
ANTHONY DAVID WOLF
Ph. D.

PART I
NONLINEAR FREE ENERGY BEHAVIOR OF 2-ARYL-2-NORBORNYL CATIONS

PART II
^{19}F AND ^{1}H NMR STUDY OF AN EQUILIBRIUM AMONG ARYLBICYCLOOCTYL CATIONS

Thesis for the Degree of Ph. D.
MICHIGAN STATE UNIVERSITY
ANTHONY DAVID WOLF
1972

This is to certify that the

thesis entitled

PART I. NONLINEAR FREE ENERGY BEHAVIOR OF 2-ARYL-2-NORBORNYL CATIONS

PART II: ^{19}F AND ^{1}H NMR STUDY OF AN EQUILIBRIUM AMONG ARYLBICYCLOOCTYL CATIONS

presented by

Anthony David Wolf

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Major professor

Date September 21, 1972

O-7639

ABSTRACT

PART I

NONLINEAR FREE ENERGY BEHAVIOR OF 2-ARYL-2-NORBORNYL CATIONS

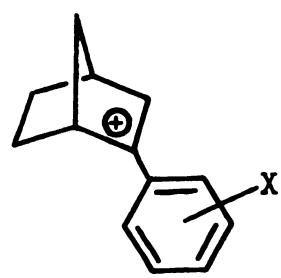
PART II

^{19}F AND ^{1}H NMR STUDY OF AN EQUILIBRIUM AMONG ARYLBICYCLOOCTYL CATIONS

By

Anthony David Wolf

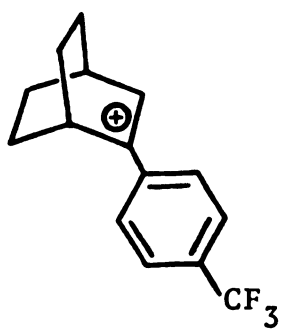
It is shown that in the graph of the H(1) versus H(3) chemical shifts for a series of 2-aryl-2-norbornyl cations 12, the linear relationship expected for a series of completely



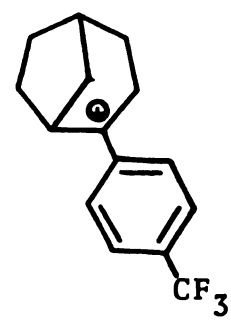
12

classical cations is not observed. Instead, nonlinear behavior ensues with cations less stable than 2-phenyl-2-norbornyl cation. It is also shown that while the non-linearity is consistent with a σ delocalized or carbon-carbon hyperconjugated description of those ions, it is not consistent with a description based on rapidly equilibrating classical ions.

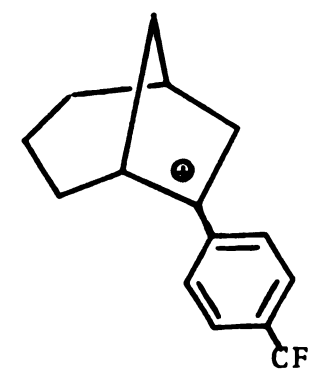
In Part II the following cations were characterized at -90°C by a ^{1}H nmr study:



2a



9a



11a

2-*p*-trifluoromethylphenyl-2-bicyclo[2.2.2]octyl cation 2a, 2-*p*-trifluoromethylphenyl-2-bicyclo[3.2.1]octyl cation 9a and 6-*p*-trifluoromethylphenyl-6-bicyclo[3.2.1]octyl cation 11a. Warming any of these cations to -60°C produced the same equilibrium mixture. By ^{19}F nmr the order of stability was found to be 11a > 2a >> 9a. The equilibrium constant between 2a and 11a at -80°C is 3.2. Other thermodynamic parameters are presented and a mechanism for the equilibrium is discussed.

PART I

NONLINEAR FREE ENERGY BEHAVIOR OF 2-ARYL-2-NORBORNYL CATIONS

PART II

^{19}F AND ^{1}H NMR STUDY OF AN EQUILIBRIUM AMONG ARYLBICYCLOOCTYL CATIONS

By

Anthony David Wolf

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1972

To Lizzie For Her

Love And Understanding

ACKNOWLEDGMENT

I would like to express my sincere appreciation to Professor Donald G. Farnum for his expert guidance, for the freedom which he always afforded to me in the laboratory and for the opportunities which he has made available to me.

To Professors David Lemal, Thomas Spencer, Charles Braun and Gordon Gribble and their graduate students ("68"-"70") at Dartmouth College, Chemistry Department, who have generously and enthusiastically contributed to my education while in the military service, I am deeply indebted.

My fellow graduate students have contributed much to this thesis. Their varied interests have served to broaden my own.

Actual laboratory contributions to this study were made by the following former undergraduates: Miss Irene Pupko, Mr. Steven Fettinger and Mr. Robert Bruggenmeier. Their enthusiasm was encouraging.

The successful completion of the nmr studies would not have been possible without the assistance of Mr. Wayne Burkhardt and Mr. Eric Roach.

ACKNOWLEDGMENT (Continued)

Over the past two and one half years I have had the following support for which I am thankful.

March 1970 - June 1970	Teaching Assistantship
June 1970 - September 1971	Research Assistantship (NSF)
September 1971 - December 1971	Teaching Assistantship
January 1972 - June 1972	Research Assistantship (NSF)
June 1972 - September 1972	Departmental Fellowship

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF TABLES

LIST OF FIGURES

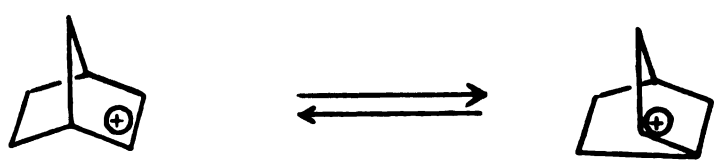
PART I

NONLINEAR FREE ENERGY BEHAVIOR OF 2-ARYL-2-NORBORNYL CATIONS

INTRODUCTION

Thorough reviews on the subject of norbornyl cations are already available in the literature.[1-5] We will simply restate the controversial aspects of the problem which have been formulated elsewhere[1,2] and we will focus on those experiments which are relevant to our results.

The nonclassical ion problem has been formulated so as to require a distinction between two alternative descriptions of the norbornyl cation.[1] That is the norbornyl cation is a rapidly equilibrating pair of classical ions 1a and 1b[6] or it is a σ delocalized cation[7] 2.



1a 1b

2

Three main foundations have been summarized as support for the latter description of the ion.[1,2]

(1) Unusually fast rates of solvolysis for *exo* norbornyl derivatives.

(2) Predominantly *exo* substitution.

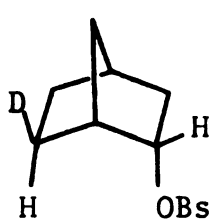
(3) Large *exo/endo* rate ratios.

The first point no longer seems to be tenable when suitable model systems are chosen for comparison.[1,8] Neither does the preponderance of *exo* substitution in solvolysis demand a nonclassical description of norbornyl cations.[1] Tortional effects seem to control the stereochemistry observed in many reactions of norbornyl systems.[9] The remaining point concerns the *exo/endo* rate ratios observed for norbornyl derivatives. Brown argues that tertiary norbornyl derivatives give rise to *exo/endo* rate ratios on the order observed for the parent norbornyl system. For example it has now been established that 2-phenyl-2-norbornyl cation is a classical cation,[10] yet the solvolysis of the *exo/endo* *p*-nitrobenzoates in this system yield rate ratios which are not significantly different from the ratio observed in the parent norbornyl system.[11] Furthermore it has been shown that these differences arise predominantly in the transition state for solvolysis rather than in the ground state.[12,13] Thus either the norbornyl cation is classical or there must be a unique interpretation for the origin of the *exo/endo* rate ratio in this cation if the nonclassical description would obtain. Schleyer

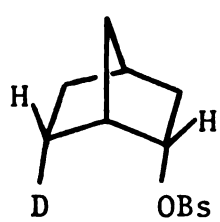
has offered a resolution.[9] He suggests that tortional and nonbonded interactions in the tertiary *endo* derivatives might largely be responsible for the observed *exo/endo* rate ratios.[9] Thus the original basis of support for nonclassical character in norbornyl cations must be rejected, since it has been shown that these criteria are not specific in indicating nonclassical character.

Deuterium isotope effects in the transition state for solvolysis of norbornyl derivatives and studies of stable norbornyl cations are not adequately explained by classical norbornyl cations. In the following we cite examples of the latter which are pertinent to our results.

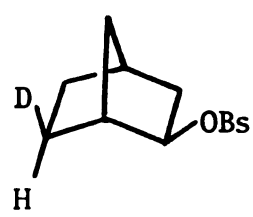
Studies of kinetic isotope effects in the solvolysis of the following systems was reported simultaneously by two different groups.[14,15] No isotope effect was observed



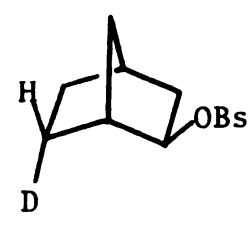
3a



3b



4a



4b

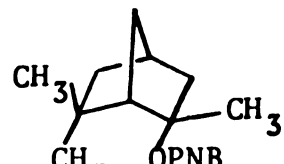
for solvolyses of the *endo* brosylates 3a and 3b.[14,15] It was reported that this result was consistent with the γ isotope effect expected for solvolysis via a classical cation.[14,15] In the *exo* brosylates 4a and 4b however, a 10%

positive isotope effect was observed for deuterium in either the *exo* or the *endo* position at C-6.[14,15] It was concluded that these isotope effects were too large to be accounted for by classical transition states.[14,15]

It seems significant that *exo*-6-D 4a *and endo*-6-D 4b 2-*exo*-brosylates *both* have large γ isotope effects. It is difficult to account for these on the basis of solvent effects and steric interactions in the solvolysis of the *exo* derivatives.[14]

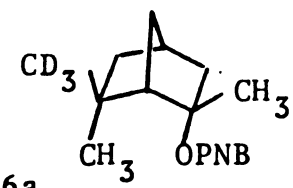
The absence of a kinetic isotope effect in the solvolysis of the *endo* brosylates 3a and 3b is interesting* since other

* Kinetic isotope effect studies by Karabatsos and Smith[16] on 2,6,6-trimethyl-*endo*-norbornyl-*p*-nitrobenzoates 5

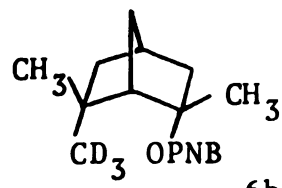


5

have indicated that a substantial isotope effect is operating (based on enthalpy only) in both the *exo*-6-trideuteriomethyl



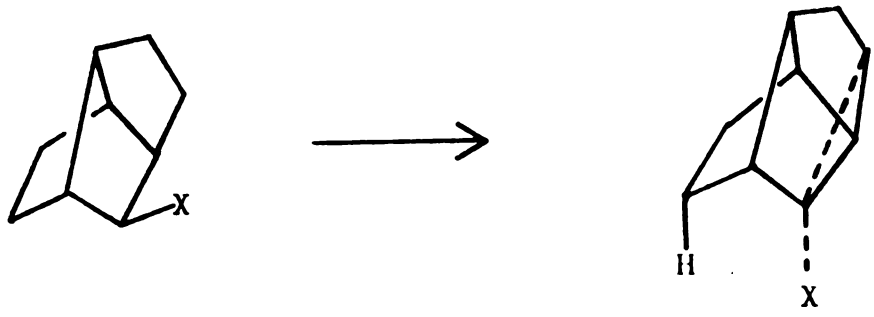
6a



6b

system 6a (k_H/k_D = .78) and the *endo*-6-trideuterio methyl system 6b (k_H/k_D = .74). This isotope effect is only revealed however when the kinetics are obtained as a function of temperature. The enthalpy contribution to the isotope effect is offset by a compensating entropy of activation. k_H/k_D values based on free energy are greater than 1.00 over the temperature range studied with one exception!

experiments have indicated that steric deceleration may play at least some role in the solvolysis of *endo* norbornyl derivatives.[1,17] An interesting tricyclic derivative of brexane 7a offers the opportunity to evaluate the relative



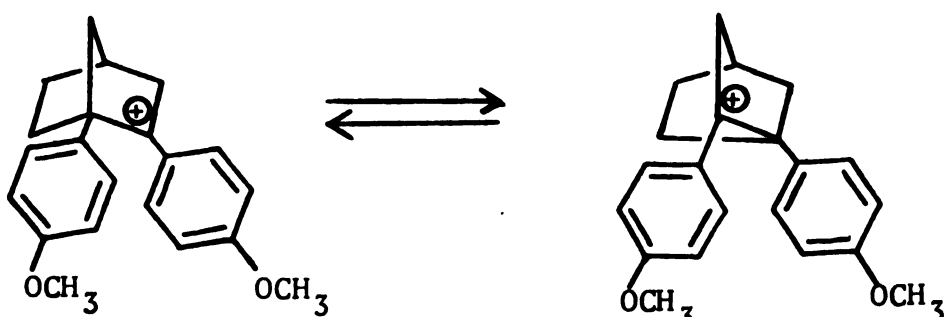
7a 7b

importance of anchimeric assistance or steric deceleration in the transition state for solvolysis of *exo* and *endo* norbornyl derivatives respectively.[5,18] This system is unique in that the leaving group X in 7b suffers similar tortional restraints and non-bonded interactions as does *endo*-norbornyl, while at the same time it is set up geometrically for anchimeric assistance as is *exo*-norbornyl. This compound was found to solvolyze at 66% of the rate of *exo*-norbornyl (or 33% of the rate of ionization of *exo*-norbornyl) or 225 times faster than *endo*-norbornyl.[5] A crude correlation of these results with the rate ratio observed with the parent norbornyl derivative leads to an estimate of 66% anchimeric assistance in *exo* norbornyl and

33% steric deceleration in *endo* norbornyl in the transition state for solvolyses of these compounds.*

If it is assumed that a carbonium ion in a medium which does not solvate positive charges very well is structurally identical to a carbonium ion formed in solvolytic media, then the results obtained from the study of carbonium ions in super acid has direct bearing on the nonclassical ion problem.

The direct observation of the rapidly equilibrating and presumably classical 1,2-dianisylnorbornyl cations 8a and 8b[19] supports the proposal of rapidly equilibrating



8a 8b

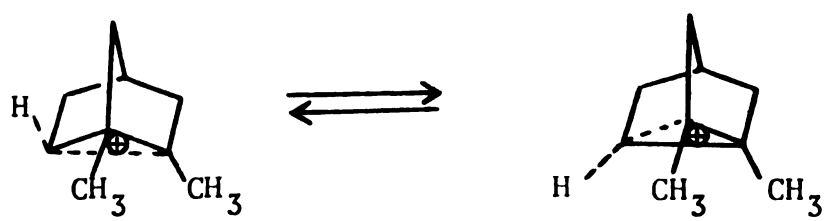
---

* Swartz has indicated that other factors may be contributing in part (or in total) to the observed rate of solvolysis of the 2-brexyl derivative 7a. For example, the slower rate of solvolysis of 2-brexyl relative to *exo*-norbornyl might in part be due to a poorer geometry for anchimeric assistance in the former case. It is also pointed out "that relative to *endo*-norbornyl the 2-brexyl compounds have *less* tortional relief of 1,2-eclipsing strain, *more* hindered backside solvation of the incipient ion and possible extra *endo* hindrance to ionization."[5]

---

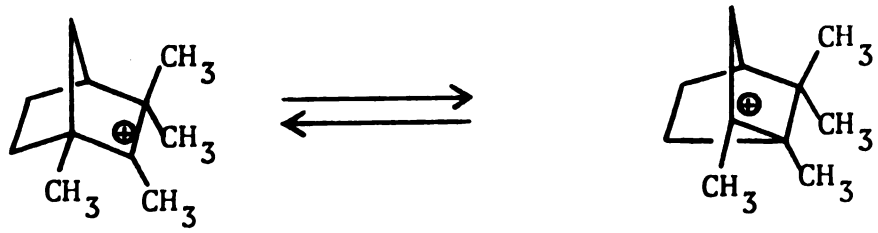
structures for norbornyl cations. Indeed the interconversion between 8a and 8b is rapid on an nmr time scale even at -70°C. It has been argued that the behavior of this cation is not unexpected. The carbonium ion center is greatly stabilized by the *p*-anisyl group and should not require σ delocalization.[20] This latter proposal has been rejected on the basis that absence of nonclassical character in this system would represent a loss of > 6 kcal/mole nonclassical resonance energy.[1] At the same time it was proposed that steric repulsion between the anisyl groups might inhibit nonclassical resonance, but that the steric problem should be absent in the 1,2-dimethylnorbornyl derivatives.[1]

The 1,2-dimethylnorbornyl cation is indeed a most interesting cation. It has been characterized as a partially C-6H σ delocalized equilibrating cation 9a and 9b on the



9a 9b

basis of a comparison of ^{13}C and ^{1}H nmr spectra with model compounds.[21] The equilibrium in a related system 10a and 10b has been observed directly and does not depend on the use of model compounds.[22] The equilibrium between 10a and



10a 10b

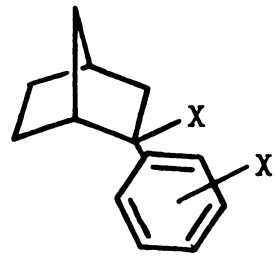
10b is fast on an nmr time scale even at -130°C but it is detected by the temperature dependence of the methyl resonances in these two cations of slightly different structure.[22] This observation lends support to the proposed equilibrium between 9a and 9b.

With the above examples of rapidly equilibrating cations in mind one might wonder if there is indeed a rapid equilibrium between 1a and 1b. The energy barrier to interconversion of 8a and 8b must be greater than it is for the interconversion of 9a and 9b as no broadening of the nmr resonances is observed even at -140°C in the latter case while broadening is observed at -70°C in the former case. Thus one might argue that the expected barrier to interconversion of 1a and 1b would be even lower than it is for 10a and 10b either on an electronic basis, a steric basis or both.

The cnmr and pnmr studies[23] of the parent norbornyl cation however indicate the presence of a species which cannot be accounted for by two rapidly equilibrating *classical*

structures. Further support for this conclusion comes from the photoelectron spectrum[24] of the norbornyl cation. On the basis of the above studies it was concluded that the norbornyl cation is best described as a symmetrical σ delocalized nonclassical ion 7.[23]

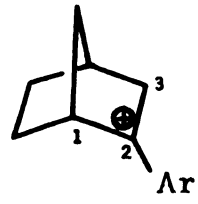
If one assumes for the moment that nonclassical character has been demonstrated for norbornyl cations then the following experiments reported by Brown and Takeuchi present a dilemma.[25,26a] They have correlated the rates of solvolysis of a number of 2-aryl-2-*exo*-norbornyl derivatives 11 with $\sigma^{\oplus}$ values.[25,26a] They found that the correlation was linear with none of the curvature expected if σ delocalization



11

were an important factor.[26a] One would expect that σ delocalization would alter the linear dependence of log k on $\sigma^{\oplus}$. It was pointed out that the studies were carried out over 60% of the reactivity range from *p*-anisyl-2-norbornyl to norbornyl without any indication of σ delocalization.[26a] These observations coupled with the observed *exo/endo* rate ratios led the authors to conclude

that participation if present in norbornyl cation cannot be large.[26a] It seems intuitively unreasonable to us that the norbornyl cation should be the only derivative of norbornane exhibiting charge leakage to C(1). Our primary goal was to try to resolve this inconsistency. Accordingly we have prepared a number of 2-aryl-2-norbornyl cations 12



12

in which the aryl group is varied so as to make increasing electron demands at the carbonium ion center which in turn makes increasing electron demands on the norbornyl skeleton especially at C(2) and C(3). The effect of increasing positive charge on the chemical shift of H(1) and H(3) is a shift to lower field for these protons.

On the basis of earlier work[10] our hypothesis was that a graph of the chemical shift of H(1) versus the chemical shift of H(3)* should be linear with increasing positive charge (Figure 1) provided there is no change in the mechanism for transmission of the charge to each of the sites under consideration. This can be stated in another way; the

---

* We have plotted the average shift of H(3) *exo* and H(3) *endo*.

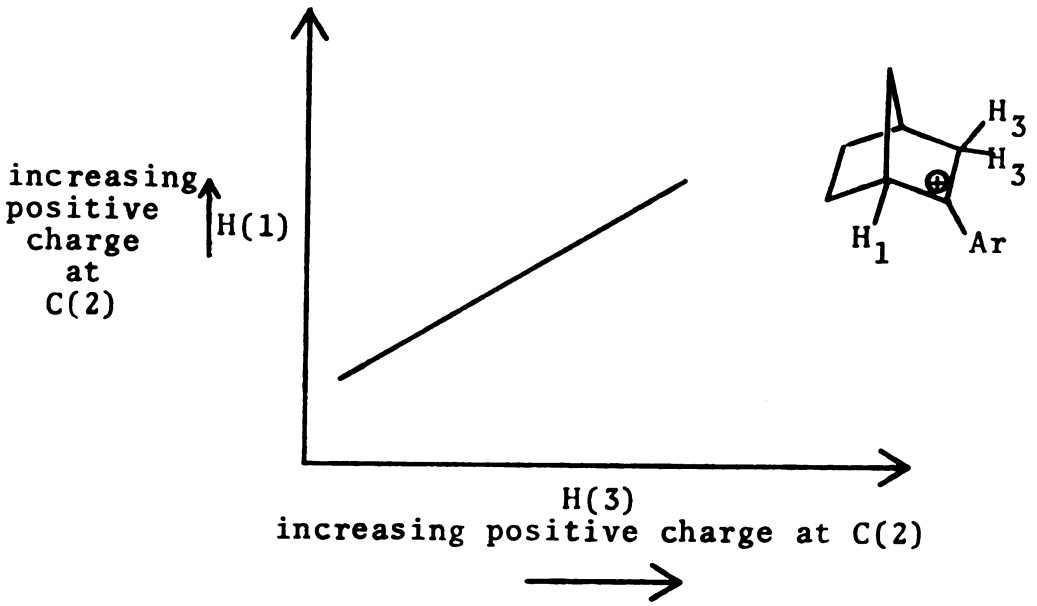


Figure 1. Graph of H(1) vs. H(3) for classical norbornyl cations with no charge leakage to C(1).

chemical shift difference between H(1) and H(3) will be constant for classical arylnorbornyl cations.

A deviation in the linear relationship between H(1) and H(3) will be observed if charge leakage to C(1) occurs by σ delocalization [13] or by a mechanism which alters the mode of charge transmission to C(1) relative to C(3) or *vice versa* (Figure 2). This can be stated differently; the chemical shift difference between H(1) and H(3) should increase relative to this same difference in a classical

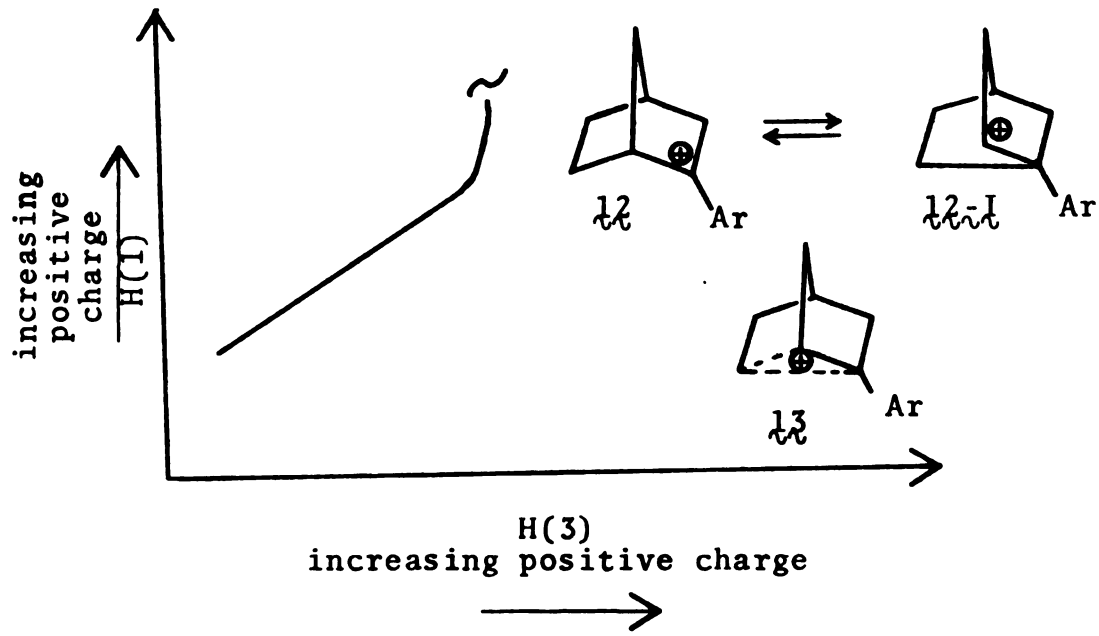
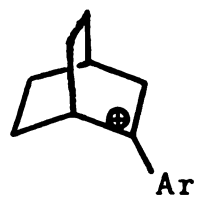


Figure 2. Graph of H(1) vs. H(3) for norbornyl cations with charge leakage to C(1).

cation if charge leakage to C(1) becomes an additional factor in the origin of these particular chemical shifts. Charge leakage to C(1) will have the effect of *increasing* the chemical shift of *H(1)* relative to its value in a classical cation while *decreasing* the chemical shift of *H(3)* relative to its value in a classical cation. Thus the chemical shift difference between H(1) and H(3) should increase.

In the interest of having a model system for comparison to 12 we have also examined the H(1) and H(3) chemical shifts in a corresponding series of 2-aryl-2-bicyclo[2.2.2]-octyl cations 14. This system is known to have less tendency

to exhibit those properties usually associated with σ



14

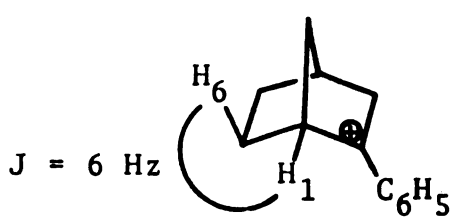
delocalization.[10] Thus a plot of H(1) vs. H(3) with increasing positive charge at C-2 should be linear or any nonlinearity observed should "lag behind"[10] any non-linearity observed for the arylnorbornyl systems 12.

RESULTS

General Discussion of Experimental Data in Tables 1 and 2

Standard procedures were used to prepare the cations for this study. The details are presented in the experimental section. The chemical shifts of the protons of interest i.e. H(1) and H(3) in cations 12 and 14 are listed in tables 1 and 2 respectively. The data were obtained at 100 MHz.

The chemical shift of proton H(1) in cation 12a is reported as a range of values τ 5.68-5.71 because this resonance appeared as a shoulder (actually the lower field portion of a broad doublet) of the methyl resonance of the *p*-methoxy group. That this assignment was correct was verified by decoupling experiments. It was reported previously that in 2-phenyl-2-norbornyl cation 12i, H(1) is coupled to H(6) *exo* with an unusually large coupling



12i

constant.[10] When 12a was irradiated in the region in which H(6) *exo* was expected to absorb the shoulder due to H(1)

Table 1. H(1) and H(3)[a] Chemical Shifts[b] in 2-Aryl-2-norbornyl Cations[c]

Cations 12	Aryl Group	H(1)	H(3)	Δν(Hz)[c]
a[e]	*p*-$CH_3OC_6H_4$	5.68-5.71	6.72	br s[d]
b	*p*-HOC_6H_4	5.64	5.59	br s[d]
c	3,4-$(CH_3)_2$-C_6H_3	5.34	6.48	9
d	*p*-$CH_3C_6H_4$	5.32	6.46	10
e	*p*-FC_6H_4	5.27	6.42	11
f	*p*-ClC_6H_4	5.22	6.38	14
g	*p*-BrC_6H_4	5.22	6.47	19
h	*p*-IC_6H_4	5.25	6.63	28
i[f]	C_6H_5	5.17	6.34	14
j	*m*-BrC_6H_4	5.09	6.32	16
k	*m*-ClC_6H_4	5.08	6.32	17
l	*p*-$CF_3C_6H_4$	4.93	6.25	22
m	3,5-$(CF_3)_2C_6H_3$	4.75	6.20	26
n	3,5-$(Cl)_2$-4-$\overset{\oplus}{N}(CD_3)_2H$	4.63	6.34	-
p	3,5$(Cl)_2$-4-CN			

[a]Average chemical shift of H(3) *exo* and H(3) *endo*.

[b]τ values relative to internal standard of tetramethylammonium tetrafluoroborate (τ 6.87)[26b] (100 MHz).

[c]Determined at -60°C unless otherwise indicated (H(3)*exo*-H(3)*endo*).

[d]Center of H(3) *exo*, H(3) *endo* multiplet.

[e]12a (30°), 2n (-100°).

[f]Literature values.

Table 2. H(1) and H(3) Chemical Shifts[a] in 2-Aryl-2-bicyclo[2.2.2]octyl Cations[b]

Cations 14	Aryl Group	H(1)	H(3)
a	*p*-$CH_3OC_6H_4$	6.03	6.42
b	3,4-$(CH_3)_2C_6H_3$	5.75	6.17
c	*p*-$CH_3C_6H_4$	5.74	6.15
d	*p*-FC_6H_4	5.68	6.09
e	*p*-ClC_6H_4	5.66	6.09
f	*p*-BrC_6H_4	5.65	6.19
g	*p*-IC_6H_4	5.66	6.36
h[c]	C_6H_5	5.57	6.02
i	*m*-BrC_6H_4	5.53	5.96
j	*m*-ClC_6H_4	5.52	5.95
k[d]	*p*-$CF_3C_6H_4$	5.33	5.83
l	3,5-$(CF_3)_2$-C_6H_3	5.15-5.29	5.78

[a] τ values relative to internal standard of tetramethylammonium tetrafluoroborate (τ 6.87).[26b]

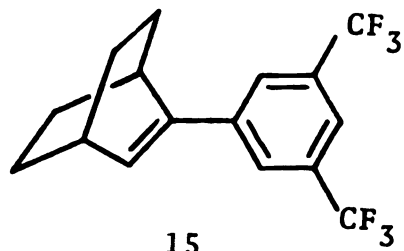
[b] Determined at -60°C unless otherwise indicated.

[c] Literature values.

[d] 14k (-80°C).

collapsed under the *p*-CH_3O resonance thereby confirming the assignment. The range τ 5.68-5.71 is the limit over which the center of the H(1) resonance should be found.

The chemical shift of H(1) in cation 14l is also reported as a range of values albeit for a completely different reason. Careful ionization of olefin 15 in FSO_3H/SO_2ClF to which was



15

added SbF_5 (to insure complete ionization) at -120°C gave a mixture of cations as noted by the nmr spectrum at -100°C. Since the cation of interest was a minor component of the mixture identification of H(1) was not possible. However the range of τ values in which H(1) should absorb is reported. The broad singlet (2H) for H(3) in 14l (τ 5.78) could be identified.

The observation that a mixture of cations results on ionization of 15 has led us to make a thorough study of the equilibration that occurs among certain aryl bicyclooctyl cation isomers. We have reported these results elsewhere.[27]

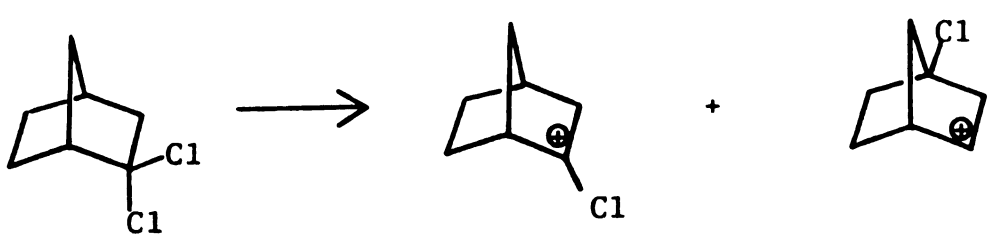
All chemical shifts are reported at -60°C for cations 12 and 14 with the exceptions of cations 12i, 14h, (literature values[10]) 12a, 12n and 14k.

The chemical shifts of cation 12a mentioned above are reported at -30°C. This was due to the fact that at this temperature H(1) is better resolved from the *p*-CH_3O resonance. At -60°C resolution of H(1) is quite poor, because of viscosity broadening by FSO_3H.

The chemical shifts of cation 14k are reported at -90°C, since at -60°C, this cation is rapidly converted to a mixture of cations in which 14k is a minor component.[27] The activation energy for rearrangement of 14l is less than it is for cation 14k. Thus we were able to determine its chemical shifts prior to rearrangement.

Cation 12n undergoes a rapid Wagner-Meerwein, 6,2-hydride shift,[28] [29] Wagner-Meerwein rearrangement. At -60°C the H(1) and H(3) resonances are broadened due to averaging with other protons in the system. This interesting rearrangement will be discussed in detail in a later section.

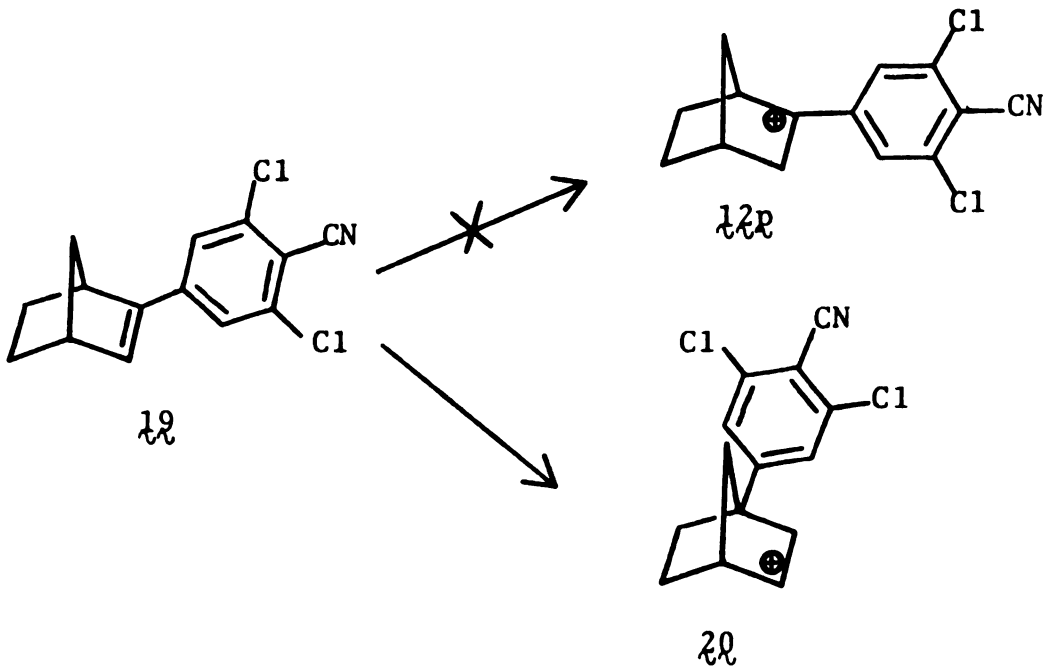
It has been reported that under some conditions of ionization 2,2-dichloronorbornane 16 yields a mixture



16 17 18

of both 2-chloronorbornyl cation 17 and protonated 4-chloro-2-norbornyl cation 18.[30] We have never been able to observe

cation 12p. Ionization of olefin 19 in $FSO_3H/SbF_5/SO_2ClF$



even at temperatures lower than -100°C produced cation 20. This assignment was based on a comparison of the nmr spectrum of 20 with that reported for 18 and the 2-norbornyl cation 2 (Table 3).[30]

Table 3. Proton Chemical Shifts (τ values) in Related 2-Norbornyl Cations

Cation	H(1), H(2) H_6 *exo*, H_6 *endo*	H(3), H(5) H(7)	H(4)	Ar
18[a]	4.70	7.58		
2[a]	4.65	7.80	6.85	
20[b]	4.62	7.52		2.14

[a]Chemical shift relative to capillary tetramethylsilane.

[b]Chemical shift relative to internal tetramethylammonium tetrafluoroborate.

There is a broad singlet (2H) at 2.14 which is assigned to the two aromatic protons.* There is another broad singlet (4H) at lower field which is assigned to H(1), H(2), H(6) *exo* and H(6) *endo*. These protons are equivalent as a result of a rapid 6,1,2-hydride shift.[30] As a result of this same rearrangement H_3, H_5 and H_7 are also equivalent. Thus this spectrum is consistent with the assigned structure and analogous to those of 18 and 2 which have already been characterized.[30]

Since we found it necessary to report some of the data at temperatures other than -60°C and since the chemical shift difference between H(1) and H(3) for 12 and 14 is important to the interpretation of our data we determined the change in these chemical shifts over a 100°C temperature range (-60° to +40°). These data are reported in Table 4.

---

* We do not know for certain if the -CN group in 20 is protonated. The chemical shift of the aromatic protons in 20 is .51 ppm to lower field compared to the aromatic protons in olefin 19 and .21 ppm to lower field compared to the corresponding 2-aryl-2-*endo*-norbornanol. Olah and coworkers have reported that alkyl nitriles are completely protonated in $FSO_3H/SbF_5/SO_2$.[31] This report coupled with the shift of the aromatic protons to lower field compared to starting materials suggests that the CN group is protonated.

Table 4. The Effect of a 100°C Temperature Difference (-60° to +40°) on the Chemical Shifts of H(1) and H(3) in 12.

Cation	H(1) (-60°)	H(3)[a] (-60°)	H(1) (+40°)	H(3)[a] (+40°)	ΔH(1)[b]	ΔH(3)[c]
12a	-	6.75	-	6.72	-	3
12d	5.33	6.46	5.37	6.51	4	5
12e	5.27	6.42	5.32	6.47	5	5
12f	5.22	6.41	5.28	6.46	6	5
12g	5.22	6.47	5.29	6.54	7	7
12h	5.25	5.63	5.31	6.70	6	7
12i	5.16	6.35	5.19	6.39	3	4

[a]Average chemical shift of H(3) *exo* and H(3) *endo*.

[b]H(1) (+40°) - H(1) (-60°) (value in Hz).

[c]H(3) (+40°) - H(3) (-60°) (value in Hz).

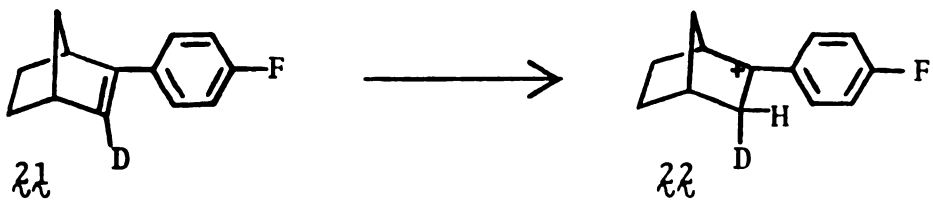
There is a distinct shift to higher field for protons H(1) and H(3) in every cation in Table 3 when the temperature is raised 100°C. The explanation for this observation is not clear. What is clear however is that this effect is operating to the same magnitude and in the same direction (i.e. higher field with increasing temperature) for both H(1) and H(3). Thus the chemical shift difference between protons H(1) and H(3) is constant over a wide temperature range and our interpretation of the data in Table 1 should not be significantly affected by any temperature variation. It is interesting nevertheless that the magnitude of this effect is variable from one cation to another. We will return to this point when we discuss the *p*-halogen cations.

A noteable observation concerns the multiplicity of the resonance due to the H(3) *exo* and H(3) *endo* proton in cation 12. As mentioned earlier we reported the average chemical shift here since an AB quartet having a variable chemical shift difference is observed. For example in cation 12a and 12b the H(3) *exo* and H(3) *endo* protons give a broad singlet in the nmr spectrum. However in all the other cations of the aryl norbornyl series the H(3) *endo* proton is the lower field component of an AB quartet having a chemical shift difference dependent upon the magnitude of

the positive charge at C(2)* (except for cations 12f, 12g and 12h which will be discussed). As more potent electron withdrawing aryl groups are placed at C(2), the magnitude of the chemical shift difference $\Delta\nu$ between H(3) *exo* and H(3) *endo* increases as shown in Table 1.**

---

* We would like to correct several chemical shifts reported earlier for 2-phenyl-2-norbornyl cation.[10] H(3) *exo* and H(3) *endo* should be interchanged. This is based on the observation that in the nmr spectrum of cation 22 produced from partially deuterated olefin 21 the higher

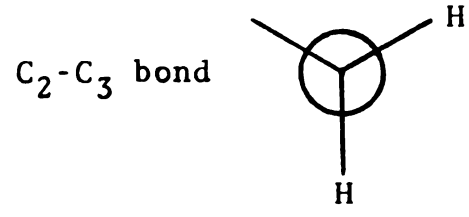


field portion of the AB quartet due to H(3) *exo* and H(3) *endo* has collapsed and is of greater intensity than the lower field component of the quartet. Assuming *exo* protonation by FSO_3H H(3) *endo* must be at lower field. In extending this assignment to the other cations in series 12 (except 12f, 12g and 12h which we are not assigning) it is assumed that no factors are operating that would interchange H(3) *exo* and H(3) *endo*.

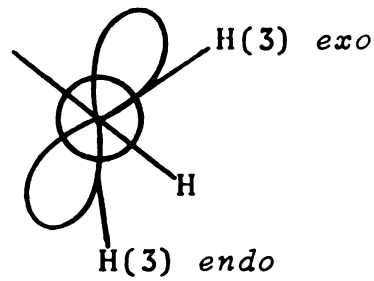
Proton H(6) *endo* should also be interchanged with an H(5) proton in cation 12i.[10] This reassignment is based on decoupling and DISST experiments (to be described), in cation 12l. We assume that these assignments will hold for 2-phenyl-2-norbornyl cation.

** We will show later that this effect is independent of charge leakage to C(1).

A possible explanation for the selective deshielding of H(3) *endo* (or shielding of H(3) *exo*) might be due to selective hyperconjugation of H(3) *endo* over H(3) *exo* with the p orbital at the carbonium ion center. Models indicate however that introduction of an sp^2 center into a perfectly eclipsed norbornane 23 leads to a cation 24 in which the *p*-orbital is symmetrically disposed with respect to these



23



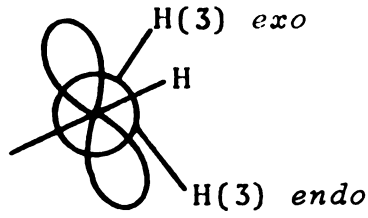
24

two protons. It is difficult in this case to see why H(3) *endo* should be affected differently than H(3) *exo* by a variable positive charge of C(2).

Twisting the cation causes the six-membered ring to approach a twist boat conformation. In cyclohexane the twist boat is an energy minimum with respect to the boat conformation.[32] In fact X-Ray diffraction studies and calculated conformations for a number of 2-substituted norbornanes indicate that these molecules are twisted. Thus there is at least a possibility that the cations 12 are also twisted.[33]

Counterclockwise rotation around the C_2-C_3 bond in 24 has the effect of aligning the p-orbital at C-2 with

H(3) *endo* while its relation to H(3) *exo* approaches an orthogonal one 25. Thus in the counterclockwise twisted



25

cation there is a greater potential for interaction of the p-orbital at C(2) with H(3) *endo*.

Whether or not relief of eclipsing interactions would actually warrant twisting is speculative at best, especially since there does not seem to be any reason to prefer the counterclockwise twisted ion over the clockwise twisted ion.*

It seems likely that some other factor is responsible for the observed variation in $\Delta\nu$ for H(3) *exo* and H(3) *endo* in cations 12. One possible explanation might be due to the effect of solvation. As charge builds up at C(2) there should be a tighter association of the cation center with the solvent. This could have the net effect of shielding H(3) *exo* relative to H(3) *endo*.[34]

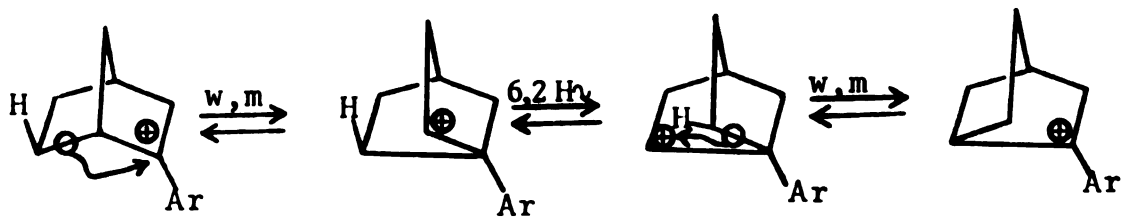
---

* In fact, since *exo* H migrates faster than *endo* H in the 3,2-shift, there is reason to prefer the other conformation.

Hydride Shifts in 2-Aryl-2-norbornyl Cations

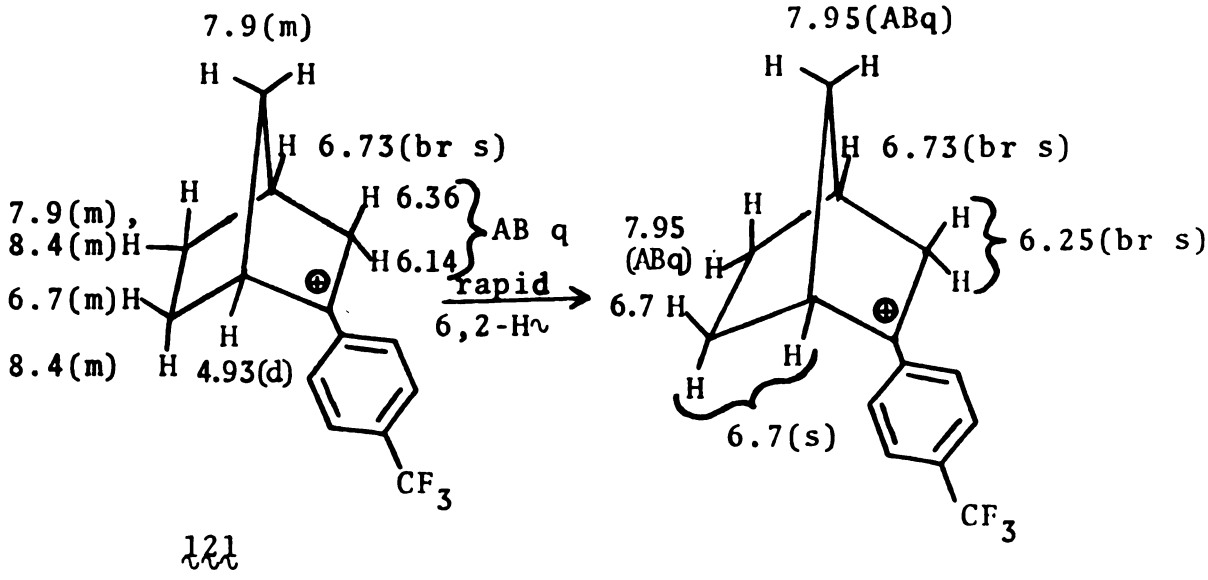
One of the most interesting phenomena encountered in this study concerns the Wagner-Meerwein, 6,2-hydride shift, Wagner-Meerwein rearrangement which we have observed for a number of cations in the norbornyl series 12. This rearrangement is formally depicted in Scheme 1, and it is

Scheme 1



12 12-I

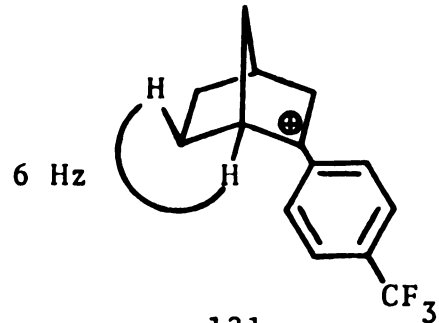
degenerate. A considerable simplification of the nmr spectrum is observed because of the symmetrization which is imposed when the hydride shift in 12-I is rapid on an nmr time scale as shown below for cation 121. The complicated multiplets at higher field for protons on C(5) and C(7) collapse to an AB quartet centered at 7.95, while the aromatic protons and H(4) remain invariant. The H(3) *exo* and H(3) *endo* AB quartet collapses to a singlet.



121

H(6) *endo* and H(1) average to a singlet with the same chemical shift as H(6) *exo*. Thus it was not possible to tell whether H(6) *endo*, H(1) and H(6) *exo* were all exchanging or if only H(6) *endo* and H(1) were exchanging while H(6) *exo* was remaining invariant. We were able to distinguish between those two possibilities by using The Double Irradiation Spin Saturation Transfer (DISST) Technique that was applied recently by Sorensen, Huang and Ranganayakulu to methyl substituted norbornyl cations.[35]

The success of the DISST technique depends upon the half-life for chemical exchange being shorter than the half-life for proton relaxation. At -10°C the coupling of H(6) *exo* to H(1) in cation 121 is nearly wiped out as a



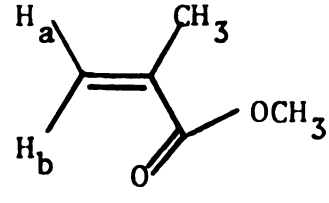
121

result of the onset of chemical exchange. If H(1) is irradiated at this temperature (exchange is slow), the two proton multiplet at highest field decreases by 25% (or 50% of the integrated intensity of H(6) *endo*).* The integral in the region in which H(6) *exo* and H(4) absorb is *increased*[36] by 25% which corresponds to an increase of approximately 50% for H(6) *exo*! Presumably this represents an increase in the intensity of H(6) *exo* rather than H(4). Thus H(6) *exo* is not exchanging with H(1) or H(6) *endo*. H(6) *exo* also increases in intensity by 45-50% on irradiation of H(6) *endo* in the absence of chemical exchange. This is a large positive Nuclear Overhauser Effect. 50% is the maximum enhancement for protons that is predicted from theory.[36]

---

* This observation allows us to assign the chemical shift of H(6) *endo* - see footnote, p. 24.

A recent review[36a] cites many examples of chemical systems in which the Nuclear Overhauser Effect (NOE) has been observed. However there were no cases of molecules cited having geminal methylene groups exhibiting an NOE enhancement. This may simply be a result of a practical problem. A substantial chemical shift difference between the observed and irradiated protons (25 Hz)[36b] is necessary for a successful determination of an NOE enhancement. In most structures having geminal methylene protons the chemical shift difference between these protons is generally small. In 2-substituted norbornyl cations however the chemical shift difference between the geminal protons at C(6) can be substantial. For example in cation 121 the difference between H(6) *exo* and H(6) *endo* is 170 Hz. The closest analogues reported in the literature are structures having geminal methylidene protons. In these cases the protons are also very close together (in space as are geminal methylene protons) and the NOE enhancements are large. For example in methyl methacrylate 28 irradiation of H(a) gives rise to a 48% increase in the integrated intensity of H(b).[37]

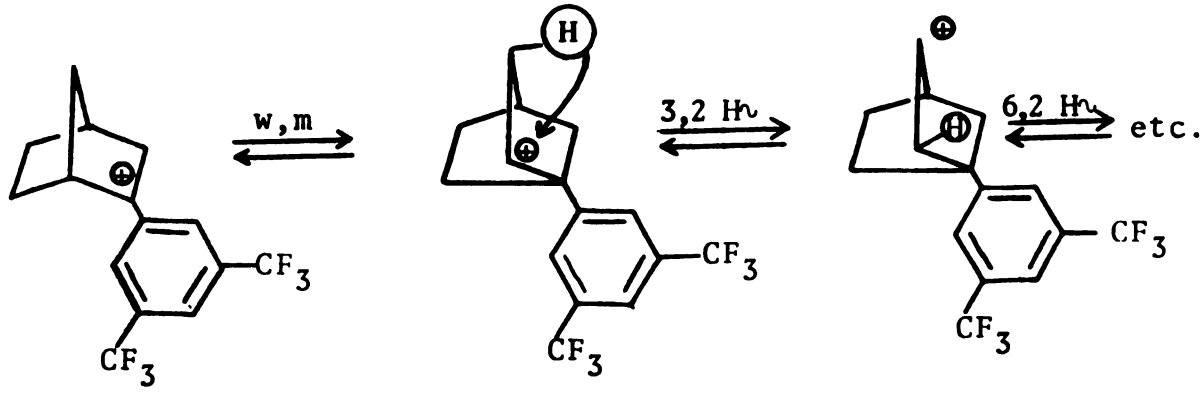


28

Table 5 summarizes the approximate coalescence temperatures for 6,2 Hν in several cations. Cation 12p presumably would have a 6,2 Hν with a temperature dependence which parallels norbornyl cation.[29]

We also list in Table 5 the temperature for which we observe the onset of a second reversible process. We believe that this broadening is a result of a 3,2-hydride shift completely analogous to the 3,2 Hν in norbornyl cation.[38] The cations decompose however before this process results in complete coalescence.

Cation 12m, already undergoing rapid 6,2 Hν at +69°, undergoes further changes due to a 3,2 Hν. The AB quartet due to protons on C_5 and C_7 collapses to a very broad signal



12m 12m-I 12m-II

(58 Hz - width at half height). At lower field the signals due to protons on C_1, C_3, C_4 and C_6 collapse to a broad singlet also. This process is reversible. The expected

Table 5. Data on Hydride Shifts in 12 at 100 MHz

Cation	6,2 Hν[a]	3,2 Hν
12i	+40°	-
12k	+80°	-
12l	+20	+60°[b]
12m	-40°	+70°[c]
12n	-40°-0°	+30 to +40°[b]
12p	<-80°	-

[a]Approximately lowest temperature for which complete coalescence is observed as a result of 6,2 Hν.

[b]Temperature at which broadening is observed as a result of 3,2 Hν.

[c]See text.

singlet which would result from total exchange of all protons in the system is not observed since the sample decomposes.

DISCUSSION

Figures 3 and 4 contain in graphic form the information presented in Tables 1 and 2 respectively. Before discussing the meaning of the data we will first note several features wich are apparent from the graphs. First the ordering of the points in general follows the $\sigma^{\oplus}$ values for these substituents.[39] A strong electron releasing group places relatively little positive charge at C(2); hence the nmr chemical shifts of protons H(1) and H(3) occur at relatively high field while a strong electron withdrawing group places relatively more positive charge at C(2); hence the nmr chemical shifts of H(1) and H(3) occur at relatively lower field. There are several exceptions to this trend which are noteworthy. For example in the arylnorbornyl series of cations (Figure 3) a *p*-methoxy substituent stabilizes a positive charge better than a *p*-hydroxy group. This is opposite to what would be expected on the basis of $\sigma^{\oplus}$ values.[39] One possible explanation involves a rapid protonation equilibrium between cations 12b and 12b-I. Since it would be expected that 12b-I would have H(1)

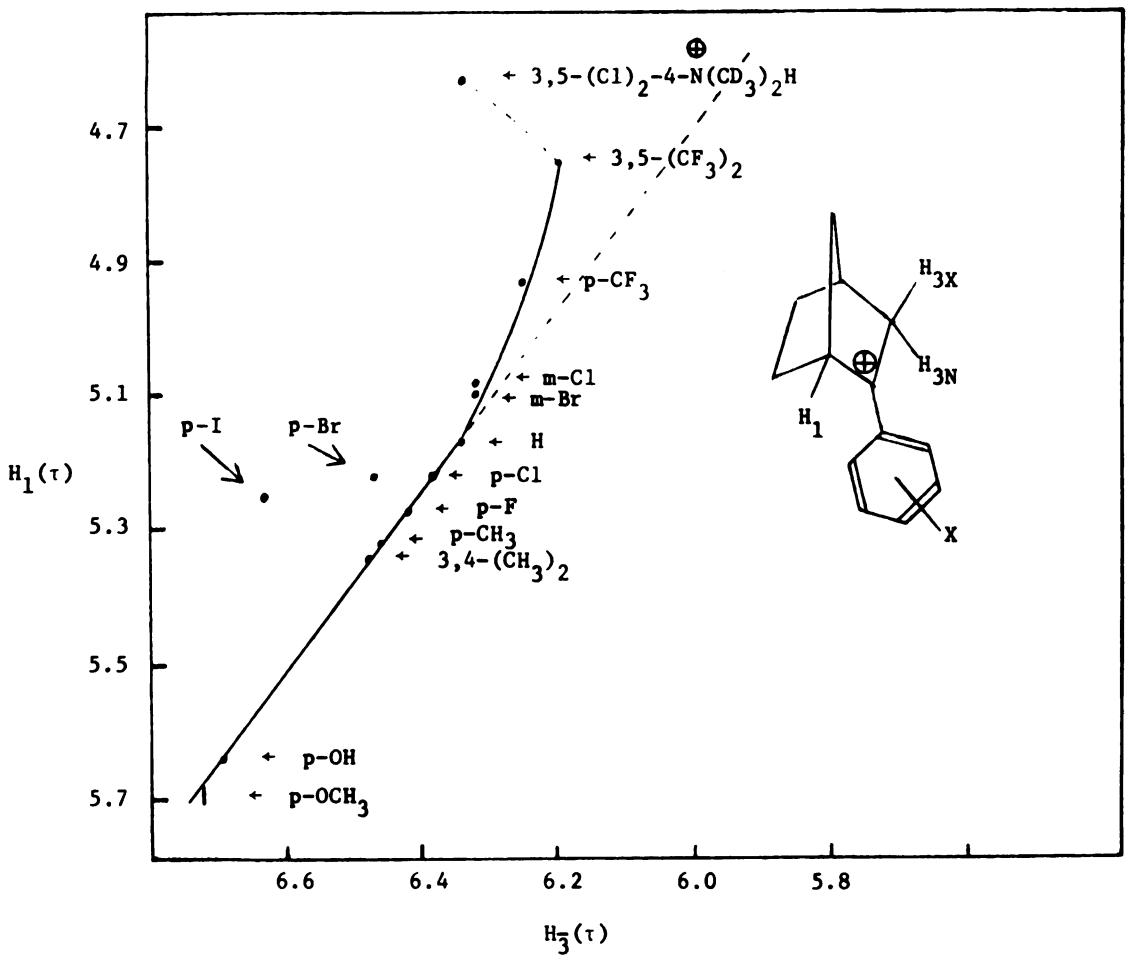


Figure 3. Graph of H(1) vs. H(3) chemical shifts in 2-aryl-2-norbornyl cations 12.

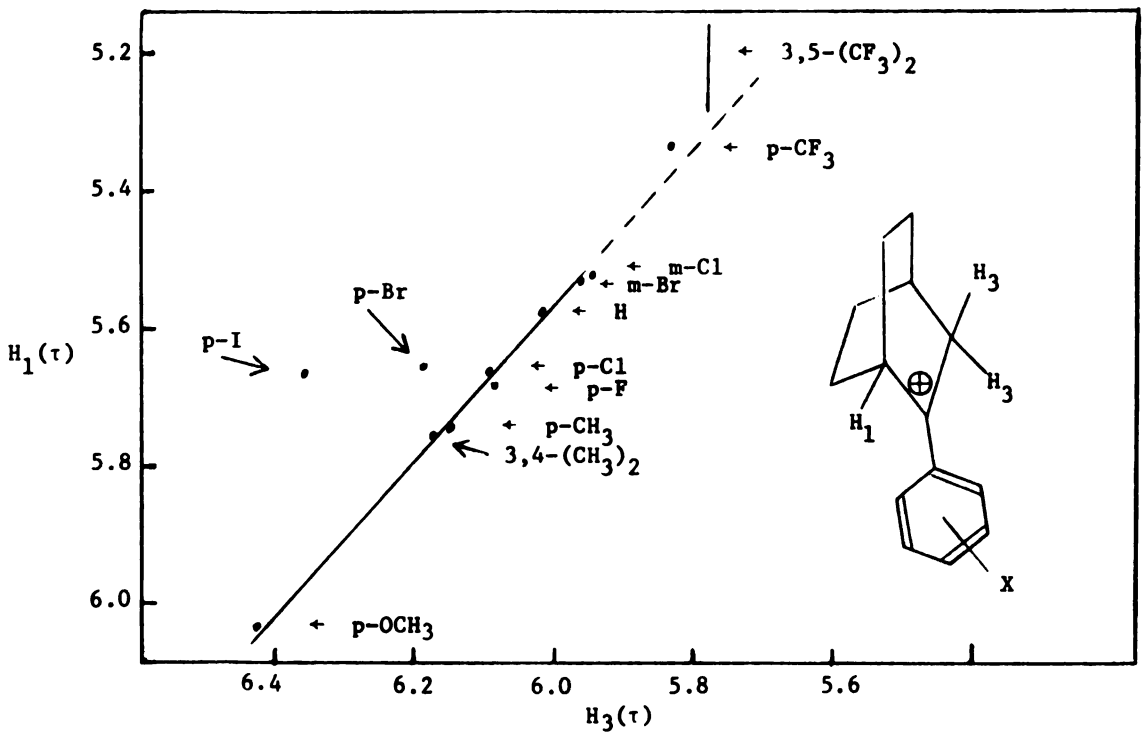
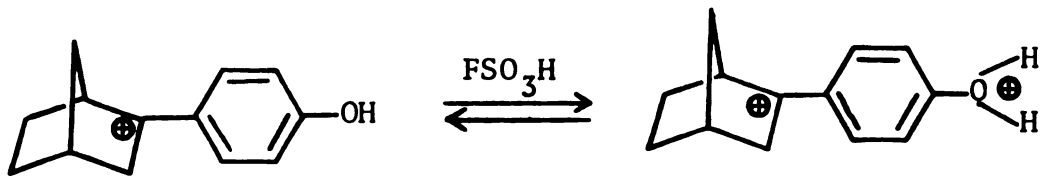


Figure 4. Graph of H(1) vs. H(3) chemical shifts in 2-aryl-2-bicyclo[2.2.2]octyl cations 14.



12b 12b-I

and H(3) chemical shifts at considerably lower field than 12b, the averaging due to the rapid equilibrium would cause the *observed* values of H(1) and H(3) for 12b to be at lower field than expected.* This argument will hold as long as the extent of protonation of cation 12b is greater than it is for 12a. It is not at all clear however why this should be the case.

A second possible explanation for the above observations lies in the origin of the $\sigma^{\oplus}$ values. Brown and Okamoto[39] have reported $\sigma^{\oplus}$ values for *p*-HO and *p*-CH_3O substituents

---

* The chemical shift difference between H(1) and H(3) in the averaged cation should be the same as that difference in cation 12b (as long as charge leakage to C(1) is not extensive in the other component of the equilibrium i.e. cation 12b-I). The net effect would be a displacement of the point for *p*-HOC_6H_4 - derivative to lower field along the straight line position of the curve shown in Figure 3.

---

which they have calculated from the data of various reactions. These results are shown in Table 6.

Table 6. $\sigma^{\oplus}$ Values Calculated From Various Reactions[39]

Reaction	A[a]	B[b]	C[c]
ρ	-12.14	-4.32	-3.44
p-HO	- .969	- .933	- .833
p-CH_3O	- .826	- .736	- .721

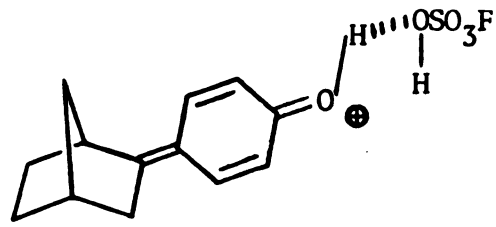
[a]Uncatalyzed bromination of aromatic derivatives in acetic acid at 25°C.[40]

[b]Protonolysis of substituted triphenylmethylsilanes by perchloric acid in aqueous methanol at 51.2°.[41]

[c]Ionization of triphenylcarbinols in aqueous sulfuric acid.[42,43]

In the case of reaction A it has been postulated that the observed substituent effects simply reflect more effective hyperconjugation by H versus CH_3.[40] On the other hand to explain the results in reaction B Earborn has claimed that equally important to any hyperconjugative effect would be a hydrogen bonding interaction between

solvent and hydroxyl group in determining the relative $\sigma^{\oplus}$ values for *p*-HO and *p*-CH_3O.[41] An explanation of our result based on solvent effects would indicate that in 12b



12b

weakening of the protonated oxygen-hydrogen bond by the weak base FSO_3H would be much less important than it would be for solvents used in the determination of $\sigma^{\oplus}$ values in Table 6. Thus there might be a reversal of these two $\sigma^{\oplus}$ values in FSO_3H.

A curved line* in the case of Figure 3 and a straight line in the case of Figure 4 satisfactorily accommodate the bulk of data in Tables 1 and 2 respectively. There is some unusual effect which is present in the case of the

---

* We have not included the point for 12n in the curve. Since the chemical shift of H(3) is not known with complete certainty. Labeling experiments are necessary to verify this assignment. The present assignment is based on the fact that at -100°C the 6,2 Hν in 12n is slow on an nmr time scale, but H(3) *exo*, H(3) *endo* and H(6) *exo* are undistinguishable. At higher temperatures a broad singlet is formed at τ 6.34 before H(1) (and presumably H(6)*endo*) coalesce to a broad singlet in the same region of the spectrum. This singlet is probably due to the averaged H(3) *exo* and H(3) *endo* protons.

p-halogen substituted cations however which causes those points to fall "off the line" in *both* the aryl norbornyl and arylbicyclooctyl series. We can estimate from $\sigma^{\oplus}$ values that the *p*-halogen derivatives should fall between phenyl ($\sigma^{\oplus} = 0$)[39] and *m*-bromo ($\sigma^{\oplus} = .405$).[39] and would have H(1) and H(3) chemical shifts at about τ 5.12 and τ 5.32 respectively. The approximate chemical shift differences between observed and expected values are shown in Table 7* along with the chemical shift differences between H(3) *exo*

Table 7. Chemical Shift Deviations in *p*-Halogen Cations

p-Halogen	σ^{+} [a]	ΔH_1 (Hz)[b]	ΔH_3 (Hz)[c]	$\Delta\nu$[d]
p-Cl (12f)	.114	9Hz	5 Hz	14 Hz
p-Br (12g)	.150	9Hz	15 Hz	19 Hz
p-I (12h)	.135	12Hz	31 Hz	28 Hz

[a]Values from Ref. 39.

[b]τ H(1) observed - τ H(1) expected.

[c]τ H(3) observed - τ H(3) expected.

[d]Chemical shift difference between H(3) *exo* and H(3) *endo*.

---

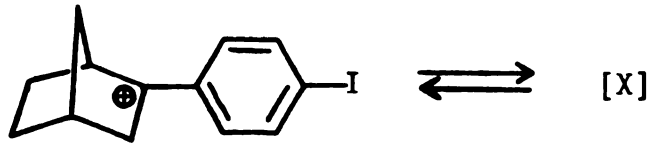
* The chemical shift difference between observed and expected values for H(1) and H(3) in the *p*-halogen bicyclooctyl analogues is of about the same magnitude as it is for the norbornyl series. For simplicity only the norbornyl derivatives are discussed.

---

and H(3) *endo*. While H(1) is relatively constant, H(3) is variable and in the case of the *p*-iodo derivatives the magnitude is rather dramatic. H(3) is shifted to higher field approximately 31 Hz. We have also included the chemical shift difference between H(3) *exo* and H(3) *endo* ($\Delta\nu$) to point out further that there is some unusual effect operating in the *p*-halogen derivatives. We pointed out earlier that $\Delta\nu$ increased with increasing positive charge at C(2). A comparison of the *p*-halogen derivatives with the other data given in Table 1 indicates that for *p*-Br and *p*-I $\Delta\nu$ is larger than expected. This does not mean that there is more positive charge at C-2 in these ions, since the chemical shifts for H(1) and H(3) are at higher field than expected.

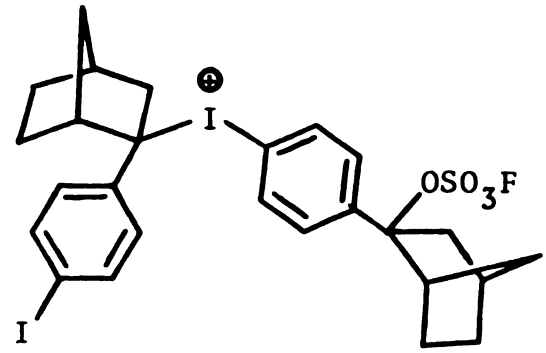
It also should be pointed out that the general features of the *p*-halogen cation nmr spectra are typical of other 2-aryl-2-norbornyl cations. We noted earlier (p. 22) that the temperature effects on chemical shifts in cations 12f, 12g and 12h were larger than for the other derivatives studied.

While we have not discovered the nature of the effect causing the deviations observed in the *p*-halogen cations, the above observations point to a temperature dependent equilibrium which favors the *p*-halogen cation (or its nmr equivalent). The other species [X] in the equilibrium in the case of 12h for example should have the effect of



12h

decreasing charge at C(2) so that H(1) and H(3) appear at higher field than expected while at the same time $\Delta\nu$ should be larger than expected on the basis of $\sigma^{\oplus}$ values and the trend set for $\Delta\nu$ by the other cations in Table 1. Furthermore the equilibrium contribution of [X] should be much less important for the *meta*-halogen derivatives.* A possible structure for [X] (though not a very satisfying one) is the "trapped dimer" 29. We have investigated this possibility



29

by a dilution study. The following concentrations of 2-*p*-iodophenyl-2-*endo*-norbornanol were dissolved in 1 ml of FSO_3H; 150 mg, 30 mg, and 3 mg. The nmr spectrum of

---

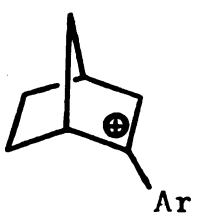
* *Meta*-halogen derivatives in both series 12 and 14 cannot be largely different from their true values. (See Figures 3 and 4).

---

each of these solutions was obtained at -20°C and a comparison of H(1) and H(3) chemical shifts was made. There were no detectable chemical shift differences between the 150 mg and 30 mg solutions. The time averaged nmr spectrum of the 3 mg/ml solution showed H(1) and H(3) shifted to lower field by about 2 Hz. This result is certainly not conclusive. A more dramatic effect on H(3) as compared to H(1) would have been expected. More dilute solutions were not studied as the limits of the instrumentation available have been reached.

Deno has calculated $\sigma^{\oplus}$ values for a number of substituents from four independent reaction series and he has noted that $\sigma^{\oplus}$ values calculated for *p-halogens* do not show good agreement.[43] Thus unusual behavior for *p*-halogen derivatives is not unique for the arylnorbornyl and aryl-bicyclooctyl cations.

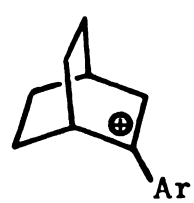
It was pointed out in the introduction that charge leakage to C(1) would be detectable in a series of 2-aryl-2-norbornyl cations 12 by nonlinear behavior in a graph of



12

H(1) vs. H(3) chemical shifts. Figure 3 illustrates just this relationship. The fractional distribution of charge at C(2) remains constant from 2-*p*-methoxyphenyl through 2-phenylnorbornyl cation.* Substituents more electron withdrawing than phenyl however lead to a "break" in the linear relationship between H(1) and H(3). This effect is rather dramatic in the case of cations 12l and 12m. For H(1) chemical shifts of 4.93 and 4.75, the H(3) chemical shifts should be within ½ Hz in each case of the straight line. They are off the line by 8 Hz and 17 Hz respectively!

By contrast the behavior of H(1) and H(3) chemical shifts in 2-aryl-2-bicyclooctyl cations 14 with increasing positive charge is linear from *p*-methoxyphenyl through



14

---

* We have made a least squares fit of this portion of the data (except cations 12a, 12g and 12h). For a given value of H(1), H(3) was fitted by a least squares method. The standard deviation for 6 points was ½ Hz. The slope was .74

---

meta-chlorophenyl. With cation 14k it seems likely that we are observing the onset of charge leakage to C(1). This effect is not nearly so dramatic in this case as it is in the norbornyl system. H(1) at τ 5.33 should have H(3) within 1 Hz of the line.* H(3) is 4 Hz from the line. Due to the uncertainty in the H(1) chemical shift of 14l, the data do not permit any further conclusion concerning the electronic structure of these cations.

Could the "break in the line" in Figure 3 be associated with any other factor besides charge leakage to C(1)? In particular could the break be associated with the curious behavior of H(3) *exo* and H(3) *endo* with increasing positive charge. The onset of a detectable chemical shift difference between these two protons occurs before cation 13c ($\Delta\nu$ = 9 Hz), well before any nonlinearity is observed so that it does not seem reasonable that the "break" should be attributable to this effect.

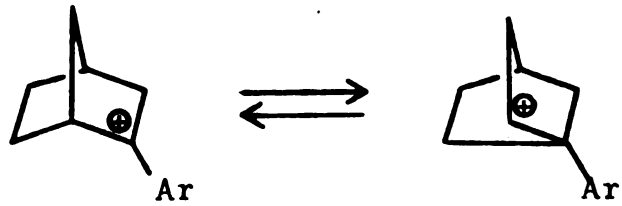
There is some possibility that the break may be due to an anisotropy effect of the phenyl ring whereby the phenyl rotates slightly as charge increases at C(2), perhaps as a result of some better orientation of solvent. If this is the case this effect in the 2-aryl-2-bicyclooctyl systems fortuitously lags behind the effect in the 2-aryl-2-norbornyl cation.

---

* A least squares fit of the points for cations 14a, 14b, 14c, 14d, 14e and 14h has a slope of .87. The deviation of these points is 1 Hz.

Having established that the nonlinearity in Figure 3 can be associated with charge leakage to C(1), what is the mechanism by which this occurs? The following two possibilities have already been presented:

(1) Rapidly equilibrating classical cations 12 and 12-I



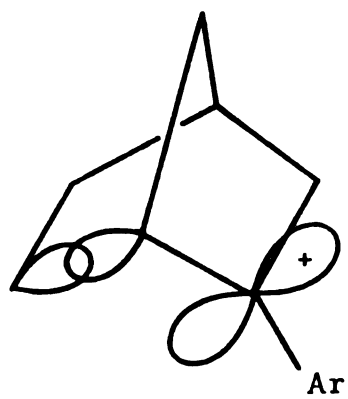
12 12-I

(2) A σ delocalized ion 13

13

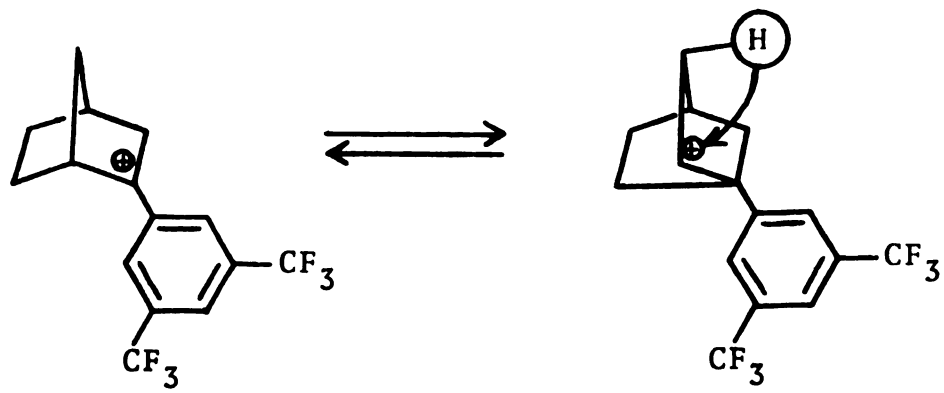
A third and currently acceptable possibility is also considered:

(3) A carbon-carbon hyperconjugated cation 30.[44,45]



30

Each of the three cases can superficially accommodate our results. We could expect that in each case the mode of charge transmission relative to a classical ion would be attended by the interaction shown. By what means do we distinguish these possibilities? Assuming that the aryl group will not significantly alter the rate of a 3,2 hydride shift in 12m-I relative to the known rate for norbornyl cation



12m 12m-I

we can estimate the percentage of 12m-I that could be present at +70°C. The rate constant for a 3,2 H$^{\sim}$ at +70°C is 6.5×10^5 sec^{-1}.* For cation 12m we observe broadening at +70°C (see Table 5). Assuming a rate of 71 sec^{-1}** the ratio

---

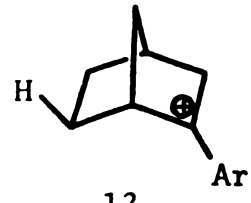
* Extrapolated from data in Ref. 23.

** The AB quartet ($\Delta\nu$ = 32 Hz) at high field for protons on H(5) and H(7) has almost collapsed to a broad singlet. We can estimate k = 71 sec^{-1} based on the equation for coalescence $\tau = \sqrt{2}\,(\pi\delta H)^{-1}$.[46]

of 12m-I/12m would be 1.1 x 10^{-4} (i.e. 7.1 x 10/6.5 x 10^{5}). Based on a chemical shift of 10 ppm[47] for a proton on a carbon with a full positive charge a concentration of 1.1 x 10^{-4} for 12m-I would lead to a shift for H(1) in 12m by .11 Hz or .001 ppm. Assuming the deviation from the line is due to equal contributions from a downfield shift of H(1) and an upfield shift of H(3), then H(1) is .1 ppm* off the line - 100 x more than accounted for by equilibrating classical ions.

We pointed out earlier that a Hammet sigma-rho plot for solvolysis of 2-aryl-2-*exo*-norbornyl *p*-nitrobenzoates is linear.[26] Yet we observe nonclassical character in the cation before it appears in the solvolysis. It seems intuitively reasonable that the electronic demands made by a developing cationic center should be less than the demands made by a fully developed cation.

We have observed a remarkable effect on the classical shift of H(6) *exo* protons in cations 12. For example in



12

* This value is obtained by dropping a line (which makes a 45° angle with a vertical line from 12m) from the point for 12m to the extended line for a classical ion. The point of intersection has coordinates for 12m if it were classical. This point is .1 ppm from the vertical or horizontal lines from 12m.

12a H(6) *exo* appears at τ 7.47, while in 12m it appears at τ 6.5. The chemical shift difference between them is about 100 Hz. This is the same value as the chemical shift difference between H(1) in these two systems! While it is difficult to distinguish H(6) *endo* it seems unlikely that there is a chemical shift difference of more than 40 Hz in these two systems. Clearly some factor which depends upon the magnitude of the charge at C(2) is responsible for the effect on H(6) *exo*. Perhaps C(6)H σ delocalization[21] or a hyperconjugative interaction is operating here.

In view of the greater effect of the positive charge on H(6) *exo* relative to H(6) *endo*, it is interesting that the isotope effects in 4a and 4b are the same.

In summary our data have shown that 2-aryl-2-norbornyl cations with stabilizing substituents ($\sigma^{\oplus}$ <0) cannot be adequately represented by classical electronic structures. Destabilizing substituents ($\sigma^{\oplus}$ >0) lead to cations having increased contributions from σ delocalized or carbon-carbon hyperconjugating interactions.

EXPERIMENTAL

Melting points (uncorrected) were measured on a Thomas-Hoover capillary melting point apparatus. Infrared spectra were taken on a Perkin-Elmer 137 instrument. NMR spectra were measured at 60 MHz on a Varian T-60 or A 56/60 D or at 100 MHz on a Varian HA-100 instrument. (Tetramethylammonium tetrafluoroborate (τ = 6.87)[26a] was used as an internal standard for carbonium ion spectra.) Mass spectra were measured on a Hitachi Perkin-Elmer RMU-6 instrument.

Carbonium Ions

The acid to be used was chosen so as to ensure complete ionization of the carbonium ion precursor; essentially identical spectra were obtained in acids differing significantly in acidity.

The carbonium ions were formed in the following way. The carbonium ion precursor was dissolved in a suitable solvent and then added slowly dropwise to the rapidly stirred acid (under N_2 atm.) For example, $CFCl_3$ was a convenient solvent for many of the carbonium ion presursors when FSO_3H was used. If very low temperatures were desired

and/or any SbF_5 was added to the FSO_3H, then SO_2ClF (25-75%) and/or SO_2F_2 (25-75%) was used as the solvent for the precursor. About a 5 wt % final solution concentration of the carbonium ion was found to be ideal in most cases. The sample was then transferred to the nmr tube.

Carbonium Ion Precursors

The alcohols used for this study were formed by the reaction of the desired organometallic reagent with the appropriate ketone - 2-norbornanone or bicyclo[2.2.2]-octan-2-one.[48,49] The organometallic reagent was formed by the Grignard Reaction[50] or the halogen-metal inter-conversion reaction[51] (HMIR).

General Procedure for Alcohol Synthesis Using the HMIR

Ether was distilled into a dried 50 ml. 3-neck flask containing a weighed amount of the desired aryl halide. The flask was equipped with a low temperature thermometer, a magnetic stirring bar, N_2 inlet and 15 ml constant pressure addition funnel. About a 10-30% by volume solution of the aryl halide in ether was used. The solution was cooled to about -40° using a Dry Ice-acetone bath. To this solution was added dropwise a 10% molar excess (over the halide) of commercially available butyllithium in hexane. The reaction was kept between -30° and -40° during the addition and then allowed to warm to -10° for about five minutes. After the addition of the butyllithium was

complete, the temperature of the reaction mixture was again lowered to -40°C. A solution of the ketone (one equivalent) in anhydrous ether was added at a rate such that the temperature of the reaction mixture did not rise above -30°. Following the addition of the ketone, the Dry Ice-acetone bath was permanently removed and the temperature of the reaction mixture was allowed to warm slowly to room temperature. The reaction mixture was then hydrolyzed with saturated aqueous NH_4Cl solution and extracted with ether. Drying the ether solution with $MgSO_4$ followed by evaporation of the ether led to a crude oil or solid which was then purified.

The desired organometallic reagent was formed from the aryl bromide except in the case of *p*-iodophenyllithium. In this case *p*-diiodobenzene was used. All the aryl halides were commercially available with the exception of 4-bromo-2,6-dichlorobenzonitrile and 4-bromo-2,6-dichloro-N,N-dimethylaminobenzene. The latter compound was prepared in 95% yield by methylation of 2,6-dichloro-4-bromo-aniline[52] with dimethyl sulfate. 4-Bromo-2,6-dichlorobenzonitrile was prepared according to the procedures of Gassman and Fentiman.[52]

Tables 8 and 9 are a summary of the pertinent synthetic and spectral data on compounds prepared by the methods mentioned above.

Table 8. Preparation of 2-Aryl-2-*endo*-Norbornanols[a,b]

Aryl Group	% Yield	mp or bp (pressure)	Molecular Formula	C, %		H, %		X,[n]		N, %		Mass Spec. (parent peak) m/e(Calcd)	m/e Found
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found		
p-$CH_3OC_6H_4$[c,d]	40	46.5-47.0°[c]	$C_{14}H_{16}O$	-	-	-	-	-	-	-	-	-	-
p-HOC_6H_4[e]	38	146-147.5°	$C_{12}H_{16}O_2$	76.42	76.25	7.90	7.68	-	-	-	-	204	204
3,4-$(CH_3)_2$-C_6H_3[f]	55.8	130-145°[g] (.6-1 mm)	$C_{15}H_{20}O$	83.28	83.62	9.32	8.93	-	-	-	-	216	216
p-$CH_3C_6H_4$[h,d]	69.2	46-47°	$C_{14}H_{18}O$	83.12	82.70	8.97	8.91	-	-	-	-	202	202
p-IC_6H_4[f]	61.2	98.99°	$C_{13}H_{15}IO$	49.68	49.80	4.81	4.85	40.41	40.36	-	-	314314	314
p-BrC_6H_4	70.2	93-94.5°	$C_{13}H_{15}BrO$	58.42	58.38	5.66	5.62	29.92	29.94	-	-	268,266	268,266
p-ClC_6H_4[d]	68.8	85-86.5°	$C_{13}H_{15}ClO$	70.09	69.90	6.79	7.12	15.92	15.85	-	-	224,222	224,222
p-FC_6H_4	45.2	63-64°	$C_{13}H_{15}FO$	75.66	75.86	7.38	7.44	9.21	9.18	-	-	206	206
C_6H_5[h,j]	70.0	41-42°	$C_{13}H_{16}O$	-	-	-	-	-	-	-	-	-	-
m-ClC_6H_4[k]	27	42-43.5°	$C_{13}H_{15}ClO$	70.36	-	6.73	-	15.79		-	-	224,222	224,222
m-BrC_6H_4	40.2	54.5-56.5°	$C_{13}H_{15}BrO$	58.42	58.47	5.66	5.68	29.92	29.90	-	-	268,266	268,266
p-$CF_3C_6H_4$	32.6	64.0-65.5°	$C_{14}H_{15}F_3O$	65.58	65.79	5.94	5.97	22.23	22.27	-	-	256	256
3,5-$(CF_3)_2$-C_6H_3	54.5	75.0-76.5°	$C_{15}H_{14}F_6O$	55.56	55.67	4.35	4.40	35.15	35.08	-	-	324	324
3,5-$(Cl)_2$-4-$N(CH_3)_2$-C_6H_2[l]	59.9	152-158° (.3 mm)	$C_{15}H_{19}Cl_2NO$	59.98	-	6.43	-	23.61	-	4.66	4.89	301,299	301,299
3,5-$(Cl)_2$-4-CN-C_6H_2[m]	24.4	102.5-103.0°	$C_{14}H_{13}Cl_2NO$	59.59	59.59	4.64	4.61	25.13	25.18	4.96	4.89	283,281	283,281

[a] *Endo* alcohol unless otherwise indicated; [b] The organometallic reagent was prepared by the halogen-metal interconversion reaction unless otherwise indicated; [c] Olefin; [d] See ref. 50; [e] The lithium reagent was prepared at 0°C. It was then refluxed for 2½ hrs. prior to the addition of 2-norbornanone (at the reflux temperature); [f] The lithium reagent was prepared at 0°C. It was then stirred at room temperature for 2 hours prior to the addition of 2-norbornanone (at room temperature); [g] Short path distillation; [h] The organometallic reagent was prepared by the Grignard reaction; [i] Butyllithium in hexane was added to *p*-diiodobenzene at -20°C. The temperature was then raised to +10°C. After all of the *p*-diiodobenzene dissolved the temperature was lowered to -20°C. 2-Norbornanone was then added; [j] See ref. 50; [k] Not analyzed. [l] Satisfactory elemental analysis was not obtained; [m] The lithium reagent was prepared by adding the aryl bromide to butyllithium below -60°C. The ketone was then added. At all times the reaction was kept below -60°C;[52] [n] X refers to the appropriate halogen atom.

Table 9. Preparation of 2-Aryl-2-bicyclo[2.2.2]octanols[a]

Aryl Group	% Yield	mpt or bpt	Molecular Formula	C, %		H, %		X,[o] %		N, %		Mass Spec (parent peak)	
				Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	m/e (Calcd)	m/e (Found)
p-$CH_3OC_6H_4$[b,c,d]	18.5	56.5-58.0[b]	$C_{15}H_{18}O$	-	-	-	-	-	-	-	-	214	214
3,4-$(CH_3)_2$-C_6H_3[e]	70.4	60-100°/.3 mm[f]	$C_{16}H_{22}O$	-	-	-	-	-	-	-	-	230	230
p-$CH_3C_6H_4$[b,d,g]	76	100°/.33 mm[b]	$C_{15}H_{18}$	90.85	89.45	9.15	9.07	-	-	-	-	198	198
p-IC_6H_4[h,i,j]	60	100°/.2-.4 mm[f]	$C_{14}H_{17}IO$	-	-	-	-	-	-	-	-	328	328
p-BrC_6H_4[i]	-	120°/5-10 mm[k]	$C_{14}H_{17}BrO$	-	-	-	-	-	-	-	-	282,280	
p-ClC_6H_4[i,j]	40-60	125-145°/3 mm[k]	$C_{14}H_{17}ClO$	-	-	-	-	-	-	-	-	238,236	238,236
p-FC_6H_4	8.6[l]	55-56°	$C_{14}H_{17}FO$	76.29	76.10	7.84	7.78	8.62	8.62	-	-	220	220
C_6H_5[m]	45.4	135-152°/15 mm	$C_{14}H_{18}O$	-	-	-	-	-	-	-	-	-	-
m-BrC_6H_4	55	60°/.25 mm[f]	$C_{14}H_{17}BrO$	59.78	59.75	6.10	6.06	28.43	28.42	-	-	282,280	282,280
m-ClC_6H_4[i]	42	60°/.3 mm[f]	$C_{14}H_{17}ClO$							-		238,236	238,236
p-$CF_3C_6H_4$[b,n]	25.5	90°/10 mm[b,f]	$C_{15}H_{15}F_3$	71.38	70.98	6.04	6.04	22.58	-	-	-	252	252
3,5-$(CF_3)_2C_6H_3$[b,n]	19.8	98-99°[b]	$C_{16}H_{14}F_6$	60.00	59.55	4.41	4.24	35.59	36.17	-	-	320	320

[a]Alcohol unless otherwise indicated. Alcohols were prepared by the halogen-metal interconversion reaction unless otherwise indicated; [b]Olefin; [c]Dehydrated with $KHSO_4$ during distillation (see ref. 50); [d]The organometallic reagent was prepared by the Grignard reaction; [e]The lithium reagent was prepared at 0°C. It was then stirred at room temperature for 2 hrs. prior to the addition of bicyclo[2.2.2]octan-2-one (at room temperature); [f]Molecular distillation; [g]Dehydrated by overheating the alcohol; [h]Butyllithium in hexane was added to *p*-diiodobenzene at -20°C. The temperature was then raised to +10°C. After all the *p*-diiodobenzene dissolved the temperature was lowered to -20°C. Bicyclo[2.2.2]octan-2-one was then added; [i]Not analyzed; [j]Partial dehydration during distillation; [k]Short path distillation; [l]The yield of crude product was actually much greater than this value. Molecular distillation of the crude product produced a mixture of alcohol and olefin from which the alcohol was obtained pure after three recrystallizations from hexane. The yield of pure product was reduced in the fractional crystallizations; [m]See ref. 10; [n]The alcohol was dehydrated in the presence of H_2SO_4 by heating to the boiling point under reduced pressure; [o]X refers to the appropriate halogen atom.

The nmr and ir spectra of the alcohols and olefins in the norbornyl and bicyclooctyl series of compounds were consistent with the assigned structures. The following are typical nmr spectra for an alcohol and olefin in each series of compounds.

Norbornyl System

2-*p*-iodophenyl-2-*endo*-norbornanol

Nmr (CCl_4) τ 2.51 (AA'BB', $\Delta\nu$ = 26 Hz, J_{AB} = 9 Hz, 4H), 7.70 (m, 4H), 8.43 (m, 7H).

2-*p*-methoxyphenyl-2-norbornene

Nmr (CCl_4) τ 3.04 (AA'BB', $\Delta\nu$ = 31 Hz, J_{AB} = 9 Hz, 4H), 3.96 (d, J = 3.5 Hz, 1H), 6.28 (s, 3H), 6.76 (br s, 1H), 7.06 (br s, 1H), 8.12-9.0 (m, 6H).

Bicyclooctyl System

2-*p*-fluorophenylbicyclo[2.2.2]octan-2-ol

Nmr (CCl_4) τ 2.58 (m, 2H), 3.09 (m, 2H), 7.5-8.8 (m, 13H)

2-*p*-methoxylphenylbicyclo[2.2.2]oct-2-ene*

2.98 (AA'BB', $\Delta\nu$ = 31 Hz, J_{AB} = 9 Hz, 4H), 3.62 (dd, J = 7 Hz, 2 Hz, 1H), 6.22 (s, 3H), 6.98 (br s, 1H), 7.38 (br d, J = 7 Hz, 1H), 8.52 (AB q, $\Delta\nu$ = 17 Hz, J = 9 Hz, 8H).

* Decoupling experiments showed that the 2 Hz coupling at 3.62 is between the olefinic proton and the broad singlet at 6.98. Comparison of a 100 MHz spectrum with a 60 MHz spectrum of this compound indicates that the absorption centered at 8.52 is indeed an AB quartet (or two overlapping AB quartets with similar chemical shifts).

PART I

REFERENCES

REFERENCES

1. H. C. Brown, *Chem. Brit.*, 199 (1966).
2. *ibid.*, *Chem. Eng. News.*, 45, 87 (Feb. 13, 1967).
3. G. D. Sargent, *Quart. Rev. Chem. Soc.*, 20, 299 (1966).
4. P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, New York, N. Y., 1965.
5. T. D. Swartz, "Solvolytic Studies of Brendyl, Brexyl and Norbornyl Systems," Ph.D. Thesis, Johns Hopkins University, Baltimore, Maryland, 1966.
6. H. C. Brown, "The Transition State," Special Publication, No. 16, (The Chemical Society, London, 1962), pp. 140-158, 174-178.
7. S. Winstein and D. S. Trifan, *J. Amer. Chem. Soc.*, 71, 2935 (1949).
8. G. E. Gream, *Rev. Pure and Appl. Chem.*, 16, 25 (1966).
9. P. von R. Schleyer, *J. Amer. Chem. Soc.*, 89, 701 (1967).
10. D. G. Farnum and G. Mehta, *J. Amer. Chem. Soc.*, 91, 3256 (1969).
11. H. C. Brown, F. Chloupek, and Min-Hon Rei, *J. Amer. Chem. Soc.*, 86, 1248 (1964).
12. H. L. Goering and C. B. Schewene, *J. Amer. Chem. Soc.*, 87, 3516 (1965).

13. Min-Hon Rei and H. C. Brown, *J. Amer. Chem. Soc.*, 88, 5335 (1966).

14. B. L. Murr, A. Nikon, T. D. Swartz, and N. H. Werstrik, *J. Amer. Chem. Soc.*, 89, 1730 (1967).

15. J. M. Jerkunica, S. Borcic, and D. E. Sunko, *J. Amer. Chem. Soc.*, 89, 1732 (1967).

16. V. F. Smith, Ph.D. Thesis, Michigan State University, 1972.

17. P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Amer. Chem. Soc.*, 87, 375 (1967).

18. A. Nikon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. D. Giorgio, *J. Amer. Chem. Soc.*, 87, 1613, 1615 (1965).

19. P. von R. Schleyer, D. C. Kleinfelter and H. G. Richey, Jr., *J. Amer. Chem. Soc.*, 85, 479-81 (1963).

20. S. Winstein, Reaction Mechanism Conference, Brookhaven, N. Y., Sept. 5, 1962.

21. G. A. Olah, J. R. DeMember, C. Y. Lui, and R. D. Porter, *J. Amer. Chem. Soc.*, 93, 1442 (1971).

22. T. S. Sorensen and K. Ranganayakulu, *Tetrahedron Letters*, 2447 (1972).

23. G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Amer. Chem. Soc.*, 92, 4627 (1970).

24. G. A. Olah, G. D. Mateescu and J. Louise Riemenschneider, *J. Amer. Chem. Soc.*, 94, 2529 (1972).

25. H. C. Brown and K. Takeuchi, *J. Amer. Chem. Soc.*, 90, 2691 (1970).

26. (a) K. Takeuchi and H. C. Brown, *J. Amer. Chem. Soc.*, 90, 2694 (1970).

(b) D. G. Farnum, *J. Amer. Chem. Soc.*, 89, 2970 (1967).

27. D. G. Farnum and A. D. Wolf, submitted for publication.

28. J. A. Berson and P. W. Grubb, *J. Amer. Chem. Soc.*, 81, 4016 (1965).

29. B. M. Benjamin and C. J. Collins, *ibid.*, 88, 1556 (1966).

30. G. A. Olah, P. R. Clifford, and C. L. Jewell, *J. Amer. Chem. Soc.*, 92, 5531 (1970).

31. G. A. Olah and T. E. Klousky, *J. Amer. Chem. Soc.*, 90, 4666 (1968).

32. E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Inc., New York, N. Y., p. 206.

33. C. Altona and M. Sundaralingam, *J. Amer. Chem. Soc.*, 92, 1995 (1970).

34. G. J. Karabatsos, private communication.

35. E. Huang, K. Ranganayakulu and T. S. Sorensen, *J. Amer. Chem. Soc.*, 94, 1779, 1781 (1972).

36. (a) J. H. Nogle and R. E. Schirmer, "The Nuclear Overhauser Effect," Academic Press, New York, N. Y., (1971).

(b) R. A. Bell and J. K. Saunders, *Can. J. Chem.*, 48, 1114 (1970).

37. T. Fukumi, Y. Arata, and S. Fujiwara, *J. Mol. Spectros*, 27, 443 (1968).

38. M. Saunders, P. von R. Schleyer, and G. A. Olah, *J. Amer. Chem. Soc.*, 80, 5679 (1964).

39. H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 80, 4979 (1958).

40. P. B. D. de la Mare, *J. Chem. Soc.*, 4450 (1954).

41. C. Earborn, *ibid.*, 4858 (1956).

42. N. C. Deno and A. Schriesheim, *J. Amer. Chem. Soc.*, 77, 3051 (1955).

43. N. C. Deno and W. L. Evans, *ibid.*, 79, 5804 (1957).

44. T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, 93, 5715 (1971).

45. R. Hoffmann, L. Radom, J. A. Pople, P. von R. Schleyer, W. J. Hebre, and L. Salem, *J. Amer. Chem. Soc.*, 94, 6221 (1972).

46. J. D. Roberts, "Nuclear Magnetic Resonance," McGraw-Hill, Inc., New York, N. Y., 1959, p. 64.

47. D. G. Farnum, *J. Amer. Chem. Soc.*, 89, 2970 (1967).

48. P. K. Freeman, D. M. Balls, and D. J. Brown, *J. Org. Chem.*, 33, 2211 (1968).

49. J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner, and M. Hine, *J. Amer. Chem. Soc.*, 77, 594 (1955).

50. D. C. Kleinfelter and P. von R. Schleyer, *J. Org. Chem.*, 26, 3740 (1961).

51. R. G. Jones and H. Gilman, "Organic Reactions," Wiley, New York, N. Y., 1951, p. 339.

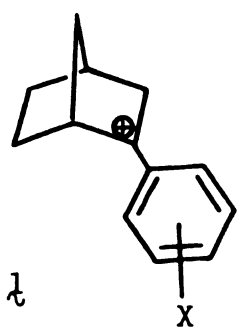
52. P. G. Gassman and A. F. Fentiman, Jr., *Tet. Let.*, 1021 (1970).

PART II

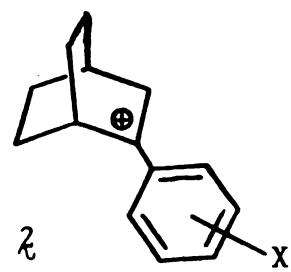
^{19}F AND ^{1}H NMR STUDY OF AN EQUILIBRIUM AMONG ARYLBICYCLOOCTYL CATIONS

INTRODUCTION

Recently we have found it desirable to examine certain chemical shifts in a series of 2-aryl-2-norbornyl cations 1 and 2-aryl-2-bicyclo[2.2.2]octyl cations 2.[1] During the course



1



2

2a, X=*p*-CF_3

2b, X=*p*-F

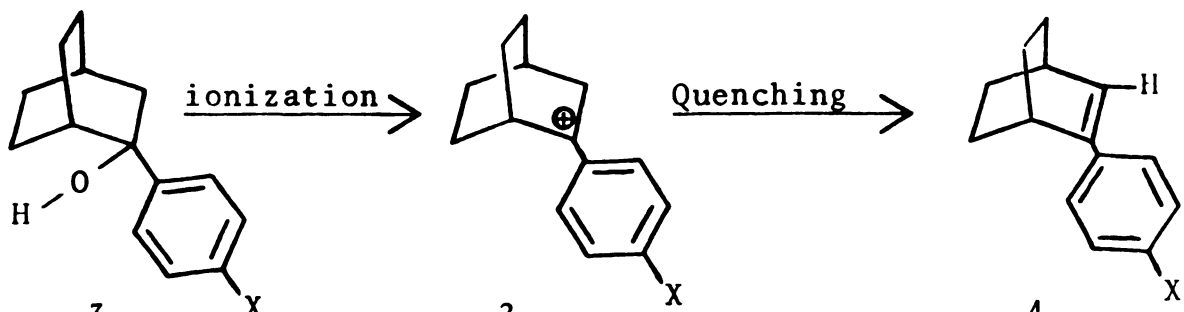
of this study we observed that upon ionization of their respective precursors at -78° cations of type 2 in which X was a strongly electron withdrawing substituent e.g. 2a, X = *p*-CF_3, gave proton nmr spectra substantially different from cations in which X was electron donating e.g. 2b, X = *p*-F.[1] Since chemical shifts in the former case indicated that the aryl group(s) was still at a carbonium ion center, it seemed likely that 2a might have rearranged to one or more new arylcarbonium ions under the ionizing conditions. Since these circumstances would permit the determination of equilibrium constants among those cations present, we explored

the hypothesis further. Thus, isomeric arylbicyclooctyl alcohols were prepared and examined under similar conditions of ionization. The results of these studies are described below.

RESULTS AND DISCUSSION

Proton Nmr Studies

Careful ionization of *p*-trifluoromethylbicyclo-[2.2.2]octan-2-ol **3a** in FSO_3H/SO_2ClF at temperatures



3

3a

3b

2

2a, X = CF_3

2b, X = F

2c, X = H

4

4a, X = CF_3

4b, X = F

lower than -100°C gave rise to the 2-*p*-trifluoro-methylphenyl-2-bicyclo[2.2.2]octyl cation **2a**. The nmr spectrum of **2a** is shown in Figure 1. The AA'BB' system centered at τ 1.45 ($\Delta\nu$ = 67 Hz, J = 9 Hz, 4H) is assigned to the *p*-trifluoromethylphenyl group. That this group is at a carbonium ion center[2] is evident when one compares the large chemical shift difference ($\Delta\nu$ = 67 Hz) between the *ortho* and *meta* protons in cation **2a** with the smaller difference in the starting material **3a** ($\Delta\nu$ = 0). Furthermore the chemical shift

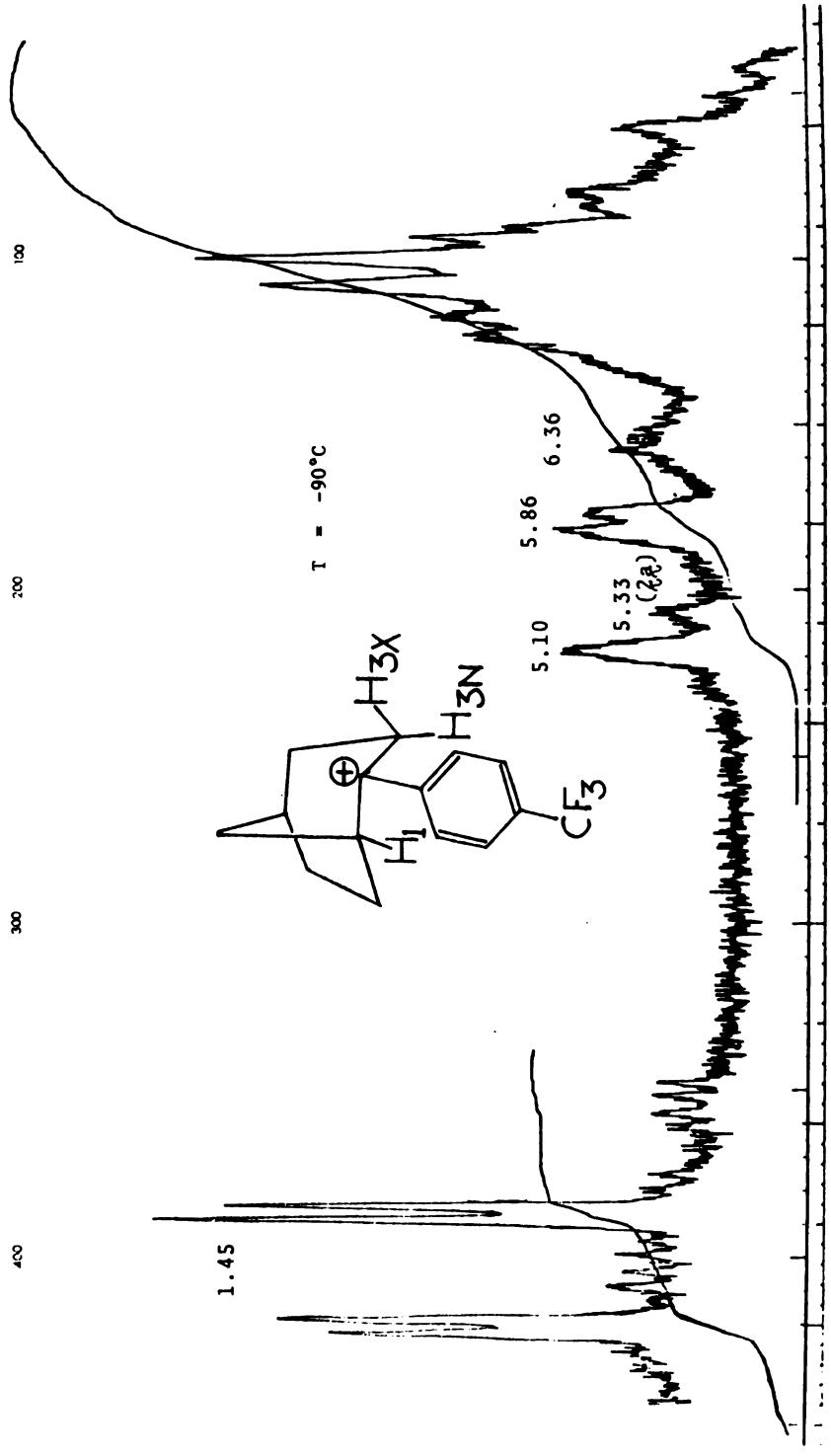


Figure 2. 100 MHz spectrum of 9a at -100°C

of the aryl group in 2a is greater than 1 ppm to lower field than in the alcohol 3a (τ 2.50). The broad singlet (1H) at τ 5.33 is assigned to the bridgehead proton H(1) α to the carbonium ion center, while the broad singlet (2H) at τ 5.83 is assigned to the methylene group α to the carbonium ion center. Deuterium labeling at C(3) in 2a gives rise to a spectrum in which the absorption at 5.83 is essentially wiped out. There are nine other hydrogens at higher field which were not assigned. This spectrum is quite similar (as expected) to the previously reported and more stable cation 2c.[3]

That cations 2 do indeed have the 2-bicyclo[2.2.2]octyl skeleton was confirmed by recovery experiments. Quenching of cation 2a in pentane/aq. Na_2CO_3 at 0°C gave bicyclo[2.2.2]-octene (4a) in 55% yield and bicyclo[3.2.1]oct-6-ene (17a) in 45% yield.* The origin of 17a will be discussed later. Quenching of 2b** gave essentially pure 4b, which can be produced by simply overheating alcohol 3b on distillation. The nmr spectra of olefins 2 are quite characteristic of their structure. For example, in 4b there is a multiplet (4H) centered at τ 2.85 assigned to the p-fluorophenyl group. A

---

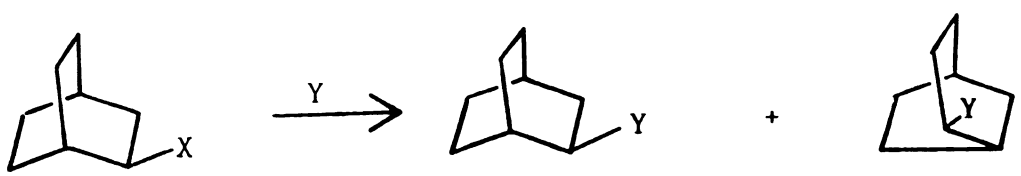
* See Experimental Section.

** The fluorophenyl derivative 2b gives the same basic spectrum as 2a. It is more stable to rearrangement than 2a but it also will rearrange when warmed to 0°C.

---

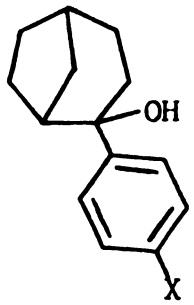
doublet of doublets τ 3.55 (J = 7 Hz, 2 Hz, 1H) is assigned to the single olefinic proton. A broad singlet τ 6.97 (1H) is assigned to H(1). Irradiation of this broad singlet leads to collapse of the 3.55 absorption to a doublet (J = 7 Hz). A broad doublet (J = 7 Hz) at τ 7.35 (1H) is assigned to H(4). Irradiation at τ 3.55 leads to collapse of the broad doublet to a broad single verifying the coupling between H(3) and H(4). There is an "AB quartet" (8H) at higher field (τ 8.50) which is assigned to the remaining four pairs of methylene protons on C_5, C_6, C_7 and C_8. While one would predict two AB quartets on symmetry grounds one for C_5, C_8 and (one for C_6, C_7), in actuality the chemical shifts of these quartets are so similar that no further resolution of the observed singlet "AB quartet" was obtained even at 100 MHz.

Warming 2a to -60°C in the nmr probe produces material with an nmr spectrum identical with that of the material obtained by ionization of 3a at -78°C. The chemical shift of the aryl group in this material indicated that one or more new aryl carbonium ions were present. It is well known from solvolytic studies of bicyclooctyl derivatives 5 that they



5 6 7

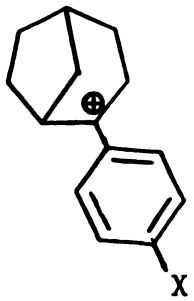
generally yield approximately equal molar mixtures of compounds 6 in which the initial skeleton is retained and 7 in which the initial skeleton has rearranged to the [3.2.1] system.[4] With the consideration that 2a might have rearranged to 9a we attempted to prepare that cation. While ionization of 8a* at -78°C did indeed give material having a spectrum



8

8a, X = CF_3

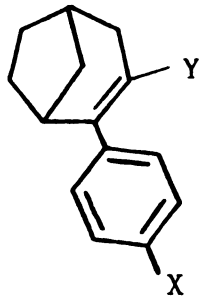
8b, X = F



9

9a, X = CF_3

9b, X = F



10

10a, X = F, Y = H

10b, X = F, Y = D

identical to that of rearranged 2a, ionization of 8a at <-100°C produced material having a different spectrum! That spectrum, assigned to structure 9a,** is shown in Figure 2.***

---

* Probably a mixture of *exo* and *endo* isomers.

** There are other materials present besides 9a. This will be discussed in the section on F^{19} nmr.

*** We are not assigning a conformation to cations 9 as our data do not permit distinction between the chair or boat conformation. It has been reported recently that the 2-methyl-2-bicyclo[3.2.1]octyl cation exists in the boat conformation.[5]

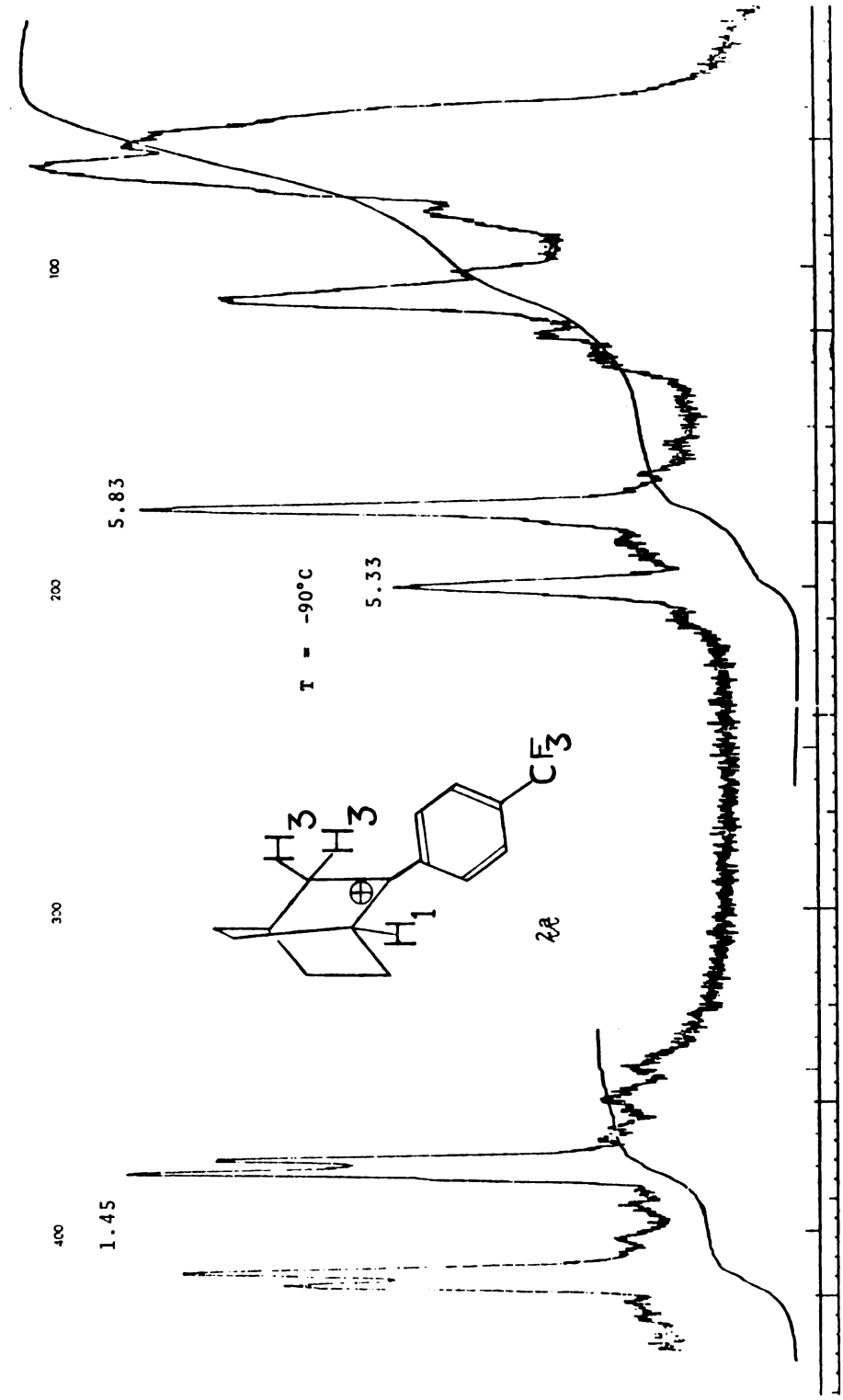


Figure 1. 100 MHz spectrum of 2a at -90°C

There is a *p*-$CF_3C_6H_4$ group (τ 1.45) at a carbonium ion center. The broad singlet at τ 5.10 (1H) is assigned to the bridgehead proton H(1).* The methylene protons α to the carbonium ion center are not magnetically equivalent as they were in structure 2a and they give rise to a highly coupled AB pattern with one component at τ 5.86 (1H) and the other at τ 6.36 (1H).

Since 9a is rather unstable towards rearrangement, labeling and quenching studies were carried out on the more stable cation 9b. This cation gives the same basic spectrum as cation 9a.

Labeling at C(3) in 9b gives rise to a spectrum in which the highly coupled AB pattern is nearly wiped out. In an attempt to make nmr assignments for each of the α-methylene protons and to obtain information on the conformation of 9 deuterated olefin 10b was prepared. Treatment of 10b with FSO_3H/SO_2ClF at -105°C gave deuterated 9b having a spectrum in which the α-methylene signals were about

---

* The broad singlet of low intensity at τ 5.33 is due to 2a. It has a counterpart of double intensity at τ 5.83 under the low field portion of the "AB quartet" of 9a. It has not been possible to produce this cation completely free from 2a. Even in the case of the more stable cation 9b, there is some 2b which is always present on ionization of 8b even at temperatures as low as -110°C to -120°C.

equally reduced in intensity and in which there was a sharpening of that portion of the AB system at lowest field. Apparently 10b is protonated equally well from both top and bottom. Thus we were not able to assign the methylene protons on the basis of these labeling experiments.

In order to convince ourselves completely that cations 9 do have the 2-substituted [3.2.1] skeleton we quenched 9b in pentane/Na_2CO_3 at -78°C and obtained the two olefins 10a and 4b in 55% and 17% yield respectively.* There was also 32% of unidentified material which was composed of at least two compounds having vpc retention times longer than the olefins. Olefin 10a could also be produced by treatment of 8b with *p*-toluenesulfonyl chloride-pyridine at 110°C in a sealed tube for 10 hrs.**

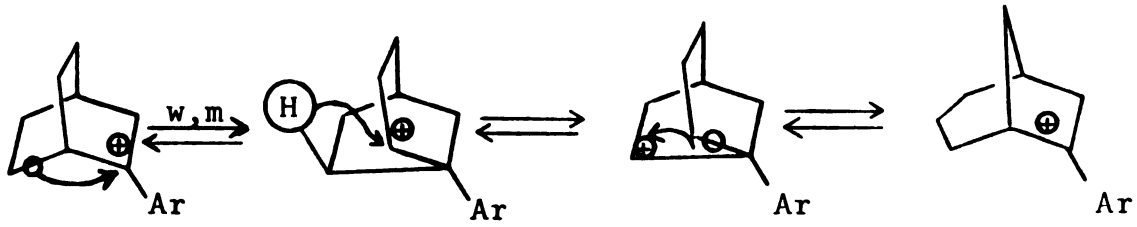
We have reported elsewhere[1] that 2-aryl-2-norbornyl cations 1 in which X is a strongly electron withdrawing group undergo the well known "Wagner-Meerwein, 6,2-hydride shift," rearrangement very rapidly on an nmr time scale. In cations 1 this rearrangement is degenerate. It is interesting to examine the outcome of this same rearrangement in cations 2. In this case, as is shown in Scheme 1, a new cation 11 having the 6-substituted bicyclo[3.2.1]octyl skeleton is produced.

---

* See Experimental Section.

** Based on a procedure for dehydration of isomeric methylbicyclooctanols.[6]

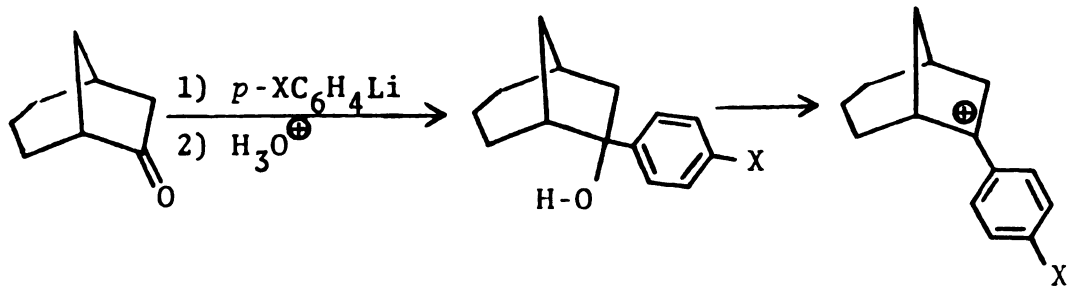
Scheme 1



2 11

Ar = *p*-XC_6H_4

In order to examine the possibility that 2a (and 9a) rearranged to cation 11a we prepared alcohol 12a as shown below.



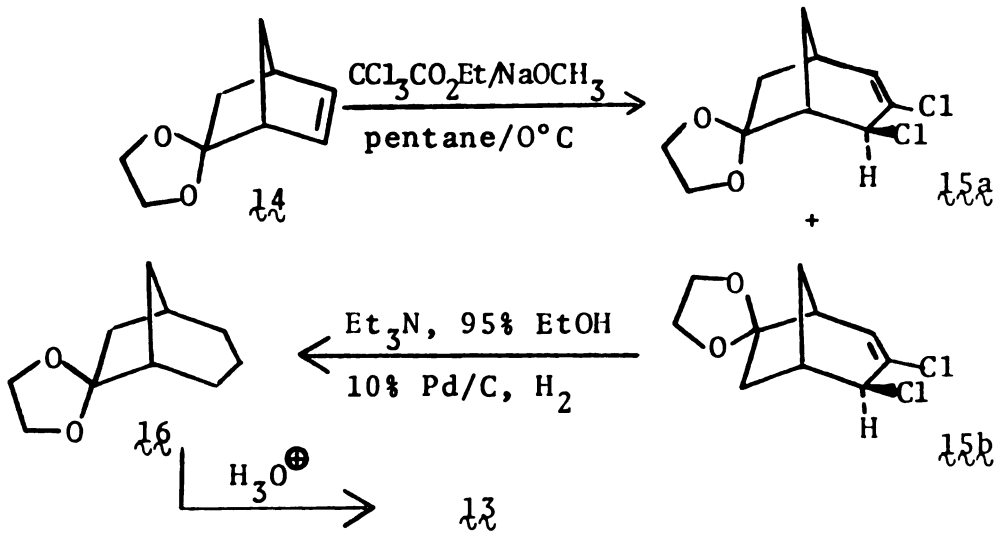
13 12 11

12a, X = CF_3 11a, X = CF_3

12b, X = F 11b, X = F

Although there are literature procedures available for the synthesis of 13[7-10] we have independently prepared it in good yield (48% based on 2-norbornenone ethylene ketal 4) according to Scheme 2. By integration of the two olefinic protons (having J = 7.6, 7.2 Hz) or the two *endo* C_4 protons

Scheme 2



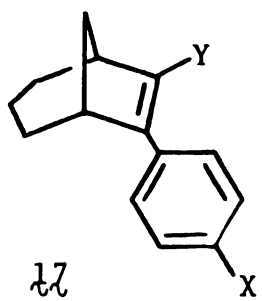
(having J = 2.7, 2.8 Hz) it was possible to determine that CCl_2 addition* to 14 produced 15a and 15b in about a 1:1 ratio. The stereochemical assignment at C(4) was based on a comparison of the observed coupling constants to those for the adduct between norbornene and CCl_2[12] (J H_1, H_2 = 7.0 Hz, J H_3, H_4 = 2.8 Hz). Because of the similarity between 15a and 15b the chemical shifts were not assigned. The mixture was not separated since each of the components yield the desired product 16 on reduction. Hydrolysis of 16 yielded ketone 13, which, on treatment with *p*-$CF_3C_6H_4Li$ followed by

---

* Same conditions that were used for CCl_2 addition to norbornene.[11]

hydrolysis, gave alcohol 12a.*

Ionization of 12a in FSO_3H/SO_2ClF <-100°C produced cation 11a. The nmr spectrum of 11a at -90°C is reproduced in Figure 3. There is an AA'BB' system ($\Delta\nu$ = 65 Hz, J = 9 Hz, 4H) centered at τ 1.45 attributable to the *p*-$CF_3C_6H_4$ group at the carbonium ion center. The broad singlet at τ 5.13 (1H) is assigned to the bridgehead proton H(1) α to the carbonium ion center. The methylene protons on C(3) give rise to the AB quartet centered at τ 5.83 (J = 24 Hz) in which the higher field component is further coupled. Deuterium labeling at C(3) in 11a essentially wipes out the AB pattern. Preparation of olefin 17b (partially deuterated) and ionization of this compound below -100°C. gave a spectrum in which the lowest



17

17a, X = CF_3, Y = H

17b, X = CF_3, Y = D

17c, X = F, Y = H

---

* Although we have no evidence on the stereochemistry of 12 it seems likely that it is the *endo* alcohol. The reactions of *p*-XC_6H_4Li (X = F, CF_3), with ketone 13 yield predominantly one product with a sharp melting point. 2-Norbornanone, a ketone of similar structure is attacked preferentially from the *exo* side of the molecule by nucleophiles.

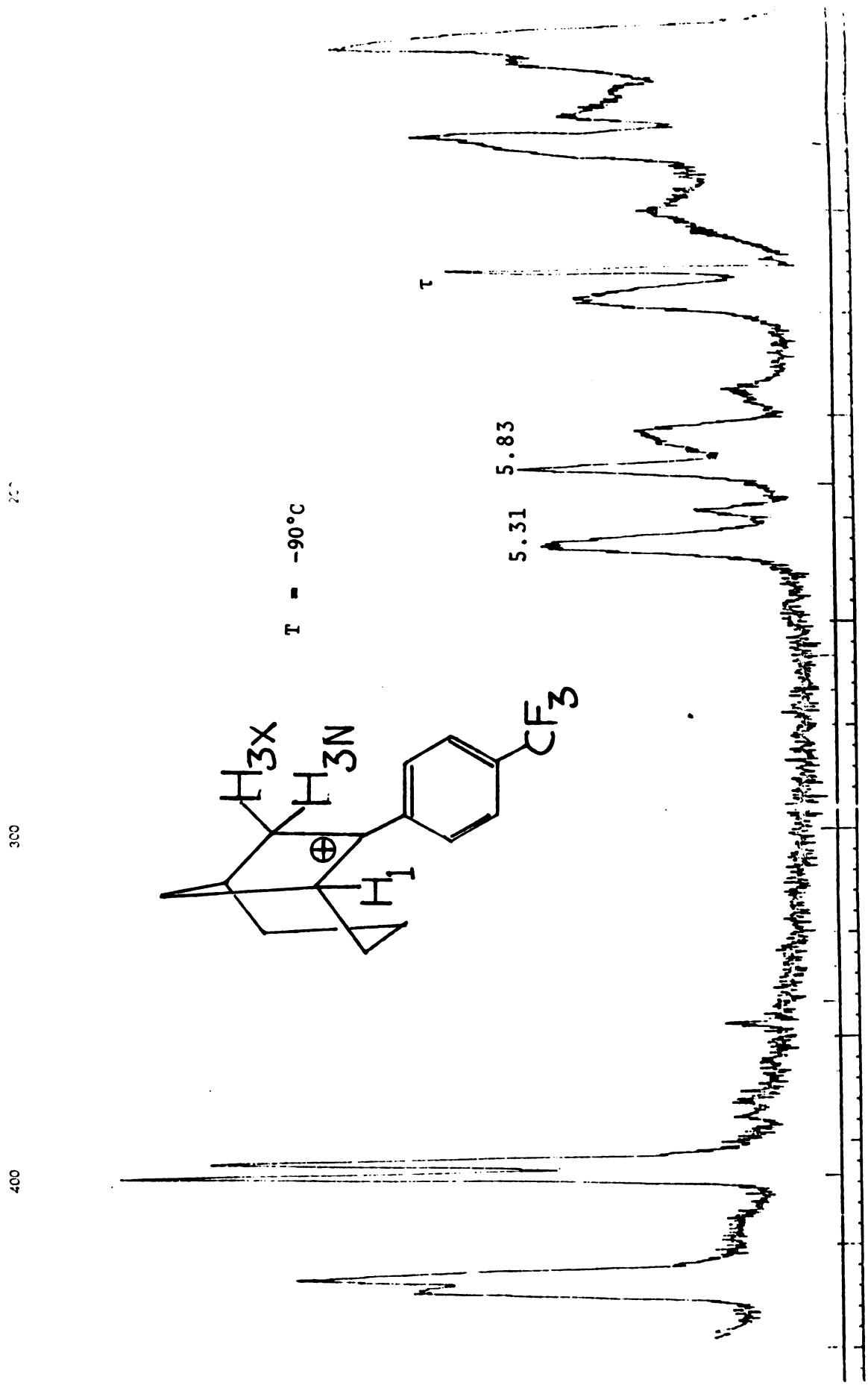


Figure 3. 100 MHz spectrum of 11a at -90°C.

field component of the AB quartet was greatly reduced in intensity while the highest field component collapsed to a broad singlet. Assuming predominantly *exo* protonation by FSO_3H in 17b,* the *endo* proton is then the lowest field proton while the *exo* proton is at highest field.

While we have not quenched cation 11a directly, it was mentioned earlier that olefin 17a is produced on quenching cation 2a. We believe that cation 11a is actually the source of olefin 17a. 17a was identified by comparison with identical material produced by dehydration of 12a with *p*-toluenesulfonyl chloride in pyridine.[6] Furthermore quenching cation 11b yields olefin 17c (80% of recovered material) as the major product.

When cation 11a was warmed to -60°C in the nmr instrument the spectrum obtained indicated that 11a had produced the same material as cations 2a and 9a on warming to -60°C. It was now evident by a comparison of the nmr spectra of the mixture and 11a that cation 11a was a major component in the mixture.

---

* Similar behavior is observed for 2-*p*-fluorophenyl-2-norbornene of similar structure.[1]

Fluorine Nmr Studies.

From the proton nmr studies of the mixture produced by either cations 2a, 9a or 11a it was not possible to tell exactly how much of each of the cations were present or if any other materials were present. Monitoring the ^{19}F resonance (a sharp singlet) of the *p*-$CF_3C_6H_4$ group in the cations proved to be a convenient method for following the formation of the mixture from each of the cations and for obtaining quantitative information on both the total number of cations (and other materials having a $CF_3C_6H_4$ group) and the relative amounts of each present.* Using this method we were able to determine that the mixture produced from 2a and 11a is virtually identical and consists almost exclusively of these two cations. The equilibrium constant measured at -80°C by integration of the ^{19}F resonances is 3.2 favoring cation 11a.

Ionization of 8a at <-100°C produces cation 9a along with several other materials (up to 40%) which have not been identified and which have ^{19}F resonances at lower field than

---

* While the *p*-FC_6H_4 derivatives of the cations were also examined, this group proved to be a less convenient probe (at 56 MHz - the conditions of exploratory runs), since the ^{19}F resonance was broad. This was due to coupling with the aromatic protons.

2a, 9a or 11a. We believe these latter compounds probably arise from irreversible reactions of the starting material during the ionization process since the amounts of these materials produced were variable in different experiments while their total percentage remained relatively constant on warming 9a.*

When 9a is warmed to -80°C it disappears and produces the equilibrium ratio of 2a and 11a. A summary of the quantitative data obtained from the ^{19}F studies in the equilibrium between these cations is shown in Table 1.

Table 1. Thermodynamic Data from ^{19}F NMR Experiments at 94.1 MHz

Cation	9a	← 9Hz[a] →	2a	← 7Hz →	11a
% (-80°C)	<2		30		70

2a ⇌ 11a (-80°C)

K = 3.2	ΔG = -450 cal
K^{+50} = 1.6	ΔH = -700 cal
T_{inv}[b] = 200°	ΔS = -1.5 eu

[a] Chemical shift differences between ^{19}F resonances

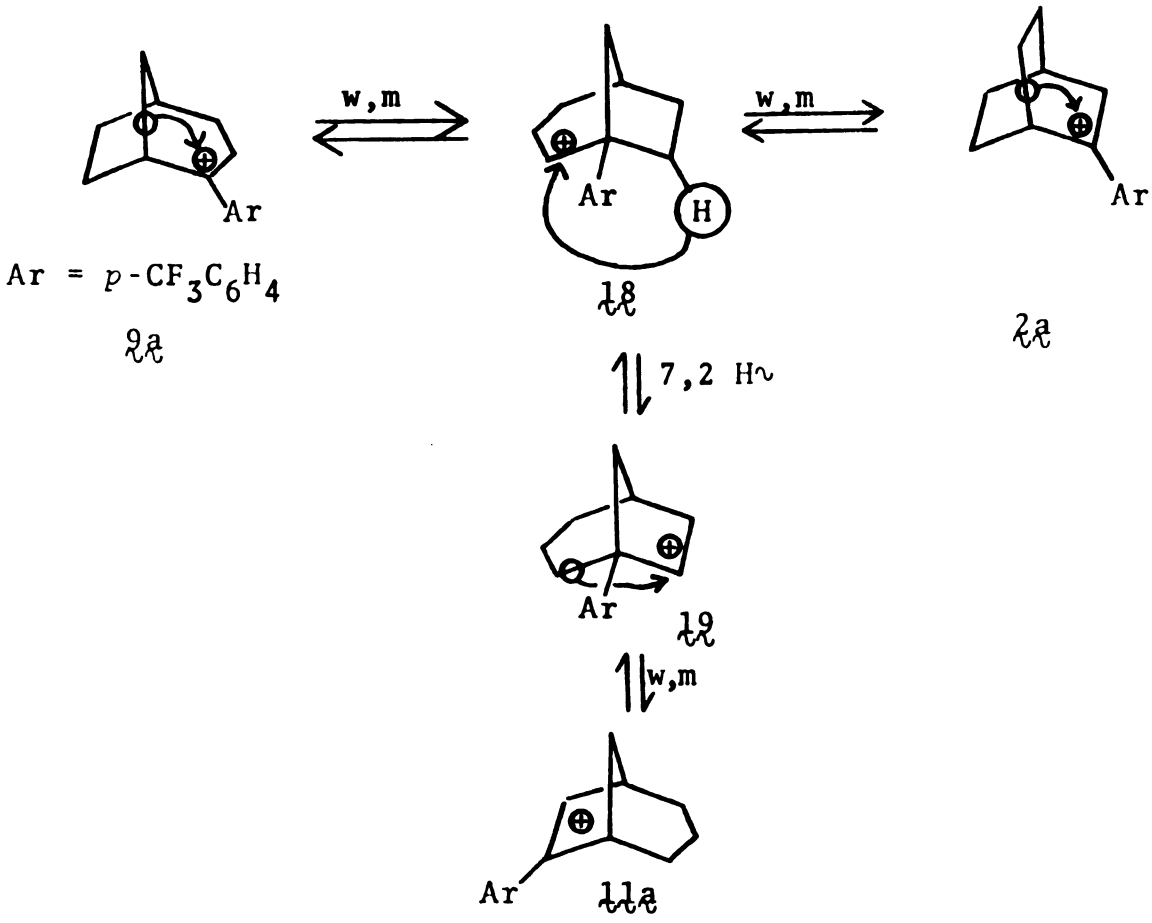
[b] Inversion temperature

* The equilibrium mixture produced from 2a or 11a was essentially free from of these materials.

Note that the figure of <2% of 9a in the equilibrium mixture is certainly an upper limit as 2% would have been detectable. The equilibrium constant between 2a and 11a was measured between -90°C and -40°C and the thermodynamic constants were extracted from this data. Note that there is an entropy factor whose origin is not completely obvious which favors cation 2a. To the extent that these extrapolations are correct we have calculated that above +200°C (the inversion temperature) cation 2a would be more stable than 11a!

From both the ^{19}F and ^{1}H nmr studies we have obtained data which support the mechanism shown in Scheme 3.

Scheme 3



First we re-emphasize that we are dealing with a true equilibrium. Thus, cations 2a, 9a and 11a can each be observed prior to any significant rearrangement, and, on warming 2a, 9a or 11a, the same mixture* of cations in the same ratio is produced.

A second important fact related to the mechanism was obtained by observing the approach to equilibrium starting from cation 9a (^{19}F method). We were able to detect that an initial buildup of cation 2a occurred while 11a became predominant as the equilbrium was approached. This indicated that cation 2a was formed at a faster rate than 11a, but 11a was more stable. The secondary cation 18 seems to be a reasonable intermediate in the transformation of 9a into 2a and 11a. One would expect that the rate of partitioning of 18 between 2a dnd 19 (which rearranges to 11a) would favor 2a as observed. The partitioning of 18 to 2a involves a Wagner-Meerwein rearrangement which yields an arylcarbonium ion ie. 2a. The partitioning of 18 to 19, a secondary carbonium ion, involves a 7,2 hydride shift (7,2 H$\sim$). Some of the stability of the arylcarbonium ion 2a ought to show up in the transition state to its formation. Even if cation 19 is more stable than 18, one would expect a larger activation

---

* Though 9a is not detectable in this mixture it very likely is an accessible intermediate.

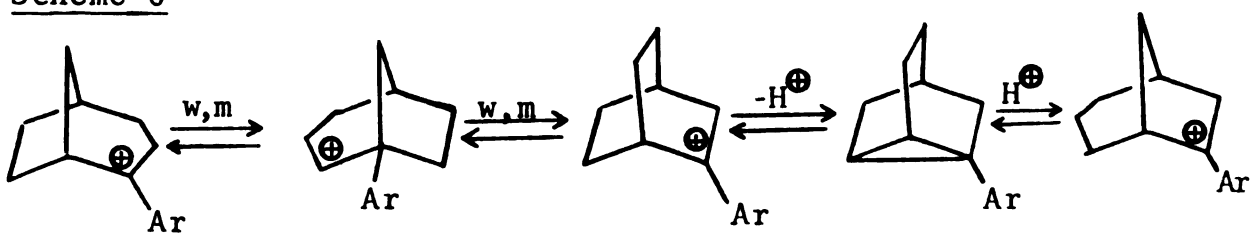
---

energy for this 7,2 H∿ than for the W,M transformation* of 18 → 2a.

A third observation is that in the transformation of 2a into 11a, the methylene group α to the carbonium ion center remains bonded to the carbon containing the aryl group. Equilibration of 2a labeled with deuterium at C(3) produces 11a with the C(7) methylene α to the carbonium ion center also labeled with deuterium.

An alternative mechanism which accounts for the observed results and avoids a direct 7,2 hydride shift is of the type 9a ⇄ 2a ⇄ 11a as shown in scheme 6. The required 7,2 hydride

Scheme 6



9a 18 2a 20 11a

shift is accomplished indirectly via the cyclopropane intermediate 20. Evidence against intermediates of type 20 was obtained by Parker and coworkers[13] in their studies of the

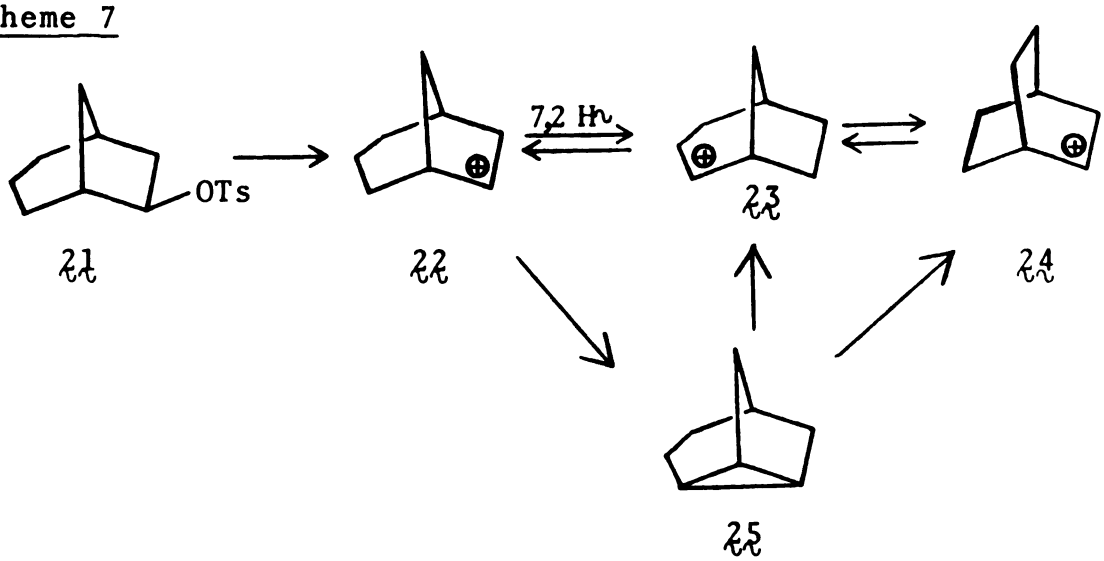
---

* It has been suggested elsewhere that the absolute rate of bond shifting in bicyclic systems is greater than the rate of hydride shifting.[4]

---

buffered acetolysis of the unsubstituted bicyclo[3.2.1]-6-toluene-*p*-sulfonates **21** (Scheme 7). They observed products

Scheme 7



resulting from trapping of **22**, **23** and **24**. They considered that leakage of **22** into **23** and **24** might be occurring indirectly via the cyclopropane **25** rather than by direct 7,2 hydride shift. However, a comparison of the products obtained when **25** was submitted to the acetolysis conditions with those obtained from **21** indicated that the mechanism involving **25** could be operative to no more than 20%.[13] Assuming that the aryl group does not significantly enhance proton loss from **11a**, then the arylcyclopropane **20** should not be an important intermediate in the conversion of **2a** to **11a**. Furthermore one would expect that proton loss to form a cyclopropane would compete even less effectively with 7,2 hydride shift in FSO_3H than in buffered acetic acid. Hydride shifts of

this type are unusual, but nevertheless are well documented in the structurally related norbornyl systems.[1,14,15]

EXPERIMENTAL

General Procedures

Melting points (uncorrected) were measured on a Thomas-Hoover capillary melting point apparatus. Infra-red spectra were measured on a Perkin-Elmer Model 137 instrument. Mass spectra were measured on a Hitachi Perkin-Elmer RMU-6 instrument. Proton and fluorine nmr spectra were taken at 60 MHz on a Varian T-60 or A 56/60 D or at 100 MHz on an HA 100 instrument. Proton chemical shifts are reported in τ values versus tetramethylammonium tetrafluoroborate (τ 6.87)[2] as an internal standard.

Carbonium Ion Preparation

The fluorophenylbicyclooctyl cations were generally formed by ionization of the respective starting materials at -78°C in FSO_3H. The *p*-trifluoromethylphenylcarbonium ions were ionized at temperatures lower than -100°C. In the latter case the alcohol or olefin to be ionized was dissolved in sulfurylchlorofluoride (1 ml) and cooled to -78°C. This solution was added slowly dropwise to a rapidly stirred mixture of FSO_3H (1 ml) in SO_2ClF (1-2 ml) (N_2 atm.) at <-100°C. About a 5 wt % final solution concentration of the

Table 2. Proton Chemical Shifts in Arylbicyclooctyl Cations

System	Cation	*p*-XC_6H_4	Bridgehead Proton	α-Methylene Protons
2-[2.2.2]	2a, X = CF_3	1.45 (AA'BB', $\Delta\nu$ = 67 Hz, J = 9 Hz, 4H)	5.33 (br s, 1H)	5.83 (br s, 1H)
	2b, X = F	1.13 (m, 2H), 2.39 (m, 2H)	5.68 (br s, 1H)	6.09 (br s, 2H)
2-[3.2.1]	9a, X = CF_3	1.45 (AA'BB', $\Delta\nu$ = 65 Hz J = 9 Hz, 4H)	5.10 (br s, 1H)	5.86 (m, 1H), 6.36 (m, 1H)
	9b, X = F	1.07 (m, 2H), 2.37 (m, 2H)	5.39 (br s, 1H)	6.04 (m, 1H), 6.63 (m, 1H)
6.[3.2.1]	11a, X = F	1.44 (AA'BB', $\Delta\nu$ = 65 Hz J = 9 Hz, 4H)	5.31 (br s, 1H)	5.83 (ABq, J = 24 Hz, 2H)
	11b, X = CF_3	1.17 (m, 2H), 2.36 (m, 2H)	5.62 (br s, 1H)	6.12 (ABq, J = 24 Hz, 2H)

carbonium ion was prepared. The sample was then transferred to nmr tubes which were maintained below -100°C by a liquid N_2-pentane mixture.

The pertinent chemical shifts of carbonium ions prepared in this study are listed in Table 2.

General Synthetic Procedures

Ketones

Bicyclo[3.2.1]octan-2-one was commercially available. Bicyclo[2.2.2]octan-2-one[16,17] and bicyclo[3.3.0]octan-2-one[18] were prepared according to literature procedures.

Bicyclo[3.2.1]octan-6-one

Although there were literature procedures available for the synthesis of the title compound,[7-10] it was prepared independently and in good yield by the following method.

Addition of dichlorocarbene to 2-norbornenone ethylene ketal 14

Dichlorcarbene was generated from ethyltrichloroacetate according to Jefford's procedure[11] for the addition of $:CCl_2$ to norbornene. The crude product was poured into H_2O and extracted 3 times with pentane. The pentane extracts were dried with $MgSO_4$ and pentane was stripped off on a rotary evaporator. The unreacted starting materials were distilled from the product at 90°/.3 mm leaving a reddish-black oil which was carried on to the next step. 64 g of ketal yielded

100 g of the crude oil. The nmr spectra of the oil indicated that the major products were (15a) and (15b) one of which was slightly predominant. Nmr (mixture CCl_4): τ 3.80, 3.95 (two doublets, J = 7.5 Hz, 1H), 5.50, 5.80 (two doublets, J = 3 Hz, 1H), 6.15 (m, 4H), 7.50 (m, 2H), 8.10 (m, 2.8 Hz).

Formation of 16 by catalytic hydrogenation of 15a and 15b

The 100 g of crude material from the preceeding step was split into two 50 g samples which were each hydrogenated in the following way: 50 g of a mixture of crude 15a and 15b was dissolved in 100 ml of Et_3N and 150 ml of 95% EtOH. To this mixture was added 4 g of 10% Pd/C. The mixture was hydrogenated on a Paar apparatus (The pressure drop was 53 psi). The crude product was poured into H_2O and extracted three times with pentane. The crude products from each run were combined and the crude ketal was distilled from polymeric material and then redistilled. There was some hydrolysis of the ketal in this process, but this was not critical since the entire mixture was carried on to the next step for hydrolysis. Nmr (purified sample of ketal, CCl_4) τ 3.84, (m, 4H), 2.4-1.0 (m, 12H).

Hydrolysis of ketal 16

The entire product from the preceeding step was treated with 300 ml of pentane, 200 ml of H_2O and 2 ml of conc. H_2SO_4. The mixture was stirred for 6 hrs at room temperature. The crude product was poured into saturated aqueous $NaHCO_3$. The

solution was extracted three times with pentane and the pentane solution was then dried over $MgSO_4$ and the pentane solvent evaporated. The crude product was sublimed at 82° at water aspirator pressure. The yield was 25 g based on 64 g of norbornenone ethylene ketal (48% overall yield). Nmr (CCl_4) 7.5 (br s, 1H), 7.65-9.0 (m, 9H). ir ν_{max}^{neat} 2990, 1750 (Lit.,[13] ν_{max} 1743 cm^{-1}). mp 149-153° (Lit.,[8] 155-157°).

Synthesis of Alcohols

The alcohols used in this study were all synthesized by reaction of the desired organometallic reagent with the appropriate ketone. The organometallic reagents were all formed by the halogen-metal interconversion reaction. In a typical experiment ether was distilled into a dried 50 ml 3-neck flask containing a weighed amount of the aryl bromide. The flask was equipped with a low temperature thermometer a magnetic stirring bar, N_2 inlet and 15 ml constant pressure addition funnel. About a 10-30% solution of the aryl halide in ether was used. The solution was cooled to about -40°C using a Dry-Ice acetone bath. To this solution was added dropwise a 10% molar excess (over the halide) of commercially available butyllithium in hexane. The reaction was kept between -30° and -40°C during the addition. The mixture was then warmed to -10°C for about five minutes. After the addition of the butyllithium wss completed, the temperature was again lowered to about -40°C. A solution of the ketone (one equivalent) was added at a rate such that the temperature of the reaction mixture did not rise above -30°C. Following

addition of the ketone the Dry-Ice acetone bath was permanently removed and the temperature of the reaction mixture was allowed to warm slowly to room temperature. The reaction mixture was then hydrolyzed with saturated NH_4Cl solution and extracted with ether. Drying the ether solution with $MgSO_4$ followed by evaporation of the ether led to a crude oil which was then purified.

The following Tables are a summary of the pertinent synthetic and spectral data on compounds prepared by the method mentioned above.

Labeling Experiments

3,3-dideuteriobicyclo[2.2.2]octan-2-one

2.0 g of bicyclo[2.2.2]octan-2-one,[16,17] 6 ml of dioxane, 3 ml of 99.77% D_2O and a catalytic amount of NaOH were refluxed for 45 hrs. The reaction product was diluted with H_2O, then extracted with pentane. The pentane extract was evaporated and the residue was sublimed (150° at 3 mm).

3,3'-dideuteriobicyclo[3.2.1]octan-2-one

1.5 g of commercially available ketone was treated with 10 ml of 99.77% D_2O and 1 ml of trifluoroacetic anhydride. The sample was heated at 60°C for 12 hrs, then poured into aqueous $NaHCO_3$. Extraction with pentane followed by sublimation of the crude product obtained by evaporation of the pentane yielded 1.3 g of deuterated material.

Table 3. Preparation of 2-Aryl-2-Bicyclo[2.2.2]octanols[a]

System	Aryl Group	Yield	Mpt. or B. pt	C%		H%		F%		Mass Spectra	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	m/e(Calcd)	m/e(found)
2-[2.2.2]	p-FC_6H_4	8.6[b]	55-56°	76.29	76.10	7.84	7.78	8.62	8.62	220	220
	p-$CF_3C_6H_4$[c]	52.2	60° at .3 min[d]	-	-	-	-	-	-	270	270
	p-$CF_3C_6H_4$[e]	43.2	60° at .3 min[d]							272	272(60.3%), 271(34.5%), 270(5.2%)
2-[3.2.1]	p-FC_6H_4[c]		80° at .3 min[d]	-	-	-	-	-	-	220	220
	p-FC_6H_4[e]		80° at .3 min[d]							222	222(80.2%), 221(17.4%), 220(2.4%)
	p-$CF_3C_6H_4$	77.8	71-74°[f]	66.66	66.64	6.31	6.36	21.11	21.10	270	270
	p-$CF_3C_6H_4$[e]	60.2	60° at .2-.4 mm[d]							272	272(78.5%), 271(18.4%), 270(3.1%)
6-[3.2.1]	p-FC_6H_4[c]	78	73-74°	-	-	-	-	-	-	220	220
	p-$CF_3C_6H_4$	32	75-75.5°	66.66	66.78	6.31	6.21	21.11	21.30	270	270
	p-$CF_3C_6H_4$[g]	55.3	74-77.5°							272	272(51.4%), 271(43.1%), 270(5.2%)

[a] All solids were crystallized from heptane.

[b] The yield of crude product was actually much greater than this value. Molecular distillation of the crude product yielded a mixture of alcohol and olefin from which the alcohol was obtained pure after three recrystallizations from hexane. The yield of pure product was reduced in the fractional crystallization process.

[c] Not analyzed.

[d] Molecular distillation.

[e] Deuterated at C(3).

[f] Possibly a mixture of *exo* and *endo* alcohols.

[g] Deuterated at C(7).

Table 4. Nmr and ir Data of Isomeric Arylbicyclooctanols

System	Aryl Group	ir (cm^{-1})[a]	nmr (τ)[b,c]
2-[2.2.2]	*p*-FC_6H_4[d]	3356(s), 2880(s), 860(m), 831(s), 815(s)	2.58 (m, 2H), 3.09 (m, 2H), 7.5-8.8 (m, 13H)
	p-$CF_3C_6H_4$	3450(s), 2950(s), 1630(m), 835(s)	2.50 (s, 4H), 7.4-9.0 (m, 13H)
2-[3.2.1]	*p*-FC_6H_4	3450(s), 2950(s), 1620(s), 835(s), 815(s)	2.50 (m, 2H), 3.04 (m, 2H), 7.4-9.0 (m, 13H)
	p-$CF_3C_6H_4$[d,e]	3330(s), 2850(s), 1620(s), 840(s)	2.35 (s, 4H), 7.3-9.0 (m, 13H)
6-[3.2.1]	*p*-VC_6H_4[d,e]	3350(m), 2890(s), 1620(m), 858(m), 845(m), 828(m), 815(m)	2.50 (m, 2H), 2.92 (m, 2H), 7.3-9.0 (m, 13H)
	p-$CF_3C_6H_4$[d]	3450(w), 2950(s), 1640(w), 858(m), 830(w)	2.4 (s, 4H), 7.2-8.8 (m, 13H)

[a] neat ir sample unless otherwise indicated

[b] CCl_4 was the nmr solvent unless otherwise indicated

[c] TMS was used as internal nmr standard for all spectra

[d] Nujol mull

[e] $CDCl_3$ was used as the nmr solvent

[f] Freon 114-B2 was used as the nmr solvent

7,7'-dideuteriobicyclo[3.2.1]octan-6-one

This material was deuterated using a procedure similar to that of Farnum and Mehta[3] for the preparation of 3,3'-dideuterionorbornan-2-one. 3.0 g of bicyclo[3.2.1]octan-6-one, 20 ml of 99.77% D_2O and 2 ml of trifluoroacetate anhydride were heated for 60 hrs at 100°C. The product was neutralized with Na_2CO_3, and then taken up in pentane solution. The pentane solution was washed with two 10 ml portions of D_2O. It was then dried with $MgSO_4$ and the pentane was evaporated on a rotary evaporator. The crude product was sublimed (80°/water aspirator pressure) yielding 2.1 g of labeled material.

Recovery Experiments

In a typical experiment the nmr sample itself was quenched. This was done by quickly decanting the sample into a quenching solution which was maintained at the desired temperature. The quenching solution was agitated vigorously with a vibro-mixer. The quenched material was then extracted with a suitable solvent. The following table summarizes the extractable products which were identified in a series of experiments.

Elimination Experiments

In a typical experiment 250 mg of 2-*p*-fluorophenyl-bicyclo[3.2.1]octan-2-ol was treated with 250 mg of absolute pyridine and 500 mg of *p*-toluenesulfonylchloride.[6] This mixture was heated in a sealed tube for 10 hrs at 110°. The

Table 5. Quenching Products From Several Isomeric Arylbicyclooctyl Cations

System	Aryl Group	Quenching Conditions	Products
2-[2.2.2]	*p*-FC_6H_4	Pentane/Na_2CO_3/-78°	2-*p*-fluorophenylbicyclo[2.2.2]-oct-2-ene[a]
	p-$CF_3C_6H_4$	Pentane/aq. NO_2CO_3/0°	2-*p*-trifluoromethylphenylbicyclo-[2.2.2]oct-2-ene (55%) 6-*p*-trifluoromethylphenylbicyclo-[3.2.1]oct-6-ene (45%)
2-[3.2.1]	*p*-FC_6H_4	Pentane/Na_2CO_3/-78°	2-*p*-fluorophenylbicyclo[3.2.1]-oct-2-ene (51%) 2-*p*-fluorophenylbicyclo[2.2.2]-oct-2-ene (17%) and 32% unidentified products[b,c]
6-[3.2.1]	*p*-FC_6H_4	MeOH/Na_2CO_3/-78°	6-*p*-fluorophenylbicyclo[3.2.1]-oct-6-ene (77%)[d] and 23% unidentified products

[a]No other detectable products. This is based on integration of the characteristic olefinic proton in this system.

[b]60% recovery of material.

[c]The unidentified material is comprised of at least two compounds. There were two peaks having a longer retention time than the olefins (20% SE-30).

[d]Based on integration of the olefinic proton.

crude reaction mixture was poured into $NaHCO_3$ solution. Extraction of the bicarbonate solution with pentane, drying with $MgSO_4$, and removal of the solvent with a rotary evaporator yielded a crude oil. This material was pumped at .3 mm pressure in order to remove the last traces of pyridine. Nmr analysis of the product indicated a mixture of 80% of the desired 2-*p*-fluorophenylbicyclo[3.2.1]oct-2-ene and 2% of 2-*p*-fluorophenylbicyclo[2.2.2]oct-2-one. The desired olefin can be obtained essentially pure by preparative gas chromatography on 1,2,3-tris(cyanoethoxy)-propane at 135°.

Nmr ($CFCl_3$) τ 2.65 (m, 2H), 3.05 (m, 2H), 4.35 (m, 1H), 6.9-9.0 (m, 10H).

The following table gives the nmr spectra for a representative olefin from each bicyclooctyl system studied.

Table 6. Nmr Spectra of Representative Olefins Prepared by Dehydration[a]

System	Olefin	Chemical Shifts
2-[2.2.2]	2b	CCl_4, 2.85 (m, 4H), 3.55 (dd, J = 7 Hz, 2 Hz, 1H), 6.97 (br s, 1H), 7.35 (br d, 5 = 7 Hz, 1H), 8.50 (AB q, 8H)
2-[3.2.1]	10b	$CFCl_3$, 2.85 (m, 4H), 4.35 (m, 1H), 7.0-9.0 (m, 10H)
6-[3.2.1]	17a	CCl_4, 2.45 (s, 4H), 3.65 (d, J = 6 Hz, 1H), 7.0 (br s, 1H), 7.30 (br s, 1H), 7.5-8.1 (m, 2H), 8.3-8.7 (m, 6H)

[a]TMS was used as internal standard.

PART II

REFERENCES

REFERENCES

1. D. G. Farnum and A. D. Wolf, submitted for publication.
2. D. G. Farnum, J. Amer. Chem. Soc., 89, 2970 (1967).
3. D. G. Farnum and G. Mehta, J. Amer. Chem. Soc., 91, 3256 (1969).
4. H. Kwart and J. L. Irvine, J. Amer. Chem. Soc., 91, 5541 (1969).
5. G. A. Olah, G. Liang, J. R. Wiseman and J. A. Chang, J. Amer. Chem. Soc., 94, 4927 (1972).
6. W. Kraus and R. DeWald, Ann. Chem., 689, 21 (1965).
7. V. N. Ipatieff, J. E. Germain, W. W. Thompson and H. Pines, J. Org. Chem., 17, 252 (1952).
8. K. B. Wiberg and B. A. Hess, Jr., ibid., 31, 2250 (1966).
9. W. Szarkowska-Szpaczek, Roczniki Chemii, 36, 235 (1962).
10. D. Komppa, T. Hirn, W. Rohrmann and S. Beckmann, Ann., 521, 242 (1936).
11. C. W. Jefford, J. Gunsher, D. T. Hill, P. Brun, J. LeGras and B. Waegell, Org. Syn., 51, 60 (1971).
12. C. W. Jefford, S. Mahajan, J. Waslyn and B. Waegell, J. Amer. Chem. Soc., 87, 2184 (1965).
13. R. A. Appelton, J. C. Fairlee, R. McCrindle and W. Parker, J. Chem. Soc., C, 1716 (1968).

14. G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras and C. Y. Lui, J. Amer. Chem. Soc., 92, 4627 (1970).

15. M. Saunders, P. von R. Schleyer and G. A. Olah, ibid., 86, 5680 (1964).

16. J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner and M. Hine, J. Amer. Chem. Soc., 77, 594 (1955).

17. P. K. Freeman, D. M. Balls and D. J. Brown, J. Org. Chem., 33, 2211 (1968).

18. A. C. Cope, H. H. Lee and H. E. Petree, J. Amer. Chem. Soc., 80, 2849 (1958).