

$^{13}\text{C}$  NUCLEAR MAGNETIC  
RESONANCE STUDIES OF  
2-ARYL-2-NORBORNYL CATIONS

Thesis for the Degree of M. S.  
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BING LUN LAM  
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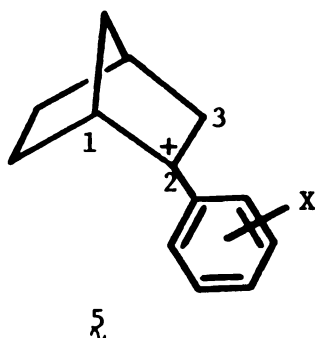
# ABSTRACT

## $^{13}\text{C}$ NUCLEAR MAGNETIC RESONANCE STUDIES OF 2-ARYL-2-NORBORNYL CATIONS

By

Bing Lun Lam

A plot of the  $^{13}\text{C}(1)$  versus  $^{13}\text{C}(3)$  chemical shifts for a series of 2-aryl-2-norbornyl cations  $\xi$ , shows a change in slope for cations less



stable than 2-m-chlorophenyl-2-norbornyl cation. The result is consistent with a change from classical ion to non-classical ion character. It is also shown that the  $^{13}\text{C}$  nmr shifts of p-halogen substituted norbornyl cations do not show the marked deviation from linearity shown in the earlier PMR studies. This result is consistent with an earlier proposal that these ions are in rapid equilibrium with dimeric ions which show large magnetic anisotropic effects on the PMR chemical shifts.

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OF 2-ARYL-2-NORBORNYL CATIONS

By

Bing Lun Lam

A THESIS

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1973

62354

## DEDICATION

To my parents for their affection and to my brother and sister-in-law  
for their moral support.

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I am grateful to Professor Donald G. Farnum who has provided me with the opportunity to complete this work. His guidance, interest and intellectual inspiration are deeply appreciated.

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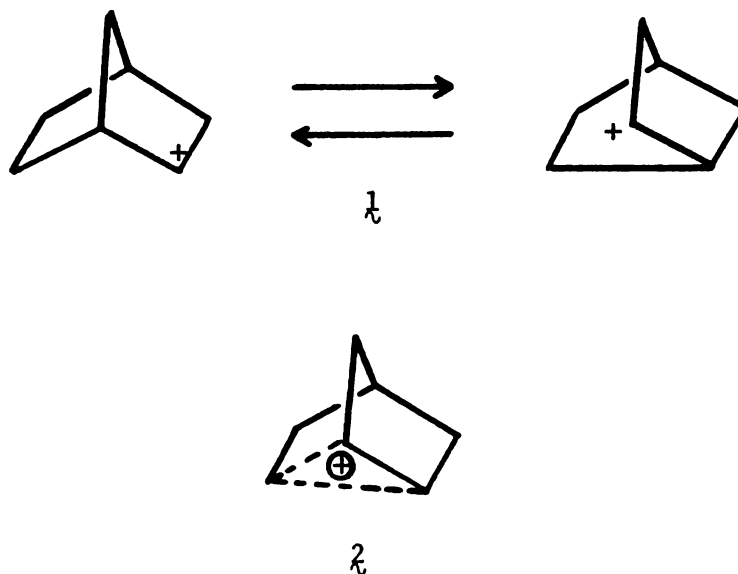
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## **INTRODUCTION**

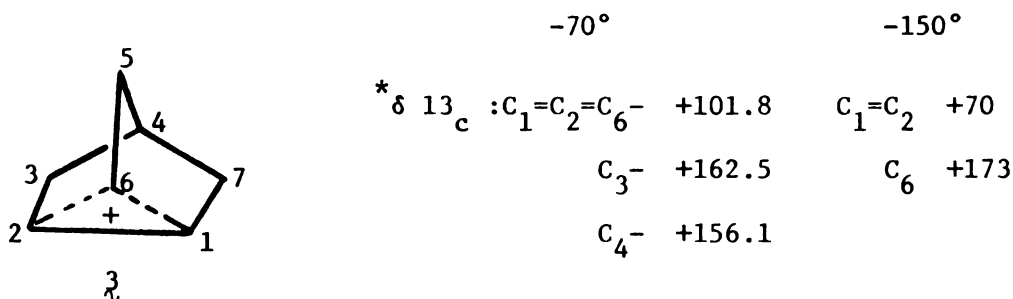
## INTRODUCTION

An early application of strong acid solvents was the use of 100%  $\text{H}_2\text{SO}_4$  for the preparation of stable solutions of carbonium ions such as the triphenylcarbonium ion  $(\text{C}_6\text{H}_5)_3\text{C}^+$ .<sup>1</sup> More recently a large variety of different carbonium ions has been prepared and observed in various highly acidic media. For example, t-butanol is completely converted to the trimethylcarbonium ion in  $\text{HSO}_3\text{F}-\text{SbF}_5-\text{SO}_2$  at  $-60^\circ$ .<sup>2</sup> The potential of this method to generate and observe stable carbonium ions at variable temperature by spectroscopic methods has been applied to the controversial question of whether the norbornyl cation is an equilibrating pair of classical ions  $1$  or a  $\sigma$  delocalized non-classical ion  $2$ .<sup>3</sup>



Schleyer, Saunders and Olah in 1964 first examined the 2-norbornyl cation and observed its PMR spectrum in solution starting from 2-fluoro-exo-norbornane in  $\text{SbF}_3-\text{SO}_2$  at room temperature and  $-140^\circ$ .<sup>4</sup> They concluded that even at  $-140^\circ$ , the PMR method does not necessarily differentiate between the rapidly equilibrating classical structures or the

non-classical structure of the 2-norbornyl cation because its time scale is much slower than the expected rapid exchange of equilibrating forms. More recently Olah obtained the low temperature Carbon-13 ( $^{13}\text{C}$ ) spectrum of the norbornyl cation by the Internuclear Double Resonance (INDOR) method and provided a strong case for a non-classical structure  $\lambda$ .<sup>5</sup>



At -150° the observed two carbon resonance at 70 ppm is not compatible with the expected value of 16.5 ppm from two equilibrating classical carbonium ion centers. The  $\sigma$  delocalized non-classical nature is further supported by a photoelectron spectrum of the norbornyl cation.<sup>6</sup>

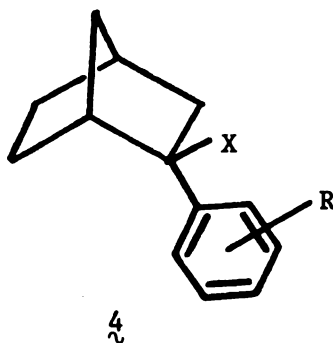
According to Winstein a basic tenet of the non-classical theory is that the more stable the cationic center the less stabilization that center will require from the rest of the molecule and the less important participation should be.<sup>7</sup> Consequently we should expect to find a marked decrease in those characteristics associated with participation as we move along a series to more and more stable cations. Therefore, one is not entirely surprised by Olah's study and conclusion that the 2-methyl-2-norbornyl cation is closer to the classical than to the completely non-classical structure.<sup>8</sup> One might point out that, in going from the parent norbornyl to the 2-methyl-2-norbornyl system, one is comparing a secondary with a tertiary center. Now if one changes the 2-substituent in the

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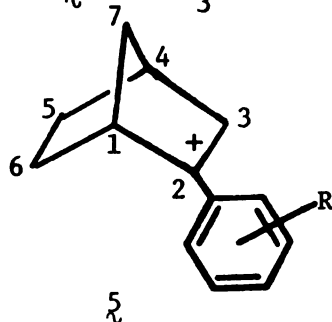
\*In parts per million from  $^{13}\text{CS}_2$ .

norbornyl system to a phenyl group, one would expect the cationic center to be greatly stabilized. Indeed, that 2-phenyl-2-norbornyl cation is classical has been demonstrated by an extensive PMR study<sup>9</sup> and confirmed by Olah's <sup>13</sup>CMR studies.<sup>8</sup>

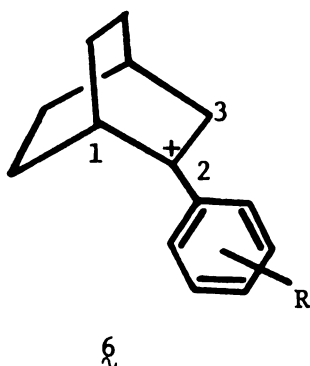
At this point, a dilemma in our trend of thought is presented by H.C. Brown and K. Takeuchi.<sup>10,11</sup> They correlated the rate of solvolysis of a number of 2-aryl-2-exo-norbornyl derivatives  $\text{4}$  with  $\sigma^+$  values.



They found that the correlation was linear with none of the curvature expected if  $\sigma$  delocalization became an important factor for any of the derivatives. Such a plot would not be linear if  $\sigma$  delocalization were operative even though the study covered only 60% of the reactivity range from 2-p-anisyl-2-norbornyl to the 2-norbornyl system. It seems intuitively unreasonable that 2-norbornyl cation would be the only norbornyl derivative to exhibit  $\sigma$  delocalization. To resolve this puzzling inconsistency, A.D. Wolf carried out an extensive PMR study of a number of 2-aryl-2-norbornyl cations  $\text{5}$  in  $\text{HSO}_3\text{F}$ .<sup>12</sup>



The aryl group is varied to decrease electron donation to the carbonium ion center ( $C_2$ ) which, in turn, increases the electron demand on the norbornyl skeleton--especially at C(1) and C(3). Such an effect will show up in a down field shift of H(1) and H(2) in the PMR spectrum. Therefore, providing there is no other mechanism for leaking charge to C(1) and C(3), the charge effect felt by C(1) and C(3) would be directly proportional to the variation of charge density at the carbonium ion center C(2). In other words, a linear relationship would be expected by plotting the chemical shift of H(1) versus that of H(3) for the different 2-aryl-2-norbornyl cations, if the cations are classical. As it turned out, a linear relationship was not observed for the complete series, but a change in slope was obtained for cations less stable than 2-phenyl-2-norbornyl cations (Figure 1). By contrast, the behavior of the H(1) and



H(3) chemical shift for a similar series of 2-aryl-2-bicyclooctyl cations **6** is linear from p-methoxyphenyl through meta-chlorophenyl, (Figure 2). Such deviation from the initial linearity leads to the conclusion that one is observing the onset of non-classical character in these 2-aryl-2-norbornyl cations.

The recent development of Fourier Transform (FT) Nuclear Magnetic Resonance Spectroscopy<sup>13</sup> has made versatile <sup>13</sup>CNMR studies not only practical but also comparable with PMR in terms of experimental ease and

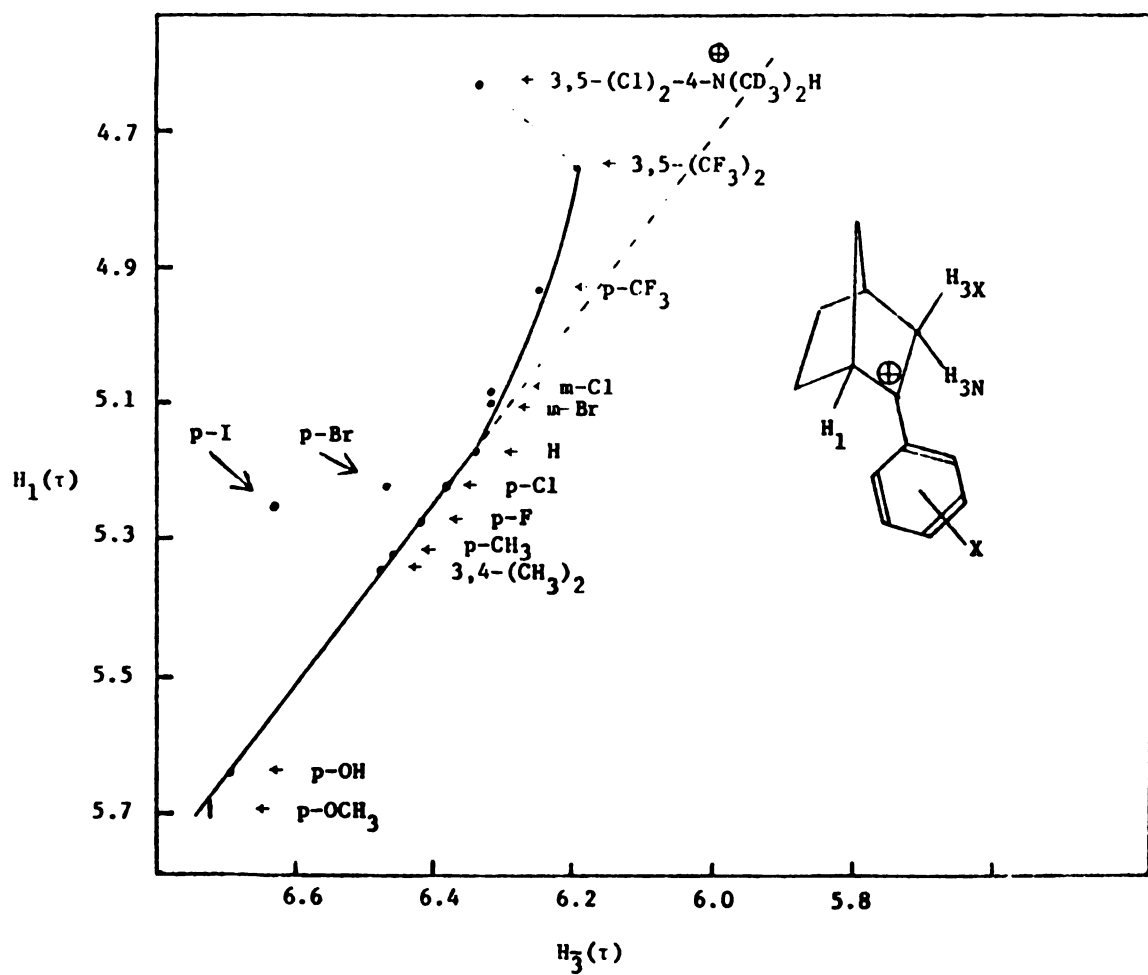


Figure 1.<sup>8</sup> Graph of  $H_1$  vs.  $H_3$  chemical shifts in 2-aryl-2-norbornyl cations **5**.

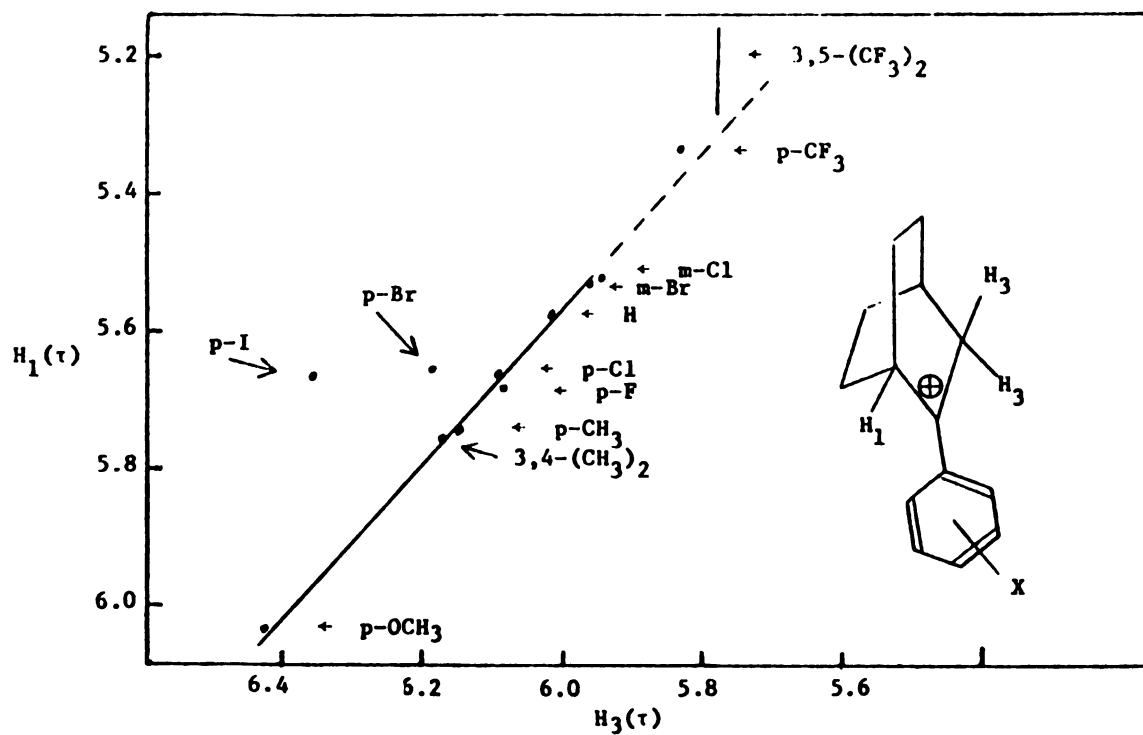


Figure 2.<sup>8</sup> Graph of  $H(1)$  vs.  $H(3)$  chemical shifts in 2-aryl-2-bicyclo[2.2.2]octyl cations  $\delta$ .



quality. In particular the sensitivity of the  $^{13}\text{C}$  chemical shift to charge distribution<sup>14</sup> offers another challenging testing ground for the conclusion drawn from Wolf's PMR studies. With this in mind, we set forth with the following studies.

## **RESULT AND DISCUSSIONS**

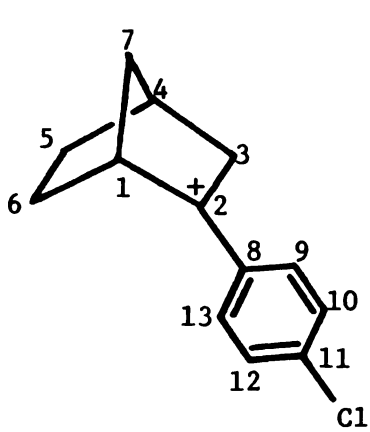
## RESULTS AND DISCUSSION

The feasibility of studying various cations at probe temperature was studied using the PMR spectrum as a measure of approximate lifetime. It was concluded that the  $^{13}\text{C}$ NMR spectrum could be obtained at probe temperature for the 2-aryl-2-norbornyl cations where the aryl groups are: p-methoxyphenyl; 2,3-dimethylphenyl; p-chlorophenyl; m-bromophenyl and p-iodophenyl. Spectra of the other cations were obtained at low temperature.

In all cases hydrogen decoupled spectra were obtained. An off-resonance decoupling experiment was performed on a few samples to help make spectral peak assignments. In these experiments, non-protonated carbon, CH,  $\text{CH}_2$ , and  $\text{CH}_3$  were observed as a singlet, doublet, triplet and quartet respectively.

A  $^{13}\text{C}$ NMR spectrum of 2-p-chlorophenyl-2-norbornyl cation  $\lambda$  in  $\text{FSO}_3\text{H}$ - $\text{FSO}_3\text{D}$  is displayed in Figure 3. The chemical shift assignments are shown in Table 1.

TABLE 1.  $^{13}\text{C}$  Chemical Shifts for Cation  $\lambda$

	$^{13}\text{C}$ Chemical Shifts for Cation $\lambda$	
	Carbon	$\delta$ (TMS)
 <p style="text-align: center;"><math>\lambda</math></p>	C(1)	59.9
	C(2)	257.5
	C(3)	50.9
	C(4)	40.2
	C(5)	34.7
	C(6)	42.0
	C(7)	25.9
	C(8,10,12)	133.5
	C(11)	162.2
	C(9,13)	142.2

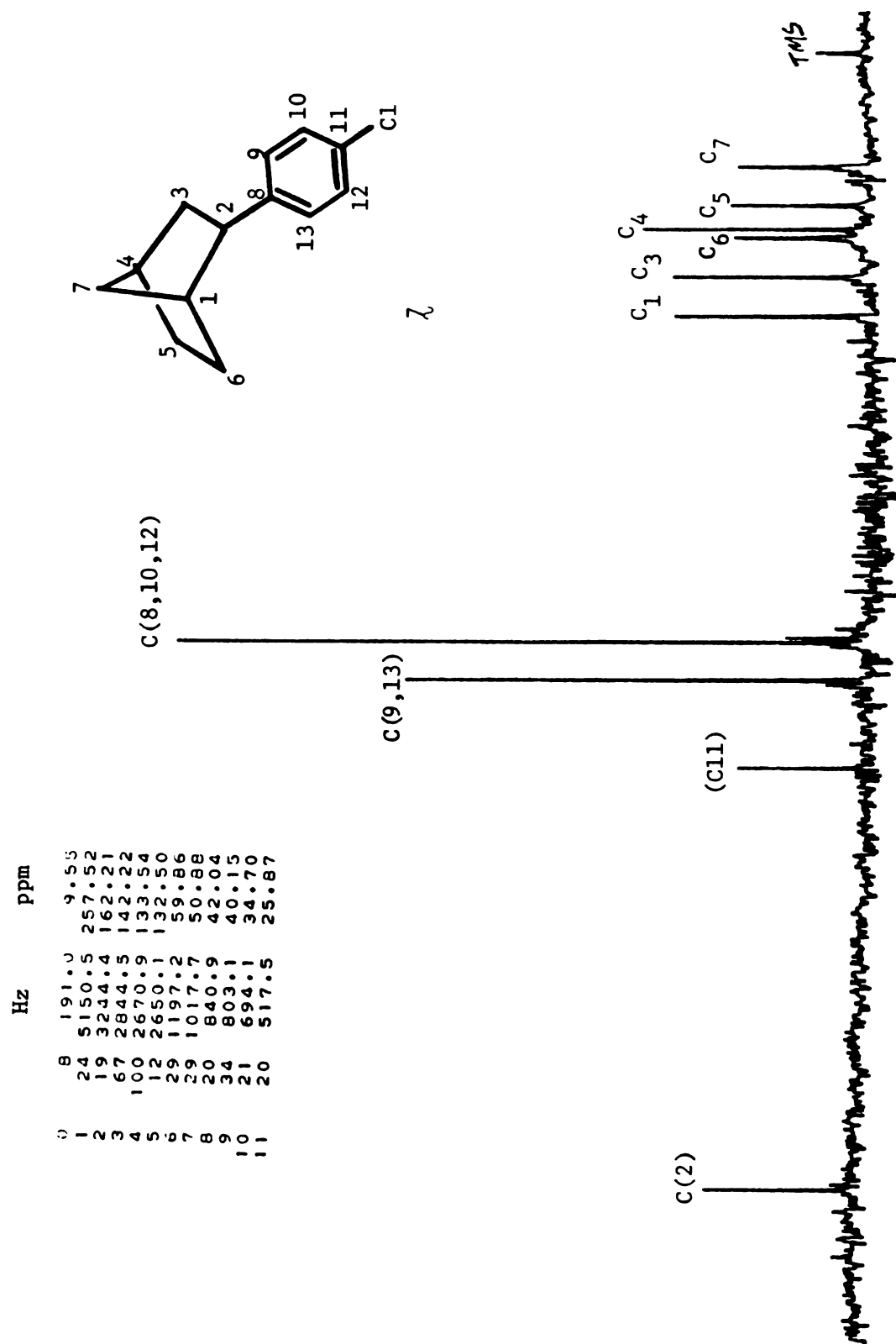
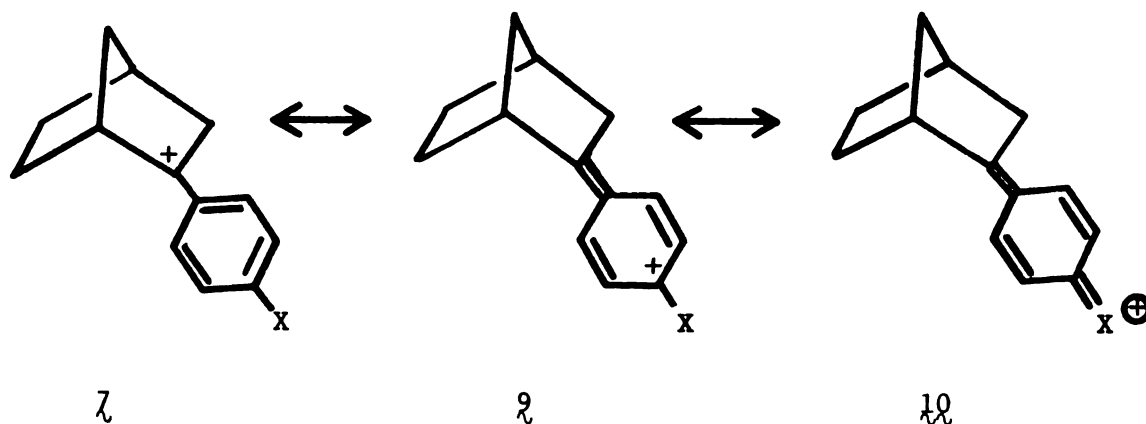


Figure 3.  $^{13}\text{C}$  NMR spectrum of 2-p-chlorophenyl-2-norbornyl cation  $\lambda$ .

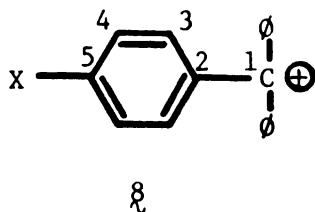
The order of assignment of the  $^{13}\text{C}$  chemical shifts for the norbornyl skeleton illustrated in Table 1 remains constant in the series of cations studied. Since the total  $^{13}\text{C}$  spectra of 2-substituted-2-norbornyl cations have not been reported in the literature, direct comparison of our assignments with others is not possible. However the  $^{13}\text{C}$  chemical shifts of C(1) and C(2) of the 2-phenyl-2-norbornyl cation in  $\text{FSO}_3\text{H}$  were obtained by Olah<sup>15</sup> using the INDOR method and were reported to be  $62 \pm 2$  ppm\* and  $258.6 \pm 2$  ppm\* respectively. Our FT  $^{13}\text{C}$  chemical shift values of C(1) and C(2) are 59.8 ppm and 257.8 ppm respectively. These values compare favorably with those reported by Olah.

Returning to Figure 3 and the  $^{13}\text{C}$  chemical shift values (Table 1) for 2-p-chlorophenyl-2-norbornyl cation, a comment would be appropriate concerning our assignment of the lower field singlet in the aromatic region to C(11) rather than C(8) of the aromatic ring. The relative importance of the resonance structures  $\lambda$  and  $\lambda Q$  (Scheme 1) to the stabilization of Cation  $\lambda$  is not obvious. In a recent study of para-substituted triphenyl-carbonium ions  $\delta$ <sup>16</sup> it was found that the chemical shift value for C(5)

SCHEME 1



\*Reported here as  $\delta(\text{TMS})$  using the conversion value  $\delta\text{CS}_2 = 192.8$ .



decreased while C(2) changed much less as the para substituent changed from a methoxy to a Fluoro group. Our chemical shifts are close to those reported for C(2) and C(5) of the appropriately substituted triaryl-carbonium ions.

Included in Table 2 is a listing of the  $^{13}\text{C}$  chemical shifts of interest, i.e., C(1), and C(3). A plot of the  $^{13}\text{C}$  chemical shift of C(1) versus C(3) is shown in Figure 4. In this graph the  $^{13}\text{C}$  chemical shifts for the 3,5-bis(trifluoromethylphenyl) substituted cation are plotted as a range of values.

Setting aside the significance of the graph in Figure 4 for later discussion, let us focus on several features of this graph.

As stated in the introduction, a strong electron releasing group places relatively little positive charge at C(2) of the norbornyl system while a strong electron withdrawing group places relatively more positive charge at C(2). An increase in charge density at C(2) causes the  $^{13}\text{C}$  chemical shift of C(3) and C(1) to shift to lower field. This trend is apparent from the ordering of points with the electron releasing capacity of the substituent as indicated by their  $\sigma^+$  values.<sup>17</sup> In fact a similar empirical relationship exists for the cationic center C(2) chemical shift and  $\sigma^+$  values (refer to Table 3). However a quantitative correlation is not obtained when one plots  $\sigma^+$  values for the different substituents on phenyl for cation  $\mathfrak{5}$  versus the  $^{13}\text{C}(2)$  chemical shift. The observed scatter of the points may be an inherent deviation obtained when one

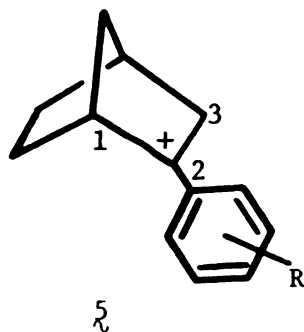


TABLE 2.  $^{13}\text{C}$  Chemical Shifts\* for C(1), C(3) of Cation 5

Cation 5	R	C(1)	C(3)
a	p-OCH <sub>3</sub>	53.5	47.2
b	3,4(CH <sub>3</sub> ) <sub>2</sub>	57.1	49.6
c	p-Cl	59.86	50.8
d	p-I	59.76	50.87
e <sup>1</sup>	H	59.34	50.47
f	m-Br	59.83	50.86
g <sup>1</sup>	m-Cl	61.45	51.27
h <sup>1</sup>	p-CF <sub>3</sub>	63.75	52.23
i <sup>2</sup>	3,5(CF <sub>3</sub> ) <sub>2</sub>	66.7-67.4	52.4-53.9

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\* ppm from capillary TMS.

1) Determined at -80°.

2) C(1) and C(2) are reported as a range of values, spectrum was determined at -90°.

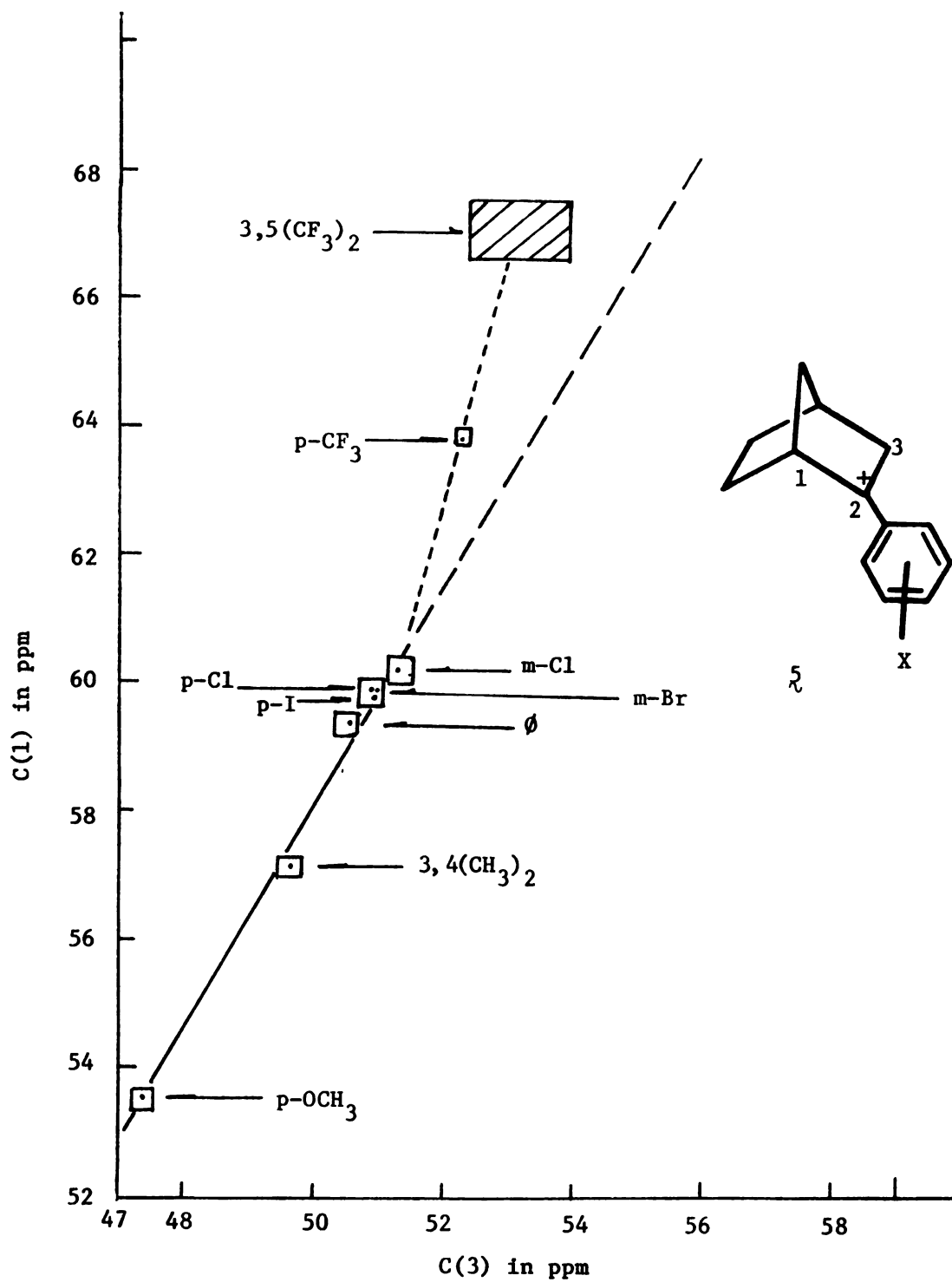


Figure 4. Graph of  $^{13}\text{C}(1)$  vs  $^{13}\text{C}(3)$  chemical shifts in 2-aryl-2-norbornyl cations  $5$ .

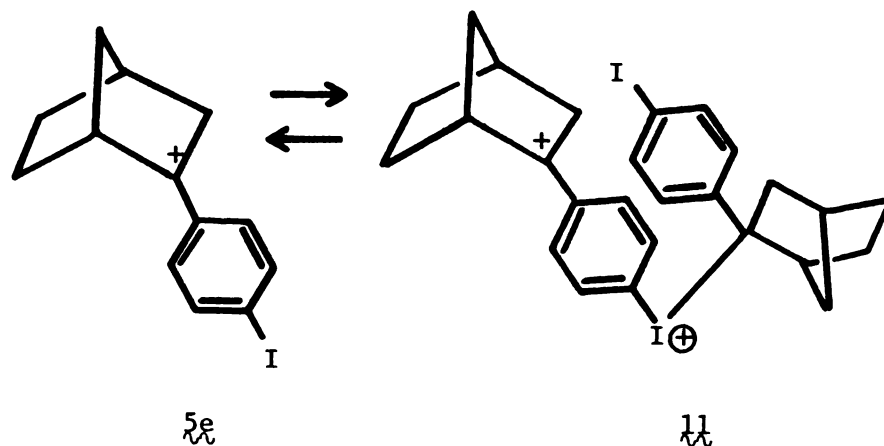


TABLE 3. Listing of  $\sigma^+$  Values Versus C(2) Chemical Shift  
in 2-aryl-2-norbornyl Cations  $5_{\lambda}$ .

Cation $5_{\lambda}$	Aryl Group	C(2)	$\sigma^+$
a	p-OCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	223.3	-0.764
b	3,4(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	230.6	-0.375
c	p-ClC <sub>6</sub> H <sub>5</sub>	257.5	0.112
e	C <sub>6</sub> H <sub>5</sub>	257.8	0.
f	m-BrC <sub>6</sub> H <sub>5</sub>	257.8	0.391
d	p-IC <sub>6</sub> H <sub>5</sub>	258.9	0.132
g	m-ClC <sub>6</sub> H <sub>5</sub>	262.44	0.373
i	3,5(CF <sub>3</sub> ) <sub>2</sub>	263.2	1.04
h	p-CF <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	264.7	0.61

extrapolates  $\sigma^+$  values, which were determined under solvolytic conditions, to these strong acidic media.

It has been shown in Wolf's<sup>8</sup> proton NMR studies that there was some unusual effect operating in the p-halogen substituted cations which caused these points to "fall off the line" in the 2-aryl-2-norbornyl cation series (Figure 1). Interestingly enough, such gross deviations are not observed for the p-halogen substituted cations in this <sup>13</sup>CNMR study. A simple resolution to this puzzling discrepancy may be found in the different response of PMR and <sup>13</sup>CNMR to diamagnetic effects. Available calculations agree that the paramagnetic term normally dominates <sup>13</sup>C chemical shifts and the anisotropy term, which depends only on the spatial relationship between the nucleus being observed and the anisotropic group, is relatively insignificant in <sup>13</sup>CNMR.<sup>18</sup> Therefore, a logical explanation is that there exists some sort of neighboring anisotropy effect for the p-halogen substituted cations in FSO<sub>3</sub>H. This explanation is consistent with Wolf's suggestion of a dimer  $\lambda\lambda$  in equilibrium with the cation  $\zeta e$ .



Another possibility is the reorientation of the aromatic ring in Cation  $\zeta e$  such that the protons on C(3) are affected by its anisotropy. Whatever the explanation, one thing is demonstrated clearly. The p-halogen substituted cations are on the line.

In this study the linearity ranges from the p-methoxyphenyl to m-chlorophenyl substituted cation, while the "break" from linearity starts after the 2-phenylnorbornyl cation in Wolf's PMR studies. Again this difference in "break" point may be due to a neighboring anisotropy experienced by the m-halogen substituted cations  $\bar{\lambda}$ . Such anisotropic effects would not be unexpected in view of the much larger effect that caused the p-halogen substituted cations to "fall off the line".

Now we will turn our attention to the significant implication of Figure 4.

The basic assumption in Wolf's PMR study<sup>8</sup> is that the chemical shift difference between H(1) and H(3) will be constant for classical aryl-norbornyl cations. This hypothesis, though well illustrated by the Proton NMR studies, was weakened by the unaccountable behavior of the p-halogen substituted cations. The smooth linearity, ranging from the p-methoxy substituted to the m-chlorophenyl substituted cation, shown in Figure 4 strengthens the hypothesis.

Similar to the proton studies, a non-linear behavior in the graph of  $^{13}\text{C}(1)$  shifts versus  $^{13}\text{C}(3)$  shifts signifies charge leakage of the cationic center C(2) to C(1). Such deviation from initial linearity is demonstrated in Figure 4 with the "break" at the m-chlorophenyl substituted cation. Thus the more reliable  $^{13}\text{C}$  chemical shift plot has confirmed the general picture obtained from previous PMR studies for a similar series of 2-aryl-2-norbornyl cations.

In summary, our data have demonstrated the following points:

(1) There is a qualitative relationship between the  $\sigma^+$  value and the charge density at the cationic center.

(2) The marked deviation from linearity exhibited by p-halogen substituted cations in the PMR studies of Wolf is apparently due to

diamagnetic effects, since the  $^{13}\text{C}$  chemical shifts of the p-halogen substituted cations show the expected linearity.

(3) The change in slope exhibited in the  $^{13}\text{C}$  nmr correlation of Figure 4 for cations more electron demanding than 2-m-chlorophenylnorbornyl signifies a change from classical to non-classical ion character.

## EXPERIMENTAL

## EXPERIMENTAL

### <sup>13</sup>CNMR Spectra

Most <sup>13</sup>CNMR spectra were obtained at 20 MHz on a Varian CFT-20 Pulse Fourier Transform (FT) Spectrometer using 20% FSO<sub>3</sub>D as internal pulse deuterium lock in 10 mm. O.D. sample tubes. Some spectra were obtained on a Varian XL-100 Pulse FT spectrometer in 12 mm sample tubes through the courtesy of Dow Chemical Co., Midland, Michigan.

All chemical shift assignments were made with reference to capillary TMS with a  $\pm 0.1$  ppm tolerance.

### Preparation of Carbocations

Appropriate amounts of carbocation precursor were dissolved in a chosen solvent, generally CFC1<sub>3</sub>. The solution was transferred to an NMR sample tube and was cooled at -80° in a Dry Ice-isopropanol bath. After 3 minutes, a layer of SO<sub>2</sub>ClF (25% by volume) was introduced without mixing with the solution of precursor. Under N<sub>2</sub>, FSO<sub>3</sub>H was pipetted into the sample tube slowly and carefully to avoid mixing. After 10 minutes at -80°, the contents of sample tube were rapidly mixed well. For samples that needed to be observed at probe temperature, the sample tube was put under very high vacuum to evacuate volatile components. In general, the carbocation solutions were prepared at approximately 20% weight concentration.

### Preparation of 2-aryl-2-endo-norbornanols

The alcohols used for this work were prepared by reacting the appropriate organometallic reagents with commercially available

2-norbornanone. The organometallic reagents were formed either by Grignard reaction<sup>19</sup> or by the halogen-metal interconversion reaction<sup>20</sup> (HMIR) starting with aryl bromide except in the case of p-iodo-phenyl lithium, when aryl iodide was used.

#### Typical procedure for preparing Alcohols using the HMIR Method

Ether was distilled into a dried 50 ml 3 neck flask containing a weighted amount of desired arylhalide to make up a 10-30% by volume solution. The flask was equipped with a low temperature thermometer, a magnetic stirring bar, N<sub>2</sub> inlet and a 15 ml constant pressure addition funnel. The arylhalide solution was cooled to -40° using a Dry-Ice-acetone bath. A 10% molar excess (over halide) of commercial n-butyllithium in hexane was added dropwise while keeping the reaction temperature between -30° and -40°. Then it was allowed to warm to -10° for 5 minutes and lowered back to -40°. A solution of norbornanone (one equivalent) in anhydrous ether was added at a rate such that the temperature of the reaction mixture did not rise above -30°. After addition of ketone was completed, the reaction mixture was warmed up to room temperature and hydrolyzed with cold saturated aqueous NH<sub>4</sub>Cl solution and extracted with ether. Drying the ether solution with MgSO<sub>4</sub> followed by evaporation of the ether led to a crude oil or solid which was then purified by fractional molecular distillation or by recrystallization with hexane.

Melting points and boiling points reported for the following compounds are the same as recorded by Wolf<sup>8</sup> unless indicated otherwise.

- (I) 2-p-methoxyphenyl-2-endo-bicyclo[2,2,1]heptanol  
38% yield from HMIR; b.p. 82° at 3mm (Rec. 100°-150° at 8 mm)<sup>8</sup>
- (II) 2-(3,4.-dimethylphenyl)-2-endo-bicyclo[2,2,1]heptanol  
55% yield from HMIR; b.p. 130°-145° at 0.5 mm.
- (III) 2-p-idodophenyl-2-endo-bicyclo[2,2,1]heptanol  
60% yield from HMIR; m.p. 99°
- (IV) 2-p-chlorophenyl-2-endo-bicyclo[2,2,1]heptanol  
68% yield from HMIR; m.p. 86°
- (V) 2-m-chlorophenyl-2-endo-bicyclo[2,2,1]heptanol  
27% yield from HMIR, b.p. 105° at 4.5 mm. (Rec. m.pt. 42-43.5°)<sup>8</sup>
- (VI) 2-m-Bromophenyl-2-endo-bicyclo[2,2,1]heptanol  
40% yield from HMIR; m.p. 54.5°-56°
- (VII) 2-p-trifluoromethylphenyl-2-endo[2,2,1]heptanol  
32.6% from HMIR; m.p. 65-66°
- (VIII) 2-[3,5,bis(trifluoromethylphenyl)]-2-endo-bicyclo[2,2,1]heptanol  
54% yield from HMIR; m.p. 75°-76°
- (IX) 2-phenyl-2-endo-bicyclo[2,2,1]heptanol  
50% yield from HMIR; m.p. 40-41°



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