

0-315-13285-X

61195

NAME OF AUTHOR/NOM DE L'AUTEUR Aravamuthan Varadarajan

TITLE OF THESIS/TITRE DE LA THÈSE "Homoaromaticity in Homotropylium Cations"

UNIVERSITY/UNIVERSITÉ McMaster

DEGREE FOR WHICH THESIS WAS PRESENTED /  
GRADE POUR LEQUEL CETTE THÈSE FUT PRÉSENTÉE Ph.D.

YEAR THIS DEGREE CONFERRED/ANNÉE D'OBTENTION DE CE DEGRÉ 1983

NAME OF SUPERVISOR/NOM DU DIRECTEUR DE THÈSE Dr. R.F. Childs

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HOMOAROMATICITY IN HOMOTROPYLIUM  
REACTIONS

By

© ARAVAMUTHAN VARADARAJAN, M.Sc.

A thesis

Submitted to the School of Graduate Studies  
in partial fulfilment of the requirements  
for the degree of  
Doctor of Philosophy

McMaster University

(April 1983)

HOMOAROMATICITY  
IN  
HOMOTROPYLIUM CATIONS

TO MY PARENTS

DOCTOR OF PHILOSOPHY (1983)

McMASTER UNIVERSITY  
Hamilton, Ontario

TITLE: Homoaromaticity in Homotropylium Cations

AUTHOR: Aravamuthan Varadarajan, M.Sc. (University of Madras)

SUPERVISOR: Professor R.F. Childs

NUMBER OF PAGES: xviii, 282

## ABSTRACT

Investigations on the structure and stability of homotropylium cations are presented in this thesis. These studies were necessitated by the lack of direct experimental evidence for homoaromatic delocalization and stabilization. The more commonly used NMR method has been shown to be inadequate.

The structure of 2-hydroxyhomotropylium cation was determined. In spite of the crystallographic disorder encountered, the cyclopropane bond lengths could be obtained. The internal cyclopropane bond (1.626(8) Å) was found to be longer than the other two cyclopropane bonds (1.488(7) Å). The structure of this cation was found to be in very good agreement with that calculated by Haddon for the parent homotropylium cation using MINDO/3. On the basis of the close similarity of the solid state and solution  $^{13}\text{C}$  NMR spectra of the 2-hydroxyhomotropylium cation, it was concluded that this cation has the same structure in both solution and the solid state. Structural studies on other model compounds fully confirm that the homotropylium cation is homoaromatic.

A calorimetric approach was used to gauge the energetic importance of homoaromaticity. Heats of protonation of several alicyclic ketones were measured. The heat of protonation of 2,3-homotropone was found to be more exothermic than that of cyclohepta-2,4-dienone by

2.9 kcal/mole. It was concluded that homoaromatic delocalization results in a significant stabilization of the homotropylium cation.

The chemistry of the homotropylium cations was examined. The acid catalyzed rearrangements of 8,8-dimethyl-2,3-homotropone and the circumambulatory rearrangements in homotropylium cations were studied in detail. Site preference for the methyl and hydroxy substituents in the seven-membered ring was probed by estimating the relative energies of the four possible positional isomers. It was found that these substituents prefer positions 2 and 4.

The protonation of homotroponeirontricarbonyl complexes was carried out in different acid media to contrast the properties of the classical cations generated with those of the homotropylium cations.

A new approach, based on the experimental determination of the structure and energy of the homoaromatic system under consideration, has been proposed in order to define homoaromaticity.

## ACKNOWLEDGEMENTS

I am greatly indebted to Professor R.F. Childs for his excellent supervision, inspirational guidance, patience and continued encouragement throughout the entire period of this work. Carrying out this research with him has been an extremely rewarding experience. Financial support from him and McMaster University is greatly appreciated.

I thank the following people for their assistance in various parts of the project: Dr. M.J. McGlinchey (ring current calculations), Dr. P.K. Ummat, Dr. M. Zeya (crystal structure studies), Dr. D.L. Mulholland and Ms. S. Yeroushalmi (calorimetry). The help from the technical staff is acknowledged.

I would like to thank my colleague, Dr. B.D. Dickie for helpful discussions in and outside chemistry during the period of our study as well as for his help in drawing the diagrams. Dr. M. Zeya, Miss L. Martins, Mrs. M. Pankratz, Miss C.V. Rogerson, Dr. C. Blackburn and Mr. G.S. Shaw are thanked for proof reading various sections of this thesis. The commendable typing skills, patience and consideration of Miss K. Stockman is greatly appreciated. A note of thanks goes to Dr. D.P. Santry for providing his office space and good humour while this thesis was written.

Finally, I thank all my friends for their concern and well-wishes on my behalf and my family for unfailing support, encouragement sympathetic understanding and love.



## TABLE OF CONTENTS

	Page
DESCRIPTIVE NOTE	
ABSTRACT	
ACKNOWLEDGEMENTS	
INTRODUCTION	
CHAPTER I HOMOAROMATICITY AND THE HOMOTROPYLIUM CATION	1
I. GENERAL BACKGROUND	1
II. HOMOTROPYLIUM CATIONS	5
1. Early Observations Regarding the Structure of Homotropylium Cation	5
a. <i>NMR Studies</i>	5
b. <i>UV Studies</i>	11
c. <i>Diamagnetic susceptibility Studies</i>	12
2. Further Studies on Homotropylium Cation	13
a. <i>Structure</i>	13
b. <i>Stability</i>	15
3. Theoretical Studies on Homotropylium Cation	17
a. <i>Bonding and Structure</i>	17
b. <i>Energetics</i>	23

	Page
4. Substituted Derivatives of Homotropylium Cation	25
5. Reactions of Homotropylium Cations	25
III. OBJECTIVES OF THE PRESENT STUDY	40
RESULTS AND DISCUSSION	
CHAPTER 2      STRUCTURAL STUDIES ON HOMOTROPYLIUM SALTS	43
1. Isolation and Attempts on Crystallization of the Salts of Parent Homotropylium Cation	43
a. <i>Homotropylium Hexachloroantimonate</i>	43
b. <i>Homotropylium Hexafluoroantimonate</i>	44
2. Structural Studies on 2-hydroxyhomotropylium hexachloroantimonate <u>69</u>	44
a. <i>Isolation and Characterization</i>	45
b. <i>Crystal Structure Studies</i>	50
c. <i>Discussion of the Molecular Structure of the 2-hydroxyhomotropylium Cation</i>	53
3. Structural Studies on the Bicyclo[5.1.0]-octadienyliumirontricarbonyl tetrafluoroborate <u>28</u>	58
a. <i>Isolation and Characterization</i>	58
b. <i>Crystal Structure Studies and Discussion of the Molecular Structure of 28</i>	58
4. Structural Studies on "Protonated 4,5-benzo-2,3-homotropone"	63
a. <i>Isolation and Characterization</i>	64
b. <i>Crystal Structure Studies and Discussion of the Molecular Structure</i>	65

	Page
5. Conclusion	80
6. Some Comments on the Use of the Ring Current Model for Homotropylium Cation	84
a. <i>Geometry of Homotropylium Cation</i>	97
b. <i>Factors Contributing to the Chemical Shift Difference for the Methylene Protons</i>	98
 CHAPTER 3	
HEATS OF PROTONATION OF ALICYCLIC KETONES BY SOLUTION CALORIMETRY. A THERMODYNAMIC INVESTIGATION OF THE HOMOAROMATIC STABILIZATION.	101
1. Heats of Protonation and $pK_a$ Values	101
2. Heats of Protonation and Relative Stabilities	102
3. Experimental Approach	103
4. Effects of Conjugation	107
5. Effects of Cyclic Conjugation	109
6. A Comparative Study of Trends in Conjugative Effects Observed by Other Methods	109
a. <i>Cationic Systems</i>	109
b. <i>Neutral Systems</i>	110
7. Comparison of Heats of Protonation with $pK_a$ values	111
8. Steric Effects and Heats of Protonation	112
9. Comparison of the Heats of Protonation of Cyclooctatrienone <u>109</u> and Homotropone <u>104</u>	113
10. Aromatic Stability vs Homoaromatic Stability. The Possible Role of Strain Energy.	114
11. Conclusion	123

	Page
CHAPTER 4	
I. REARRANGEMENT OF 8,8-DIMETHYL-2,3-HOMOTROPONE CATALYZED BY BRØNSTED AND LEWIS ACIDS	127
1. Rearrangement Studies	127
a. Brønsted Acids	127
b. Lewis Acids	131
2. Rationale for the Failure of the Equilibration Attempt	133
3. Rationale for Products Formation	136
a. Formation of Isobutyrophenone <u>128</u>	137
b. Formation of 2-isopropyltropone <u>127</u>	139
c. Formation of 2-isobutenylphenol <u>129</u>	140
d. The Possible Roles of Lewis Acids	141
4. Conclusion: Estimation of the Relative Free Energies of Various Cations Observed in FSO <sub>3</sub> H Solutions of <u>107</u>	142
II. INTERACTION OF LEWIS ACIDS WITH THE HOMOTROPONES <u>104</u> AND <u>107</u>	146
1. <sup>1</sup> H NMR Study	146
2. Scale of Relative Strengths of Lewis Acids	148
3. Correlation of Δδ Values with Lewis Acid Strengths	150
a. Probable Cause for the Large Δδ Values Observed for the Complexes	150
b. Probable Cause for the Variation of Δδ with Lewis Acid Strengths	150
4. Δδ Values and Reactivity of Lewis Acids	154
5. Conclusions	154

	Page
CHAPTER 5      STUDIES ON THE REARRANGEMENTS IN 8,8-DIMETHYL- HOMOTROPYLIUM AND 8,8-DIMETHYLBICYCLO[3.2.1]- OCTADIENYLIUM CATIONS -	157
1. Protonation of 8,8-dimethylbicyclo[5.1.0]- octa-3,5-dien-2-ol 155	159
2. Preparation and Protonation of 2-deutero- 8,8-dimethylbicyclo[5.1.0]octa-3,5-dien- 2-ol 155-d	162
3. Protonation of 8,8-dimethylbicyclo[3.2.1]- octa-3,6-dien-2-ol 156	165
4. Protonation of Bicyclo[3.2.1]octa-3,6- dien-2-ol 167	166
5. Protonation of Bicyclo[3.2.1]octa-3,6- dien-2-one 169	170
6. Protonation of 2,8,8-trimethylbicyclo- [5.1.0]octa-3,5-dien-2-ol 157 and 2,8,8- trimethylbicyclo[3.2.1]octa-3,6-dien-2- ol 158	172
a. Protonation of 2,8,8-trimethylbicyclo- [5.1.0]octa-3,5-dien-2-ol 157	172
b. Identity of Cation A	174
c. Identity of Cation B	176
d. Identities of Cations C, D and E	179
e. Protonation of 2,8,8-trimethylbicyclo- [3.2.1]octa-3,6-dien-2-ol 158	179
f. Possible Mechanisms for the Formation of Various Cations	186
7. Conclusions	
a. Substituent Dependence of the "Equili- brium" Between the Homotropylium and the Bicyclo[3.2.1]octadienyl Cations	192
b. Relative Energies of Various Isomers	194
c. The Nature of Delocalization Present in the Bicyclo[3.2.1]octadienyl Cation	196

	Page
CHAPTER 6	
PROTONATION OF HOMOTROPONEIRONTRICARBONYL AND CYCLOOCTATRIENONEIRONTRICARBONYL COMPLEXES	200
1. Preparation of Homotroponeirontri- carbonyl Complexes	201
2. Protonation in $CF_3COOH$	202
3. Protonation in $H_2SO_4$	211
4. Protonation in $FSO_3H$	218
5. Protonation of Cyclooctatrienoneiron- tricarbonyl <u>217</u> in weaker acids	220
6. Deuteration Studies	221
7. Quenching of Carbon-protonated Cations	225
8. Some Mechanistic Aspects	226
9. Conclusions	234
CONCLUDING REMARKS	236
EXPERIMENTAL	
CHAPTER 7	
EXPERIMENTAL METHODS	238
1. Instrumental Techniques	238
2. Purification of Solvents and Reagents	239
3. Synthetic Aspects	239
a. Preparation of Homotropylium Hexachloroantimonate <u>5</u>	240
b. Preparation of Homotropylium Hexafluoroantimonate <u>5</u>	241
c. Preparation of 2-hydroxyhomo- tropylium Hexachloroantimonate <u>69</u>	241
d. Preparation of bis(5,6-benzo-8,8- dideuterobicyclo[5.1.0]octa-3,5-dien- 2-one)hydrogen hexachloroantimonate <u>115</u>	243

	Page
e. Preparation of 2-deuterobicyclo- [5.1.0]octa-3,5-dien-2-ol 155-d	243
f. Preparation of 8,8-dimethylbicyclo- [3.2.1]octa-3,6-dien-2-ol 156	244
g. Preparation of 2,8,8-trimethylbicyclo- [5.1.0]octa-3,6-dien-2-ol 157	245
h. Preparation of 2,8,8-trimethylbicyclo- [3.2.1]octa-3,6-dien-2-ol 158	245
i. Preparation of Isopropyltropylium Hexachloroantimonate 159	246
j. Preparation of Cyclooctatrienoneiron- tricarbonyl 217	247
4. Calorimetric Measurements	247
5. Acid-Catalyzed Rearrangements of 8,8- dimethyl-2,3-homotropone 107	249
a. General Isomerization Procedure	249
b. Product Characterizations	249
i. Rearrangement Catalyzed by $CF_3COOH$	249
ii. Rearrangement Catalyzed by <i>p</i> - toluenesulfonic acid	250
iii. Rearrangement Catalyzed by $BCl_3$	250
iv. Rearrangement Catalyzed by $BF_3 \cdot OEt_2$	251
6. Preparation of Lewis Acid Complexes of 2,3-homotropone 104 and 8,8-dimethyl- 2,3-homotropone 107	251
7. Protonation Studies on the Iron Complexes 197, 198, 199 and 217	252
a. Method of Protonation	252
b. Quenching of the Protonated Metal Carbonyl Complexes	252
c. Measurement of Rate Constants	253

	Page
8. Rearrangement Studies on Homotropylium and Bicyclo[3.2.1]octadienyl <sup>+</sup> Cations	253
a. Protonation of the Bicyclic Alcohols 155, 156, 167, 157 and 158 at low temperatures	253
b. Protonation of Bicyclo[3.2.1]octa-3,6-dien-2-one 169 and kinetics of Isomerization of the Conjugate Acid 173	254
c. Low Temperature Protonation of 155-d and Kinetics of Deuterium Scrambling in 50-d	254
d. Quenching of the Cation 154	255
9. Crystal Structure Determinations	256
a. 2-Hydroxyhomotropylium Hexachloroantimonate 69	256
i. Collection of the x-ray data	256
ii. Solution of the Structure	256
b. Bis(5,6-benzo-8,8-dideuterobicyclo[5.1.0]octa-3,5-dien-2-one)hydrogen Hexachloroantimonate 115	260
c. Bicyclo[5.1.0]octadienyliumirontriacetyl tetrafluoroborate 28	260
REFERENCES	268



LIST OF TABLES

Number		Page
1	Examples of homoaromatic cations	6
2	Homotropylium cation derivatives	26
3	Examples of ring inversion process in homotropylium cations	33
4	$^{13}\text{C}$ NMR chemical shifts for <u>69</u>	48
5	Selected interatomic distances ( $\text{\AA}$ ) and angles (deg) in <u>69</u>	55
6	Comparison of calculated interatomic distances and angles of <u>5</u> with those found for <u>69</u>	57
7	Selected interatomic distances ( $\text{\AA}$ ) and angles (deg) in <u>28</u>	61
8	$^1\text{H}$ NMR chemical shift data for the ketone <u>114-d<sub>2</sub></u> , the cation <u>82-d<sub>2</sub></u> and the "hexachloroantimonate salt of <u>82-d<sub>2</sub></u> "	66
9	$^2\text{H}$ NMR chemical shift data for the ketone <u>114-d<sub>2</sub></u> , the cation <u>82-d<sub>2</sub></u> and the "hexachloroantimonate salt of <u>82-d<sub>2</sub></u> "	67
10	$^{13}\text{C}$ NMR chemical shift data for the ketone <u>114-d<sub>2</sub></u> , the cation <u>82-d<sub>2</sub></u> and the "hexachloroantimonate salt of <u>82-d<sub>2</sub></u> "	68
11a	Selected interatomic distances ( $\text{\AA}$ ) and angles (deg) in <u>115</u>	71
11b	Bond lengths ( $\text{\AA}$ ) and angles (deg) involving hydrogen atoms in <u>115</u>	72
11c	Best planes, dihedral angles and torsional angles (deg) in <u>115</u>	73
12	Some examples of short O-H-O bonds	75
13	Calculated ring current contribution ( $\delta'$ ) to the chemical shifts for methylene protons in <u>5</u>	87

Number		Page
14	Calculated ring current contribution ( $\delta'$ ) to the chemical shifts for the methylene protons in <u>5</u>	91
15	Calculated ring current contributions ( $\delta'$ ) to the chemical shifts for the methylene protons in <u>5</u>	96
16	Calorimetric data	106
17	Estimation of standard enthalpies of formation of <u>2,3-homotropone 104</u> and <u>cycloocta-2,4,6-trienone 109</u>	115
18	Estimation of standard enthalpies of formation of <u>8,8-dimethyl-2,3-homotropone 107</u> and <u>8,8-dimethyl-bicyclo[3.2.1]octa-3,6-dien-2-one 101</u>	121
19	Products obtained on isomerization of <u>107</u>	129
20	Estimation of the standard entropies of formation of <u>8,8-dimethyl-2,3-homotropone 107</u> and <u>8,8-dimethyl-bicyclo[3.2.1]octa-3,6-dien-2-one 101</u>	134
21	Chemical shift differences ( $\Delta\delta$ ) for $C_8$ -hydrogens and $C_8$ -methyls observed for complexes of <u>2,3-homotropone 104</u> and <u>8,8-dimethyl-2,3-homotropone 107</u> with various Lewis acids	149
22	$^1H$ NMR spectra of various cations	160
23	$^{13}C$ NMR chemical shifts for cations <u>153</u> and <u>177</u>	178
24	$\Delta\delta$ values for the protons $H_3$ , $H_4$ , $H_6$ and $H_7$ in some bicyclo[3.2.1]octadienyl systems	198
25	$^1H$ NMR data for the <u>homotroponeirontricarboxyls 197</u> , <u>198</u> and <u>199</u>	203
26	$^{13}C$ NMR data for <u>homotroponeirontricarboxyls 197</u> , <u>198</u> and <u>199</u>	204
27	$^1H$ NMR data for cations <u>200</u> , <u>201</u> and <u>202</u>	205
28	$^{13}C$ NMR data for cations <u>200</u> , <u>201</u> and <u>202</u>	208
29	$^{13}C$ NMR data for neutral and protonated cyclopropylmethyl ketone <u>211</u> and <u>212</u>	209
30	$^1H$ NMR data for cations <u>214</u> , <u>215</u> , <u>216</u> and <u>218</u>	212

Number		Page
31	$^{13}\text{C}$ NMR data for cations <u>205</u> , <u>214</u> , <u>218</u> and <u>216</u>	217
32	Rate Constants for some of the isomerization processes occurring in protonated homotroponeiron-tricarbonyls	228 <sup>b</sup>
33	$\Delta\delta$ values in protonated homotropones and their irontricarbonyl complexes	235
34	Crystal data for <u>69</u>	257
35	Atomic positional parameters ( $\times 10^4$ ) and temperature factors ( $\text{\AA}^2$ ) for 2-hydroxyhomotropylum hexachloroantimonate <u>69</u>	259
36	Crystal data for <u>115</u>	261
37	Atomic positional parameters ( $\times 10^4$ ) for non-hydrogen atoms in <u>115</u>	262
38	Temperature factors ( $\text{\AA}^2$ ) ( $\times 10^3$ ) for non-hydrogen atoms in <u>115</u>	263
39	Coordinates of hydrogen atoms ( $\times 10^3$ ) in <u>115</u>	264
40	Atomic positional parameters ( $\times 10^4$ ) for non-hydrogen atoms in <u>28</u>	265
41	Temperature factors ( $\text{\AA}^2 \times 10^3$ ) for non-hydrogen atoms in <u>28</u>	266
42	Atomic positional parameters ( $\times 10^3$ ) for hydrogen atoms in <u>28</u>	267

## LIST OF FIGURES

Number		Page
1	Some homologues of tropylium cation	4
2	Energy profile for the ring inversion process in homotropylium cation	16
3	MINDO/3 structure for the homotropylium cation (a) bond distances and (b) interplanar angles	21
4	Haddon's revised energy profile for the ring inversion process in homotropylium cation	24
5	$^1\text{H}$ NMR spectrum of 2-hydroxyhomotropylium cation (a) 2,3-homotropone in $\text{D}_2\text{SO}_4$ and (b) 2-hydroxyhomotropylium hexachloroantimonate in $\text{SO}_2$	46
6	Solution ( $\text{D}_2\text{SO}_4$ ) and solid state (CPMAS) $^{13}\text{C}$ NMR spectra of <u>69</u>	49
7	The packing of $[\text{C}_8\text{H}_8(\text{OH})^+][\text{SbCl}_6^-]$ within the unit cell	52
8	Structure of 2-hydroxyhomotropylium cation (a) the cation $\text{C}_8\text{H}_8(\text{OH})^+$ showing the atom numbering and selected interatomic distances and (b) the cation $\text{C}_8\text{H}_8(\text{OH})^+$ showing the dihedral angles between the planes of atoms	54
9	$^1\text{H}$ NMR spectrum of bicyclo[5.1.0]octadienylirontricarbonyl cation <u>28</u> (a) cyclooctatetraeneirontricarbonyl <u>27</u> in $\text{H}_2\text{SO}_4$ and (b) bicyclo[5.1.0]octadienylirontricarbonyl tetrafluoroborate in $\text{SO}_2$	59
10	Structure of bicyclo[5.1.0]octadienylirontricarbonyl cation <u>28</u> showing atom numbering and selected interatomic distances	62
11	$^1\text{H}$ NMR spectra of the neutral and the protonated ketone <u>114-d<sub>2</sub></u> (a) <u>114-d<sub>2</sub></u> in $\text{CDCl}_3$ , (b) <u>114-d<sub>2</sub></u> in $\text{D}_2\text{SO}_4$ and (c) the hexachloroantimonate salt of the protonated ketone <u>114-d<sub>2</sub></u> in $\text{CD}_2\text{Cl}_2$	69

Number		Page
12	Structure of bis(5,6-benzo-8,8-dideuterobicyclo [5.1.0]octa-3,5-dien-2-one)hydrogen hexachloro-antimonate 115 showing atom numbering and selected interatomic distances.	76
13	A perspective view of bis(5,6-benzo-8,8-dideuterobicyclo[5.1.0]octa-3,5-dien-2-one)hydrogen hexachloro-antimonate 115	79
14	Plots of $\Delta\delta$ values vs relative strengths of Lewis acids for the complexes of (a) 8,8-dimethyl-2,3-homotropone and (b) 2,3-homotropone	152
15	$^1\text{H}$ NMR spectrum of a solution of the alcohol 157 in $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ (a) at $-100^\circ\text{C}$ and (b) at $-70^\circ\text{C}$ for 1 hour	173
16	$^{13}\text{C}$ NMR spectrum of a solution of the alcohol 157 in $\text{CD}_2\text{Cl}_2/\text{SO}_2\text{ClF}/\text{FSO}_3\text{H}$ (a) at $-80^\circ\text{C}$ , (b) after warming at $-50^\circ\text{C}$ for 5 minutes and (c) spectrum obtained by subtracting spectrum (a) from spectrum (b)	177
17	$^1\text{H}$ NMR spectrum of a solution of the alcohol 158 in $\text{CD}_2\text{Cl}_2/\text{SO}_2\text{ClF}/\text{FSO}_3\text{H}$ at $-100^\circ\text{C}$	181
18	$^1\text{H}$ NMR spectrum of a solution of the alcohol 158 in $\text{SO}_2\text{ClF}/\text{FSO}_3\text{H}$ (a) at $-80^\circ\text{C}$ for 10 minutes, (b) at $-60^\circ\text{C}$ for 10 minutes and (c) spectrum of the intermediate 180 obtained by subtracting spectrum (b) from spectrum (a)	182
19	Estimates of the free energies of various cations relative to that of 2,8,8-trimethylhomotropylum cation 153	195
20	$^1\text{H}$ NMR spectrum of 2,3-homotroponeirontricarbonyl 197 in different media (a) in $\text{CDCl}_3$ , (b) in $\text{CF}_3\text{COOH}$ and (c) in $\text{H}_2\text{SO}_4$	206
21	$^1\text{H}$ NMR spectrum of cyclooctatrienoneirontricarbonyl 217 in protic and deuterated acids (a) in $\text{H}_2\text{SO}_4$ and (b) in $\text{D}_2\text{SO}_4$	214

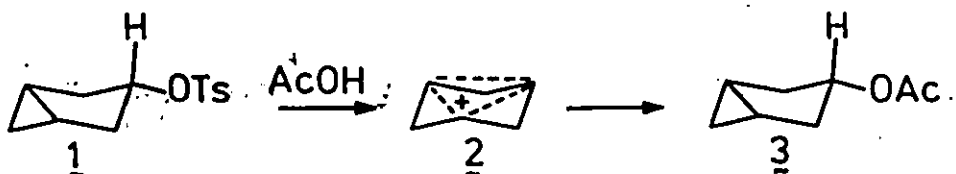
INTRODUCTION

## CHAPTER 1

### HOMOAROMATICITY AND THE HOMOTROPYLIUM CATION

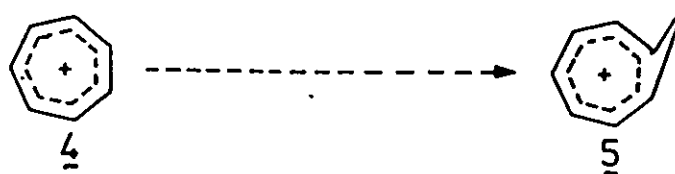
#### I. GENERAL BACKGROUND

The past two decades have seen wideranging efforts directed toward theoretical and experimental studies on homoaromatic systems.<sup>1-4</sup> The concept of homoaromaticity was originally proposed by Winstein to explain the nature of the intermediate 2, (a trishomocyclopropenyl cation) formed in the solvolysis of 1, cis-bicyclo[3.1.0]hex-3-yl tosylate 1.<sup>5-7</sup>



In simple terms, "homoaromatic species" result from the cyclic delocalization of  $(4n+2)\pi$  electrons in systems where the aromatic pericycle is interrupted by one or more methylene bridges.

A homoaromatic species, such as the homotropylium cation 5, can be conceptually derived by the homologation of the parent aromatic system. In this case the tropylium cation is the parent aromatic system.

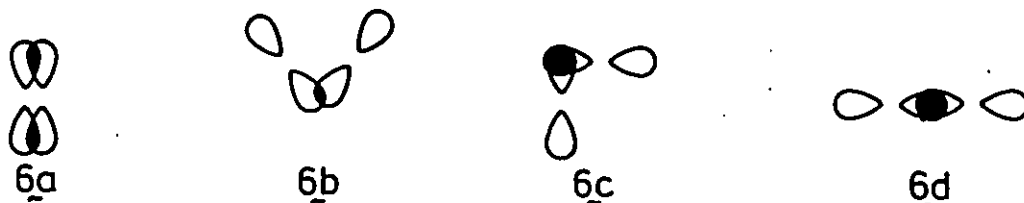


tropylium

homotropylium

The orbital interaction between the two non-adjacent  $\pi$  centres, in an ion such as 5, is thought to be maintained, inspite of the interposition of the methylene group between them. This interaction is expected to be considerably reduced in the homoaromatic species 5 as compared to its aromatic parent 4.

Some idea of the nature of bonding between the two carbons that are separated by the methylene group can be gained by considering the ways in which two p orbitals can formally interact. Paquette has suggested that there are four possible modes of overlap 6a - 6d for two interacting p orbitals.<sup>8</sup>



→ increasing  $\sigma$  contribution

The first mode 6a is the normal parallel overlap for a p-p  $\pi$  bond (such as in 4a). Case 6b corresponds to a homoaromatic interaction which lies between a p-p  $\pi$  bond and a p-p  $\sigma$  bond. (5a is an example of this case). Although Paquette differentiates 6b and 6c, in actual fact 6c differs from 6b in degree rather than kind. Overlap of the type shown in 6c is believed to occur in certain bicycloaromatic compounds.<sup>9,10</sup>



The end-on overlap 6d leading to a  $\sigma$  bond is postulated to occur in the transition state for pericyclic reactions such as Diels-Alder reactions (eg., between a diene and an olefin 7).



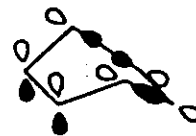
4a

p-p  $\pi$



5a

homoaromatic



7

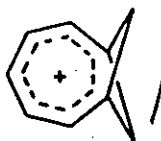
p-p  $\sigma$

Homoaromatic systems can, in principle, be neutral, cationic or anionic. They can be further categorized as monohomoaromatic, bishomoaromatic, trishomoaromatic and higher (poly) homoaromatic species. The terms mono, bis, tris, etc., refer to the number of C-C  $\sigma$  bonds in the aromatic parent that have been interrupted by an  $sp^3$  centre and not to the number of methylene groups that have been included in the homoconjugation of a particular side of the aromatic parent ring. Thus 12 is still formally a monohomotropylium cation (one interruption in the  $\sigma$  backbone of the tropylium ring), although incidentally calculations suggest that 12 has no special stability.<sup>11-13</sup> The relative disposition of the methylene groups can lead to different regio (eg., 8, 9, 10 and 11) and stereo (eg., 10, 13, 11 and 14) isomers in higher homoaromatic systems. Favorable evidence for homoaromatic character has been found only in the case of cis isomers.<sup>14-16</sup> Some of the various possibilities for the homologues of the tropylium cation 4, are summarized in Figure 1.

Theoretical studies do not support homoaromatic delocalization in neutral molecules.<sup>17</sup> In the case of anionic homoaromatic species,



Homotropylium  
cation 5



1,1-bishomotropylium  
cation 8  
(Haddon's dihomotropylium  
cation)



1,2-bishomotropylium  
cation 9



1,3-cis-bishomotropylium  
cation 10



1,4-cis-bishomotropylium  
cation 11



not a bishomotropylium  
cation 12



1,3-trans-bishomotropylium  
cation 13



1,4-trans-bis-  
homotropylium cation 14



heptahomotropylium  
cation 15

Figure 1 Some Homologues of Tropylium Cation.

theoretical calculations have yielded conflicting results.<sup>3,18-24</sup>

Experimental evidence for the presence of homoaromaticity in anions and neutral systems is by no means unambiguous or "totally overwhelming". Only in the case of cations have theoretical and experimental evidence been favorable for the existence of homoaromaticity. Some examples of homoaromatic cations are listed in Table I.

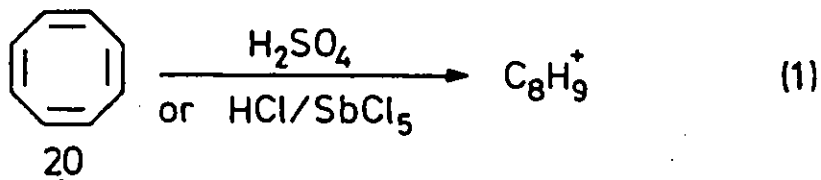
Homoaromatic interaction is expected to be more pronounced in monohomoaromatic rather than bis or higher homoaromatic cations.<sup>4,42</sup> Of the monohomoaromatic cations, the homotropylium cation is seemingly the best established. However many basic questions remain to be answered. Its structure and chemistry form the topic of this thesis.

## II. HOMOTROPYLIUM CATIONS

### 1. Early Observations Regarding the Structure of Homotropylium Cation





#### a. *NMR Studies*

Pettit and co-workers observed that protonation of cyclooctatetraene 20 in strong acids produced a new cationic species,  $C_8H_9^+$  (Equation 1).<sup>51</sup>






The  $^1H$  NMR spectrum of the cation obtained in these reactions was found to consist of four multiplet signals with the chemical shift values of  $\delta$  8.6, 6.6, 5.2 and -0.6 parts per million (ppm) with relative areas 5, 2, 1 and 1 respectively. Pettit considered three possible structures, namely, the planar cyclooctatrienylium 21, the bicyclo[5.1.0]

Table 1  
Examples of Homoaromatic Cations

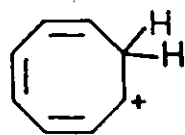
Cation	Method of Study	Reference
Monohomocyclopropenyl cation	Direct observation by NMR	25,26
Cyclobutenium ion 16	X-ray structure of a derivative	27
 16	Theoretical studies	12,13,18,21,28
Bishomocyclopropenyl cation	Direct observation by NMR	29
7-Norbornenyl cation 17	Solvolysis studies	30-33
 17		
Trishomocyclopropenyl cation 2	Direct observation by NMR	34,35
 2	Solvolysis studies	5-7,36,37
	Theoretical studies	38-40
Monohomotropylium cation 5	Will be discussed separately in Part II	
 5		

..... continued

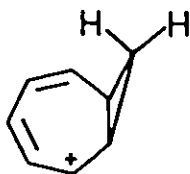
Table 1 (continued)

Cation	Method of Study	Reference
Bishomotropylium cations	Direct observation by NMR	14,41,42
1,3-bishomotropylium cation 10		
 10		
1,4-bishomotropylium cations 18 and 19		
 18	Direct observation by NMR	43-47
 19	Direct observation by NMR Solvolysis studies	45,48-50 45

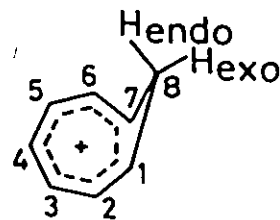
octadienyl 22 and the homotropylium 5 structures for the cation generated.



21



22



5

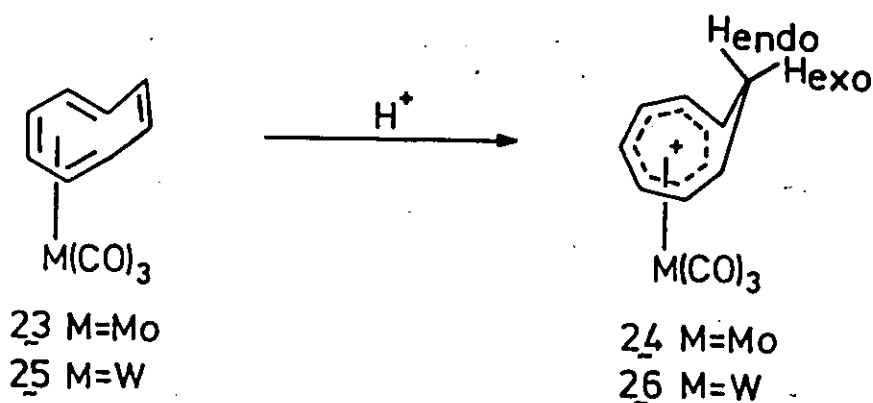
The characteristic NMR spectrum ruled out the planar structure 21 for the cation. Though Pettit referred to this cation as the bicyclo[5.1.0] octadienyl cation 22, he suggested that there was extensive involvement of the internal cyclopropyl bond in 22. Interaction of the p orbital components on C<sub>1</sub> and C<sub>7</sub> with the p orbitals on the adjacent C<sub>2</sub> and C<sub>6</sub> atoms was suggested to form a "pseudoaromatic" ring, somewhat analogous to tropylium cation 4, as implied in structure 5. Therefore Pettit proposed the name "homotropylium" for this cation. The large difference in chemical shifts of the endo and exo protons ( $\Delta\delta = 5.8$  ppm) was taken as evidence for the existence of an induced ring current in this cation.

Winstein made a further analysis of the NMR spectrum of the cation C<sub>8</sub>H<sub>9</sub><sup>+</sup>.<sup>52</sup> The marked dissimilarity in the chemical shifts and coupling constant values of the cyclopropyl protons in homotropylium cation and various model cyclopropyl compounds led Winstein to discount the bicyclooctadienyl structure 22.<sup>52</sup> The average chemical shift of the vinyl protons was found to be markedly similar to that of the protons of tropylium cation 4.<sup>53</sup> Winstein concluded that homotropylium cation could be best represented as having an open cyclopropane structure 5

rather than a fully formed cyclopropane structure 22. Pettit also came to similar conclusions.<sup>54</sup>

Deno disagreed with the view that the open cyclopropane structure is representative of homotropylium cation.<sup>55</sup> Deno stated that the properties of this cation are in accord with structure 22 and that no unusual hybridization other than cyclopropyl conjugation is required to rationalize the stability. His statement, which had no experimental (or theoretical) support, was discounted by further experimental studies that ensued.

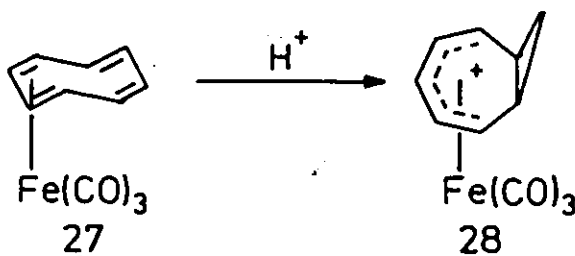
Winstein and coworkers observed that on protonation of cyclooctatetraenemolybdenumtricarbonyl 23, the homotropyliummolybdenumtricarbonyl cation 24 was formed.<sup>52</sup> The NMR spectrum of 24 was markedly similar to that of 5. The tungsten analogue 25 behaved similarly to produce 26 on protonation.<sup>1</sup>



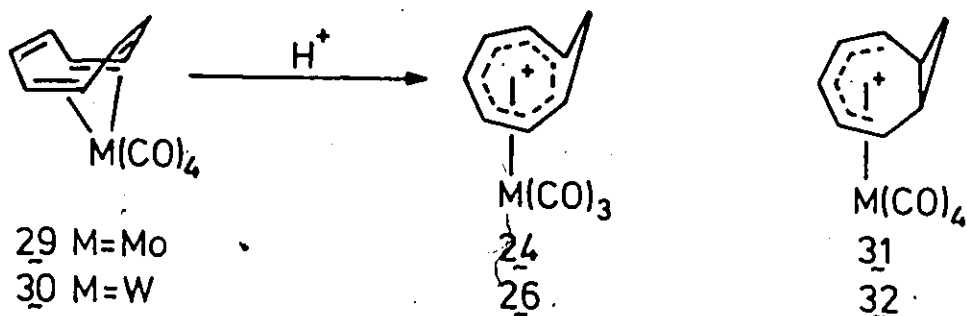
The bicyclooctadienyl cation structure for these complexes was ruled out on the basis of the  $6\pi$  electron requirement of these transition metals in the complexes 24 and 26. The NMR spectra were inconsistent with the cyclooctatrienyl structure as the methylene protons had a significant difference in their chemical shift values. ( $\Delta\delta = 3.5$  ppm).<sup>1,52</sup> Only

a homotropylium-like structure (with an open cyclopropyl unit) could account for the observed spectra.

The protonation behavior of cyclooctatetraeneirontricarbonyl 27 stood in sharp contrast. No homotropylium cation was observed in this case. The NMR spectrum was interpreted in terms of a bicyclo[5.1.0]octadienyliumirontricarbonyl cation 28, with an intact cyclopropane unit.<sup>56,57</sup>

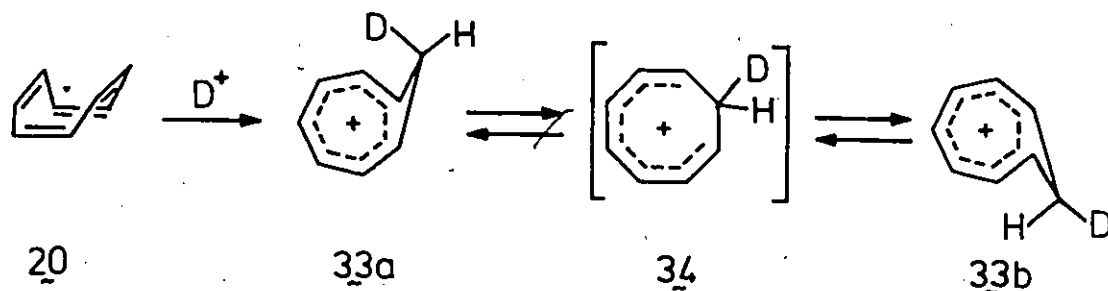


It is interesting to note that protonation of cyclooctatetraene molybdenum and tungsten tetracarbonyls 29 and 30 led to the formation of 24 and 26, respectively, with the loss of CO. The classical cations 31 and 32 were not formed. The stability associated with a non-classical cation was suggested as a possible reason.<sup>1,58</sup> These studies on metal complexes ruled out the bicyclic structure 22 and strongly supported the nonclassical structure 5 for homotropylium cation.





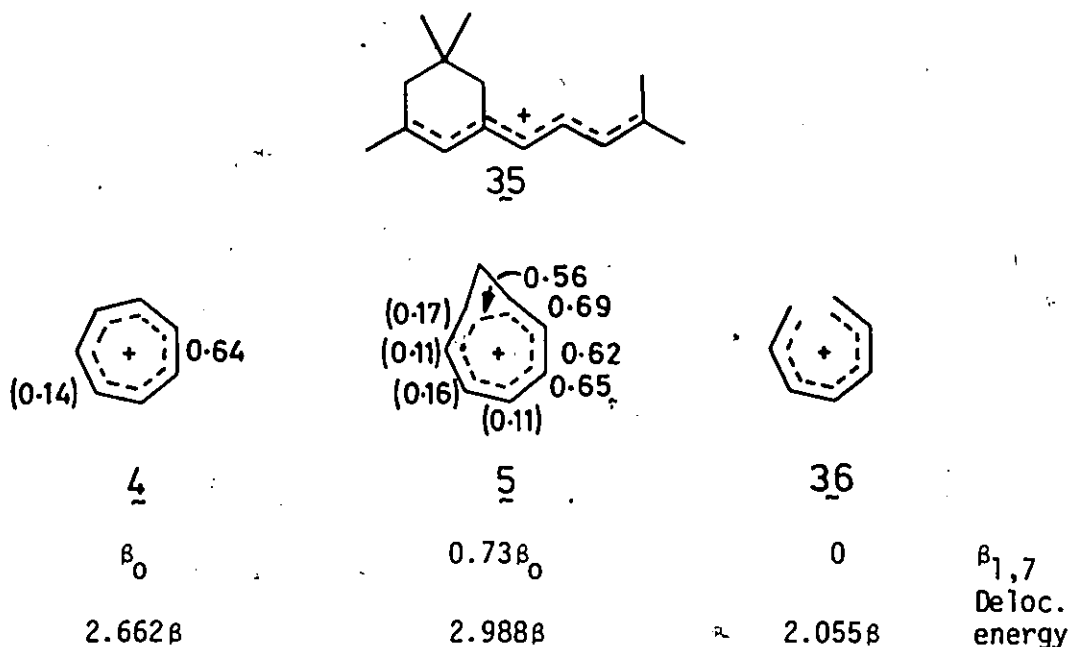
Winstein and co-workers found that deuteration of cyclooctatetraene 20 in  $D_2SO_4$  at  $-10^\circ$  was stereoselective (to the extent of  $\sim 80\%$ ).<sup>53</sup> Deuterium incorporation occurred preferentially from the endo side. Continued NMR observation showed that at equilibrium the intensities of the methylene proton signals approached the value corresponding to half a proton in each position. The activation barrier ( $\Delta G^\ddagger$ ) associated with this endo-exo equilibration process was found to be 22.3 kcal/mole. Winstein suggested that the equilibration process 33a  $\rightarrow$  33b might proceed by ring inversion through a planar form 34 as the transition state. He concluded that free energy of the classical cation 34 must be at least 22.3 kcal/mole higher than that of the homoaromatic cation 33.



#### b. UV Studies

Further evidence for the structure of homotropylium cation came from the ultraviolet absorption studies on the homotropylium cation.<sup>53</sup> The two  $\lambda_{max}$  values, 232.5 nm ( $\log \epsilon$  4.52) and 313 nm ( $\log \epsilon$  3.48) observed for homotropylium cation are higher than those of tropylium cation ( $\lambda_{max}$  217 nm,  $\log \epsilon$  4.61 and  $\lambda_{max}$  273.5 nm,  $\log \epsilon$  3.63) but much less than that expected for a planar cyclooctatrienylium cation. (For example, a  $\lambda_{max}$  of 470 nm was observed for the heptatrienyl cation 35).<sup>59,60</sup> The HMO excitation energy for the tropylium ion and a planar cyclooctatrienylium cation were calculated to be 1.692  $\beta$  and 0.765  $\beta$ , where

$\beta$  is the resonance integral. Using the reasonably good correlation between the HMO excitation energy and frequency of the long-wavelength absorption maximum that exists for a number of carbocations, Winstein obtained an approximate HMO excitation energy of  $1.45 \beta_0$  for homotropylium cation.<sup>61</sup> This corresponds to the 1,7 resonance integral ( $\beta_{1,7}$ ) value of  $0.73 \beta_0$  and the 1,7 bond order of 0.56. The HMO bond order and charge density values for homotropylium cation 5, tropylium cation 4 and heptatrienylium cation 36, obtained by Winstein and co-workers are given below:<sup>45</sup>



### c. Diamagnetic Susceptibility Studies

The evidence for the existence of a ring current in homotropylium cation came from the volume diamagnetic susceptibility of 5 measured by Dauben and co-workers.<sup>62</sup> Like benzene and tropylium cation, homotropylium cation clearly showed significant exaltation of diamagnetic susceptibility. The exaltation value is the difference between the measured diamagnetic

susceptibility value and that calculated for a nonaromatic model. The numbers reported in literature vary and hence the exact magnitude of the exaltation value is open to question.<sup>1,2</sup>

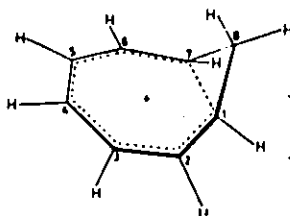
## 2. Further Studies on Homotropylium cation

### a. Structure

A high resolution 251 MHz NMR spectrum of 5 in  $\text{FSO}_3\text{H-SO}_2\text{ClF}$  at  $-60^\circ$  was obtained by Winstein and coworkers.<sup>63</sup> The downfield multiplet signal of the five vinyl protons previously observed in the low field NMR spectrum of 5 resolved into three essentially first order triplets in the high field NMR spectrum. The chemical shifts and coupling constants for the vinyl protons could be measured accurately.

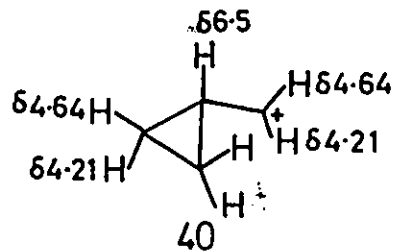
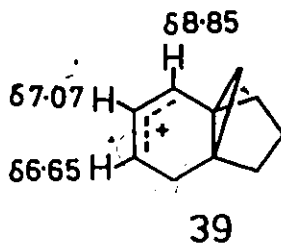
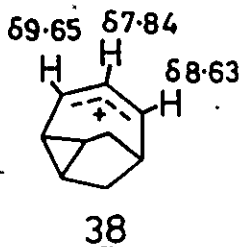
The analysis of the coupling constant data suggested that the 7-membered ring is nonplanar with the  $\text{C}_3\text{-C}_4\text{-C}_5$  segment being slightly tilted away from the plane defined by  $\text{C}_1\text{-C}_2\text{-H}_2$  (or  $\text{C}_7\text{-C}_6\text{-H}_6$ ). This results in a nonzero dihedral angle between  $\text{H}_3(\text{H}_5)$  and  $\text{H}_2(\text{H}_6)$  (37). A similar suggestion was put forward to account for the dihedral angle between  $\text{H}_2(\text{H}_6)$  and  $\text{H}_1(\text{H}_7)$ . On the basis of a study of models it was suggested that the  $\text{C}_3\text{-C}_4\text{-C}_5$  segment is tilted toward  $\text{C}_8$  and the "7-membered" ring was nonplanar.

$\text{H}_{1,7}$ :	$\delta$	6.48
$\text{H}_{2,6}$ :	$\delta$	8.39
$\text{H}_{3,5}$ :	$\delta$	8.57
$\text{H}_4$ :	$\delta$	8.27
$\text{H}_{8\text{exo}}$ :	$\delta$	5.13
$\text{H}_{8\text{endo}}$ :	$\delta$	-0.73



37

The chemical shifts for the vinyl protons revealed the charge distribution in  $C_2-C_6$  to be quite different from that occurring in model cyclopropyl carbanyl cations. In 5 most of the positive charge is located on the carbon  $\beta$  to the cyclopropane ring. But in the model systems, 38 and 39 most of the charge was found to be located on the carbon adjacent ( $\alpha$ ) to the cyclopropyl ring.<sup>64,65</sup> The  $J_{gem}$  value (7.2 Hz) observed for the methylene protons in 5 was found to be larger than that (3.2 Hz) observed for the cyclopropylcarbanyl cation 39.<sup>65</sup> Unlike cyclopropyl carbanyl cations, in 5, the  $J_{trans}$  value was found to be larger than  $J_{cis}$ .<sup>52,66,67</sup> Also, the average  $J_{13C,H}(CH_2)$  value of 180 Hz observed in cyclopropyl carbanyl cation 40 was found to be significantly larger than the average value of 159 Hz for  $J_{13C,H}(CH_2)$  found in 5.<sup>68,69</sup> These observations are consistent with electron delocalization in 5, involving homoallylic participation of the cyclopropane ring, where only one of the cyclopropane bonds is used to an appreciable extent.



The  $^{13}C$  NMR chemical shifts in 5 have been measured independently by Olah and Schröder.<sup>25,42,70</sup> The two studies disagree with regard to the assignment of chemical shifts for the vinyl carbons.<sup>71</sup> Nonetheless,

the extensive deshielding of carbons 1 and 7 is suggestive of their involvement in cyclic delocalization of the positive charge. Olah has pointed out that the difference in chemical shifts for the carbons  $C_1$  and  $C_4$  (22.4 ppm) is much smaller than those observed in monocyclic pentadienyl cations (54.4 - 89 ppm).<sup>42</sup> The coupling constant values observed for the methylene carbon ( $J_{13C,H}(CH_2) = 159.2, 155.8$  Hz) indicate no appreciable cyclopropane ring formation or the involvement of  $C_8$  in charge delocalization.<sup>25</sup>

The structural studies performed, so far, thus rely heavily on the NMR data. No direct structural data on homotropylium cation or its derivatives are available.

#### b. Stability

Quantitative and direct information of the thermodynamic (relative or absolute) stability of homotropylium cation is lacking.

Winstein attributed the exo-endo equilibration process occurring in the 8-deuteriohomotropylium cation 33 to a ring inversion process proceeding via a possible planar cyclooctatrienylium cation 34.<sup>53</sup> If 34 were indeed the transition state then the homotropylium cation is more stable than the linearly conjugated analogue by 22.3 kcal/mole (Figure 2). The obvious difficulty in establishing the nature of the transition state limits the use of this data. At that time alternative mechanisms for such a process were not considered.

Feldman and Flythe used electrochemical methods to measure the stabilities of trivalent carbon species.<sup>72</sup> In a cyclic voltammetry study, it was observed that the (two electron) reduction potential (0.92 V) of 5 in 14M  $H_2SO_4$  was 0.3 V more negative than that of dibenzo-

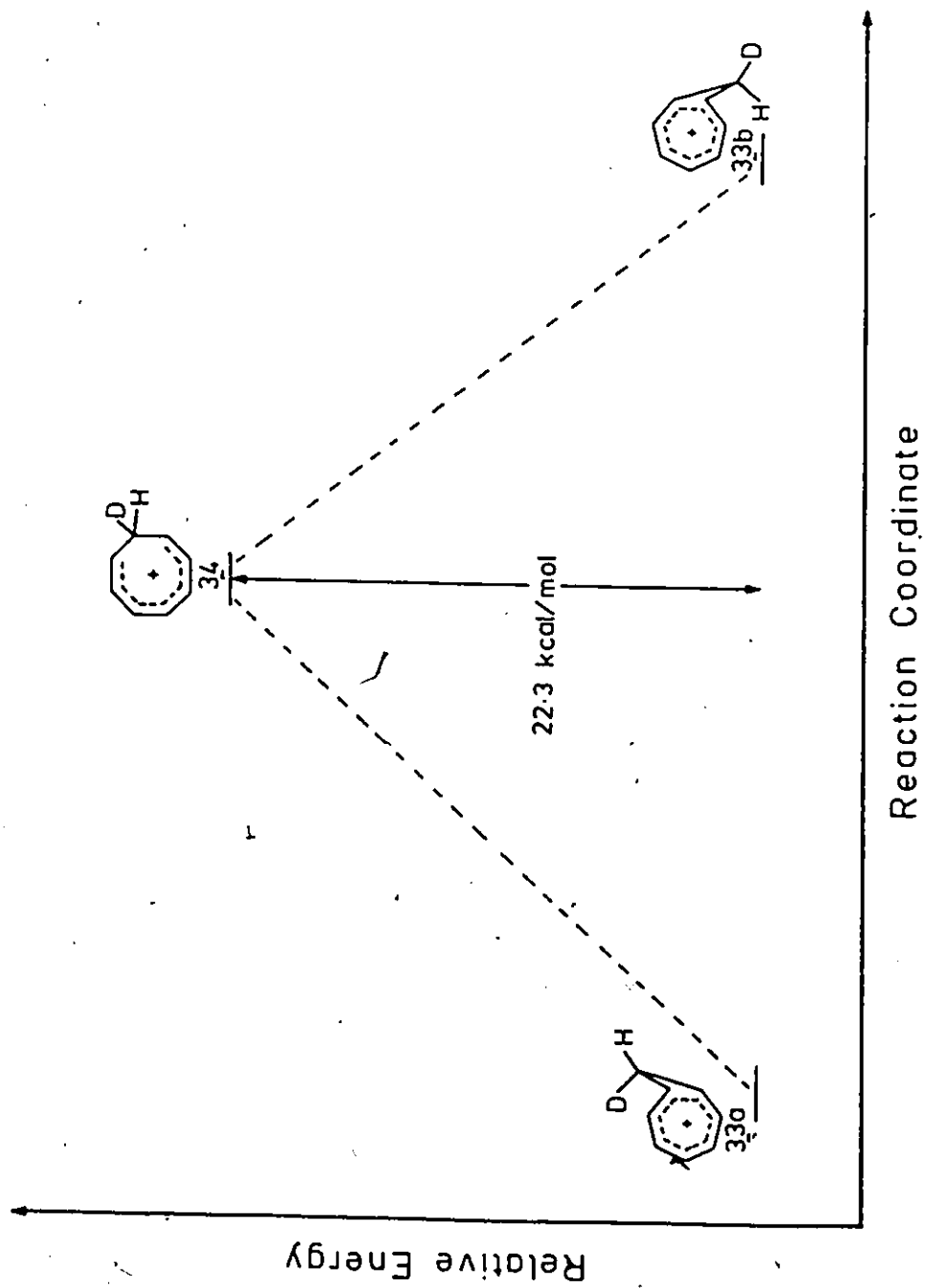


Figure 2 Energy Profile for the Ring Inversion Process in Homotropylium Cation.

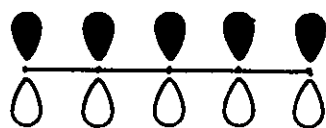
tropylium cation but 0.3 V less negative than that of tropylium cation 4.<sup>73</sup> This relative ordering follows their low energy electronic transitions (longest wavelength absorption maxima of 275 nm for 4, 313 nm for 5 and 530 nm for dibenzotropylium cation). But the reduction processes occurring in each case are different and hence a meaningful correlation can not be obtained.

It is with this lack of experimental information in mind that one needs to look into the theoretical studies on homotropylium cation.

### 3. Theoretical Studies on Homotropylium Cation

#### a. *Bonding and Structure*

The first detailed attempt to develop a theoretical approach to the nature of homoaromatic bonding and stability of homotropylium cation was that of Hehre.<sup>74</sup> In his orbital model for homoaromatic stability, Hehre considered the interaction of the lowest occupied (symmetric) molecular orbital of pentadienyl cation moiety ( $\chi_1s$ ) with the highest occupied symmetric ( $\psi_2s$ ) and antisymmetric ( $\psi_2a$ ) Walsh orbitals of the cyclopropane unit.



$\chi_1(S)$



$\psi_2(S)$

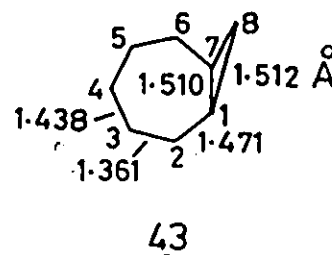


$\psi_3(A)$

Homotropylium cation 5 can then gain stabilization by forming a  $6\pi$  electrons Hückel aromatic system 41, by the interaction of symmetric cyclopropane Walsh function  $\psi_2s$  with the pentadienyl  $\pi$  system  $\chi_1s$ .

Alternatively, an  $8\pi$  electron Möbius aromatic system 42, can be visualized

to result from the interaction of the antisymmetric cyclopropane Walsh function  $\psi_2A$ , with the pentadienyl  $\pi$  system,  $\chi_1S$ . 41 would lead to a closed cyclopropane structure 22 and 42 to an open cyclopropane structure 5. Though initially Hehre suggested that both modes of electron delocalization are operative in practice, he later abandoned the Möbius model.

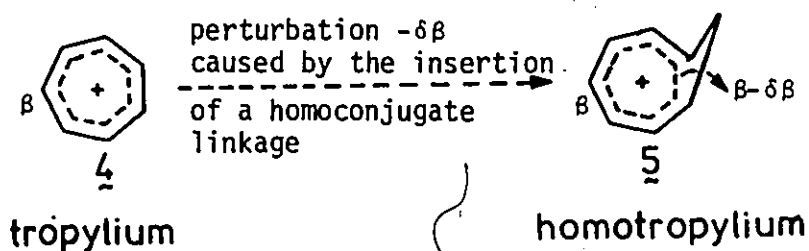


Hehre's ab initio STO-3G calculations on the equilibrium geometry for the homotropylium cation (with the seven membered ring constrained to be planar) produced a structure 43 with the homoconjugate linkage having a length of 1.512 Å. This value is not too far from the C-C bond length in cyclopropane itself (1.504 Å, theoretical and 1.510 Å, experimental).<sup>75,76</sup> All the three bonds of the cyclopropane unit were almost equal in length. In other words, the resulting structure showed it to be a bicyclo[5.1.0]-octadienyl cation 22 which is quite inconsistent with all the previously reported properties of the system.<sup>1,2</sup>

Haddon applied the perturbational molecular orbital (PMO) method to extract information regarding the difference in properties (such as



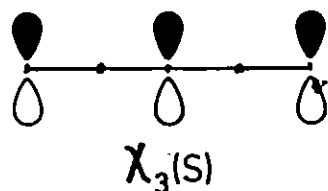
energy, charge density and bond orders) of homoaromatic systems with reference to their parent aromatic systems.<sup>71</sup> In this treatment he considered the homoaromatic system to be a perturbed form of the aromatic system, in which the resonance integral of one bond is reduced as a result of the homoconjugate linkage. The presence of an "open" cyclopropane unit is implied in this treatment.



Information regarding the influence of a single homoconjugate linkage on the  $\pi$  electron energy, the effect of a second homoconjugate linkage on the homoaromatic stability, the effects of substituents, charge density distribution and prediction of homoaromaticity in annelated systems could be obtained.<sup>77</sup> Though not entirely in agreement with the experimental observations, the results of these calculations were, by and large, good when the simplicity of the theory was taken into account.

In a second approach to the problem of homoaromaticity and the mechanism of homoconjugation, Haddon considered the interaction between an intact cyclopropane and the residual  $\pi$  system.<sup>78</sup> The conclusions reached in this case were the same as those obtained from his PMO treatment, which considered the cyclopropane unit to be relatively "open".<sup>71</sup> For example, the highest-occupied, degenerate (symmetric) cyclopropane

ish orbital ( $\psi_2S$ ) can have positive interaction with the (symmetric) lowest unoccupied molecular orbital (LUMO,  $\chi_3S$ ) of pentadienyl cation. Transfer of electron density from cyclopropane to the pentadienyl unit leads to the lengthening of the internal cyclopropane bond, in the case of 5.



Haddon re-examined the geometry of homotropylium cation using the semi-empirical MINDO/3 method with full geometry optimization, allowing the seven-membered ring to relax from planarity.<sup>79</sup> The energy minimum corresponding to this nonplanar geometry was found to be 3 kcal/mole lower than that for the geometry with a planar seven-membered ring. This effect has been ascribed to the improved overlap of the  $p\pi$  orbitals of the incipient pentadienyl cation with the symmetric HOMO of the cyclopropane Walsh function. The convex deformation of the seven membered ring and the out of plane bending of the C-H bond have been suggested to operate in concert to facilitate this interaction. The elongation of the homoconjugate linkage to 1.621 Å is in favor of an open cyclopropane structure 5 (Figure 3).<sup>13</sup>

There is an obvious disagreement between Hehre's ab initio calculations and the MINDO/3 calculations of Haddon regarding the geometry of 5. This is due to the partial geometry optimization with the seven-membered ring restricted to planarity and also to the inadequacy of the calculation

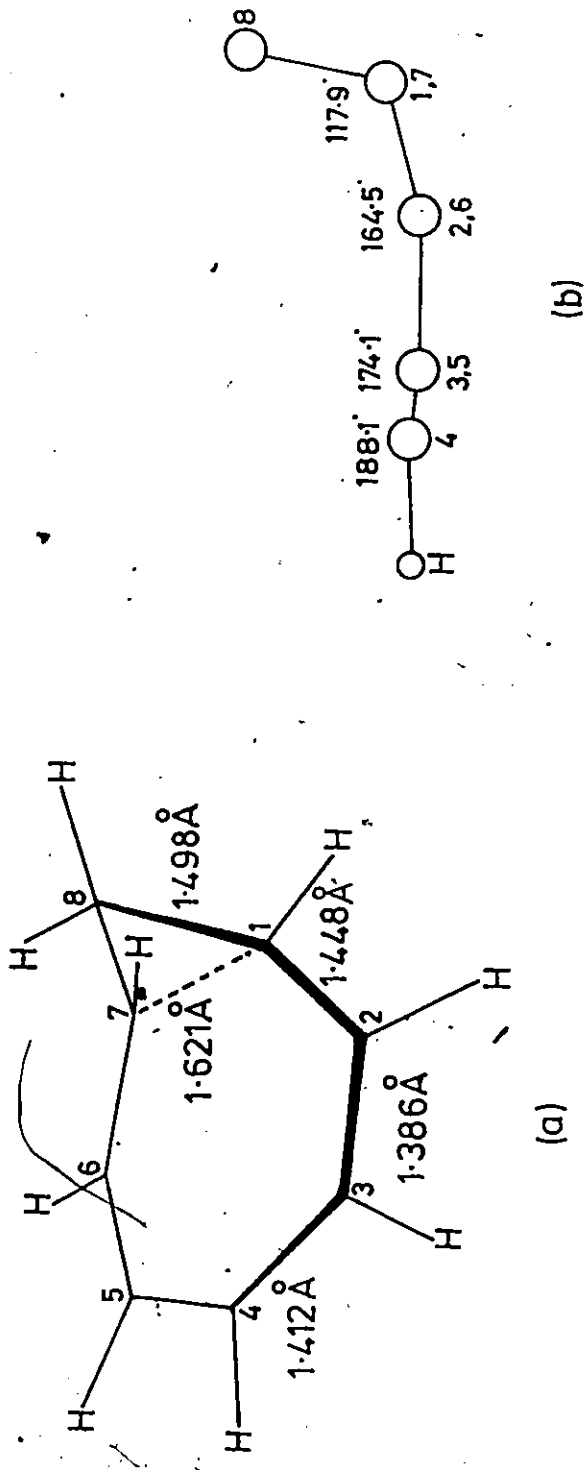


Figure 3 MINDO/3 Structure for the Homotropylium Cation

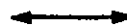
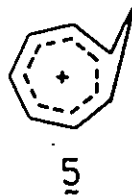
(a) Bond Distances and (b) Interplanar Angles.

technique employed by Hehre.<sup>13</sup>

Haddon has recently performed extensive ab initio (STO-2G, STO-3G and 4-31G) as well as semi-empirical (MINDO/3) calculations on homotropylium cation **5**.<sup>13</sup> Ab initio STO-2G geometry optimization for the homotropylium cation **5** yielded a homoconjugate bond length of 1.578 Å. This has brought the ab initio calculations in line with the MINDO/3 studies, FMO theory and Winstein's picture of an open cyclopropane unit in homotropylium cation.

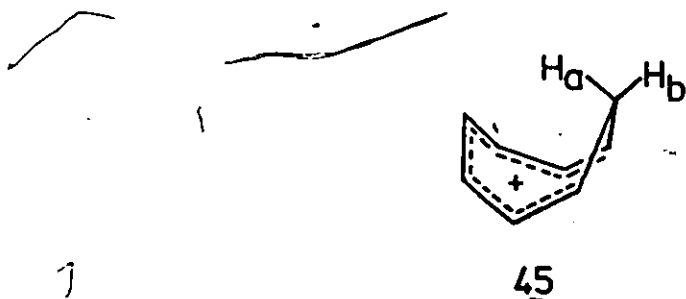
Haddon's calculations brought forth certain well-defined trends in homoaromatic cations.<sup>13</sup> Haddon concluded that in homoaromatic species such as **5**, "non planarity in the basal plane, shortened bondlengths between the polyenyl and bridge fragments, bond equalization in the polyenyl segment and lengthening of the homoconjugate linkage operate in concert to confer homoaromatic character" (eg. Figure 3).

Haddon calculated the STO-3G  $\pi$  type localized molecular orbitals (LMO) on the STO-2G structure for **5**.<sup>13</sup> The  $\pi$  type LMOs here indicate the conjugation of an intact cyclopropane unit with a pentadienyl cation in which each component has retained its integrity **44**. Haddon argues that on the basis of the LMO picture, homotropylium cation should be regarded as a resonance hybrid between the fully delocalized ion **5** and one with an intact cyclopropane unit **22**, in which the contribution from the former predominates.



b. Energetics

Homotropylium cation and the planar cyclooctatrienylium cation 21 (the transition state proposed by Winstein for the ring inversion or bridge flipping process occurring in homotropylium cation) were found to be markedly nonplanar when fully optimized.<sup>13</sup> Ab initio calculations indicated that the nonplanar cyclooctatrienylium cation 45 lies no more than 10 kcal/mole higher in energy than homotropylium cation. Haddon suggested 45 as an intermediate in the ring inversion process.



"Homoaromatic interaction" is supposed to be present in 45.<sup>77,80</sup> This is revealed by the consistent trend toward bond equalization (when compared to acyclic models) and the 1,7 interatomic distance of 2.303 Å. The geometry of the ring allows the 1,7 overlap beneath the ring. Haddon's revised energy profile for the ring inversion process 5 → 5' is shown in Figure 4.

Homoaromatization energy has been redefined as the energy difference between 5 and 45 (< 10 kcal/mole) instead of that between 5 and 21 (22.3 kcal/mole).<sup>13,53</sup> To quote Haddon, "The very existence of homoaromaticity is a matter of a few kcal/mole". Jorgensen probed the energetic importance of homoaromaticity using MINDO/3, EH (extended Hückel) and PMO calculations.<sup>12</sup> His calculations yielded the conclusion

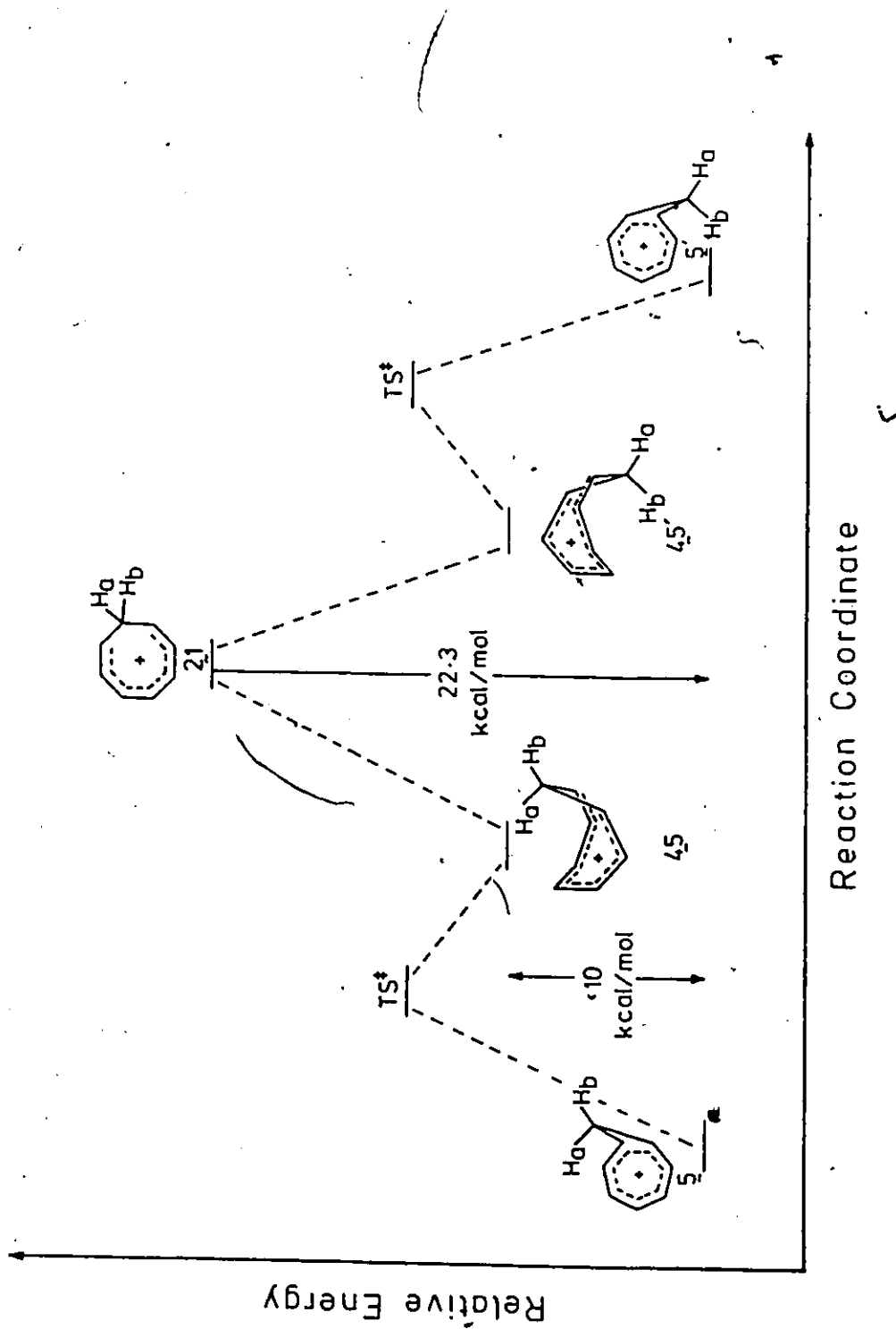


Figure 4 Haddon's Revised Energy Profile for the Ring Inversion Process in Homotropylium Cation 5.



Table 2

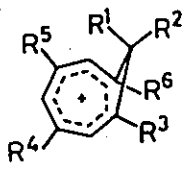
Homotropylium Cation Derivatives

Systems	$\Delta\delta$ (ppm) <sup>a</sup>	Reference
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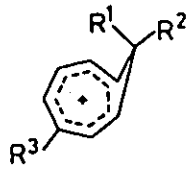
A. Metal Complexes

46	M=Cr		4.45	81
24	M = Mo		3.62	81
26	M = W		3.51	81

B. Alkyl and aryl derivatives

				
47	$R^3=CH_3, R^1=R^2=R^4=R^5=R^6=H$		5.0	82
48	$R^3=C_6H_5, R^1=R^2=R^4=R^5=R^6=H$		5.33	82
49	$R^3=R^4=R^5=R^6=CH_3, R^1=R^2=H$		2.72	83
50	$R^3=R^4=R^5=R^6=H, R^1=R^2=CH_3$		2.84 <sup>c</sup>	84

C. 8-Substituted derivatives<sup>b</sup>

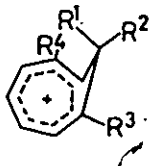
				
51	$R^1=Cl, R^2=R^3=H$ ; 52 $R^1=R^3=H, R^2=Cl$		5.69-5.8	85-89
53	$R^1=Br, R^2=R^3=H$ ; 54 $R^1=R^3=H, R^2=Br$		6.061	86,88
55	$R^1=R^3=H, R^2=I$			86
56	$R^1=R^3=H, R^2=OH$			86



57	$R^1 = \text{SO}_2(\text{SbF}_5)_2$ $R^2 = R^3 = \text{H}$	58	$R^2 = \text{SO}_2(\text{SbF}_5)_2$ $R^1 = R^3 = \text{H}$	5.33	90-92
59	$R^1 = \text{SO}_2(\text{SbF}_5)_2$ $R^2 = \text{H}, R^3 = \text{CH}_3$	60	$R^2 = \text{SO}_2(\text{SbF}_5)_2$ $R^1 = \text{H}, R^2 = \text{CH}_3$	4.03	92
61	$R^1 = \text{SO}_2(\text{SbF}_5)_2$ $R^2 = R^3 = \text{CH}_3$	62	$R^2 = \text{SO}_2(\text{SbF}_5)_2$ $R^1 = R^3 = \text{CH}_3$	2.31 <sup>c</sup>	92

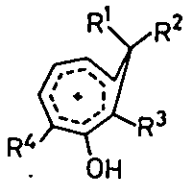
D. Hydroxy derivatives

i. 1-Hydroxy derivatives



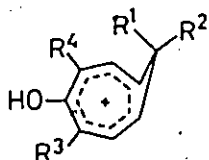
63	$R^3 = \text{OH}, R^1 = R^2 = R^4 = \text{H}$	3.08	93
64	$R^3 = \text{OCH}_3, R^1 = R^2 = R^4 = \text{H}$	3.1, 3.25	94, 95
65	$R^3 = R^4 = \text{OH}, R^1 = R^2 = \text{H}$	2.67	96
66	$R^3 = \text{OH}, R^2 = R^4 = \text{H}, R^1 = \text{CH}_3$	1.56 <sup>b,c</sup>	
67	$R^3 = \text{OH}, R^1 = R^4 = \text{H}, R^2 = \text{CH}_3$	3.86 <sup>b</sup>	84
68	$R^3 = \text{OH}, R^4 = \text{H}, R^1 = R^2 = \text{CH}_3$	1.95 <sup>c</sup>	84

ii. 2-Hydroxy derivatives



69	$R^1 = R^2 = R^3 = R^4 = \text{H}$	3.1	97
70	$R^1 = R^3 = R^4 = \text{H}, R^2 = \text{COOC}_2\text{H}_5$		98
71	$R^1 = \text{CH}_3, R^2 = R^3 = R^4 = \text{H}$	1.17 <sup>b,c</sup>	84
72	$R^2 = \text{CH}_3, R^1 = R^3 = R^4 = \text{H}$	3.13 <sup>b</sup>	84
73	$R^1 = R^2 = \text{CH}_3, R^3 = R^4 = \text{H}$	1.24 <sup>c</sup>	84
74	$R^1 = R^2 = R^3 = \text{CH}_3, R^4 = \text{H}$	1.63 <sup>c</sup>	84
75	$R^1 = R^2 = R^4 = \text{CH}_3, R^3 = \text{H}$	1.74 <sup>c</sup>	84

iii. 4-Hydroxy derivatives



76	$R^1=R^2=R^3=R^4=H$	4.6	99
77	$R^1=R^2=H, R^3=R^4=CH_3$	5.0	100
78	$R^1=R^2=CH_3, R^3=R^4=H$	1.62 <sup>C</sup>	84
79	$R^1=R^2=R^3=CH_3, R^4=H$	2.13 <sup>C</sup>	84

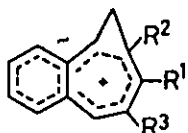
E. Benzannelated derivatives

i. Monobenzo derivatives

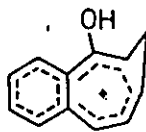


80

3.86 101



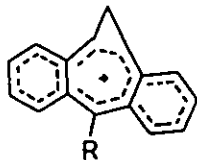
81	$R^1=R^2=R^3=H$	5.34	16
82	$R^1=OH, R^2=R^3=H$	2.41	16,102
83	$R^1=OH, R^2=R^3=CH_3$	2.29	102
84	$R^1=OH, R^2=R^3=(CH_2)_n$		103
	$n=5,7,9,10,12$		



85

2.3 15

ii. Dibenzo derivatives

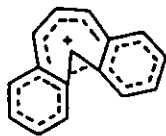


86	R=H	4.67	104
87	R=OH	3.96	104



88

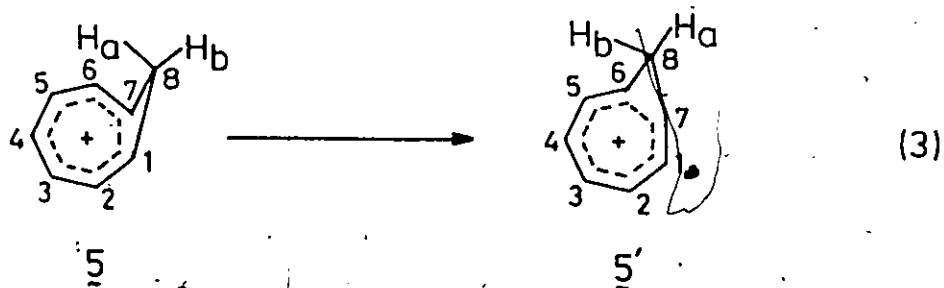
3.2	105
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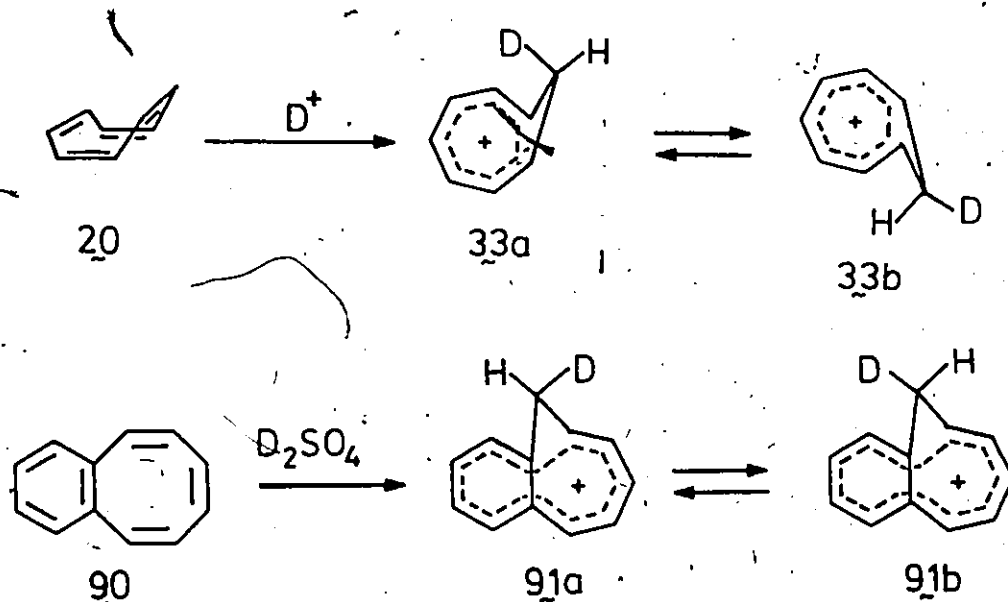
89

2.31	106
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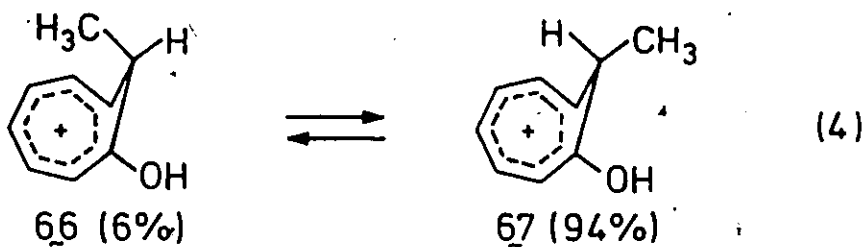
- a  $\Delta\delta$  is the difference in chemical shifts for the endo and exo protons on the methylene carbon.
- b Obtained from the difference in chemical shifts for the endo proton of the exo isomer and exo proton of the endo isomer.
- c  $\Delta\delta$  values for methyl groups.

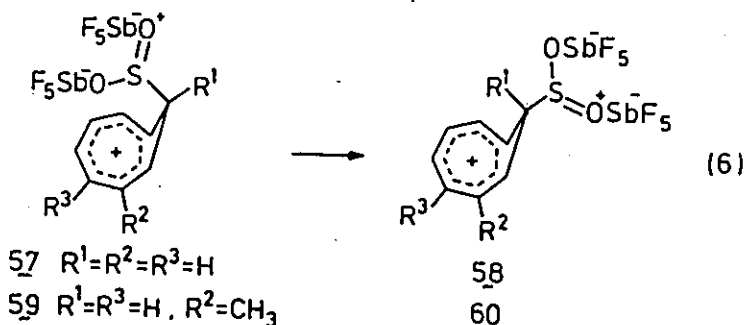
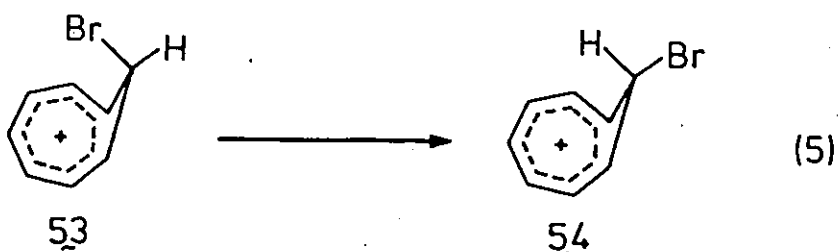


The ring inversion process was observed first by Winstein in the deuteration studies on cyclooctatetraene 20 as mentioned earlier, and later by Pettit in the case of deuteration of benzocyclooctatetraene 90.<sup>53,101</sup>

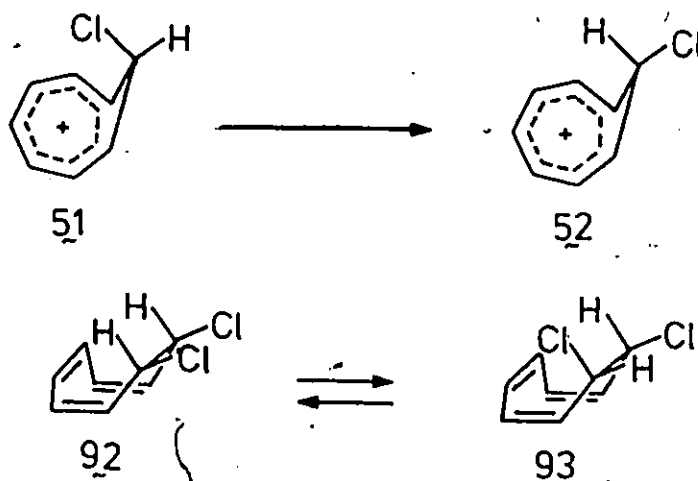


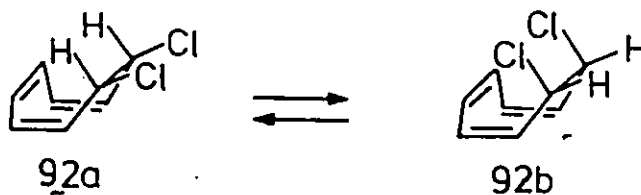
In the case of a deuterium substituent on  $C_8$  an equal proportion of 8-exo and 8-endo isomers is observed at equilibrium. With bulkier  $C_8$  substituents, the inversion process leads to the 8-exo isomer as the major or the only observable isomer (equations 4, 5 and 6).<sup>84,88,90,92</sup>





The sterically preferred 8-exo isomers are thermodynamically more stable. In the case of the 8-methyl-1-hydroxyhomotropylum cations 66 and 67, the exo isomer 67 was found to be 1.48 kcal/mole more stable than the endo isomer 67.<sup>84</sup> In the case of 8-chlorohomotropylum cations, the 8-exo isomer 52 is calculated to be more stable than the 8-endo isomer 51 by at least 2 kcal/mole.<sup>89</sup> This value was arrived at from an extensive study of the conversion of the endo isomer 52 to the exo isomer 53, the cis-trans interconversion of 7,8-dichlorocyclooctatrienes 92 and 93 and the exo-endo ring inversion in the cis-7,8-dichlorocyclooctatrienes 92a and 92b.<sup>89</sup>





The energy profiles for the ring inversion process based on Winstein's and Haddon's proposals are given in Figures 2 and 4.<sup>53,13</sup> Electron donating substituents at C<sub>7</sub> in 5, that can stabilize the possible planar cyclooctatrienyl cation transition state 21, lower the barrier to the inversion process.<sup>84,94</sup> Table 3 lists some examples of the inversion process and the reported activation barriers.

The original mechanism proposed by Winstein for the ring inversion process (equation 2), did not consider the possibility of the intervention of a circumambulatory rearrangement (equation 3).<sup>53</sup>

A circumambulatory rearrangement is defined as "a molecular rearrangement in which an atom or group of atoms migrates around the periphery of a ring in such a way that during a series of such reactions, the atom or group of atoms can become bonded to any of the ring carbons."<sup>107</sup>

This type of rearrangement has been observed in several systems. A typical example is shown in equation 7 for the bicyclo[3.1.0]hexenyl cation 94. In this system this degenerate isomerization has been observed to occur with a low activation barrier (15 kcal/mole for 94 and lower in the case of methyl substituted derivatives).<sup>108,112</sup>

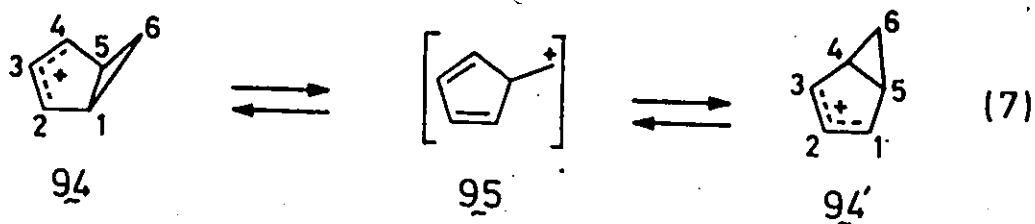
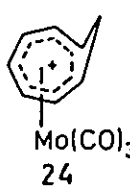
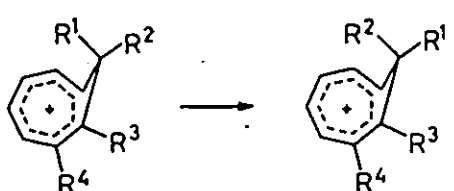


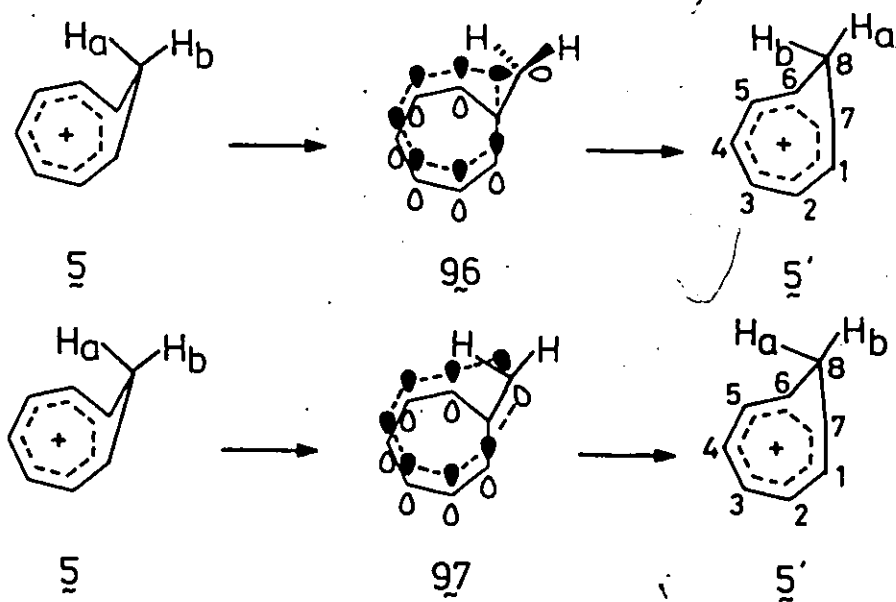
Table 3

Examples of ring inversion process in homotropylium cations

System	Activation barrier $\Delta G^\ddagger$ (kcal/mole)	Reference
 <p>Mo(CO)<sub>3</sub> 24</p>	>16*	52
		
<u>34a</u> $R^1=D$ ; $R^2=R^3=R^4=H$ ; <u>34b</u> $R^2=D$ , $R^1=R^3=R^4=H$	22.3	53
<u>51</u> $R^1=Cl$ , $R^2=R^3=R^4=H$ ; <u>52</u> $R^2=Cl$ , $R^1=R^3=R^4=H$	22.6	85,89
<u>63</u> $R^3=OH$ , $R^1=R^2=R^4=H$	>20*	93
<u>64a</u> $R^3=OCH_3$ , $R^1=D$ , $R^2=R^4=H$ ;	19.6	94
<u>64b</u> $R^3=OCH_3$ , $R^2=D$ , $R^1=R^4=H$		
<u>66</u> $R^3=OH$ , $R^1=CH_3$ , $R^2=R^4=H$ ;	17.1	84
<u>67</u> $R^3=OH$ , $R^2=CH_3$ , $R^1=R^4=H$		
<u>71</u> $R^4=OH$ , $R^1=CH_3$ , $R^2=R^3=H$ ;	>27*	84
<u>72</u> $R^4=OH$ , $R^2=CH_3$ , $R^1=R^3=H$		

\* Limiting values.

In homotropylium cations, this rearrangement process can occur via an eclipsed transition state 96 which is favored by the orbital symmetry rules<sup>113</sup> but disfavored by the least motion principle.<sup>114-117</sup> It can also occur via a bisected transition state 97 which is orbital symmetry forbidden but least motion allowed.

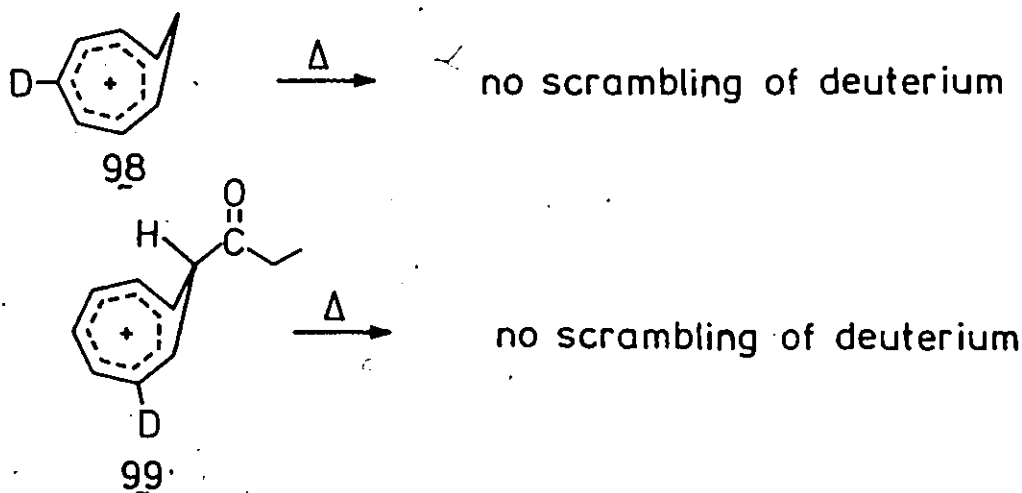


The migration via the eclipsed transition state 96 leads to the retention of configuration around the migrating centre while the bisected transition state leads to an inversion of configuration around the carbon that migrates. In other words, the endo-exo integrity of groups on C<sub>8</sub> would be lost in a symmetry allowed process but retained in a symmetry forbidden process.

It is therefore possible to visualize the endo-exo interconversion process 5 → 5' (equation 2) to occur via the symmetry allowed 1,6 migration of the C<sub>8</sub> methylene (equation 3). But in the case of homotropylium cations with substituents attached to the seven-membered ring, the ring inversion proceeds without the scrambling of the substituents.



in the seven-membered ring (equations 4,6 and reaction 64a + 64b, Table 3).<sup>84,92,94</sup> This rules out the circumambulatory rearrangement process as being responsible for the ring inversion. Further support came from the experiments of Berson and Jenkins.<sup>118</sup> In their studies of the thermal reaction of 4-deuteriohomotropylium cation 98 and 2-deuterio-exo-8-carboethoxyhomotropylium cation 99, no scrambling of the labels was observed. Instead, the cations underwent decomposition on heating.



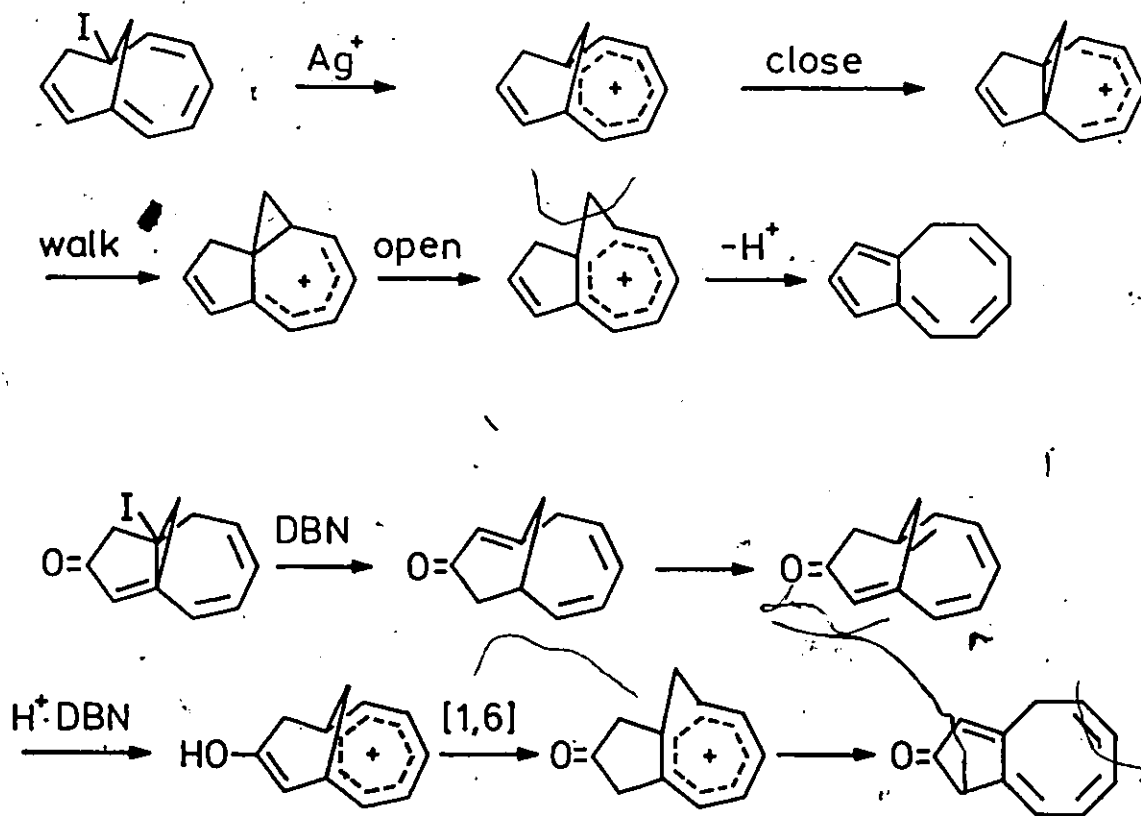
Berson and Jenkins have placed an experimental lower bound of 26-27 kcal/mole for the barrier to the degenerate circumambulatory process in these systems. This higher energy process, therefore, cannot be involved in the ring inversion process which has a lower activation energy. Berson and Jenkins have suggested that the loss of homoaromaticity in the transition state, as well as the inefficient orbital overlap in the transition state due to the twisting motion of the migrating carbon in the allowed pathway, could lead to the lack of occurrence of such a process.

The lack of experimental observation of the circumambulatory process led Hehre to examine the process by means of theoretical studies

using ab initio STO-3G calculations.<sup>74</sup> In the discussion of the theoretical studies on the structure of homotropylium cation, it has been mentioned before that due to defects in geometry optimization and in the method of calculation, the results of Hehre are inconsistent with those of Haddon and with experimental observations.<sup>13,74</sup> Quantitative significance, therefore, cannot be attached to Hehre's results, but qualitative conclusions regarding the trends observed must still hold. Hehre concluded that migration of the methylene through the symmetry allowed transition state was associated with a high barrier, owing to the loss of homoaromatic stability in the transition state. The migration via symmetry forbidden process was calculated to involve an even larger energy of activation. Stabilization of the charge that develops on the migrating carbon in the transition state, by two methyl substituents on the migrating carbon, was calculated to lower the energy barrier to migration. In fact, in such a case, Hehre's calculations showed that the symmetry forbidden process would be the favored mode.

The search for circumambulatory processes in homotropylium cation had gone unrewarded for quite some time. Recently Scott and Brunsvold reported the first instance of the migration of an unsubstituted methylene in homotropylium cations.<sup>119</sup> It was proposed that the steric factors arising from the bridging of the homoconjugate linkage favor the easy closure to the classical cation, facilitating the circumambulatory migration. These reactions are represented in Scheme 1.

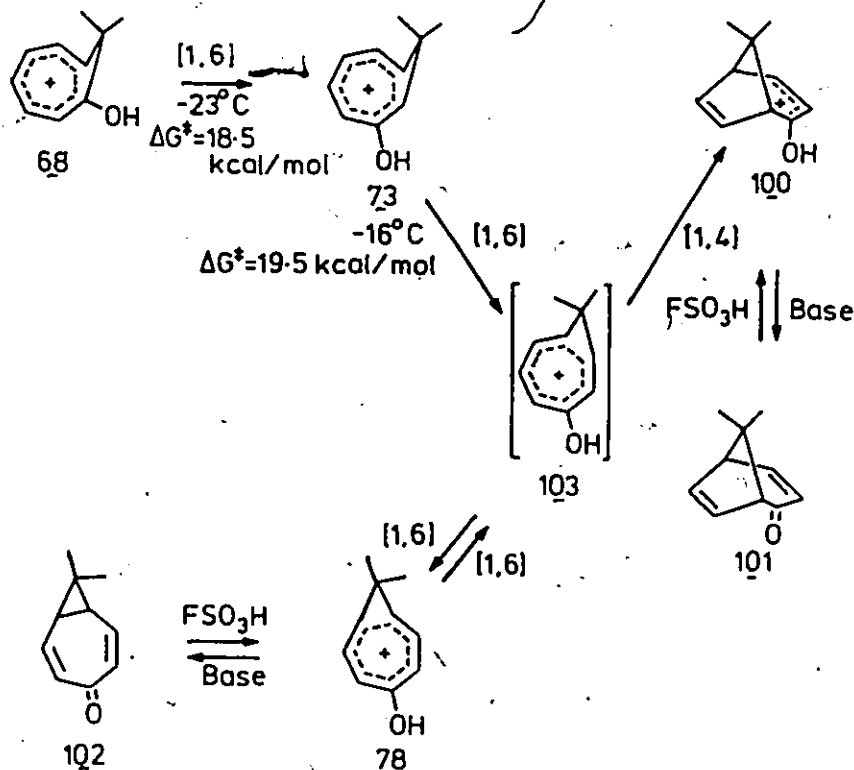
Childs and Rogerson were the first to observe circumambulatory rearrangements in homotropylium cations.<sup>84</sup> They observed that 8,8-dimethyl-1-hydroxyhomotropylium cation 68 isomerized to the 2-

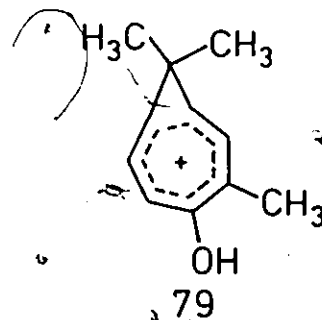
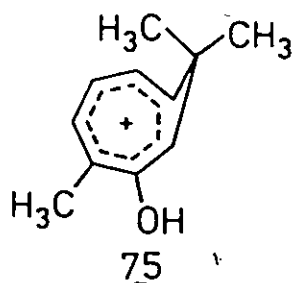
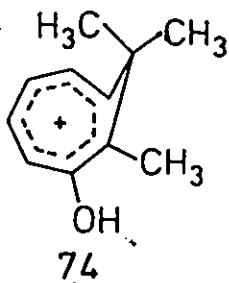


Scheme 1

2-hydroxy isomer 73, at  $-23^{\circ}\text{C}$ . The activation free energy of such a process was found to be 18.5 kcal/mole. In agreement with Hehre's suggestion, the dimethyl substitution at  $\text{C}_8$  has permitted ground state circumambulation in homotropylium cations. The lower limit for the difference in activation energy associated with the migration of  $\text{C}_8$  with one and two methyl groups was found to be 6.5 kcal/mole. This suggests that  $\text{C}_8$  bears substantial positive charge in the transition state, which is in line with the prediction of Hehre.

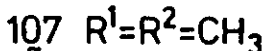
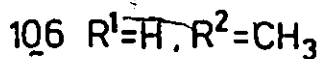
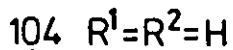
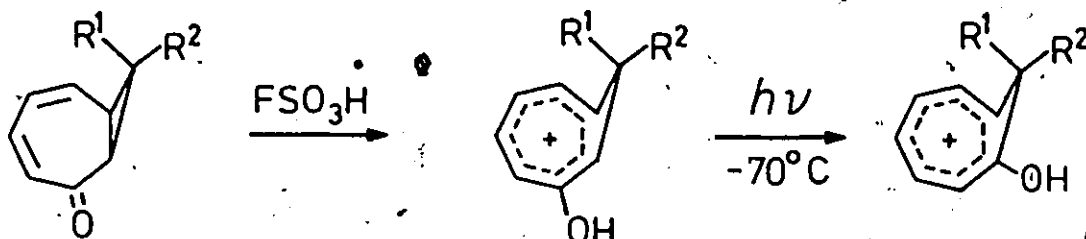
The 2-hydroxy isomer 73 underwent a further series of rearrangements at somewhat higher temperatures ( $-16^{\circ}\text{C}$ ), eventually forming 100, the protonated form of bicyclo[3.2.1]octa-3,6-diene-2-one 101. The 8,8-dimethyl-4-hydroxyhomotropylium cation 78 was found to be an observable intermediate.



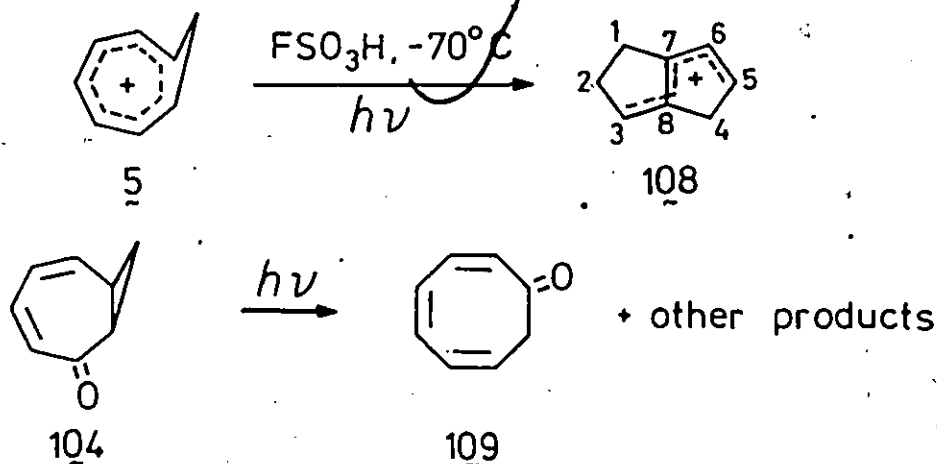


The mechanism of the rearrangement was examined by following the course of the reactions of cations 74 and 75, which had methyl label in the ring positions 1 and 3 respectively. Again, the 4-hydroxy isomer 79 was an observable intermediate. It was shown that the rearrangement proceeded via a 1,6 sigmatropic shift and the 3-hydroxyhomotropylium cation 103 was an unobserved intermediate.

Childs and Rogerson have also observed circumambulatory rearrangements in the excited state of homotropylium cations.<sup>84</sup> Irradiation of the 2-hydroxyhomotropylium cations 69, 71, 72 and 73, at  $-70^{\circ}\text{C}$ , led to the production of the corresponding 1-hydroxy isomers 63, 66, 67 and 68, respectively. The conversion of 71 to 66 proceeded with 94% stereoselectivity. This observation showed that this excited state rearrangement occurred very largely via the "bisected" transition state 97, in accord with orbital symmetry rules and the least motion principle.



It is to be noted that the irradiation of homotropylium cation 5 itself, gave 1,2-dihydro-4H-pentalenyl cation 108.<sup>120,121</sup> Irradiation of unprotonated 2,3-homotropone 104 gave cyclooctatrienone 109 as a minor product.<sup>122</sup> The occurrence of circumambulations in these cases, however, is uncertain.



### III. OBJECTIVES OF THE PRESENT STUDY

It is clear that there is a great need for definitive structural evidence for homoaromaticity.<sup>4</sup> As mentioned before,  $^1H$  NMR spectroscopy has been the primary method of studying the homoaromatic species. The existence of cyclic delocalization is inferred from the induced diamagnetic ring current proposed to account for the unusual proton chemical shifts.

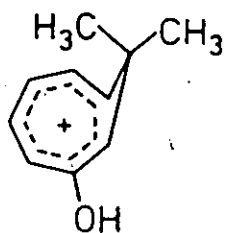
At the present time the concept of aromaticity itself is questioned and a critical test or an unambiguous criterion to define the concept is needed.<sup>123-125</sup> The ring current theories and their use as a criterion for aromaticity in general, have not escaped criticism.<sup>126-130</sup> Some measure of support comes from Haddon's recent proposal of a unified theory linking ring current to resonance energy and aromatic character

in Hückel annulenes.<sup>131-133</sup> But limitations on the use of ring current in NMR studies as a criterion for aromaticity still continue to exist.

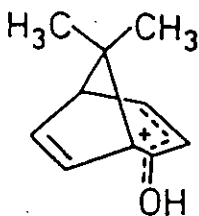
Definitive evidence for homoaromatic delocalization could be obtained if the molecular structure of homotropylium cation could be determined. The present study is therefore aimed at attempts to determine the structure of homotropylium cations by means of X-ray structural analysis on single crystals of these cation salts.

The stability of homotropylium cations is the next question addressed. It has always been stated that homoaromaticity bestows a system with enhanced stability. Theoretical attempts have been made by Hehre, Jorgensen and Haddon in this regard.<sup>12,13,74</sup> But experimental attempts to quantify the energy associated with and hence the stability of these systems are lacking. Even if it is not possible to measure the absolute stabilities of these ions due to experimental difficulties, estimates regarding their relative stabilities are highly desirable. To this end, a calorimetric investigation of the thermodynamic importance of conjugation and homoconjugation has been undertaken.

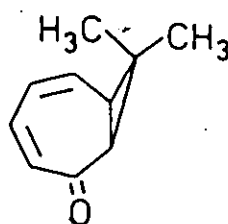
A further attempt to evaluate the energetic consequences of homoaromaticity was made using the cations 73 and 100. These cations represent two extremes, 73 being homoaromatic and 100 being nonaromatic or even antihomoaromatic. The approach used involved the attempt to estimate relative difference in energy between the ketones 107 and 101 and comparison of this value with that between the cations 73 and 100.



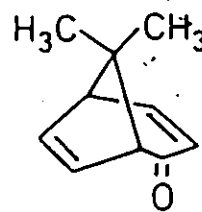
73



100



107



101

The circumambulatory rearrangements of homotropylium cations warrant further study. Occurrence of such rearrangements has been well established in the case of hydroxyhomotropylium cations with two methyl substituents on  $C_8$ . It would be of interest to extend this study to nonhydroxy systems. Methyl substitution in the 7-membered ring of these cations would indicate relative stability of and hence the site preference of methyl groups in the different isomers, besides aiding in the observation of the degenerate rearrangements.

Finally, it would be of interest to compare the properties of a homoaromatic system with a structurally similar nonhomoaromatic system. As mentioned before, an irontricarbonyl group would effectively convert a nonclassical  $6\pi$  homoaromatic cation to a classical  $4\pi$  5C penta-dienylic cation. In this regard, iron complexes having the homotropylium cation precursors as ligands were studied under comparable conditions.

The results of these studies are reported in succeeding chapters.



RESULTS AND DISCUSSION.

## CHAPTER 2

### STRUCTURAL STUDIES ON HOMOTROPYLIUM SALTS

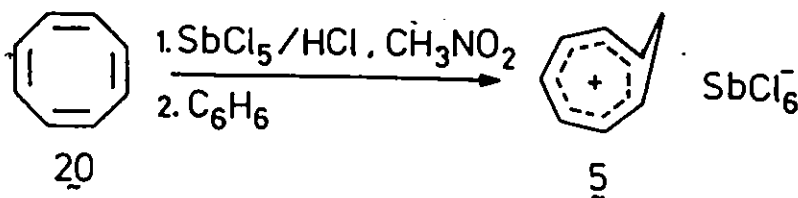
Homoaromatic delocalization in homotropylium cation 5 has been inferred primarily from NMR techniques.<sup>1-4</sup> Due to the limitation of this technique for use as the only criterion for homoaromaticity, a direct method of structural analysis by x-ray diffraction becomes important.

#### 1. Isolation and Attempts on Crystallization of the Salts of Parent Homotropylium Cation

##### a. *Homotropylium Hexachloroantimonate*

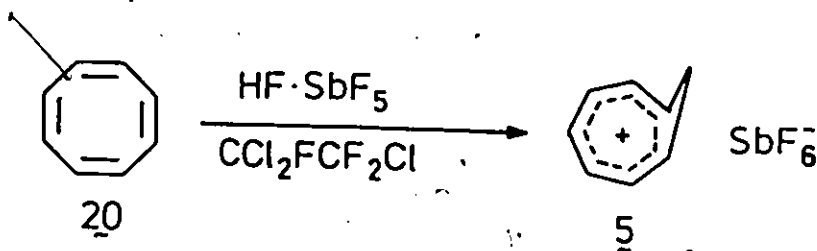
The system of choice for the structural study, namely, the homotropylium cation itself, has been obtained in the solid state as its hexachloroantimonate salt by Pettit and coworkers.<sup>51</sup> Previous attempts in this laboratory to obtain crystalline material from this solid were not successful.<sup>134</sup>

Considerable further work in this direction was undertaken by the author of this thesis. The hexachloroantimonate salt was prepared from cyclooctatetraene 20 by the method of Pettit.<sup>51</sup> All the attempts to recrystallize the solid using a wide variety of solvents and techniques were unsuccessful.



b. *Homotropylium Hexafluoroantimonate*

In the hope of obtaining crystalline sample of 5, it was decided to isolate the cation with different counterions. A "hexafluoroantimonate" salt of 5 was obtained by the reaction of cyclooctatetraene with  $\text{HF} \cdot \text{SbF}_5$  (1:1 mixture) using  $\text{CCl}_2\text{F} \cdot \text{CF}_2\text{Cl}$  as the solvent. The NMR spectrum of a  $\text{SO}_2$  solution of the yellow solid obtained from this reaction was found to be identical to that of homotropylium cation previously reported.<sup>51</sup> Like the hexachloroantimonate salt, this solid also failed to give suitable crystals on recrystallization. Satisfactory elemental analysis could not be obtained for this salt, probably due to the indefinite stoichiometry of the counterion.



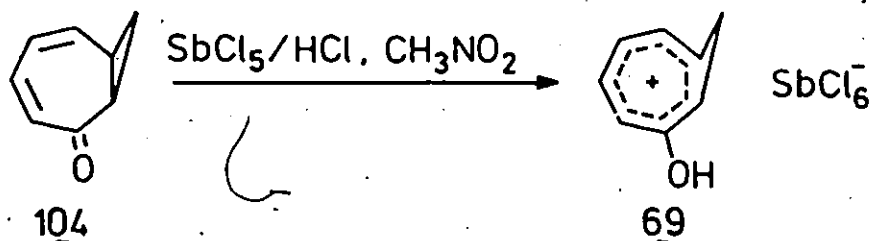
As attempts to isolate the cation 5 with various other counterions were unsuccessful, attention was turned to the derivatives of homotropylium cation.

2. Structural Studies on 2-Hydroxyhomotropylium Hexachloroantimonate 69

The 2-hydroxyhomotropylium cation 69 has been claimed to be homoaromatic on the basis of its NMR spectrum.<sup>84,97</sup> This cation was chosen as the next alternative for structural analysis, particularly as the hexachloroantimonate salt has been isolated previously as a solid.<sup>97</sup> In this case the effort was more successful.

a. Isolation and Characterization

The 2-hydroxyhomotropylum cation 69 was prepared as its hexachloroantimonate salt in a manner similar to that described by Holmes and Pettit.<sup>97</sup> 2,3-homotropone 104 was added to a mixture of HCl and SbCl<sub>5</sub> in nitromethane and the resulting mixture diluted with benzene to precipitate a yellow salt from solution.



The <sup>1</sup>H NMR spectrum of 69 in SO<sub>2</sub> was very similar to that of 104 when protonated in H<sub>2</sub>SO<sub>4</sub> (Figure 5).<sup>97</sup> The <sup>1</sup>H NMR spectrum of the salt consists of a sharp singlet at δ 8.0 ppm attributed to the resonance of -OH proton, a multiplet at δ 7.7 ppm corresponding to the resonances of H<sub>4</sub> and H<sub>6</sub>, a multiplet at 7.0 ppm for the resonances of H<sub>3</sub> and H<sub>5</sub>, a multiplet at δ 3.78 ppm for those of H<sub>1</sub>, H<sub>7</sub> and H<sub>8</sub> exo and a multiplet of δ 0.5 ppm for that of H<sub>8</sub> endo. The principal difference between the spectrum of the salt in SO<sub>2</sub> and that of the protonated ketone in H<sub>2</sub>SO<sub>4</sub> lies in the position of the -OH resonance. In the latter case, rapid exchange of the proton on oxygen with the solvent pool is expected to occur.

The <sup>13</sup>C NMR spectrum of 69 was obtained for solutions of the ketone 104 in D<sub>2</sub>SO<sub>4</sub> and of the hexachloroantimonate salt of 69 in CD<sub>2</sub>Cl<sub>2</sub>. Signal assignments were made by selective proton decoupling

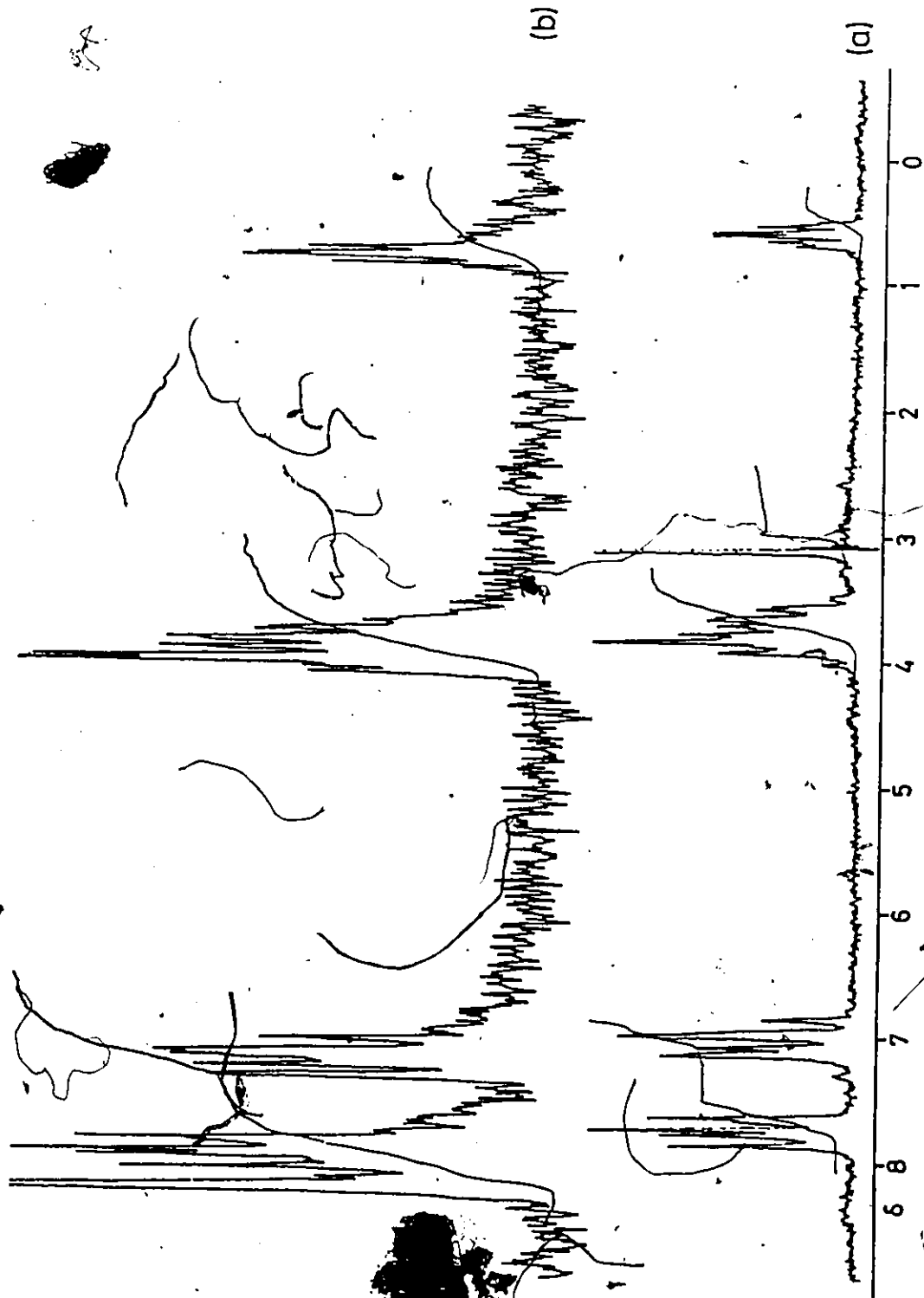
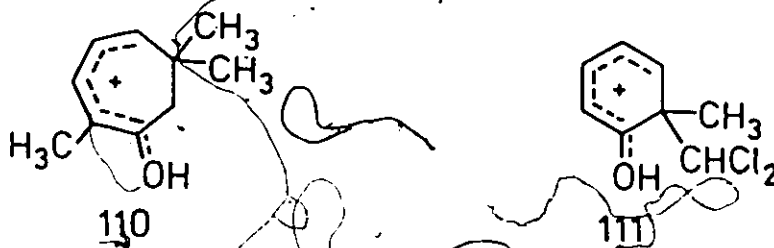


Figure 5  $^1\text{H}$  NMR Spectrum of 2-hydroxyhomotropylum Cation (a)  $2,3$ -homotropone in  $\text{D}_2\text{SO}_4$  and (b) 2-hydroxyhomotropylum hexachloroantimonate in  $\text{SO}_2$ .

and by comparison with the  $^{13}\text{C}$  NMR spectra of protonated eucarvone 110 and other protonated dienones, eg., 111.<sup>135,136</sup> The data are given in Table 4.



It can be seen from the data in Table 4 that the two solution spectra are again very similar. It can be concluded that the cation present in the  $\text{CD}_2\text{Cl}_2$  solution of the salt obtained by the treatment of homotropone 104 with a mixture of  $\text{HCl}$  and  $\text{SbCl}_5$  is the same as that generated from 104 in  $\text{D}_2\text{SO}_4$ . The question arises as to whether the salt in the solid state is still ionic.

The narrow-line  $^{13}\text{C}$  NMR spectrum of the solid salt was obtained under cross-polarization magic angle spinning (CPMAS) conditions by Drs. C.A. Fyfe and R.E. Wasylishen at the University of Guelph.

Isotropic chemical shifts can be obtained by this technique and these can be compared with those observed for solution spectra. From Table 4 and Figure 6, it can be seen that there is a close similarity between the positions of the resonances in the  $^{13}\text{C}$  NMR spectra of the cation 69 in the solid state and in solution. (The broadness of the  $^{13}\text{C}$  signals in the solid state spectrum is probably caused in part by quadrupolar interactions of the chlorines in the counterion and is not considered to be a significant factor.) The maximum difference in

Table 4

<sup>13</sup>C NMR Chemical Shifts of 69

Solvent or Phase	Chemical Shift (ppm) <sup>b</sup>							
	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>
D <sub>2</sub> SO <sub>4</sub>	52.5 <sup>a</sup>	199.0	127.0 <sup>c</sup>	155.6	119.6 <sup>c</sup>	152.5	56.3 <sup>a</sup>	28.4
CD <sub>2</sub> Cl <sub>2</sub>	51.2 <sup>a</sup>	199.7	126.9 <sup>c</sup>	154.9	120.5 <sup>c</sup>	152.0	56.0 <sup>a</sup>	28.2
solid	54.5	194.1	127.7	157.0	119.1	151.9	60.4	30.2

a,c Assignments may be reversed.

b Chemical shifts are referred to CD<sub>2</sub>Cl<sub>2</sub> (δ 53.6 ppm) in CD<sub>2</sub>Cl<sub>2</sub>; CDCl<sub>3</sub> (internal, δ 76.95 ppm) in D<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>OH (external, δ 49.17 ppm) for the solid.

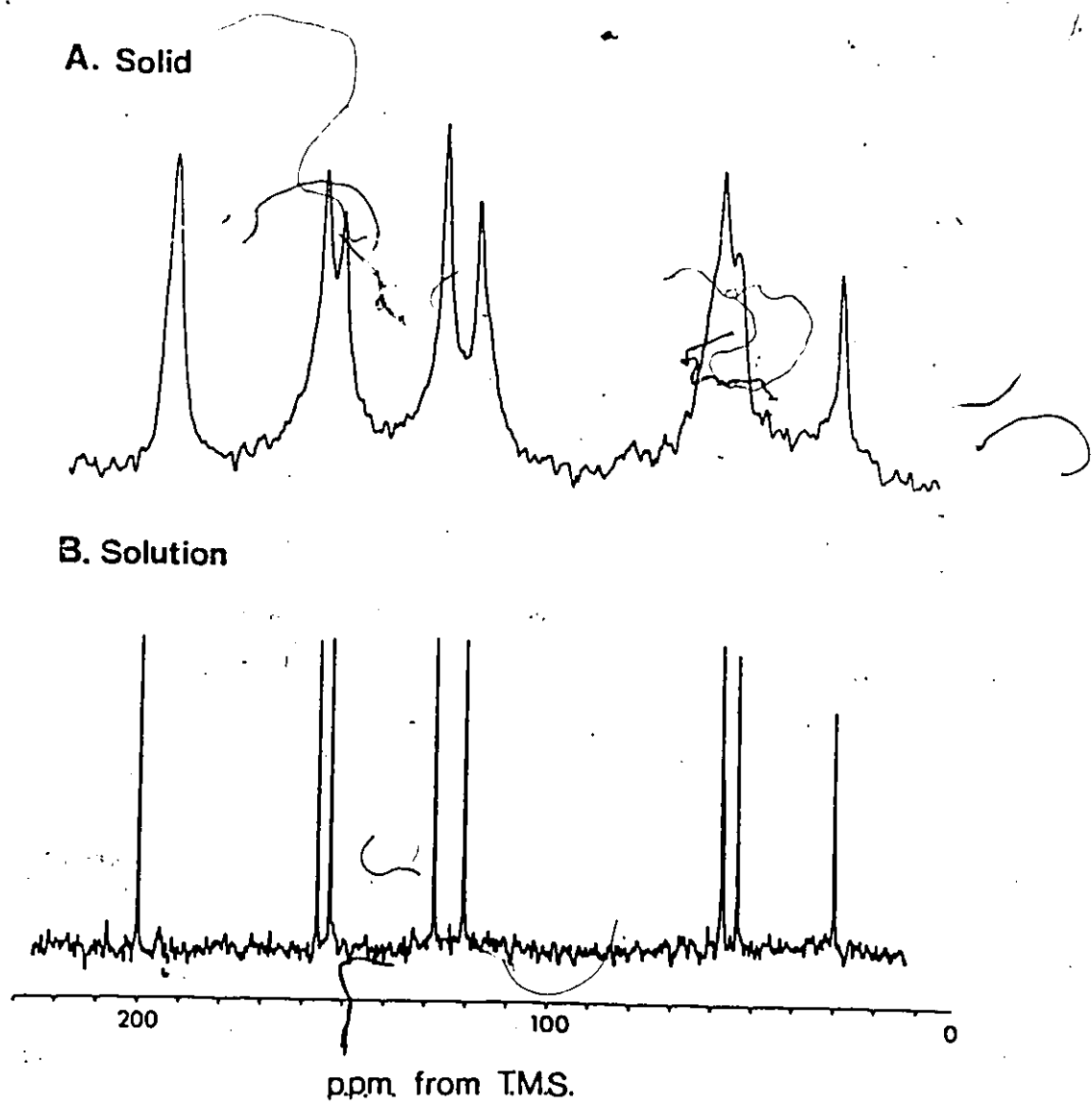


Figure 6 Solution ( $\text{D}_2\text{SO}_4$ ) and Solid State (CPMAS)  $^{13}\text{C}$  NMR Spectra of 69.



chemical shifts observed between the two spectra is 5.6 ppm for the  $C_2$  (protonated carbonyl carbon) resonance. Greater cation-anion interaction via hydrogen bonding in the solid state is a possible cause for the observed difference. Other chemical shift differences are significantly smaller. Overall it can be concluded that there are no substantial differences in the structure or charge distribution of 69 as a crystalline solid or as a solution in  $CD_2Cl_2$  or  $H_2SO_4$ .

b. *Crystal Structure Studies*

Single crystals suitable for x-ray diffraction studies were obtained by slow crystallization of the salt from  $CH_2Cl_2$  solution at  $-20^\circ C$ . The x-ray structure determination of this salt was performed by Dr. C.J.L. Lock and Mr. R. Faggiani of the Department of Chemistry at McMaster University.<sup>137</sup>

An initial solution of the structure was obtained with satisfactory refinements. In this refinement, the cation was present in the crystal in only one enantiomeric form. Due to certain unusual features noted in this structure for both the anion and the cation, it was decided to check the optical purity of the system under investigation. Solutions of the ketone 104, bulk salt of 69 and a single crystal of 69 in methylene chloride were all examined for optical activity using a polarimeter. None of the solutions exhibited any significant optical rotation at several wavelengths. As this evidence ruled out that 69 was enantiomerically pure, the x-ray diffraction data was re-examined.

A second solution was carried out in a different space group with the asymmetric cation having crystallographic disorder. This disorder was treated using a refinement with half occupancy for the

oxygen atom on either side of the "pseudo mirror plane" bisecting the cation 69. A satisfactory solution was thus obtained.



The disorder arises because there is no discrimination for the position of the hydroxy function during the packing of the cation. In other words, the -OH group could be randomly oriented on either side of the "pseudo mirror plane", as far as the crystal packing is concerned. This disorder does not affect the accuracy of the bond lengths in the cyclopropane ring (apart from making the C<sub>1</sub>-C<sub>8</sub> and C<sub>7</sub>-C<sub>8</sub> bond lengths equal, out of necessity). It does, however, show up in the large temperature factors for C<sub>3</sub>, C<sub>4</sub> and oxygen atoms. In examining the bond lengths around the "seven-membered ring", it is important to bear in mind the large errors quoted.

The packing arrangement of the cations and anions in the unit cell is shown in Figure 7. The structure is comprised of alternate layers of anions and cations. Within the cation layer, disordered cations are arranged in paired chains. Thus a cation, which resembles a half-closed hand is related to another in the adjacent chain, as though the hands were interlinked fingertips to fingertips. The cation is hydrogen bonded to the SbCl<sub>6</sub><sup>-</sup> ions. The SbCl<sub>6</sub><sup>-</sup> anions form a regular array. All interactions appear to be weak ionic or Van der Waals forces and thus packing considerations do not appear to be important in

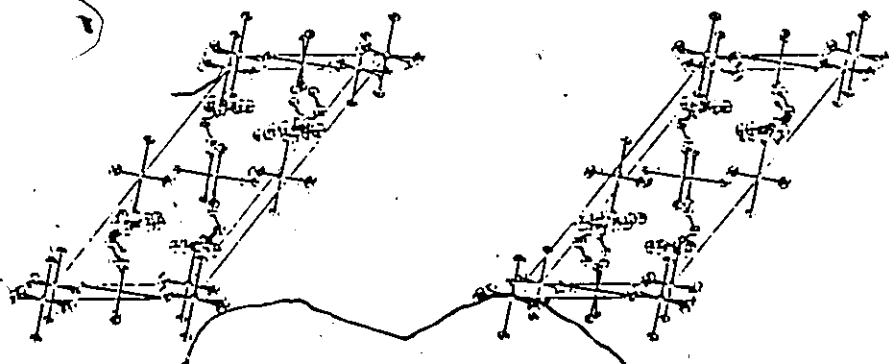


Figure 7. The packing of  $[\text{C}_8\text{H}_8(\text{OH})^+][\text{SbCl}_6^-]$  within the unit cell. The two oxygen atoms (each of half occupancy) of the disordered cation are shown. The view is down  $b$ , and  $a$  and  $c^*$  are parallel to the bottom and side of the page, respectively (temperature factors of the cation are isotropic for simplicity).

determining the conformation of the cation. This is in accord with the conclusions reached previously from a comparison of the solution and solid state  $^{13}\text{C}$  NMR spectra.

c. Discussion of the Molecular Structure of the 2-Hydroxyhomocyclopropylm Cation

The molecular structure of the cation is illustrated in Figures 8(a) and 8(b) and selected interatomic distances and angles are given in Table . It can be seen that the "seven-membered ring" of the cation exists as a shallow boat with the bridging  $\text{C}_8$  carbon held directly over this ring.

The bondlengths of the formal cyclopropane unit of this structure for the cation 69 are noteworthy. The homoconjugate  $\text{C}_1\text{-C}_7$  distance of  $1.626(8) \text{ \AA}$  is significantly longer than the C-C bond in free cyclopropane ( $1.510 \text{ \AA}$ ).<sup>76</sup> The  $\text{C}_1\text{-C}_8$  distance of  $1.488(7) \text{ \AA}$  is not very different from that of a normal cyclopropane.

It is interesting to note that the  $\text{C}_1\text{-C}_2$  (or  $\text{C}_6\text{-C}_6$ ) distance of  $1.422(12) \text{ \AA}$  is considerably shorter than that anticipated for the average of two single bonds.<sup>138,139</sup>

The disorder also leads to a short C-O bond length ( $1.182(12) \text{ \AA}$ ) with a large associated standard deviation. The normal C=O bond length in aldehydes and ketones is  $1.215 \text{ \AA}$ .<sup>138</sup> No special significance can be attached to this value.

From these bond distances and angles one can conclude that cation 69 can be regarded as a homoaromatic cation. The lengthening of the  $\text{C}_1\text{-C}_7$  bond compared to the normal C-C bonds in cyclopropane and the substantial

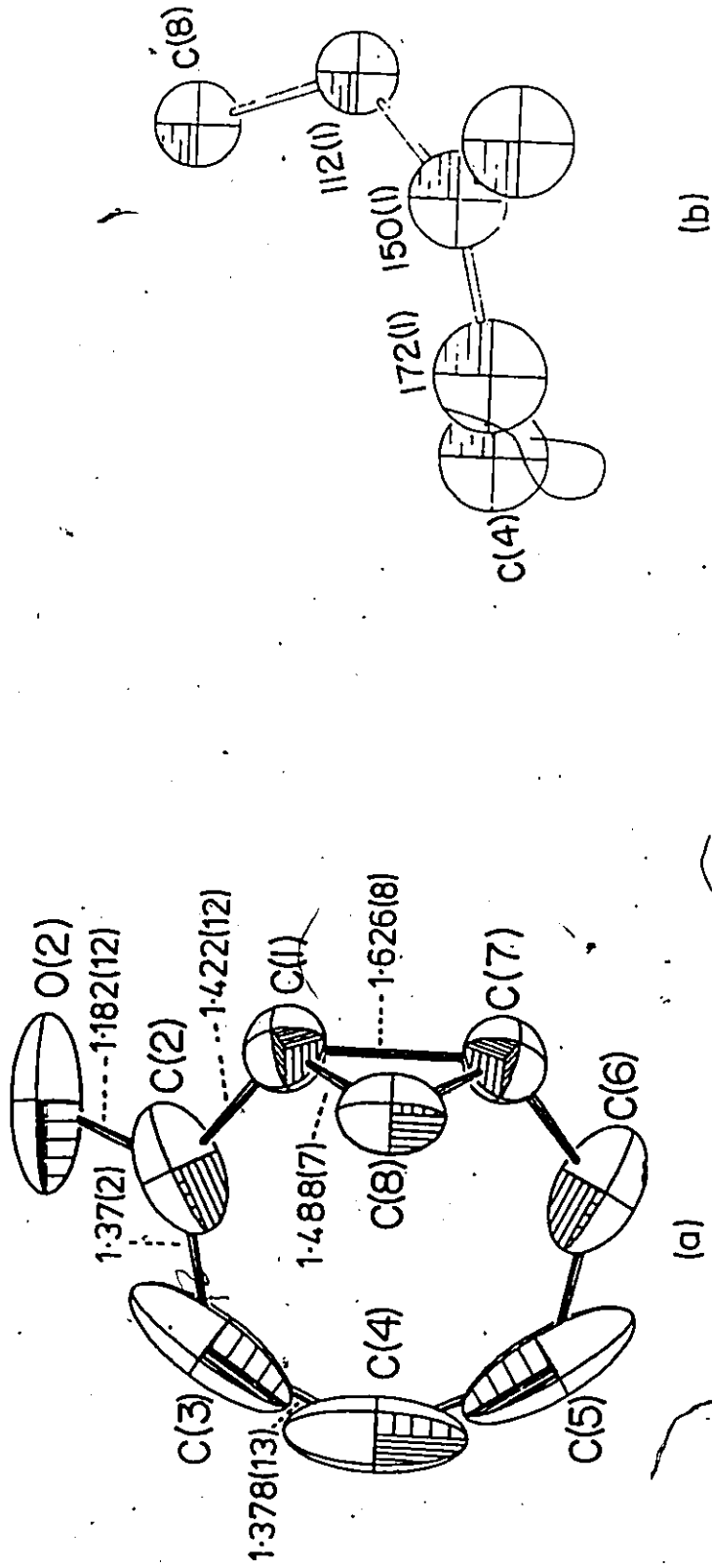


Figure 8 Structure of 2-hydroxyhomotropylium cation (a) the cation  $C_8H_8(OH)^+$  showing the atom numbering and selected interatomic distances and (b) the cation  $C_8H_8(OH)^+$  showing the dihedral angles between the planes of atoms (temperature factors are isotropic for simplicity).

Table 5

Selected Interatomic Distances (Å) and Angles (deg) in 69

Sb(1)-Cl(11)	2.363(2)	Sb(1)-Cl(12)	2.350(2)	Sb(2)-Cl(21)	2.365(2)
Sb(2)-Cl(22)	2.365(1)	C(1)-C(2)	1.422(12)	C(2)-C(3)	1.368(16)
C(3)-C(4)	1.378(13)	C(1)-C(8)	1.488(7)	C(1)-C(7)	1.626(8)
C(2)-O(2)	1.182(12)				

Possible hydrogen bonds

O(2)...Cl(22) <sup>a</sup>	3.292(9)	O(2)...Cl(11)	3.15(1)	O(2)...Cl(12) <sup>b</sup>	3.332(9)
Cl(11)-Sb(1)-Cl(12)	90.4(1)	Cl(11)-Sb(1)-Cl(12) <sup>a</sup>	89.6(1)	Cl(12)-Sb(1)-Cl(12) <sup>a</sup>	90.4(1)
C(12)-Sb(1)-Cl(12) <sup>c</sup>	89.6(1)	Cl(21)-Sb(2)-Cl(22)	90.3(1)	Cl(21)-Sb(1)-Cl(21) <sup>d</sup>	89.7(1)
Cl(22)-Sb(2)-Cl(22) <sup>d</sup>	90.1(1)	Cl(22)-Sb(2)-Cl(22) <sup>e</sup>	89.9(1)	C(8)-C(1)-C(2)	121.8(3)
C(1)-C(2)-C(3)	128.9(7)	C(2)-C(3)-C(4)	127(1)	C(3)-C(4)-C(5)	130(1)
C(7)-C(1)-C(2)	127.0(7)	C(8)-C(1)-C(7)	56.9(3)	C(1)-C(8)-C(7)	66.2(4)
C(1)-C(2)-O(2)	115(1)	C(3)-C(2)-O(2)	117(1)		

a-f Atoms are related to those given in Table 2 by a, -x, y, -z; b, x, -y, z;

c, -x, -y, -z; d, l-x, y, -z; e, l-x, l-y, -z; f, x, l-y, z. C(5), C(6),

C(7) are related to atoms C(3), C(2), C(1) respectively by f.

shortening of the  $C_1-C_2$  distance from that for a regular C-C single bond are exactly in accord with the delocalization involving only the internal cyclopropane bond. Further, the shallow boat conformation adopted by the cation fully supports the view that the nonplanarity of the 7-membered ring greatly improves the overlap of orbitals on  $C_1$  and  $C_7$ .<sup>13</sup>

The structural trends observed here agree remarkably well with those predicted in general by Haddon for homoaromatic species.<sup>13</sup> The bond distances and angles observed for the 2-hydroxyhomotropylium cation 69 have very close agreement with those obtained by Haddon for the parent homotropylium cation 5, using the theoretical calculations.<sup>13,79</sup> Some of these values are reproduced in Table 6.

The cation 69 is a little more bent than the calculations had indicated for the parent cation 5. The agreement between the calculated and observed bond lengths is excellent. This agreement is all the more remarkable in view of the fact that a substantial part of the positive charge in 69 would be localized on the oxygen atom of the hydroxy group, thereby reducing the extent of cyclic delocalization.

It is possible to estimate the bond order for the  $C_1-C_7$  bond in 69 using the distance (1.626(8) Å) obtained from this study and the empirical bond valence method developed by Brown.<sup>140</sup> For C-C bonds, this method essentially consists of establishing a relationship between the lengths and bond orders of single, double and triple bonds. From this method, a bond order of 0.76 was obtained for the  $C_1-C_7$  bond in 69. As mentioned earlier, Winstein obtained a value of 0.56 for the  $C_1-C_7$  bond order in the parent homotropylium cation 5, from UV spectral data.<sup>53</sup>

Table 6

Comparison of Calculated Interatomic Distances  
and Angles of 5 with Those Found for 69

Cation	Method	Distances $\overset{\circ}{\text{A}}$					Dihedral Angle $^{\circ}$	
		C <sub>1</sub> -C <sub>8</sub>	C <sub>1</sub> -C <sub>7</sub>	C <sub>1</sub> -C <sub>2</sub>	C <sub>2</sub> -C <sub>3</sub>	C <sub>3</sub> -C <sub>4</sub>	a	b
5	X-ray	1.488	1.626	1.42(1)	1.37(2)	1.38(2)	152(1)	110(1)
3	MINDO/3 <sup>c</sup>	1.498	1.621	1.449	1.387	1.412	164.5	117.9
3	STO-2G <sup>c</sup>	1.516	1.578	1.479	1.379	1.425	158.1	108.5

<sup>a</sup> C<sub>2</sub>C<sub>3</sub>C<sub>5</sub>C<sub>6</sub> - C<sub>1</sub>C<sub>2</sub>C<sub>6</sub>C<sub>7</sub> dihedral angle

<sup>b</sup> C<sub>1</sub>C<sub>2</sub>C<sub>6</sub>C<sub>7</sub> - C<sub>1</sub>C<sub>7</sub>C<sub>8</sub> dihedral angle

<sup>c</sup> Reference 13

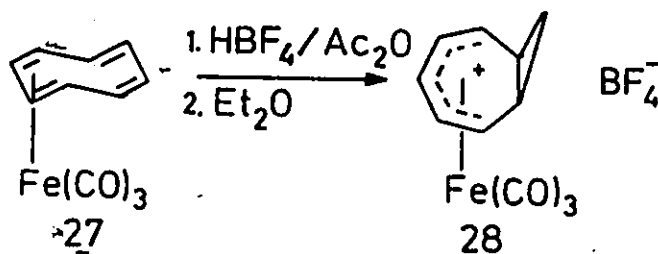


3. Structural Studies on the Bicyclo[5.1.0]octadienylirontricarbonyl Tetrafluoroborate 28

It is important to compare the length of the C<sub>1</sub>-C<sub>7</sub> homoconjugate linkage in 2-hydroxyhomotropylium cation 69 with that of a fully formed cyclopropyl bond in a structurally similar environment. The bicyclo[5.1.0]-octadienylirontricarbonyl tetrafluoroborate salt 28 would be suitable for such a study. It has already been mentioned that Winstein chose cation 28 as a nonhomoaromatic model system in his study of homotropylium cation, 5, and its molybdenumtricarbonyl complex, 24.<sup>58</sup> The cation 28 has previously been isolated as a solid salt by Schrauzer and by Wilkinson and coworkers.<sup>141,56,57,134</sup>

a. *Isolation and Characterization*

The cation 28 was prepared as its tetrafluoroborate salt according to the procedure of Wilkinson and coworkers.<sup>56,57</sup> Cyclooctatetraeneirontricarbonyl 27 was reacted with HBF<sub>4</sub> in acetic anhydride and the tetrafluoroborate salt of the cation 28 was isolated by precipitation from the solution with the addition of ether.



The <sup>1</sup>H NMR spectrum of 28 in SO<sub>2</sub> (Figure 9) and its IR spectrum as a KBr pellet were identical to those previously reported.<sup>57,58</sup>

b. *Crystal Structure Studies and Discussion of the Molecular Structure of 28*

Single crystals suitable for x-ray diffraction work were obtained by recrystallization of the salt from SO<sub>2</sub>. The crystal structure was

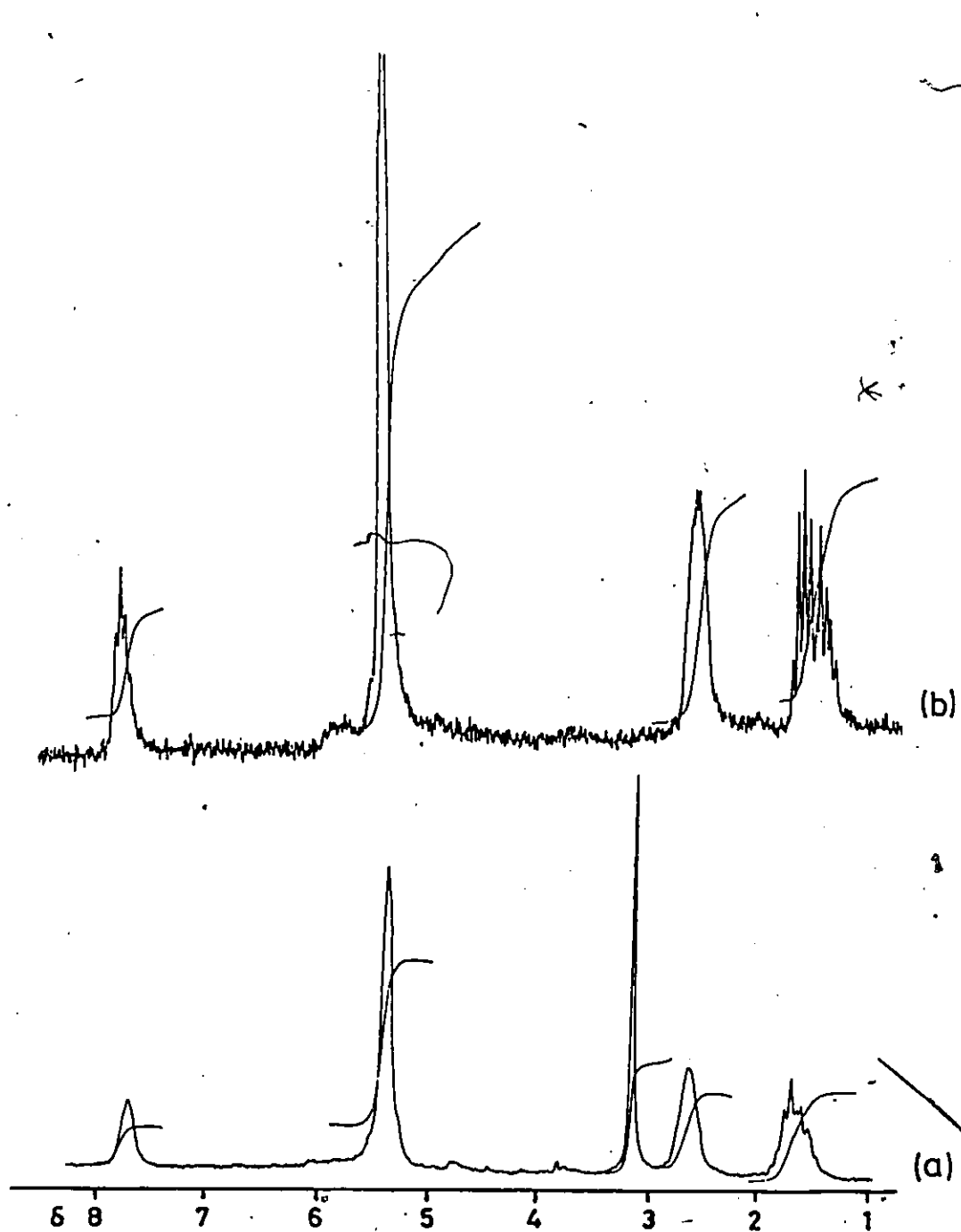


Figure 9  $^1\text{H}$  NMR Spectrum of bicyclo[5.1.0]octadienylirontricarbonyl cation 28. (a) Cyclooctatetraeneirontricarbonyl 27 in  $\text{H}_2\text{SO}_4$  and (b) Bicyclo[5.1.0]octadienylirontricarbonyl tetrafluoroborate in  $\text{SO}_2$ .

solved by Dr. C.J.L. Lock and Mr. R. Faggiani of McMaster University, using standard methods. Selected interatomic distances and angles are given in Table 7.

The structural features of the cation 28 are displayed in Figure 10. The structure consists of a planar cyclopentadienyl unit linked to the cyclopropane moiety with the C<sub>8</sub> methylene carbon situated right over the ring. There is an overall similarity between the conformation of ring carbons in 28 to that of the 2-hydroxyhomotropylium cation 69. The cyclopropyl group and the Fe(CO)<sub>3</sub> group are oriented on opposite sides of the seven-membered ring.

The important C<sub>1</sub>-C<sub>7</sub> bond distance in the iron complex 28 is 1.474 Å. This is quite different from that observed for 69 (1.626(8) Å). This value of 1.474 Å is in the range expected for a normal cyclopropane bond. The external cyclopropane bonds C<sub>1</sub>-C<sub>8</sub> and C<sub>7</sub>-C<sub>8</sub> have lengths of 1.498 Å. These bond distances are in agreement with earlier proposals that 28 has a fully formed cyclopropane ring. The ~~C<sub>1</sub>-C<sub>2</sub> and C<sub>6</sub>-C<sub>7</sub>~~ bond distances of 1.488 Å also reveal the lack of interaction of the cyclopropane unit with the pentadienyl unit. This value is similar to those found for the bond distance between a metal coordinated and the adjacent uncoordinated carbon atoms in complexes such as 112 and 113.<sup>142,143</sup> These bond distances are summarized in the diagrams below.

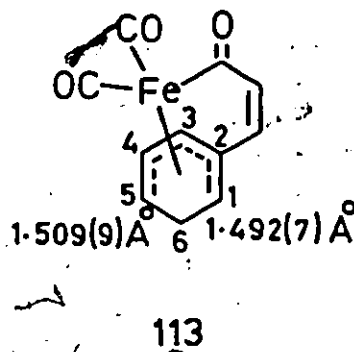
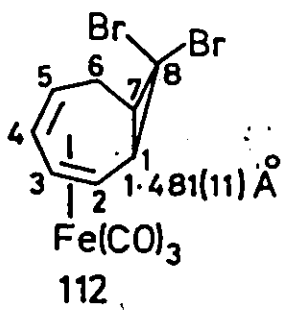


Table 7

Selected Interatomic Distances (Å) and Angles (deg) in 28

C <sub>1</sub> -C <sub>2</sub>	1.488(10)	C <sub>11</sub> -O <sub>3</sub>	1.133(9)	C <sub>1</sub> -H <sub>1</sub>	0.89(7)
C <sub>1</sub> -C <sub>7</sub>	1.474(11)	C <sub>1</sub> -Fe	3.070(7)	C <sub>2</sub> -H <sub>2</sub>	0.87(8)
C <sub>1</sub> -C <sub>8</sub>	1.498(11)	C <sub>2</sub> -Fe	2.226(6)	C <sub>3</sub> -H <sub>3</sub>	0.95(8)
C <sub>2</sub> -C <sub>3</sub>	1.395(10)	C <sub>3</sub> -Fe	2.097(7)	C <sub>4</sub> -H <sub>4</sub>	0.95(7)
C <sub>3</sub> -C <sub>4</sub>	1.402(10)	C <sub>4</sub> -Fe	2.098(7)	C <sub>5</sub> -H <sub>5</sub>	0.95(8)
C <sub>4</sub> -C <sub>5</sub>	1.400(10)	C <sub>5</sub> -Fe	2.121(7)	C <sub>6</sub> -H <sub>6</sub>	0.88(8)
C <sub>5</sub> -C <sub>6</sub>	1.393(11)	C <sub>6</sub> -Fe	2.239(7)	C <sub>7</sub> -H <sub>7</sub>	0.85(8)
C <sub>6</sub> -C <sub>7</sub>	1.495(11)	C <sub>7</sub> -Fe	3.081(8)	C <sub>8</sub> -H <sub>8a</sub>	1.01(8)
C <sub>7</sub> -C <sub>8</sub>	1.497(12)	C <sub>9</sub> -Fe	1.816(7)	C <sub>8</sub> -H <sub>8b</sub>	0.91(8)
C <sub>9</sub> -O <sub>1</sub>	1.133(9)	C <sub>10</sub> -Fe	1.799(7)		
C <sub>10</sub> -O <sub>2</sub>	1.137(8)	C <sub>11</sub> -Fe	1.829(7)		
C <sub>7</sub> -C <sub>1</sub> -C <sub>2</sub>	117.2(6)	C <sub>6</sub> -C <sub>7</sub> -C <sub>1</sub>	116.5(6)		
C <sub>8</sub> -C <sub>1</sub> -C <sub>2</sub>	119.8(6)	C <sub>8</sub> -C <sub>7</sub> -C <sub>1</sub>	60.5(5)		
C <sub>8</sub> -C <sub>1</sub> -C <sub>7</sub>	60.5(5)	C <sub>8</sub> -C <sub>7</sub> -C <sub>6</sub>	119.5(7)		
C <sub>3</sub> -C <sub>2</sub> -C <sub>1</sub>	128.2(6)	C <sub>7</sub> -C <sub>8</sub> -C <sub>1</sub>	59.0(5)		
C <sub>4</sub> -C <sub>3</sub> -C <sub>2</sub>	125.5(6)	H <sub>8a</sub> -C <sub>8</sub> -H <sub>8b</sub>	118.5(65)		
C <sub>5</sub> -C <sub>4</sub> -C <sub>3</sub>	124.0(6)	O <sub>1</sub> -C <sub>9</sub> -Fe	177.4(7)		
C <sub>6</sub> -C <sub>5</sub> -C <sub>4</sub>	124.7(6)	O <sub>2</sub> -C <sub>10</sub> -Fe	179.1(7)		
C <sub>7</sub> -C <sub>6</sub> -C <sub>5</sub>	129.0(7)	O <sub>3</sub> -C <sub>11</sub> -Fe	179.3(7)		

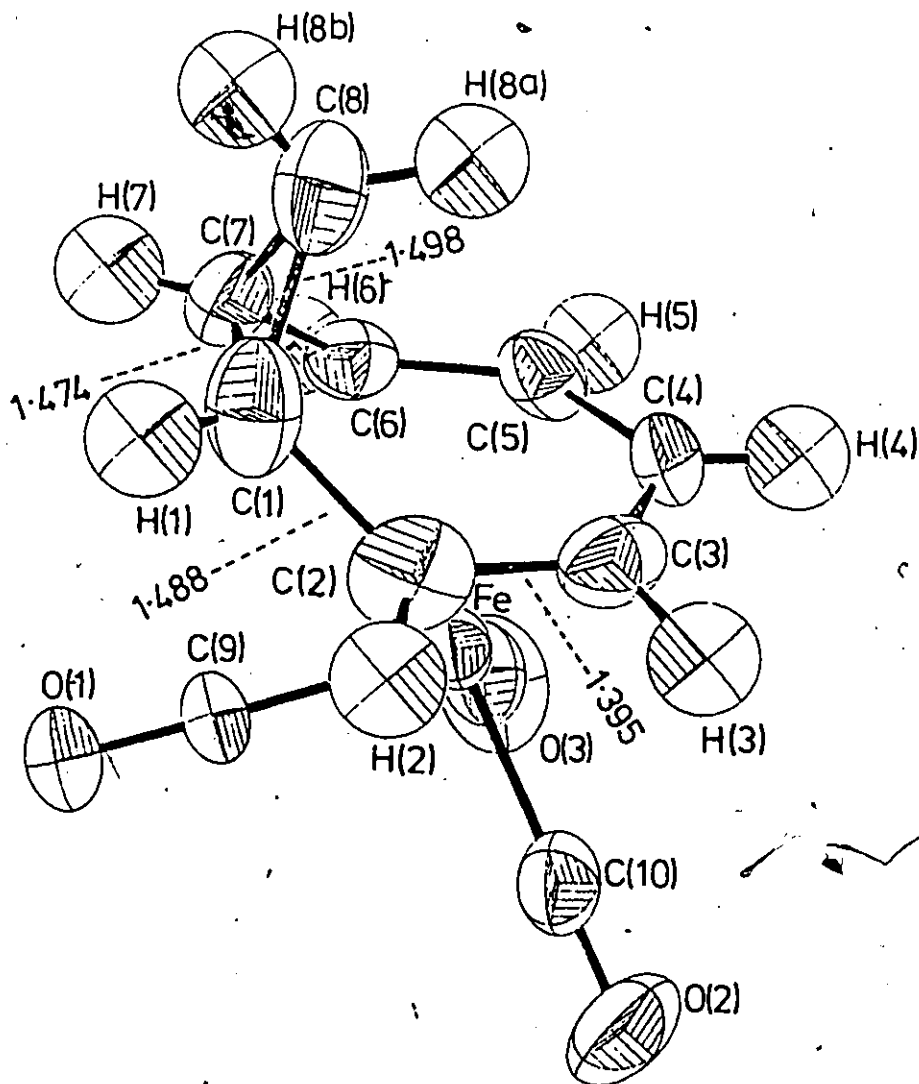


Figure 10 Structure of bicyclo[5.1.0]octadienylirontricarbonyl cation 28 showing atom numbering and selected interatomic distances.

2 The carbon-carbon bond distances in the pentadienyl unit of 28 are all almost identical. This once again indicates that delocalization is restricted to this segment. The iron-carbon distances, both for the carbonyl and for the organic moiety, and the carbon-oxygen bond distances are all in the expected ranges.

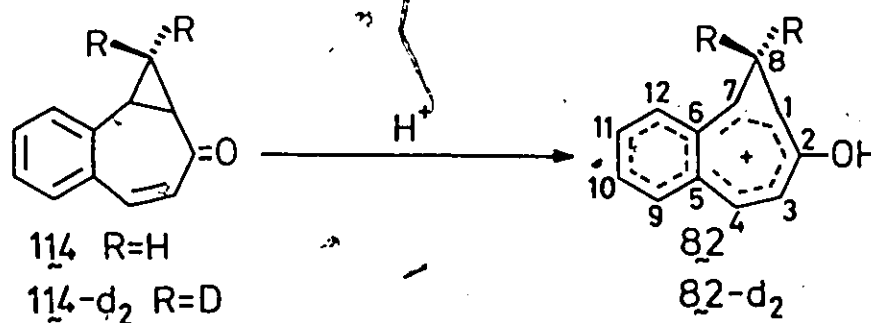
The marked structural differences of cations 69 and 28 fully confirm the conclusions reached earlier on the basis of the NMR evidence for the difference in delocalization observed for 28 and for 5.<sup>1,2</sup> The short  $C_1-C_7$  and the long  $C_1-C_2/C_6-C_7$  interatomic distances of 1.474 Å and 1.49 Å respectively, are in sharp contrast to those of 69. These differences substantiate the existence of cyclic delocalization in 69.

7 It is to be noted that in both 69 and 28,  $C_8$  is situated above the rest of the "7-membered ring", leading to similar spatial orientation of the methylene protons. This means that the differences in the chemical shifts for the protons on  $C_8$  cannot be explained in terms of large differences in structural arrangement. Rather, the original Winstein, concept of an induced ring current in homotropylium cation(s), can be considered to be one of the factors causing the large differences in the chemical shifts for the  $C_8$  protons resonances.

#### 4. Structural Studies on "Protonated 4,5-benzo-2,3-homotropone"

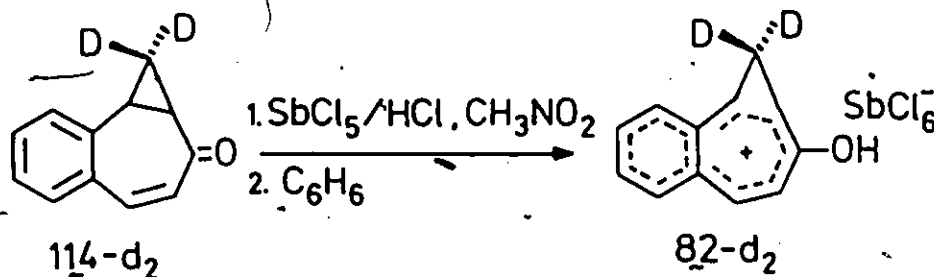
To establish a structural criterion for homoaromaticity, it is desirable to determine the structures of more than one homotropylium cation. It was decided to determine the structure of 82, a benzannelated derivative of 69. The 2-hydroxy-5,6-benzohomotropylium cation, 82, obtained by the protonation of 114, has been characterized previously by NMR spectroscopy and suggested to be homoaromatic.<sup>16,102,144</sup> The

precursor ketone 114-d<sub>2</sub> (doubly deuterated at the bridging methylene carbon) was available\* and this was used in an attempt to isolate 82-d<sub>2</sub> as a solid. The replacement of hydrogens by deuteriums should not affect the structure of the cation 82.



*a. Isolation and Characterization*

A similar procedure to the one used to isolate the solid salt of 2-hydroxyhomotropylium cation 69 was followed. The ketone 114-d<sub>2</sub> was added to a solution of  $\text{SbCl}_5$  and  $\text{HCl}$  in  $\text{CH}_3\text{NO}_2$ . Benzene was added to precipitate the solid. Unlike the case of 2-hydroxyhomotropylium cation, a solid salt did not precipitate readily. Instead a greenish yellow viscous mass separated from the solution. This subsequently solidified into a greenish yellow solid.



\* The ketone 114-d<sub>2</sub> was synthesized by H.A. Corver in this laboratory. <sup>144</sup>  
 The systematic name for this ketone is 5,6-benzo-8,8-dideutero-bicyclo[5.1.0]octa-3,5-dien-2-one, on which the numbering of the atoms, in the text, is based.

The  $^1\text{H}$ ,  $^2\text{H}$  and  $^{13}\text{C}$  NMR data for the ketone  $114\text{-d}_2$ , the cation  $82\text{-d}_2$  in  $\text{D}_2\text{SO}_4$  and for the hexachloroantimonate salt prepared above and dissolved in  $\text{CD}_2\text{Cl}_2$ , are reported in Tables 8, 9 and 10, respectively. The resonances of all protons in the salt isolated were shifted downfield as compared to the neutral ketone  $114\text{-d}_2$ . The relative magnitudes of these downfield shifts observed in the case of the salt are less than those observed for the cation  $82\text{-d}_2$  generated in strong acids. The  $^1\text{H}$  NMR spectra of the ketone  $114\text{-d}_2$ , the cation  $82\text{-d}_2$  in  $\text{D}_2\text{SO}_4$  and the isolated salt in  $\text{CD}_2\text{Cl}_2$  are shown in Figure 11.

Noticeable differences were also observed in the  $^2\text{H}$  NMR chemical shifts for the  $\text{C}_8$ -deuteriums (Table 9). The chemical shift difference for the exo and endo deuteriums on  $\text{C}_8$  ( $\Delta\delta$ ) in the salt was 1.62 ppm. This is considerably larger than that for the ketone  $114\text{-d}_2$  (0.22 ppm) but less than that observed for the cation  $82\text{-d}_2$  in  $\text{D}_2\text{SO}_4$  (2.34 ppm).

The  $^{13}\text{C}$  chemical shifts for the cation  $82\text{-d}_2$  in  $\text{D}_2\text{SO}_4$  and for the isolated salt, Table 10 are also different. These differences in  $^1\text{H}$ ,  $^2\text{H}$  and  $^{13}\text{C}$  NMR spectra led one to suspect that the cation isolated as the salt was not the same as that generated in strong acid solutions of the ketone in  $114\text{-d}_2$ . Despite these differences the system still seemed to be homoaromatic (e.g.,  $\Delta\delta$  for  $\text{C}_8$  deuteriums = 1.62 ppm) and it was decided to perform an x-ray structural analysis on the isolated salt.

*b. Crystal Structure Studies and Discussion of the Molecular Structure*

Single crystals suitable for x-ray diffraction were obtained by slow crystallization of the solid salt from  $\text{CH}_2\text{Cl}_2$  at  $-20^\circ\text{C}$ . The



Table 8

$^1\text{H}$  NMR Chemical Shift Data for the Ketone 114- $d_2$ , the Cation 82- $d_2$   
and the "Hexachloroantimonate Salt of 82- $d_2$ "<sup>a</sup>

Compound/Solvent (int. std., $\delta$ ppm)	H <sub>1</sub>	H <sub>7</sub>	H <sub>9</sub> - H <sub>12</sub> (Ar - H)	H <sub>4</sub>	H <sub>3</sub>
116 - $d_2$ /CCl <sub>4</sub> <sup>b</sup> (TMS, $\delta$ 0.0 ppm)	2.47(b,s)		7.43-7.16 (m)	6.73(d) (J=13.3Hz)	5.87(dd) (J=13.3, 1Hz)
82 - $d_2$ /D <sub>2</sub> SO <sub>4</sub> ( $(\text{CH}_3)_4\text{N}^+\text{BF}_4^-$ , $\delta$ 3.1ppm)	3.17(dd) (J=7.5, 3Hz)	3.9(d) (J=7.5Hz)	7.9-7.56 (m)	8.06(d) (J=12Hz)	6.7(dd) (J=12, 3Hz)
"82 - $d_2$ SbCl <sub>6</sub> "/CD <sub>2</sub> Cl <sub>2</sub> (CHCl <sub>2</sub> , $\delta$ 5.3 ppm)	2.97(b,d) (J=7.1Hz)	3.31(b,d) (J=8.3Hz)	7.64-7.42 (m)	7.64-7.42 (m)	6.43(dd) (J=12, 2.2Hz)

<sup>a</sup> b:broad; d:doublet; dd:doublet of doublets; m:multiplet; s:singlet

<sup>b</sup> ref. 146.

Table 9

$^2\text{H}$  NMR Chemical Shift Data for the Ketone 114-d<sub>2</sub>,  
the Cation 82-d<sub>2</sub> and the "Hexachloroantimonate Salt of 82-d<sub>2</sub>"

Compound/Solvent (int. std., $\delta$ ppm)	$D_{\text{gexo}}$	$D_{\text{gendo}}$	$\Delta\delta = D_{\text{exo}} - D_{\text{endo}}$
<u>117-d<sub>2</sub></u> /CDCl <sub>3</sub> (CDCl <sub>3</sub> , $\delta$ 7.27 ppm)	1.90	1.68	0.22
<u>82-d<sub>2</sub></u> /H <sub>2</sub> SO <sub>4</sub> (CDCl <sub>3</sub> , $\delta$ 7.27 ppm)	3.51	1.17	2.34
" <u>82-d<sub>2</sub></u> SbCl <sub>6</sub> "/CH <sub>2</sub> Cl <sub>2</sub> (CHDCl <sub>2</sub> , $\delta$ 5.3 ppm)	3.04	1.42	1.62

Table 10

$^{13}\text{C}$  NMR Chemical Shift Data for the Ketone 114-d<sub>2</sub>, the Cation 82-d<sub>2</sub> and the "Hexachloroantimonate Salt of 82-d<sub>2</sub>"

Compound/Solvent (int. Std., $\delta$ ppm)	C <sub>2</sub>	C <sub>1</sub> <sup>a</sup>	C <sub>7</sub> <sup>a</sup>	C <sub>5</sub> , C <sub>6</sub> , C <sub>9</sub> , C <sub>10</sub> , C <sub>11</sub> , C <sub>12</sub> (Ar-C)	C <sub>4</sub>	C <sub>3</sub>	C <sub>8</sub>
116-d <sub>2</sub> /CDCl <sub>3</sub> (CDCl <sub>3</sub> , $\delta$ 76.95 ppm)	198.3	29.2	40.7	133.6, 131.0, 129.7, 126.6	138.8	126.4	14.5(b)
82-d <sub>2</sub> /D <sub>2</sub> SO <sub>4</sub> (CDCl <sub>3</sub> , $\delta$ 76.95 ppm)	205.7	44.3	46.81	142.2, 138.2, 136.8, 131.1 130.3, 12-.1	159.4	115.8	28.7(b)
"82-d <sub>2</sub> SbCl <sub>6</sub> " / CD <sub>2</sub> Cl <sub>2</sub> (CD <sub>2</sub> Cl <sub>2</sub> , $\delta$ 53.6 ppm)	207.2	41.4	43.4	141.4, 136.8, 134.6, 131.4, 130.4, 128.5	153.8	119.1	26.1(b)

<sup>a</sup> Assignments may be reversed.

<sup>b</sup> Broad

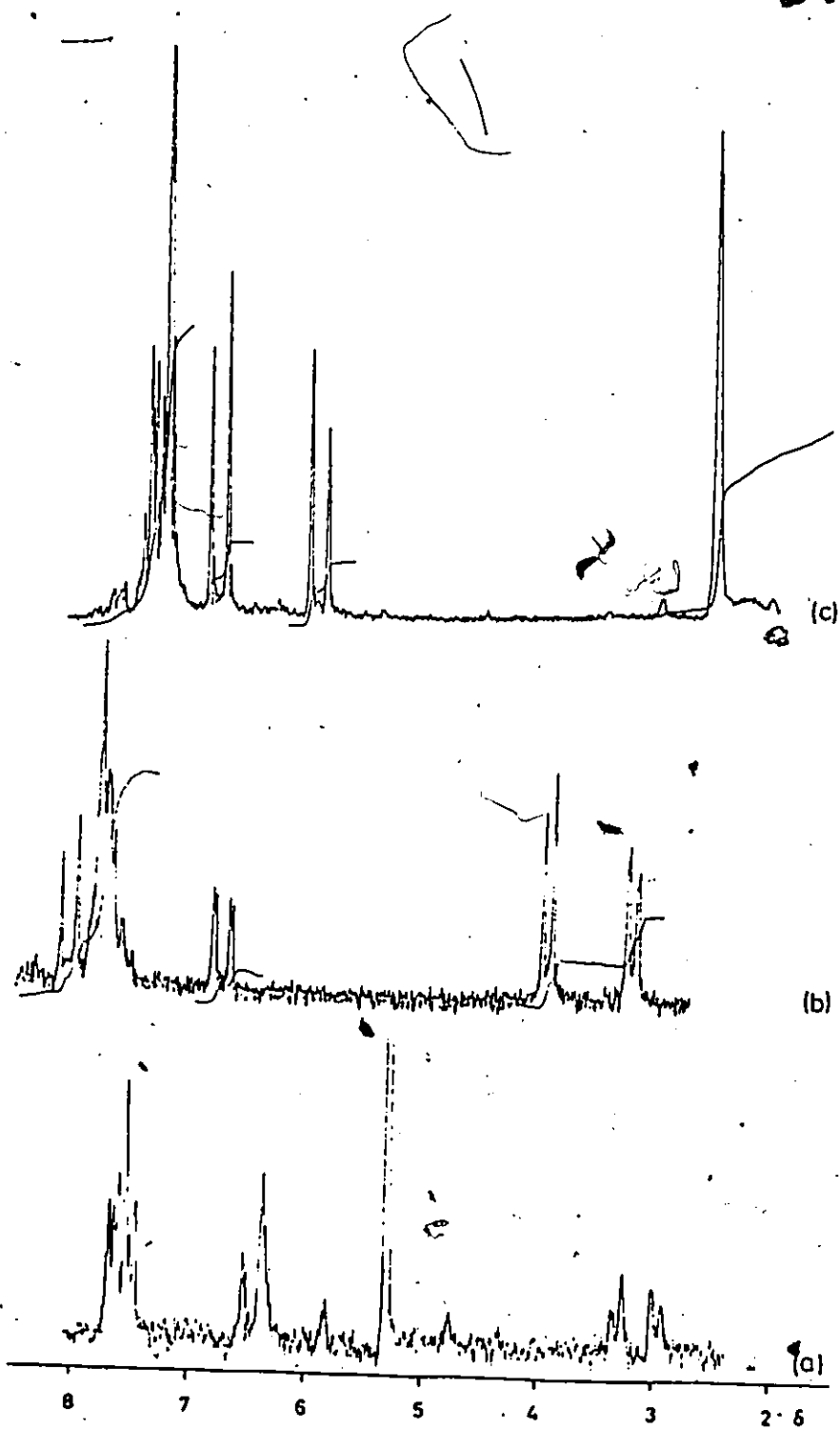
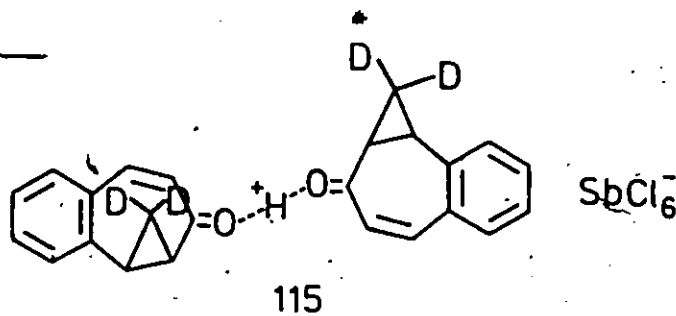


Figure 11  $^1\text{H}$  NMR Spectra of the neutral and the protonated ketone 114-d<sub>2</sub>  
(a) 114-d<sub>2</sub> in  $\text{CDCl}_3$ , (b) 114-d<sub>2</sub> in  $\text{D}_2\text{SO}_4$  and (c) the hexa-  
chloroantimonate salt of the protonated ketone 114-d<sub>2</sub> in  $\text{CD}_2\text{Cl}_2$ .

crystal structure of this salt was again solved by Dr. C.J.L. Lock and Mr. R. Faggiani of the Department of Chemistry at McMaster University. Selected interatomic distances and angles are given in Table 11.

The x-ray studies revealed that in the unit cell of the crystal there is only one  $\text{SbCl}_6^-$  counterion for every two organic moieties. In other words, the crystalline material isolated is not a simple 1:1 hexachloroantimonate salt of cation 82-d<sub>2</sub>.

The very short O-O distance of 2.44(1) Å between the oxygens of the two carbonyls in these moieties is strongly suggestive of the existence of a very short and strong hydrogen bond. The proton, which could not be located by the x-ray method, is likely to be bound to the two oxygen atoms of the carbonyl groups. In other words, the system would appear to be an intermolecular hydrogen bonded species, namely a bis(5,6-benzo-8,8-dideuterobicyclo[5.1.0]octa-3,5-dien-2-one)-hydrogen hexachloroantimonate 115.



The occurrence of such very short hydrogen bonds is not unusual. Several species have been reported in the literature, in which strong hydrogen bonds of the type N-H-N, F-H-F, O-H-O and F-H-O occur.<sup>145-147</sup>

Speakman has defined "very short" O-H-O bonds as hydrogen bonds in which the O...O distance is less than 2.5 Å.<sup>148</sup> In a typical

Table 11a

Selected Interatomic Distances (Å) and Angles (deg) in 115

C(1)-C(2)	1.439(10)	C(2)-C(3)	1.425(10)	C(3)-C(4)	1.341(8)
C(4)-C(5)	1.446(7)	C(5)-C(6)	1.413(7)	C(6)-C(7)	1.484(7)
C(7)-C(8)	1.471(9)	C(8)-C(1)	1.515(9)	C(1)-C(7)	1.544(8)
C(2)-O	1.289(6)	C(5)-C(9)	1.402(7)	C(9)-C(10)	1.376(9)
C(10)-C(11)	1.350(10)	C(11)-C(12)	1.376(9)	C(12)-C(6)	1.393(7)
O-O'	2.435(12)	Sb-Cl(1)	2.372(1)	Sb-Cl(2)	2.377(1)
Sb-Cl(3)	2.376(2)	Sb-Cl(4)	2.353(2)		
C(8)-C(1)-C(2)	119.0(6)	C(7)-C(1)-C(2)	124.2(5)	C(1)-C(2)-C(3)	124.1(5)
C(2)-C(3)-C(4)	128.5(5)	C(3)-C(4)-C(5)	132.3(5)	C(4)-C(5)-C(6)	125.6(5)
C(5)-C(6)-C(7)	125.7(5)	C(6)-C(7)-C(1)	125.9(5)	C(6)-C(7)-C(8)	121.8(5)
C(8)-C(1)-C(7)	57.5(4)	C(1)-C(7)-C(8)	60.2(4)	C(7)-C(8)-C(1)	62.3(4)
C(1)-C(2)-O	116.2(7)	C(3)-C(2)-O	119.5(7)	C(4)-C(5)-C(9)	115.4(5)
C(6)-C(5)-C(9)	118.9(5)	C(5)-C(9)-C(10)	121.1(6)	C(9)-C(10)-C(11)	120.5(6)
C(10)-C(11)-C(12)	120.0(5)	C(11)-C(12)-C(6)	121.1(6)	C(12)-C(6)-C(5)	118.2(5)
C(12)-C(6)-C(7)	115.8(5)	<del>C(2)-O-H(13)</del>	115.9(4)		
Cl(1)-Sb-Cl(2)	90.4(1)	Cl(1)-Sb-Cl(3)	90.1(1)	Cl(1)-Sb-Cl(4)	89.9(1)
Cl(2)-Sb-Cl(3)	89.0(1)	<del>Cl(2)-Sb-Cl(4)</del>	91.0(1)	Cl(3)-Sb-Cl(4)	180.0(1)

Table 11b

Bond Lengths (Å) and Angles (deg) Involving Hydrogen Atoms in 115

C(1)-H(1)	1.0	C(3)-H(3)	1.1	C(4)-H(4)	1.1
C(7)-H(7)	1.1	C(8)-D(1)	1.0	C(8)-D(2)	0.7
C(9)-H(9)	1.1	C(10)-H(10)	1.1	C(11)-H(11)	1.2
C(12)-H(12)	0.9				
C(8)-C(1)-H(1)	119	C(7)-C(1)-H(1)	118	C(2)-C(1)-H(1)	110
C(2)-C(3)-H(3)	115	C(4)-C(3)-H(3)	116	C(3)-C(4)-H(4)	126
C(5)-C(4)-H(4)	101	C(6)-C(7)-H(7)	107	C(1)-C(7)-H(7)	123
C(8)-C(7)-H(7)	112	C(1)-C(8)-D(1)	120	C(1)-C(8)-D(2)	106
C(7)-C(8)-D(1)	123	C(7)-C(8)-D(2)	112	D(1)-C(8)-D(2)	120
C(5)-C(9)-H(9)	121	C(9)-C(10)-H(10)	126	C(10)-C(11)-H(11)	132
C(10)-C(9)-H(9)	115	C(11)-C(10)-H(10)	114	C(12)-C(11)-H(12)	108
C(11)-C(12)-H(12)	123	C(6)-C(12)-H(12)	115		

Errors in CH bonds were 0.1 Å and in C-C-H angles 6°. The D-C-D error was 10°.

Table 11c

Best Planes, Dihedral Angles and Torsional Angles (deg) in 115

Plane	Distance of Atom from Plane (Å)
1. C(3)C(4)C(5)	
2. C(2)C(3)C(5)C(6)	C(2) 0.071(6) C(3) -0.075(6), C(5) 0.044(4) C(6) -0.048(6), C(9) 0.372(6), C(12) 0.229(6) 0 0.626(6)
3. C(1)C(2)C(6)C(7)	C(1) 0.019(6), C(2) -0.011(6), C(6) 0.007(6) C(7) -0.015(6); 0 0.581(6)
4. C(1)C(7)C(8)	
5. C(5)C(6)C(9)C(10)C(11)C(12)	C(5) -0.003(4), C(6) 0.015(6), C(9) -0.011(6), C(10) 0.019(6), C(11) -0.004(6), C(12) -0.014(6) C(4) -0.087(6), C(7) 0.192(6) 0 -0.083(6)
6. C(1)C(2)C(3)	
<u>Dihedral Angles</u>	
Plane 1 - Plane 2	171(1)
Plane 2 - Plane 3	155°(1)
Plane 3 - Plane 4	108(1)
Plane 2 - Plane 5	166°(1)
<u>Torsional Angles</u>	
C(8)C(1)C(2)C(3)	352
C(1)C(2)C(3)C(4)	33.6
C(2)C(3)C(4)C(5)	2.1
C(8)C(1)C(7)C(6)	-109.6
C(4)C(5)C(6)C(12)	174.6
C(3)C(4)C(5)C(9)	160.9
C(8)C(7)C(6)C(5)	-44.6
C(7)C(6)C(5)C(4)	-11.5
C(6)C(5)C(4)C(3)	-15.6
C(8)C(7)C(1)C(2)	105.2
C(7)C(6)C(5)C(9)	172.1
C(1)C(7)C(6)C(12)	-156.4



hydrogen bond, the O...O distance is of the order of  $2.8 \text{ \AA}$ .<sup>149</sup>

Both x-ray and neutron diffraction methods have been used in these structural studies. Some examples are given in Table 12.<sup>150,151</sup> In many examples reported in the literature the O-O distances range from  $2.51 \text{ \AA}$  to  $2.29 \text{ \AA}$ .<sup>152,153</sup>

This hydrogen bridged structure for the hexachloroantimonate salt 115 offers some explanation for the earlier NMR observations. The extent of cyclic delocalization, if it occurs at all in 115, is expected to be considerably reduced when compared to other homotropylium cations such as 82-d<sub>2</sub> in strong acids. Since the proton is shared by two ketone molecules, only half the positive charge is transferred to each carbonyl oxygen. Further transmission of the charge into the carbocyclic fragment would be less significant in 115 as compared to 82-d<sub>2</sub>. Consequently the salt 115 can be expected to exhibit a lower  $\Delta\delta$  value for the deuteriums on C<sub>8</sub> and smaller downfield shifts for ring protons as compared to cation 82-d<sub>2</sub> in strong acids.

In any case, the structural features of the salt 115 must be examined carefully before any conclusions regarding cyclic delocalization can be reached.

Selected bond lengths in cation 115 are displayed in Figure 12. The strong hydrogen bonding in cation 115 perturbs the system significantly to cause slight changes in some of the bond distances. However, the "key" internal cyclopropane bond length (C<sub>1</sub>-C<sub>7</sub>) is only  $1.544(8) \text{ \AA}$ . This is much shorter than the corresponding bond length of  $1.626 \text{ \AA}$  observed in 69 and is not significantly different from that of free cyclopropane ( $1.510 \text{ \AA}$ ).<sup>76</sup> The other two cyclopropane bond distances are also not

Table 12

Some Examples of Short O-H-O Bonds

Compound	$\gamma(0\dots0)\overset{\circ}{\text{A}}$	Diffraction Method	Reference
$\text{Na}^+ [\text{H}(\text{CH}_3\text{COO})_2]^-$	2.444(10)	x-ray	154
Sodium hydrogen diacetate	2.475(14)	neutron	155
$\text{N}_2\text{H}_5^+ [\text{H}(\text{COO})_2]^-$	2.450(4)	x-ray	156
Hydrazinium hydrogen oxalate	2.457(7)	neutron	157
$[(\text{CH}_3\text{CO}\cdot\text{NH}_2)_2\text{H}]^+ \text{Cl}^-$	2.4507(14)	x-ray	158
Acetamide hemihydrochloride			

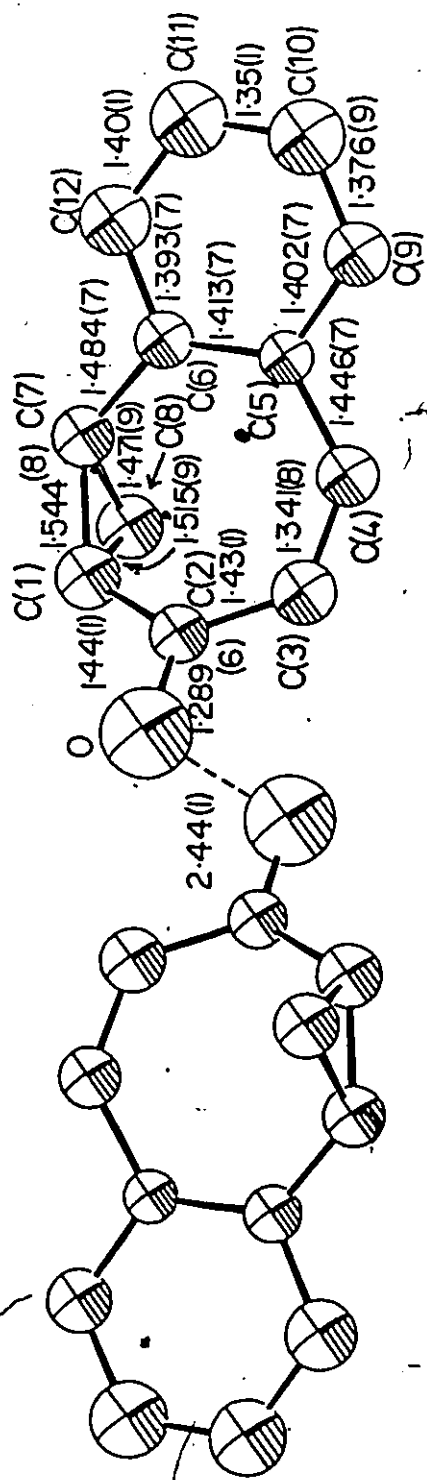


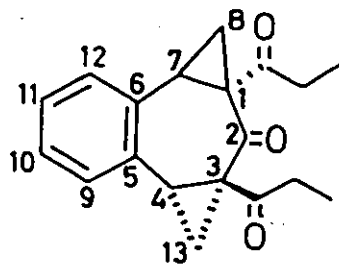
Figure 12 Structure of bis(5,6-benzo-8,8-dideuterobicyclo[5.1.0]octa-3,5-dien-2-one)-hydrogen hexachlorantimonate 115 showing atom numbering and selected interatomic distances.

substantially different from that of free cyclopropane (1.471(9) Å and 1.515(9) Å respectively for the C<sub>7</sub>-C<sub>8</sub> and C<sub>1</sub>-C<sub>8</sub> bonds). The C<sub>1</sub>-C<sub>2</sub> bond distance (1.44(1) Å) is very slightly shorter than that for a carbon linked to a carbonyl carbon (1.506 Å).<sup>138</sup> The other bond distances in the seven-membered ring are in the expected range for conjugated systems.<sup>138</sup> These bond distances suggest that cation 115 cannot be regarded as a substantially delocalized homotropylium cation such as 69. The extent of homoaromatic delocalization (if any) occurring in 115 must be extremely small.

The carbon-oxygen bond length for the carbonyl group is 1.289(6) Å which is longer than the normal value (1.215 Å) found for C=O bonds in ketones and aldehydes.<sup>138</sup> The C-O single bond distances are 1.426 Å in saturated aliphatic alcohols and ethers and 1.36 Å in phenols.<sup>138</sup> Perturbations of similar nature have been found for other systems with short hydrogen bonds. For example, the C=O and C-N and C-C bond distances in rhombohedral acetamide change from their respective values of 1.243(4) Å, 1.336(4) Å and 1.510(3) Å to 1.2654(10) Å, 1.3045(10) Å and 1.4858(13) Å respectively in acetamide hemihydrochloride.<sup>159,158</sup>

Since single crystals of the parent ketone 114-d<sub>2</sub>, suitable for x-ray diffraction could not be obtained, its structure could not be determined. Therefore the extent of structural perturbation due to hydrogen bonding, occurring in the 7-membered ring could not be analyzed. However, the structure of the trans-benzobishomotropone derivative 116 has been reported in the literature.<sup>160</sup> This could serve as a suitable model compound for 115.

C<sub>1</sub>-C<sub>2</sub>: 1.485(11)  
 C<sub>2</sub>-O: 1.191(9)  
 C<sub>1</sub>-C<sub>8</sub>: 1.530(11)  
 C<sub>1</sub>-C<sub>7</sub>: 1.542(11)



C<sub>7</sub>-C<sub>8</sub>: 1.477(11)  
 C<sub>6</sub>-C<sub>7</sub>: 1.505(12)  
 C<sub>6</sub>-C<sub>5</sub>: 1.404(13)

116

The bond lengths reported for 116 have substantial standard deviations associated with them and too detailed a comparison is not meaningful. However, one of the internal cyclopropyl bonds C<sub>1</sub>-C<sub>7</sub> in 116 is just as long (1.542(11) Å) as the C<sub>1</sub>-C<sub>7</sub> bond in 115. Other relevant bond distances in 116 are comparable to corresponding distances in 115. The carbon-oxygen bond distance for the carbonyl in 116 (1.191 Å) is considerably shorter than that in 115. The C<sub>1</sub>-C<sub>2</sub> distance in 116 is only slightly longer than that in 115. The close similarity in the two structures confirms that 115 is not an extensively delocalized homotropylium derivative like 69.

Figure 13 represents another perspective view of the cation 115. The benzene ring is relatively planar. The rest of the framework deviates from planarity. It is interesting to see that the dihedral angles reported in Table 11c for 115 are very similar to those observed for 69.

The cation 115 is thus a case in point where there is disagreement between NMR and direct structural methods with regard to the extent of cyclic delocalization occurring in it. The NMR studies indicate that there is considerable delocalization occurring in 115 (though to a lesser

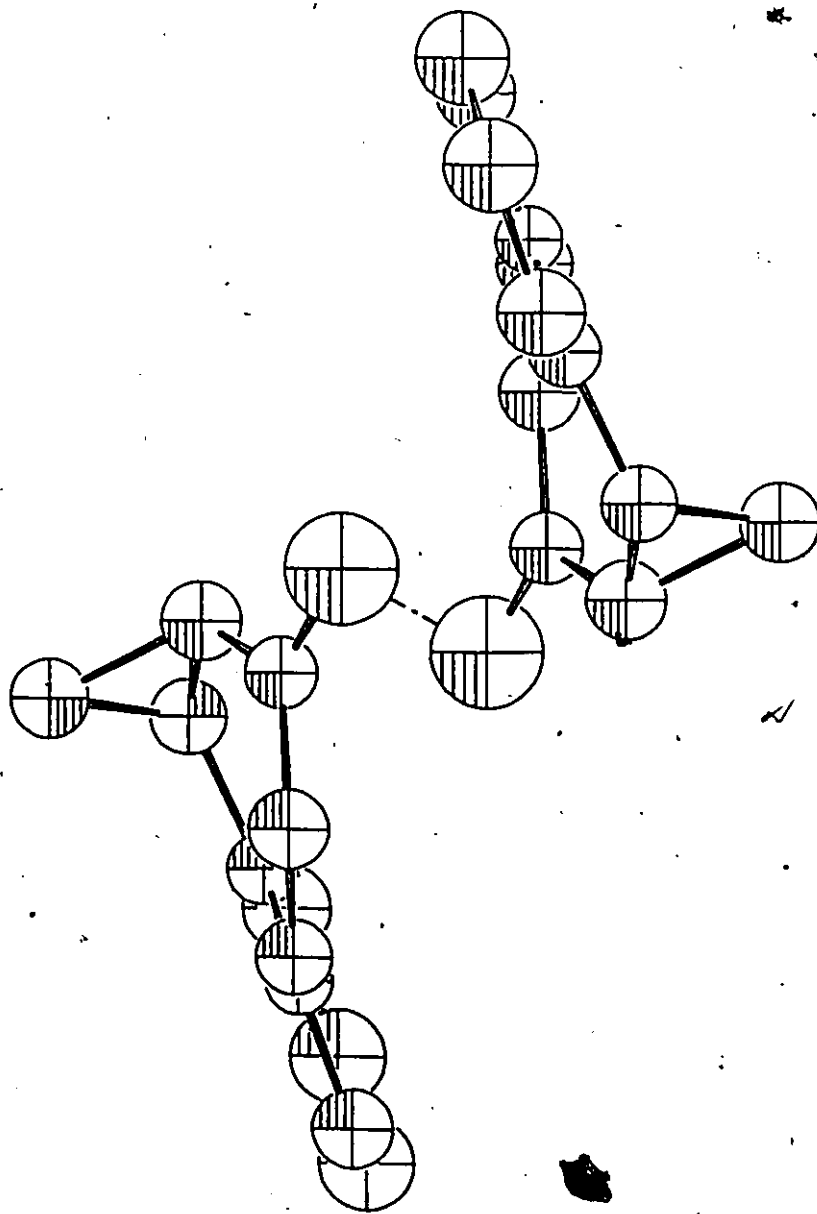


Figure 13 A perspective view of bis(5,6-benzo-8,8-dideuterobicyclo[5.1.0]octa-3,5-dien-2-one)hydrogen hexachloroantimonate 115.

extent compared to  $82-d_2$ ). The structural parameters observed hardly support this.

Hydrogen bridged ketones of the type  $115$  have not been observed before. In this context, it is unusual for the ketone  $114-d_2$  to yield the cation  $115$  and not the corresponding homotropylium cation  $82-d_2$ . More systems of similar nature must be examined before the factors determining this difference in behaviour can become apparent.

### 5. Conclusion

For defining aromaticity, molecular structure, molecular energetics and magnetic effects have been used as three important criteria.<sup>161</sup> The same three criteria can also be applied to define homoaromaticity. It should be mentioned that all three criteria are relative and depend on the model used for comparison. The use of magnetic effects such as the nuclear magnetic resonance (NMR) behaviour, diamagnetic susceptibility exaltation etc., as a criterion for homoaromaticity has been mentioned before. The use of molecular structure as a criterion for homoaromaticity is considered here.

Based on the structures of 2-hydroxyhomotropylium cation  $69$  and the related model compounds  $28$  and  $115$  as well as Haddon's proposals resulting from theoretical calculations, the following structural requirements are considered necessary for defining homoaromaticity.<sup>13</sup>

The group of atoms forming the cyclic array must have suitable spatial disposition for cyclic conjugation to occur. This spatial arrangement is particularly important for the orbitals forming the "homoconjugate bond" to have the most favorable overlap possible. This situation leads to a "nonplanar" arrangement for the basal plane.

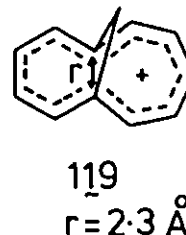
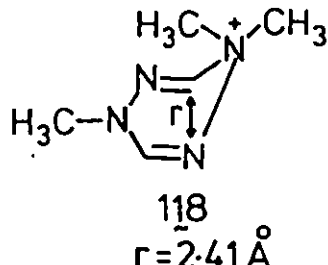
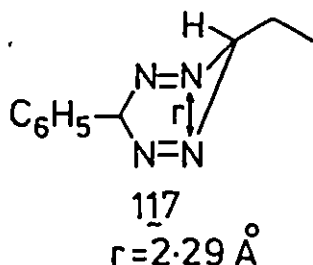
Calculations by Haddon for the homotropylium cation have shown

that such a nonplanar arrangement greatly improves the overlap of orbitals forming the "homoconjugate linkage". This leads to a lowering of energy for the system.<sup>13,79</sup> The bond lengths in the polyenyl segment should be in between those of single and double bonds for the atoms in question. Haddon has predicted a tendency toward bond equalization. The bonds between the polyenyl segment and the bridge fragment would therefore be expected to be shortened from the normal distance for a single bond. A comparison with the corresponding bond lengths in a nonhomoaromatic model compound is implicit in these statements.

The interatomic distance between the atoms forming the "homoconjugate linkage" is also very important. If this distance is too short (as in the free cyclopropane itself) the system would obviously have a "localized cyclopropyl bond" restricting delocalization to the polyene segment only. One such example is the iron complex 28. For the hydrogen bridged cation 115, again, the short internal cyclopropane bond length shows the lack of significant involvement of this bond in cyclic conjugation, contrary to NMR results.

If the transannular distance is too large (for example, greater than  $2.2\text{\AA}$ ) the transannular interactions will be too weak to be of any beneficial value energetically. Some examples for this category are the tetrazines 117 and 118 and bicyclo[5.4.1]dodecapentanylium cation 119.<sup>162-164</sup> It should be noted that all these systems have been claimed to be homoaromatic on the basis of NMR studies.<sup>165-167</sup>

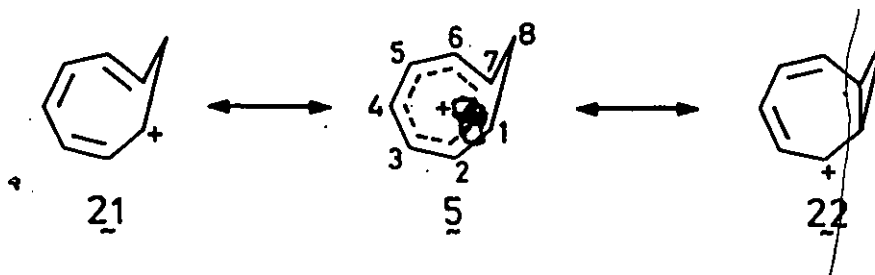




The obvious question to address is what could be a reasonable length for this homoconjugate linkage. Based on the structure of 69, the only homoaromatic cation examined thus far, it is hard to arrive at a definite answer. One would obviously expect a range of bond lengths that are considerably longer than 1.51 Å (free cyclopropane bond length) but considerably shorter than 2.2 Å (transannular distances in annulenes).<sup>76,168</sup>

In the case of homotropylium cations, this distance would be expected to be dependent on the nature and position of substituents. At least for this system it is possible to make speculative predictions regarding the length of the "homoconjugate bond" on the basis of substituent effects.

In the case of the parent homotropylium cation, the fully closed structure 22 and the open cyclooctatrienylium structure 21 can be considered to contribute to the hybrid 5.



An electron donating substituent such as an -OH group at position 2 would preferentially help to stabilize the positive charge in this position. Hence the closed structure corresponding to 22 would be expected to contribute more to the resultant hybrid. This would result in a somewhat shorter C<sub>1</sub>-C<sub>7</sub> bond for the 2-hydroxy derivative 69, compared to the parent cation 5.

An -OH group at position 1, on the other hand, would preferentially localize the positive charge at this position. This would be expected to increase the contribution from the open structure corresponding to 21 to the resonance hybrid. The C<sub>1</sub>-C<sub>7</sub> interatomic distance would be longer in this case compared to the parent cation 5. Clearly, any test for the validity of this prediction warrants further structural studies on the parent cation 5 and the 1-hydroxy derivative 63.

Since definitive experimental evidence is lacking, it is necessary to resort to rough empirical calculations on bond orders for support. In the case of the parent cation, an equal contribution from 21 and 22 would be expected to lead to a bond order of approximately 0.5, for the C<sub>1</sub>-C<sub>7</sub> bond. For the 2-hydroxy derivative 69, an increased contribution from 22 would result in an increase in the bond order for the corresponding bond. The estimated C<sub>1</sub>-C<sub>7</sub> bond order values of 0.56 and 0.76 in 5 and 69, respectively, can be taken as crude qualitative support for the predictions mentioned above.<sup>53,137</sup> It should also be remembered that the methods used to obtain these values are different in both cases.

In conclusion, it is necessary that a system meets all the structural requirements stated earlier, before it can be considered to

fulfill the structural criterion for homoaromaticity. The presence of one structural feature, such as a long cyclopropyl bond, is, by itself, not a sufficient support for the structural criterion.

An important point to consider now is the relationship among all the three criteria of homoaromaticity, namely, structure, energetics and magnetic effects. In other words, it is necessary to determine how the structural parameters can be linked to the molecular energetics (such as the resonance energy) and to the magnetic effects (such as the induced ring current).

The dire shortage of information in this regard makes it difficult to come to a conclusion. A large number of "homoaromatic systems" have to be re-examined on the basis of the three criteria mentioned above in order to attempt at a correlation.

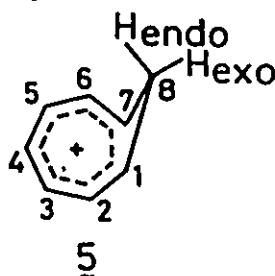
It is hoped that future studies will be directed towards rigorously defining the concept of homoaromaticity rather than finding "new homoaromatic systems". All systems should be tested to see if they fulfill all the three criteria mentioned above, before being described as "homoaromatic".

The 2-hydroxyhomotropylium cation meets the structural and magnetic requirements. The following chapter reports the results from investigations of this system with regard to the energetic requirements for homoaromaticity.

#### 6. Some Comments on the use of the Ring current Model for Homotropylium Cation

As already mentioned, Pettit explained the unusual features of the NMR spectrum of homotropylium cation 5 on the basis of the existence of

a ring current in the system.<sup>51</sup> Pettit realized the need to invoke the ring current in order to explain the large difference in chemical shifts ( $\Delta\delta = 5.8$  ppm) for the exo and endo protons on  $C_8$ .<sup>51</sup> The endo proton, being held over the ring is shielded due to the induced ring current while the exo proton, which was considered by Pettit to be almost coplanar with the ring, is deshielded.<sup>51,54</sup> On the basis of the data reported by Johnson and Bovey, Pettit suggested that the large  $\Delta\delta$  value of 5.8 ppm indicates that the size of this ring current is of the same order of magnitude as that present in benzene.<sup>54,126</sup>



Winstein came to similar conclusions regarding the existence of a ring current in 5.<sup>52</sup> According to Winstein the large chemical shift difference for exo and endo protons could be well accounted for by the ring current model.<sup>53</sup>

The only ring current calculation reported for homotropylium cation in the literature was that by Winstein.<sup>1</sup> Based on its spectral similarity to the tropylium cation 4, Winstein used a tropylium-like ring radius of  $1.6 \text{ \AA}$  and a 6-electron induced ring current in his calculation. The coordinate distances for the two protons on  $C_8$  from the centre of the seven-membered ring were estimated from molecular models. Based on the Johnson-Bovey equation, Winstein calculated the incremental shift for  $H_{\text{endo}}$  and  $H_{\text{exo}}$  due to the ring current to be 5.4

and -0.14 ppm respectively. The calculated  $\Delta\delta$  value of 5.54 ppm agreed well with the observed difference of 5.8 ppm. No details are available of Winstein's assumptions, etc. in obtaining these values.

In this present work an attempt was made to recalculate this chemical shift difference using a computer program written by Dr. McGlinchey and A. Agarwal of this Department.<sup>128,215</sup> It was hoped that the improved computational techniques used here would lead to a better understanding of this phenomenon. The evaluation of the elliptical integrals, used in this ring current calculation, as the sum of the first 29 terms of the infinite series would reduce errors due to truncation.

The results of the present calculation based on the same coordinates and ring radius reported by Winstein for different values of the current loop separation are reported in Table 13. It is likely that Winstein must have used a loop separation of about 1 Å. Thus the present calculations showed that Winstein's results could be reproduced.

Though these calculations seemingly support Winstein's conclusion that the ring current accounts for the observed chemical shift difference between the two protons, there are certain disturbing features that makes its validity doubtful.

i) The coordinates for the protons were calculated from molecular models. These are not reliably accurate. The calculated increments to the chemical shifts due to the ring current are very sensitive to the coordinates of the protons used. Therefore calculations based on wrong geometry would lead to unreliable results. The values reported by Winstein for the coordinates of the protons indicate that the seven-membered ring is planar and the cyclopropyl group is bent away from the

Table 13

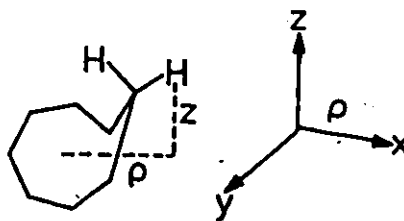
Calculated Ring Current Contribution ( $\delta'$ ) to the Chemical Shifts for Methylene Protons in 5<sup>a,b</sup>

Loop Separation	$\delta'$ for H <sub>endo</sub> (ppm)	$\delta'$ for H <sub>exo</sub> <sup>c</sup> (ppm)	$\Delta\delta$ (ppm)
0.00	4.81	-0.03	4.84
0.94	5.41	-0.31	5.72
1.00	5.49	-0.34	5.83
1.02	5.52	-0.36	5.88
1.28	5.95	-0.99	6.94

<sup>a</sup> Ring radius  $\delta = 1.6 \text{ \AA}$

<sup>b</sup> Coordinates for the protons (reported by Winstein, ref. 1).

proton	P(x) 0 Å	Z 0 Å
H <sub>endo</sub>	0.81	1.70
H <sub>exo</sub>	2.60	1.37



<sup>c</sup> Negative sign shows deshielding.

basal seven-membered ring.

ii) The magnitude of shielding for the endo proton calculated on the basis of this model is far greater than the magnitude of the deshielding for the exo proton. From the magnitudes of the chemical shifts of  $\delta$  5.1 and -0.76 ppm, for  $H_{\text{exo}}$  and  $H_{\text{endo}}$ , measured experimentally, it would appear that the converse is true.<sup>63</sup> For example, the chemical shift for methylene protons in the absence of ring current is suggested to be  $\delta$  1.36 ppm, on the basis of calculations by McGlinchey and coworkers.<sup>215</sup> If this suggestion is valid, then, the ring current contribution to the shielding of endo proton would be 2.12 ppm and that for the deshielding of the exo proton would be 3.74 ppm. The average value of chemical shifts for methylene protons on  $C_8$  in the structurally similar, nonhomoaromatic cation 28 is  $\delta$  1.44 ppm. Even the use of this value instead of  $\delta$  1.36 ppm for the methylene proton reference would not change the outcome.

iii) The need for the empirical separation of the current loops in the case of calculations for aromatic systems has been questioned.<sup>128</sup> The use of such a loop separation in the case of homoaromatic systems is even less valid. It is well-known that in the latter systems, the orbital overlap is restricted to only one side (namely, the lower side) of the basal plane.

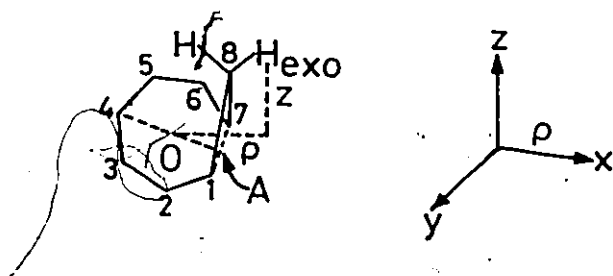
These foregoing arguments against the conclusions of the calculations based on Winstein's data warranted a re-examination of these calculations in the light of the experimental geometry for the 2-hydroxyhomotropylium cation 69. As previously mentioned, the geometry obtained from x-ray crystallography for the 2-hydroxy derivative is in very good agreement with the geometry of the parent cation 5, calculated

theoretically by Haddon.<sup>13</sup> It is interesting to note that in this crystallographic geometry for 69, C<sub>8</sub> is tilted towards the seven-membered ring and not away from it. This geometry, being different from that inferred from Winstein's data, would be expected to give different results.

The crystallographic coordinates for the hydrogens on C<sub>8</sub> were not reported in the crystallographic study for the 2-hydroxy derivative 69.<sup>137</sup> (The hydrogen atoms in 69 could not be located by x-ray diffraction due to the disorder present in the crystal). However, these coordinates were calculated using the regular geometries for a cyclopropyl group, since the crystallographic coordinates for all the carbon atoms in 69 are known. A standard C-H bond length of 1.08 Å and H-C-H angle of 114° were used in this calculation.<sup>216</sup> The crystallographic coordinates calculated for these hydrogens were then transformed to the orthogonal cartesian coordinates, measured in Ångstroms, with respect to a crystallographic (heavy atom) origin. These coordinates had to be referred to the centre of the seven-membered ring as the origin in order to be used in the ring current calculation. For the nonplanar seven-membered ring the midpoint of the line joining C<sub>4</sub> and A (the midpoint of the line joining C<sub>1</sub> and C<sub>7</sub>) was considered to represent the "centre" of the seven-membered ring. The coordinates of the hydrogens on C<sub>8</sub> were then referred with respect to this new origin. The radius (r) of the circular loop inscribing the (nonplanar) seven-membered ring was calculated as the average distance of the carbon atoms C<sub>1</sub> to C<sub>7</sub> from the centre of the ring. These values are summarized in Scheme 2,



Scheme 2



radius,  $\gamma = 1.61 \text{ \AA}$

Proton	$\rho(x)$ $\text{\AA}$	Z $\text{\AA}$
H <sub>endo</sub>	0.6388	1.8521
H <sub>exo</sub>	2.4500	1.8184

Due to the crystallographic mirror-plane symmetry restriction imposed to solve the crystal structure, the y coordinates of these hydrogens were zero ( $C_4$ , O, A, H<sub>endo</sub> and H<sub>exo</sub> lie in this plane).

These data were then used to calculate the ring current contribution to the incremental shifts for these protons using the same program mentioned earlier.<sup>128,216</sup> For the sake of completeness, calculations were made with finite as well as zero separation between the current loops.

As shown by the results presented in Table 14, the present

Table 14

Calculated Ring Current Contribution ( $\delta'$ ) to the Chemical  
Shifts for the Methylene Protons in 5<sup>a,b</sup>

Loop Separation $\overset{\circ}{\text{A}}$	$\delta'$ for H <sub>endo</sub> (ppm)	$\delta'$ for H <sub>exo</sub> (ppm)	$\Delta\delta$ (ppm)
0.00	4.49	0.55	3.94
0.50	4.63	0.51	4.12
1.00	5.06	0.38	4.68
1.28	5.44	0.25	5.19
1.50	5.81	0.12	5.69

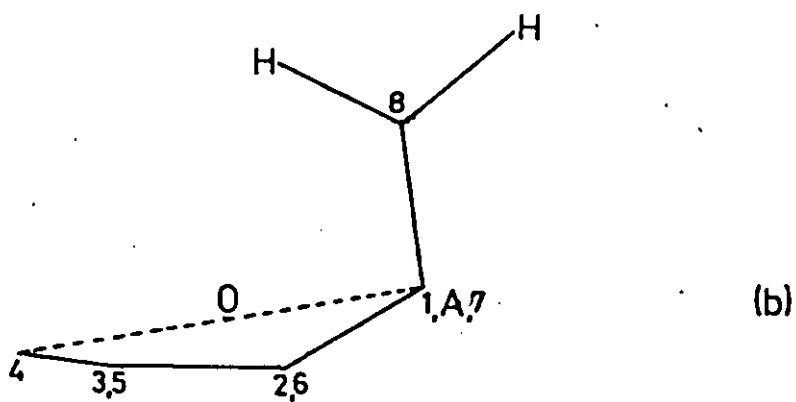
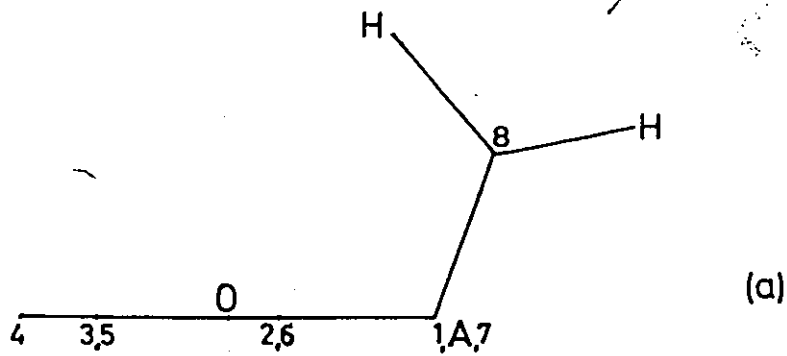
<sup>a</sup> Based on the present data reported in Scheme 2.

<sup>b</sup> Positive and negative signs indicate shielding and deshielding, respectively, due to the ring current.

study indicates that both the protons on  $C_8$  experience shielding due to the ring current. The  $\Delta\delta$  values for the small loop separations are considerably lower than those calculated with the coordinates used by Winstein (Table 13). However, it is interesting to note that larger values of  $\Delta\delta$ , close to the experimentally observed value, can be obtained if loop separations of 1.28 Å or more are employed. The  $\Delta\delta$  value (3.94 ppm, Table 14) calculated for zero loop separation is very close to the experimentally measured  $\Delta\delta$  value (3.1 ppm) for the 2-hydroxyhomotropylium cation, the geometry of which was made use of in the present study.

Further calculations were made using different sets of coordinates for the hydrogens  $H_{\text{endo}}$  and  $H_{\text{exo}}$  and different values for the ring radius. These coordinates and radii were the results of different choices for the centre of the ring (such as, for example, centre of the "best"-plane  $C_2C_3C_5C_6$  etc). These calculations did not lead to any improvement of the situation.  $\Delta\delta$  values in all these cases were much lower and calculations yielded positive shielding increments for both the protons due to the ring current.

Based on the experimental geometry for 69 and the calculated coordinates for the exo and endo hydrogens on  $C_8$ , and the relative orientation of the methylene hydrogens and  $C_8$  with respect to the centre of the ring could be traced. This can be compared with the model employed by Winstein. These results are summarized in Scheme 3. On comparing these models the reasons for the differences in the values reported in Tables 13 and 14 become obvious. The ring current calculation for the non planar structure has placed  $H_{\text{exo}}$  in the shielding region. It is interesting to



Scheme 3

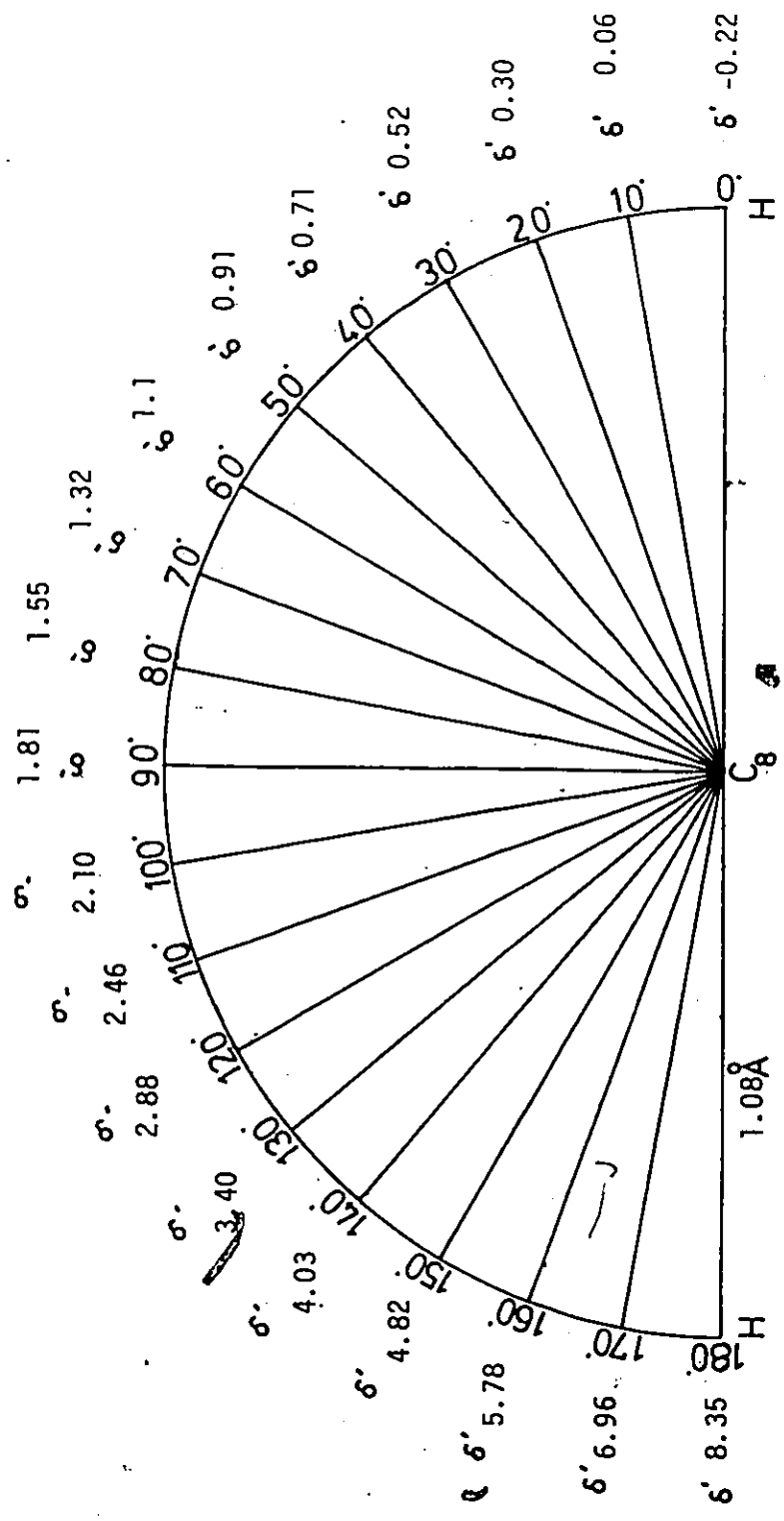
Side projection of homotropylium cation based on (a) Winstein's model, and (b) the crystallographic geometry of 2-hydroxyhomotropylium cation.

note that according to this geometry,  $H_{\text{endo}}$  would be located at a position close to the centre of the ring and would experience greater shielding. Since both the protons are shielded, based on this calculation, the chemical shift difference is expected to be less (than 5.86 ppm).

It is possible that the assumption of a regular cyclopropyl geometry for the C-H bond length and H-C-H bond angle used in the calculation of the coordinates of the hydrogens is incorrect. It is conceivable that at a different orientation of the C-H bond, the exo proton may undergo shielding due to the ring current and the  $\Delta\delta$  values will increase to the expected value of 5.86 ppm. To test this possibility, a profile map was traced for one of the protons on  $C_8$ . This profile took the shape of a semi-circle with  $C_8$  as the centre and the C-H bond length (1.08 Å) as the radius. Shielding contributions from the ring current (for zero loop separation) were calculated at positions corresponding to every 10° increments with respect to the reference line, (which is parallel to the  $C_4$ -O-A axis shown in Scheme 2). The results are summarized in Scheme 4.

As can be seen from Scheme 4, that only at the extreme position around the periphery of the semi-circle does the proton on  $C_8$  experience deshielding due to the ring current. At all other positions, both the protons on  $C_8$  would experience shielding no matter what their relative orientations are, if the geometry of the homotropylium cation is the same as that of its 2-hydroxy derivative.

Further, from Scheme 4, it can be seen that large values of  $\Delta\delta$ , close to the observed value of 5.86, result when the two hydrogens make an angle of 150° or 160° at  $C_8$ . The shielding contributions for the protons at these two positions are listed in Table 15.



Scheme 4

Table 15

Calculated Ring Current Contribution ( $\delta'$ ) to the Chemical Shifts for the Methylene Protons in 5<sup>a,b</sup>

H-C-H Angle °	$\delta'$ for H <sub>endo</sub> (ppm)	$\delta'$ for H <sub>exo</sub> (ppm)	$\Delta\delta$ (ppm)
150°	5.78	0.06	5.72
160°	5.78	-0.22	6.00

<sup>a</sup> A zero loop separation was employed.

<sup>b</sup> Positive and negative signs indicate shielding and deshielding, respectively, due to the ring current.

Thus, from this calculation, only for an almost linear disposition of the two hydrogens, or only with the use of an arbitrary loop separation of 1.28 Å, were large  $\Delta\delta$  values, close to that observed for homotropylium cation, obtained. However, such a distorted arrangement for  $H_{\text{endo}}$ ,  $C_8$  and  $H_{\text{exo}}$  is unrealistic and the need to use a loop separation has no justification.

From this exercise, the following conclusion can be reached: the large magnitude of the difference in chemical shifts for the protons on  $C_8$  in homotropylium cation 5 cannot be fully accounted for, on the basis of the ring current, if 5 has the nonplanar geometry similar to its 2-hydroxy derivative 69. This shows that either (a) 5 has a geometry very different from that of 69, or (b) other factors besides ring currents contribute (significantly) to the observed chemical shift difference for the methylene protons.

a. *Geometry of Homotropylium Cation*

As already mentioned, the MINDO-3 geometry for 5 is in very good agreement with the experimental geometry of 69.<sup>13,79,137</sup> Further, it has been reported that MINDO/3 calculations can reproduce reasonable molecular geometry.<sup>13</sup> The hydroxy group in 69 can be expected to cause some changes in bond lengths for the seven-membered ring when compared to the parent cation 5. It has already been mentioned that the charge localization by the hydroxy group can be expected to alter the internal cyclopropyl bond length. However, it is not expected to change substantially the overall geometry of the cation. In other words, the orientation of the cyclopropyl group relative to the seven-membered ring can not be expected to vary widely. As can be seen from the structural studies on



69, 28 and 115, the molecular geometry of the bicyclo[5.1.0]octadienyl systems does not seem to vary, in spite of the differences in the nature and extent of cyclic delocalization, present in these systems. Therefore, it is unlikely that the geometry of 5 should be very different from that of 69.

Experimental support for the nonplanar geometry comes from the values of the coupling constants for the protons in the seven-membered ring of 5.<sup>63</sup> Such a geometry would tilt the cyclopropyl group (and therefore  $C_8$ ) toward the centre of the ring and not away from it, as the data of Winstein (Table 13) would indicate. This would place both the hydrogens in the shielding zone due to the ring current. Therefore neither the deshielding for  $H_{\text{endo}}$  nor a large value for  $\Delta\delta$  could be expected to result from this ring current. The x-ray structural determination of 5 would, indeed, help to solve the problem with certainty.

b. *Factors Contributing to the Chemical Shift Difference for the Methylene Protons*

If the geometry of the cation 5 is similar to (or the same as) the one used in this calculation, then other factors besides ring current must contribute to the chemical shifts for the two protons in question. The calculated ring current contribution to the  $\Delta\delta$  value of 3.94 ppm for 5 compared to the observed value of 5.86 ppm indicates that contributions from these other factors cannot be ignored.

(i) One of the factors to be considered is the chemical shift value for the methylene protons in the absence of a ring current. The important question to bear in mind is whether the value of the chemical shift

for both the protons is the same. The assumption that the chemical shift value is the same for both the protons in the absence of the ring current is implicit in the calculation of  $\Delta\delta$ . In many molecules, due to the free internal motion, the chemical shift value for the geminal protons of a methylene group would average to be the same. For example, in large cycloalkanes the average value for the chemical shift of methylene protons is reported to be  $\delta$  1.30 ppm.<sup>218</sup> In a study of the ring current calculations of [10]-paracyclophane, Agarwal and coworkers obtained a better fit between the experimental and calculated chemical shifts for the methylene protons, if the above value was changed to 1.36 ppm.<sup>215</sup> This once again is an average value for both the methylene protons.

However, in the present case these methylene protons form part of a "formal" cyclopropane. It is necessary in this case to consider the shielding effect of cyclopropane itself. Cyclopropane also has a ring current and this has been the subject of a considerable number of studies.<sup>217-219</sup> However, the difference in chemical shift for the geminal protons in many cyclopropane derivatives is small and is usually in the range 0 to 0.5 ppm, depending on the substituents.<sup>217</sup> In the case of the cyclopropyl carbanyl cation itself (40), this difference is only 0.43 ppm.<sup>68</sup>

Perhaps a more pertinent model to consider in this case, would be the structurally similar nonhomoaromatic bicyclo[5.1.0]octadienylum-irontricarbonyl cation 28: The chemical shifts for the cyclopropyl (methylene) protons are  $\delta$  1.35 and 1.53 ppm. The  $\Delta\delta$  value of 0.18 ppm in this case is by no means significant. Further their average value of  $\delta$  1.44 ppm is closer to that reported for methylene protons ( $\delta$  1.36

ppm).<sup>215</sup>

Thus it would seem that the exo and endo protons on C<sub>8</sub> of the homotropylium cation may not have widely different chemical shifts in the absence of the ring current due to the delocalization in the seven-membered ring. In other words, this difference may not be more than 0.5 ppm as in the case of cyclopropyl compounds.<sup>217</sup> Therefore it would seem that the assumption implied in the calculation of  $\Delta\delta$  value is not unreasonable.

ii) The next important factor is the local anisotropy. In the case of aromatic systems local anisotropy contributions (resulting from the electron circulation around each carbon in the ring) to the chemical shifts of the protons have been shown to be significant.<sup>128</sup> For [10]-paracyclophane 151 the magnitude of this contribution has been shown to be about half that due to the ring current contribution.<sup>128</sup> It is likely that in the case of 5, local anisotropy contributions also have to be considered to account for the proton chemical shifts. However, these contributions cannot be calculated, as the <sup>13</sup>C shielding tensors for the seven-membered ring cations are not available.<sup>215</sup>

In the case of the systems such as the tetrazines 117 and 118, the foregoing conclusions can offer some explanation for the observed discrepancy between the conclusions based on NMR studies and x-ray crystallography.<sup>162,163,165,166</sup> Thus, the present study has once again reiterated the need for structural determination to define homoaromaticity, as the conclusions reached from the NMR methods can only have limited value.



## CHAPTER 3

### HEATS OF PROTONATION OF ALICYCLIC KETONES BY SOLUTION CALORIMETRY.

#### A THERMODYNAMIC INVESTIGATION OF THE HOMOAROMATIC STABILIZATION.

It has been mentioned earlier that experimental studies on the measurement of the stability associated with homoaromatic systems are lacking. Experimental values for the stability can, in principle, be obtained by measuring the energy change associated with the formation of the "homoaromatic system" and comparing with that of a structurally similar nonhomoaromatic system. Absolute heats of formation of those two systems under consideration, usually measured in the vapour phase, can be used for such a study. However the extrapolation of the gas phase results to the much needed solution phase data is difficult.

Experimentally, it is easier to measure relative values of energies that are, in principle, associated with the heats of formation, preferably in solution. To this end a calorimetric determination of the heats of protonation of several ketones (with varying degrees of unsaturation), based on the method of Arnett and coworkers, was undertaken.<sup>169,170</sup>

#### 1. Heats of Protonation and $pK_a$ values

The heat of protonation of a carbonyl compound is a measure of the enthalpy difference between the carbonyl base and its conjugate acid (equation 10). In much the same way the  $pK_a$  of the conjugate acid is a measure of the free energy difference between the conjugate acid and

the carbonyl base (equation 9). The relationship between the free energy and enthalpy of protonation for the process represented by equation (8) has been discussed in detail by Arnett and Scorrano.<sup>171</sup>



$$\Delta G_{\text{protn}}^{\circ} = RT \ln K_a = -2.303 RT \text{p}K_a \quad (9)$$

$$\Delta H_{\text{protn}} = \Delta H_f(\text{conj. acid}) - \Delta H_f(\text{base}) \quad (10)$$

Arnett and coworkers found that there was a linear relationship (equation 11) between the heats of protonation of several amines and the experimentally measured  $\text{p}K_a$  values of their conjugate acids.<sup>170</sup> This relation was further extended to carbonyl compounds.<sup>169</sup>

$$-\Delta H_{\text{protn}} = (1.78\text{p}K_a + 28.1)\text{kcal/mol} \quad (11)$$

Deviations from this linear correlation were noted for several carbonyl bases and these were suggested to be due to discrepancies in the  $\text{p}K_a$  values. This has been dealt with in detail by Arnett.<sup>169,171</sup> It has been suggested that the enthalpy of protonation of the carbonyl compounds is a better measure of their relative basicities.<sup>169</sup>

## 2. Heats of Protonation and Relative Stabilities

The difference in heats of protonation measured for structurally related ketones will, to a large extent, reflect the relative stability of the protonated ketones. The stability of a protonated ketone, in turn, depends on the ability of substituents to stabilize a positive charge. For example, in a series of structurally related ketones with

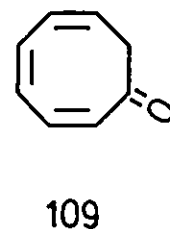
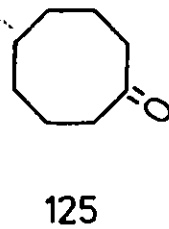
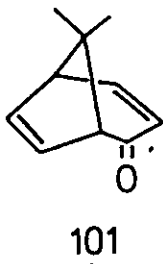
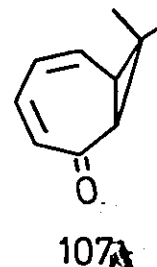
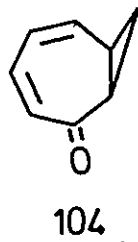
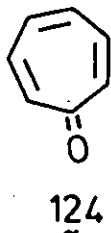
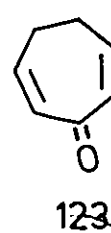
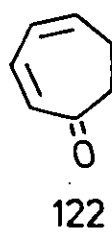
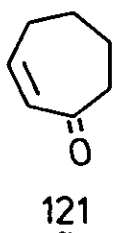
varying degrees of conjugation, the differences in the heats of protonation would be a measure of the differences in the conjugative stabilities of the protonated bases. The effects of conjugation are expected to be less pronounced in the case of the neutral ketones as compared to their conjugate acids.<sup>172,173</sup> In other words, these differences in the heats of protonation set a lower limit for the differences in stabilities of the conjugate acids. When extended to suitable model cyclic ketones, with extended conjugation, this approach can be used to bring out the importance of cyclic conjugation occurring in these systems. The present study takes advantage of this method.

### 3. Experimental Approach

The calorimetric measurement of heats of protonation is made possible by the fact that protonation of carbonyl compounds in  $\text{FSO}_3\text{H}$  is generally a clean reaction giving stable cationic products. The high acidity ( $H_0 = -15$ ) of the medium makes the protonation of the ketones a quantitative process.<sup>171</sup> Comparison of the heats of protonation of the ketones is possible because all measurements are made in the same medium ( $\text{FSO}_3\text{H}$ ).

The calorimeter used to measure the heats of protonation of the ketones 120-124, 104, 107, 101, 128 and 109 in  $\text{FSO}_3\text{H}$  ( $\Delta H_{\text{FSO}_3\text{H}}$ ), was similar in design but smaller in size than that employed by Arnett and Petro.<sup>174</sup> The ketones were introduced by means of a microliter syringe directly into the well-stirred acid. The changes in temperature were measured by means of corresponding variations in electrical resistance of a thermistor bead, incorporated into a Wheatstone bridge-circuit. The calorimeter was calibrated electrically by measuring the temperature

change for a known amount of heat input. Details of the experimental procedure have been described elsewhere.<sup>173,175</sup> Heats of protonation of all ketones except 107 were measured at ambient temperatures. Since the cation from 107 undergoes thermal isomerization at ambient temperatures, the heat of protonation of 107 had to be measured at  $-20^{\circ}\text{C}$ .<sup>84</sup>



In each case, control experiments were carried out to check for the completeness and cleanliness of the protonation as well as for the

kinetic stability of the conjugate acids under the calorimetric conditions. These control experiments involved the protonation of the individual carbonyl compounds in  $\text{FSO}_3\text{H}$ , separately, at somewhat higher concentration under conditions simulating those used for calorimetry. The resulting solutions were examined by  $^1\text{H}$  nmr. In each case, clean protonation on the carbonyl oxygen was observed. The  $^1\text{H}$  nmr spectra corresponded to those previously reported or those expected for the resulting cations.<sup>176-181,97,84,83</sup>

The measured heats of protonation in  $\text{FSO}_3\text{H}$ ,  $\Delta H_{\text{FSO}_3\text{H}}$ , have to be corrected for the heat capacity term for the neutral ketone resulting from the difference in temperature between the calorimeter and the sample as well as for the heat necessary for separation of the solute molecules to infinite dilution in solution. This latter quantity corresponds to the heat of sublimation or vaporization of the ketone. These corrections were made by measuring the heat of solution of the ketones in an inert solvent,  $\text{CCl}_4$  ( $\Delta H_{\text{CCl}_4}$ ), and subtracting this value from  $\Delta H_{\text{FSO}_3\text{H}}$ . The resulting quantity,  $\Delta H_{\text{protn}}$  (equation 12) corresponds to the heat of protonation of the ketones in the gas phase. Justification of this correction has been dealt with in great detail by Arnett and co-workers.<sup>169-171,182,183</sup>

$$\Delta H_{\text{protn}} = \Delta H_{\text{FSO}_3\text{H}} - \Delta H_{\text{CCl}_4} \quad (12)$$

These values along with the  $\text{pK}_a$  values calculated from equation 11, are reported in Table 16.

In the case of cycloheptanone <sup>120</sup> the  $\Delta H_{\text{protn}}$  value of  $-18.5 \pm 1.3$  kcal/mole obtained in the present study, compared well with that ( $-18.2 \pm 0.2$  kcal/mole) quoted by Arnett and coworkers.<sup>169</sup>



Table 16  
Calorimetric Data

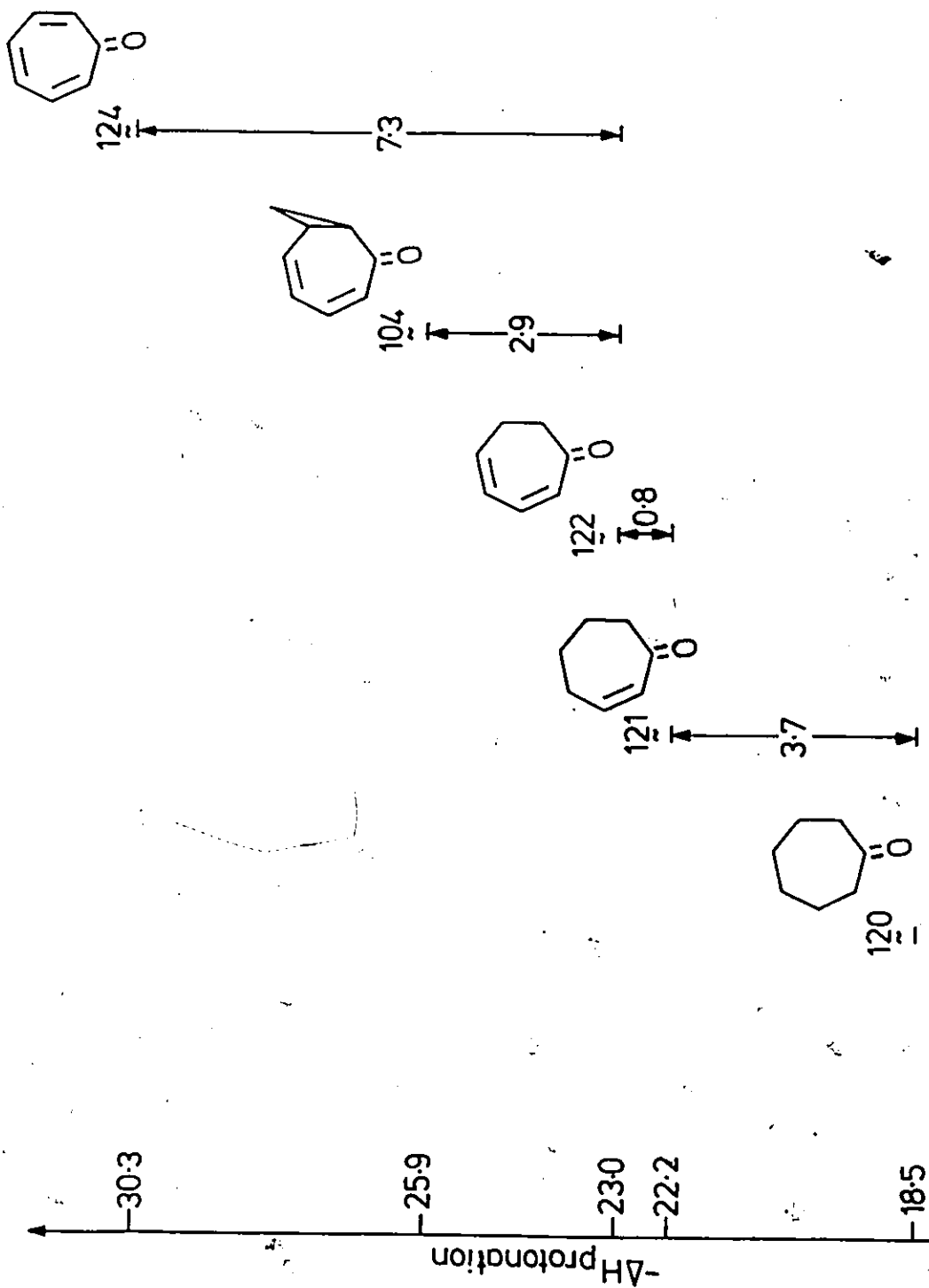
Ketone	Temp. °C	$\Delta H_{\text{FSO}_3\text{H}}$ kcal/mole	$\Delta H_{\text{CCl}_4}$ kcal/mole	$\Delta H_{\text{protn}}$ kcal/mole	$\text{pK}_a$ (Calcd.)*
<u>120</u>	25	-18.5 ± 1.3	0.0 ± .04	-18.5 ± 1.3	-5.4
<u>121</u>	30	-21.9 ± .9	+0.31 ± .01	-22.2 ± .9	-3.3
<u>123</u>	25	-21.5 ± .3	+0.50 ± .02	-22.0 ± .3	-3.4
<u>122</u>	30	-22.0 ± .3	+1.0 ± .5	-23.0 ± .8	-2.9
<u>124</u>	30	-28.5 ± .2	+1.8 ± .1	-30.3 ± .3	1.2
<u>104</u>	25	-25.1 ± .8	+0.77 ± .06	-25.9 ± .9	-1.2
<u>107</u>	-20	-25.4 ± .8	-2.47 ± .1	-23.0 ± .9	-2.9
<u>101</u>	26	0	0	-20.2 ± .4	-4.4
<u>125</u>	25	-19.3 ± .2	+0.32 ± .03	-19.6 ± .2	-4.8
<u>109</u>	25	-23.4 ± .7	+0.76 ± .04	-24.2 ± .7	-2.6

\* From equation 11.

#### 4. Effects of Conjugation

The trends in variation of the heats of protonation with changes in the extent of conjugation for the ketones 120, 121, 122, 124 and 104 are summarized in Scheme 5. The difference in the values of the heats of protonation ( $\Delta\Delta H_{\text{protn}}$ ) for cycloheptanone 120 and cycloheptenone 121 is 3.7 kcal/mole. In a related work carried out in this laboratory comparable differences were obtained with other pairs of saturated and unsaturated ketones.<sup>173</sup> This value translates into a  $pK_a$  difference of about 2.3 units.<sup>169,170</sup> The experimentally measured differences in  $pK_a$  for the conjugate acids of  $\alpha,\beta$ -unsaturated ketones and their saturated analogues vary between 3.5 and 4.45 units.<sup>184-86</sup> The use of different acidity scales in the experimental determination of  $pK_a$  values of the conjugate acids of these ketones could be a likely cause for this discrepancy.<sup>184-187</sup> The consistency of the values obtained by calorimetric method, where such discrepancies are not encountered, gives a better idea of the difference in basicities of the saturated and the corresponding unsaturated ketones.

Introduction of a second double bond in conjugation with the first does not cause considerable difference in basicity of the seven-membered ring ketones as compared to the effect of the first double bond. This is shown by the  $\Delta H_{\text{proton}}$  values of the cycloheptadienones 128 and 123 not being significantly greater than that of 121. While measuring the  $pK_a$  values of the conjugate acids of several steroidal ketones, Zalewski and Dunn have similarly noted that the effect of the second double bond in enhancing the  $pK_a$  values is small.<sup>188</sup>



Scheme 5

(All values in kcal/mole)

## 5. Effects of Cyclic Conjugation

The introduction of the third double bond in these cyclic ketones causes a very large effect with regard to  $\Delta H_{\text{protn}}$ . This is shown by the large difference in the values for the heats of protonation of cycloheptadienone 122 and tropone 124 ( $\Delta\Delta H_{\text{protn}} = 7.3$  kcal/mole). Tropone 124, with a  $\Delta H_{\text{protn}}$  value of  $-30.3$  kcal/mole is the most basic of the ketones studied in this series. This large  $\Delta H_{\text{protn}}$  value is a distinct variation from the previously observed smooth trend and reflects the stability associated with the aromatic hydroxytropylium cation. Arnett and coworkers observed that ketones, such as 2,6-dimethyl-4-pyrone, which also can form  $(4n+2)$  aromatic systems on protonation, have similar very large heats of protonation in  $\text{FSO}_3\text{H}$ .<sup>169</sup>

2,3-Homotropone 104, also exhibits a large  $\Delta H_{\text{protn}}$  value ( $-25.9 \pm 0.9$  kcal/mole). The significant difference in  $\Delta H_{\text{protn}}$  values of homotropone 104 and the dienone 122 ( $\Delta\Delta H_{\text{protn}} = 2.9$  kcal/mole) fully substantiates the conclusion reached previously that 69 is a homoaromatic cation. As in the case of tropone 124, this large value of  $\Delta H_{\text{protn}}$  is a marked change from the systematic variation in the heats of protonation observed for the ketones 120, 121 and 122. It is instructive to compare the results of the present study and the effect of variation of delocalization energy with increase in conjugation in acyclic and cyclic systems studied by means of other methods.

## 6. A Comparative Study of Trends in Conjugative Effects Observed by Other Methods

### a. Cationic Systems

In the case of linear systems thermodynamic data for a series of

conjugated cations is not available. However, theoretical calculations are available which give some indication of the delocalization energies in these systems. For the allyl cation, the barrier to rotation (the energy difference between the fully conjugated planar form and the non-conjugated perpendicular form) can be considered as the delocalization energy.<sup>189</sup> Though experimental values of rotational barriers are available for substituted allylic cations, such values are not available for pentadienyl, heptatrienyl and other conjugated cations. Therefore one is restricted to the use of estimates based on theoretical methods. In this regard the rotational barriers for twisting the terminal C<sub>1</sub>-C<sub>2</sub> bonds in allyl, pentadienyl and heptatrienyl cations calculated by Baird using the Dewar method have been chosen for comparison.<sup>190</sup> It is to be noted that the trends are more important than the absolute values themselves. The calculated rotational barriers for allyl, pentadienyl and heptatrienyl cations are 38, 51 and 57 kcal/mole respectively. With the introduction of a second double bond, the increment in the barrier is only  $\frac{1}{3}$  of the original value. The increment for the third double bond is even less. Thus the incremental change in delocalization energy decreases with increase in conjugation and is expected to level off as the chain length increases. However, the present study shows that, in cyclic cations, where the extended conjugation leads to aromatic or homoaromatic delocalization, the increment in delocalization energy is actually enhanced.

b. *Neutral Systems*

The heats of hydrogenation of cyclic olefins measured by Kistiakowski and coworkers serve as the thermodynamic data for comparing

the energetic effect of conjugation in neutral systems.<sup>191,192,193</sup> For linearly conjugated systems, the increment in the heats of hydrogenation due to the introduction of each additional double bond decreases gradually. This can be seen from the values of -26.5, -51.3 and -72.8 kcal/mole observed for the heats of hydrogenation of cycloheptene, cyclohepta-1,3-diene and cyclohepta-1,3,5-triene, respectively.<sup>191</sup> In the case of the olefinic series with six-membered ring, the extension of conjugation leads ultimately to an aromatic system with cyclic delocalization. This is reflected by a break or discontinuity in the variation of the heats of hydrogenation. The heats of hydrogenation values of -28.6, -55.4 and -49.8 kcal/mole observed for cyclohexene, cyclohexa-1,3-diene and benzene, respectively, illustrate this point.<sup>192,193</sup> In fact, the difference between the calculated ( $-28.6 \times 3 = -85.8$  kcal/mole) and the observed (-49.8 kcal/mole) heats of hydrogenation of benzene has been proposed as the resonance energy (36 kcal/mole) of benzene.<sup>161</sup> The discontinuity in the trend observed for the heats of hydrogenation of the six-membered ring unsaturated hydrocarbons was one of the arguments for the proposal of molecular energetics as a criterion for aromaticity.<sup>161</sup> Such a criterion can be extended to homoaromaticity, on the basis of the discontinuity in the trend observed, in the present study, for the heats of protonation of the series of ketones mentioned earlier.

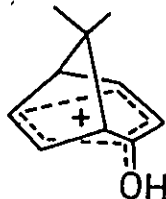
#### 7. Comparison of Heats of Protonation with $pK_a$ Values

The experimental  $pK_a$  values reported for the conjugate acids of ketones 120, 104 and 124 are -6.9, -2.8 and -0.6 respectively.<sup>185,186,97,194</sup> All these  $pK_a$  values were based on  $H_0$  acidity scale. It is therefore possible to compare these  $pK_a$  values with the values of the heats of

protonation of the corresponding conjugate bases. The differences in  $\Delta H_{\text{protn}}$  found for these ketones are roughly 1.78 times the corresponding differences in  $\text{pK}_a$  values quoted above. This observation is in line with the correlation between the  $\text{pK}_a$  values and heats of protonation reported by Arnett (equation 11).<sup>169</sup>

#### 8. Steric Effects and Heats of Protonation

The  $\Delta H_{\text{protn}}$  of 107 is some 2 kcal/mole less than that of 104. The presence of a gem dimethyl substituent on the cyclopropyl carbon contributes considerably to the lowering of heats of protonation in this case. A similar effect was observed by Childs and coworkers in the case of some methyl substituted bicyclo[3.1.0]hex-3-en-2-ones.<sup>173</sup> It is likely that this effect results from the steric hindrance to solvation of the cations in the acid medium. Arnett and coworkers have observed a reduction in solvation energy with increase in the bulkiness of substituents in benzenium ions.<sup>195</sup> This type of lowering of solvation energies due to steric hindrance to solvation has also been observed in the calorimetric studies of neutral molecules such as ketones and alkenes as well as anions such as the alkoxide ions.<sup>196-198</sup> It is likely that the lower heat of protonation of the ketone 101, as compared to cyclohexenone ( $-22.1 \pm 0.6$  kcal/mole) arises from such an effect mentioned above.<sup>173</sup> Other destabilizing effect of electronic origin, in the resulting cation (such as bishomoantiaromatic delocalization 126) would seem to be an unlikely cause.<sup>84,173</sup>



9. Comparison of the Heats of Protonation of Cyclooctatrienone 109 and Homotropone 104

In the present study, the corresponding series of 8-membered ring ketones is incomplete. However, it is interesting to note that the difference in the heats of protonation of cyclooctanone 125 and cyclooctatrienone 109 is relatively small ( $\Delta\Delta H_{\text{protn}} = 4.6$  kcal/mole). This difference in the heats of protonation is less than that between cycloheptanone 120 and homotropone 104 ( $\Delta\Delta H_{\text{protn}} = 7.4$  kcal/mole).

While the heats of protonation of cyclooct-2-en-1-one and cycloocta-2,4-dien-1-one were not measured, it is likely that they are larger than that of cyclooctanone by much the same magnitude as the differences observed for the corresponding seven-membered ring ketones. In other words, cycloocta-2,4-dien-1-one might be expected to have a heat of protonation of about -24 kcal/mole which is approximately the same value as that measured for cyclooctatrienone 109 (-24.2 kcal/mole). Therefore, the question arises as to whether homoaromatic stabilization is present in 63 and if so, why the heat of protonation of 109 is not larger. This can be answered by comparing the relative energies of the ketones 104 and 109 and those of their conjugate acids 63 and 69.

As will be shown in the following chapter, there is good evidence to suggest that the difference in free energies of formation of 1-hydroxyhomotropylium cation 63 and 2-hydroxyhomotropylium cation 69 in  $\text{FSO}_3\text{H}$  is only of the order of 1kcal/mole. Since differences in entropy effects are expected to be small for these isomeric cations, it is likely that there is a corresponding difference in the enthalpies of formation of the two cations 63 and 69.



The heats of formation of the ketones 109 and 104 are not available. However, estimates of their heats of formation in the gas phase can be obtained using Benson's rules for the additivity of the enthalpies of formation of various groups in a molecule.<sup>199,200</sup> Such an estimate leads to a value of about 0.5 kcal/mole for the difference in enthalpies of formation of the ketones in question (Table 17). It can be seen that the sum of the differences in enthalpies of the starting ketones and product cations (1.5 kcal/mole) is roughly the same as the difference in heats of protonation of the two ketones (1.7 kcal/mole). Thus the lower heat of protonation of cyclooctatrienone can be expected to result from the differences in relative stabilities of the two ketones 109 and 104 as well as those of the conjugate acids 63 and 69. Scheme 6 illustrates this point. The thermodynamic consistency of the numbers shown in Scheme 6 supports the validity of the various estimates made.

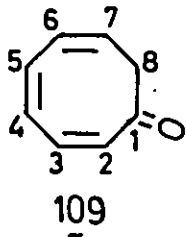
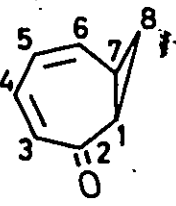
10. Aromatic Stability vs Homoaromatic Stability. The Possible Role of Strain Energy.

The difference in the heats of protonation of 122 and 104 (2.9 kcal/mole) is approximately  $\frac{2}{5}$  times as large as that between 122 and 124 (7.3 kcal/mole) (Scheme 5). This comparison suggests that homoaromatic delocalization is less effective than conventional aromatic delocalization in stabilizing the seven-membered ring cation.

The difference in the conjugative abilities of cyclopropyl group and the double bond is unlikely to be the main cause for this observation. From a study of the heats of protonation of ketones conjugated with a carbon-carbon double bond and with a cyclopropyl ring, Childs and

Table 17

Estimation of Standard Enthalpies of Formation of  
2,3-homotropone 104 and cycloocta-2,4,6-trienone 109<sup>a</sup>

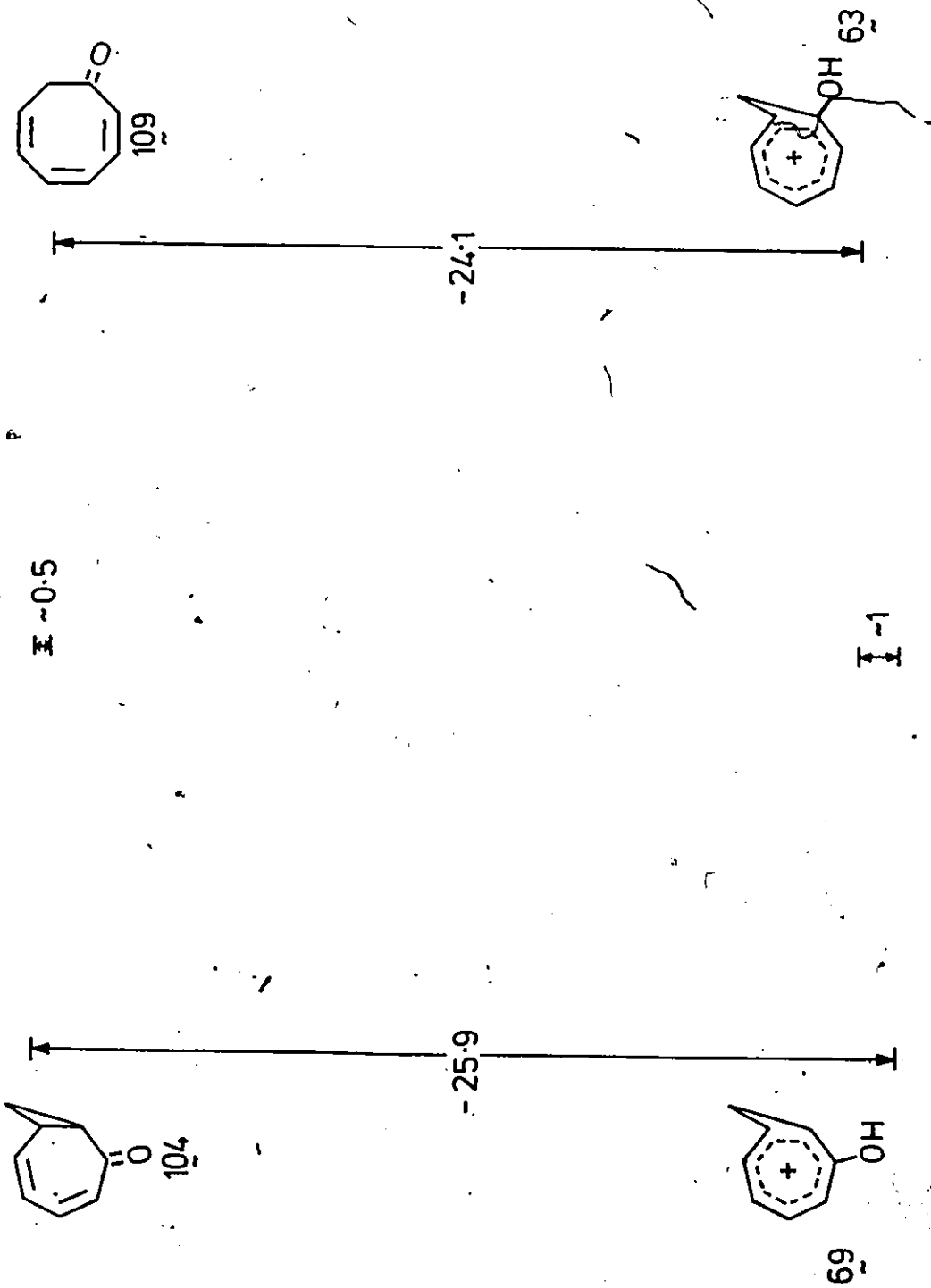
Molecule	Group <sup>b,c</sup>	Heat of formation kcal/mole	
 <p>109</p>	1 <u>CO</u> (Cd) (C)	-31.4	
	2 <u>Cd</u> (Cd) (CO)	8.9 <sup>d</sup>	
	4 3-6 <u>Cd</u> (Cd) <sub>2</sub>	7.42x4 <sup>d</sup>	
	7 <u>Cd</u> (C) (Cd)	8.88	
	8 <u>C</u> (Cd) (CO)	-3.8	
	3) Correction for cis C=C	1x3	
	Correction for the ring	8.9 <sup>e</sup>	
	$\Delta H_f^0$ (total)	<u>24.16</u>	
	 <p>104</p>	2 <u>CO</u> (Cd) (C)	-31.4
		3 <u>Cd</u> (CO) (Cd)	8.9 <sup>d</sup>
2 4,5 <u>Cd</u> (Cd) <sub>2</sub>		7.42x2 <sup>d</sup>	
6 <u>Cd</u> (Cd) (C)		8.88	
7 <u>C</u> (H) <sub>2</sub> (C) <sub>2</sub>		-4.95	
8 <u>C</u> (C) <sub>2</sub> (Cd)		-1.48	
1 <u>C</u> (CO) (C) <sub>2</sub>		-1.7	
2 Correction for cis C=C		1x2	
Correction for the ring		29.6 <sup>f</sup>	
$\Delta H_f^0$ (total)		<u>24.69</u>	

..... continued

Table 17 (continued)

- a Based on the values reported by Benson and coworkers. 199,200
- b The carbons in parentheses are the groups attached to the carbon in question (the underlined carbon; the superscript denotes its position in the ring).
- c Cd denotes an olefinic carbon; CO, a carbonyl carbon and C, a saturated carbon.
- d Estimates.
- e Correction for cycloocta-1,3,5-triene
- f Correction for bicyclo[5.1.0]octane

$$\Delta\Delta H_f^0 = \Delta H_f^0 \text{ 104} - \Delta H_f^0 \text{ 109} = 24.7 - 24.2 = 0.5 \text{ kcal/mole}$$



Scheme 6

(All values in kcal/mole)

coworkers observed that the cyclopropyl group is as effective as a double bond in enhancing the stability of a protonated ketone.<sup>173</sup> As mentioned before, the strain energy associated with the "cyclopropyl" ring in the homoaromatic species can be expected to be one of the main factors reducing the relative energetic importance of homoaromatic delocalization. (The less efficient overlap of the interacting orbitals in homoaromatic systems as compared to aromatics could be another possible factor. However, this cannot be directly ascertained by the present experimental study).

In order to evaluate the relative importance of strain energy and delocalization energy, it was decided to make use of the thermodynamic cycle given in Scheme 7. This cycle takes advantage of the previously reported facile rearrangement of the conjugate acid of 107 to that of 101.<sup>84</sup>

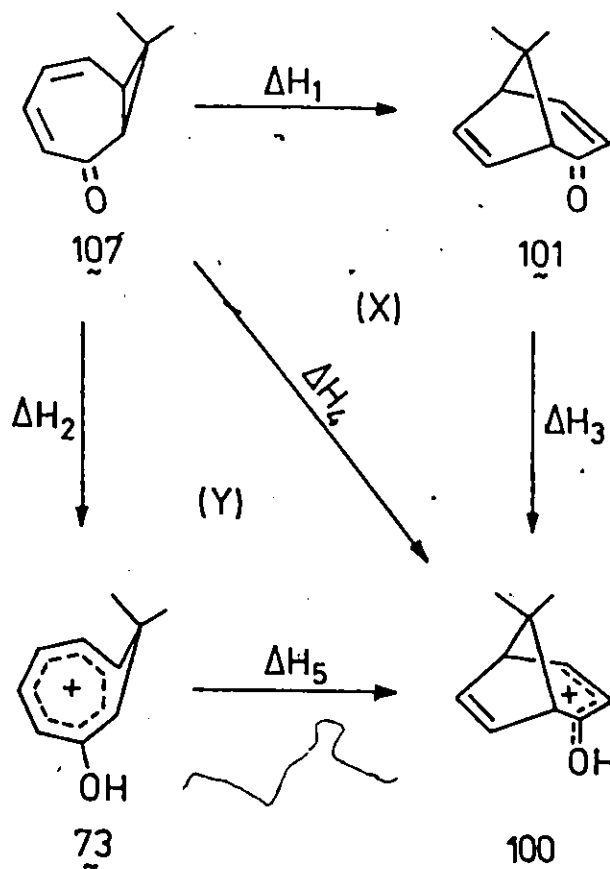
Considering the two half cycles x and y, in Scheme 7, one can obtain the following relationships among these enthalpy changes (equations 13 and 14):

$$\Delta H_1 = \Delta H_4 - \Delta H_3 \quad (13)$$

$$\Delta H_5 = \Delta H_4 - \Delta H_2 \quad (14)$$

$\Delta H_2$  and  $\Delta H_3$  are the heats of protonation of ketones 107 and 101, measured previously.  $\Delta H_4$  could be obtained by measuring the heat evolved when the ketone 107 is introduced into the acid at a higher temperature at which rapid and quantitative rearrangement to 100 occurs. Knowing  $\Delta H_2$ ,  $\Delta H_3$  and  $\Delta H_4$  one could calculate  $\Delta H_1$  and  $\Delta H_5$ .

$\Delta H_1$  is mainly a measure of the difference in strain energy



Scheme 7

$\Delta H_1$  = Enthalpy difference between 107 and 101.

$\Delta H_2$  = Heat of protonation of 107 (at low temperatures).

$\Delta H_3$  = Heat of protonation of 101.

$\Delta H_4$  = Sum of the enthalpies of protonation and rearrangement of ketone 107 at ambient temperatures.

$\Delta H_5$  = Enthalpy difference between the conjugate acids 73 and 100.

= Enthalpy change for the rearrangement of 73 to 100.

between the two isomeric ketones 107 and 101. This value could then be approximated to the difference in strain energy between the cations 73 and 100.  $\Delta H_5$  is a measure of the differences in both the delocalization energy and the strain energy between the cations 73 and 100. A comparison of  $\Delta H_5$  and  $\Delta H_1$  would therefore indicate the relative importance of strain energy over delocalization energy in the homoaromatic cation 73 relative to that of 100.

Control experiments had to be run for checking the quantitative-ness and cleanliness of protonation of 107 and of the rearrangement of the conjugate acid 73 at the same temperature as that employed in the calorimetric measurements. Protonation and rapid NMR analysis of the ketone in  $\text{FSO}_3\text{H}$  at  $30^\circ\text{C}$ , under conditions mentioned earlier, showed "relatively" clean conversion to the conjugate acid 101. The reaction, however, was extremely sensitive even to small amounts of impurities in  $\text{FSO}_3\text{H}$  and reproducible results could not be obtained, if the acid was not rigorously purified.

Calorimetric measurements were unsuccessful. At  $30^\circ\text{C}$ , the rearrangement was not rapid enough to go to completion during the time of measurements. At elevated temperatures, ( $+60$  to  $+65^\circ\text{C}$ ) abnormally high and scattered values were obtained and considerable charring was noticed. Therefore the crucial value of  $\Delta H_4$  could not be obtained.

An estimate for the enthalpy difference  $\Delta H_1$  between the ketones 107 and 101 can be obtained from their calculated gas phase heats of formation based on the group additivity parameters reported by Benson.<sup>199,200</sup> The ketone 101 was found to be more stable than 107 by about 18.3 kcal/mole (Table 18). Using this value for  $\Delta H_1$ , it is possible to formally complete the cycles x and y shown in Scheme 7. The estimated values of

Table 18

Estimation of Standard Enthalpies of Formation of  
 8,8-dimethyl-2,3-homotropone 107 and  
 8,8-dimethylbicyclo[3.2.1]octa-3,6-dien-2-one 101<sup>a</sup>

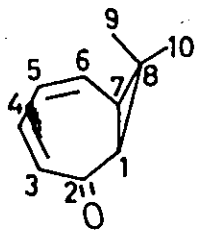
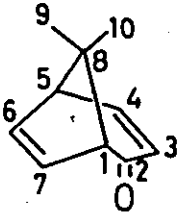
Molecule	Group <sup>b,c</sup>	Heat of formation kcal/mole
 <p>107</p>	2 <u>CO</u> (C) (Cd)	-31.4
	3 <u>Cd</u> (CO) (Cd)	8.9 <sup>d</sup>
	2 4,5 <u>Cd</u> (Cd) <sub>2</sub>	7.42x2 <sup>d</sup>
	6 <u>Cd</u> (Cd) (C)	8.88
	7 <u>C</u> (Cd) (C) <sub>2</sub>	-1.48
	1 <u>C</u> (CO) (C) <sub>2</sub>	-1.7
	8 <u>C</u> (C) <sub>4</sub>	0.5
	2 9,10 <u>C</u> (H) <sub>3</sub> (C)	-10.08x2
	2 Correction for cis C=C	1.0x2
	Correction for the ring	<u>29.6<sup>e</sup></u>
	$\Delta H_f^0$ (total)	<u>9.98</u>
 <p>101</p>	2 <u>CO</u> (Cd) (C)	-31.4
	3 <u>Cd</u> (CO) (Cd)	8.9 <sup>d</sup>
	3 4,6,7 <u>Cd</u> (Cd) (C)	8.88x3
	5 <u>C</u> (Cd) <sub>2</sub> (C)	-1.13 <sup>d</sup>
	1 <u>C</u> (Cd) (CO) (C)	-1.7
	8 <u>C</u> (C) <sub>4</sub>	0.5
	2 9,10 <u>C</u> (H) <sub>3</sub> (C)	-10.08x2
	2 Correction for cis C=C	1.0x2
	Correction for the ring	<u>8.1<sup>f</sup></u>
		$\Delta H_f^0$ (total)



Table 18 (continued)

- a Based on the values reported by Benson and coworkers.<sup>199,200</sup>
- b The carbons in parentheses are the groups attached to the carbon in question (the underlined carbon; the superscript denotes its position in the ring).
- c Cd denotes an olefinic carbon; CO, a carbonyl carbon and C, a saturated carbon.
- d Estimates.
- e Correction for bicyclo[5.1.0]octane.
- f Sum of the corrections for cyclohexanone and cyclopentene.

$$\Delta\Delta H_f^{\circ} = \Delta H_f^{\circ} 107 - \Delta H_f^{\circ} 101 = 10 - (-8.3) = 18.3 \text{ kcal/mole.}$$

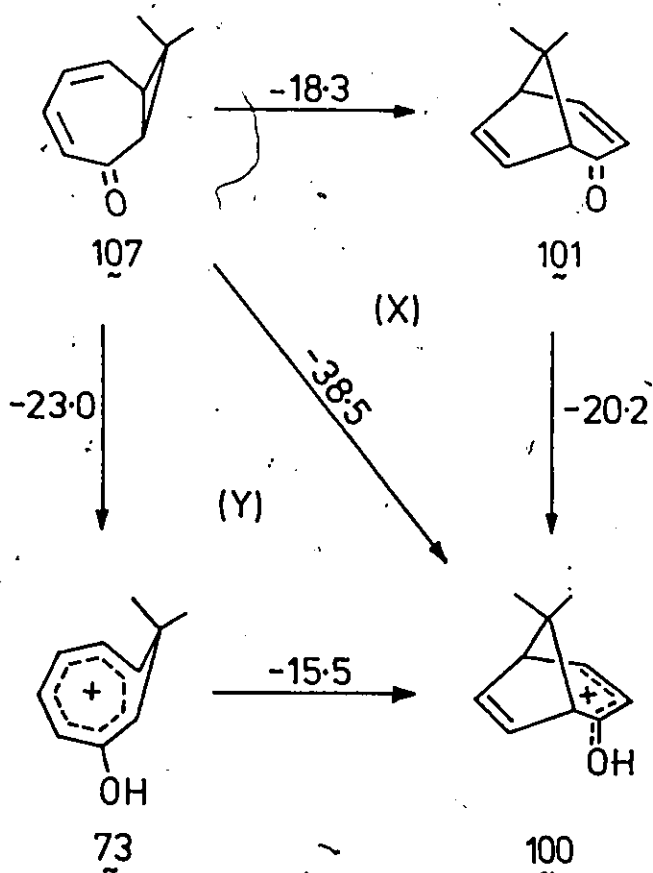
$\Delta H_4$  and  $\Delta H_5$  would be -38.5 kcal/mole and -15.5 kcal/mole, respectively (Scheme 8).

If the difference in strain energies of the cations 73 and 100 is approximately the same as that of the ketones 107 and 101, the difference in delocalization energies between the homoaromatic cation 73 and the nonaromatic cation 100 would be expected to be about 2.8 kcal/mole. This value of 2.8 kcal/mole (which is also equal to the difference in the heats of protonation of ketones 107 and 101) agrees well with the difference in the heats of protonation observed for cycloheptadienone 122 and 2,3-homotropone 104 ( $\Delta\Delta H_{\text{protn}} = 2.9$  kcal/mole).

It would thus seem likely that the protonated bicyclo[3.2.1]octa-3,6-dien-2-one 101 does not suffer from any significant destabilization of electronic origin (such as bishomoantiaromatic delocalization 126).<sup>84</sup> Further, the stabilization gained from homoaromatic delocalization is unlikely to be significant enough to offset the strain energy present in systems such as 73. Thermodynamic consistency of these estimates could be further checked if the energy difference between the ketones 107 and 101 could be experimentally measured accurately by other methods.

## 11. Conclusion

On the basis of the present study, one can conclude that a homoaromatic system has to fulfill the third and very important criterion of molecular energetics. This criterion demands that the "homoaromatic" system exhibit a higher stability than what is expected for a structurally similar and closely related model system which is devoid only of the cyclic delocalization. Where a suitable model system is lacking, a series of related systems differing only in the extent of conjugation



Scheme 8

(All values in kcal/mole)

$$\begin{aligned}\Delta H_{\text{delocalization}} &= -18.3 - (-15.5) \\ &= -2.8 \text{ kcal/mole}\end{aligned}$$

should be considered. Any abrupt discontinuity, noted for the system in question, in the measurement of energies related to delocalization energy, from the relatively steady trend observed for the rest of the series, can be taken to infer homoaromatic stability in this system. It is to be noted that the situation presented here is comparable to that proposed and observed for an aromatic system such as benzene, as mentioned earlier.<sup>161</sup>

It is hard to predict what could be the relative magnitude of the stabilization energy expected in general for homoaromatic delocalization. This will depend on the system under investigation, and the model system used for reference. The extent of delocalization and hence the delocalization energy will also depend on the substituents present. Clearly, more work needs to be done in this regard.

It is therefore worthwhile to recall, once again the results of theoretical studies carried out on the homoaromatic stability in homotropylium cation. Jorgenson's theoretical estimate for this value is approximately 15 kcal/mole.<sup>12</sup> The value (22.3 kcal/mole) reported for the barrier to ring inversion process in homotropylium cation is therefore too high to be considered as a measure of the homoaromatic delocalization energy.<sup>53</sup> In fact Haddon's revised estimate of this barrier, based on theoretical calculations, for the above process is substantially lower (less than 10 kcal/mole).<sup>13</sup> Haddon has, in fact, concluded that homoaromatic stabilization is only a matter of a few kcal/mole.

The present study is in agreement with Haddon's conclusion. At least when compared to the magnitude of stabilization due to aromatic

delocalization, that due to homoaromatic delocalization is relatively small.

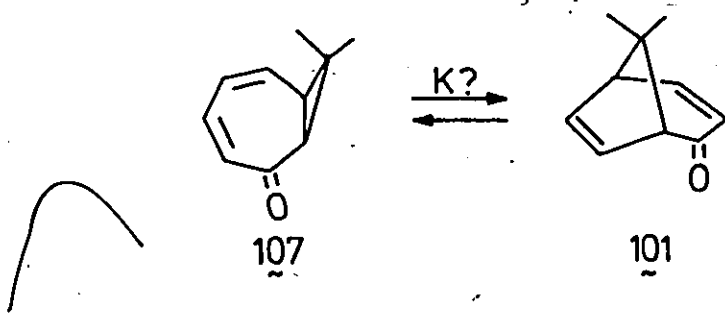
Empirical estimates of (strain) energy difference between the cations 73 and 100, based on Benson's group additivity parameters for the corresponding ketones 107 and 101 suggest that the stabilization energy due to cyclic delocalization in a homoaromatic system such as 73 is likely to be considerably less than its strain energy. The following chapter deals with a different experimental attempt to measure the energy difference between the two ketones 107 and 101.

CHAPTER 4

I. REARRANGEMENTS OF 8,8-DIMETHYL-2,3-HOMOTROPONE CATALYZED BY BRØNSTED AND LEWIS ACIDS

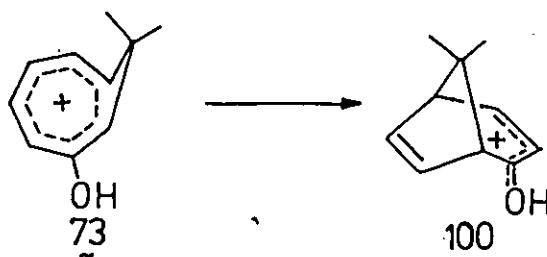
1. Rearrangement Studies

Prior to the calorimetric studies described in the previous chapter, attempts were made to establish a chemical equilibrium between the two ketones 107 and 101. If an equilibrium could be set up between these two ketones, their free energy difference could be obtained from the value of the equilibrium constant measured. The outcome of such attempts, which involved the use of weak Bronsted and Lewis acids as catalysts, is discussed here.<sup>201</sup>



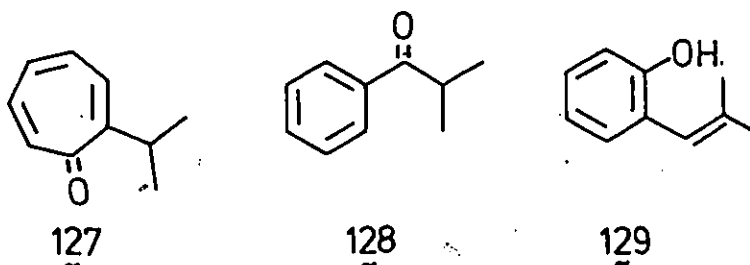
a. *Brønsted Acids*

In strong acids such as  $\text{FSO}_3\text{H}$ , the protonated form of the ketone, 73 was quantitatively converted to that of 100.<sup>84</sup> A similar result was obtained in 96%  $\text{H}_2\text{SO}_4$ .



It was decided to use low concentrations of weaker Brønsted acids so that the homotropone 107 would not be completely protonated and converted to 73. Exploratory reactions were carried out on a small scale and monitored directly by  $^1\text{H}$  NMR spectroscopy of the solutions. Preliminary observations showed that 101 was not formed under these conditions but a series of other compounds such as 2-isopropyltropone 127, isobutyrophenone 128 and 2-isobutenylphenol 129 was produced.

In order to gain further insights into the nature of the rearrangement processes involved, further reactions were carried out at higher concentrations of the acids. These results are summarized in Table 19.



In a 0.15M solution of  $\text{CF}_3\text{COOH}$  in  $\text{CCl}_4$ , 107 was found to isomerize cleanly to 2-isopropyltropone 127. Solutions of  $\text{HCl}$  in  $\text{CDCl}_3$  and  $\text{CCl}_3\text{COOH}$  in  $\text{CCl}_4$  also caused the clean isomerization of 107 to 127. The structure of 127 was established by comparison of its spectra and GLC retention time with that of an authentic sample prepared by the method of Noyori and coworkers.<sup>202</sup> In this method tropone 104 was

Table 19  
Products Obtained on Isomerization of 107

Acid Medium	Acid Conc. (M)	Ketone Conc. (M)	Temp. °C	Time <sup>a</sup> hr	Products (%) <sup>b</sup>			
					101	127	128	129
FSO <sub>3</sub> H	-	0.20	0	2	100	-	-	-
CF <sub>3</sub> COOH/CCl <sub>4</sub>	0.18	0.14	70	16	-	100	-	-
CF <sub>3</sub> COOH/CCl <sub>4</sub>	6.0	0.07	70	16	-	53	47	-
CF <sub>3</sub> COOH	-	0.05	25	4	-	<2	82 <sup>c</sup>	-
CCl <sub>3</sub> COOH/CCl <sub>4</sub>	0.6	0.20	70	10	-	100	-	-
HCl/CDCl <sub>3</sub>	-	0.07	25	1	-	100	-	-
TSOH.H <sub>2</sub> O/CCl <sub>4</sub> <sup>d</sup>	0.01	0.14	75	3	-	-	100	-
BCl <sub>3</sub> /CDCl <sub>3</sub>	0.012	0.09	25	<1	-	-	100	-
BCl <sub>3</sub> /CDCl <sub>3</sub>	0.26	0.05	25	<1	-	-	-	100
BF <sub>3</sub> .O(Et) <sub>2</sub> /CCl <sub>4</sub>	0.07	0.14	70	3	50	-	50	-
BF <sub>3</sub> /CDCl <sub>3</sub>	<0.1	0.05	25	1	100	-	-	-
BF <sub>3</sub> /CDCl <sub>3</sub>	0.02	0.08	25	4	-	-	-	100
TiCl <sub>4</sub> /CDCl <sub>3</sub>	0.006	0.07	25	0.5	-	-	-	100
SbCl <sub>5</sub> /CDCl <sub>3</sub>	0.11	0.06	25	0.5	100	-	-	-

<sup>a</sup> Times given are those approximately required for complete reaction.

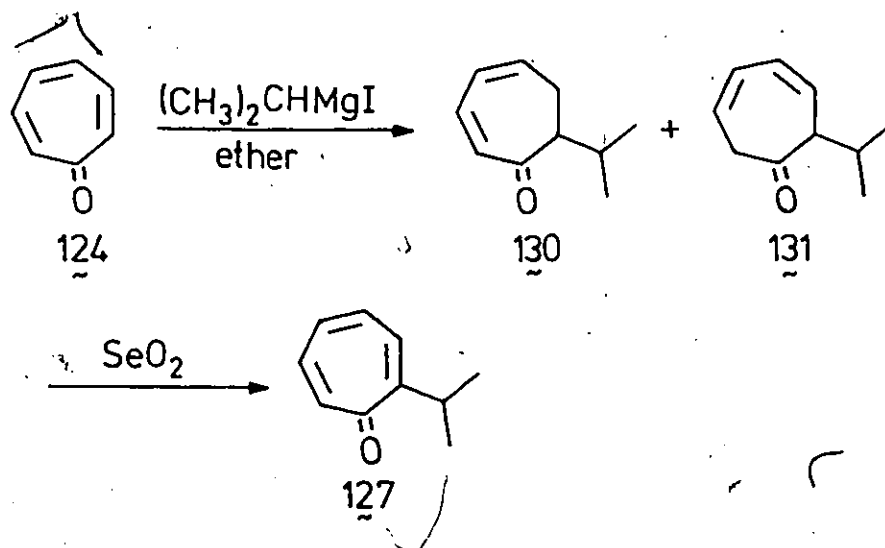
<sup>b</sup> Yields are based on <sup>1</sup>H NMR and GLC analyses. Recovered yields are about 10% lower.

<sup>c</sup> Other minor products present.

<sup>d</sup> p-toluenesulfonic acid. The acid was not completely soluble in CCl<sub>4</sub>.



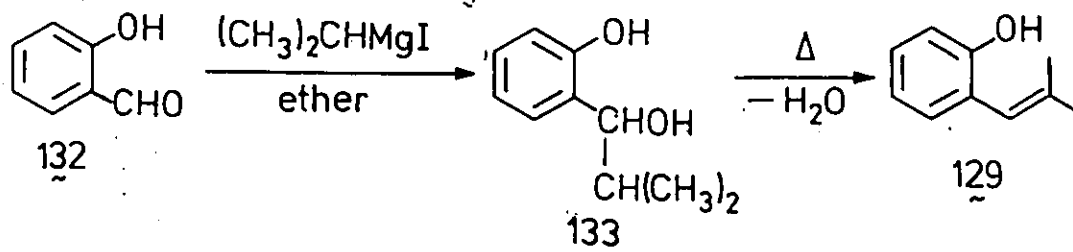
reacted with isopropylmagnesium iodide and the resulting mixture of products 130 and 131 was oxidized to give 2-isopropyltropone 127.



Increasing the concentration of  $\text{CF}_3\text{COOH}$  in  $\text{CCl}_4$  beyond 0.15M resulted in the production of an additional product. This was identified as isobutyrophenone 128 on the basis of comparison of the spectroscopic properties and GLC retention time with an authentic commercial sample. When  $\text{CF}_3\text{COOH}$  itself was used as a solvent, 128 was the major product present and only traces of 127 could be detected. Ketones 127 and 128 were not interconverted under the reaction conditions.

A different product resulted when p-toluenesulfonic acid hydrate was used as the catalyst. 2-Isobutenylphenol 129 was obtained as the product, when 107 was heated at  $70^\circ$  with small amounts of this acid in  $\text{CCl}_4$ . The structural identity of 129 was established by comparing its spectral properties with those of an authentic sample synthesized by the method of Pauly and coworker.<sup>203</sup> This method involves the dehydrative distillation of the product (133) of the Grignard reaction between salicylaldehyde 132 and isopropylmagnesium iodide, to

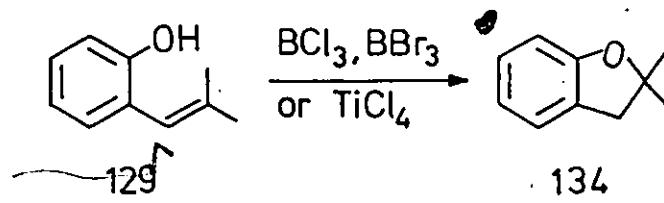
give 129.



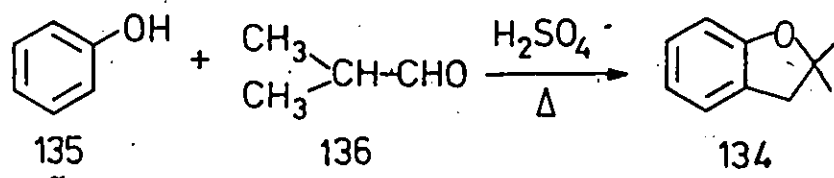
Attempts were made to establish the equilibrium between 107 and 101 by starting with the ketone 101. This approach was again unsuccessful. While the solutions of the ketone 101 in  $\text{FSO}_3\text{H}$  were stable at ambient temperatures, they underwent decomposition to uncharacterized material on warming to higher temperatures. Heating a solution of 101 in  $\text{CCl}_4$  with  $\text{CF}_3\text{COOH}$  of concentration 0.18M at  $70^\circ$  for 4 hours caused its decomposition to uncharacterized products. Neither 8,8-dimethyl-2,3-homotropone 107, nor products such as 127 - 129, thereof, could be detected under any of these conditions.

b. *Lewis Acids*

Lewis acid catalysts were also used in an attempt to effect the equilibration of the starting 8,8-dimethyl-2,3-homotropone 107 with the ketone 101. No evidence for the existence of such an equilibrium was obtained. However, the treatment of 107 with various Lewis acids resulted in the formation of the same products as those obtained with Brønsted acids (Table 19). The only difference was that with Lewis acids such as  $\text{BCl}_3$ ,  $\text{BBr}_3$  and  $\text{TiCl}_4$ , the phenol 129 underwent further cyclization to give the dihydrobenzofuran 134.



The dihydrobenzofuran was characterized by comparison of its spectral properties with those of an authentic material prepared by literature methods reported previously.<sup>204,205</sup> In this method the furan derivative 134 was obtained by the condensation of isobutyraldehyde 136 with phenol 135 in presence of  $\text{H}_2\text{SO}_4$ .



In order to probe the mechanistic possibilities for the rearrangement process observed, further reactions of 107 were carried out at ambient temperatures using higher concentrations of Lewis acids. The reaction conditions and the relative amounts of products obtained, for the rearrangements of 107 described below, are summarized in Table 19.

With catalytic amounts of  $\text{BCl}_3$  in  $\text{CDCl}_3$ , the phenol 129 was obtained from 107 as the only product. At higher concentrations of  $\text{BCl}_3$  in  $\text{CDCl}_3$  the product of cyclization, namely the furan 134, was obtained from 107. Catalytic amounts of  $\text{BBr}_3$  and  $\text{TiCl}_4$  in  $\text{CDCl}_3$ , converted 107 to the furan derivative 134. Catalytic amounts of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  in  $\text{CCl}_4$  at  $70^\circ\text{C}$ , on the other hand, led to the formation of 101 and 128 in equal proportions from 107, while an excess of  $\text{BF}_3$ ,  $\text{SbCl}_5$  or  $\text{SbF}_5$  in  $\text{CDCl}_3$

caused 107 to isomerize cleanly to 101.

In the case of reactions with molar excess of the Lewis acids, it would appear from  $^1\text{H}$  NMR evidence that the ketone 107 is completely complexed. Further, control experiments showed that besides the cyclization of 129 to 134, the products did not interconvert in the presence of Lewis' acids.

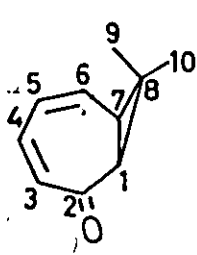
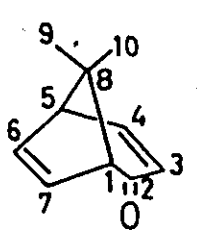
Attempts to establish an equilibrium between the two ketones 107 and 101 by using 101 as the starting material and Lewis acids as catalysts were also unsuccessful. For example, heating a  $\text{CCl}_4$  solution of the ketone 101 with catalytic amounts of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  led only to the gradual decomposition of the starting material.

## 2. Rationale for the Failure of the Equilibration Attempt

It is clear that by using weak protic or Lewis acid catalysts, it is not possible to equilibrate the two ketones 107 and 101. This can be explained by comparing the calculated free energies of formation of these ketones. As mentioned earlier, the bicyclo[3.2.1]octadienone 101 is calculated to be more stable than its homotropone isomer 107 by approximately 18.3 kcal/mole. Based on Benson's group additivity parameters, the entropy difference between the ketones 107 and 101 can be estimated.<sup>199</sup> A value of 1.5 cal/mole/deg is obtained as the calculated difference in entropy (Table 20). At  $25^\circ\text{C}$ , this corresponds to a value of 0.5 kcal/mole. Subtracting this entropy contribution, from the enthalpy difference one obtains a value of 17.8 kcal/mole, as the free energy difference between the two ketones in the gas phase. In an inert solvent like  $\text{CCl}_4$ , the solvation energies of the ketones 107 and 101 can be considered to be very small. Therefore the value of

Table 20

Estimation of the Standard Entropies of Formation of 8,8-dimethyl-2,3-homotropone 107 and 8,8-dimethylbicyclo[3.2.1]octa-3,6-dien-2-one 101<sup>a</sup>

Molecule	Group <sup>b,c</sup>	Entropy of formation cal/mole/deg
 <p>107</p>	2 $\underline{CO}$ (C) (Cd)	15.01 <sup>d</sup>
	3 $\underline{Cd}$ (CO) (Cd)	9.6 <sup>d</sup>
	2 $4,5 \underline{Cd}$ (Cd) <sub>2</sub>	-14.2x2 <sup>d</sup>
	6 $\underline{Cd}$ (Cd) (C)	-14.6
	7 $\underline{C}$ (Cd) (C) <sub>2</sub>	-11.7
	1 $\underline{C}$ (CO) (C) <sub>2</sub>	-12.0
	8 $\underline{C}$ (C) <sub>4</sub>	-35.1
	2 $9,10 \underline{C}$ (H) <sub>3</sub> (C)	30.41x2
	Correction for the ring	48.0 <sup>e</sup>
		$\Delta S_f^0$ (total)
 <p>101</p>	2 $\underline{CO}$ (Cd) (C)	15.01 <sup>d</sup>
	3 $\underline{Cd}$ (CO) (Cd)	9.6 <sup>d</sup>
	3 $4,6,7 \underline{Cd}$ (Cd) (C)	-14.6x3
	5 $\underline{C}$ (Cd) <sub>2</sub> (C)	-11.7 <sup>d</sup>
	1 $\underline{C}$ (Cd) (CO) (C)	-12.0
	8 $\underline{C}$ (C) <sub>4</sub>	-35.1 <sup>d</sup>
	2 $9,10 \underline{C}$ (H) <sub>3</sub> (C)	30.41x2
	Correction for the ring	47.3 <sup>f</sup>
	$\Delta S_f^0$ (total)	30.13

..... continued

Table 20 (continued)

- a Based on the values reported by Benson and coworkers. 199
- b The carbons in parentheses are the groups attached to the carbon in question (the underlined carbon; the superscript denotes its position in the ring).
- c Cd denotes an olefinic carbon; CO, a carbonyl carbon and C, a saturated carbon.
- d Estimates.
- e Sum of the corrections for cycloheptane and cyclopropane.
- f Sum of the corrections for cyclohexene and cyclopentene.

$$\Delta \Delta S_f^0 = \Delta S_f^0 \text{ 107} - \Delta S_f^0 \text{ 101} = 31.63 - 30.13 = 1.5 \text{ cal/mole/deg.}$$

$$\text{At } 25^\circ\text{C, } T\Delta S_f^0 = 1.5 \times 298/1000 = 0.45 \text{ kcal/mole} \approx 0.5 \text{ kcal/mole.}$$

$\Delta G^0$  for the conversion of 107 to 101

$$\begin{aligned} \Delta G^0 &= \Delta H^0 - T\Delta S^0 \\ &= -18.3 - (-0.5) = -17.8 \text{ kcal/mole.} \end{aligned}$$

Equilibrium constant K for the process 107  $\rightleftharpoons$  101

$$\begin{aligned} K &= e^{-\Delta G^0/RT} \\ &= 9.1 \times 10^{13} \end{aligned}$$

9/15

17.8 kcal/mole can be considered as the free energy difference of 107 and 101 in solution. Once again, the bicyclooctadienone 101 is the more stable of the two. The value of  $1.1 \times 10^{13}$  estimated for the "hypothetical" equilibrium constant serves as an explanation for the failure of the attempts to establish an equilibrium.

This argument can be extended to the cations 100 and 73. The enthalpy difference between the cations 73 and 100 has previously been estimated to be about 15.5 kcal/mole. Again, the entropy difference between the cations 73 and 100 can be assumed to be the same as that between their neutral precursors. Therefore, the difference in free energy of the cations 100 and 73 would be about 15 kcal/mole which corresponds to an equilibrium constant of  $1.0 \times 10^{11}$ . The extremely favorable energetic preference for the bicyclo[3.2.1]octadienyl system, relative to the bicyclo[5.1.0]octadienyl system, (both in the protonated and neutral species) would be expected to rule out any possibility for the establishment of an equilibrium between the two.

### 3. Rationale for Products Formation

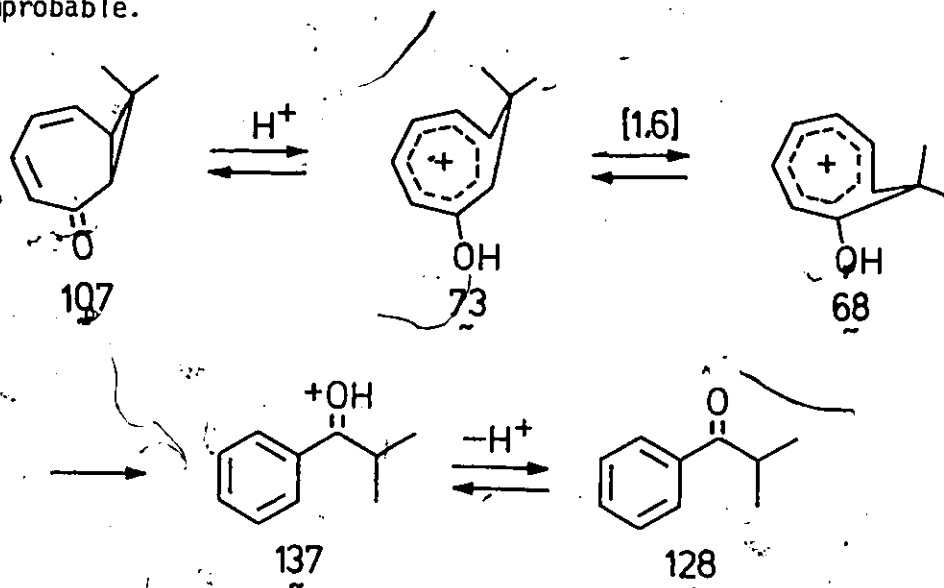
Extensive mechanistic studies on the different isomerization pathways observed have not been carried out. However, it is possible to propose tentative explanations for the formation of various products on the basis of the (acid) medium dependence on the relative energies of these paths.

In the highly acidic  $\text{FSO}_3\text{H}$  medium, where the ketones are fully protonated, 73 isomerized to 103 and then to either 78 or 100.<sup>84</sup> The bicyclic ketone 101 was reported to be the only product obtained when the reaction mixture was worked up and none of the products such as

127, 128 and 129 was reported to be present.<sup>84</sup> This obviously raises the question as to why these products are not formed in  $\text{FSO}_3\text{H}$ . The formation of 127, 128 and 129 (or 130) from the reaction of 107 with weaker Brønsted acids and certain Lewis acids suggests that in these cases various unobserved covalent intermediates rather than simple cationic intermediates are formed.

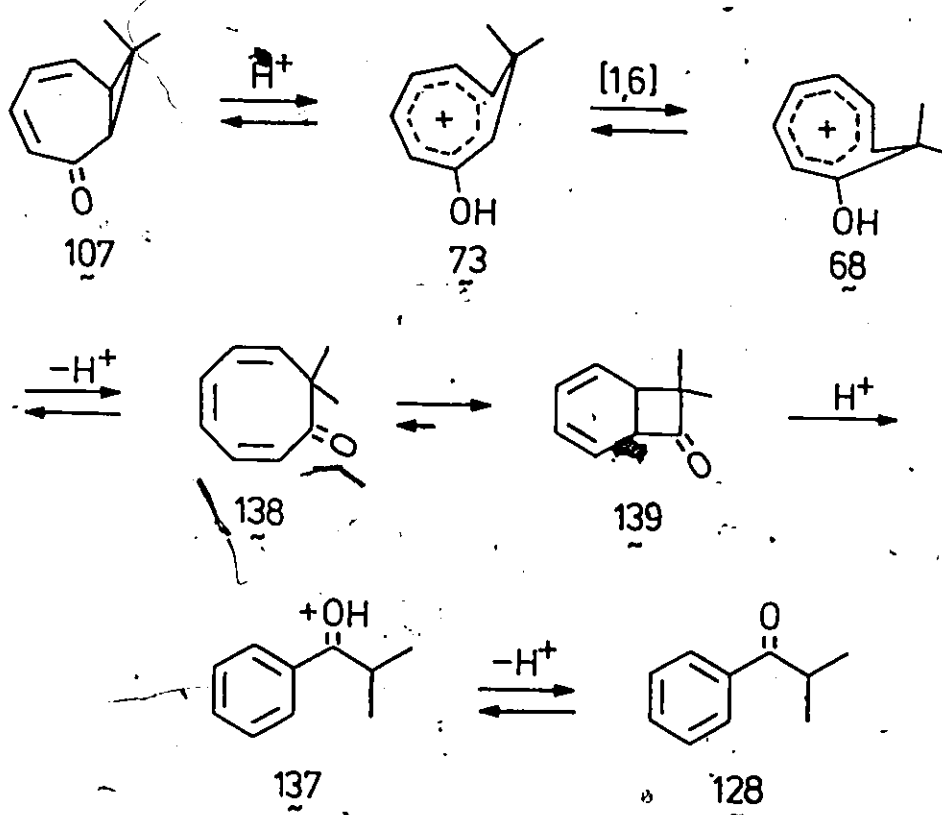
a. *Formation of Isobutyrophenone 128*

The formation of the aromatic ketone 128 can be accounted for on the basis of a circumambulatory rearrangement of the cation 73 to 68, followed by the isomerization of the 1-hydroxyhomotropylium cation derivative 68 to the protonated aromatic ketone 137. The rearrangement of 1-hydroxyhomotropylium derivatives to cationic derivatives of aromatic ketones has been observed previously.<sup>84,93,94</sup> However, the absence of such a reaction in  $\text{FSO}_3\text{H}$  makes the occurrence of this pathway in weaker acids improbable.



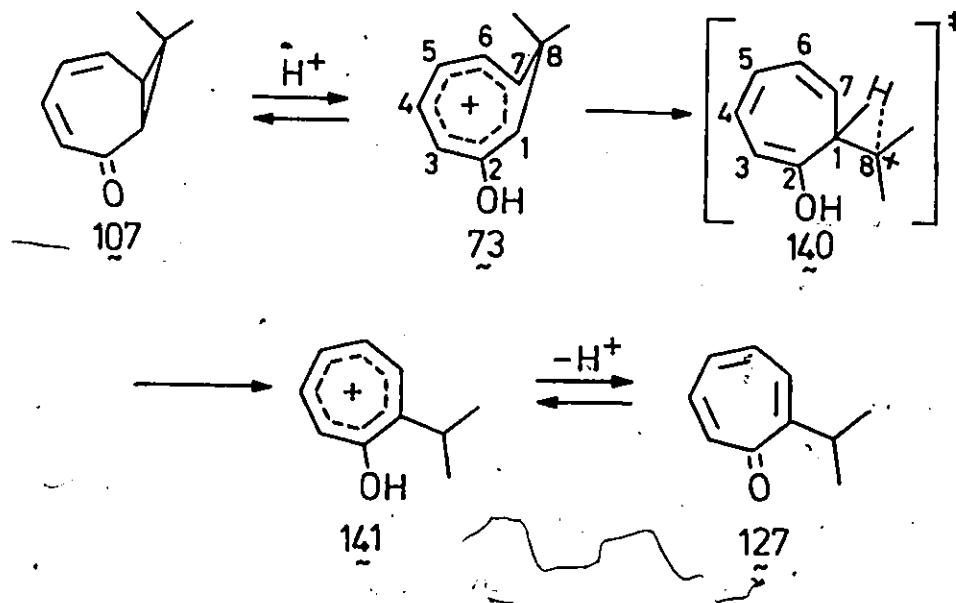


It is likely that with a weaker acid, 68 could undergo deprotonation to yield the cyclooctatrienone 138. It is known that 138 preferentially exists as its bicyclic valence tautomer 139.<sup>206,207</sup> It has been shown that protonation of 139 results in the irreversible formation of 137.<sup>84</sup> These protonation-deprotonation steps account for the difference in behavior of 107 in weaker acids and in  $\text{FSO}_3\text{H}$ .



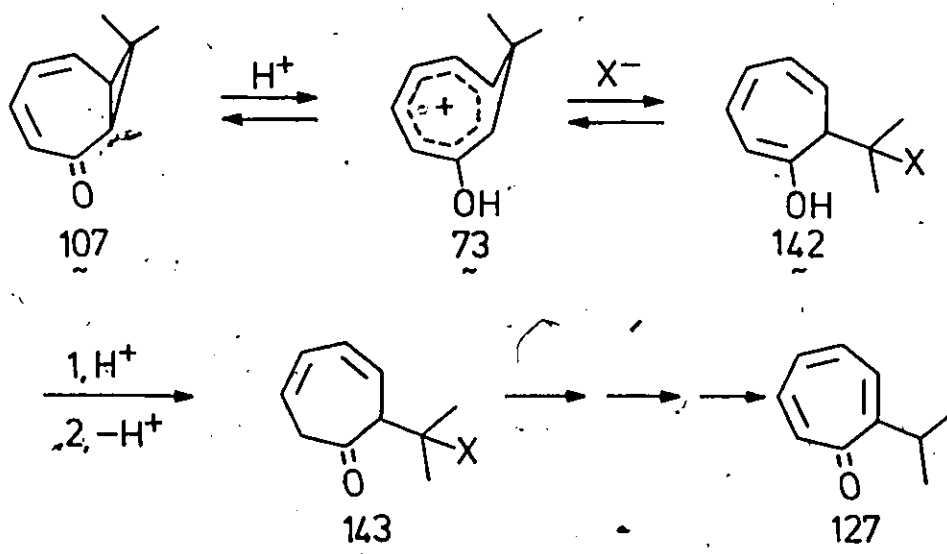
b. Formation of 2-isopropyltropone 127

The formation of 127 could be considered to result from a hydride shift from  $C_7$  to  $C_8$  in 73 or a species closely related to 73. It has been suggested by Hehre that there is considerable development of positive charge on  $C_8$  in the symmetry allowed transition state for the circumambulatory rearrangement of these cations.<sup>74</sup> Results of his ab initio calculations indicated that the transition state could be partially stabilized by bridging the migrating carbon  $C_8$  with the hydrogen on the adjacent carbon  $C_7$ , 140.<sup>74</sup> Such a process could facilitate the hydride shift.



However, 127 is formed only in weak acid media and if this were the mechanism, there is no reason why it should not also occur in  $FSO_3H$ . It is therefore more appropriate that the mechanism for formation of 127 involves a nucleophilic attack at  $C_8$  to give 142. This enol, 142, could undergo ketonization to 143 via protonation

preferentially at C<sub>2</sub>. Examples for such a process have been reported in the literature.<sup>208-210</sup> Loss of the nucleophile X<sup>-</sup>, hydride shift and proton loss from the ketone intermediate 143 would eventually lead to 127.

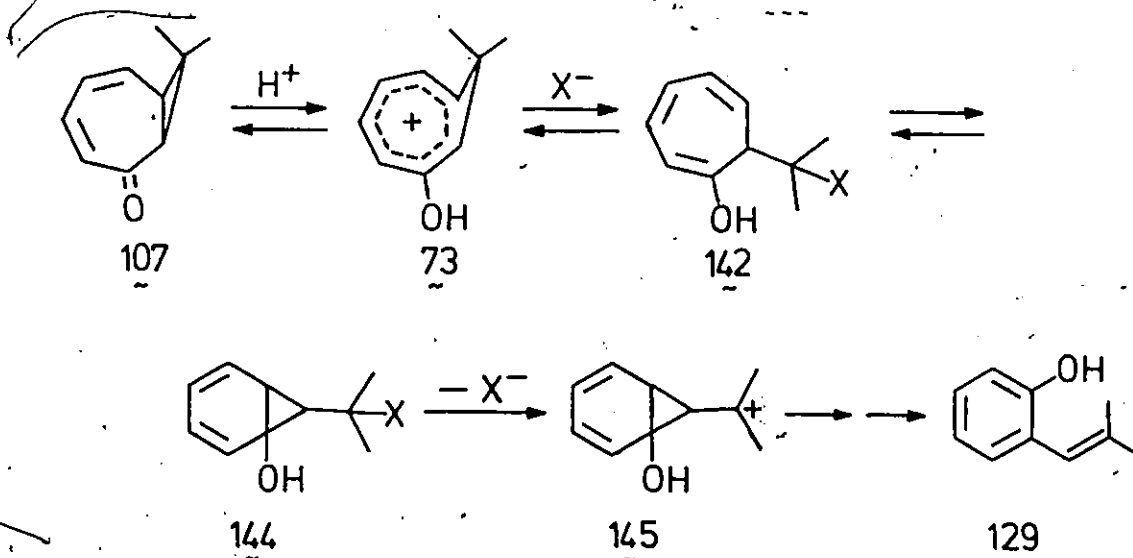


With CF<sub>3</sub>COOH, both 127 and 128 are produced from 107 (Table 19). The tropone 127 is the major product when small amounts of the acid are used in a nonpolar medium (CCl<sub>4</sub>) where ion pairing and hence nucleophilic attack are more likely to occur. Increasing the amount of the acid would enhance the polarity of the medium. Consequently, less nucleophilic capture to give 127 and an increase in the relative amount of 128 might be expected.

c. Formation of 2-isobutenylphenol 129

The enol intermediate 142 could also undergo reionization prior to ketonization. It has been shown in several cases, that ionization

of cycloheptatrienecarbonyl systems occurs from their norcaradiene valence tautomers to yield styrene derivatives.<sup>211-213</sup> In this case ionization of 142 could proceed via 144. This could serve as a potential route for the formation of 2-isobutenylphenol 129.



d. *The Possible Roles of Lewis Acids*

The Lewis acid catalyzed reactions offer some measure of support for the suggestions mentioned above. With an excess of a strong Lewis acid such as BF<sub>3</sub>, SbCl<sub>5</sub> or SbF<sub>5</sub>, a situation similar to that occurring with FSO<sub>3</sub>H would be encountered. The fully complexed ketone 107 would be expected to give 101 as the final product. With catalytic amounts of BF<sub>3</sub>, decomplexation steps, similar to the deprotonation steps encountered in the case of protic acids, could occur and these could lead to the aromatic ketone 128 as the final product. A Lewis acid such as BF<sub>3</sub> would not be expected to dissociate a fluoride from the complex that could react at C<sub>8</sub>. Therefore the tropone 121 or the phenol 129 are not expected to be present in the product mixture.

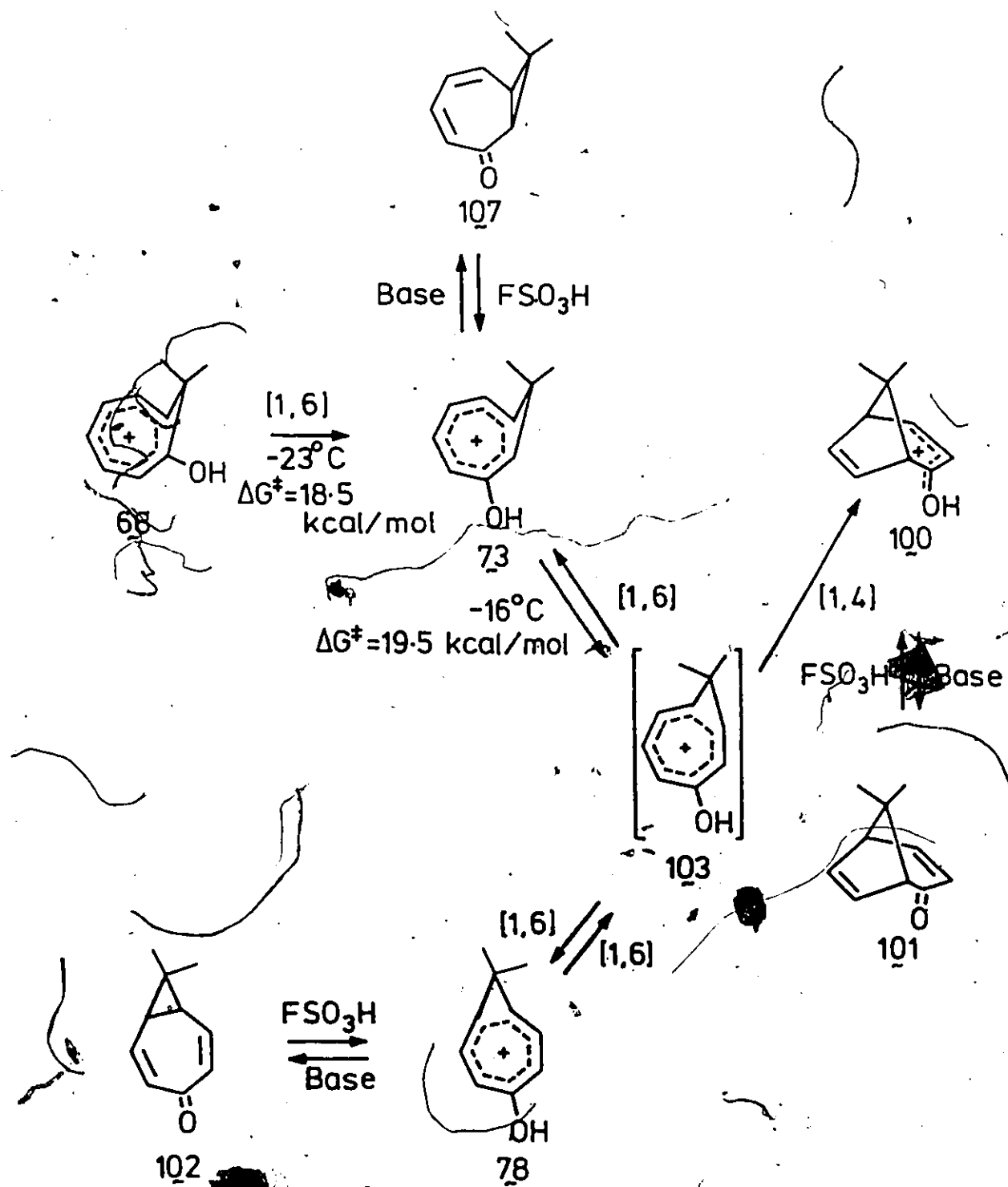
However, Lewis acids such as BCl<sub>3</sub>, BBr<sub>3</sub> and TiCl<sub>4</sub>, led to the

formation of the phenol 129 or the furan 134. This would seem to involve the attack at C<sub>8</sub> of a halide such as chloride or bromide resulting from the dissociation of these Lewis acid complexes of 107. Certainly in the cases of BCl<sub>3</sub> and BBr<sub>3</sub> this dissociation is not unexpected (in view of the well-known cleavage of ethers by Lewis acids like BBr<sub>3</sub>) and probably also occurs from the bisketone complexes of TiCl<sub>4</sub>. In the absence of a protic acid, ketonization of 142 to give 127, might be expected to be slower than reionization and formation of 129.

Thus, the processes such as protonation-deprotonation (or complexation-decomplexation) and nucleophilic attack on C<sub>8</sub> can satisfactorily account for the difference in behavior of 107 Lewis and weaker Brønsted acid media as compared to that in strong acid media.

#### 4. Conclusion: Estimation of the Relative Free Energies of Various Cations Observed in FSO<sub>3</sub>H Solutions of 107

In conclusion, it is worthwhile to reconsider the reactions observed in FSO<sub>3</sub>H solutions of 107 (Scheme 9).<sup>84</sup> In this acid 68 thermally rearranged to 73, suggesting that 73 is thermodynamically more stable than 68. At higher temperatures 73 rearranged to 78 and 100 via the possible intermediacy of 103.<sup>84</sup> The results obtained in the present study suggest that the barrier for the isomerization of 73 to 68, an unobserved reaction in FSO<sub>3</sub>H due to the equilibrium position between the two cations, is lower than that for the conversion of 73 to 103. This, in turn, suggests that the ground state energy difference between 78 and 73 can only be of the order of 1 kcal/mole. This corresponds to an equilibrium constant of 7.5 for the equilibrium between these two cations. In other words only 12% of 68 would be



Scheme 9

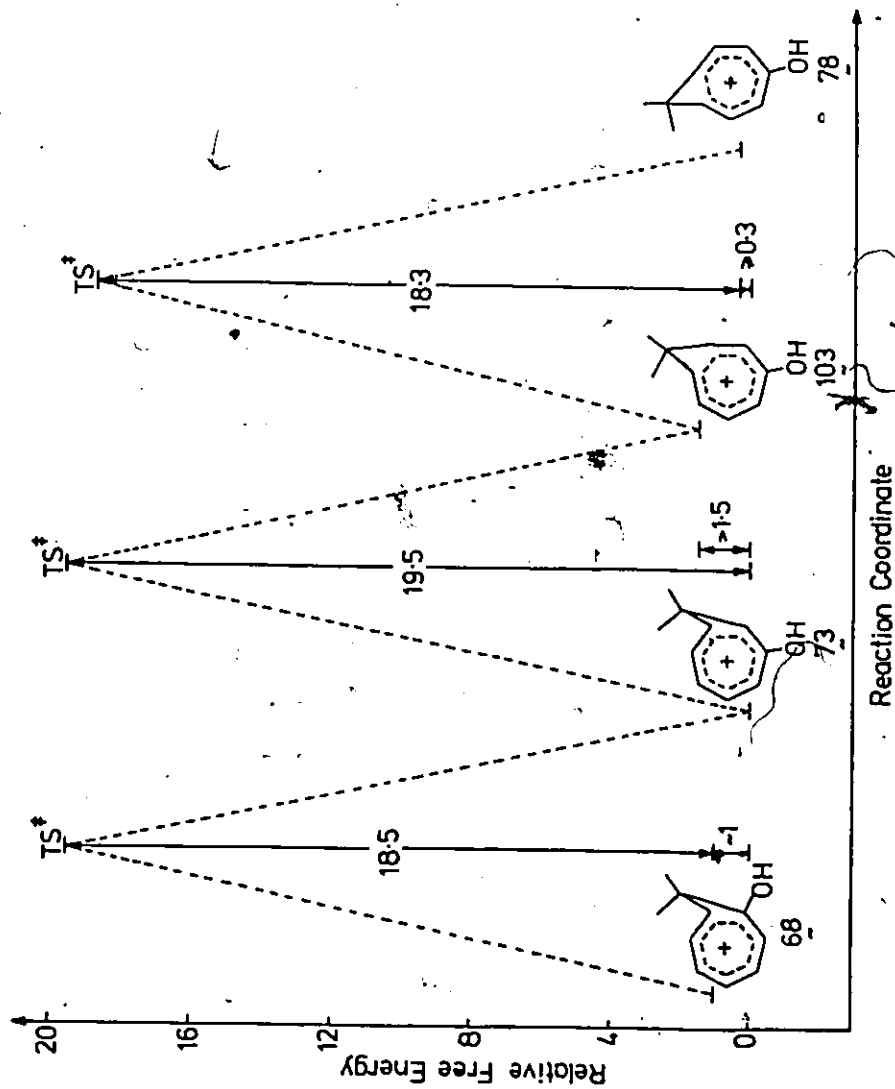
present in this equilibrium.

It has been reported that the maximum concentration of 78 detected during the course of rearrangement of 73 to 100 at  $-16^{\circ}\text{C}$  was 16%.<sup>84</sup> The corresponding concentration of 73 was 60%.<sup>84</sup> If these concentrations are assumed to be their relative equilibrium concentrations, under these conditions, one would obtain a value of 1.9 for the hypothetical equilibrium constant between 73 and 78, after correcting for their statistical distribution. This corresponds to a minimum free energy difference of approximately 0.3 kcal/mole at  $-16^{\circ}\text{C}$  between 73 and 78, with 73 being the more stable of the two species.

Though the presence of cation 103 could not be detected, it is likely that a minimum concentration of roughly 5% would not escape detection.<sup>84</sup> Once again, if this amount of the 3-hydroxy isomer 103 is assumed to be present in equilibrium with the 2-hydroxy isomer 73, a value of 19 could be estimated for the hypothetical equilibrium constant between 73 and 103. This corresponds to an estimated minimum free energy difference of approximately 1.5 kcal/mole between these two cations.

It has already been estimated that the cation 100 would be more stable than 73 by about 15 kcal/mole. 100 is the most stable of all the cations observed in the rearrangements of 73 in  $\text{FSO}_3\text{H}$ , under the conditions reported.<sup>84</sup> These results are summarized in Scheme 10. It should be noted that the estimates are very approximate and that the relative magnitudes are more important than their absolute values themselves.

These suggestions regarding the relative stabilities of various 8,8-dimethylhydroxyhomotropylium cations were found to be useful for a study of the circumambulatory rearrangements of trimethylhomotropylium cations. This will be discussed in the next chapter.



Scheme 10

(All values in kcal/mole. Free energies of activation taken from reference 84.)

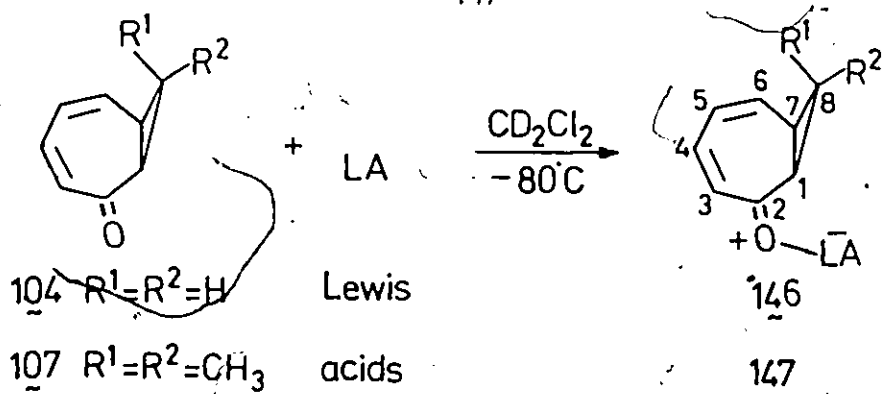


## II. INTERACTION OF LEWIS ACIDS WITH THE HOMOTROPONES 104 and 107

### 1. $^1\text{H}$ NMR Study

As mentioned earlier, the reactions of 8,8-dimethyl-2,3-homotropone 107 with Lewis acids were monitored by  $^1\text{H}$  NMR. It was observed that the chemical shift difference ( $\Delta\delta$ ) for the endo and exo methyl proton resonances in the starting complexes was dependent on the Lewis acid used. It is of interest to probe the relationship between the nature of the Lewis acid and the  $\Delta\delta$  values observed for the complexes. To this end, a further NMR investigation of the complexes of the homotropes 104 and 107 with various Lewis acids was undertaken.

2,3-homotropone 104 and 8,8-dimethyl-2,3-homotropone 107 were chosen because they were available and because their expected structural similarity would make the comparative study more meaningful. The acids used in this study were  $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{BBr}_3$ ,  $\text{SnCl}_4$ ,  $\text{TiCl}_4$  and  $\text{SbCl}_5$ . Deuterated methylene chloride was used as the solvent. It has been reported that the solvent is not reactive to the Lewis acids.<sup>214</sup> The complexes (represented by 146 and 147) were prepared by adding a ten fold excess of the Lewis acids to ( $\sim 0.1\text{M}$ ) solutions of the ketones in  $\text{CD}_2\text{Cl}_2$  kept at  $-78^\circ$  in an NMR tube, under argon. The larger excess of the Lewis acid was used to ensure that the Lewis bases would be almost completely complexed. The NMR spectra had to be run at  $-80^\circ$  owing to the instability of the complexes. The dimethylhomotropone 107 was extremely reactive to all Lewis acids except  $\text{SnCl}_4$ , even at low temperatures. The reaction of  $\text{BBr}_3$  with 107 was extremely rapid even at  $-80^\circ$  so that measurement of proton chemical shift values could not be done with a good accuracy.



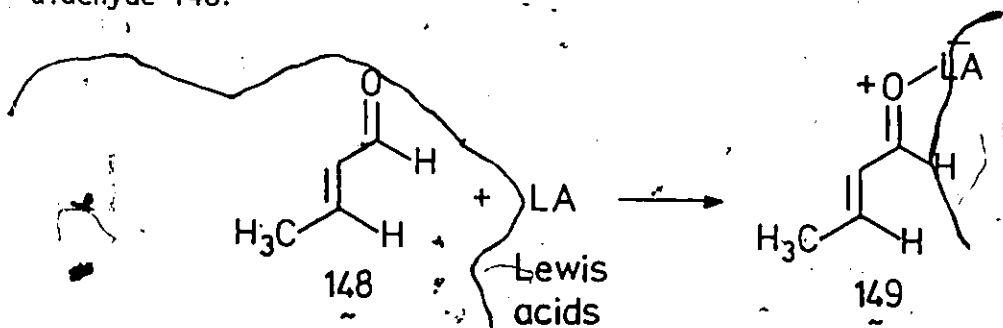
Complex formation was evident from the downfield shifts of the resonances for all the protons attached to the seven-membered ring relative to the neutral ketones. This behaviour resembled that observed on protonation of the ketones 104 and 107 in strong acid media. The overlap of many of the resonances for the protons in the seven-membered ring as well as the difficulty in obtaining a well-resolved spectrum at low temperatures, made signal assignments for these protons a difficult task. Therefore, the chemical shifts for these protons could not be considered for any comparative study.

The resonances for the hydrogens or the methyl groups attached to  $\text{C}_8$  underwent marked changes on complexation, similar to those observed on protonation of the ketones 107 or 104. Upon complex formation, the resonance for the exo hydrogen or methyl group on  $\text{C}_8$  experienced a downfield shift while that for the endo hydrogen or methyl group underwent an upfield shift relative to the neutral ketones 107 or 104. For the complexes of 104, the chemical shift corresponding to the endo proton resonance could be measured without difficulty as it was far removed from the rest of the resonances. The resonance for the exo proton was not always well-resolved from those of  $\text{H}_1$  and  $\text{H}_7$  protons in all the complexes. However, this did not pose any serious problem as the central position of the overlapping broad multiplets served as an

adequate measure of the chemical shift for the proton in question. No difficulty was encountered in the measurement of the chemical shifts for the exo and endo methyl resonances. Thus, in all the cases the  $\Delta\delta$  values could be obtained from these measured chemical shift values (Table 21). From Table 21, it is obvious that in both the series of complexes of 104 and 107, the  $\Delta\delta$  values are dependent on the Lewis acids used.

## 2. Scale of Relative Strengths of Lewis Acids

Childs and coworkers have established a scale for the relative strengths of Lewis acids.<sup>214</sup> This scale was based on the magnitudes of the chemical shift differences for the  $H_3$  proton resonances observed for the Lewis acid complexes of crotonaldehyde 149 relative to the neutral aldehyde 148.<sup>214</sup>



The  $H_3$  proton in crotonaldehyde is far removed from the interacting Lewis acid. Therefore the magnitude of the induced shift would be a measure of the ability of the Lewis acid to withdraw electron density away from (or conversely, donate positive charge to) the conjugated system. In simpler terms, the  $^1H$  NMR based scale of Lewis acid strengths is a relative measure of the extent of the positive charge donated to the conjugated system.

Table 21

Chemical Shift Differences ( $\Delta\delta$ ) for  $C_8$ -Hydrogens and  $C_8$ -Methyls  
Observed for Complexes of 2,3-homotropone 104 and 8,8-dimethyl-2,3-  
homotropone 107 with Various Lewis Acids

Lewis Acid	Relative Acid Strength	$\Delta\delta$ Values Observed (ppm)	
		104	107
None	0.0	0.45	0.34
$SnCl_4$	0.52	1.91	0.78
$TiCl_4$	0.66	3.49	1.39
$BF_3$	0.77	2.57	1.02
$SbCl_5$	0.85	3.2	1.21
$BCl_3$	0.93	3.14	1.18
$BBr_3$	1.00	3.55	1.30

### 3. Correlation of $\Delta\delta$ Values with Lewis Acid Strengths

It is of interest to see if such a correlation could be extended to the complexes of the homotropones, in view of the differing  $\Delta\delta$  values observed. A correlation could be expected on the basis of a consideration of (a) the probable cause for the large  $\Delta\delta$  values observed on complexation and hence (b) the probable cause for the variation of these  $\Delta\delta$  values with the nature (or the strength) of the Lewis acid.

#### a. *Probable Cause for the Large $\Delta\delta$ Values Observed for the Complexes*

The hydrogens or methyls on  $C_8$  are removed from the centre of interaction (namely, the carbonyl oxygen and the Lewis acids). Any chemical shift difference noticed for the protons in question could not be considered to arise from the direct electronic, steric or through space interaction of the Lewis acids with these hydrogens/methyls on  $C_8$ . Local anisotropy effects due to the Lewis acids are, therefore, unlikely to contribute to the observed behavior. The chemical shift differences observed for the hydrogens (or methyls) on  $C_8$  could thus be ascribed to the factor(s) resulting from the cyclic delocalization of the positive charge donated by the Lewis acid. One such important (or possibly predominant) factor is the ring current associated with the cyclic delocalization. However, as emphasized in an earlier chapter there are other factors besides ring current that can contribute significantly to the differences in chemical shifts for the exo and endo protons.

#### b. *Probable Cause for the Variation of $\Delta\delta$ with Lewis Acid Strengths*

Within each series of the complexes 146 and 147 the structural geometry was assumed to be constant. If this assumption is valid, then

geometric contributions to the variation in  $\Delta\delta$  values observed can be neglected. The differences in  $\Delta\delta$  values observed on complexation with different Lewis acids can, therefore, be considered to reflect in some measure, the differences in the magnitudes of ring current and hence, the extent of charge delocalization occurring in each case. These in turn, would depend on the extent of the positive charge donated to the seven-membered ring, by the Lewis acid, depending on its relative strength. It is, therefore, reasonable to expect that complexes of the homotropones with Lewis acids of different acid strengths should exhibit different  $\Delta\delta$  values, with possibly a linear relationship between the two. Such an expectation assumes that other factors which contribute to the  $\Delta\delta$  values may also show a linear relationship with the Lewis acid strengths.

A linear correlation was indeed found, when the  $\Delta\delta$  values observed for the complexes homotropones 146 and 147 reported in Table 21 were plotted against the scale of Lewis acid strengths set up by Childs and coworkers (Figure 14). The correlation coefficient in both cases was 0.992. It can be seen from Table 21 and Figure 14 that the  $\Delta\delta$  values for the  $TiCl_4$  complexes of the ketones 104 and 107 are anomalously high. Therefore the corresponding data points were not taken into account and only the rest of the data (in Table 21) were fitted with least squares.

The values of the slopes obtained for the plots of the two sets of complexes 146 and 147 were 3.06 and 0.96 ppm, respectively. These values for the slopes suggest that the  $\Delta\delta$  values for hydrogens on  $C_8$  are more sensitive to the extent of delocalization (and ring current) than those for the methyl groups on  $C_8$  which are located relatively

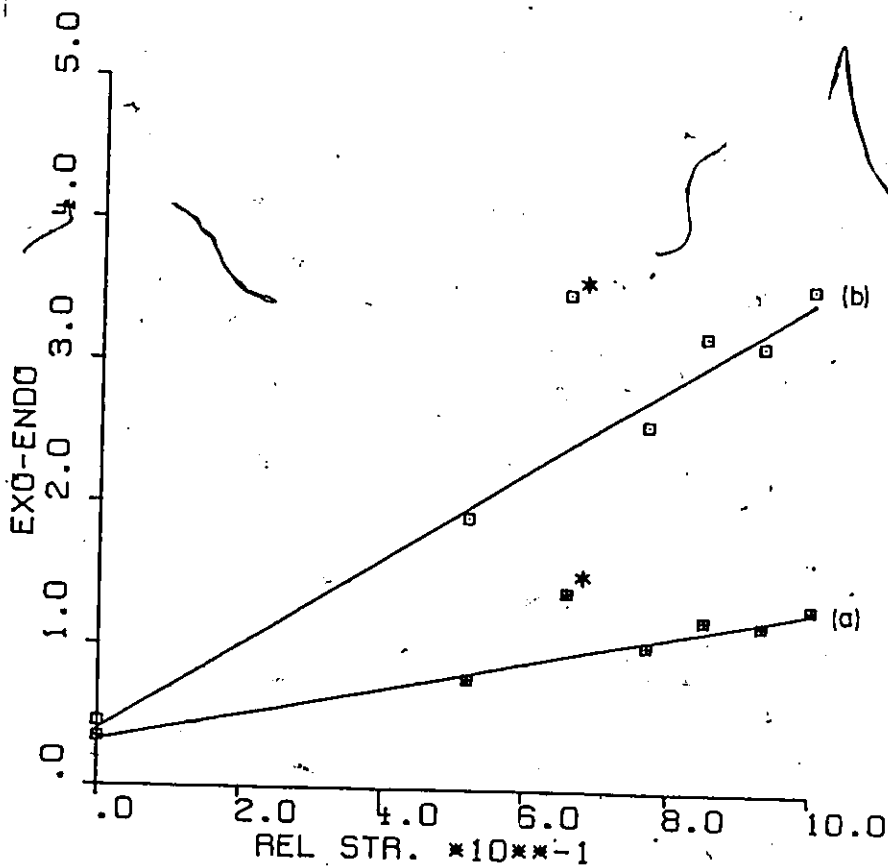


Figure 14 Plots of  $\Delta\delta$  values vs relative strengths of Lewis acids for the complexes of (a) 8,8-dimethyl-2,3-homotropone and (b) 2,3-homotropone. (\*Data points not included in the least-squares fits).

farther away from the centre of the ring. The  $\Delta\delta$  values corresponding to the neutral ketones had to be considered in the extrapolation of the least squares fit because no  $\Delta\delta$  value corresponding to the acid strength range 0 to 0.5 was measured in this study. The values of the y-intercepts for the plots of the 2,3-homotropone complexes 146 and 147 obtained by this extrapolation method were 0.4 and 0.32 respectively. As mentioned earlier, the geometries of the bicyclo[5.1.0]octadienyl systems such as 69, 28 and 115 do not seem to vary significantly. On this basis, the neutral ketones 104 and 107 can be expected to have the same relative geometry. The values for the y-intercept in these cases can be considered to reflect in some measure the cyclic delocalization occurring in the seven-membered ring. However, these systems have a fully formed cyclopropyl group and as mentioned earlier, the chemical shift differences for geminal cyclopropyl protons have been known to vary by as much as 0.5 ppm.<sup>217</sup> The values of y-intercepts for the two ketones would thus indicate the magnitude of the effect of the ring current due to the three-membered ring rather than the seven-membered ring. In other words, these y-intercepts can be considered as a measure of the respective  $\Delta\delta$  values for the hydrogens and methyls on  $C_8$  in the absence of cyclic delocalization in the seven-membered ring.

It has been assumed that the induced ring current contributes significantly to the observed  $\Delta\delta$  values. It has been mentioned earlier, that other factors (such as local anisotropy) would also contribute to the observed chemical shift differences. However, the present study shows that even if they contribute significantly to the  $\Delta\delta$  values, they also seem to exhibit a linear correlation with Lewis acid strengths.



The order of magnitudes of the  $\Delta\delta$  values generally followed the order of the relative acid strengths. However,  $\text{TiCl}_4$  complexes of both the ketones showed abnormally high  $\Delta\delta$  values. This could be either due to the fact that the  $\text{TiCl}_4$  complexes have different geometry from the rest of the complexes or these complexes cannot be regarded as simple 1:1 complexes of the Lewis acids with the ketones. The actual reason is not clear.

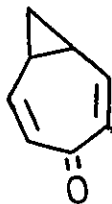
#### 4. $\Delta\delta$ Values and Reactivity of Lewis Acids

The rates of rearrangement of the homotropone 107 in presence of these Lewis acids have not been measured. However, these rates, in general, would be expected to follow the order of Lewis acid strengths and hence the magnitudes of  $\Delta\delta$  values. The duration of reaction times reported in Table 19 for the completion of the rearrangements of 107 in presence of molar excess of Lewis acids are, in general, in agreement with this prediction. As mentioned earlier, reaction of 107 with  $\text{SnCl}_4$  was the slowest and its reaction with  $\text{BBr}_3$  (excess) was the fastest observed. The anomalous behaviour of  $\text{TiCl}_4$  was further reflected in its reaction with 107. The ketone reacted rapidly with excess  $\text{TiCl}_4$  to give 2-isopropyltropone 125 and an unidentified product. This behavior is not in line with the explanations proposed earlier for the formation of products in these rearrangements.

#### 5. Conclusions

The present study suggests that the  $\Delta\delta$  values can be correlated to the difference in the extent of delocalization, if the ring current originating from such a delocalization contributes significantly to the observed  $\Delta\delta$  values. (It must be assumed that other factors which also

contribute to the  $\Delta\delta$  values also show corresponding systematic variations.) For the Lewis acid complexes of homotropones this difference is brought about by changing a remote substituent, the size of which is unlikely to contribute to the structural geometry of the complexes. Any changes in bond lengths observed for the seven-membered ring in these complexes, would be expected to result from the changes in the extent of delocalization. This would especially be true for the length of the internal ( $C_1-C_7$ ) cyclopropane bond. A structure-spectra correlation could be attempted if the crystal and molecular structures of these complexes could be determined. For example, it would be interesting to see in a related series of complexes, the relationship between the homoconjugate bond lengths and the  $\Delta\delta$  values, if there is any. Complexes of 4,5-homotropone 150, in which the methylene hydrogens are farthest removed from the interacting carbonyl group and the Lewis acids would be good candidates for this study. It is hoped that future attempts on structural determination would be directed toward this goal, as this might possibly link structural criterion for homoaromaticity with the magnetic effects criterion.



150

If, on the other hand, a correlation between the NMR parameters (such as  $\Delta\delta$ ) and the structural parameters (such as length of the  $C_1-C_7$  bond) is not obtained, it will reflect a breakdown of the structure-ring

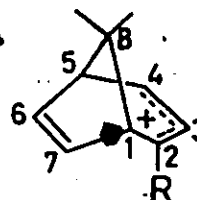
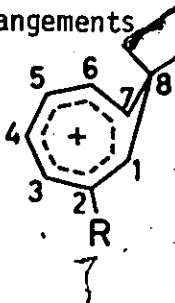
current relationship. It would also indicate that the other factors contributing to  $\Delta\delta$  values do not exhibit a linear correlation with structure.

CHAPTER 5

STUDIES ON THE REARRANGEMENTS IN 8,8-DIMETHYLHOMOTROPYLIUM AND 8,8-DIMETHYL-BICYCLO[3.2.1]OCTADIENYL CATIONS

The circumambulatory rearrangements in 8,8-dimethylhomotropylium cations with a hydroxy substituent in the ring have been studied in detail by Childs and Rogerson.<sup>84</sup> These studies, and those reported in the previous chapter, have given information regarding the relative stabilities of the hydroxy substituted 8,8-dimethylhomotropylium and 8,8-dimethyl-bicyclo[3.2.1]octadienyl systems (eg., 73 and 100). In these systems it is expected that the hydroxy group would localize the positive charge to a certain extent on oxygen. Because of this, a reduction in cyclic delocalization could be anticipated in the case of homotropylium cations. It would be of interest to examine these systems preferably without any substituent or with substituents that would exert a smaller perturbation on the homotropylium ring. Some work had already been started in this laboratory on the rearrangements of the unsubstituted and methyl substituted 8,8-dimethylhomotropylium and bicyclo[3.2.1]octadienyl cations (50, 153, 152 and 154).<sup>220</sup> Further studies were made by the author to complete this work and to investigate the nature of the intermediates formed in these rearrangements

- 73 R=OH
- 50 R=H
- 153 R=CH<sub>3</sub>

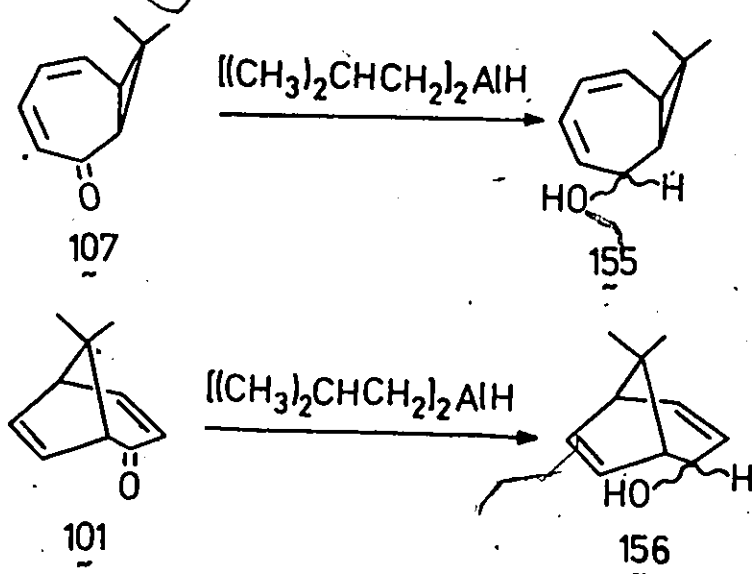


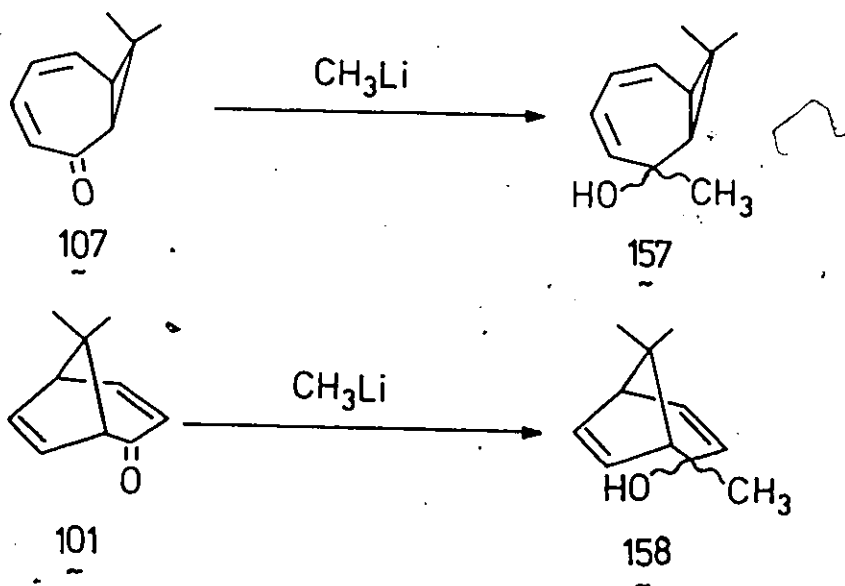
- 100 R=OH
- 152 R=H
- 154 R=CH<sub>3</sub>

Childs and Rogerson have reported the formation of 8,8-dimethyl-homotropylum cation 50 by the protonation of the secondary alcohol 155.<sup>84</sup> This alcohol was obtained by the reduction of the homotropone 107 with diisobutylaluminum hydride.<sup>84</sup>

The secondary alcohol 156 which is the precursor for the cation 152 was obtained by a similar reduction of 101. The tertiary alcohols 157 and 158 were prepared by the reaction of methyllithium with the ketones 107 and 101 respectively.

It would appear from the NMR spectra of the product(s) resulting from the hydride reductions that a mixture of both the endo and exo stereoisomers was produced. On the other hand, the methyllithium reactions gave predominantly one isomer. Purification of the secondary alcohols by distillation gave only one (the more volatile) isomer. The alcohols were characterized by their NMR and IR spectra. Their accurate molecular weights were determined by high resolution mass spectrometry. The stereochemistry of the final products has not been established. This, however, is not of concern, since the hydroxy group would be lost as water on protonation of these alcohols.





1. Protonation of 8,8-dimethylbicyclo[5.1.0]octa-3,5-dien-2-ol 155

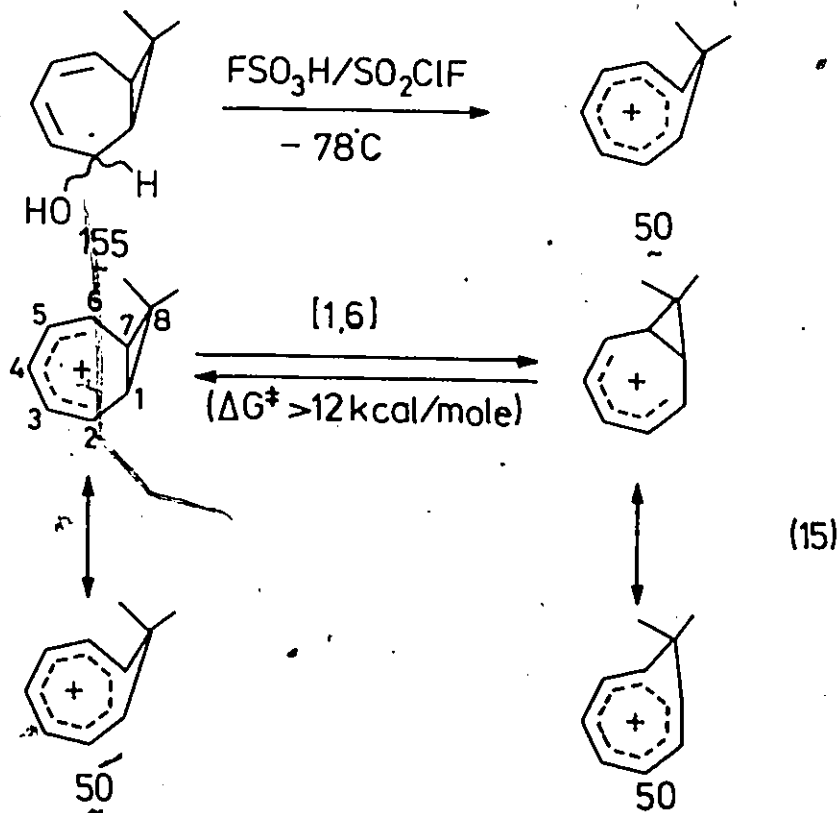
Childs and Rogerson have reported that protonation of 155 in  $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$  at  $-78^\circ\text{C}$  gave 50.<sup>84</sup> The NMR spectrum of 50 was reported to consist of broad singlets at  $\delta$  8.17 for the vinyl protons and at  $\delta$  5.26 for the protons on  $\text{C}_1$  and  $\text{C}_7$  as well as singlets at  $\delta$  2.36 and  $\delta$  -0.48 respectively for the exo and endo methyl protons on  $\text{C}_8$  (Table 22).<sup>84</sup> This  $^1\text{H}$  NMR spectrum is consistent with the homotropylium structure for 50. The signal corresponding to the resonance for the exo methyl protons was relatively broad at lower temperatures but it sharpened as the temperature was raised. This possibly could arise from restricted rotation of the exo methyl group at lower temperatures.

No evidence for the averaging of the ring proton resonances in the NMR spectra of 50 was observed at temperatures up to  $-50^\circ\text{C}$ .<sup>84</sup> Degenerate circumambulatory rearrangements such as that represented by equation 15, if occurring, would therefore be slow on the NMR time scale ( $\Delta G^\ddagger > 12$  kcal/mole).

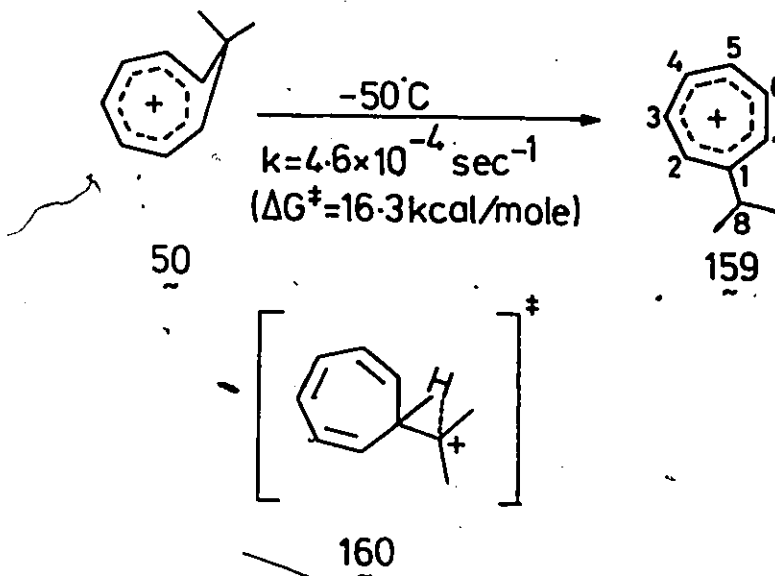
Table 22  
<sup>1</sup>H NMR Spectra of Various Cations

Cation	Temp. °C	Chemical Shifts (δ) <sup>a</sup> , b, c, d							
		H <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	H <sub>8</sub>	
50 <sup>f</sup>	-78			8.17(b,s)			5.26(b,s)		(2.36)(exo,s) (-0.48)(endo,s)
159	-50			9.07(b,s)					3.68(m, J=6.5Hz) (1.56)(d, J=6.5Hz)
173	34		6.33(dd) (J=10, 2Hz)	9.00(dd) (J=10, 11Hz)	3.86(m) (J=3Hz)	7.26(t) (J=4.5Hz)	3.93(m) (J=3Hz)	6.56(t) (J=4.5Hz)	3.0(t) (J=1.5, 4.5Hz)
153	-80		(2.84)(s)	8.03(m)				4.86(b,s)	(2.37)(exo,s) (-0.15)(endo,s)
177	-70			8.03(m)		8.03(m)		4.86(b,s)	(2.37)(exo,s) (-0.27)(endo,s)
183	-30		(3.12)(m) <sup>e</sup>	(3.09)(m) <sup>e</sup>		8.85(m)			3.5(m)
154	-120		(3.08)(s)	7.86(b,s)	9.55(b,t)	4.04(b,s)	7.35(b,d) <sup>e</sup>	4.04(b,s)	7.17(b,s) <sup>e</sup>
180 <sup>e</sup>	-60		(3.2)(s)	5.38(m)	4.27(m)	4.50(m)	6.37(m)	4.05(d) (J=8Hz)	-5.96(m) (1.54)(s) (1.13)(s)

<sup>a</sup> In CD<sub>2</sub>Cl<sub>2</sub>/SO<sub>2</sub>-Cl<sub>2</sub>/FSO<sub>3</sub>H medium.    <sup>d</sup> b:broad, s:singlet, d:doublet, dd:doublet of doublet, t:triplet, m:multiplet  
<sup>b</sup> CHCl<sub>3</sub> internal reference (δ 5.3).    <sup>e</sup> Assignments tentative.  
<sup>c</sup> Chemical shifts in parentheses are for methyl groups.    <sup>f</sup> Ref. 84.

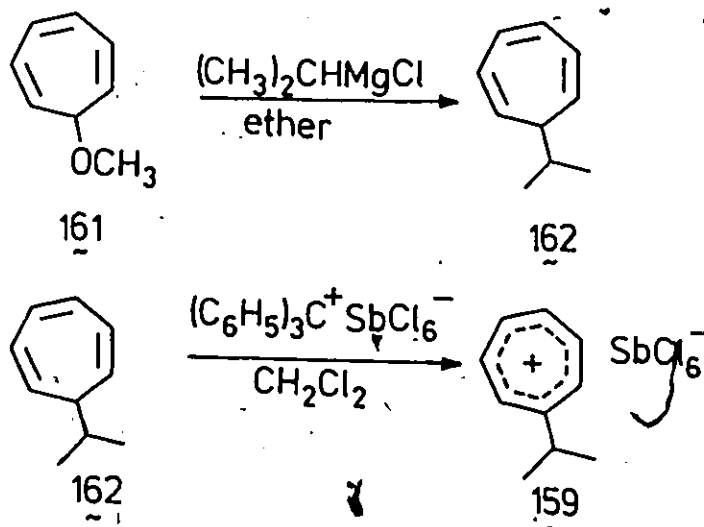


At  $-50^\circ\text{C}$ , 50 was observed to isomerize irreversibly to the isopropyltropylium cation 159.<sup>84</sup> The rate constant for this process at  $-50^\circ\text{C}$  was  $4.6 \times 10^{-4} \text{ sec}^{-1}$  ( $\Delta G^\ddagger = 16.3 \text{ kcal/mole}$ ). This isomerization process is consistent with Hehre's picture of a hydrogen-bridged transition state 160 for the circumambulatory-rearrangement in homotropylium cation.<sup>74</sup>





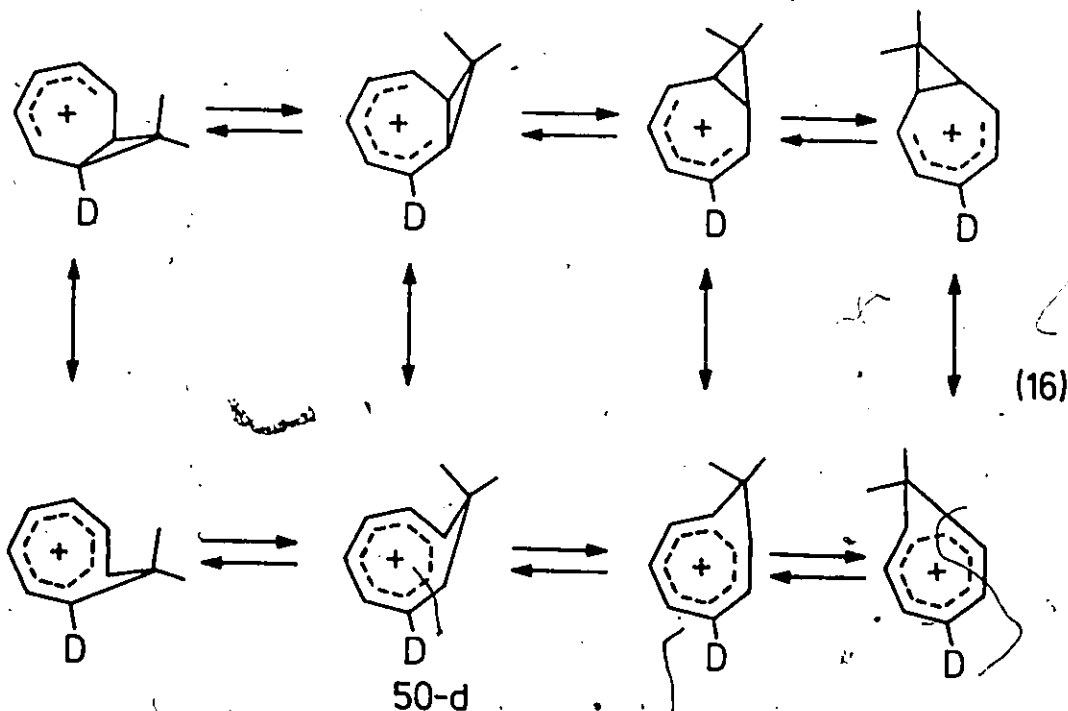
In the present study, the identity of 159 was established by its independent synthesis using a modification of the procedure reported by Nozoe and coworkers.<sup>221</sup> 7-Methoxycycloheptatriene 161 was treated with isopropylmagnesium chloride to get 7-isopropylcycloheptatriene 162. Hydride abstraction from 162 with triphenylmethyl hexachloroantimonate yielded isopropyltropylium hexachloroantimonate 159. The <sup>1</sup>H NMR spectrum of this material in CD<sub>2</sub>Cl<sub>2</sub> was identical to that of the cation obtained by the rearrangement of 50 in FSO<sub>3</sub>H solutions.



2. Preparation and Protonation of 2-deutero-8,8-dimethylbicyclo[5.1.0]-octa-3,5-dien-2-ol, 155-d.

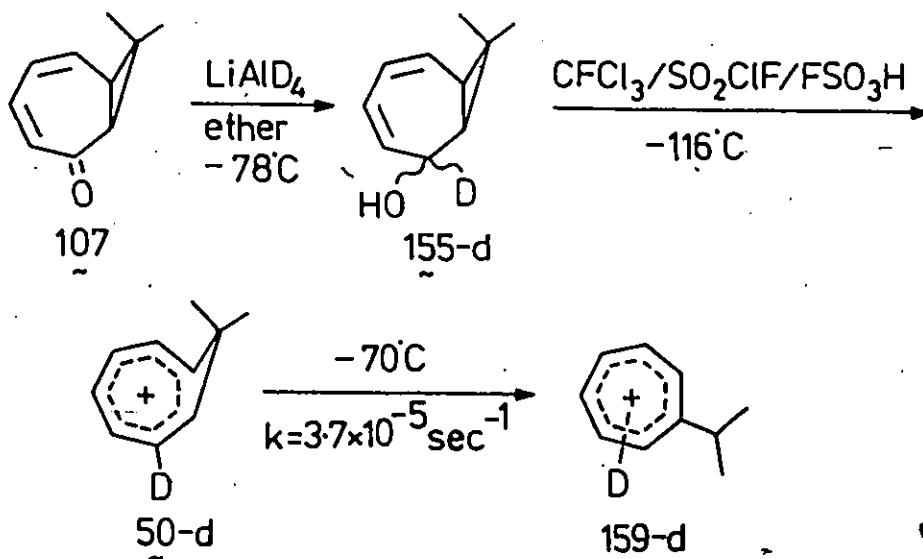
In an attempt to detect circumambulatory rearrangement in 50, it was decided to label the seven-membered ring with a deuterium atom. A degenerate circumambulatory rearrangement would distribute the label equally over all the seven carbons (equation 16). This process could in principle be followed experimentally by observing the increase in intensity of the signals for the vinyl protons H<sub>2</sub>-H<sub>6</sub> and decrease in the intensity of the signal for the methine protons H<sub>1</sub> and H<sub>7</sub>, in the

$^1\text{H}$  NMR spectrum. For example, the intensity of the signal for the vinyl protons  $\text{H}_2\text{-H}_6$  would change from the relative value of 4 in the starting cation before the rearrangement to 4.29 after complete equilibration and that of the signal for the methine protons  $\text{H}_1$  and  $\text{H}_7$  would change from the starting relative value of 2 to the final value of 1.71. In other words, the ratio of the relative intensities of these two signals would increase from the starting value of 2 to the final value of 2.51 after complete equilibration. As can be expected, the magnitudes of these intensity changes would be small and difficult to measure.



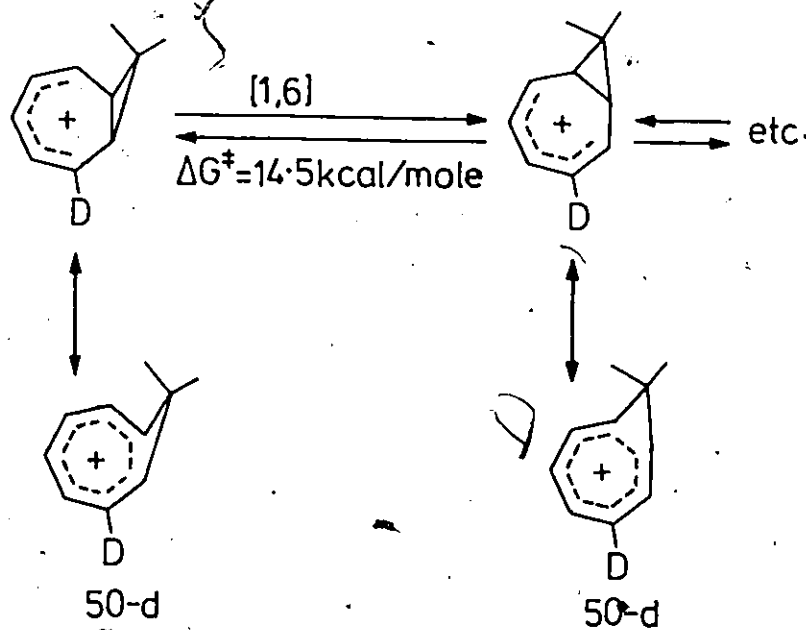
The alcohol, 155-d was prepared by the lithium aluminum deuteride reduction of the ketone 107 in ether at  $-78^\circ\text{C}$ . One major isomer was obtained under these conditions, the stereochemistry of which was not established. Protonation of this alcohol in  $\text{CFC}_1_3\text{-SO}_2\text{ClF-FSO}_3\text{H}$  medium at  $-116^\circ\text{C}$  led to the formation of 50-d. On warming from  $120^\circ\text{C}$  to  $-70^\circ\text{C}$  in steps of  $10^\circ\text{C}$ , the ratio of the integrals for the vinyl and

the methine proton signals in the  $^1\text{H}$  NMR spectrum of 50-d increased from 1.9 to 2.55. At  $-70^\circ\text{C}$  this value remained constant at  $2.45 \pm .09$  for several minutes. On the basis of the predictions made earlier, this observation would indicate the occurrence of deuterium label scrambling in 50-d, possibly via a circumambulation of the cyclopropyl group (equation 16). Continued observation of the same sample at  $-70^\circ\text{C}$  by NMR, showed that the intensities of the signals for all the protons decreased slowly with time. This could be attributed to the slow formation ( $k = (3.7 \pm .06) \times 10^{-5} \text{ sec}^{-1}$ ) of the isopropyltropylium cation 159-d.



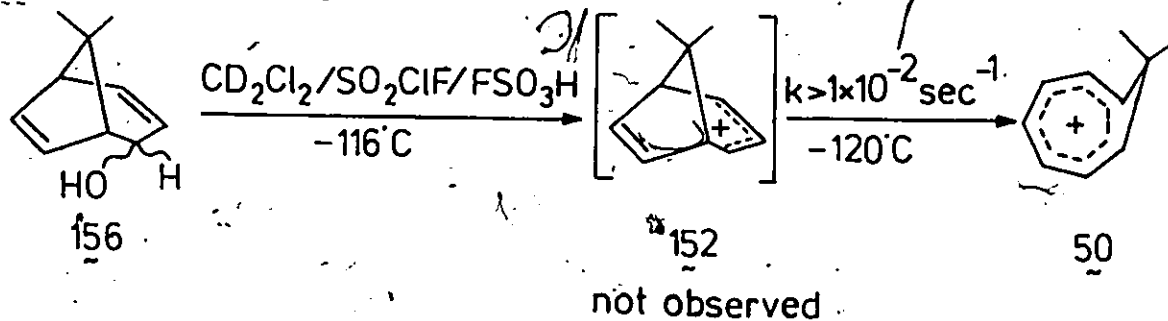
In a further attempt, observations were made on the cation 50-d at  $-90^\circ\text{C}$ , in order to obtain the rate constant for the deuterium scrambling process. Conversion to the isopropyltropylium cation 159-d would be expected to slow down considerably at this temperature. Measurement of the increase in the relative intensity (peak height) of the signal for the vinyl proton with time yielded a rate constant of

$(2.01 \pm .09) \times 10^{-5} \text{ sec}^{-1}$  corresponding to a free energy of activation of 14.5 kcal/mole for the deuterium scrambling process. This could be considered as the minimum value for the free energy of activation for the circumambulation in the parent cation 50-d, if the label scrambling proceeded via circumambulation.



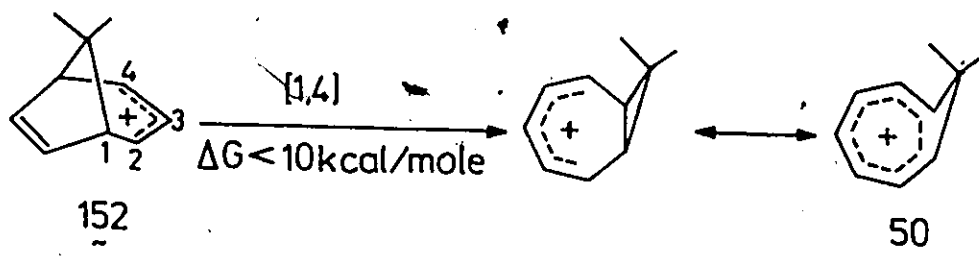
3. Protonation of 8,8-dimethylbicyclo[3.2.1]octa-3,6-dien-2-ol 156

Protonation of the secondary alcohol 156 in  $\text{FSO}_3\text{H-SO}_2\text{ClF-CD}_2\text{Cl}_2$  medium at  $-116^\circ\text{C}$  and NMR observation of the solution within three minutes, in the temperature ranges  $-120^\circ$  to  $-100^\circ\text{C}$  showed that the homotropylium cation 50 was the only species present. There was no evidence for the presence of cation 152. The half life of this cation must be less than a minute ( $k > 1 \times 10^{-2} \text{ sec}^{-1}$ ). At higher temperatures 50 rearranged to 159 as observed before.



Hart has observed various rearrangements in the permethylated derivative of the bicyclo[3.2.1]octadienyl cation, 163.<sup>222-224</sup> This cation was reported to undergo various processes such as circumambulation (equation 17), 1,2 bridge shift (equation 18) and cyclopropylcarbonyl rearrangement, which resulted eventually in the formation of the bicyclo[3.3.0]octadienyl cation 166 (equation 19).<sup>224</sup> The processes are summarized in Scheme 11.

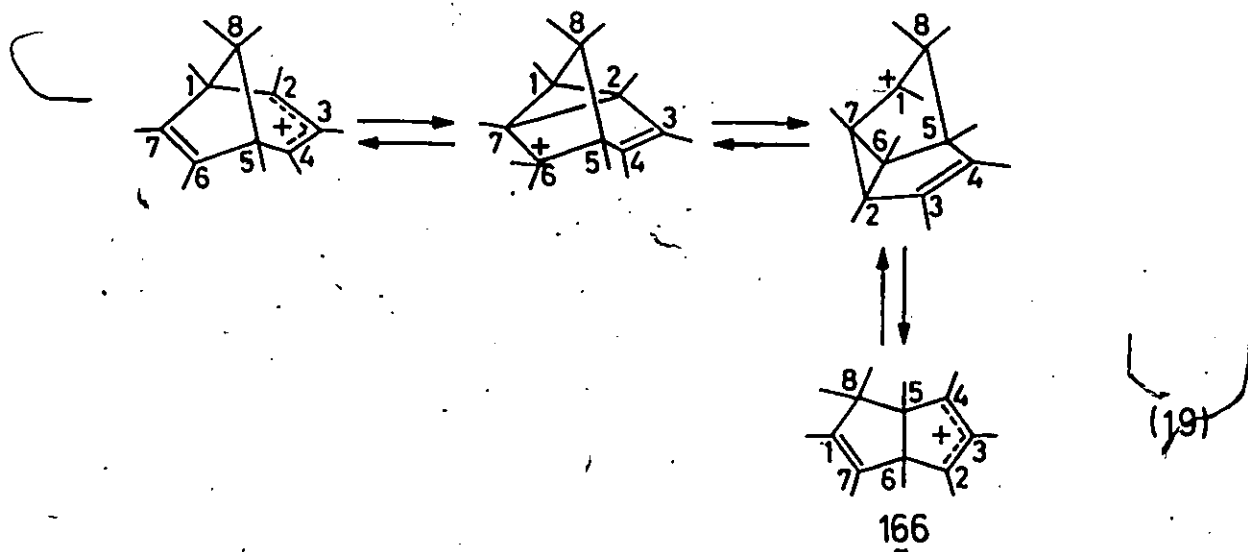
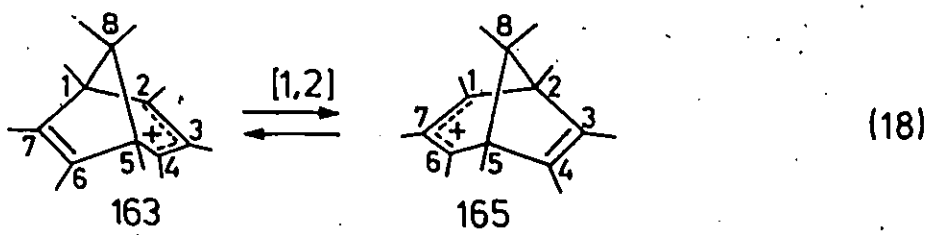
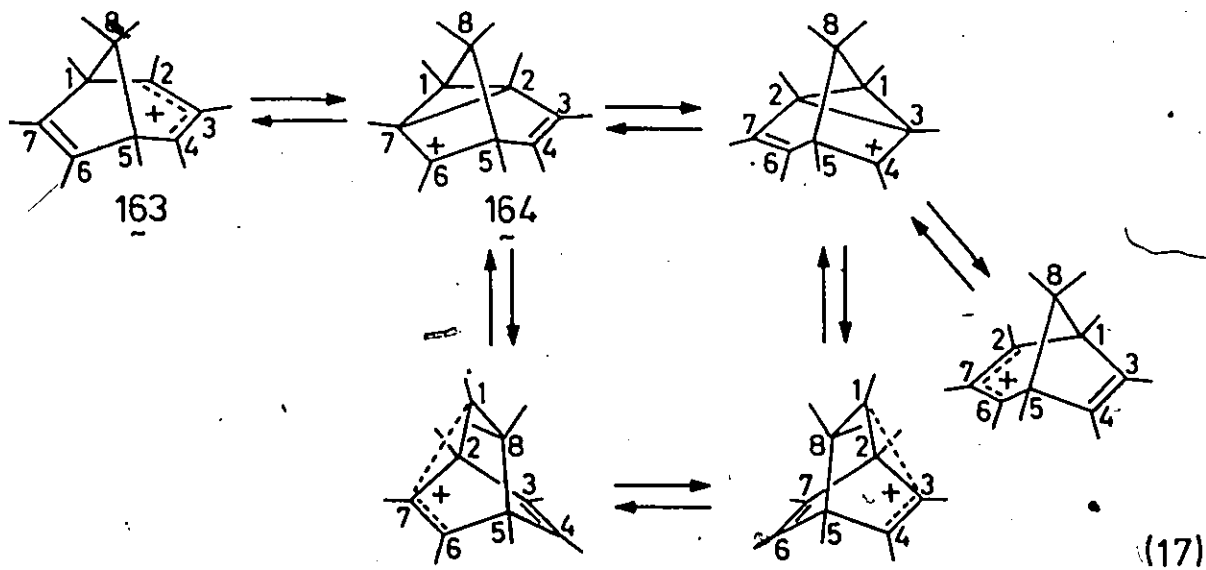
These processes have also been observed in cations containing fewer methyl groups.<sup>222-224</sup> It is interesting that Hart has not observed the formation of any homotropylium cation in these systems. The formation of 50 from 156 reported in the present work is unprecedented. The cation 50 could be formed by the 1,4 migration of C<sub>8</sub> in the unobserved cation 152.



As in the case of homotropylium cations, the methyl groups would be expected to stabilize the positive charge developing at C<sub>8</sub> in the transition state for this migration and thus facilitate this process. To test this, an attempt was made to observe the parent bicyclo[3.2.1]-octadienyl cation 168 from its alcohol precursor 167.

#### 4. Protonation of bicyclo[3.2.1]octa-3,6-dien-2-ol 167

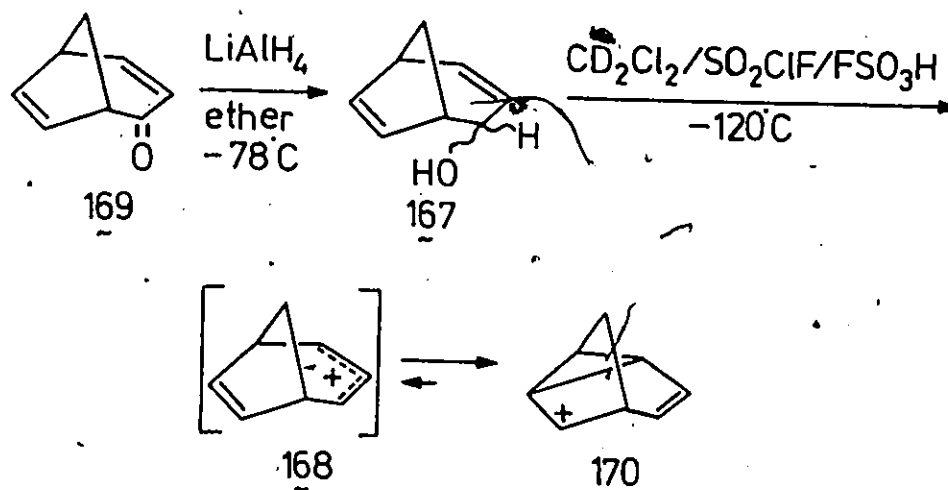
The alcohol 167 was obtained as a mixture of exo and endo isomers from the lithium aluminum hydride reduction of the ketone 169



Scheme 11  
(Reference 224)

at  $-78^{\circ}\text{C}$  in ether, by Diaz and coworkers.<sup>225</sup> Hart reported the formation of polymeric material on protonation of this alcohol.<sup>224</sup>

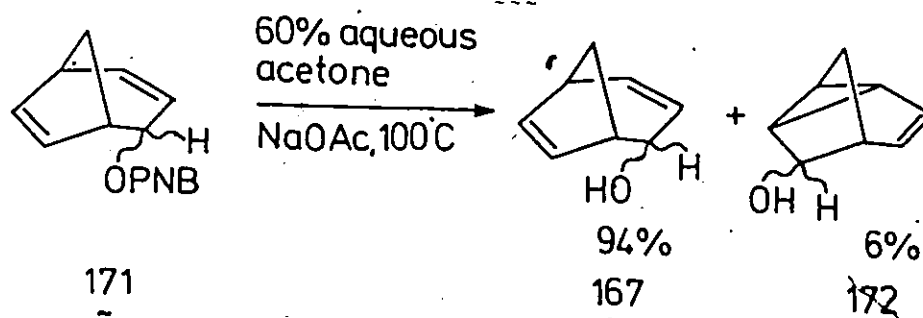
In the current study, 167 was protonated in a  $\text{CD}_2\text{Cl}_2\text{-SO}_2\text{ClF- FSO}_3\text{H}$  solution at  $-116^{\circ}\text{C}$ .  $^1\text{H}$  NMR analysis of this solution at  $-110^{\circ}\text{C}$  revealed the occurrence of extensive polymerization as shown by broad baseline hump in the upfield region. However, distinct multiplets at  $\delta$  6.25, 5.8, 5.3, 4.85, 3.44 and 2.09 and two other less intense signals at  $\delta$  2.98 and 2.42 could be seen. There was no signal in the downfield region. The absence of the downfield resonances corresponding to protons of the allylic cations would indicate that the starting cation 168 was not present in this solution. The resonances at  $\delta$  6.25, 5.8, 5.3, 4.85 and 3.44 are suggestive of a cyclopropylcarbinyl cation such as 170.<sup>\*</sup> For the parent cyclopropylcarbinyl cation (40) itself, the proton resonances occur at  $\delta$  6.5, 4.64 and 4.21.<sup>68</sup>



not observed

\* 170 is considered as a distinct cation and not as a resonance structure for the allylic cation. An explanation will be given later.

The cyclopropylcarbiny l cation structure for 170 would not seem to be unreasonable, in the light of the solvolysis experiments of Diaz and coworkers on the p-nitrobenzoate esters 171.<sup>225</sup> Besides the epimeric alcohols 167, small amounts of the epimers of the tricyclic alcohol 172 were also obtained.<sup>225</sup> The formation of 172 could be expected to result from an ion such as 170, under solvolytic conditions.



The cation 170 was found to be unstable at temperatures above  $-40^{\circ}\text{C}$  and undergo a general decomposition.

The pronounced instability of the bicyclooctadienyl cation 168, could possibly be due to the inductive effects of the second double bond rather than any bishomoantiaromatic delocalization, in 168. On the contrary, Diaz and coworkers attributed the rate retardation for the solvolysis of the p-nitrobenzoate 171 relative to its monoene analog to the antihomoaromatic character of the intermediate cation 168.<sup>225</sup>

Jefford and coworkers studied the isomeric  $\text{C}_8\text{H}_9$  cations extensively using the MINDO/3 method.<sup>226</sup> The calculated gas phase heats of formation ( $\Delta H_f$ ) for various cations such as 168 and 170 can serve as a guide for the relative stability of these cations in solution. The reported  $\Delta H_f$  values of 245.81 kcal/mole and 243.36 kcal/mole for 170 and 168 respectively, are close together.

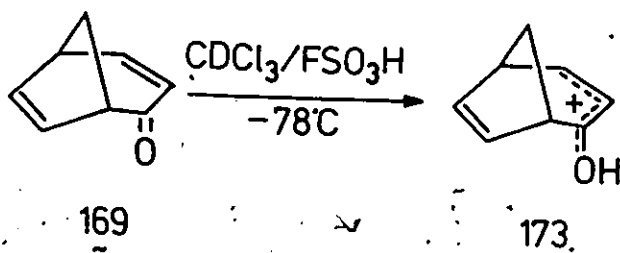
It is instructive, however, to compare the  $\Delta H_f$  value (243.36



kcal/mole) for 168 with that of homotropylium cation 5 (210.16 kcal/mole) calculated by Haddon, also using MINDO/3.<sup>13,79</sup> The homoaromatic isomer is more stable than its nonhomoaromatic counterpart by about 33 kcal/mole. In solution, some degree of attenuation of this difference can be anticipated due to the difference in the solvation energies of the two cations. Yet, the homotropylium cation would still be expected to be considerably more stable than cation 168. On this basis a facile conversion of 168 to 5 would be expected. However, the lack of occurrence of such a process suggests that the transition state for this rearrangement would have a high activation energy. Stabilization of the incipient positive charge at C<sub>8</sub> in the transition state by a gem dimethyl substituent is likely to lower this energy. The facile conversion of 152 to 50 seems to be in agreement with this suggestion.

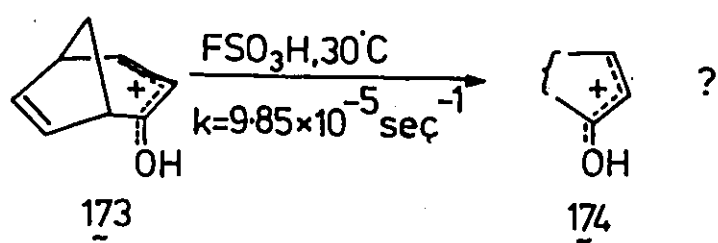
5. Protonation of bicyclo[3.2.1]octa-3,6-dien-2-one 169

In an attempt to observe the cation containing the bicyclo[3.2.1]octa-3,6-dienyl skeleton, protonation of the ketone 169 was carried out. Extraction of 169 from CDCl<sub>3</sub> into FSO<sub>3</sub>H at low temperatures (-78°C) gave a cation 173 whose <sup>1</sup>H NMR spectrum was unchanged on warming the solution up to ambient temperatures. The proton chemical shifts measured for the cation 173 were fully consistent with the assigned structure. The signal assignments were made on the basis of the similarity of the spectrum of 173 to that of its 8,8-dimethyl derivative 100.<sup>84</sup>



At ambient temperatures, the cation 173 rearranged slowly to give a new cation 174. The rate constant for this process was measured to be  $(9.85 \pm 0.17) \times 10^{-5} \text{ sec}^{-1}$  at  $30^\circ\text{C}$  ( $\Delta G^\ddagger = 23.3 \text{ kcal/mole}$ ).

The  $^1\text{H}$  NMR spectrum of the product cation 174 consisted of multiplets at  $\delta$  8.59, 6.76, 5.26, 3.83, 2.8, 2.53 and 2.39 each corresponding to one proton. The absence of upfield signals shows that 174 is not a homotropylium cation derivative. The signals at  $\delta$  8.59 and  $\delta$  6.76 are typical for the olefinic protons of protonated  $\alpha, \beta$ -unsaturated ketones. Thus it would appear that this enone segment is maintained in the product cation 174. The multiplet at  $\delta$  3.83 could be ascribed to the signal for the resonance of the bridgehead protons, based on its similarity of appearance to those of the bridgehead protons in 173. However, due to the complexity of the upfield signals, a definite structure for 174 could not be assigned. It is interesting to note that the cation 100 obtained from the protonation of 101 in  $\text{FSO}_3\text{H}$  did not undergo any rearrangement at ambient temperatures.



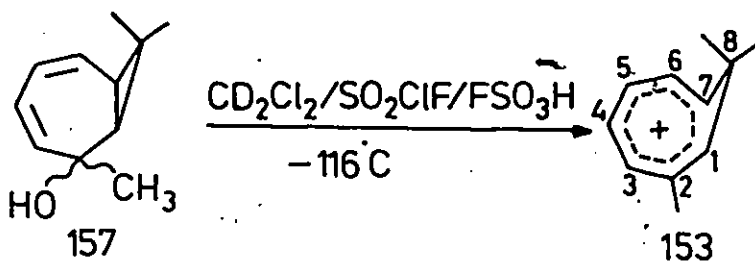
Labelling the seven-membered ring with a methyl substituent would facilitate the detection of the circumambulation processes in the homotropylium and the bicyclooctadienyl cations. Further, the effect of the methyl substituent on the relative stabilities of the various isomers could be obtained from such a study. To this end, the tertiary alcohols

157 and 158 were protonated at low temperature and the resulting cations studied by NMR spectroscopy.

6. Protonation of 2,8,8-trimethylbicyclo[5.1.0]octa-3,5-dien-2-ol 157  
and 2,8,8-trimethylbicyclo[3.2.1]octa-3,6-dien-2-ol 158

a. Protonation of 2,8,8-trimethylbicyclo[5.1.0]octa-3,5-dien-2-ol 157

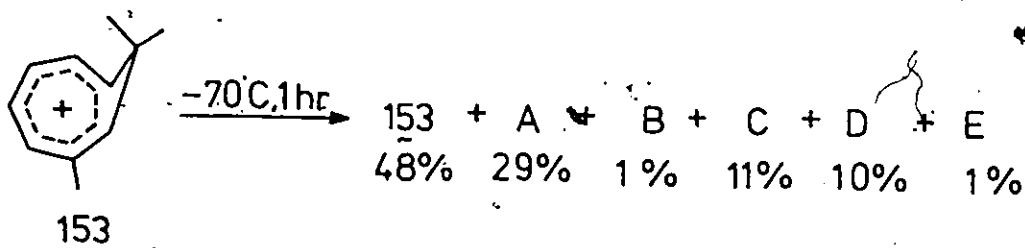
The alcohol 157 was protonated in  $\text{CD}_2\text{Cl}_2\text{-SO}_2\text{ClF-FSO}_3\text{H}$  medium at  $-116^\circ\text{C}$ . The  $^1\text{H}$  NMR spectrum of the resulting cation was observed at  $-120^\circ\text{C}$  (Figure 15). This NMR spectrum is very similar to that of 50 but for the additional methyl resonance at  $\delta$  2.84 (Table 22, Figure 15). The broadening of the signal for the exo methyl resonance ( $\delta$  2.37) at low temperature was used to distinguish this signal from that for the methyl group at  $\text{C}_2$  ( $\delta$  2.84). This cation was stable up to  $-80^\circ\text{C}$ .



Warming the solution above  $-80^\circ\text{C}$  resulted in the formation of other species, observed by the appearance of several signals in the  $^1\text{H}$  NMR spectrum. From the number of signals for the methyl protons, it was inferred that at least five different cations, A - E, besides 153 were present in the solution (Figure 15). At  $-75^\circ\text{C}$  the rate constant for the decrease in concentration of 153 was found to be approximately  $1.4 \times 10^{-4} \text{ sec}^{-1}$ . Cation 153 did not disappear completely on heating. For example, at  $-70^\circ$ , after 1 hour, the relative concentrations of 153, A, B, C, D and E were 48, 29, 1, 11, 10 and 1% respectively.



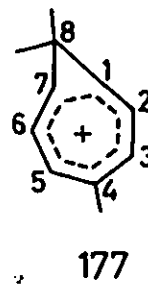
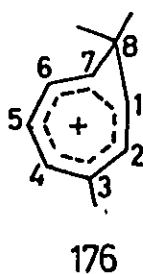
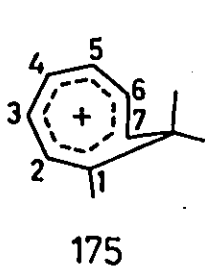
Figure 15  $^1\text{H}$  NMR spectrum of a solution of the alcohol 157 in  $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$  (a) at  $-100^\circ\text{C}$  and (b) at  $-70^\circ\text{C}$  for 1 hour.



Cations A and B exhibited methyl signals at  $\delta$ -0.27 and  $\delta$ -0.45 respectively. The upfield positions of these resonances are characteristic of endo (hydrogen or methyl) substituents in homotropylium cations. On this basis, species A and B are likely to be two isomeric homotropylium cations. The methyl resonances for the rest of the species C, D and E occurred at comparatively lower fields and these cations would not be expected to be homotropylium cations.

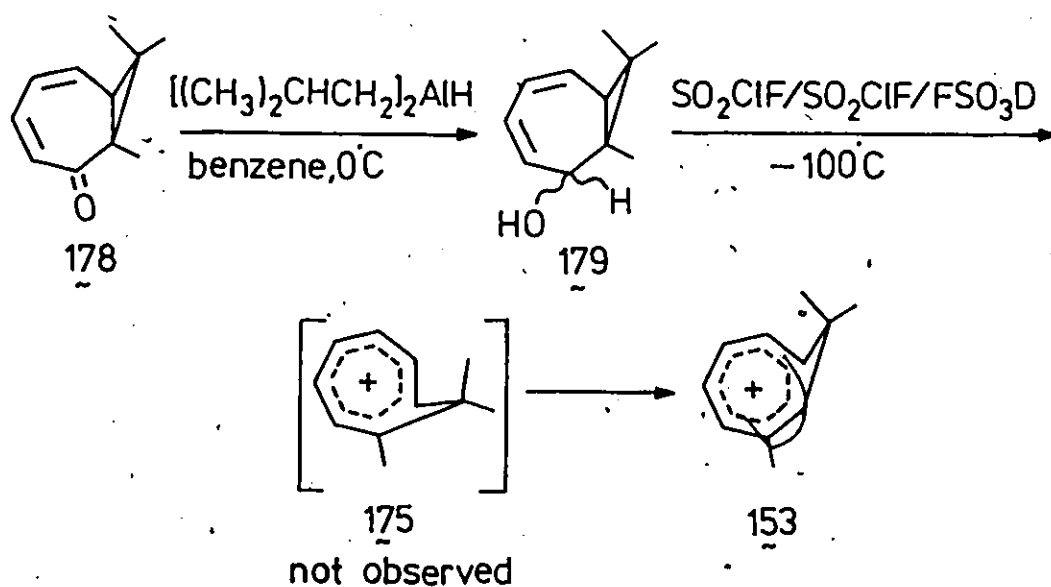
b. Identity of Cation A

The proton NMR signals for A closely resembled those of 153. In fact the only observable differences were the positions of the resonances for the endo methyl ( $\delta$ -0.27) and the methyl substituent on the seven-membered ring ( $\delta$  2.87). The chemical shifts for the vinyl and the bridgehead methine protons were identical to those in 153 (Table 22). This would suggest that A is an isomeric homotropylium ion. Three other homotropylium cations are possible, 175, 176, and 177.



Earlier work done in this laboratory ruled out structure 175

for A.<sup>220</sup> Childs obtained the 1,8,8-trimethylbicyclo[5.1.0]octa-3,5-dien-2-ol 179 by the diisobutylaluminum hydride reduction of 1,8,8-trimethyl-2,3-homotropone 178.<sup>220</sup> Protonation of this alcohol in  $\text{SO}_2\text{ClF}-\text{SO}_2\text{F}_2-\text{FSO}_3\text{H}$  medium was carried out at  $-120^\circ\text{C}$ . Observation of the resulting product by  $^1\text{H}$  NMR at  $-110^\circ\text{C}$  showed that only 153 was present.<sup>220</sup> No evidence for the presence of 175 was found.<sup>220</sup>



It would therefore seem unlikely that A could be 175. A could now be represented by either 176 or 177. Structure 176 for A was discounted on the basis of two observations. (i) In the case of hydroxy substituted 8,8-dimethylhomotropylium cations the 3-hydroxy isomer 103 was found to be less stable than the 4-hydroxy isomer 78. A methyl substituent could be expected to exert a similar influence on the basis of its charge stabilizing effect. Since cation A is the next most abundant species in the reaction mixture (29% at  $-70^\circ\text{C}$ ), it would seem likely that A is 177. (ii) Further support came from the  $^{13}\text{C}$  NMR studies of Childs on the rearrangement of 153.<sup>220</sup> Initial observation of this

cation at  $-80^{\circ}\text{C}$  gave a spectrum (Figure 16) consistent with the assigned structure.<sup>220</sup> After warming for 5 minutes at  $-50^{\circ}\text{C}$ , the  $^{13}\text{C}$  NMR spectrum was recorded again at  $-80^{\circ}\text{C}$ . A complex set of signals was obtained. Besides 153 two other intermediates (one major and one minor) appeared to be present. By means of spectral subtraction techniques, the spectrum of the intermediates was obtained.<sup>220</sup> The symmetric nature of the spectrum of the major intermediate is consistent with the structure 177 (Figure 16).

The signal assignments for the various carbon resonances in 153 and 177 were based on the similarity between the  $^{13}\text{C}$  NMR spectra for these cations and those for the 2-hydroxy and 4-hydroxyhomotropylium cations 69 and 76.<sup>137,227</sup> The  $^{13}\text{C}$  NMR chemical shifts for 153 and 177 are reported in Table 23.

Additional signals observed in the  $^{13}\text{C}$  NMR spectra (Figure 16) during the course of the rearrangement of 153 at  $-50^{\circ}\text{C}$  were attributed tentatively to the cation C (the minor intermediate). The chemical shift values for these resonances were  $\delta$  124.4, 121.4, 82.9, 78.4, 66.6, 62.5, 57.6, 52.0, 51.4, 33.3 and 18.7. The first two signals could be considered as the resonances for the vinyl carbons and the last two for the methyl carbons. Definite assignment, however, could not be made for the rest of the carbons.

c. *Identity of the Cation B*

The species B was present in very small quantities (about 1% at  $-70^{\circ}\text{C}$ ). The only distinguishing feature was the resonance at  $\delta$  -0.45 ppm. The rest of the resonances were either too weak to be noticed or buried in other strong signals. Higher proportions of this cation were observed in experiments to be described later and it is clear that the

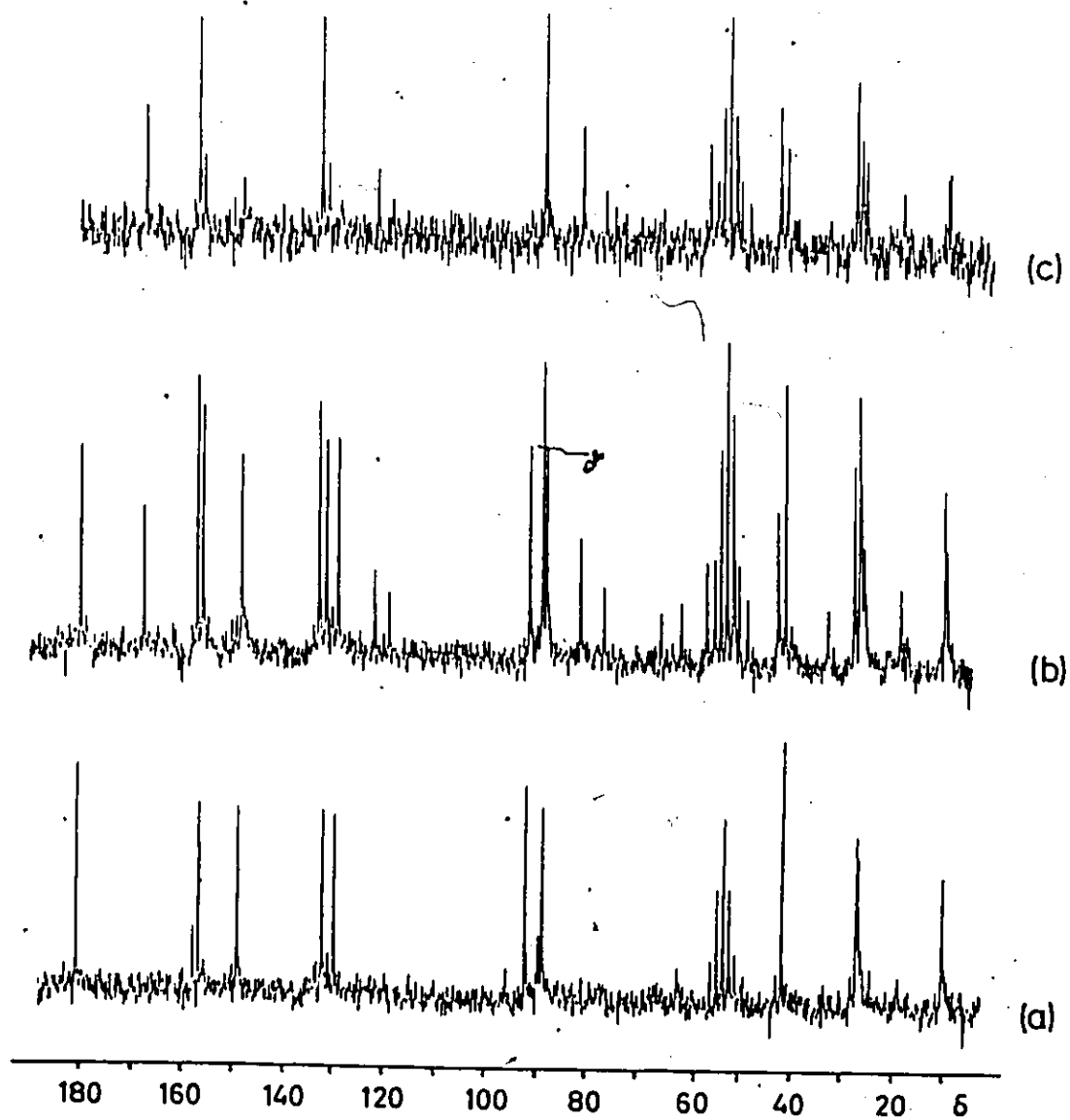


Figure 16  $^{13}\text{C}$  NMR spectrum of a solution of the alcohol 157 in  $\text{CDCl}_2/\text{SO}_2\text{ClF}$   $\text{FSO}_3\text{H}$  (a) at  $-80^\circ\text{C}$ , (b) after warming at  $-50^\circ\text{C}$  for 5 minutes and (c) spectrum obtained by subtracting spectrum (a) from spectrum (b).



Table 23

<sup>13</sup>C NMR Chemical Shifts for Cations 153 and 177<sup>a</sup>

Cation	Chemical Shifts (δ) <sup>b</sup>										
	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	8-CH <sub>3</sub> exo	8-CH <sub>3</sub> endo	CH <sub>3</sub> (ring)	
153	183.0	133.9 <sup>c</sup>	158.6	150.7	131.6 <sup>c</sup>	93.1 <sup>d</sup>	89.8 <sup>d</sup>	41.9 <sup>e</sup>	27.0	9.9	26.6 <sup>e</sup>
177	159.8	135.3	170.3	135.3	159.8	90.5	90.5	43.5 <sup>f</sup>	28.1	9.6	26.1 <sup>f</sup>

<sup>a</sup> in FSO<sub>3</sub>H-SO<sub>2</sub>ClF medium at -80°C.

<sup>b</sup> Relative to CD<sub>2</sub>Cl<sub>2</sub> internal standard (δ 53.6).

c-f Assignments may be reversed.

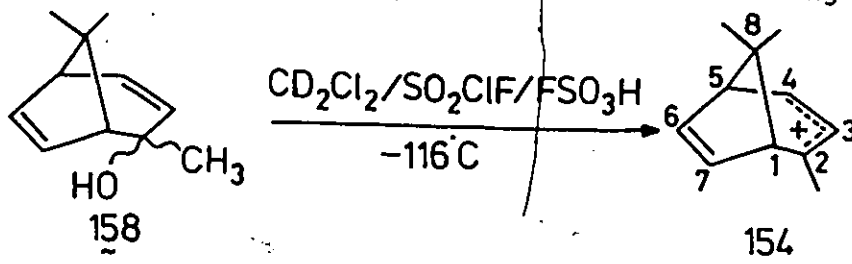
resonance at  $\delta$ -0.45 must not be simply considered as noise but must be taken seriously. The unusually high chemical shift value of  $\delta$  -0.45 would correspond to an endo methyl resonance in homotropylium cations. The only possible choice left now is the 3,8,8-trimethylhomotropylium cation 176.

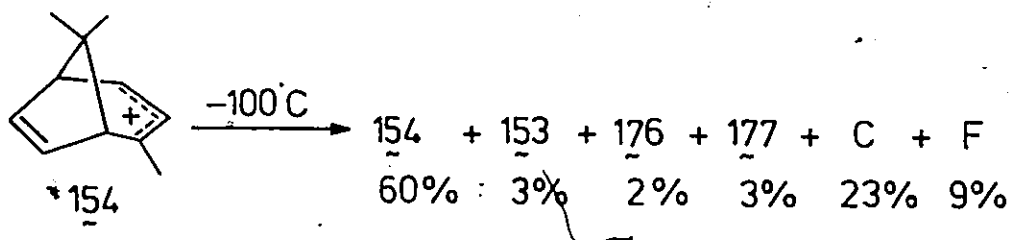
d. *Identities of Cations C, D and E*

Cations C, D and E appeared to be structurally related to one another. Further, they did not appear to be homotropylium cations. Evidence for the structure of C came from the protonation of 158, while cations D and E were not identified.

e. *Protonation of 2,8,8-trimethylbicyclo[3.2.1]octa-3,6-dien-2-ol 158*

The tertiary alcohol 158 was protonated at  $-116^{\circ}\text{C}$  and the  $^1\text{H}$  NMR spectrum observed at  $-120^{\circ}\text{C}$ . Unlike the protonation of the secondary alcohol 156, the parent cation 154 was observed in this case. The proton resonances at  $\delta$  9.55, 7.86 and 3.08 (methyl) were strongly suggestive of a methyl substituted allyl cation. For example, the chemical shifts reported for the 1-methylcyclohex-2-enyl cation were  $\delta$  9.73, 8.08 and 3.36 (methyl).<sup>228</sup> The allylic resonances and the other resonances at  $\delta$  7.35, 7.17, 4.04, 1.58 and 1.30 in the NMR spectrum are consistent with structure 154 for this cation (Table 22). The methyl resonances of 154 did not correspond to those of C, D or E. The introduction of a methyl group would be expected to have a stabilizing effect on 154.





Although cation 154 was sufficiently stable to be observed at  $-120^\circ\text{C}$ , it underwent further reactions even at these temperatures. Slow conversion to the three homotropylium cations 153, 176 and 177 was evident from the appearance of the three methyl resonances in the upfield region. In addition, cation C observed earlier was also formed and initially was the most abundant of the rearrangement products.

At  $-100^\circ\text{C}$ , at least six cations appeared to be present (Figure 17). Three of these were homotropylium cations 153, 176 and 177, present to the extent of 3%, 3% and 2% respectively. The starting bicyclo[3.2.1]-octadienyl cation 154 was the major species (60%). The cationic species C was present to the extent of 23%. 9% of cation F was also present.

The  $^1\text{H}$  NMR spectrum of C formed in the rearrangement of 154 was obtained by a spectral subtraction technique (Figure 18). This spectrum consisted of multiplets of  $\delta$  6.37, 5.96, 5.38, 4.5 and 4.27 and singlets at  $\delta$  3.20, 1.54 and 1.13 (Table 22). There were no downfield signals attributable to any allylic or other such cationic species.

The cyclopropylcarbinyl structure 180 for the cation C was assigned on the basis of its NMR spectrum and comparison with similar systems. The signals at  $\delta$  6.37 and 5.96 can be ascribed to the olefinic proton resonances, those at  $\delta$  5.38, 4.5 and 4.27 to the cyclopropyl and the bridgehead proton resonances and those at  $\delta$  3.20,

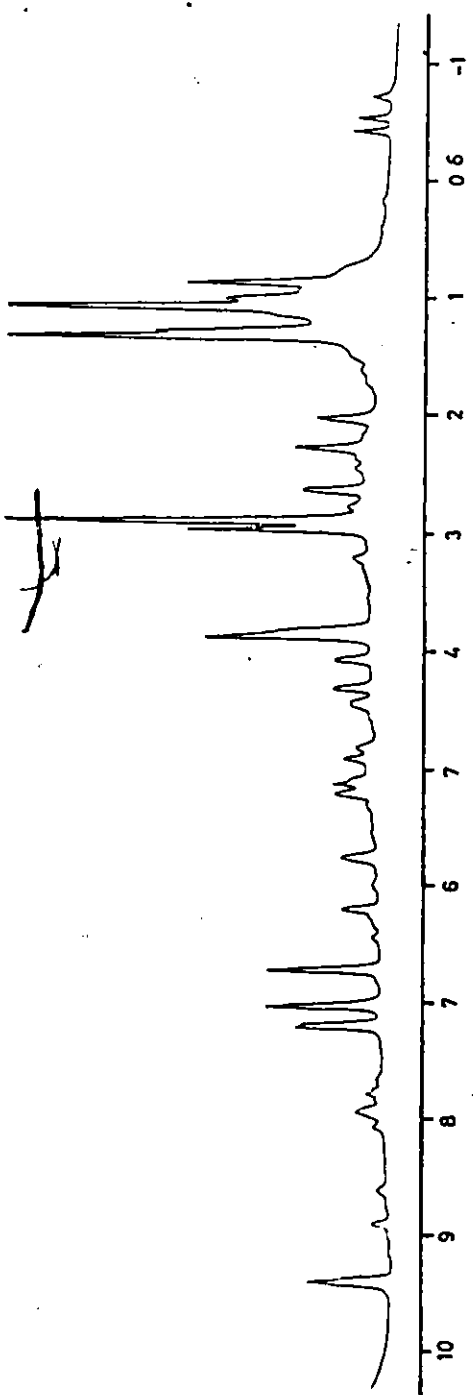


Figure 17 <sup>1</sup>H NMR spectrum of a solution of the alcohol 158 in CD<sub>2</sub>Cl<sub>2</sub>/SO<sub>2</sub>ClF/FSO<sub>3</sub>H at -100°C.

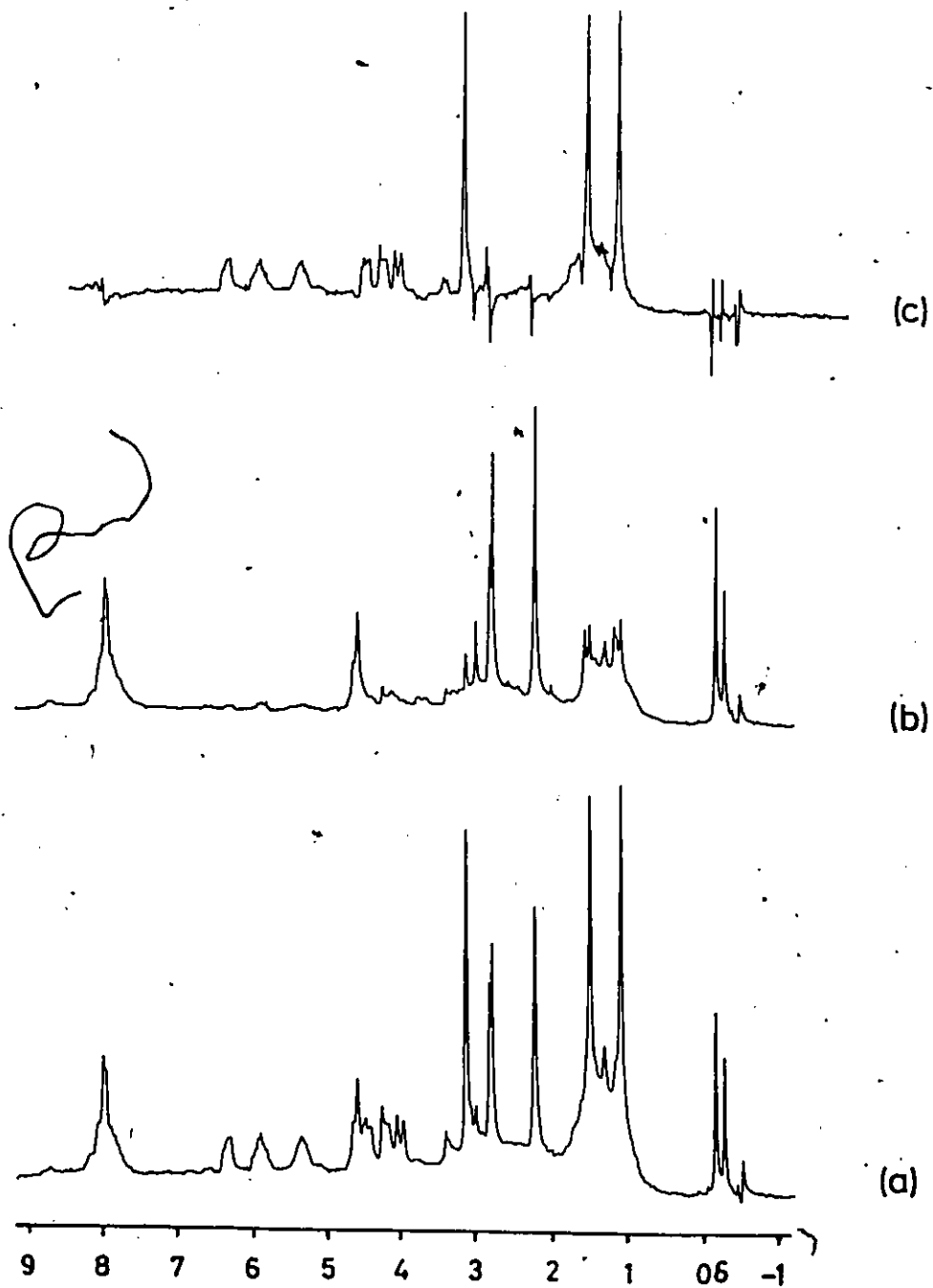
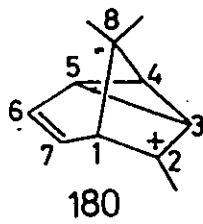
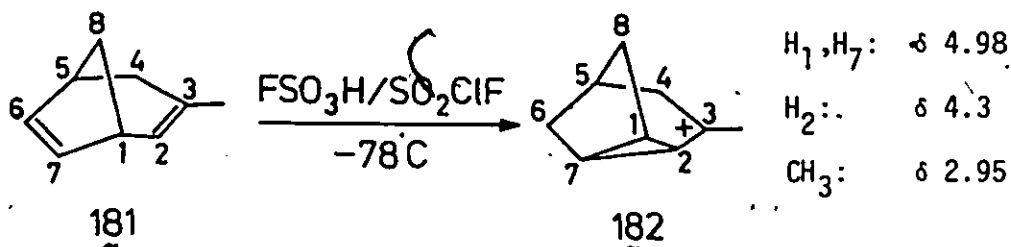


Figure 18  $^1\text{H}$  NMR spectrum of a solution of the alcohol 158 in  $\text{SO}_2\text{ClF}/\text{FSO}_3\text{H}$  (a) at  $-80^\circ\text{C}$  for 10 minutes, (b) at  $-60^\circ\text{C}$  for 10 minutes and (c) spectrum of the intermediate 180 obtained by subtracting spectrum (b) from spectrum (a).

1.54 and 1.13 to the methyl proton resonances. The significant downfield shift for the methyl proton resonance at  $\delta$  3.20 adjacent positive charge.



Although individual signal assignments could not be made with certainty for all the methine protons, their resonances occurring in the upfield region are strongly suggestive of a cyclopropylcarbinyl cation species.<sup>68</sup> There were close similarities between the spectrum of this cation and that of 170, obtained by the protonation of the parent alcohol 167. Olah and coworkers have reported that protonation of 3-methylbicyclo[3.2.1]octa-2,6-diene 181 in  $\text{FSO}_3\text{H-SO}_2\text{ClF}$  at  $-78^\circ\text{C}$  results in the formation of the 3-homonortricyclyl cation 182.<sup>229</sup> The  $^1\text{H}$  NMR chemical shifts reported for the cyclopropylcarbinyl moiety in 182 are similar to those observed for the cation 180.<sup>229</sup>



Species F was present only in small amounts (9%). The distinct signal at  $\delta$  2.54 was used to estimate its relative concentration. This signal is typical for the proton resonance of a methyl group

attached to an olefinic carbon. Further there were two other signals for methyl resonances at  $\delta$  1.36 and 1.22, overlapping with that for the methyl resonance at  $\delta$  1.30 for the major rearrangement product 180. However due to the difficulty in locating the rest of the signals in the complex NMR spectrum, the cation F could not be assigned a definite structure. At best, it is possible to conclude that F is not a homotropylium cation.

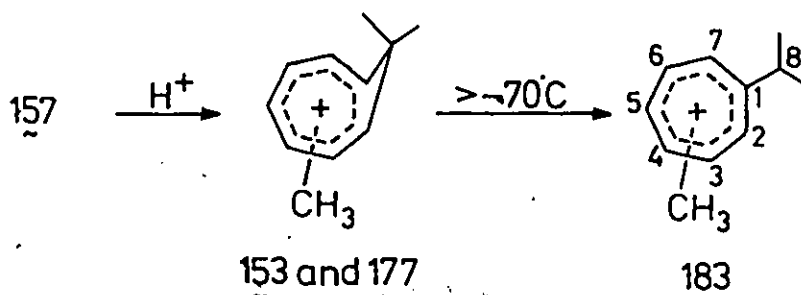
On raising the temperature to  $-80^{\circ}\text{C}$  the starting cation 154 disappeared almost completely, increasing the relative concentration of the cyclopropylcarbanyl cation 180 substantially. The relative concentrations of the homotropylium cations 153, 176 and 177 also underwent notable increase. It was found that the 3-methyl isomer of the homotropylium cations was present in relatively higher concentrations at lower temperatures (about 6%) as compared to its concentration at higher temperatures (1%) in solutions of 153.

On warming the solution to  $-70^{\circ}\text{C}$  the concentration of the 3,8,8-trimethylhomotropylium cation 176 decreased in favor of the other two homotropylium cations 153 and 177. The concentration of 180 also decreased.

Warming the solution obtained from the protonation of 157, in steps of  $10^{\circ}\text{C}$  to  $-30^{\circ}\text{C}$ , resulted in the slow formation of two more cationic species, with concomitant disappearance of the homotropylium cations 153 and 177 ( $\Delta G^{\ddagger}$  - 14 kcal/mole). The NMR spectra of these cations consisted of a broad singlet at  $\delta$  8.85, a multiplet at  $\delta$  3.5, a doublet at  $\delta$  1.51 and two singlets at  $\delta$  3.12 and 3.09 (Table 22).

Based on the spectral similarity to the isopropyltropylium cation

159, these cations were identified as the isomeric methyl derivatives 183 of isopropyltropylium cation 159. From ratio of the intensities of the methyl signals at  $\delta$  3.12 and 3.09, these isomeric cations were found to be present in the relative ratio of 4:3. The exact location of the methyl groups in these cations was not found.



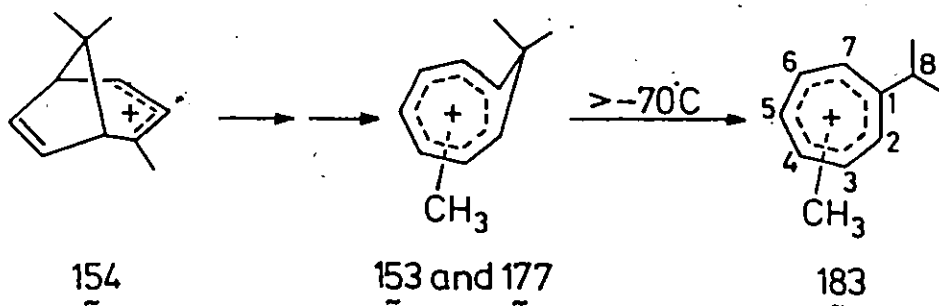
Over a large range of temperatures the relative ratios of the 2-methyl and 4-methylhomotropylium cations 153 and 177 remained constant (63:37 for 153:177). This suggests the two cations are in equilibrium.

The species represented by 180, D and E, underwent changes at these temperatures ( $-70$  to  $-20^\circ C$ ) as shown by the signals for their methyl resonances. However, due to the complexity of the spectra, and due to the difficulty in identifying the species D and E, these changes could not be interpreted.

~~At~~ Above  $-20^\circ C$  the conversion to the isopropyltropylium cations 183 was rapid. At ambient temperatures, ~~all~~ the species observed at low temperatures disappeared. The isomeric mixture of the cation 183 was the dominant species.

Comparable changes were observed when the solution of the cation 154 was warmed above  $-70^\circ C$ .

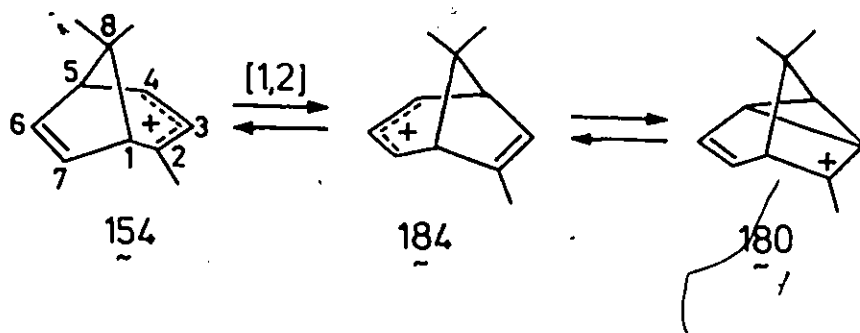




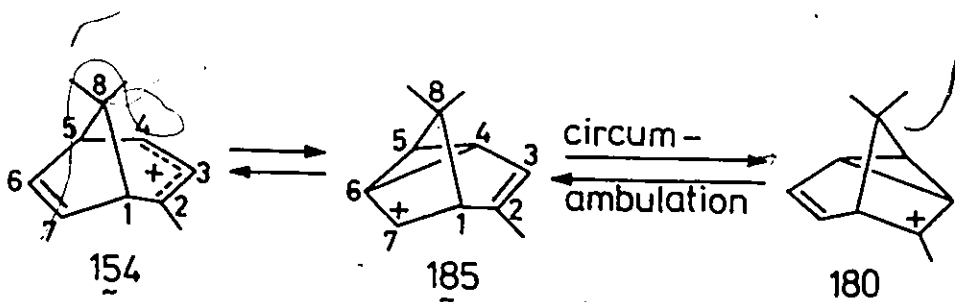
In order to deduce the nature of the intermediates formed in the rearrangement of 154, an attempt to quench its solution in  $\text{FSO}_3\text{H}$  at  $-78^\circ\text{C}$  with methanolic  $\text{NaHCO}_3$  was made. This resulted in the formation of a mixture of products, as indicated by GLC analysis. However, due to the small amounts of products obtained after gas chromatographic separation, their characterization could not be carried out.

f. Possible Mechanisms for the Formation of Various Cations

As has already been mentioned, Hart observed 1,2 bridge shifts in the rearrangement of the nonamethylbicyclo[3.2.1]octadienyl cation 163 (equation 18, Scheme 11).<sup>224</sup> Such a shift can also be expected to occur in 154, producing (small amounts of) the less stable isomer 184. This cation, in turn, could form the cyclopropylcarbinyll cation 180. Comparable examples of the formation of tricyclic systems such as 180 are provided by the rearrangement of 163 to 164 (equation 17, Scheme 11) and the protonation of the diene 181 to yield 182.<sup>224,229</sup>



Alternatively, the isomeric cyclopropylcarbiny l cation 185 formed from 154 could undergo circumambulatory migration of C<sub>5</sub> from C<sub>6</sub> to C<sub>3</sub>, forming the cation 180 directly.



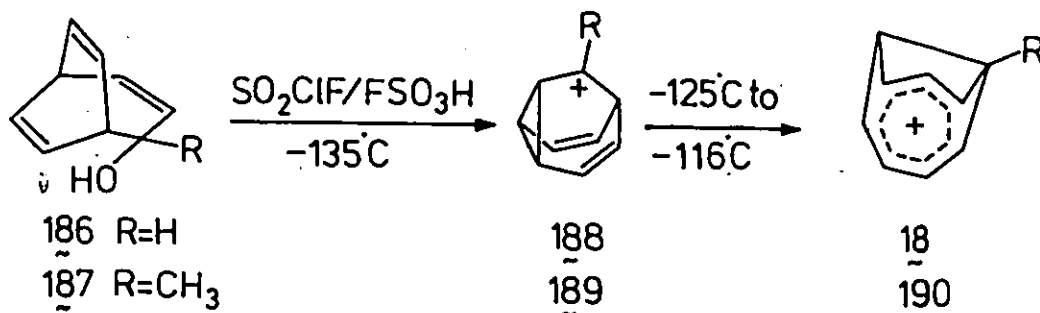
According to Hart, the circumambulatory migration process in the nonamethylbicyclo[3.2.1]octadienyl cation 163 (equation 17, Scheme 11) is at least 30 times faster than the 1,2 bridge shift (equation 18, Scheme 11).<sup>223</sup>

On this basis, it is likely that the cation 180 is formed from 154, relatively rapidly via a similar circumambulatory process. As reported in the case of the unmethylated parent cation 168, the relative stability of the cyclopropylcarbiny l cation 180 is seemingly greater than that of the bicyclic isomer 154.

The cation pair 184 and 180 along with the pair 154 and 185 are considered as equilibrating pairs rather than as resonance forms. An explanation for this will be given later. The barrier to the formation of these tricyclic cations from their bicyclic isomers can be expected to be very low. Only small changes in the relative positions of the interacting carbons are necessary to bring about this transformation.

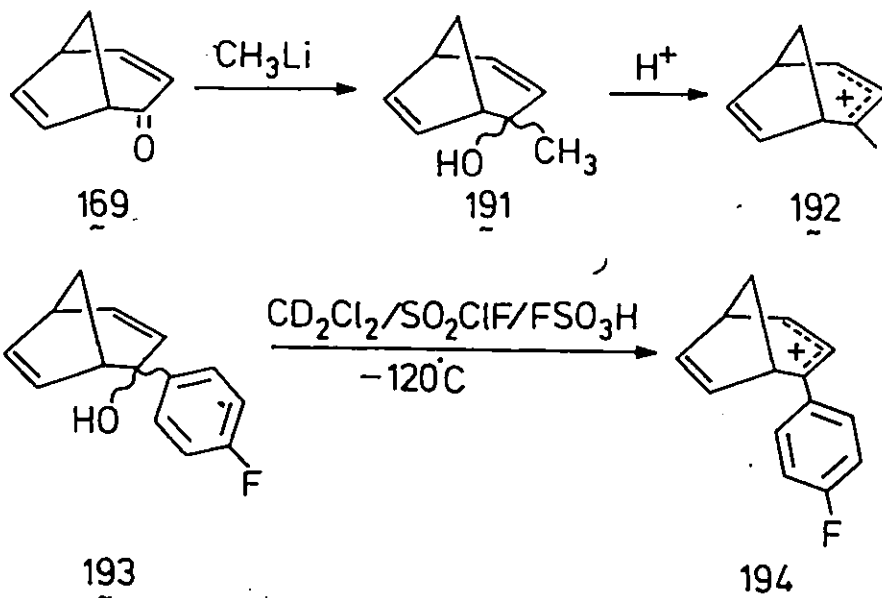
The low barrier is probably reflected in the relatively facile formation of 180 from 154 even at low temperatures.

The protonation behavior observed for the tertiary alcohol 158 is similar to that observed for the bicyclo[3.2.2]nor $\alpha$ -3,6,8-trien-2-ol 186 and its 2-methyl derivative 187.<sup>43,230</sup> The barbaralyl cations 188 and 189 rearranged to give the 1,4-bishomotropylium cation 18 and its 1-methyl derivative 190, respectively.<sup>43,230</sup>

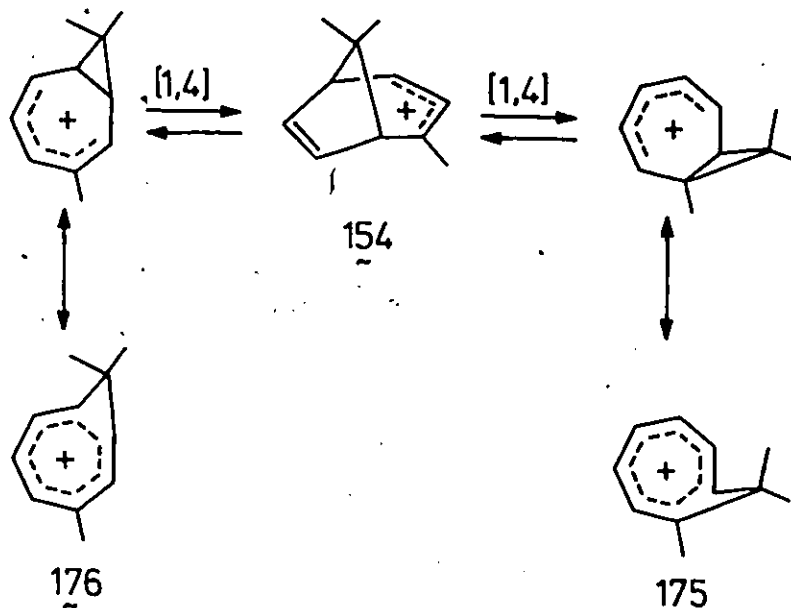


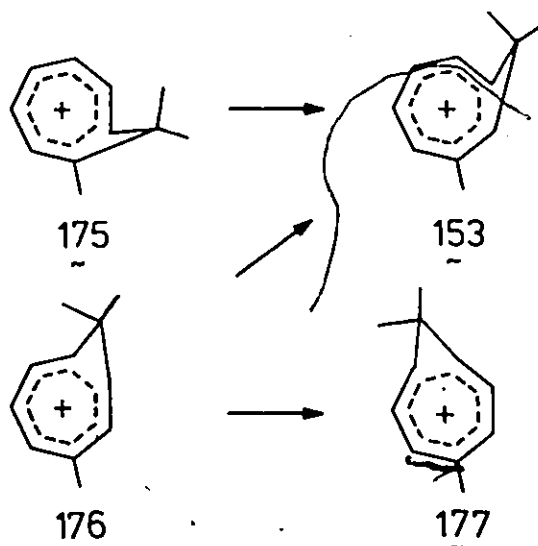
As mentioned earlier Hart and coworker have reported the formation of polymeric material on protonation of the parent alcohol 167.<sup>224</sup> In contrast the higher methylated systems formed the parent cations cleanly, which then underwent circumambulation, bridge shifts and cyclopropyl-carbinyl rearrangements (Scheme 11).<sup>224</sup> In this regard Hart has raised questions as to how far and from what positions one can strip the system of substituents and still have it undergo these rearrangements.<sup>224</sup> From this study one can infer that even with one methyl substituent at C<sub>2</sub>, it might be possible to observe the cation 192 by protonating the tertiary alcohol 191. It is interesting to note that the aryl substituted derivative 194 has recently been observed by Shin.<sup>231</sup> Protonation of the

alcohol 193 in super acid media at low temperatures led to the formation of 194.<sup>231</sup>



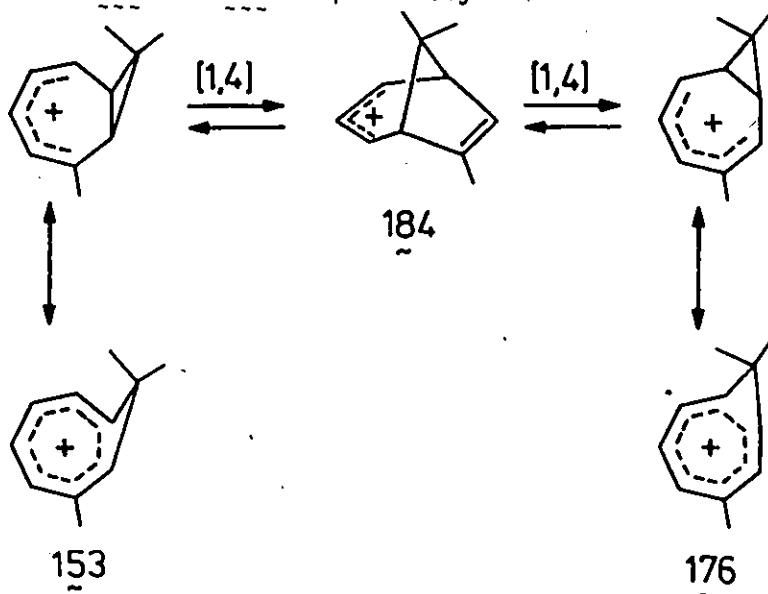
Cation 154 could form 1-methyl and 3-methylhomotropylum cations 175 and 176 by 1,4 shifts of carbon  $\text{C}_8$ . Since 1-methylhomotropylum cation 175 has already been reported to form its 2-methyl isomer 153 even at very low temperatures, 175 would not be expected to be observed in this case. Further, the 2- and 4-methylhomotropylum cations 153 and 177 respectively, would probably result from the rearrangement of 176.





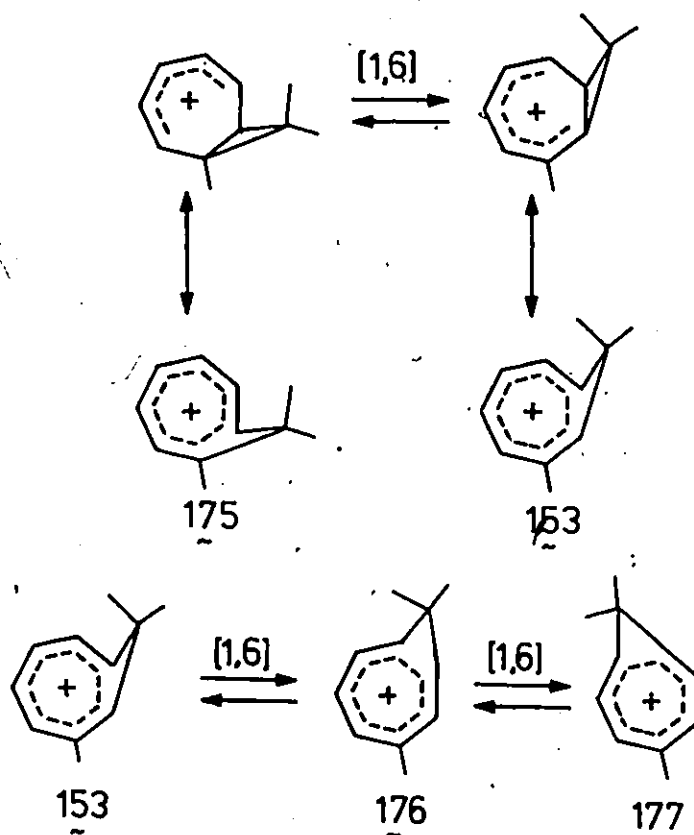
These explanations are consistent with the results of the rearrangement studies in the trimethylhomotropylium cations. At temperatures below  $-70^{\circ}\text{C}$ , the conversion of the 3,8,8-trimethylhomotropylium cation 176 to 153 and 177 is slow. Thus the concentration of 176 observed would be relatively higher (6%) in the case of the rearrangement of 154 than that of 153 reported earlier.

The bridge shift isomer 184 of the cation 154, if present, could also undergo 1,4 shifts of  $\text{C}_8$ , to give 2,8,8- and 3,8,8-trimethylhomotropylium cations 153 and 176 respectively.



It would appear that the cyclopropylcarbinyl cation 180 has no direct pathway for conversion to the homotropylium cations. Any such rearrangement would have to proceed via the bicyclo[3.2.1]octadienyl cations 154 and 184. This would mean that its conversion to the homotropylium cation would be relatively slow and would account for its observation at comparably higher temperatures ( $-70^{\circ}\text{C}$  to  $-60^{\circ}\text{C}$ ).

The rearrangement processes occurring in the trimethylhomotropylium cations can now be considered. As already reported, analogous rearrangements were observed in the hydroxy substituted 8,8-dimethylhomotropylium cations.<sup>84</sup> Therefore the rearrangements observed here in the methyl substituted systems could be visualized to occur from the 1,6 (circumambulatory) migration of the  $\text{C}_8$  carbon around the periphery of the "seven-membered" ring.



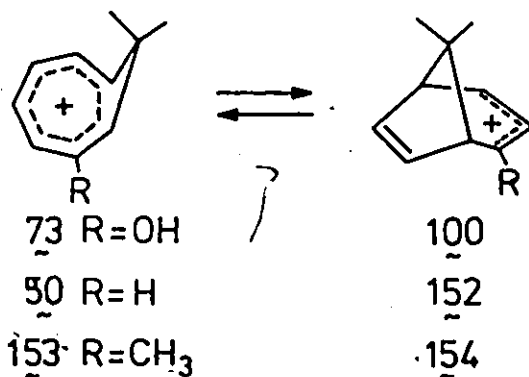
The approximate value of the rate constant for the decrease in concentration of 153 at  $-75^{\circ}\text{C}$  ( $1.4 \times 10^{-4} \text{ sec}^{-1}$ ) corresponds to a  $\Delta G^{\ddagger}$  of 14.9 kcal/mole. This can be considered as being equal to or a lower limit for the barrier to circumambulation in 153.

The formation of the cyclopropylcarbiny] cation 180 in the circumambulatory rearrangement of 2,8,8-trimethylhomotropylium cation 153 indicates that the bicyclo[3.2.1]octadieny] cation 154 could be a potential intermediate in this process.

## 7. Conclusions

### a. *Substituent Dependence of the "Equilibrium" Between the Homotropylium and the Bicyclo[3.2.1]octadieny] Cations*

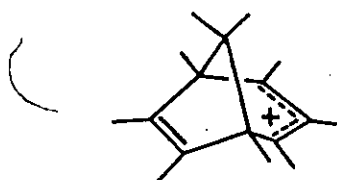
The foregoing results indicate that there is a remarkable substituent dependence of the equilibrium position between the 8,8-dimethylhomotropylium and the 8,8-dimethylbicyclo[3.2.1]octa-3,6-dien-2-ylum cations.



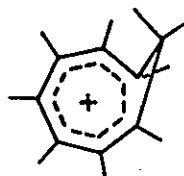
For the hydroxy derivatives 73 and 100 the equilibrium lies to the right, while for the unsubstituted cations 50 and 152, the equilibrium lies to the left. In the case of the methyl derivatives 153 and 154

both species can be detected simultaneously indicating that the equilibrium constant is close to 1.

The considerable variation of the position of the equilibrium with changes in the substituents can be explained on the basis of differences in the charge distribution for these two cations. From a simplistic point of view, the cyclic delocalization in a homotropylium ion can be thought of as resulting in a seventh of a positive charge on each of the ring carbons. On the other hand the bicyclo[3.1.0]octadienyl cations can be regarded largely as allyl cations with a half positive charge on C<sub>2</sub> and C<sub>4</sub>. Electron donating substituents on these carbons will have a much larger stabilizing effect on the bicyclo[3.2.1]octadienyl cations than on the homotropylium ions. Calculations indicate that the unsubstituted homotropylium ion is more stable than the bicyclo[3.2.1]octadienyl cation. This is shown experimentally in this work where 50 is more stable than 152. A methyl substituent on the appropriate carbons brings the two ions into about the same energy range. A hydroxy group on the other hand renders the bicyclo[3.2.1]octadienyl systems the more stable. This analysis can be extended to the nonamethyl systems of Hart, and on reflection it is not at all difficult to see why these workers never detected any homotropylium ions such as 195 in the rearrangements of cations such as 163. It may be recalled that the nonhomoaromatic cation is preferred to its homoaromatic counterpart as far as strain energy is concerned.



163



195



b. *Relative Energies of Various Isomers*

The relative energies of various methyl substituted cations can be estimated, as shown for the hydroxyhomotropylium cations in the previous chapter.

The relative concentrations of the 2,8,8-trimethyl and 4,8,8-trimethylhomotropylium cations 153 and 177 present after equilibration at  $-70^{\circ}\text{C}$  for an hour were 48% and 29% respectively. This would lead to an equilibrium constant of 1.21, after making correction for their statistical distribution. This corresponds to a free energy difference of 0.08 kcal/mole at  $-70^{\circ}\text{C}$ , in favor of the 4-methyl isomer 177. Some 1% of the 3-methyl isomer 176 was observed in equilibrium with 153. This means that the latter would be more stable than the former by 1.6 kcal/mole ( $K = 48$ ). Similarly 153 would be expected to be more stable than 180 (11%) by 0.6 kcal/mole ( $K = 4.4$ ). If 1% of the cation 154 is also assumed to be present in equilibrium, then 153 is estimated to be more stable than 154 by at least 1.6 kcal/mole ( $K = 48$ ). The same conclusion can be made for the 1,8,8-trimethyl isomer 175. These estimates are summarized in Figure 19. It should be remembered, once again, that these estimates are approximate and the relative magnitudes rather than the absolute values of the various energy differences should be taken into consideration.

It is seen that the 2,8,8-trimethyl and 4,8,8-trimethylhomotropylium cations 153 and 177 are the most stable of all the cations reported in Figure 19. Among the trimethyl homotropylium cations, the stability decreases in the order  $\underline{153} = \underline{177} > \underline{176} > \underline{175}$ . In other words this would represent the site preference of a methyl substituent in the

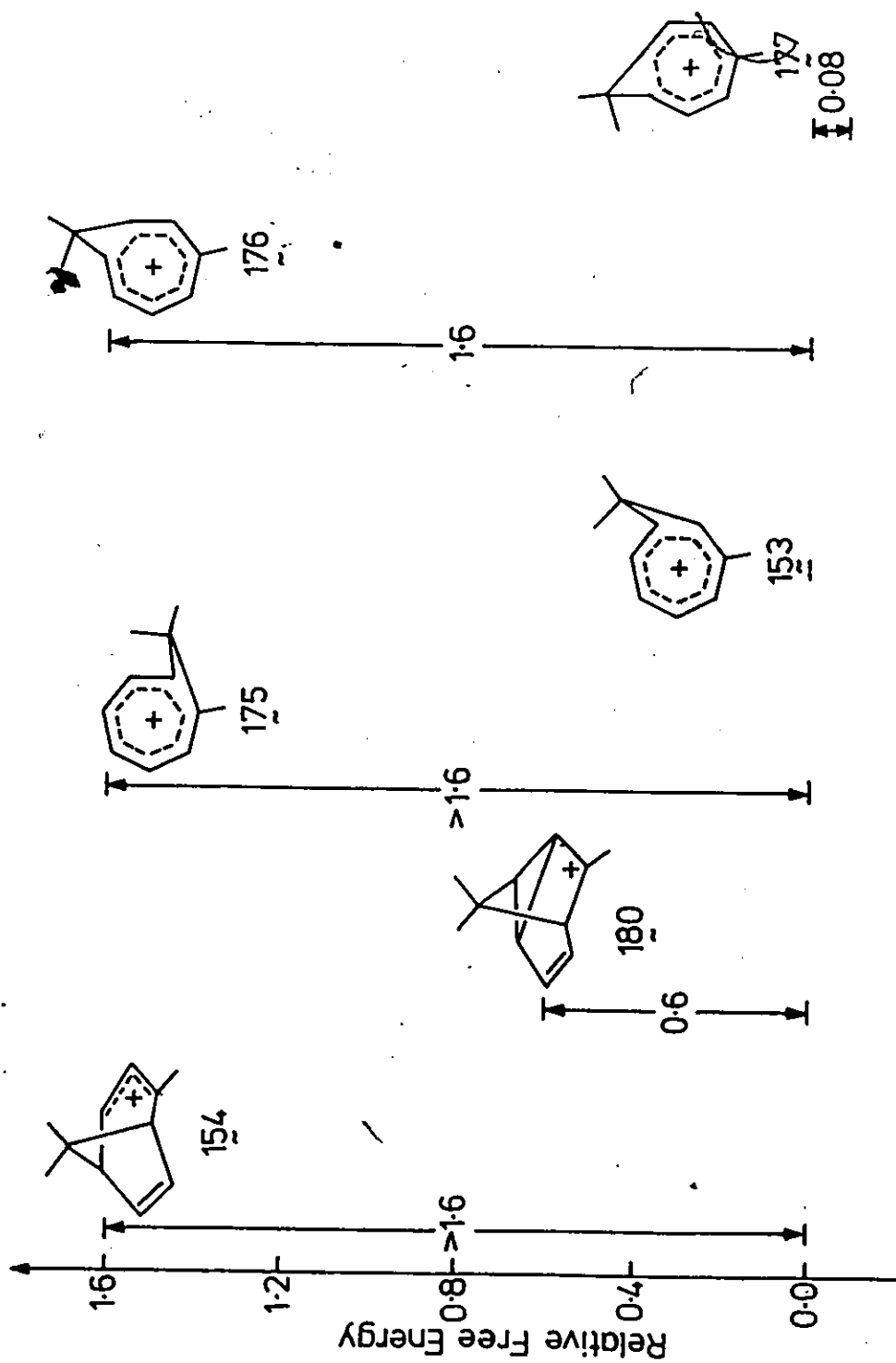


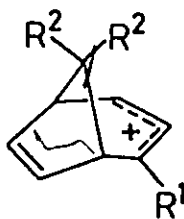
Figure 19 Estimates of the free energies of various cations relative to that of 2,8,8-trimethylhomotropylium cation 153. (All values in kcal/mole).

homotropylium cations. This order is similar to that observed in the corresponding hydroxy derivatives but for the relative positions of the 3-hydroxy and the 1-hydroxy isomers 103 and 68 respectively. In the hydroxy derivatives, the 3-substituted isomer was estimated to be less stable than its 1-substituted counterpart. The lack of direct observation of 175 and 103 as well as the assumptions used in estimating these values would be the probable causes for the differences in relative ordering.

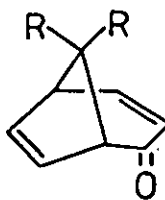
The tropylium cation derivatives are formed as final products from the homotropylium cations in all these rearrangements. This shows that the homoaromatic systems are less stable thermodynamically than the aromatic systems. Such a conclusion was reached from the calorimetric studies described earlier.

c. *The Nature of Delocalization Present in the Bicyclo[3.2.1]octadienyl Cation*

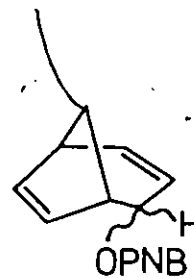
The bicyclo[3.2.1]octa-3,6-dienyl cations such as 100, 152 and 154 have been represented as allyl cations. It has been mentioned that no special destabilizing factors such as the bishomoantiaromatic delocalization operate in these systems. The calorimetric study on the ketone 101 lends support to this conclusion.<sup>173</sup> However, Diaz and coworkers concluded that the rate retardation experienced by the p-nitrobenzoate ester 171, is in line with the antihomoaromatic designation for the intermediate cation 168. Shin proposed similar conclusions by comparing the <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra of the cation 194 with those of 196.<sup>231</sup>



- 100 R<sup>1</sup>=OH, R<sup>2</sup>=CH<sub>3</sub>  
 152 R<sup>1</sup>=H, R<sup>2</sup>=CH<sub>3</sub>  
 154 R<sup>1</sup>=R<sup>2</sup>=CH<sub>3</sub>  
 173 R<sup>1</sup>=OH, R<sup>2</sup>=H



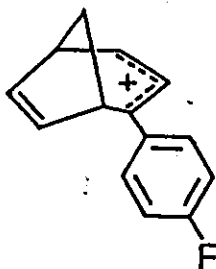
- 101 R=CH<sub>3</sub>  
 169 R=H



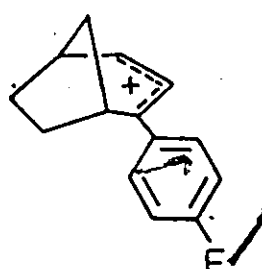
171



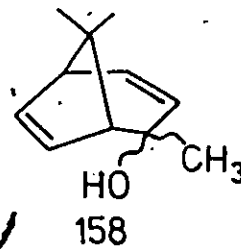
168



194



196



158

In this regard it is worthwhile to reconsider the nature of delocalization present in the bicyclo[3.2.1]octadienyl cations.

The <sup>1</sup>H NMR spectral data for the cations 154, 173 (Table 22), 100 and 194 indicate that there is no obvious paratropic effect resulting from any bishomoantiaromatic delocalization.<sup>84,231</sup> All the vinyl protons experience deshielding. Therefore, cyclic delocalization may not be important for these cations. However, comparison of the chemical shifts for H<sub>6</sub> and H<sub>7</sub> in the cations 173, 100 and 154 relative to their neutral counterparts 169, 101 and 158 respectively, suggests that transfer of some fraction of the positive charge from the allyl cation fragment to the second double bond has occurred (Table 24).

The nature and extent of this interaction is not clear. The

Table 24

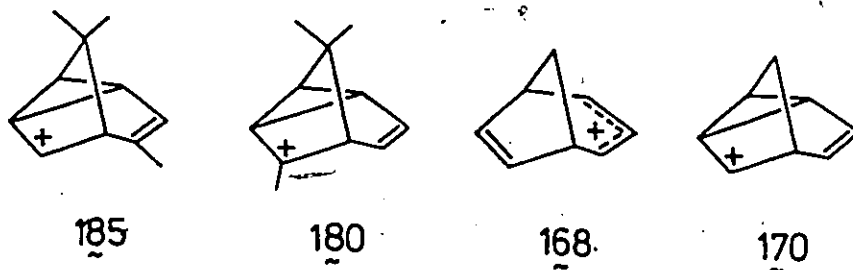
$\Delta\delta$  Values for the Protons H<sub>3</sub>, H<sub>4</sub>, H<sub>6</sub> and H<sub>7</sub> in Some  
Bicyclo[3.2.1]octadienyl Systems<sup>a,b</sup>

Systems	$\Delta\delta$ (ppm)			
	H <sub>3</sub>	H <sub>4</sub>	H <sub>6</sub>	H <sub>7</sub>
<u>169</u> + <u>173</u>	1.06	1.73	0.6	0.43
<u>101</u> + <u>100</u>	1.07	1.66	0.59	0.48
<u>158</u> + <u>154</u>	2.71	3.62	1.13	1.37

<sup>a</sup>  $\Delta\delta = \delta_{\text{cation}}(\text{FSO}_3\text{H}) - \delta_{\text{neutral}}(\text{CDCl}_3)$

<sup>b</sup> Positive sign indicates downfield shift for all the protons in question.

NMR spectra of cations such as 154 are typical of allylic cations. This indicates that there is no obvious contribution from the cyclopropyl-carbinyl cation such as 185. <sup>1</sup>H NMR spectra of related cations such as 170 and 180 are in fact distinctly different from those of cations such as 154. Further, the MINDO/3 calculations of Jefford and coworkers for the minimum energy reaction paths in various isomeric C<sub>8</sub>H<sub>9</sub> cations show two distinct energy minima corresponding to the cations 168 and 170.<sup>226</sup>

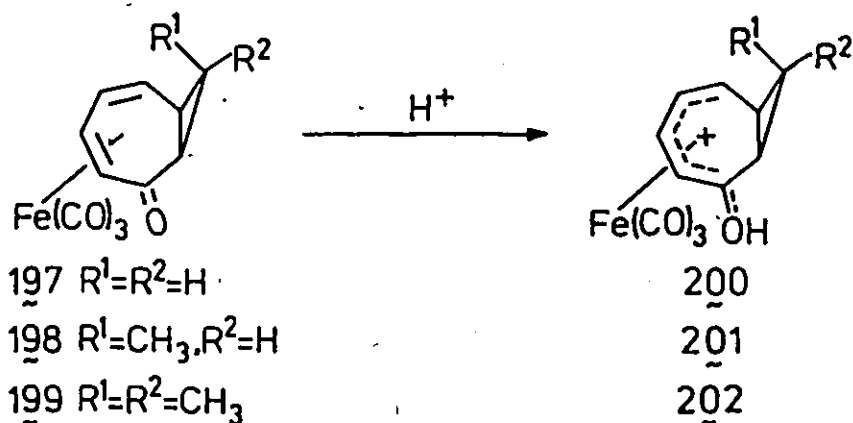


MINDO/3 calculations of Jefford and coworkers rule out any interaction of the C<sub>6</sub>-C<sub>7</sub> double bond with the allylic fragment in the bicyclo[3.2.1]octadienyl cations.<sup>226</sup> Such a conclusion was also reached by Schleyer and coworkers, using semiempirical MNDO and ab initio STO-3G calculations.<sup>19</sup> NMR spectroscopy is of limited value with regard to the structural studies of these systems. An x-ray study on the structure of the cation 100 and comparison with that of the neutral ketone 101 would be helpful in deciding whether transannular interactions occur in these systems.

CHAPTER 6

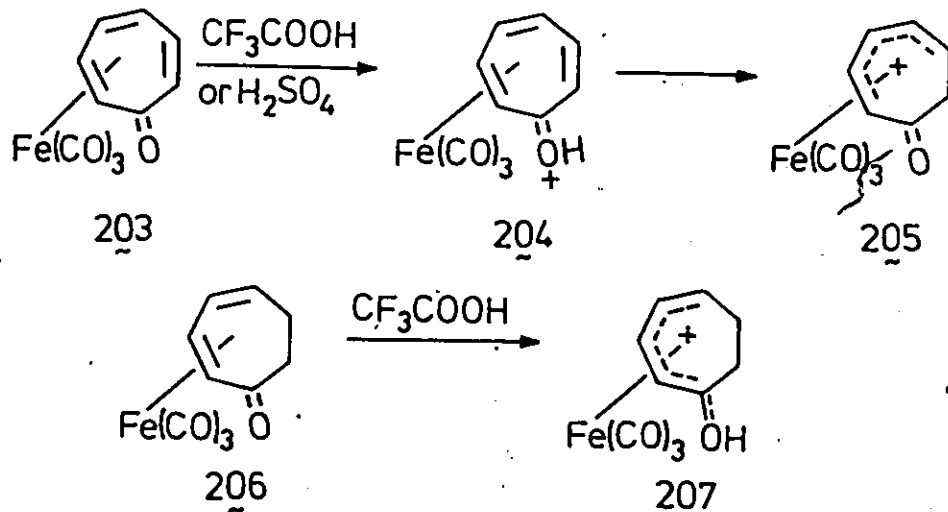
PROTONATION OF HOMOTROPONEIRONTRICARBONYL AND CYCLOOCTATRIENONEIRON-  
TRICARBONYL COMPLEXES

An irontricarboxyl moiety functions as a four electron acceptor. Complexation of an irontricarboxyl group with a homotropylium cation converts it into a classical bicyclo[5.1.0]octadienyl cation. This approach to examining the properties of the classical structure was used by Winstein and coworkers in their early studies of the homotropylium cations.<sup>1,2</sup> Recent work on the structure of the iron complex 28, reported in Chapter 2, fully confirms this view. In this chapter the protonation studies on the iron tricarboxyl complexes of the 2,3-homotropones 197, 198 and 199 are described.



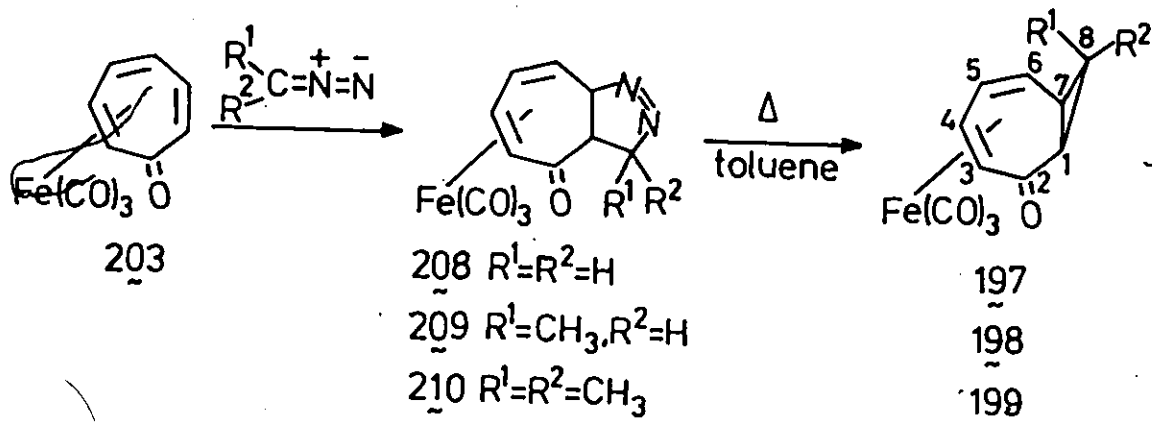
Considerable work has been done regarding the protonation of troponeirontricarboxyl 203 and its derivatives.<sup>232-235</sup> The regio and

stereochemistry of the protonation have not been defined unambiguously. However, the major processes that occur in these protonations have been shown to be an initial kinetically controlled protonation on the oxygen atom of the ketonic carbonyl and subsequent isomerization of the oxygen-protonated species 204 to the thermodynamically more stable carbon-protonated species 205.<sup>235</sup> Protonation of cycloheptadienoneirontricarbonyl 206, on the other hand, occurs solely on oxygen to give 207.



### 1. Preparation of Homotroponeirontricarbonyl Complexes

The homotropone complexes 197, 198 and 199 were prepared by the method of Franck-Neumann and Martina.<sup>236</sup>





The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data for these complexes, (Tables 25 and 26 respectively) are in agreement with some of those reported in literature.<sup>236-239</sup> Both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR signal assignments were based on those reported for the parent homotropone complex 197, as well as on decoupling experiments.<sup>237,238</sup>

## 2. Protonation in $\text{CF}_3\text{COOH}$

Dissolution of the homotroponeirontricarbonyls 197, 198 and 199 in  $\text{CF}_3\text{COOH}$  at  $0^\circ\text{C}$  gave red colored solutions which were examined at ambient temperatures by NMR spectroscopy. The  $^1\text{H}$  NMR chemical shift data for the solutions obtained are reported in Table 27.<sup>240</sup> The signal assignments were made by double irradiation methods. As can be seen from Tables 25 and 27, the resonances for the ring protons in these complexes are shifted downfield in  $\text{CF}_3\text{COOH}$  solutions relative to those in  $\text{CDCl}_3$  (Figure 20). This is suggestive of protonation on the oxygen atom of the (ketone) carbonyl group. On the other hand, the coupling constants observed for the resulting cations do not vary significantly from those of the precursors. Presumably no major geometry changes accompany this protonation process. The shifts observed for the proton resonances, on protonation of these complexes are similar to those previously reported for the oxygen protonation of troponeirontricarbonyl 203 and cycloheptadienoneirontricarbonyl 206.<sup>233,235</sup> This reinforces the conclusion that in  $\text{CF}_3\text{COOH}$  the complexes 197, 198 and 199 are protonated on the carbonyl oxygen to form the cations 200, 201 and 202 respectively. No signals were observed in the region from  $\delta$  0 to  $\delta$  -40 indicating the absence of metal hydride protons in these cations.

Table 25  
<sup>1</sup>H NMR Data for the Homotroponeirontricarboxyls 197, 198 and 199

Complex	Chemical Shifts (ppm) <sup>a,b,c</sup>							
	H <sub>1</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	H <sub>8exo</sub>	H <sub>8endo</sub>
197	1.53(m) J=6,9Hz	3.10(d) J=7.5Hz	5.74(m) J=7.5,3Hz	5.3(dd) J=7.5Hz	3.6(t) J=7.5Hz	2.0(m) J=7.5Hz	1.30(m) J=3,4.5Hz	1.00(m) J=6,4.5Hz
198	1.39(m) J=6Hz	3.13(dd) J=8,1Hz	5.7(m) J=6,2.5Hz	5.39(dd) J=8,7.5Hz	3.66(m) J=7.5,2Hz	1.6(m) J=6,6,9Hz	1.39(m) J=6Hz	(0.96)(d) J=6Hz
199	1.5(d) J=8Hz	3.2(d) J=6Hz	5.83(m) J=6,2Hz	5.6(m) J=6,1Hz	3.5(m) J=8,2Hz	1.89(t) J=8Hz	(1.1)(s) J=6Hz	(1.03)(s)

<sup>a</sup> In CDCl<sub>3</sub> with CHCl<sub>3</sub> as internal reference (δ 7.27).

<sup>b</sup> Chemical shifts in parentheses represent methyl resonances.

<sup>c</sup> s:singlet; d:doublet; t:triplet; dd:doublet of doublets; m:multiplet.

Table 26

<sup>13</sup>C NMR Data for Homotroponeirontricarboxyls 197, 198 and 199

Complex	Chemical Shifts (ppm) <sup>a</sup>					
	CO	C <sub>2</sub>	C <sub>4</sub> ,C <sub>5</sub>	C <sub>3</sub> ,C <sub>6</sub>	C <sub>1</sub> ,C <sub>7</sub> ,C <sub>8</sub>	CH <sub>3</sub>
<u>197</u>	208.8	206.0	92.2	63.5	29.3	
			87.2	62.1	27.6	
					26.6	
<u>198</u>	209.0	205.7	92.0	64.3	39.2	19.6 (endo)
			87.2	62.8	36.8	
					35.1	
<u>199</u>	209.3	205.3	90.5	66.0	41.5	30.4 (exo)
				64.6	39.8	16.7 (endo)
					38.9	

<sup>a</sup> In CDCl<sub>3</sub> with TMS internal standard (δ 0).

Table 27  
<sup>1</sup>H NMR Data for Cations 200, 201 and 202

Cations	Chemical Shifts (ppm) <sup>a,b</sup>							
	H <sub>1</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7</sub>	H <sub>8exo</sub>	H <sub>8endo</sub>
200	1.90(m)	3.4(d) J <sub>3,4</sub> =6Hz	6.69(t) J <sub>4,5</sub> =6Hz	5.53(dd) J <sub>5,6</sub> =9Hz	3.80(t) J <sub>6,7</sub> =9Hz	2.84(b,t) J <sub>7,1</sub> =7.5Hz	1.90(m)	1.90(m)
201	1.79(m)	3.46(d) J <sub>3,4</sub> =7Hz	6.69(m) J <sub>4,5</sub> =6Hz	5.59(dd) J <sub>5,6</sub> =8Hz	3.97(b,t) J <sub>6,7</sub> =8Hz	2.72(dd)	2.27(m)	(0.86)(d) J <sub>CH<sub>3</sub>,H</sub> =6Hz
202	2.00(d)	3.56(d) J <sub>3,4</sub> =7Hz	6.85(t) J <sub>4,5</sub> =7Hz	5.86(dd) J <sub>5,6</sub> =9Hz	3.84(t) J <sub>6,7</sub> =9Hz	2.99(t) J <sub>7,1</sub> =9Hz	(1.22)(s)	(1.06)(s)

<sup>a</sup> In CF<sub>3</sub>COOH with (CH<sub>3</sub>)<sub>4</sub>NBF<sub>4</sub><sup>+</sup> as internal reference (δ 3.1).

<sup>b</sup> Numbers in parentheses represent methyl group resonances.

<sup>c</sup> s:singlet; d:doublet; t:triplet; m:multiplet; b:broad; dd:doublet of doublet.

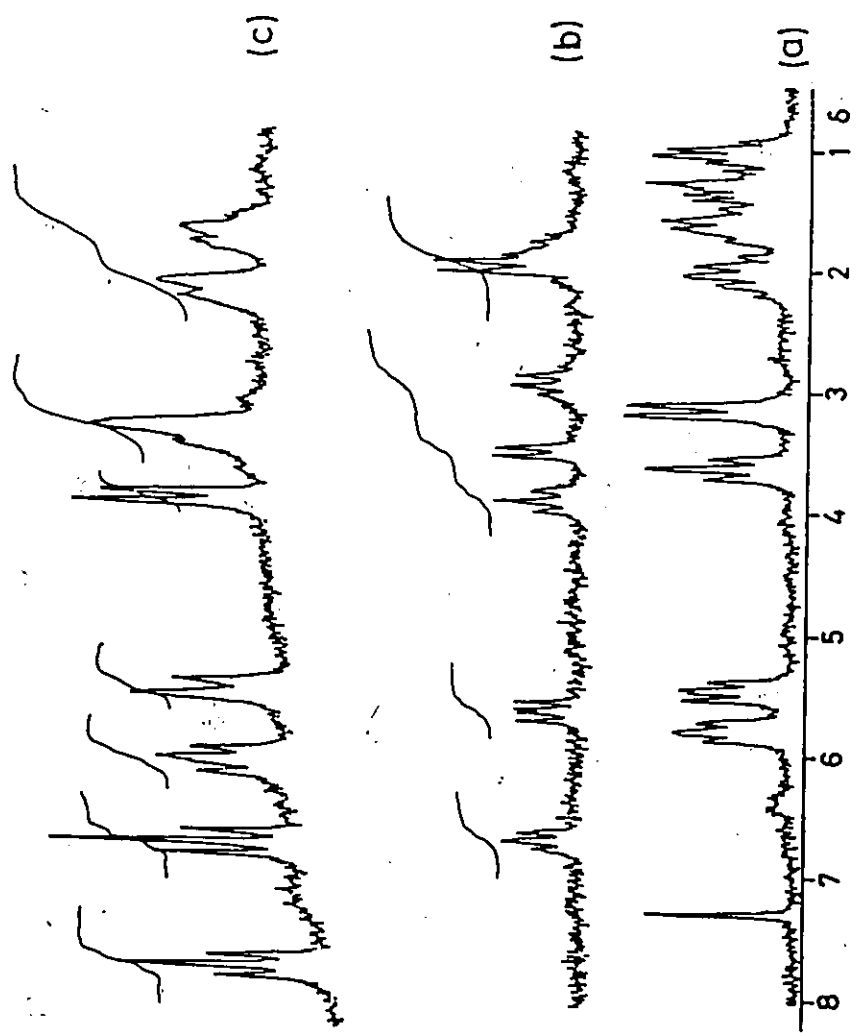
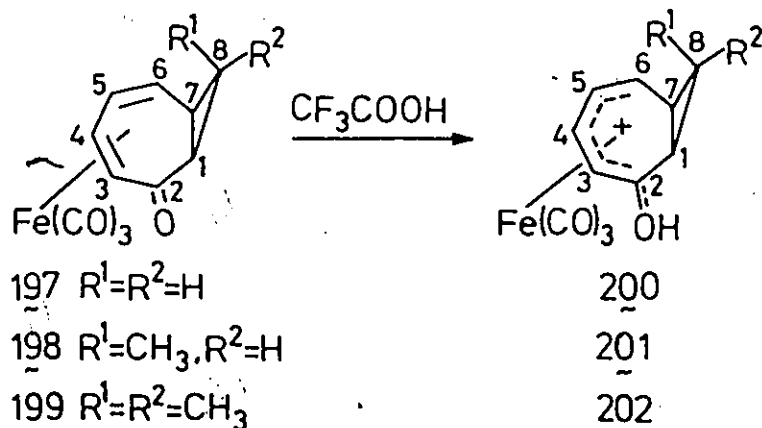


Figure 20. <sup>1</sup>H NMR spectrum of 2,3-homotroponeirontricarboxyl 197 in different media. (a) in CDCl<sub>3</sub>, (b) in CF<sub>3</sub>COOH and (c) in H<sub>2</sub>SO<sub>4</sub>.



The  $^{13}C$  NMR spectra (Table 28) of solutions of these complexes in  $CF_3COOH$  are also in accord with the oxygen-protonated structures.

Signal assignments were made on the basis of comparison of these spectra with that of the oxygen-protonated troponeirontricarbonyl 204.<sup>235</sup> It can be seen that the resonances of the coordinated carbons in the homotroponeirontricarbonyls are shifted downfield on protonation, similar to those reported for 204.

The cyclopropyl carbons also experience considerable deshielding on protonation. This would seem to suggest that delocalization of some of the positive charge to the cyclopropyl carbons by means of cyclopropylcarbinyl-type interaction occurs in these cations. This can be seen by comparing  $^{13}C$  NMR data in Table 29 for neutral (211) and protonated cyclopropyl methyl ketone (212). It is also interesting to note that the changes in chemical shifts observed for the carbons  $C_6$  and  $C_7$  on protonation of troponeirontricarbonyl 203 have been reported to resemble those observed for the protonation of  $\alpha, \beta$ -unsaturated ketones.<sup>235</sup> However, it is not easy to come to a conclusion regarding the nature of delocalization on the basis of NMR evidence alone. The bicyclo[5.1.0]-octadienylirontricarbonyl cation 28 is a case in point. The  $^{13}C$

Table 28

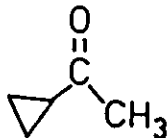
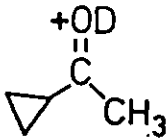
<sup>13</sup>C NMR Data for Cations 200, 201 and 202

Complex	Chemical Shifts (ppm) <sup>a</sup>					
	C <sub>0</sub>	C <sub>2</sub>	C <sub>4</sub> ,C <sub>5</sub>	C <sub>3</sub> ,C <sub>6</sub>	C <sub>1</sub> ,C <sub>7</sub> ,C <sub>8</sub>	CH <sub>3</sub>
<u>200</u>	205.9	b	90.3	66.8	40.7 39.2	
<u>201</u>	205.1	b	95.4 91.4	70.3 69.6	55.6 50.7 43.9	19.0 (endo)
<u>202</u>	204.6	211.5	94.4 92.8	72.0 66.8	64.2 56.4 42.2	15.9 (endo) 30.9 (exo)

<sup>a</sup> In CF<sub>3</sub>COOH with CDCl<sub>3</sub> internal standard (δ 76.95).

<sup>b</sup> Signals not observed due to low intensity.

Table 29  
<sup>13</sup>C NMR Data for Neutral and Protonated  
 Cyclopropylmethyl Ketone 211 and 212

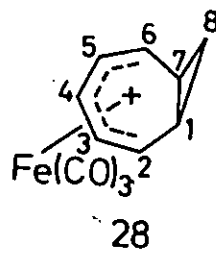
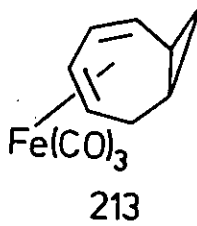
Compound	Chemical Shifts (ppm) <sup>a</sup>			
	CO	CH	CH <sub>2</sub>	CH <sub>3</sub>
 211	208.5	21.0	10.3	29.7
 212	238.7	28.5	28.5	25.9
Δδ <sup>b</sup>	30.2	7.5	18.2	-3.8

<sup>a</sup> In CDCl<sub>3</sub> and D<sub>2</sub>SO<sub>4</sub> for 211 and 212 respectively, with CDCl<sub>3</sub> internal reference (δ 76.95).

<sup>b</sup> Δδ = δ<sub>D<sub>2</sub>SO<sub>4</sub></sub> - δ<sub>CDCl<sub>3</sub></sub>; negative sign indicates an upfield shift.



chemical shift data for the neutral complex 213 have been obtained by Aumann and Knecht.<sup>241</sup> Olah and coworkers have measured the <sup>13</sup>C chemical shifts for the cation 28.<sup>242</sup> The chemical shifts reported for the cyclopropyl carbons in 213 and 28 are shown in the diagrams below. According to Olah the cyclopropyl carbons in 28 are substantially deshielded relative to other neutral cyclopropyl carbons, due to charge delocalization into the cyclopropane ring.<sup>242</sup> The normal cyclopropyl bond lengths obtained from the crystallographic studies on 28 (Chapter 1) do not seem to support this view.



<sup>13</sup> C Chemical Shifts (δ) for cyclopropyl carbons	18.0; 14.6, 14.0	35.8(C <sub>1</sub> ,C <sub>7</sub> ) 47.0(C <sub>8</sub> )
--	------------------	--

The CF<sub>3</sub>COOH solutions of these cations were stable at ambient temperatures and no thermal isomerization could be detected. Heating the NMR sample of 202 at 60°C for 30 minutes produced no change in the NMR spectrum. This is in contrast with the oxygen-protonated troponeiron-tricarbonyl complex 204 which is reported to isomerize to the carbon-protonated complex 205 at 0°C in CF<sub>3</sub>COOH.<sup>235</sup> The starting homotropone-iron-tricarbonyl complexes could be recovered by neutralization of CF<sub>3</sub>COOH. When protonation of the complexes 197, 198 and 199 was carried out in CF<sub>3</sub>COOD no deuterium incorporation (other than on oxygen) could be detected.

### 3. Protonation in H<sub>2</sub>SO<sub>4</sub>

The protonation studies were extended to other acid media. In 96% H<sub>2</sub>SO<sub>4</sub>, the oxygen protonated cations 200, 201 and 202 were formed initially. These cations could be observed by <sup>1</sup>H NMR spectroscopy at subambient temperatures. Warming these solutions to ambient temperatures resulted in the formation of new cations 214, 215 and 216 respectively. The half-life for the conversion of 200 to 214 was ca. 3 minutes at -10°C, for 201 to 215 ca. 4 minutes at 5°C and for 202 to 216 ca. 3 minutes at 34°C.

The <sup>1</sup>H NMR data for the cations 214, 215 and 216 are reported in Table 30 (Figure 20). Signal assignments were made by double irradiation methods. In all these cases an additional proton signal in the upfield region was observed. Further, the <sup>1</sup>H NMR data for these cations are somewhat similar to those reported for the carbon-protonated troponeirontricarbonyl complex 205.<sup>232,233</sup> On the basis of these observations the cyclooctadienyl-irontricarbonyl structures 214, 215 and 216 were assigned to these cations. These cations can be considered to result from the protonation at C<sub>1</sub> of the starting complexes. No signal was observed in the region between δ 0 and δ -40. This suggests that the metal hydride (Fe-H) group is absent in these final products.

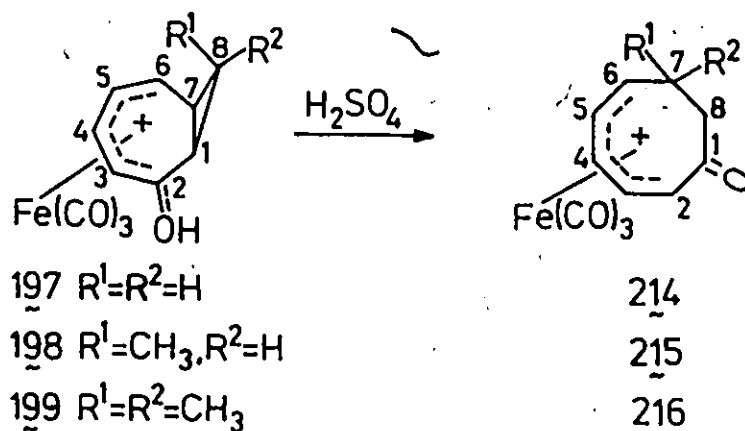


Table 30  
<sup>1</sup>H NMR Data for Cations 214, 215, 216 and 218

Cation	Chemical Shifts (ppm) <sup>a,b</sup>										
	H <sub>2</sub>	H <sub>3</sub>	H <sub>4</sub>	H <sub>5</sub>	H <sub>6</sub>	H <sub>7exo</sub>	H <sub>7endo</sub>	H <sub>8exo</sub>	H <sub>8endo</sub>		
214	4.03(d) <sup>d</sup> J <sub>2,3</sub> =7.5Hz	6.87(t) J <sub>3,4</sub> =7.5Hz	7.87(t) J <sub>4,5</sub> =8Hz	6.20(dd) J <sub>5,6</sub> =11Hz	5.60(bd) J <sub>6,7</sub> =8Hz	3.43(m)	3.43(m) <sup>d</sup>	2.28(bd) <sup>d</sup>	1.82(bd) <sup>c,d</sup>		
215	3.96(d) J <sub>2,3</sub> =7.5Hz	6.92(t) J <sub>3,4</sub> =7.5Hz	7.86(t) J <sub>4,5</sub> =8Hz	6.23(t) J <sub>5,6</sub> =10.5Hz	5.56(bt)	3.69(m)	(1.72)(d) J <sub>CH<sub>3</sub>,H</sub> =6Hz	2.16(m)	2.16(m) <sup>c</sup>		
218	4.10(s) <sup>c</sup>	(2.82)(s)	7.79(d) J <sub>4,5</sub> =7.5Hz	6.20(bt) J <sub>5,6</sub> =11Hz	5.68(hd)	3.53(m)	3.53(m) <sup>c</sup>	2.36(m) <sup>c</sup>	1.89(m) <sup>c</sup>		
216	4.07(d) J <sub>2,3</sub> =8Hz	6.89(t) J <sub>3,4</sub> =7.5Hz	7.83(t) J <sub>4,5</sub> =7.5Hz	6.07(dd) J <sub>5,6</sub> =11Hz	5.58(d)	(1.66)(s)	(1.46)(s)	2.00(m)	2.00(m) <sup>c</sup>		

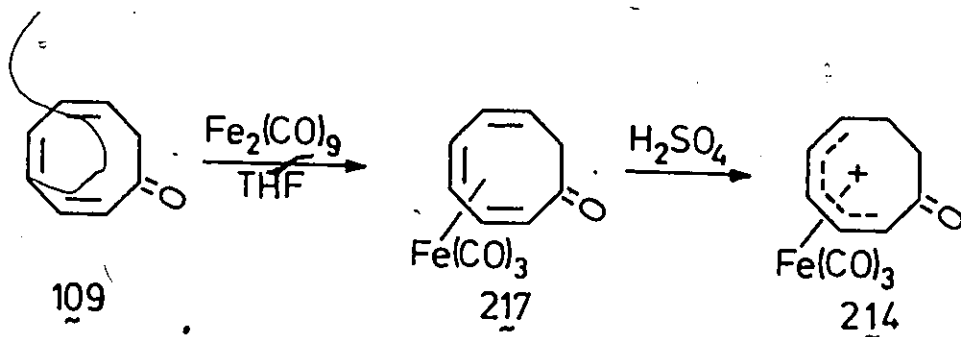
<sup>a</sup> In H<sub>2</sub>SO<sub>4</sub> with (CH<sub>3</sub>)<sub>4</sub>NBF<sub>4</sub><sup>+</sup> internal reference (δ 3.1).

<sup>b</sup> s:singlet; d:doublet; t:triplet; m:multiplet; b:broad; dd:doublet of doublet.

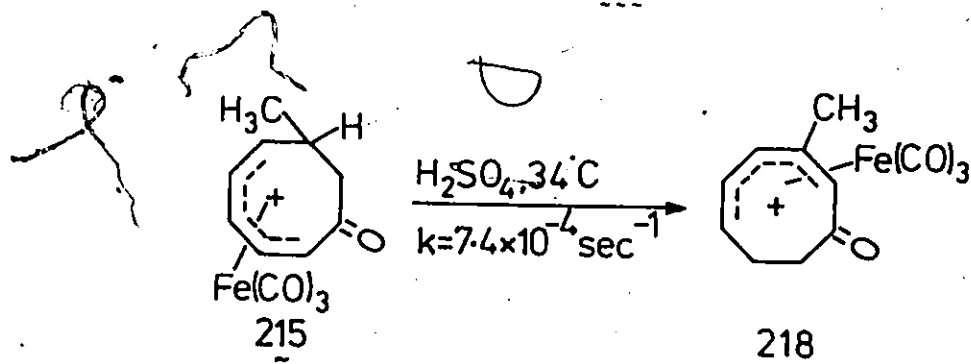
<sup>c</sup> Signals absent on protonation in D<sub>2</sub>SO<sub>4</sub>.

<sup>d</sup> Signals absent in the generation of 214 from 217 in D<sub>2</sub>SO<sub>4</sub>.

Further support for the structures of these cations came from the protonation of cyclooctatrienoneirontricarbonyl 217. The complex 217 was prepared by the reaction of cyclooctatrienone 109 with  $\text{Fe}_2(\text{CO})_9$  in THF. Protonation of 217 in  $\text{H}_2\text{SO}_4$  resulted in the formation of 214, as shown by the  $^1\text{H}$  NMR spectral identity of this cation with that of the cation generated from the protonation of homotroponeirontricarbonyl 197 at ambient temperatures (Figures 20 and 21).



Further rearrangement was observed for the cation 215 at ambient temperatures and a new cation 218 was formed. The rate constant for this process was  $7.4 \times 10^{-4} \text{ sec}^{-1}$  ( $\Delta G^\ddagger = 22.4 \text{ kcal/mole}$ ) at  $34^\circ\text{C}$ . Based on its  $^1\text{H}$  NMR spectrum the structure 218 was assigned to this cation.



Fluxional isomerization of the type mentioned above has been

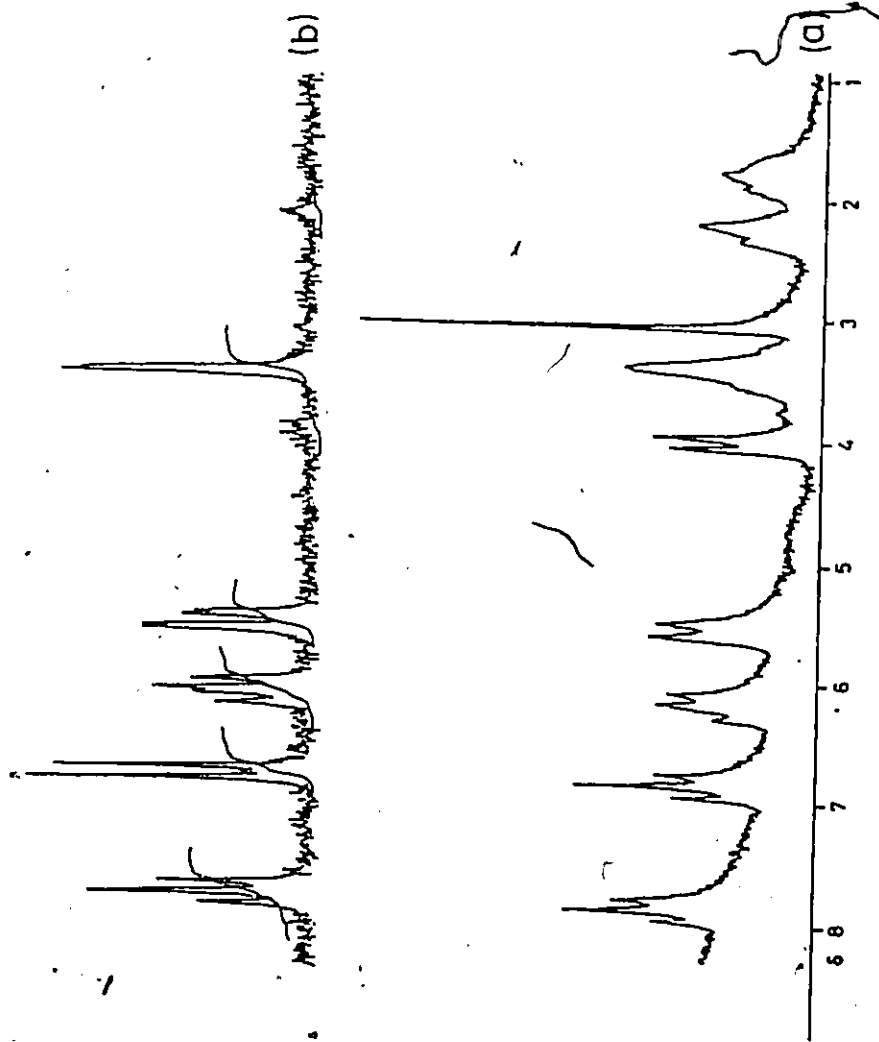
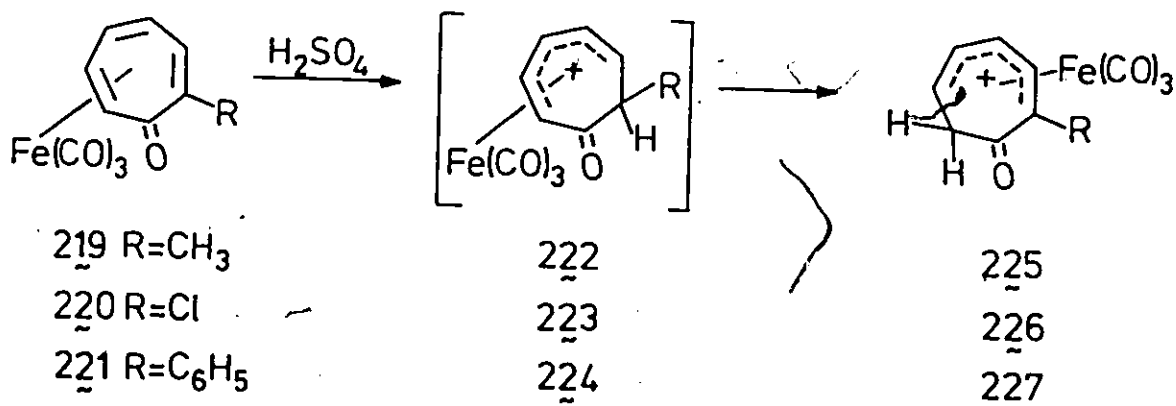
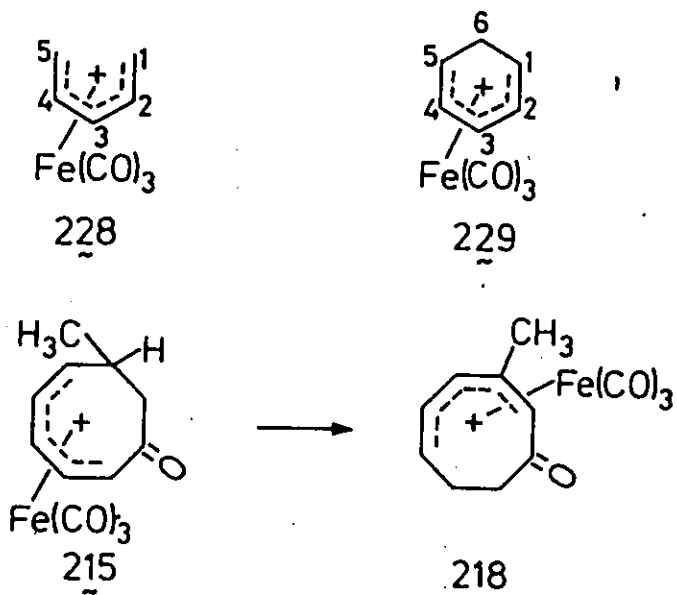


Figure 21  $^1\text{H}$  NMR spectrum of cyclooctatrienoneirontricarbonyl 217 in protic and deuterated acids. (a) in  $\text{H}_2\text{SO}_4$  and (b) in  $\text{D}_2\text{SO}_4$ .

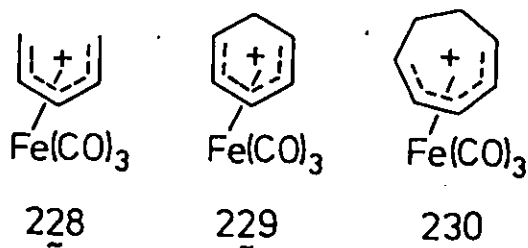
observed in the case of the carbon-protonated 7-substituted troponeirontricarboxyl cations 222-224.<sup>234</sup> Protonation of the 7-substituted troponeirontricarboxyls 219-221 resulted in the formation of the 2-substituted cations 225-227 presumably via the intermediacy of cations 222-224 respectively.<sup>234</sup>



Extended Hückel (EH) and INDO calculations have been reported in the literature for pentadienylirontricarboxyl cation 228 and cyclohexadienylirontricarboxyl cation 229.<sup>243-245</sup> These calculations indicate that there is more positive charge at carbons 2 and 4 than at carbons 3, 1 and 5. The rearrangement of cation 215 to the more stable 218 could be anticipated on this basis.



The carbon-protonated cations 214, 216 and 218 were also examined by  $^{13}\text{C}$  NMR spectroscopy. The  $^{13}\text{C}$  NMR data for the carbon protonated troponeirontricarbonyl 205, which has not been reported before, has been obtained for the sake of comparison. These data are summarized in Table 31. Partial signal assignments were based on selective proton decoupling, deuteration studies to be discussed later and comparison with the reported data for the model systems such as 228, 229 and 230.<sup>245,246</sup>



The  $^{13}\text{C}$  chemical shifts<sup>1</sup> reported in Table 31 for 205 are typical for pentadienylirontricarbonyl cations. The resonances of the two terminal carbons of the coordinated pentadienyl cations occur upfield relative to those of the three internal carbons.<sup>244,245</sup> The  $^{13}\text{C}$  chemical shifts for the carbon-protonated homotroponeirontricarbonyl cations 214, 218 and 216 are somewhat different. For these cations, the resonance of one of the terminal carbons ( $\text{C}_6$ ) in the pentadienyl unit is shifted downfield by about 20 ppm, while that of the other ( $\text{C}_2$ ) is shifted upfield by a similar magnitude, relative to 205. This would seem to suggest that, in these cases, the metal is possibly unsymmetrically bound to the pentadienyl unit, with the  $\text{C}_2$ -Fe linkage having more  $\sigma$  character. Further the resonance of the ketonic carbon ( $\text{C}_7$ ) is shifted farther downfield relative to that of 205. It is possible that some degree of further proton transfer to the (ketone) carbonyl oxygen occurs in 214, 218 and 216, although the proton chemical shifts do not seem

Table 31

<sup>13</sup>C NMR Data for Cations 205, 214, 218 and 216

Cation	Solvent Reference	Chemical Shifts (ppm)					
		CO	C <sub>1</sub>	C <sub>3</sub> , C <sub>4</sub> , C <sub>5</sub> , C <sub>6</sub>	C <sub>2</sub>	C <sub>7</sub> , C <sub>8</sub>	CH <sub>3</sub>
205 <sup>c</sup>	H <sub>2</sub> SO <sub>4</sub>	197.3	201.3	108.8 103.8 102.5 78.2	75.7 <sup>a</sup>	33.6 <sup>a</sup>	
214 <sup>c</sup>	H <sub>2</sub> SO <sub>4</sub>	192.4	236.3	111.1 105.7 100.8 99.9	54.5 <sup>a</sup>	44.1 <sup>a</sup> 32.7 <sup>a</sup>	
218 <sup>d</sup>	D <sub>2</sub> SO <sub>4</sub>	196.5	235.0	127.5 108.5 98.4 97.3	55.3 <sup>a</sup>	42.8 <sup>a</sup> 32.9 <sup>a</sup>	26.4 (endo)
216 <sup>b,c</sup>	H <sub>2</sub> SO <sub>4</sub>	192.4	233.5	111.9 109.2 106.1 97.5	55.7	58.1 43.4 <sup>a</sup>	40.5 (exo) 27.4 (endo)

<sup>a</sup> In D<sub>2</sub>SO<sub>4</sub>, observed as broad signals due to coupling with directly bonded deuterium.

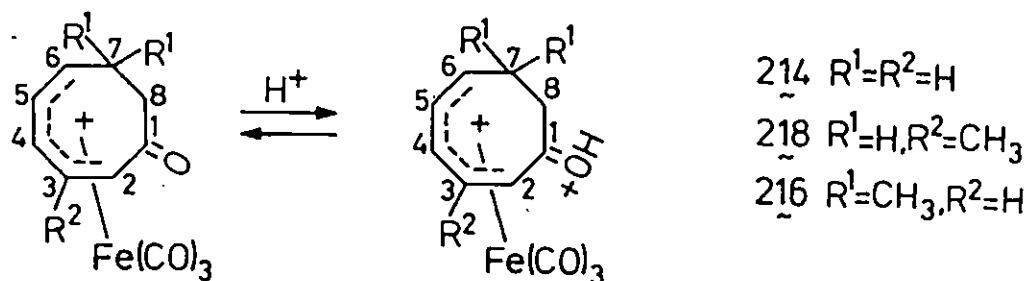
<sup>b</sup> Chemical shifts varied randomly in D<sub>2</sub>SO<sub>4</sub>.

<sup>c</sup> Reference external TMS (δ 0).

<sup>d</sup> Reference internal CDCl<sub>3</sub> (δ 76.95).



to reflect this. Conformational differences, if any, between the seven- and eight-membered rings may also play a part.



The  $^{13}C$  resonances for the carbonyl ligands in complexes 214, 218 and 216 were much broader than that in 205. This would indicate that the site exchange process which averages the resonances of the CO ligands is slow in the former set of cations.<sup>239,245</sup> It is not certain as to why this averaging process should be slow in these cations. It is possible that steric and electronic factors may play a role.<sup>239</sup> Further structural studies are necessary to account for the spectral differences of the carbon-protonated homotroponeirontricarbonyl complexes and other pentadienylirontricarbonyl cations.

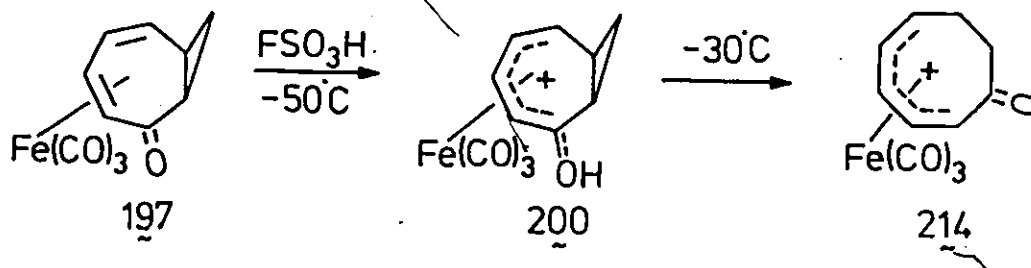
However, one can conclude that initial protonation of the homotroponeirontricarbonyl complexes occurs on the oxygen. The oxygen-protonated species then form the more stable carbon-protonated species. This proton is attached to the cyclopropyl carbon adjacent to the carbonyl group.

#### 4. Protonation in $FSO_3H$

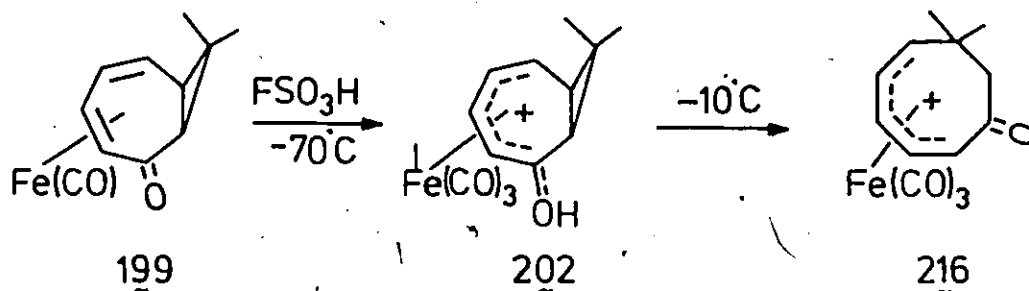
$FSO_3H$  is a very strong acid, suitable for low temperature studies. Protonation of some of the metal complexes were carried out in this medium at low temperatures with the hope of examining the processes unobservable in  $H_2SO_4$ .  $^1H$  NMR observations were made at a range of

temperatures. The processes observed were similar to those occurring in  $H_2SO_4$  medium, as revealed by comparison of the  $^1H$  NMR spectra in both acids. Some small changes in chemical shifts for the various protons of the cationic species were observed in  $FSO_3H$ , due to the change in acidity of the medium. The thermal stability of these carbon-protonated complexes at ambient temperatures was less in  $FSO_3H$  than in  $H_2SO_4$ .

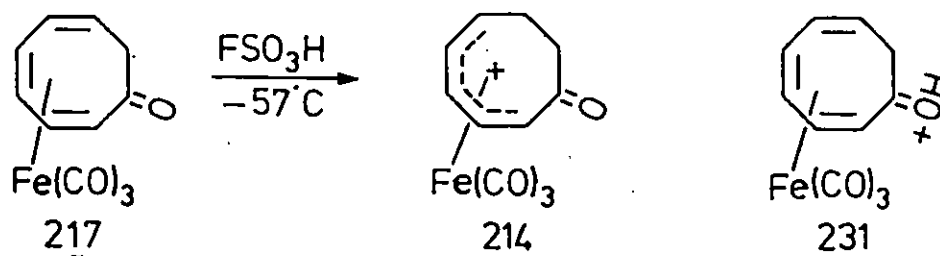
Protonation of 197 in  $FSO_3H$  at  $-78^\circ C$  and  $^1H$  NMR observation of the resulting cation at  $-50^\circ C$  showed that the oxygen-protonated cation 200 was formed in solution. Above  $-30^\circ C$  this cation isomerized to the carbon-protonated cation 214.



Protonation of 199 in  $FSO_3H$  at  $-78^\circ C$  and  $^1H$  NMR observation of the red colored solution at  $-70^\circ C$  showed the clean formation of the oxygen-protonated cation 202. This cation was stable up to  $-10^\circ C$ . Above this temperature formation of 216 along with some decomposition was evident.

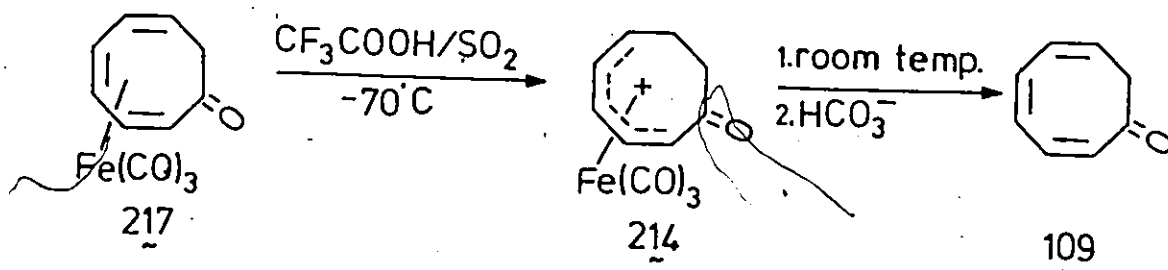


The  $^1\text{H}$  NMR spectrum of a solution of 217 in  $\text{FSO}_3\text{H}$  at  $-57^\circ\text{C}$  showed only the carbon-protonated cation 214 to be present. The anticipated oxygen-protonated species 231 was not present to any detectable extent.



#### 5. Protonation of Cyclooctatrienoneirontricarbonyl 217 in Weaker Acids

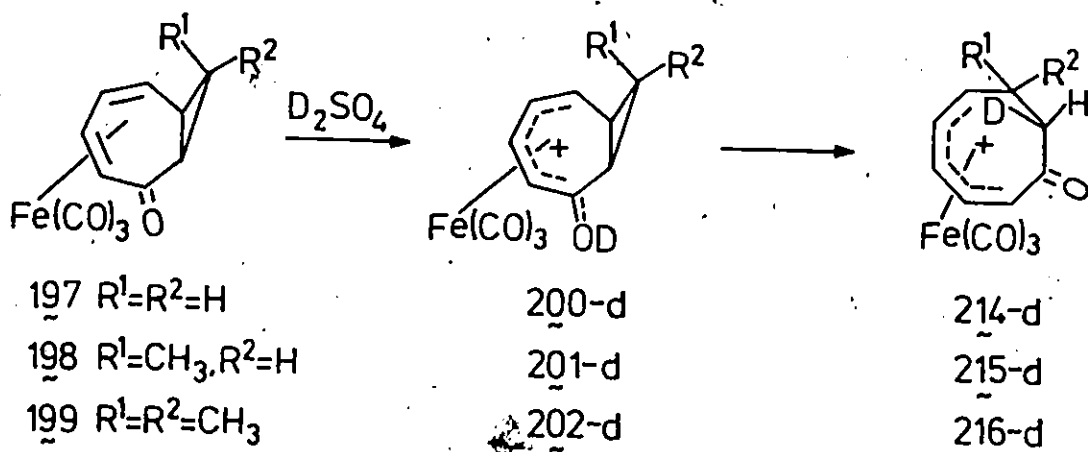
Attempts were made to observe the oxygen-protonated cyclooctatrienoneirontricarbonyl cation 231, by protonation of 217 with weaker acids. The  $^1\text{H}$  NMR spectrum of a solution of 217 in a mixture of  $\text{SO}_2$  and  $\text{CF}_3\text{COOH}$  at  $-70^\circ\text{C}$  was similar to that of 214 in  $\text{H}_2\text{SO}_4$ . As in the case of  $\text{FSO}_3\text{H}$ , some changes in chemical shifts for the protons were observed due to the change in the medium. 214 was stable in this medium up to  $-15^\circ\text{C}$ . Above this temperature and especially at ambient temperatures, decomposition occurred with the production of some solid material. It is not clear as to why a weaker acid like  $\text{CF}_3\text{COOH}$  should cause decomposition of the complex. Cyclooctatrienone 109 was obtained upon neutralizing the resulting solution. This behavior stands in contrast to that of homotroponeirontricarbonyl complexes.



Dissolution of 217 in a solution of  $\text{CF}_3\text{COOH}$  in  $\text{CDCl}_3$  and  $^1\text{H}$  NMR observation of the resulting mixture did not reveal any significant change occurring in this medium. Presumably the acid is not strong enough to cause any protonation.

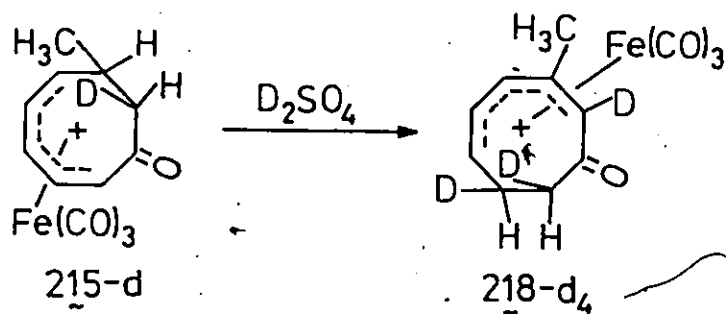
#### 6. Deuteration Studies

To confirm the position of the added proton in the carbon protonated metal complexes, similar reactions were carried out in deuterated acids. In  $\text{D}_2\text{SO}_4$ , 197, 198 and 199 initially formed the less stable oxygen-deuterated analogs of 200, 201 and 202 which subsequently rearranged to the carbon-deuterated species 214-d, 215-d and 216-d.



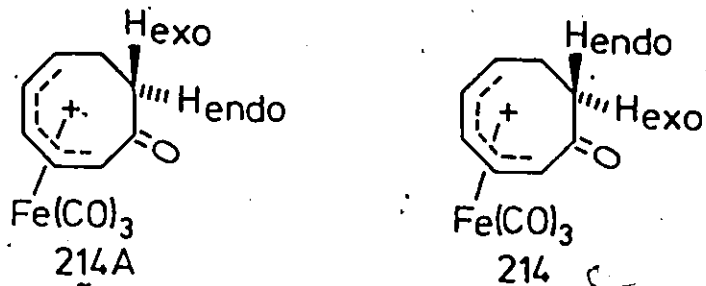
For the carbon-deuterated cation 214-d the farthest upfield signal corresponding to the  $\text{H}_{\text{endo}}$  resonance was absent in the  $^1\text{H}$  NMR spectrum. This indicates that the incorporated deuterium occupies the

endo position on  $C_8$ .<sup>\*</sup> Cation 216-d underwent no further change. 215-d rearranged to form its fluxional isomer. The rate constant for this process was  $7.1 \times 10^{-4} \text{ sec}^{-1}$  at  $34^\circ\text{C}$  ( $\Delta G^\ddagger = 22.4 \text{ kcal/mole}$ ). In this process four deuteriums were incorporated in the final cation 218-d<sub>4</sub>. These were found to be located at  $C_2$ ,  $C_7$  and  $C_8$  (both endo and exo). It is possible that this deuterium exchange accompanies the fluxional isomerization process.

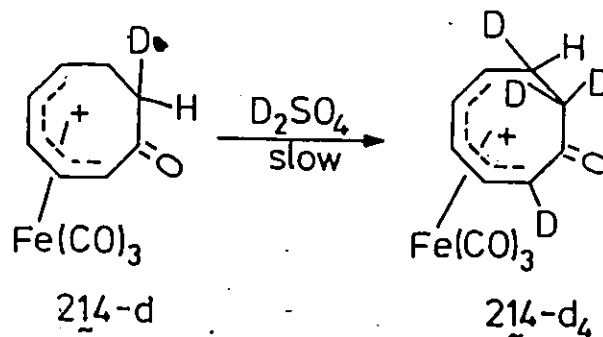


Cation 214-d underwent deuterium exchange at a much slower rate in  $\text{D}_2\text{SO}_4$  than 215-d. Slow deuterium incorporation at  $C_2$ ,  $C_7$  and  $C_8$  was evident from the reduction in intensities of the signals for the corresponding proton resonances. From the  $^1\text{H}$  NMR spectra, the approximate

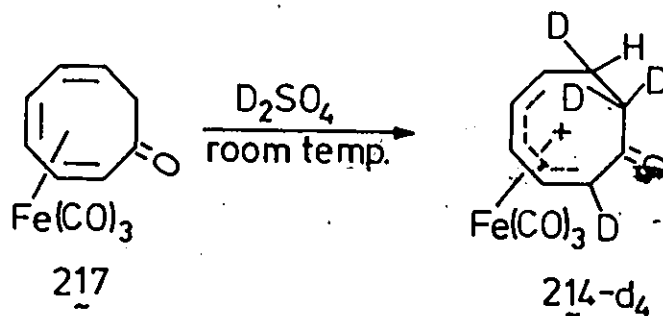
\* In the metal complex chemistry, the endo and exo designations have been commonly used to refer to the stereochemistry on the same side and the opposite side respectively, of the  $\text{Fe}(\text{CO})_3$  group (eg., 214A). However, this terminology is opposite to that followed for the homotropylium cations. For the sake of consistency, the same stereochemical designation as that used for the homotropylium cations is maintained here (eg., 214).



value of the half-life for this exchange process at room temperature was estimated to be 24 hours. Eventually cation 214-d<sub>4</sub> was formed with the incorporation of four deuteriums at C<sub>2</sub>, C<sub>7</sub> and C<sub>8</sub> (both endo and exo).

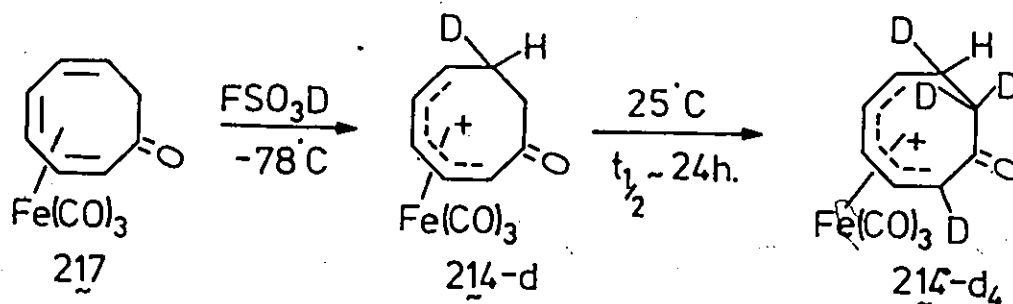


In contrast to the deuteration of the homotropone complex 197, deuterium incorporation occurred much faster when cyclooctatrienoneiron-tricarbonyl 217 was dissolved in D<sub>2</sub>SO<sub>4</sub>. <sup>1</sup>H NMR analysis of the resulting cation indicated that incorporation of four deuteriums had occurred, with one deuterium each at C<sub>2</sub> and C<sub>7</sub> and two at C<sub>8</sub> (both endo and exo) (Figure 21). After five minutes, the extent of deuterium incorporation at each of these positions was found to be approximately 67%. Kinetic measurements for these exchange reactions were not carried out. <sup>1</sup>H NMR observation of the signal intensities appeared to suggest that further exchange at C<sub>2</sub> could be slower than at C<sub>8</sub>.

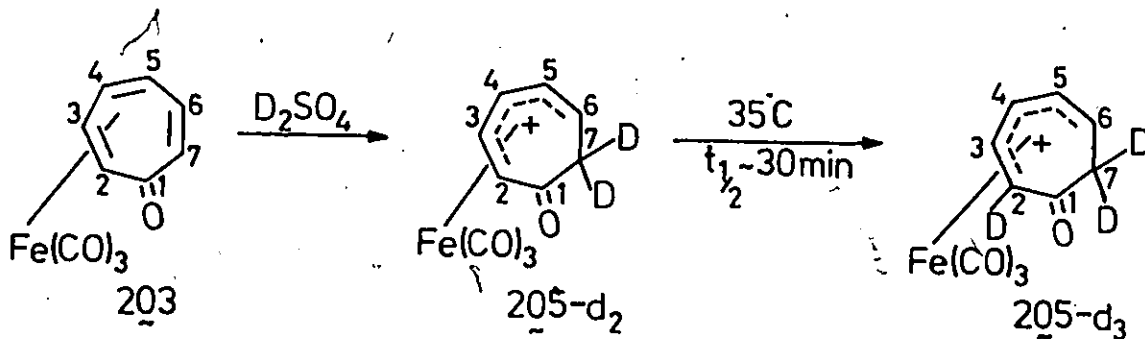


<sup>1</sup>H NMR observation of a solution of 217 in FSO<sub>3</sub>D at -78°C

showed that only one deuterium was incorporated at C<sub>7</sub>. No further incorporation of deuterium was evident until warming the solution to room temperature. At room temperature further slow incorporation of deuterium at C<sub>2</sub>, C<sub>7</sub> and C<sub>8</sub> occurred, the half-life for these exchange reactions being about 24 hours. Since the FSO<sub>3</sub>H solutions of the protonated complexes were not very stable at ambient temperatures for extended periods of time, continued <sup>1</sup>H NMR observation of this solution was not carried out.



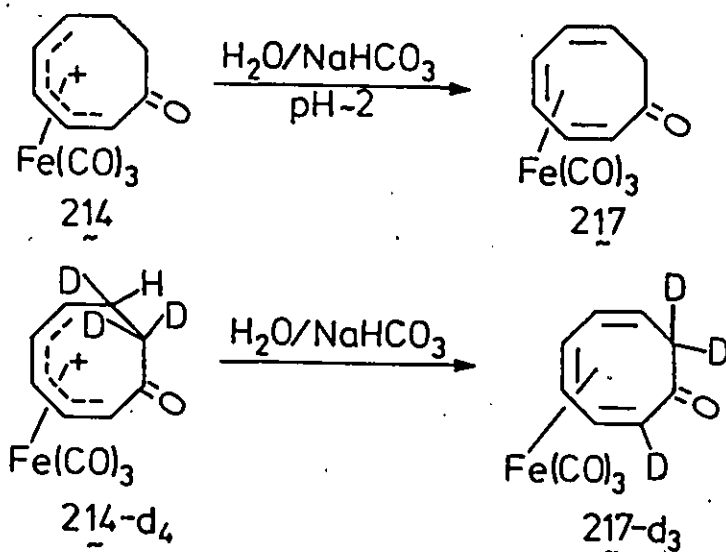
These observations are similar to the deuteration studies on troponeirontricarbonyl 203.<sup>232,233</sup> Eisenstadt and Winstein observed that incorporation of three deuteriums occurred when 203 was protonated in D<sub>2</sub>SO<sub>4</sub>.<sup>232</sup> Incorporation of deuterium at C<sub>7</sub> was observed to be much faster than at C<sub>2</sub>. In FSO<sub>3</sub>D, these processes proceeded at a much slower rate.<sup>232</sup>



The  $^{13}\text{C}$  NMR spectra of cations 214, 216 and 218 (as well as 205) in  $\text{D}_2\text{SO}_4$  confirmed the sites of deuteration (Table 31). The signals for carbons directly bonded to deuteriums were broadened due to coupling with deuterium. The extent of broadening was dependent on the extent of deuteration.

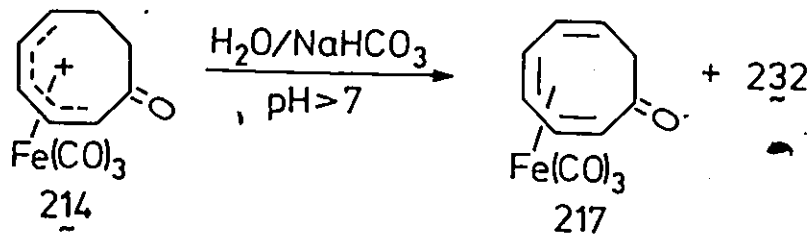
### 7. Quenching of Carbon-Protonated Cations

When  $\text{H}_2\text{SO}_4$  solutions of 214 were diluted with water deprotonation occurred. Cyclooctatrienoneirontricarbonyl 217 was the product obtained as shown by the  $^1\text{H}$  NMR spectrum.<sup>237,239</sup> Similar treatment of the cation 214-d<sub>4</sub> yielded 217-d<sub>3</sub>. From the  $^1\text{H}$  NMR spectrum of this product, it was inferred that two deuterium atoms are located at  $\text{C}_8$  and one at  $\text{C}_2$ . This confirms the original assignment regarding the sites of deuteration in 214-d<sub>4</sub>.

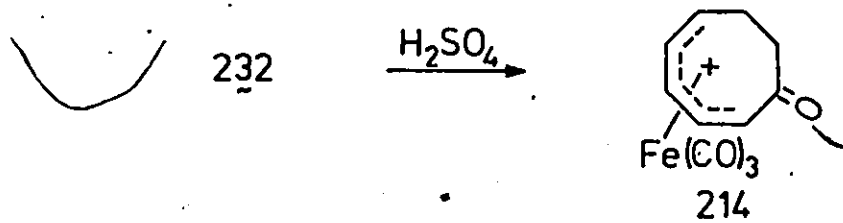


Quenching of 214 at  $\text{pH} > 7$  resulted in some decomposition with the precipitation of iron hydroxides. Under alkaline quenching conditions varying amounts of a minor product 232 were obtained besides the major product 217. These products were separated by thin layer chromatography.





The structure of 232 could not be determined with certainty. However, some of its properties are reported below: The  $^1\text{H}$  NMR spectrum of 232 consisted of multiplets at  $\delta$  5.33, 4.66, 3.08 and 2.79 - 1.63 with the approximate integration ratio of 2:1:2:3. The carbonyl stretching frequencies at 2030, 2000 and 1980  $\text{cm}^{-1}$  in its IR spectrum confirm the presence of the irontricarbonyl moiety. The presence of a dieneirontricarbonyl fragment in 232 could be inferred from its  $^{13}\text{C}$  spectrum which consisted of signals at  $\delta$  213.1, 205.1, 86.7, 86.5, 63.6, 61.2, 39.1 and 33.4. Further, cation 214 was regenerated when 232 was protonated in  $\text{H}_2\text{SO}_4$ .



Quenching of the methyl substituted derivatives 216 and 218 was unsuccessful as decomposition occurred during this process.

#### 8. Some Mechanistic Aspects

Some conclusions can be drawn regarding the protonation processes observed for these iron complexes. However, exact mechanisms for these processes cannot be proposed.

Troponeirontricarbonyl 203 and cyclooctatrienoneirontricarbonyl

217 are readily protonated on carbon by  $\text{CF}_3\text{COOH}$ . Carbon-protonation of homotroponeirontricarbons requires a stronger acid,  $\text{H}_2\text{SO}_4$ . This could be due to the latter protonation occurring on a saturated carbon.<sup>240</sup>

The rate constants for the isomerization of the oxygen-protonated 8,8-dimethyl derivative 202 to its carbon-protonated derivative 216 in  $\text{H}_2\text{SO}_4$  of different concentrations at  $34^\circ\text{C}$  are reported in Table 32. It can be seen that the rate constant decreases with decrease in acid strength. This is in agreement with the previous suggestion that protonation at the saturated carbon requires a stronger acid. The conversion of the oxygen-protonated cation to the carbon-protonated cation is slower in  $\text{D}_2\text{SO}_4$  (Table 32) owing to the isotope effect ( $\frac{k_{\text{H}}}{k_{\text{D}}} = 1.83$ ).

The oxygen-protonated cyclooctatrienoneirontricarbons complex 231 was not observed in  $\text{CF}_3\text{COOH}$  at low temperatures, while that of its tropone counterpart 204 was reported to be stable up to  $0^\circ\text{C}$ . The  $\text{C}_6\text{-C}_7$  double bond in 203 is relatively less susceptible to attack by an electrophile ( $\text{H}^+$ ) due to conjugation with the carbonyl group. In cyclooctatrienoneirontricarbons 217 this double bond is relatively free. This suggestion would assume that protonation occurs on the uncoordinated double bond, in contrast to the conclusions of Hunt and coworkers.<sup>233</sup> Eisenstadt also disagreed with Hunt's conclusion.<sup>234</sup> The exact mechanism of the transformation of the oxygen-protonated species to the carbon-protonated analogs is not known.

The deuteration experiment on 197 indicates that the incorporated deuterium occupies the endo position at  $\text{C}_8$  in the carbon-protonated cation 214-d. This cannot be taken to indicate that the initial deuteration occurs by endo attack on  $\text{C}_1$  of 197, since the role of the

Table 32

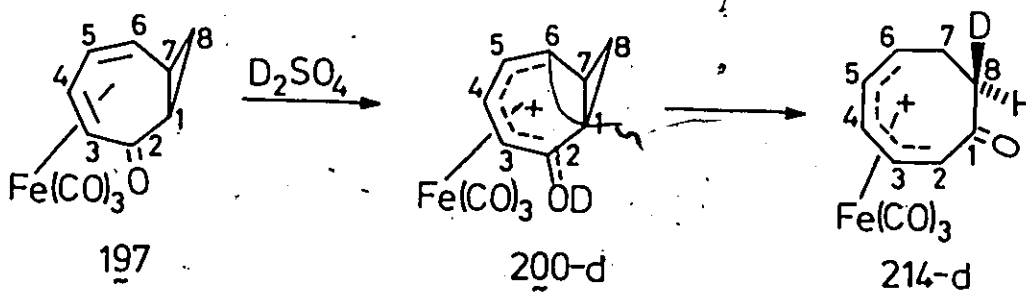
Rate Constants for Some of the Isomerization Processes  
Occurring in Protonated Homotroponeirontricarbons<sup>a,b</sup>

Process	Medium	$k \times 10^3 \text{ sec}^{-1}$	$\Delta G^\ddagger$ (kcal/mole)
<u>202-d</u> + <u>216-d</u>	96% D <sub>2</sub> SO <sub>4</sub>	1.8 ± 0.2	21.9
<u>202</u> + <u>216</u>	96% H <sub>2</sub> SO <sub>4</sub>	3.3 ± 0.2	21.5
<u>202</u> + <u>216</u>	80% H <sub>2</sub> SO <sub>4</sub>	2.7 ± 0.3	21.6
<u>202</u> + <u>216</u>	60% H <sub>2</sub> SO <sub>4</sub>	0.63 ± 0.03	22.5
<u>215</u> + <u>218</u>	96% H <sub>2</sub> SO <sub>4</sub>	0.74 ± 0.02	22.4
<u>215-d</u> + <u>218-d</u> <sub>4</sub>	96% D <sub>2</sub> SO <sub>4</sub>	0.71 ± 0.07	22.4

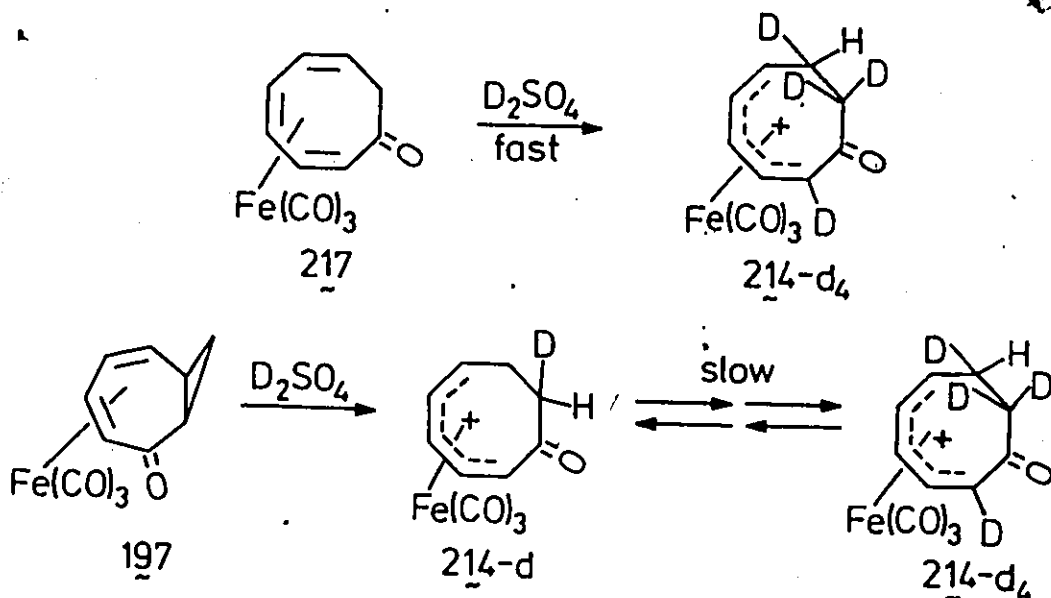
<sup>a</sup> At 34°C.

<sup>b</sup> Errors quoted are standard deviations.

intervening oxygen-protonated species 200-d is not known. However, one can conclude that this protonation is unlikely to involve the transfer of a proton via the metal atom, as this would be expected to lead to exo deuteration at C<sub>8</sub>. Further, the metal hydride signal is not observed in the <sup>1</sup>H NMR spectra of these complexes in protic acids.



Deuterium exchange for the cation generated from 197 is much slower than that from the cyclooctatrienone complex 217. This would indicate that for the latter, deuterium exchange occurs as fast as, if not faster than protonation at C<sub>7</sub>. For the homotroponeirontricarbonyl complex 197, exchange has to occur after protonation at C<sub>7</sub> to form 214, via further deprotonation-protonation processes.



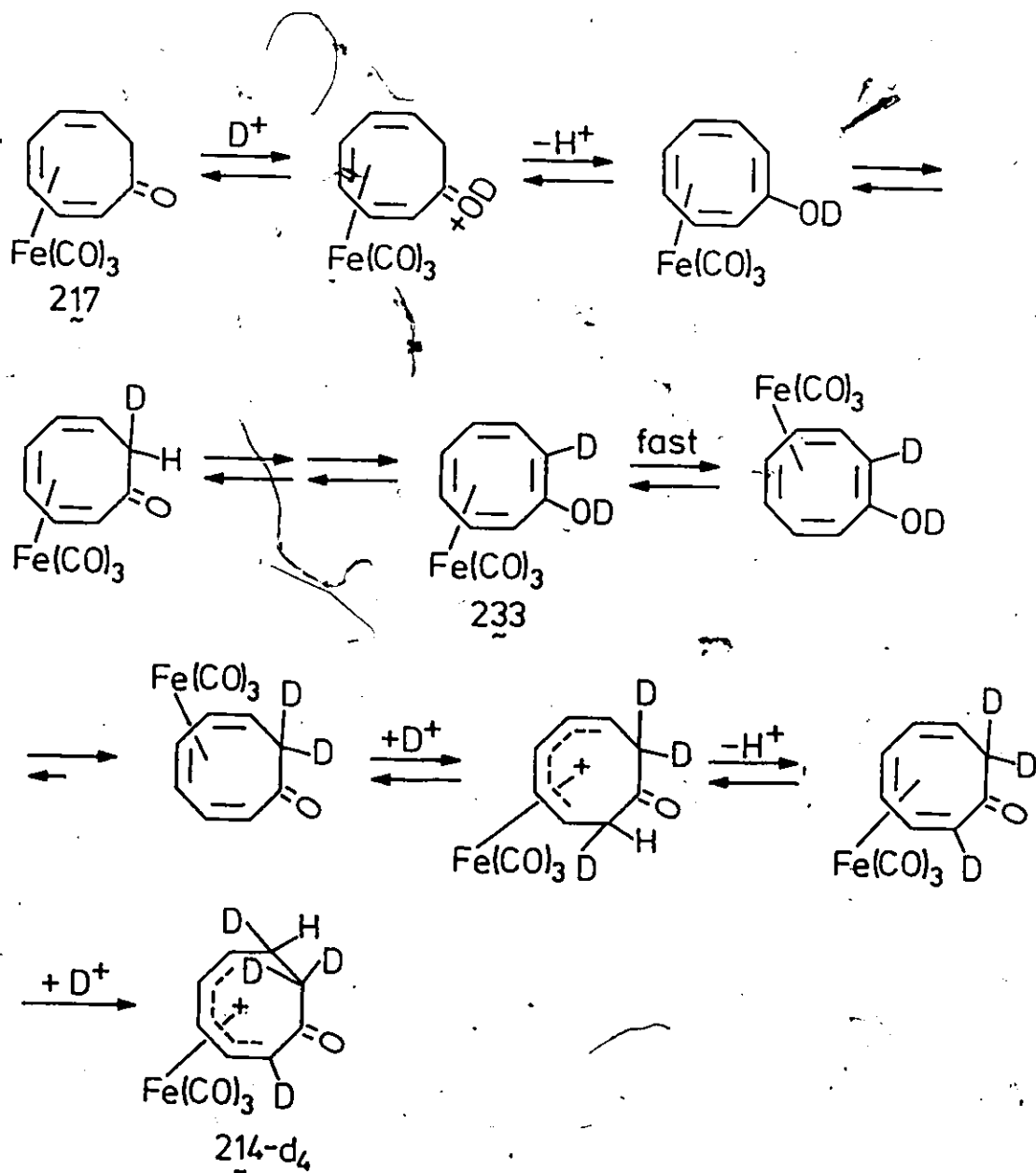


the rate constant for the fluxional isomerization process.<sup>232</sup> The rate constant ( $k = 4 \times 10^{-4} \text{ sec}^{-1}$  at  $35^\circ\text{C}$ ) for exchange at  $\text{C}_2$  of 203 was suggested as an estimate of that for the fluxional isomerization process.<sup>232</sup>

Such a mechanism can be extended to the exchange reactions of cyclooctatrienoneirontricarbonyl 217. The following observations support the above suggestion: The deuterium exchange reactions in  $\text{FSO}_3\text{D}$  are slower for 217 than in  $\text{D}_2\text{SO}_4$ . The stronger the acid, the slower will be the deprotonation steps. Further, the rate constant (Table 32) for the fluxional isomerization in the methyl substituted cation 215 is similar to that reported for the incorporation of deuterium at  $\text{C}_2$  of 203 ( $\sim 10^{-4} \text{ sec}^{-1}$  at  $35^\circ\text{C}$ ). Accordingly, deuterium incorporation at  $\text{C}_2$ , which has been proposed to occur via the fluxional isomerization process, is slower than at the other two carbons in the case of 217.

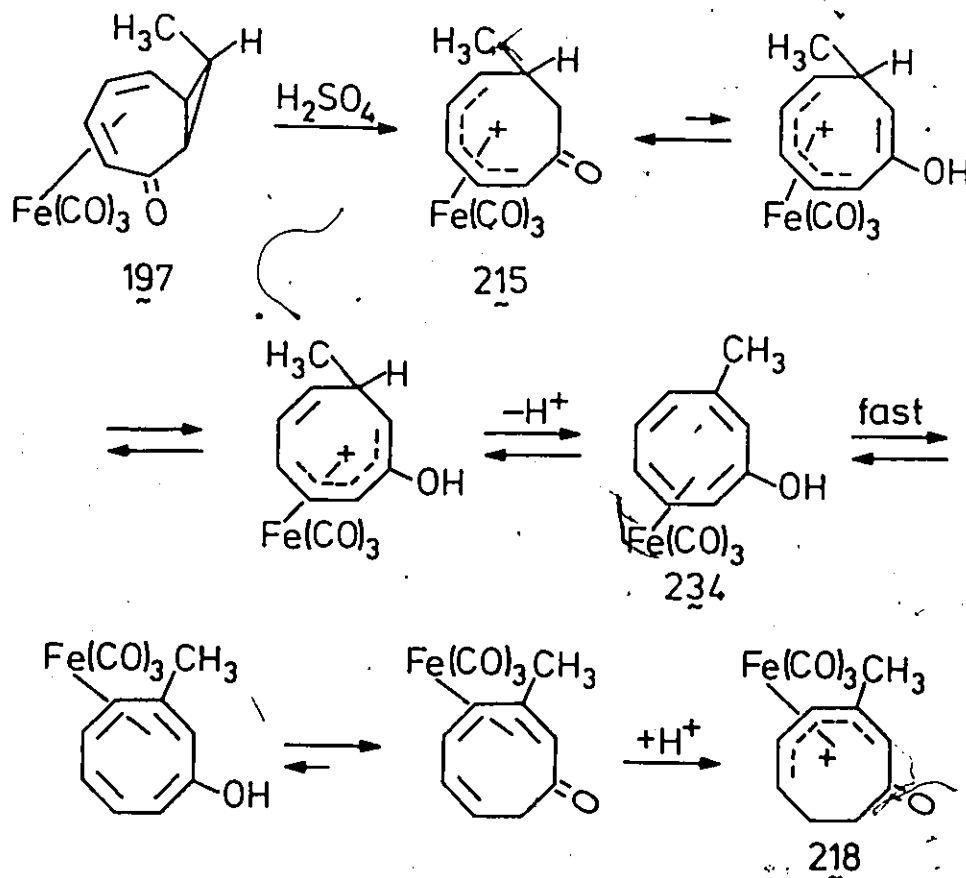
For cyclooctatrienoneirontricarbonyl 217 the exchange of two deuteriums can occur via an acid catalyzed enolization process. However, incorporation of deuterium at  $\text{C}_2$  could be better accounted for by a rapid valence tautomerism of the resulting hydroxycyclooctatetraeneirontricarbonyl followed by deuteration at  $\text{C}_2$  (of what has now become the free double bond). This process is summarized in Scheme 13.

The valence tautomerization of the irontricarbonyl group in cyclooctatetraeneirontricarbonyl 27 is an extremely facile process ( $\Delta G^\ddagger = 7.2 \text{ kcal/mole}$ ).<sup>247</sup> However, the formation and the stability of its hydroxy derivative is not established. It is likely that the formation of enolic intermediates such as 233 is slow and this could be responsible for the slower rate of fluxional isomerization and deuterium incorporation at  $\text{C}_2$ .



Scheme 13

This mechanism can be applied to the isomerization of 215 to 218. This possibility is outlined in Scheme 14.



Scheme 14

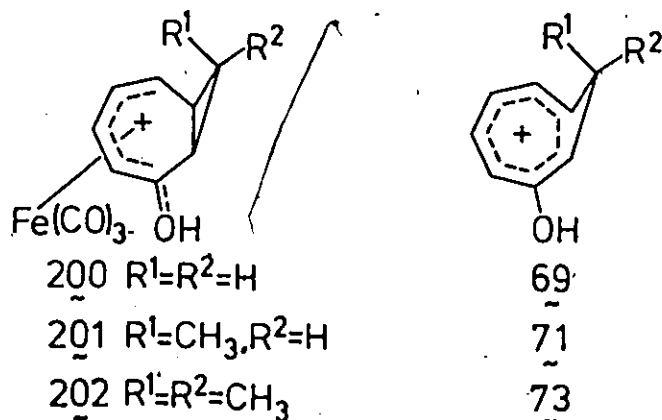
There is no definite evidence for the formation of the enol intermediates of these complexes such as 234. However, even a transient formation of these species would drive the equilibrium to the right, on account of the well-known preference of the methyl substituent for the internal carbons of a coordinated diene.<sup>248</sup> The formation of the



enol intermediates could be the slowest step. It should be realized that these mechanisms are at best tentative and further experiments are necessary to arrive at a more definite answer.

### 9. Conclusions

It is interesting to compare the properties of the oxygen-protonated homotroponeirontricarboxyls 200, 201 and 202 with those of the corresponding hydroxyhomotropylum cations 69, 71 and 73.



The difference in delocalization in the protonated forms of the complexes and the free ligands is reflected in their spectra and chemical properties. From Table 33, it can be seen that the  $\Delta\delta$  values of the proton chemical shifts for the substituents on C<sub>8</sub> are considerably smaller in the metal complexes, indicating the absence of cyclic delocalization. Similar differences have been noted earlier in the case of homotropylum and bicyclo[5.1.0]octadienylirontricarboxyl cations.<sup>1,2</sup>

Further differences can be noticed in the reactions of these systems. While 73 undergoes a facile circumambulation reaction, solutions of 202 in CF<sub>3</sub>COOH do not undergo any change on heating at 60°C

for 30 minutes. Hydroxyhomotropylium cations such as 69 or 71 do not undergo protonation or deuterium exchange on the carbon atoms. In contrast, the iron complexes 200 - 202 undergo facile protonation (deuteration) at C<sub>1</sub>. This would indicate the presence of an intact cyclopropane in these complexes. Protonation of cyclopropanes is a well-known reaction.<sup>249</sup>

Structural differences such as the presence of cyclic or linear delocalization are thus manifested in the differences in properties of these classical and nonclassical systems.

Table 33

$\Delta\delta$  Values in Protonated Homotropones and their Irontricarboxyl Complexes

Cation	$\Delta\delta$ (ppm)	Cation	$\Delta\delta$ (ppm)
<u>200</u>	0	<u>69</u>	3.1
<u>202</u>	0.16	<u>73</u>	1.24

## CONCLUDING REMARKS

The series of projects dealt with in this thesis, provide information on the structure and stability of homotropylium cations. A great number of previous investigations on this subject exist in the literature. However, they furnish little definitive evidence for the importance of homoaromatic delocalization. Most of the previous evidence for homoaromaticity in these ions and in fact, for most other supposedly homoaromatic systems, rests heavily on the presence of an induced diamagnetic ring current when the molecule or ion is placed in a magnetic field.

Definitive structural evidence obtained in the present study justifies the designation of 2-hydroxyhomotropylium cation as being homoaromatic. This conclusion is further reinforced by the thermodynamic studies which clearly show that homoaromatic delocalization has a measurable stabilizing effect on the heat of formation of homotropylium cations. Taken in conjunction, these results provide unambiguous, quantitative information on homoaromaticity.

The ring current calculations reported in this thesis deliver an important message. Using the geometry of the 2-hydroxyhomotropylium cation obtained from the crystallographic studies, the expected difference in chemical shifts for the exo and endo protons on C<sub>8</sub> of homotropylium cation was calculated. The large discrepancy found between the calculated and observed chemical shift differences serves as a warning for the use of <sup>1</sup>H NMR chemical shifts as a sole criterion for homoaromaticity.

This opens up a lot of questions about much of the previous work on homoaromaticity reported in the literature. It is suggested that future workers in the area of homoaromaticity should use the structure and energy criteria developed in this thesis and not just rely on  $^1\text{H}$  NMR data alone.

EXPERIMENTAL

## CHAPTER 7

### EXPERIMENTAL METHODS

#### 1. Instrumental Techniques

$^1\text{H}$  NMR spectra were recorded on Varian EM-390, Bruker WP-80, Bruker WH-90 and Bruker WM-250 spectrometers. Probe temperatures were measured using a methanol sample for the Varian EM-390 spectrometer and an iron-constantan thermocouple digital thermometer for the rest of the spectrometers.  $^{13}\text{C}$  and  $^2\text{H}$  spectra were run on Bruker WP-80 and Bruker WM-250 spectrometers respectively. The reference signals used to measure the chemical shifts are indicated with the data.

Infrared spectra were recorded on a Perkin-Elmer model 283 spectrometer. Optical rotations were measured using a Perkin-Elmer 241 MC polarimeter. Mass spectra were obtained from a VG7070 F mass spectrometer operating at an ionization potential of 70 eV, at 200°C. A Spex 14018 double spectrometer equipped with a Spectraphysics model 164 ion laser of wavelength 514.9 nm was used to obtain the Raman spectra. Preparative and analytical gas chromatography were carried out with Varian A-90-P3 and Varian-3700 gas chromatographs respectively. X-ray diffraction data were recorded on a Syntex P2<sub>1</sub> diffractometer. Ring current calculations were made using an HP3000 computer with a Fortran program LARC written by Agarwal.<sup>214</sup> Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected.

## 2. Purification of Solvents and Reagents

$\text{FSO}_3\text{H}$  was purged with dry nitrogen, treated with dry NaF (1 g/50 ml) and distilled. The distillate was subjected to the same treatment once again. The redistilled material was stored in small quantities (1 ml) in glass ampoules.

$\text{CF}_3\text{COOH}$  was distilled prior to use.

Lewis acids such as  $\text{SbCl}_5$ ,  $\text{BBr}_3$ ,  $\text{SnCl}_4$  and  $\text{TiCl}_4$ , which are liquids at room temperature, were doubly distilled under vacuum and stored in glass ampoules.  $\text{SbF}_5$  from a fresh commercial sample was used without purification.

$\text{CH}_3\text{NO}_2$ ,  $\text{C}_6\text{H}_6$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CCl}_4$  were refluxed over  $\text{P}_2\text{O}_5$  and distilled. Benzene was further dried with sodium wire. Fresh anhydrous ether was dried with sodium wire. Tetrahydrofuran was distilled over  $\text{LiAlH}_4$ . Deuterated NMR solvents such as  $\text{CD}_2\text{Cl}_2$  and  $\text{CDCl}_3$  were dried with activated molecular sieves (Type 4A).  $\text{SO}_2\text{ClF}$  was used as supplied.  $\text{SO}_2$  was stored over  $\text{P}_2\text{O}_5$  and distilled when required.

## 3. Synthetic Aspects

Many of the compounds used in this work have been reported previously. In these cases the literature methods were used to prepare the samples and their purity was checked by  $^1\text{H}$  NMR spectroscopy. The following is a list of such compounds along with the literature references for their preparation: 2,3-homotropone 104<sup>250</sup>, Tropone 124<sup>251</sup>, Cyclohepta-2,4-dienone 122<sup>179</sup>, cyclohept-2-enone 121<sup>210</sup>, cyclohepta-2,6-dienone 123<sup>210</sup>, 8,8-dimethyl-2,3-homotropone 107<sup>236</sup>, 8,8-dimethylbicyclo[3.2.1]octa-3,6-dien-2-one 101<sup>84</sup>, cycloocta-2,4,6-trienone 109<sup>252</sup>, 2-isopropyltropone 127<sup>202</sup>, 2-isobutenylphenol 129<sup>203</sup>, 2,2-dimethyl-2,3-dihydrobenzofuran

134<sup>204,205</sup>, 8,8-dimethylbicyclo[5.1.0]octa-3,5-dien-2-ol 155<sup>84</sup>,  
bicyclo[3.2.1]octa-3,6-dien-2-one 173<sup>253,254</sup>, bicyclo[3.2.1]octa-3,6-  
dien-2-ol 169<sup>225</sup>, 2,3-homotroponeirontricarbonyl complexes 197, 198 and  
199<sup>236</sup>, and bicyclo[5.1.0]octadienylirontricarbonyl tetrafluoroborate  
28<sup>57</sup>.

Cycloheptanone 120, cyclooctanone 125 and isobutyrophenone 128  
were obtained commercially and distilled prior to use. The preparation  
of other compounds is described below.

a. Preparation of Homotropylium Hexachloroantimonate 5.

This was prepared using a modification of the procedure described  
by Pettit and coworkers.<sup>51</sup> A reaction vessel, consisting of two limbs  
separated by a sintered frit was flame-dried on a vacuum line before use.  
SbCl<sub>5</sub> (1.6 g) and nitromethane (10 ml) were introduced into the vessel  
under a dry nitrogen atmosphere in a glove bag. The solution was cooled  
in freezing mixture (-13°C) and saturated with anhydrous HCl by means  
of a vacuum line. The vessel was closed and removed from the vacuum  
line. A solution of cyclooctatetraene 20 (0.565 g) in CH<sub>3</sub>NO<sub>2</sub> (5 ml) was  
added slowly at -11°C under dry nitrogen. The solution was stirred under  
nitrogen for ½ hour. Benzene (100 ml) was added to precipitate the salt.  
The off-white solid was dried under vacuum. The <sup>1</sup>H NMR of this solid  
in SO<sub>2</sub> was identical to that of homotropylium cation 5 generated by the  
protonation of cyclooctatetraene in H<sub>2</sub>SO<sub>4</sub>. Recrystallization of this  
material from different solvents such as CH<sub>2</sub>Cl<sub>2</sub>, SO<sub>2</sub>, and SO<sub>2</sub>ClF by cooling  
at -20°C or by the slow evaporation of the solvents at ambient temperature  
failed to give single crystals suitable for x-ray analysis.



b. Preparation of Homotropylium Hexafluoroantimonate 5

In a dry three-necked flask fitted with a nitrogen inlet, a dropping funnel and a drying tube containing drierite, was taken a solution of cyclooctatetraene (2.34 g) in  $\text{CF}_2\text{Cl}-\text{CCl}_2\text{F}$  (40 ml). The dropping funnel was charged previously with a commercial sample of  $\text{HF}\cdot\text{SbF}_5$  (5.33 g) under nitrogen in a glove bag. The solution of cyclooctatetraene was cooled to  $-25^\circ\text{C}$  and the fluoroantimonic acid was added very slowly in drops over a period of 30 minutes with constant stirring. The reaction mixture was stirred for a further 10 minutes and the yellow solid was filtered under nitrogen in the glove bag. The solid was washed with 10 - 20 ml of the same solvent and dried under vacuum at  $-25^\circ\text{C}$ . This solid was thermally less stable than its hexachloroantimonate analog. The  $^1\text{H}$  NMR spectrum of the solid in  $\text{SO}_2$  was identical to that of homotropylium cation 5 in  $\text{H}_2\text{SO}_4$ . Satisfactory elemental analysis could not be obtained for this solid.

Elemental analysis:

Calculated (for $\text{C}_8\text{H}_9^+\text{SbF}_6^-$ )	C 28.19%	H 2.66%
Calculated (for $\text{C}_8\text{H}_9^+\text{Sb}_2\text{F}_{11}^-$ )	C 17.23%	H 1.63%
Observed	C 19.21%	H 2.84%

Using the same set of solvents and techniques employed for the hexachloroantimonate salt, single crystals of this hexafluoroantimonate salt suitable for x-ray study could not be obtained.

c. Preparation of 2-hydroxyhomotropylium hexachloroantimonate 69<sup>97</sup>

This preparation was carried out in a two limbed reaction vessel in which the limbs were separated by a sintered frit. The vessel was flame-dried on a vacuum line before use. Using a glove bag,  $\text{SbCl}_5$

(1.12 g) and nitromethane (10 ml) were introduced into one limb of the reaction vessel. The solution was cooled to  $-11^{\circ}\text{C}$  and anhydrous HCl introduced to the vessel by way of a vacuum line until no more was taken up by the solution. The vessel was closed and removed from the vacuum line. With dry nitrogen passing through the vessel a solution of 2,3-homotropone 104 (0.448 g) in  $\text{CH}_3\text{NO}_2$  (5 ml) was added slowly at  $-11^{\circ}\text{C}$ . The resulting yellow solution was stirred for 1.5 h before dry benzene (100 ml) was added slowly. The precipitated yellow salt was filtered using the sintered frit and dried under a vacuum. Further crops of the salt were obtained from the filtrate. The salt was recrystallized from  $\text{CH}_2\text{Cl}_2$  at  $-20^{\circ}\text{C}$ .

Raman (sealed sample,  $-196^{\circ}\text{C}$ ): 171, 180, 282, 290, 330, and  $361\text{ cm}^{-1}$ .  $^1\text{H}$  NMR data are discussed in the text (Chapter 1).

$^{13}\text{C}$  CPMAS spectra of the solid salt were obtained at 22.6 MHz on a Bruker CXPI00 pulse spectrometer with a 'home-built' probe and spinner assembly. Proton spin locking and decoupling fields of  $\sim 40\text{ kHz}$  were used. The spinner design was of the Andrew-Beams type utilizing Kel-F spinners of  $\sim 450\ \mu\text{l}$  capacity driven by air and operated at spinning rates of approximately 3 kHz. The sample was sealed and protected in the spinner from air and moisture by teflon tape wound on the threads of the spinner cap.  $^{13}\text{C}$  NMR data are given in Table 4.

Optical rotations were measured for the ketone 104, bulk salt 69 and a single crystal of 69 at selected wavelengths. In all cases the angles of rotation measured were less than  $\pm 0.009$ .

d. Preparation of bis(5,6-benzo-8,8-dideuterobicyclo[5.1.0]octa-3,5-dien-2-one)hydrogen hexachloroantimonate 115

The title compound 115 was prepared in an evacuated, flame-dried reaction vessel. A solution of  $\text{SbCl}_5$  (0.58 g) in  $\text{CH}_3\text{NO}_2$  (2 ml) was introduced into the vessel, under nitrogen in a glove bag. The solution was saturated with HCl gas at  $-15^\circ\text{C}$  by means of a vacuum line. The vessel was removed from the vacuum line and dry nitrogen was passed through it. A solution of the ketone 114-d<sub>2</sub> (0.335 g) in  $\text{CH}_2\text{Cl}_2$  (2 ml) was added slowly at  $-15^\circ\text{C}$  with stirring under nitrogen. After stirring for another 30 minutes benzene (100 ml) was added to the reaction mixture. The product separated as a viscous greenish-yellow mass which subsequently solidified to give a greenish-yellow solid. It was filtered under nitrogen and dried under vacuum. The  $^1\text{H}$ ,  $^2\text{H}$  and  $^{13}\text{C}$  NMR data are reported in Tables 8, 9 and 10 respectively. Crystals used in the x-ray study were obtained by slow crystallization of the salt from  $\text{CH}_2\text{Cl}_2$  solution at  $-20^\circ\text{C}$ .

e. Preparation of 2-deuterobicyclo[5.1.0]octa-3,5-dien-2-ol 155-d

$\text{LiAlD}_4$  (29.1 mg) was added to a solution of 8,8-dimethylhomotropone 107 (85.3 mg) in anhydrous ether (5 ml) kept at  $-78^\circ\text{C}$  under nitrogen. The resulting heterogeneous mixture was stirred at this temperature, under nitrogen for 1 h after which time the yellow color of the starting material disappeared.  $\text{CH}_3\text{OH}$  (10 ml) was added, the solution stirred for 15 min at  $-78^\circ\text{C}$ , warmed to  $0^\circ\text{C}$  and stirred for a further 15 min. The solution was warmed to room temperature and filtered twice through celite to remove the coagulated solid. The solvent was evaporated to give the crude alcohol 155-d as a pale yellow liquid. The product was purified by bulb to bulb distillation ( $110^\circ\text{C}/7.5$  Torr) yield: 67.5 (mg).

The properties of this material were closely similar to those of the undeuterated material, 155.<sup>84</sup> In the <sup>1</sup>H NMR spectrum of 155-d, the signal at  $\delta$  4.7 corresponding to the resonance for H<sub>2</sub> in 155 was absent.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) $\delta$  : 6.03 (m, 1H, vinyl); 5.66 (m, 3H, vinyl); 1.96 (d, J=9Hz, 1H, H<sub>1</sub>); 1.63 (s, 1H, OH); 1.5 (dd, J=9, 10Hz, 1H, H<sub>7</sub>); 1.27 (s, 3H, CH<sub>3</sub>); 1.0 (s, 3H, CH<sub>3</sub>).

M.S m/e (rel. abund.%): 151 (M<sup>+</sup>, 81.3); 118 (54.3); 93 (49.6); 92 (100); 91 (56.8); 83 (95.7); 82 (43.5); 80 (64); 79 (71.2); 78 (50.7); 77 (55.8); 68 (47.1); 67 (52.2); 59 (44.6); 51 (42.4).

6. Preparation of 8,8-dimethylbicyclo[3.2.1]octa-3,6-dien-2-ol 156

A solution of 8,8-dimethylbicyclo[3.2.1]octa-3,6-dien-2-one 101 (74 mg) in 3 ml dry benzene was kept stirred under nitrogen at 0°C. 5 ml of a 1M solution of diisobutylaluminum hydride in hexane was added slowly at this temperature. The solution was stirred at this temperature for 2 h. Excess CH<sub>3</sub>OH (10 - 15 ml) was then added and the mixture stirred at room temperature for a further 15 minutes. It was then filtered through celite and the solvent evaporated to give a pale yellow oil.

<sup>1</sup>H NMR analysis of this product showed that two isomeric compounds were present in an approximate ratio of 2:1. The crude mixture was distilled bulb to bulb (100°C/7.5 Torr) and a white solid sublimed over.

Yield: 35 mg.

M.P.: 81 - 83°C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) $\delta$  : 6.23 (dd, J=6, 3Hz, H<sub>6</sub>); 5.95 (dd, J=10, 5Hz, H<sub>4</sub>); 5.70 (dd, J=6, 3Hz); 5.28 (dt, J=10, 3, 3Hz, H<sub>3</sub>); 3.80 (bs, H<sub>2</sub>); 2.21 (dd, J=5, 3Hz, H<sub>5</sub>); 2.05 (bs, H<sub>1</sub>); 1.22 (s, CH<sub>3</sub>); 1.07 (s, CH<sub>3</sub>).

IR (CS<sub>2</sub>) cm<sup>-1</sup>: 3600, 2920, 1020, 780, 735, 700.

High Res. MS (m/e): M<sup>+</sup> obsd: 162.1029

M<sup>+</sup> calcd: 162.1045.

g. Preparation of 2,8,8-trimethylbicyclo[5.1.0]octa-3,5-dien-2-ol 157

A solution of 8,8-dimethyl-2,3-homotropone (101 mg) in dry ether, (10 ml) kept under nitrogen, was cooled to -78°C. To this was added a 1.4M solution of CH<sub>3</sub>Li in ether (0.7 ml). The reaction mixture was stirred at -78°C for 1 h. After warming to 0°C, ice-cold water (5 ml) was added to quench the reaction. The ether layer was separated from the aqueous layer and the aqueous layer extracted with ether (3x10 ml). The combined ether extract was washed with water, dried over anhydrous MgSO<sub>4</sub>, filtered and the solvent removed to give a pale-yellow solid. Bulb to bulb distillation (110°C / 7.5 torr) resulted in the sublimation of the product 157 as a colorless solid.

Yield: 113.2 mg.

M.P.: 61 - 64°C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 6.00 (m, 1H, vinyl); 5.53 (m, 3H, vinyl); 1.93 (b, OH); 1.72 (dd, J=9, 2Hz, H<sub>1</sub>, H<sub>7</sub>); 1.36 (s, CH<sub>3</sub>); 1.17 (s, CH<sub>3</sub>); 1.1 (s, CH<sub>3</sub>).

IR (KBr pellet) cm<sup>-1</sup>: 3300, 2940, 1380, 1105, 970, 795, 730, 690.

High res. MS (m/e): M<sup>+</sup> obsd: 164.1207

M<sup>+</sup> calcd: 164.1201.

h. Preparation of 2,8,8-trimethylbicyclo[3.2.1]octa-3,6-dien-2-ol 158

This compound was prepared from 8,8-dimethylbicyclo[3.2.1]octa-3,6-dien-2-one 101 (140.9 mg) and a 1.4M solution of CH<sub>3</sub>Li in ether (1 ml) by the same method as that described above for 157. The crude

product was obtained as a colorless liquid. The product was purified by bulb to bulb distillation (100°C / 7.5 Torr). The oil solidified to give colorless crystals upon storage in the freezer.

Yield: 148.7 mg.

M.P.: 38 - 40°C.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ ) $\delta$  : 6.22 (dd,  $J=6,3\text{Hz}$ ,  $\text{H}_6$ ); 5.93 (dd,  $J=10,6\text{Hz}$ ,  $\text{H}_4$ ); 5.8 (dd,  $J=6,3\text{Hz}$ ,  $\text{H}_7$ ); 5.15 (dd,  $J=10,2\text{Hz}$ ,  $\text{H}_3$ ); 2.24 (dd,  $J=6,3\text{Hz}$ ,  $\text{H}_5$ ); 2.1 (m,  $J=3,2\text{Hz}$ ,  $\text{H}_1$ ); 1.57 (s, OH); 1.34 (s,  $\text{CH}_3$ ); 1.13 (s,  $\text{CH}_3$ ); 1.04 (s,  $\text{CH}_3$ ).

IR ( $\text{CS}_2$ )  $\text{cm}^{-1}$ : 3600, 3480, 2925, 1365, 1265, 1105, 1095, 915, 780, 730, 710.

High res. MS (m/e):  $\text{M}^+$  obsd: 164.1255

$\text{M}^+$  calcd: 164.1201.

*i. Preparation of isopropyltropylium hexachloroantimonate 159*

To a solution of 7-methyloxycycloheptatriene 161 (300 mg) in 15 ml dry ether, a 2M solution of isopropylmagnesiumchloride in ether (5 ml) was added slowly under nitrogen at 0°C. The solution was stirred at this temperature for 3 h. A solution of  $\text{NH}_4\text{Cl}$  (2 g) in water (15 ml) was added and the solution was stirred at 0°C for 30 min. The ether layer was removed and the aqueous layer was extracted with ether (3x10 ml). The combined organic layer was dried over anhydrous  $\text{MgSO}_4$ , filtered and the solvent evaporated to give a brown oil. Bulb to bulb distillation (80°C/7.5 Torr) of this oil yielded the pure 7-methylcycloheptatriene 162 (133.8 mg). This product was added to a solution of triphenylmethyl hexachloroantimonate (305 mg) in  $\text{CH}_2\text{Cl}_2$  (15 ml) at room temperature, under nitrogen. The mixture was kept overnight under nitrogen at room temperature when a dark solution was obtained. The solvent was evapor-

ated under vacuum and the off-white solid product 159 was washed with dry ether several times to remove triphenylmethane and the excess 7-methylcycloheptatriene 162. The crude product was recrystallized from dry  $\text{CH}_2\text{Cl}_2$  at  $-20^\circ\text{C}$  to give isopropyltropylium hexachloroantimonate 159 as colorless crystals.

Yield: 230 mg.

$^1\text{H}$  NMR ( $\text{SO}_2$ ): 9.06 (s, 5H, vinyl); 3.6 (quint,  $J=7.5$ , 1H, methine); 1.2 (d,  $J=7.5$  Hz,  $\text{CH}_3$ ).

j. *Preparation of cyclooctatrienone iron tricarbonyl* 217

Cyclooctatrienone 109 (1 g) was dissolved in THF (40 ml) which was purged with a stream of dry nitrogen.  $\text{Fe}_2(\text{CO})_9$  (3 g) was added under nitrogen. The mixture was stirred overnight (about 12 - 15 h) at room temperature under nitrogen. The solution was filtered through celite and the solvent removed under vacuum. The resulting dark solid was chromatographed on neutral alumina (activity grade III). The starting material 109 was removed by elution with low boiling pet ether. Elution with benzene gave two bands. The major yellow band gave the desired product (0.5 g) on evaporation of the solvent. The minor red band gave small amounts of a red solid which possibly was the binuclear carbonyl  $\text{C}_8\text{H}_8\text{OFe}_2(\text{CO})_6$  and was discarded.

The properties of 217 were in complete agreement with those reported previously. <sup>237,239</sup>

4. Calorimetric Measurements

The ketones were dried over molecular sieves and distilled

prior to use. Their purity was checked by  $^1\text{H}$  NMR spectroscopy and GLC.

All of the ketones were subjected to trial protonations under conditions simulating those used in the calorimetric measurements. Each of the ketones (15 - 20  $\mu\text{l}$ ) was rapidly injected from a 25  $\mu\text{l}$  syringe directly into stirred  $\text{FSO}_3\text{H}$  (3 - 5 ml) kept at the same temperature as that used in the calorimetry. In the case of the solid ketone 101 a 50% solution in  $\text{CCl}_4$  was used. The resulting solutions were examined by  $^1\text{H}$  NMR spectroscopy to verify the nature of the cations formed. The  $^1\text{H}$  NMR spectra of these protonated ketones corresponded to those reported or expected. <sup>176-181, 83, 84, 97</sup>

A modified version of the calorimeter designed by Arnett and Petro was used to measure the heats of protonation. <sup>174</sup> These modifications and the procedures used have been described in detail elsewhere. <sup>172, 175</sup> The performance of the calorimeter was checked by measuring the heat of protonation of cyclopentanone in  $\text{FSO}_3\text{H}$ . The observed value for this ketone agreed well with that reported by Arnett and coworkers. <sup>169</sup>

60 ml of  $\text{FSO}_3\text{H}$  was introduced into the dried calorimeter vessel. The acid was kept under dry nitrogen and maintained at the temperatures reported in Table 16.

The samples were introduced directly into the acid by means of a weighed 25  $\mu\text{l}$  syringe. The tip of the syringe needle was arranged to be ca. 0.5 cm above the surface of the liquid in the calorimeter. The syringe was reweighed after the introduction of the sample. The ketone was injected five to six times in a given calorimetric run. At least two such independent calorimetric runs were carried out for each ketone.



Electrical calibrations were carried out before, during and after each calorimetric run. The bicyclic ketone 101, which is a solid at room temperature, was introduced as a 50% solution in  $\text{CCl}_4$ . Appropriate corrections were made for the heat of mixing of  $\text{CCl}_4$  in  $\text{FSO}_3\text{H}$  by injecting a weighed quantity of the former into the latter.

Heats of solution in  $\text{CCl}_4$  were measured exactly in the same way, replacing  $\text{FSO}_3\text{H}$  by  $\text{CCl}_4$  in the calorimeter. The heats of solution of the ketones in  $\text{FSO}_3\text{H}$  and  $\text{CCl}_4$  and the heats of protonation were then calculated using the electrical calibrations. Each value reported in Table 16 is the arithmetic mean of several measurements. The error quoted is the standard deviation of the measurements from the mean value.

## 5. Acid Catalyzed Rearrangements of 8,8-dimethyl-2,3-homotropone 107

### a. *General Isomerization Procedure*

8,8-dimethyl-2,3-homotropone 107 (5 - 20 mg) was dissolved in  $\text{CDCl}_3$  or  $\text{CCl}_4$  (0.7 ml) in an NMR tube, the solution cooled to  $-78^\circ\text{C}$  and the appropriate amount of acid added under an argon blanket. The mixture was warmed to the specified temperature (Table 19) and the reaction monitored by  $^1\text{H}$  NMR spectroscopy. After the completion of the reaction, the mixture was poured into a saturated solution of  $\text{NaHCO}_3$ . The organic materials extracted into  $\text{CH}_2\text{Cl}_2$  (3x5-ml) and the combined extracts dried over  $\text{MgSO}_4$ . The solvent was removed in vacuo and the residue subjected to GLC and  $^1\text{H}$  NMR analyses. The results are summarized in Table 19.

### b. *Product Characterizations*

#### i. *Rearrangement catalysed by $\text{CF}_3\text{COOH}$*

Ketone 107 (20 mg) in  $\text{CCl}_4$  (1 ml) and  $\text{CF}_3\text{COOH}$  (20 mg) were mixed

and heated at 70°C for 16 h. The reaction mixture was neutralized with NaHCO<sub>3</sub>, the product extracted into CH<sub>2</sub>Cl<sub>2</sub>, and dried as above. Removal of the solvent and bulb to bulb distillation (80°C/0.1 Torr) gave 127 (19 mg).

<sup>1</sup>H NMR (CCl<sub>4</sub>, TMS) δ: 6.81 (vinyl H, 5H, m); 3.34 (methine H, m, J=6Hz); 1.14 (CH<sub>3</sub>, d, J=6Hz).

The IR and <sup>1</sup>H NMR spectra of 127 were identical to an authentic sample prepared by the method of Noyori and coworkers.<sup>202</sup>

IR (film): 2960, 1630, 1580, 1520, 780, 690 cm<sup>-1</sup>.

*ii. Rearrangement catalysed by p-toluenesulfonic acid*

Ketone 107 (20 mg) in CCl<sub>4</sub> (1 ml) was treated with p-toluenesulfonic acid hydrate (2 mg). The reaction mixture was heated at 75°C for 3 h and subsequently worked up as described above. Removal of the solvent gave the crude phenol 129 (10 mg). The phenol was purified by extraction into aqueous NaOH, washing the aqueous layer with ether; acidification of the aqueous layer, re-extraction into ether, drying (MgSO<sub>4</sub>) and solvent removal.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, TMS) δ: 7.0 (aromatic H, 4H, m); 6.2 (vinyl H, 1H, s); 5.17 (OH, 1H, s); 2.0 and 1.72 (CH<sub>3</sub>, each 3H, s).

IR (CS<sub>2</sub>): 3540, 2960, 750, 695 cm<sup>-1</sup>.

The <sup>1</sup>H NMR and IR spectra and GLC retention times of 129 were identical

to those of an independently prepared sample.<sup>203</sup>

*iii. Rearrangement catalysed by BCl<sub>3</sub>*

BCl<sub>3</sub> (30 mg) was condensed into a frozen solution of 107 (13 mg) in CDCl<sub>3</sub> (1 ml) at -78°C. The mixture was warmed to 25°C. After 1 h at this temperature, the reaction mixture was quenched and worked up as

described above. Removal of the solvent and bulb to bulb distillation (150°C/15 Torr) gave 2,3-dihydro-2,2-dimethylbenzofuran 134.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.17 and 6.83 (Aromatic H, 4H, m); 3.03 ( $\text{CH}_2$ , 2H, s); 1.46 ( $\text{CH}_3$ , 6H, s).

IR (film): 2920, 1595, 1455, 1260, 1205, 890, 745  $\text{cm}^{-1}$ .

The  $^1\text{H}$  NMR and IR spectra and GLC retention times were identical to those of an authentic sample prepared by the method of Martini and coworkers.<sup>204, 205</sup>

*iv. Rearrangement catalysed by  $\text{BF}_3 \cdot \text{OEt}_2$*

Ketone 107 (20 mg) in  $\text{CCl}_4$  (1 ml) was treated with  $\text{BF}_3 \cdot \text{OEt}_2$  (1 mg) and heated at 70°C for 3 h. Working up the reaction as described above gave a mixture of 101 and 128 (10 mg). These were separated by preparative GLC (15% SE-30 on Chromosorb W; retention times: 101, 5.8 m and 128, 6.6m, at 130°C). The properties of 101 were identical to those previously described.<sup>84</sup>

Isobutyrophenone 128,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 7.86 and 7.43 (aromatic H, 5H m); 3.45 ( $\text{CH}$ , 1H, h,  $J=7\text{Hz}$ ); 1.15 ( $\text{CH}_3$ , 6H, d,  $J=7\text{Hz}$ ).

IR (film): 2980, 1690, 1600, 1582, 1480, 1430, 1315, 1225, 1160, 970, 788, 696  $\text{cm}^{-1}$ .

The properties of 128 were identical to those of a commercial sample.

6. Preparation of Lewis Acid Complexes of 2,3-homotropone 104 and 8,8-dimethyl-2,3-homotropone 107

5.0mm NMR tubes containing solutions of the ketones 104 and 107 (12 - 15 mg) in  $\text{CD}_2\text{Cl}_2$  (1 ml) were cooled in a dry ice-acetone bath at -78°C and kept under argon. The Lewis acids (200 - 300 mg) were added under argon by means of a 100  $\mu\text{l}$  syringe, weighing the syringe with the

Lewis acid before and after addition. Gaseous acids (0.2 - 0.3 ml) were directly condensed into the NMR tube at  $-78^{\circ}\text{C}$ . The solutions were mixed with a thin quartz rod and the  $^1\text{H}$  NMR spectra run immediately at  $-80^{\circ}\text{C}$ .

7. Protonation Studies on the Iron Complexes 197, 198, 199 and 217

All the solvents were purged of oxygen by passing a stream of nitrogen through them. The complexes were dissolved in  $\text{CDCl}_3$  and filtered under nitrogen to remove suspended paramagnetic impurities prior to use. All protonations were carried out under nitrogen.

a. *Method of Protonation*

The complexes 197, 198, 199 and 217 (about 20 - 25 mg) were dissolved in a minimum volume of  $\text{CDCl}_3$  (a few drops), cooled to  $0^{\circ}\text{C}$ , cold  $\text{CF}_3\text{COOH}$  (about 0.7 - 1 ml at  $0^{\circ}\text{C}$ ) added and the resulting mixtures stirred with a thin quartz rod. Protonations with  $\text{H}_2\text{SO}_4$  were carried out in a similar manner at  $-15^{\circ}\text{C}$ . The same procedure was employed in the case of deuterated acids. Protonations with  $\text{FSO}_3\text{H}$  were carried out at  $-78^{\circ}\text{C}$ . For protonation of 217 in  $\text{CF}_3\text{COOH}$  at  $-78^{\circ}\text{C}$ , a solution of  $\text{CF}_3\text{COOH}$  in  $\text{SO}_2$  (1:4 by volume) was employed.

Samples for  $^{13}\text{C}$  NMR spectra were prepared under the same conditions using 100 - 150 mg of the complexes and 2 - 3 ml of the acids.

b. *Quenching of the Protonated Metal Carbonyl Complexes*

Quenching of the protonated metal complexes was carried out by pouring the NMR samples in ice cold water (10 ml), neutralizing with  $\text{NaHCO}_3$  to the required pH (usually about 7) and extracting with ether

(3x10 ml). The ether extract was dried over anhydrous  $\text{MgSO}_4$ , filtered and the solvent evaporated. The products were examined by  $^1\text{H}$  NMR spectroscopy. The results obtained are discussed in the text.

c. *Measurement of Rate Constants*

Commercial 96%  $\text{H}_2\text{SO}_4$  or 96%  $\text{D}_2\text{SO}_4$  were used as the acid media. 80%  $\text{H}_2\text{SO}_4$  and 60%  $\text{H}_2\text{SO}_4$  were prepared by diluting the 96% acid with appropriate amounts of distilled water.

The rate constants for conversion of  $\underline{215} \rightarrow \underline{218}$  in  $\text{H}_2\text{SO}_4$  and  $\text{D}_2\text{SO}_4$  and the conversion of  $\underline{202} \rightarrow \underline{216}$  in various acid media are reported in Table 33. The kinetics for these processes were followed by measuring the ratio of the peak heights of the methyl signals in the starting cations to those of the  $(\text{CH}_3)_4\text{NBF}_4^-$  internal standard (singlet at  $\delta$  3.1) at various time intervals. This ratio was used as a unit-free concentration term [C]. The first order rate constant  $k$  was measured from the formula  $k = \frac{1}{t} \ln \frac{C_0}{C_t}$  where  $C_0$  was the concentration at time  $t_0$  and  $C_t$  was that at time  $t$ . The reactions were followed until they were greater than 90% complete. The mean of the  $k$  values and the errors (standard deviations of the  $k$  values from the mean) are reported in Table 32. Each kinetic run was repeated once again and the results obtained were well within the errors reported.

8. Rearrangement Studies on Homotropylium and Bicyclo[3.2.1]octadienyl Cations

a.: Protonation of the Bicyclic Alcohols  $\underline{155}$ ,  $\underline{156}$ ,  $\underline{167}$ ,  $\underline{157}$  and  $\underline{158}$  at Low Temperatures

Each of the  $\underline{7}$  alcohols (20 mg) was dissolved in  $\text{CD}_2\text{Cl}_2$  (a few

drops) and cooled to  $-78^{\circ}\text{C}$  in a 5.0 mm NMR tube.  $\text{SO}_2\text{ClF}$  (about 0.2 ml) was condensed into the NMR tube at this temperature. The tube was transferred to an ether-liquid nitrogen slush bath ( $-116^{\circ}\text{C}$ ) and 1 ml of a solution of  $\text{FSO}_3\text{H}$  in  $\text{SO}_2\text{ClF}$  (1:4 v/v) at the same temperature was added to the alcohol solution. The solution was rapidly stirred with a thin quartz rod previously cooled in liquid nitrogen, to effect complete mixing. The tube was quickly transferred to the probe of the NMR spectrometer, kept at  $-120^{\circ}\text{C}$ .

b. *Protonation of Bicyclo[3.2.1]octa-3,6-dien-2-one 169 and Kinetics of Isomerization of the Conjugate Acid 173*

Protonation of the ketone 169 (20 mg) carried out at  $-78^{\circ}\text{C}$  by extraction from a frozen solution in  $\text{CDCl}_3$  (1 ml) with  $\text{FSO}_3\text{H}$  (1 ml). The NMR observations were done at  $+34^{\circ}\text{C}$ . The rate constant for the isomerization of 173 to 174 was followed by observing the change in intensity (peak heights) of the signal for  $\text{H}_4$  at  $\delta$  9.00 with time and using the same calculations as those employed for the kinetics of isomerization of iron complexes mentioned earlier. Similar calculations were performed using the peak height for the  $\text{H}_3$  proton signal at  $\delta$  6.33. The rate constant reported is the average of these two sets. The error quoted is the standard deviation.

c. *Low Temperature Protonation of 155-d and Kinetics of Deuterium Scrambling in 50-d*

This protonation was carried out exactly in the same way as that reported for the other bicyclic alcohols, but for the use of  $\text{CFCl}_3$  instead of  $\text{CD}_2\text{Cl}_2$  as the solvent in this case. Kinetics of deuterium

scrambling at  $-90^{\circ}\text{C}$  was followed by measuring the increase in the intensity (peak height) of the vinyl proton signal or the decrease in the intensity (peak height) of the bridgehead methine proton signal, with time. The treatment of the data was to obtain the rate constant was the same as that reported earlier. The error quoted in the value of  $k$  is the standard deviation of the individual values from the mean.

The rate constant for the first order decay of the 2,8,8-trimethylhomotropylium cation 153 at  $-70^{\circ}\text{C}$  was obtained by measuring the peak height of the signal for the exo methyl protons at  $\delta$  -0.15 at various time intervals and using the first order rate equation.

d. *Quenching of the Cation 154*

The alcohol 158 (25 mg) in acid-washed pentane (5 ml) was cooled in a methanol-liquid nitrogen slush bath. This cold solution was added to a mixture of  $\text{FSO}_3\text{H}$  and  $\text{SO}_2\text{ClF}$  (2 ml, 1:1 v/v) kept in the same bath. After mixing the two solutions to extract the alcohol 158 into the acid layer, the reaction mixture was transferred to a dry ice-acetone bath ( $-78^{\circ}\text{C}$ ) and kept at this temperature for 45 min. A slurry of  $\text{NaHCO}_3$  in methanol at  $-78^{\circ}\text{C}$  was added to the acid solution. Then the mixture was warmed to  $0^{\circ}\text{C}$  and water was added to complete the neutralization. The organic materials were extracted with ether (3x25 ml). The ether layer was dried with anhydrous  $\text{MgSO}_4$ , filtered and the ether removed under vacuum.  $^1\text{H}$  NMR analysis indicated the presence of a complex mixture of products. GLC analysis (on SE-30 column at  $140^{\circ}\text{C}$ ) showed at least five components to be present. Due to the small quantities of the products isolated by GLC further analyses could not be carried out.

## 9. Crystal Structure Determinations

### a. 2-Hydroxyhomotropylum hexachloroantimonate 69

#### i. Collection of the x-ray data

The crystal of 69 was mounted and sealed in a Lindemann glass capillary tube. Precession photographs showed the crystals to be single and monoclinic. Unit cell parameters were obtained from a least squares fit of  $\chi$ ,  $\phi$  and  $2\theta$  for 15 reflections in the range  $14 < 2\theta < 20^\circ$  recorded on a Syntex P2<sub>1</sub> diffractometer using MoK $_{\alpha}$  radiation ( $\lambda = 0.71096 \text{ \AA}$  at  $22^\circ\text{C}$ ). Crystal data and other numbers related to data collection are summarized in Table 34. Density was not measured due to the air instability of the sample. Reflection intensities were recorded on a Syntex P2<sub>1</sub> diffractometer using a coupled  $\theta$  (crystal) -  $2\theta$  (counter) scan. Corrections were made for Lorentz polarization effects but not for absorption. This will make a maximum error in F of 5.6%.

#### ii. Solution of the structure

A three-dimensional Patterson synthesis and a difference synthesis revealed the antimony atoms and the chlorine atoms respectively. A series of full-matrix least-squares refinements, followed by three-dimensional electron density difference syntheses revealed all the non-hydrogen atoms. The temperature factors were made anisotropic. Further refinements were made using full-matrix least-squares, minimizing  $\sum w(|F_o| - |F_c|)^2$  until the maximum shift/error was  $< 0.01$ . Throughout the refinement the scattering curves were taken from reference 255 and anomalous dispersion corrections from reference 256 were applied to the curves for antimony and chlorine.



Table 34

Crystal Data for 69

Compound	$\{C_8H_8OH^+\}[SbCl_6^-]$
fw	455.62
crystal size (mm)	rough cylinder, $r = 0.15$ , $l = 0.50$
Systematic absences	$h k l$ , $k + l = 2n + 1$
space group <sup>a</sup>	$A2/m$
unit cell parameters ( $\text{\AA}$ and deg) <sup>a</sup>	$a = 8.893(4)$ $b = 11.093(6)$ $c = 18.811(9)$ $\beta = 128.32(3)$
$V(\text{\AA}^3)$	1456(1)
Z	4
$\rho_{\text{calc}}$ g cm <sup>-3</sup>	2.078
linear abs coeff, cm <sup>-1</sup>	29.80
max $2\theta$ , quadrant	$45^\circ$ , $h$ , $k$ , $+$ $l$
std reflectns, (e.s.d., %)	3 0 -4 (1.1%) -3 -3 9 (0.5%)
temp, °C	-65(1)
no. independent reflectns.	2086
no. with $I > 3\sigma(I)$	1690
$3\sigma(I) > I > 0$	246
$I < 0$ , rejected	150
final $R_1^b$ , $R_2^b$	0.0448, 0.0696
final shift/error, max, ave.	0.0040, 0.0006
g(secondary extinction)	$5.48 \times 10^{-8}$
final diff. map	
highest peak (e/ $\text{\AA}^3$ ); location	1.2; 0.10, 0.05, 0.15
lowest valley (e/ $\text{\AA}^3$ ); location	-2.0; 0.40, 0.50, 0.0
weighting	$w = (\sigma^2 + (0.06F_o)^2)^{-1}$
error in observation of unit weight	1.060

<sup>a</sup> The cell can be transformed to the standard  $C2/m$  cell by the matrix (001/0-10/100).

<sup>b</sup>  $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ;  $R_2 = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2)^{1/2}$ .

The initial solution with the cation considered as being asymmetric gave a satisfactory refinement ( $R_1 = 0.047$ ,  $R_2 = 0.071$ ). However there were certain inconsistent features that made its validity questionable.

(1) There were obvious symmetry relationships between certain pairs of chlorine atoms and of carbon atoms. (2) It is highly unlikely that the racemic ketone 104 would yield the salt 69 in one enantiomeric form. (3) There were differences in bond distances which were expected to be nearly equivalent. Since the reversal of signs for all the atomic parameters made no difference to the refinement and since the solution of the crystal in  $\text{CH}_2\text{Cl}_2$  showed no optical rotation, it was concluded that the asymmetric cation was disordered, with a mirror plane bisecting the cation. This disorder primarily arises from the oxygen atoms having half occupancy in a site on either side of the mirror plane. Among the various methods of treating the disorder, only that using refinements with half-occupancy for the oxygen atom gave satisfactory solution. The existence of this disorder can be seen from the large temperature factors for  $\text{C}_3$ ,  $\text{C}_4$  and O, which limits the accuracy of this structure. Since all the hydrogen atoms could not be located, they were not included in the refinement. The atomic parameters for nonhydrogen atoms are given in Table 35.\* In spite of the disorder discussed above, the positions of the carbon atoms of the cyclopropane ring are well-defined.

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\* All calculations were carried out on CDC-6400 or CYBER 170/730 computers. The programs DATCO5 and DATRDN from the X-RAY 76 program were used for preliminary data treatment. The structure was solved using the SHELX package, and final refinement used the internally written programs CUDLS and SYMFOU by J.S. Stephens and J.S. Rutherford, respectively. Plane calculations used NRC-22 (M.E. Pippy and F.R. Ahmed) and diagrams were prepared using ORTEP-II (C.K. Johnson, U.S. Atomic Energy Commission Report, ORNL-5138, Oak Ridge National Research Laboratory, Oak Ridge, Tenn., 1976).

Table 35

Atomic Positional Parameters ( $\times 10^4$ ) and Temperature Factors ( $\text{\AA}^2$ )  
for 2-hydroxyhomotropylum hexachloroantimonate 69

	x	y	z
Sb(1)	0	0	0
Sb(2)	5000	5000	0
Cl(11)	1527(3)	0	1569(1)
Cl(12)	2123(2)	-1493(1)	214(1)
Cl(21)	2054(2)	5000	-241(1)
Cl(22)	3826(2)	3493(1)	-1120(1)
C(1)	1440(8)	4267(5)	2688(3)
C(2)	1771(10)	3607(6)	2149(4)
C(3)	2977(12)	3873(11)	1950(4)
C(4)	3595(13)	5000	1927(7)
C(8)	2973(11)	5000	3478(5)
O(2) <sup>a</sup>	890(19)	2700(8)	1844(7)

<sup>a</sup> Atom given half occupancy in this position. Anisotropic temperature factors given by  $\exp[-2\pi^2(h^2 a^{*2} U_{11} + \dots + 2hka^* b^* U_{12} + \dots)]$  where  $a^*$ ,  $b^*$ ,  $c^*$  are the reciprocal lattice vectors ( $\text{\AA}^{-2}$ ).

( $\times 10^4$ )

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Sb(1)	255(3)	243(3)	255(3)	-	155(2)	-
Sb(2)	232(3)	244(3)	177(3)	-	123(2)	-
Cl(11)	496(10)	836(16)	277(8)	-	235(8)	-
Cl(12)	471(7)	597(10)	665(9)	238(7)	245(7)	-123(7)
Cl(22)	384(6)	491(7)	412(6)	-68(5)	222(5)	-224(5)
Cl(21)	258(1)	289(6)	292(7)	-	175(6)	-

( $\times 10^3$ )

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)	50(3)	40(3)	37(3)	1(2)	30(2)	4(2)
C(2)	72(4)	55(4)	31(3)	24(3)	20(3)	4(2)
C(3)	77(5)	161(10)	36(3)	74(6)	30(3)	10(4)
C(4)	35(5)	197(17)	33(5)	-	22(4)	-
C(8)	39(4)	70(5)	26(3)	-	20(3)	-
O(2)	147(11)	29(4)	50(5)	3(6)	41(6)	-4(4)

b. *Bis(5,6-benzo-8,8-dideuterobicyclo[5.1.0]octa-3,5-dien-2-one)-hydrogen hexachloroantimonate 115*

The same method of data collection as that used for 69 was employed here. The solution of the structure was carried out using standard methods. The crystal data are reported in Table 36. Atomic positional parameters and temperature factors are given in Tables 37 and 38 respectively. The coordinates of hydrogen atoms can be found in Table 39.

c. *Bicyclo[5.1.0]octadienylirontricarbonyl tetrafluoroborate 28*

Single crystals suitable for x-ray diffraction were obtained from an SO<sub>2</sub> solution of the tetrafluoroborate salt 28 by slow evaporation of the solvent. This evaporation was carried out in an evacuated two limbed reaction vessel with the limb containing the solution at room temperature and the other limb cooled by running cold water from a tap.

The collection of data and the solution of the structure were performed using standard methods. The BF<sub>4</sub><sup>-</sup> anion was found to be disordered. This disorder was treated by giving two of the fluorines partial occupancies of 0.5, 0.5, 0.6, 0.2 and 0.2. Further refinements are in progress. The disorder in the anion does not affect the bond lengths in the cation to any significant extent. The atomic positional parameters and temperature factors are reported in Tables 40 and 41.

Coordinates of hydrogen atoms are given in Table 42.

Table 36  
Crystal Data for 115

Compound	$[(C_{12}H_{10}O)_2H^+][SbCl_6^-]$
fw	675.9
crystal size (mm)	needle, $l = 0.25$ ; cross section: 0.175
systematic absences	$k k l, h + k + l = 2n + 1, h \text{ or } l, h, l = 2n + 1$
space group <sup>a</sup>	I2/C
unit cell parameters <sup>a</sup>	$a \text{ \AA} = 18.336(3)$ $b \text{ \AA} = 8.056(2)$ $c \text{ \AA} = 17.982(3)$ $\beta^\circ = 99.56(2)$
$V(\text{\AA}^3)$	2619
Z	4
$\rho_{\text{calc}} (\text{g cm}^{-3})$	1.714
Temp. ( $^\circ\text{C}$ )	-35
Linear abs. coeff. ( $\text{cm}^{-1}$ )	16.94
Max $2\theta$	$45^\circ$
Standards (e.s.d.)	4 -1 -3 (0.015) 40 -4 (0.012)
No. of reflections	3334
No. with $I > 0$	2714
Unobserved	297
Final $R_1^b, R_2^b$	0.0587, 0.0547
Final shift/error max, ave.	0.006, 0.0018
Secondary extinction	0.00013
Final diff. map	
Highest peak ( $e/\text{\AA}^3$ )	0.59
Lowest valley ( $e/\text{\AA}^3$ )	-0.66
Weighting	$w = (\sigma^2 + 0.00075F_o^2)^{-1/2}$

<sup>a</sup> This non-standard setting of C2/C can be transformed to the standard cell  $a = 23.453(4) \text{ \AA}, b = 8.056(2) \text{ \AA}, c = 17.982(3) \text{ \AA}, \beta = 119.95(2)^\circ$  by the matrix  $(-10 -1/0 \ 0/001)$ .

<sup>b</sup>  $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$

$R_2 = \left\{ \frac{\sum w(|F_o| - |F_c|)^2}{\sum w F_o^2} \right\}^{1/2}$

Table 37

Atomic Positional Parameters ( $\times 10^4$ ) for Non-Hydrogen Atoms in 115

Atom	x	y	z
Sb	0	8774(1)	2500
C1(1)	206(1)	8777(2)	1232(1)
C1(2)	1297(1)	8724(2)	2936(1)
C1(3)	0	5824(2)	2500
C1(4)	0	1695(2)	2500
C(1)	1236(3)	7371(7)	5868(4)
C(2)	1719(3)	6825(9)	6538(4)
C(3)	1792(3)	5141(9)	6780(3)
C(4)	1748(3)	3762(8)	6357(3)
C(5)	1640(2)	3504(6)	5550(3)
C(6)	1383(3)	4707(7)	4997(3)
C(7)	1055(3)	6337(7)	5138(3)
C(8)	500(4)	6506(9)	5637(4)
C(9)	1850(3)	1939(7)	5319(4)
C(10)	1798(3)	1553(9)	4566(4)
C(11)	1575(3)	2707(10)	4032(3)
C(12)	1370(3)	4295(9)	4242(3)
O	2066(3)	7973(7)	6954(3)

Table 38

Temperature Factors ( $\text{Å}^2$ )( $\times 10^3$ ) for Non-Hydrogen Atoms in 115

Atom	$U_{11}$ of U	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$	$U_{eq}^*$
C(1)	44(3)	43(3)	101(5)	-24(3)	23(3)	-6(3)	61(4)
C(2)	41(3)	71(4)	76(4)	-47(4)	23(3)	-15(3)	61(4)
C(3)	34(3)	89(5)	38(3)	-13(3)	5(2)	-16(3)	53(3)
C(4)	37(3)	59(3)	41(3)	4(3)	1(2)	-5(3)	46(3)
C(5)	28(2)	38(3)	40(3)	-8(2)	1(2)	-8(2)	35(3)
C(6)	27(2)	48(3)	40(3)	-4(2)	4(2)	-6(2)	38(3)
C(7)	43(3)	47(3)	59(3)	2(3)	-3(2)	9(3)	50(3)
C(8)	40(3)	55(4)	81(5)	-11(3)	7(3)	11(3)	58(4)
C(9)	41(3)	45(3)	72(4)	-10(3)	7(3)	-2(3)	52(3)
C(10)	49(3)	66(4)	81(5)	-36(4)	16(3)	-2(3)	64(4)
C(11)	39(3)	104(6)	50(3)	-39(4)	16(3)	-16(3)	63(4)
C(12)	29(3)	90(5)	37(3)	-4(2)	4(2)	-7(3)	52(3)
O	55(3)	110(4)	123(5)	-88(4)	29(3)	-29(3)	94(5)
Sb(1)	31.9(2)	24.0(2)	34.4(3)	-	2.3(2)	-	30.0(2)
Cl(1)	52.6(7)	55.0(8)	37.7(6)	-2.8(6)	8.4(5)	-9.4(7)	48.0(7)
Cl(2)	33.7(6)	50.5(7)	52.7(7)	-13.5(7)	-0.6(5)	-11.9(6)	45.7(7)
Cl(3)	53.4(11)	27.0(9)	57.0(11)	-	-0.8(9)	-	45.8(11)
Cl(4)	63.4(13)	24.2(9)	63.8(12)	-	1.1(10)	-	50.4(11)

\*  $U_{eq} = 1/3(U_{11} + U_{22} + U_{33} + 2U_{13} \cos \beta)$ .

Table 39  
Coordinates of Hydrogen Atoms ( $\times 10^3$ ) in 115

Atom	x	y	z
H(1)	126	862	582
H(3)	193	496	738
H(4)	192	251	656
H(7)	87	692	458
D(1)	36(3)	559(7)	594(3)
D(2)	24(4)	715(9)	551(4)
H(9)	219	112	570
H(10)	193	34	433
H(11)	151	268	335
H(12)	117	501	392

Hydrogen atoms were arbitrarily given a temperature factor of roughly  $1.5 - 2$  that of the atom to which they were attached, namely  $U = 0.09$  and deuterium atoms were given  $U = 0.05$ .



Table 40  
Atomic Positional Parameters ( $\times 10^4$ ) for Non-hydrogen Atoms in 28

Atom	x	y	z
Fe	8880(1)	8771(1)	7942(1)
C <sub>1</sub>	9144(5)	10845(5)	7078(7)
C <sub>2</sub>	9412(5)	10290(5)	8035(5)
C <sub>3</sub>	10073(5)	9572(5)	8131(5)
C <sub>4</sub>	10221(4)	8803(5)	7425(6)
C <sub>5</sub>	9666(5)	8602(5)	6565(6)
C <sub>6</sub>	8946(6)	9182(6)	6245(5)
C <sub>7</sub>	8900(6)	10269(6)	6140(6)
C <sub>8</sub>	9755(6)	10855(6)	6140(6)
C <sub>9</sub>	8903(5)	8567(6)	9347(5)
C <sub>10</sub>	7780(4)	9321(5)	7933(7)
C <sub>11</sub>	8521(5)	7506(5)	7734(6)
O <sub>1</sub>	8904(5)	8473(5)	10229(4)
O <sub>2</sub>	7088(3)	9677(4)	7938(6)
O <sub>3</sub>	8305(4)	6723(4)	7596(5)
B	8283(5)	11981(7)	10040(7)
F <sub>1</sub>	9186(4)	11943(4)	9969(5)
F <sub>2</sub>	8064(4)	12249(4)	11050(5)
F <sub>3</sub> <sup>a*</sup>	8140(7)	10922(8)	10031(8)
F <sub>4</sub> <sup>a*</sup>	12792(7)	13771(8)	10342(8)
F <sub>5</sub> <sup>b*</sup>	8121(8)	12767(9)	9342(9)
F <sub>6</sub> <sup>c*</sup>	7440(22)	12304(23)	9835(27)
F <sub>7</sub> <sup>c*</sup>	7803(22)	12731(24)	4284(26)

\* These atoms have occupancies of a, 0.5; b, 0.6; and c, 0.2.

Table 41  
 Temperature Factors ( $\text{\AA}^2 \times 10^3$ ) for Non-hydrogen Atoms in 28

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Fe	28.8(5)	33.6(4)	37.3(4)	4.7(4)	0.6(4)	-0.7(4)
C <sub>1</sub>	50(5)	33(3)	69(5)	6(4)	11(4)	1(3)
C <sub>2</sub>	43(4)	40(3)	42(3)	-6(3)	2(3)	-4(3)
C <sub>3</sub>	34(4)	54(4)	42(4)	-2(3)	-6(3)	-11(3)
C <sub>4</sub>	31(4)	44(4)	69(5)	8(4)	12(3)	1(3)
C <sub>5</sub>	57(5)	40(4)	49(4)	-7(3)	13(4)	-8(3)
C <sub>6</sub>	71(6)	61(4)	32(3)	-5(3)	-1(4)	-27(4)
C <sub>7</sub>	63(5)	66(5)	50(4)	22(4)	-14(4)	-6(4)
C <sub>8</sub>	66(6)	55(5)	62(5)	21(4)	7(4)	-9(4)
C <sub>9</sub>	51(5)	61(5)	49(4)	13(3)	8(4)	-2(4)
C <sub>10</sub>	28(4)	43(4)	80(5)	9(4)	-2(4)	-2(3)
C <sub>11</sub>	46(4)	48(4)	55(5)	10(3)	7(3)	-1(4)
O <sub>1</sub>	93(5)	119(6)	43(3)	23(3)	0(3)	-10(4)
O <sub>2</sub>	37(3)	53(3)	158(7)	13(4)	-3(4)	3(3)
O <sub>3</sub>	95(5)	40(3)	94(5)	3(3)	14(4)	-17(3)
B	28(5)	62(5)	50(4)	-13(4)	-6(4)	9(4)

Table 42  
Atomic Positional Parameters ( $\times 10^3$ ) for Hydrogen Atoms in 28

Atom	x	y	z
H <sub>1</sub>	881(5)	1137(5)	724(6)
H <sub>2</sub>	927(5)	1059(6)	861(6)
H <sub>3</sub>	1041(5)	956(6)	877(6)
H <sub>4</sub>	1071(5)	837(5)	757(6)
H <sub>5</sub>	969(5)	797(6)	626(6)
H <sub>6</sub>	857(5)	887(6)	583(6)
H <sub>7</sub>	846(5)	1046(6)	577(6)
H <sub>8a</sub>	1034(5)	1049(6)	621(6)
H <sub>8b</sub>	974(5)	1141(6)	575(6)

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