

C-13 NUCLEAR MAGNETIC RESONANCE
SPECTROSCOPY AS A PROBE TO STUDY
SUBSTITUTED ARYL CARBOCATIONS

A Dissertation
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William T. Chambers
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This is to certify that the

thesis entitled

C-13 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY AS A
PROBE TO STUDY SUBSTITUTED ARYL CARBOCATIONS

presented by

William T. Chambers

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

A handwritten signature in blue ink, which appears to read "Donald G. Hamann".
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Major professor

Date 1/5/76





ABSTRACT

C-13 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY AS A PROBE TO STUDY SUBSTITUTED ARYL CARBOCATIONS

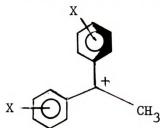
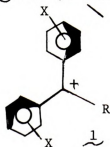
By

William T. Chambers

We have determined the carbon-13 NMR spectra of solutions of a number of aryl substituted carbocations in highly acidic media. We have observed a linear correlation of the carbon-13 chemical shift of the carbocationic centers in the arylcyclopentyl cations with those in the arylcyclohexyl and symmetrical 1,1-diaryl-1-ethyl cations. However, a plot of the carbon-13 chemical shifts of the carbocationic centers of the unsymmetrical 1-aryl-1-phenyl-1-ethyl cations vs. those of the arylcyclopentyl cations shows two reasonably linear portions of different slope.

The linear plots are as expected if the chemical shifts of the carbocationic centers of the three cation types are responding similarly to the electron donating ability of the aryl groups. The results are consistent with the commonly accepted symmetrically twisted structure

(1) for symmetrically diaryl substituted carbocations.



- 2 X = e⁻ donating
Y = Hydrogen
- X = Hydrogen
- 3 Y = e⁻ withdrawing

William T. Chambers

The change in slope for 1-aryl-1-phenyl-1-ethyl cations indicates a change in the response. This change could be accommodated by a change in structure from an unsymmetrically twisted ion in which the more coplanar electron donating aryl group was better conjugated with the carbocationic center than the more twisted phenyl (eg. 2) to one in which the more coplanar phenyl was better conjugated than the more twisted electron withdrawing aryl group (eg. 3). The different slopes would then reflect the different responses of the carbon chemical shift of the cationic center to the changing electron donating ability of a more planar aryl group as compared with that of a more twisted aryl group.

C-13 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY AS A
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By
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William T. Chambers

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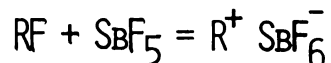
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INTRODUCTION

Not long after Gomberg discovered the first free radical, two groups^{1,2} independently proposed the existence of carbocationic species when they observed that colorless derivatives of triphenylmethane gave deep yellow solutions in concentrated sulfuric acid and formed orange complexes with metal halides. Although much evidence accumulated to support the existence of carbocations, confirmation was not obtained until Hofmann³ and Gomberg⁴ independently prepared colored anhydrous perchlorate salts, Ar_3CClO_4 , from triarylcarbinol and crystalline perchlorate acid. Although interest in carbocations has not abated from their discovery to the present time, it has only been since about 1950 that attempts to obtain crystalline salts of carbocations, other than those of triarylmethylcations, have been undertaken. These efforts were undoubtedly inspired by the theories of reaction mechanism which stemmed from investigations concerning solvolysis reactions. Since the presence of unstable carbocations as intermediates was postulated, it has only been natural to try to confirm their existence by isolation as stable salts or preparation of stable solutions.

With the development of more highly acid media, the range of carbocationic species available for study has been extended. The belief that alkyl carbocations were very unstable had to be discarded when Olah^{5,6} was able to isolate alkyl carbocationic hexafluorantimonates by

using the very simple reaction:



where R = i-Pr, t-Bu.

Although classical methods, such as conductometry, cryoscopy, and UV and IR spectroscopy, are still used to detect and establish the structure of stable carbocations, nuclear magnetic resonance spectroscopy, NMR, has more recently proved itself to be of incalculable value. Indeed, all that is necessary even for the layman to comprehend the impact that NMR has had on detection and establishment of structures of carbocation species, not to mention its impact on the rest of the chemical field, is to scan the chemical literature over the past two decades. A detailed review of the applications of NMR spectroscopy to detect and establish the structure of carbocations is beyond the scope of this text (one more than adequate review was published by Olah and Schleyer⁷). We will focus on those investigations pertinent to and directly relating to our results.

Farnum and Wolf⁸ used proton nuclear magnetic resonance spectroscopy, PNMR, to study a series of substituted 2-aryl-2-norbornyl cations. A plot of the PNMR chemical shifts of H(1) versus H(3) throughout the series of cations showed marked deviations from linearity for substituents on the aryl group more electron withdrawing than hydrogen (Figure 1). The results were consistent with the onset of nonclassical participation taking place in norbornyl cations more electron demanding than the 2-phenyl-1-norbornyl cation. A more nearly linear plot was

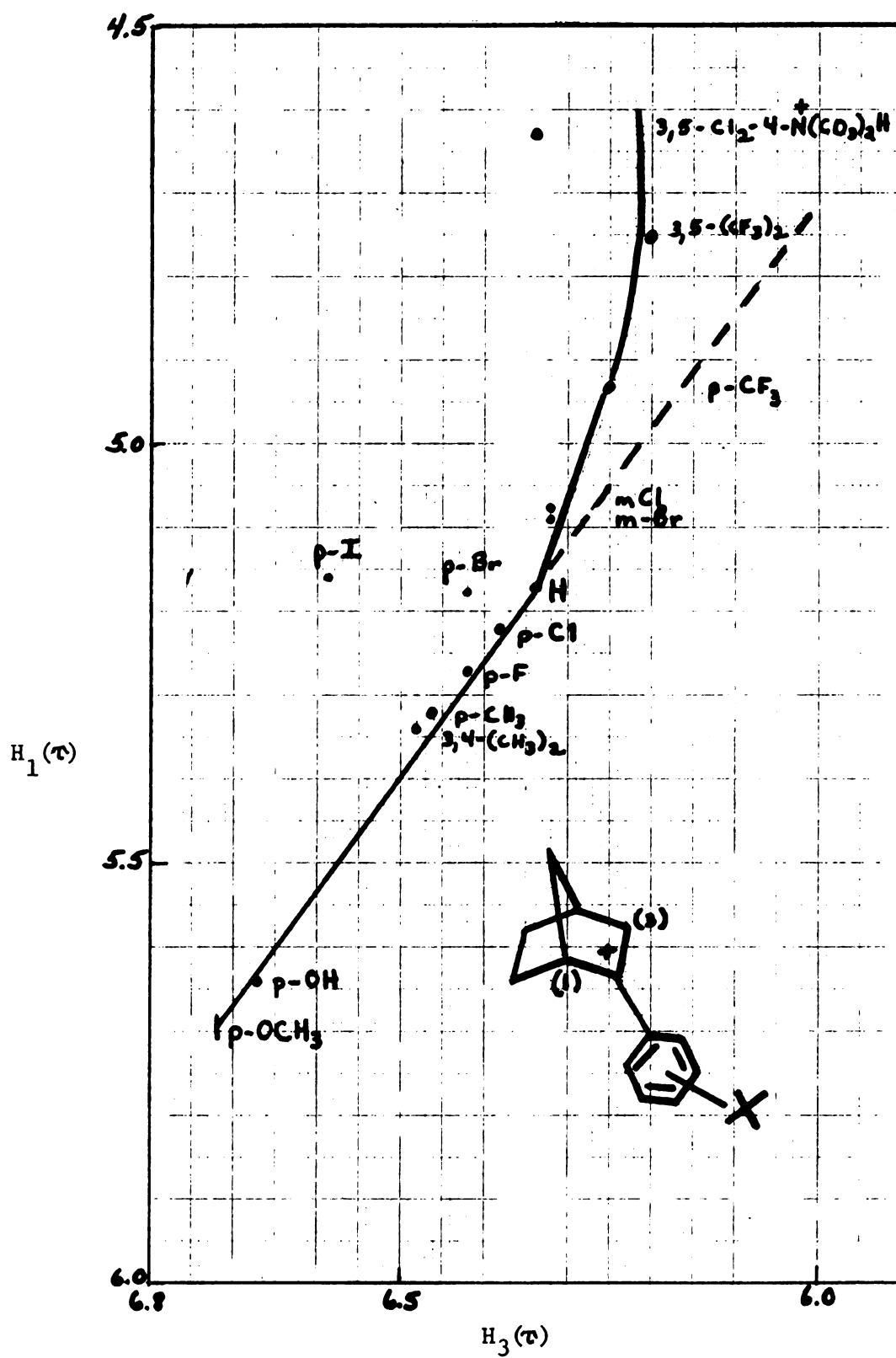
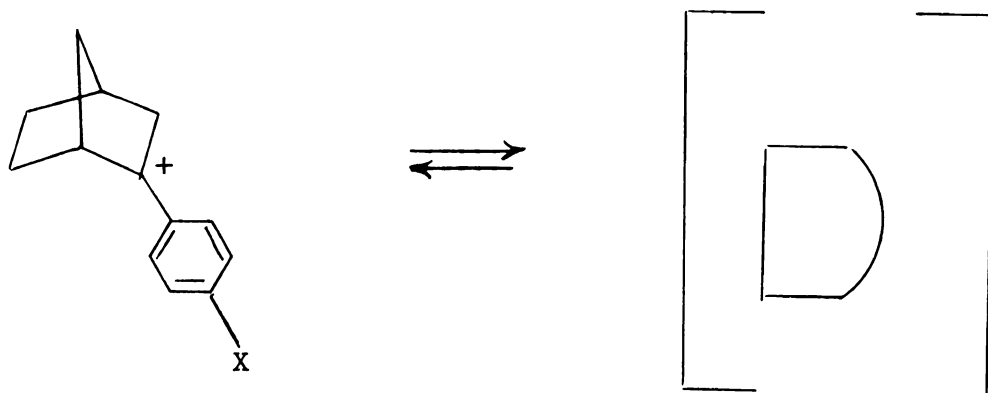


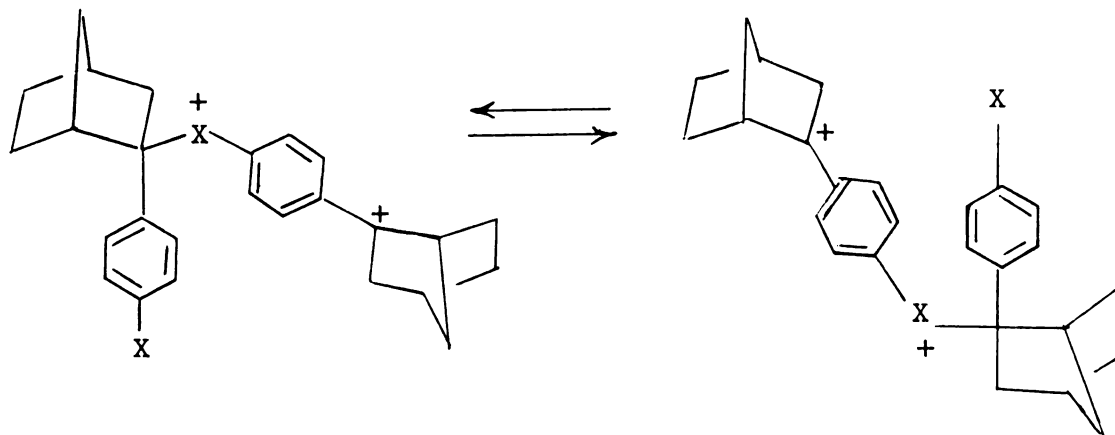
Figure 1. Graph of $H(1)$ vs. $H(3)$ chemical shifts in 2-aryl-2-norbornyl cations.

similarly obtained for a series of substituted 2-aryl-2-bicyclo (2.2.1) octyl cations (Figure 2). There was also some unusual effect which was present in the case of the parahalogen substituents which caused these points to deviate from the line in both the arylnorbornyl and the arylbicyclooctyl series. Close scrutiny of the PNMR data led these authors to postulate the presence of some other species, (D), in equilibrium with the parahalogen substituted cation.



Where X = Cl, Br, I

A possible structure of (D) is the equilibrating dimer 1



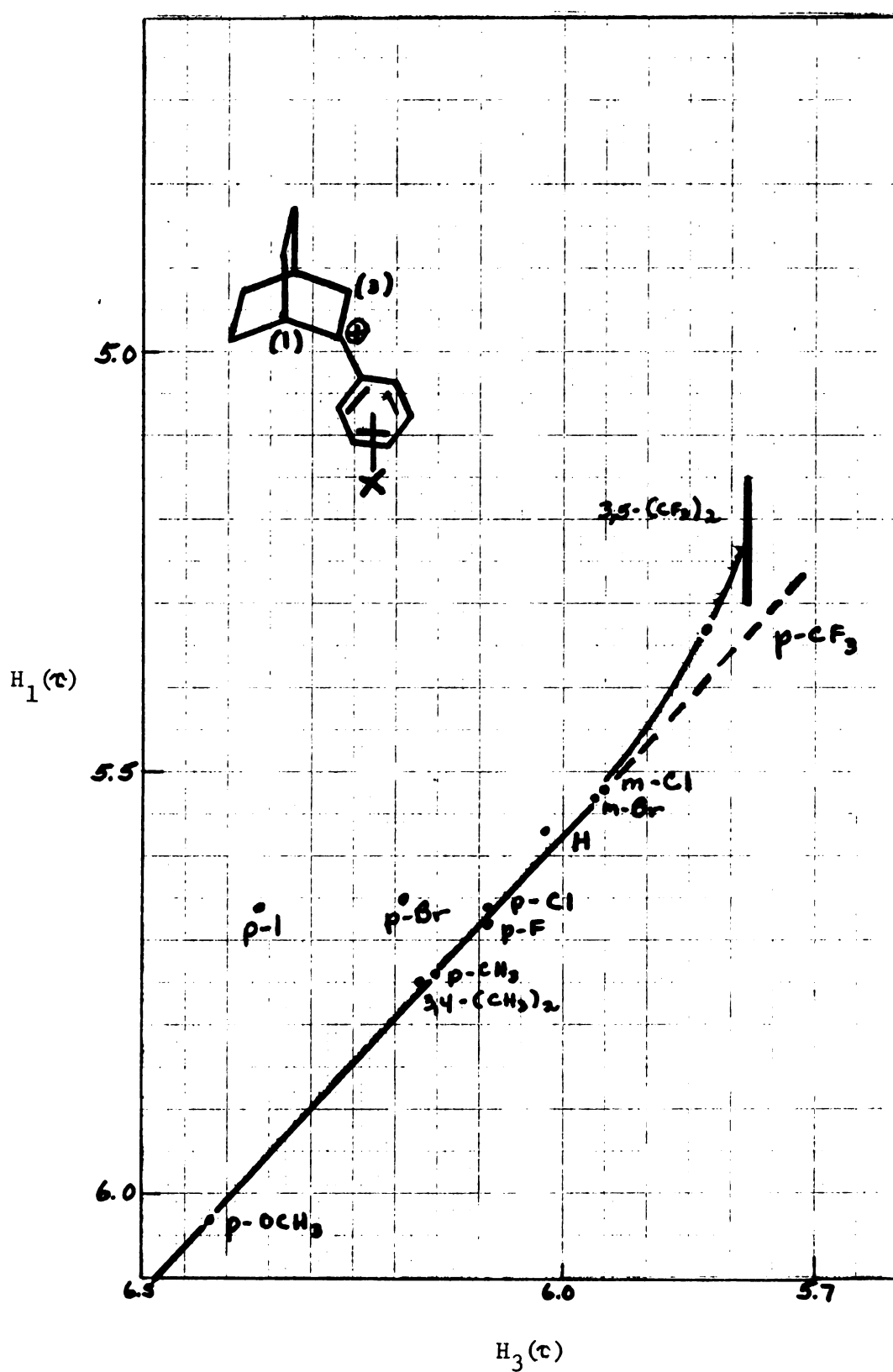


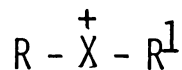
Figure 2. Graph of $H(1)$ vs. $H(3)$ chemical shifts in 2-aryl-2-bicyclo (2.2.2) octyl cations.

However, attempted detection of this equilibrium in the para iodophenyl derivative by a dilution study over a 50-fold change in concentration showed that if 1 is the species present, it is not in equilibrium with significant amounts of the monomer at the concentrations studied.

Deno⁹ has calculated σ^+ values for a number of substituents from four independent reactions and has shown that σ^+ values for para-halogens do not show good agreement. Thus the anomolous behavior of para-halogen derivatives for the 2-aryl-2-norbornyl and the 2-arylbi-cyclo[2.2.1]octyl cations is not unique.

Halonium ions represent a significant class of onium compounds and their role in electrophilic halogenation reactions is well-established. Evidence for halonium ion formation includes the result of trans addition (so-called anti addition) of the halogens to a double bond.^{10,11}

With the development of highly acidic solvents with low nucleophilicity, such as $\text{SbF}_5/\text{SO}_2(\text{SO}_2\text{ClF})$, Olah¹² has been able to prepare, directly observe and in some instances, even isolate stable chloronium, bromonium and iodonium ions of the type:



where $\text{R}=\text{R}^1 = \text{Me}, \text{Et}, \text{iPr}, \text{Norbornyl}, \text{Adamantyl}$

$\text{x} = \text{Cl}, \text{Br}, \text{I}$

and where $\text{R} = \text{Alkyl}, \text{R}^1 = \text{Aryl}$

Olah's⁷ data lend support to the idea of Farnum and Wolf⁸ that halonium ion formation was possibly occurring in their work.

Proton NMR data are also available for several series of substituted Arylmethyl alkyl carbocations.¹³ A plot of the proton chemical shift of the methyl group alpha to the carbocationic center versus σ^+ (Figures 3 through 5) shows a general correlation. However, several features become apparent on closer scrutiny. First, an appreciable amount of scatter is also observed. Second, as the aryl group becomes more electron withdrawing, the correlation becomes worse. In fact, if one looks at the plot of the secondary substituted 1-phenyl-1-ethyl cations, one sees a very large deviation from the linearity of the plot for these electron withdrawing substituents. This deviation from linearity may reflect either differences in the anisotropic effect of the various phenyl substituents and/or a leveling effect on the influence of the aryl substituent on the stability and in turn the chemical shift.

Olah⁷ has obtained PNMR spectra on the isopropyl cation and diisopropyl chloronium ion. The isopropyl cation has two absorptions, one at δ 5.00 (6H,d) and another at δ 13.8 (1H, septet), while the diisopropyl chloronium ion also has two absorptions, one at δ 2.20 (6H,d) and the other at δ 7.1 (H, septet), where the ratio of alkyl chloride to the acid is 2/1. Thus, the proton attached directly to the carbocationic center, which feels the effect of the positive charge the most, is moved upfield by 6.7 ppm.

Although the carbon-13 (CNMR) spectrum of the diisopropyl halonium ion is not reported, the CNMR spectrum of the dimethyl chloronium ion is reported and has an absorption at δ 48.6 ppm. This value is much

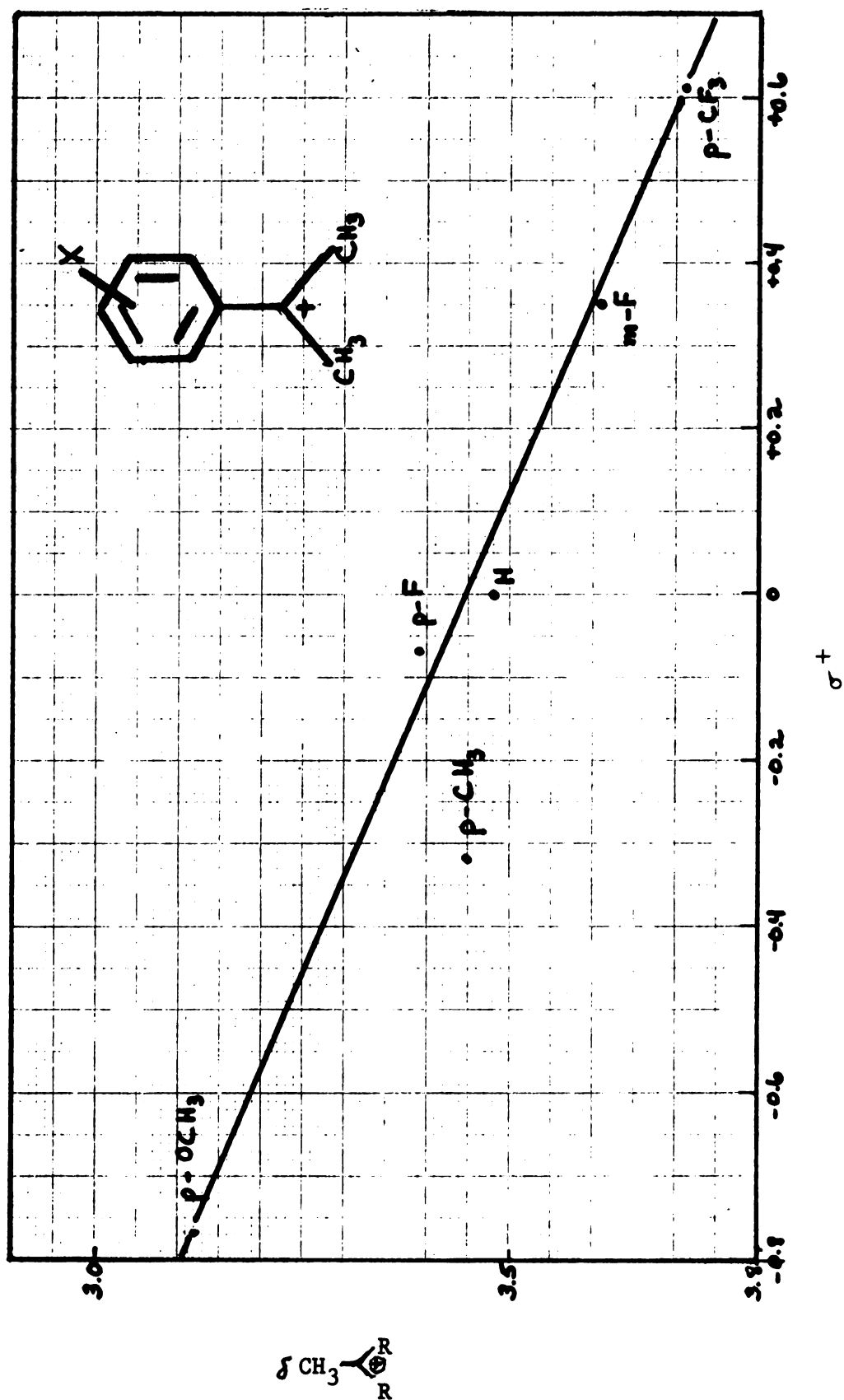


Figure 3. Correlation of PNMN chemical shift of the methyl protons alpha to the carbocationic center in 2-aryl-2-propyl cations with σ^+ .

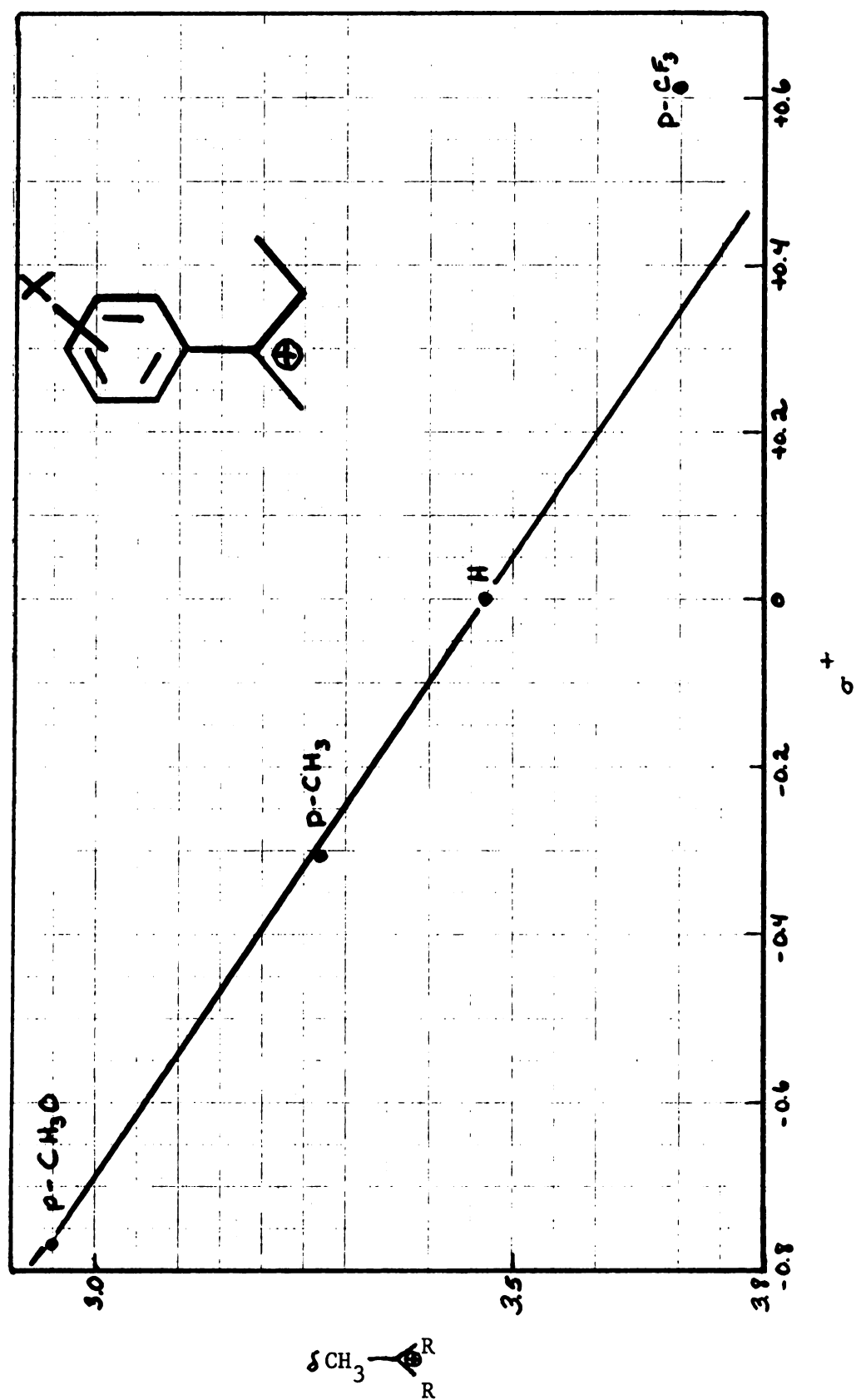


Figure 4. Correlation of PNM chemical shift of the methyl protons alpha to the carbocationic center in 2-aryl-2-butyl cations with σ^+ .

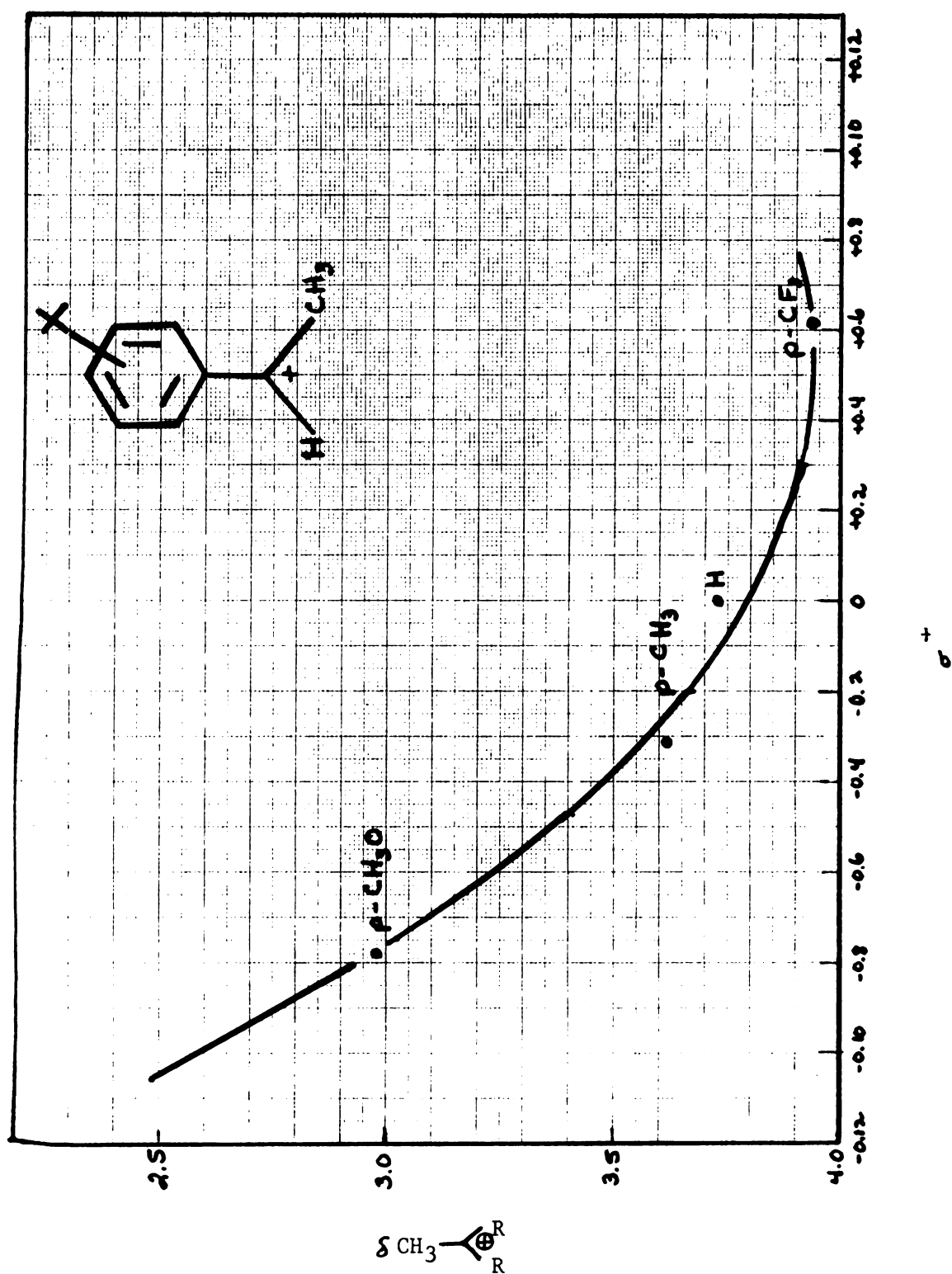


Figure 5. Correlation of PNMR chemical shift of the methyl protons alpha to the carbocationic center in 1-phenyl-1-ethyl cations with σ^+ .

closer to that of methylchloride (25.1 ppm) than that expected for the methyl cation (> 300 ppm). Hence, much of the positive charge on the dialkyl halonium ion resides on the halide and not on the carbon to which it is attached. The chemical shift of the dimethyl halonium ion indicates that its carbon is sp^3 hybridized. These results clearly demonstrate that carbon-13 chemical shifts are much more sensitive to change in bonding or geometry at the carbocationic center than PMMR chemical shifts. Since more routine carbon-13 instrumentation is now available, we thought that CNMR was an ideal probe to detect changes in bonding or geometry at the carbocationic center, such as dimeric halonium ion formation.

Olah¹³ has done some preliminary carbon-13 magnetic resonance studies on substituted aryl carbocations. In these studies he plotted the ^{13}C chemical shift of the cationic center, $\delta^{13}C^+$, versus Brown's σ^+ substituent constants (see Figures 6 through 9). If one looks at these plots, one sees a general overall correlation of $\delta^{13}C^+$ with σ^+ . However, there is a considerable amount of deviation from the arbitrary straight line drawn in these plots. It was from this work of Olah's that many of our ideas stemmed. We thought that in order to answer questions about the more intimate structural details of substituted aryl carbocations and in particular the details of the bonding at the carbocationic center, that we needed a series of substituted aryl carbocations as model systems; e.g., the substituted aryl cyclopentyl, which we could use as our standard to plot against all other substituted aryl acyclic, cyclic, and bicyclic carbocations. Our hope was

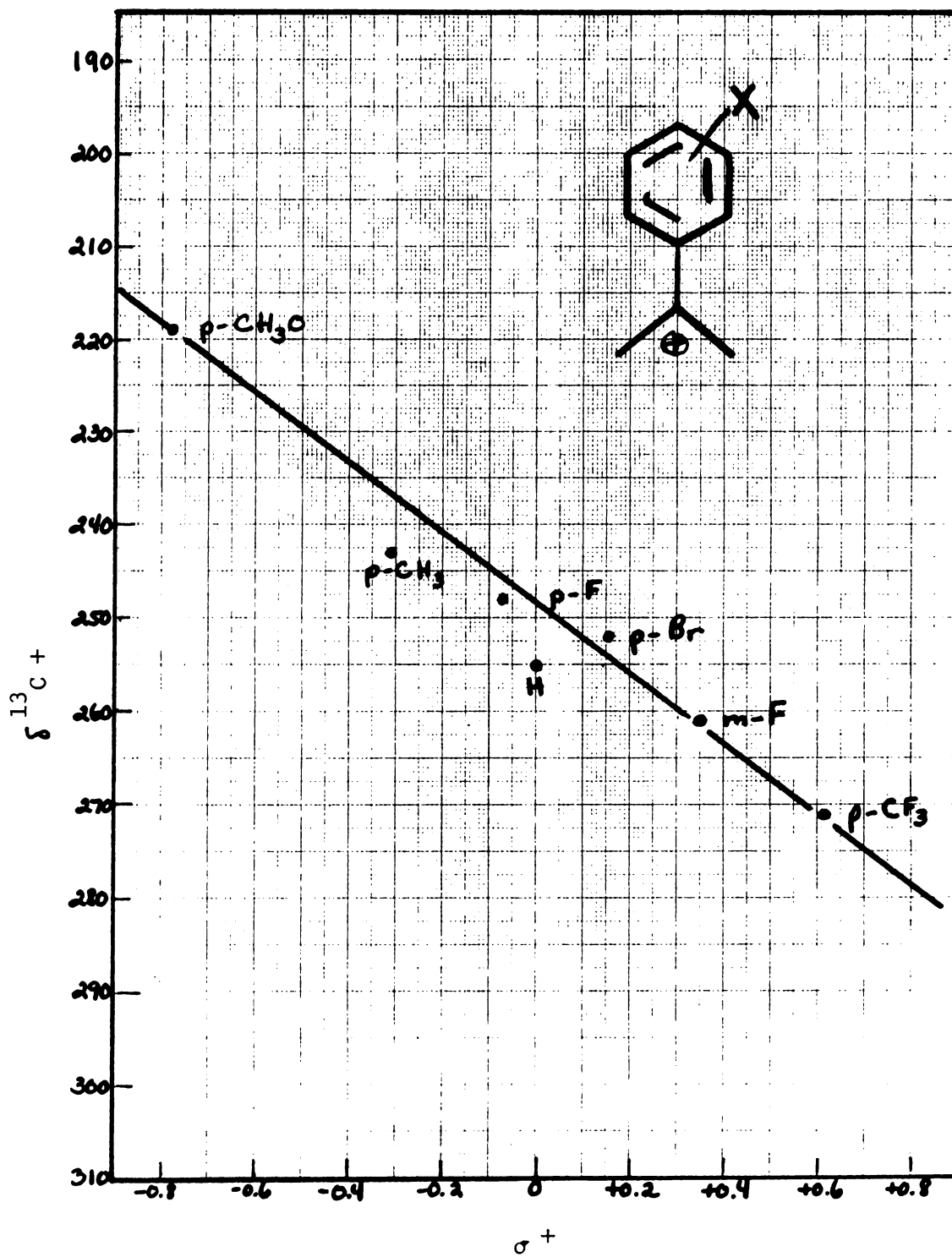


Figure 6. Correlation of 2-aryl-2-propyl cationic center chemical shift with σ^+ .

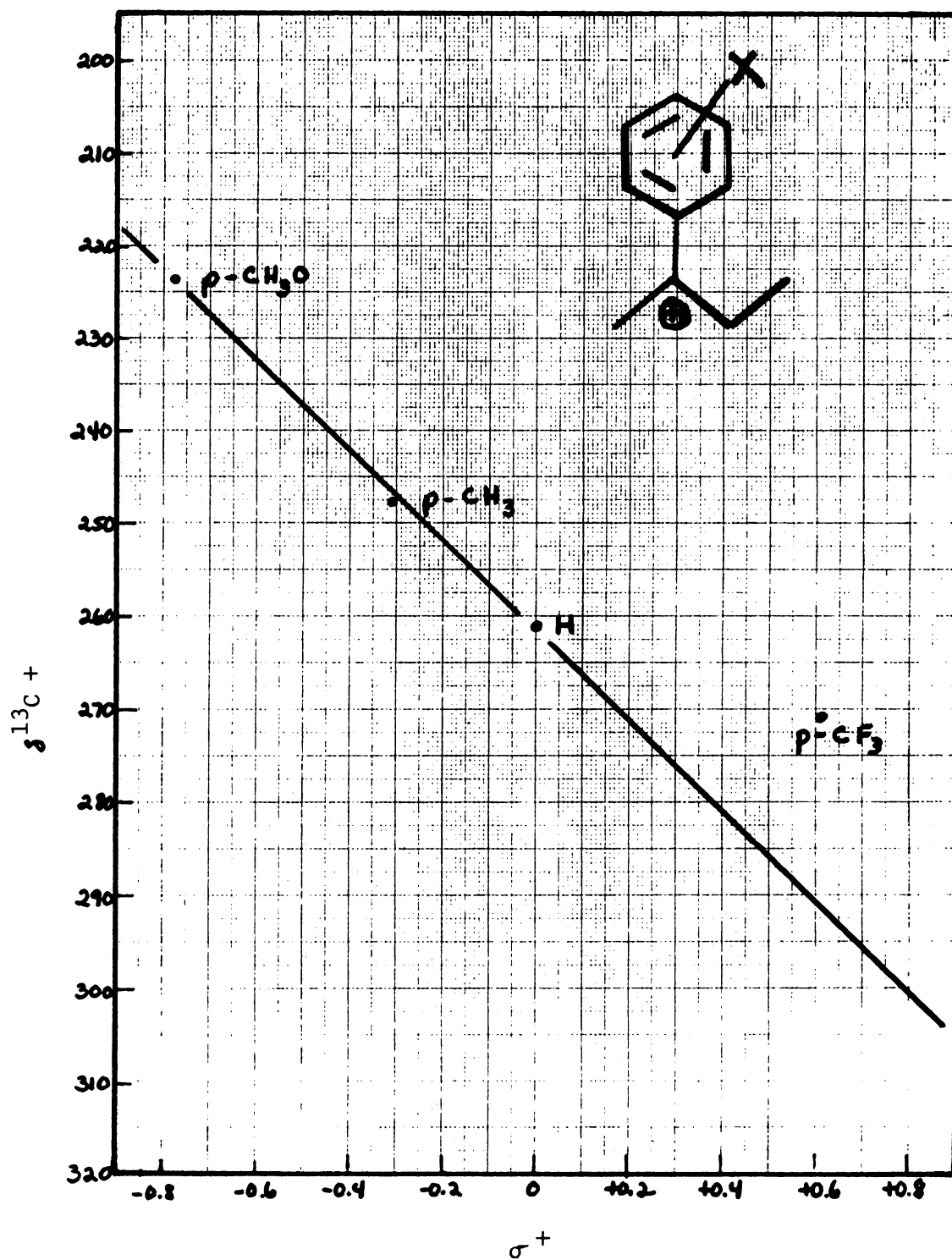


Figure 7. Correlation of 2-aryl-2-butyl cationic center chemical shift with σ^+ .

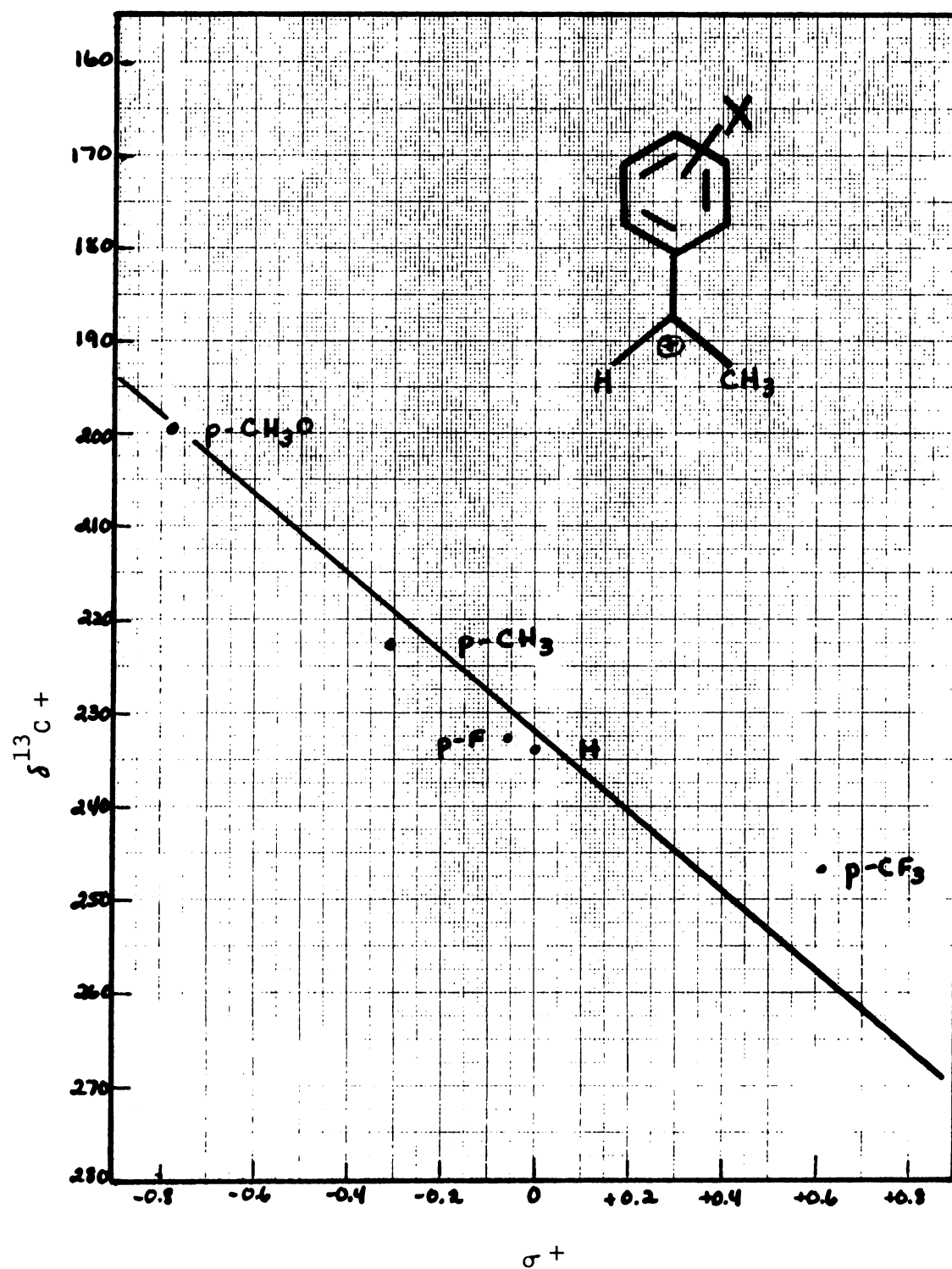


Figure 8. Correlation of 1-aryl-1-ethyl cationic center chemical shift with σ^+ .

that for similar systems a straight line would be obtained by plotting the $\delta^{13}\text{C}$ + of any series of substituted aryl carbocations versus the $\delta^{13}\text{C}$ + of our model carbocationic system if the electron demands in the systems were comparable. Any deviations from linearity could be interpreted as a qualitative change in structure of the carbocation. Some factors which might lead to such a qualitative change in structure include halonium ion formation and changes in geometry around the cationic center.

CNMR is an ideal probe to determine whether dimeric halonium ion formation does occur in substituted carbocations as postulated by Farnum and Wolf⁸, since carbon chemical shifts show a large dependence on orbital hybridization as well as electron density. We chose to compare substituted aryl cyclohexyl and cyclopentyl carbocationic systems to detect halonium ion formation. Thus, if dimeric halonium ions were formed in these systems, then the different steric constraints in these carbocations should lead to differing amounts of halonium ion formation, and to a deviation from linearity in the plot of the $\delta^{13}\text{C}$ + of the two systems.

Moreover, for the same reasons that it was good for detecting halonium ion formation, CNMR was also thought to be a good probe to detect any geometry change at the carbocationic center by the resultant deviation from linearity of a plot of the $\delta^{13}\text{C}$ + of the system in question versus the $\delta^{13}\text{C}$ + of an appropriate model system.

RESULTS

A detailed description of the preparation of the carbocations is given in the experimental section. Fourier transform nuclear magnetic resonance spectroscopy was used to obtain all carbon-13 spectra.

The substituted 1-aryl-1-phenyl-1-ethyl cation 3(a-k) and the substituted 1,1-diaryl-1-ethyl cations 4(a-d), were generated in FSO_3H at -78° from their corresponding carbinols. The spectra for these cations were recorded at -40° . The CNMR chemical shifts of the carbocationic centers for these carbocations are listed in Tables 1 and 2 respectively. In addition to the absorptions for the aryl carbons, carbon (or appropriate) aryl substituents, and carbocationic center the carbon-13 spectra showed a single high field absorption for each of these ions. In the case of the 1,1-diphenyl-1-ethyl cation, a PNMR spectrum was obtained and was found to be nearly identical with that recorded in the literature.¹⁴

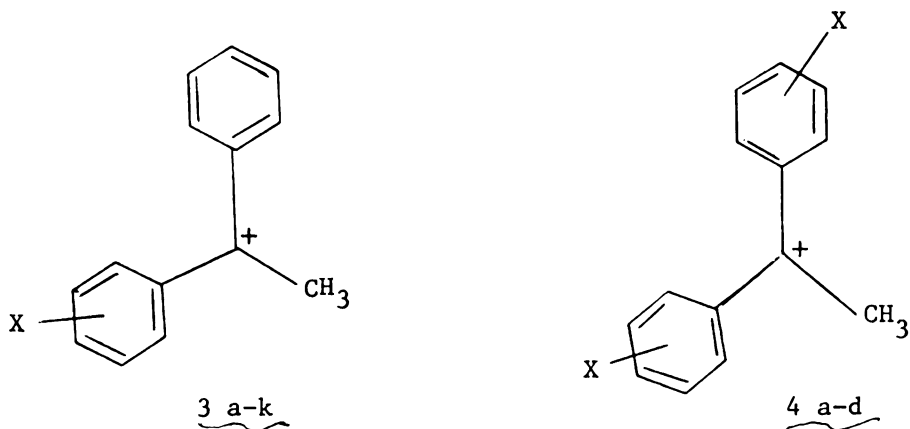


Table 1. ^{13}C chemical shifts for the carbocationic center is substituted 1-aryl-1-phenyl-1-ethyl cations.

Aryl Group	$\delta\text{C} +^*$
a) $\text{p-CH}_3\text{O-C}_6\text{H}_4$	209.
b) $3,4(\text{CH}_3)_2\text{C}_6\text{H}_3$	223.
c) $\text{p-CH}_3\text{-C}_6\text{H}_4$	224.
d) $\text{p-F-C}_6\text{H}_4$	226.
e) $\text{p-Cl-C}_6\text{H}_4$	227.
f) $\text{p-Br-C}_6\text{H}_4$	228.
g) C_6H_5	230.
h) $\text{m-F-C}_6\text{H}_4$	231.
i) $\text{m-Cl-C}_6\text{H}_4$	231.
j) $\text{p-CF}_3\text{-C}_6\text{H}_4$	233.
k) $3,5(\text{CF}_3)_2\text{-C}_6\text{H}_3$	232.

* PPM relative to external TMS.

Table 2. ^{13}C chemical shifts of the carbocationic center for the substituted 1,1-diaryl-1-ethyl cations.

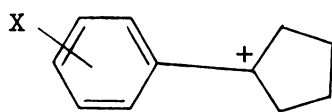
Aryl Group	$\delta\text{C} +^*$
a) $\text{p-CH}_3\text{O-C}_6\text{H}_4$	206.
b) $\text{p-CH}_3\text{-C}_6\text{H}_4$	221.
c) C_6H_4	230.
d) $\text{p-CF}_3\text{-C}_6\text{H}_4$	240

* PPM relative to external TMS.

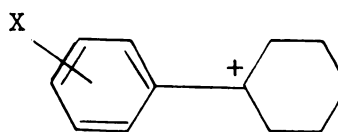
The substituted arylcyclopentyl 5(a-j) and arylcyclohexyl 6(a-h) cations were prepared in FSO_3H at -78° . The spectra were recorded at -70° . The C-13 parameters pertinent for our discussion for the carbocations are given in Tables 3 and 4 respectively.

Preparation of carbocations 5k and 6i and 6j, required much lower temperatures. Those ions were prepared in $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ with a trace of SbF_5 at -110° . Their spectra were recorded at -90° . Attempts to obtain their spectra at higher temperature only resulted in decomposition of these ions.

In addition to the aryl carbons, appropriate aryl substituents, and the carbocationic center absorptions, two high field peaks were observed for cations 5(a-k) and three high field peaks for ions 6(a-j). The PNMR spectra obtained for ions 5g and 6g were nearly identical with those reported in the literature.¹¹



5(a-k)



6(a-j)

The very similar chemical shifts for the aryl carbons in the aryl substituted cyclic carbocations investigated indicate that electron distribution in the aromatic systems are similar. Typical chemical shifts for the aryl cations are given in Table 5.

Table 3. ^{13}C chemical shifts of the carbocationic center in substituted arylcyclopentyl cations.

Aryl Group	$\delta\text{C} +^*$
a) $\text{p-CH}_3\text{O-C}_6\text{H}_4$	235.
b) $3,4(\text{CH}_3)_2\text{C}_6\text{H}_3$	257.
c) $\text{p-CH}_3\text{-C}_6\text{H}_4$	259.
d) $\text{p-F-C}_6\text{H}_4$	264.
e) $\text{p-Cl-C}_6\text{H}_4$	267.
f) $\text{p-Br-C}_6\text{H}_4$	267.
g) C_6H_5	270.
h) $\text{m-F-C}_6\text{H}_4$	277.
i) $\text{m-Cl-C}_6\text{H}_4$	277.
j) $\text{p-CF}_3\text{-C}_6\text{H}_4$	283.
k) $3,5(\text{CF}_3)_2\text{C}_6\text{H}_4$	286.

* PPM relative to external TMS.

Table 4. ^{13}C chemical shifts of the carbocationic center in substituted arylcyclohexyl cations.

Aryl Group	δC^*
a) $\text{p-CH}_3\text{O-C}_6\text{H}_4$	227.
b) $3,4(\text{CH}_3)_2\text{-C}_6\text{H}_3$	249.
c) $\text{p-CH}_3\text{-C}_6\text{H}_4$	251.
d) $\text{p-F-C}_6\text{H}_4$	256.
e) $\text{p-Cl-C}_6\text{H}_4$	259.
f) $\text{p-Br-C}_6\text{H}_4$	260.
g) C_6H_5	263.
h) $\text{m-F-C}_6\text{H}_4$	267.
i) $\text{p-CF}_3\text{-C}_6\text{H}_4$	276.
j) $3,5(\text{CF}_3)_2\text{C}_6\text{H}_3$	279.

* PPM relative to external TMS.

Table 5. Typical chemical shifts* for the aryl carbons in substituted cyclic aryl cations.

Substituent	δC_{para}	δC_{ortho}	δC_{meta}	δC_1
p-CH ₃ O	182.	146.	120.	131.
p-CH ₃	173.	143.	134.	135.
p-F	180. (J _{CF} =291. Hz)	148. (J _{CF} =15.)	121. (J _{CF} =21.)	134.
p-Cl	164.	143.	133.	135.
p-Br	156.	142.	136.	136.
p-H	154.	145.	136.	133.

* PPM relative to external TMS.

DISCUSSION

Figures 9 through 12 are plots of the carbon-13 chemical shifts of the carbocationic centers of the substituted arylcyclopentyl cations versus the carbon-13 chemical shifts of cationic centers of several series of substituted aryl cations.

There are a few features of the graphs that should be noted. First, a good linear correlation is found between the carbocationic center chemical shift of our model system (aryl cyclopentyl) and several other series of carbocationic systems. This linear correlation is consistent with the interpretation that electron demand is qualitatively the same throughout each series. Thus, the C_{13} chemical shifts of these carbocations reflect the donating ability of the aryl substituent. Second, none of the p-halogen substituents, pF, p-Cl, p-Br (see Figures 9 and 12) show any large deviation from the line. These results imply that either halonium ion formation is not taking place in these systems or that the extent of halonium ion formation is the same in these systems at the temperature and concentration studied. Certainly, the steric constraints in substituted aryl cyclopentyl, cyclohexyl, and bicyclo[3.2.1]octyl cations are different. It is our belief that if halonium ion formation occurred in these tertiary cationic systems to any appreciable extent, then much larger deviations from linearity would be observed.

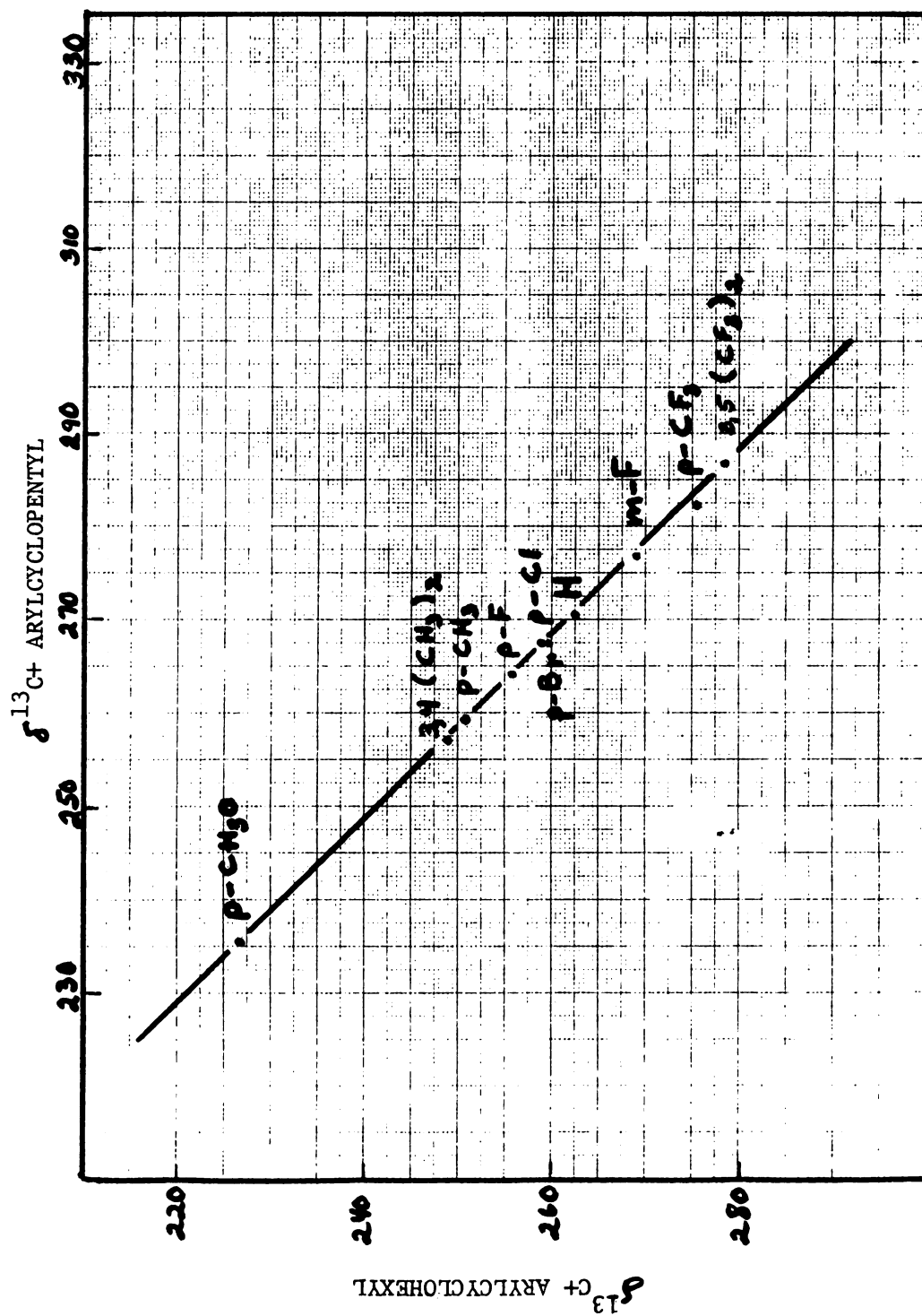


Figure 9. Graph of Arylcyclopentyl vs. Arylcyclohexyl cationic center chemical shifts.

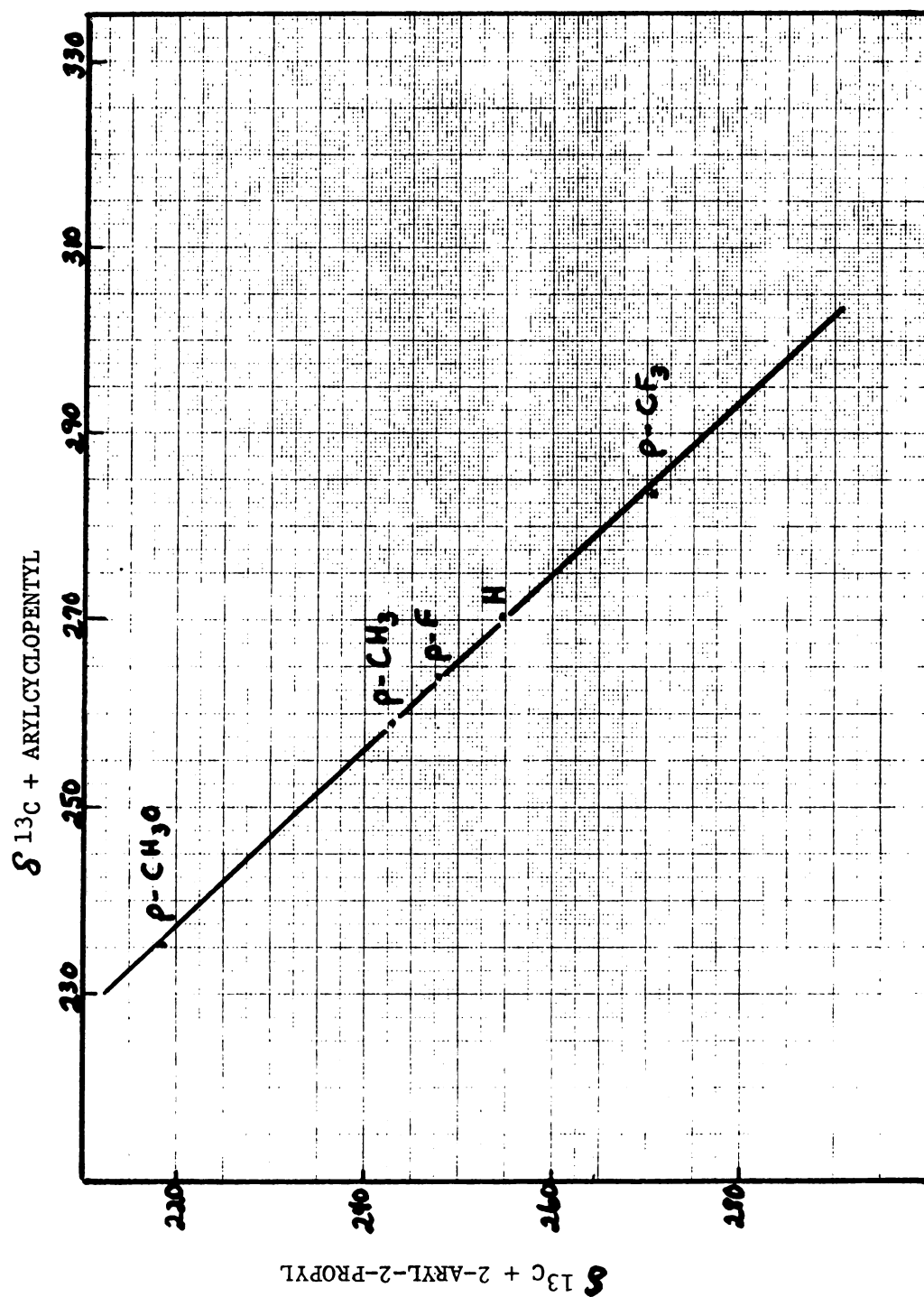


Figure 10. Graph of substituted arylcyclopentyl vs. substituted 2-aryl-2-propyl cationic center chemical shifts.

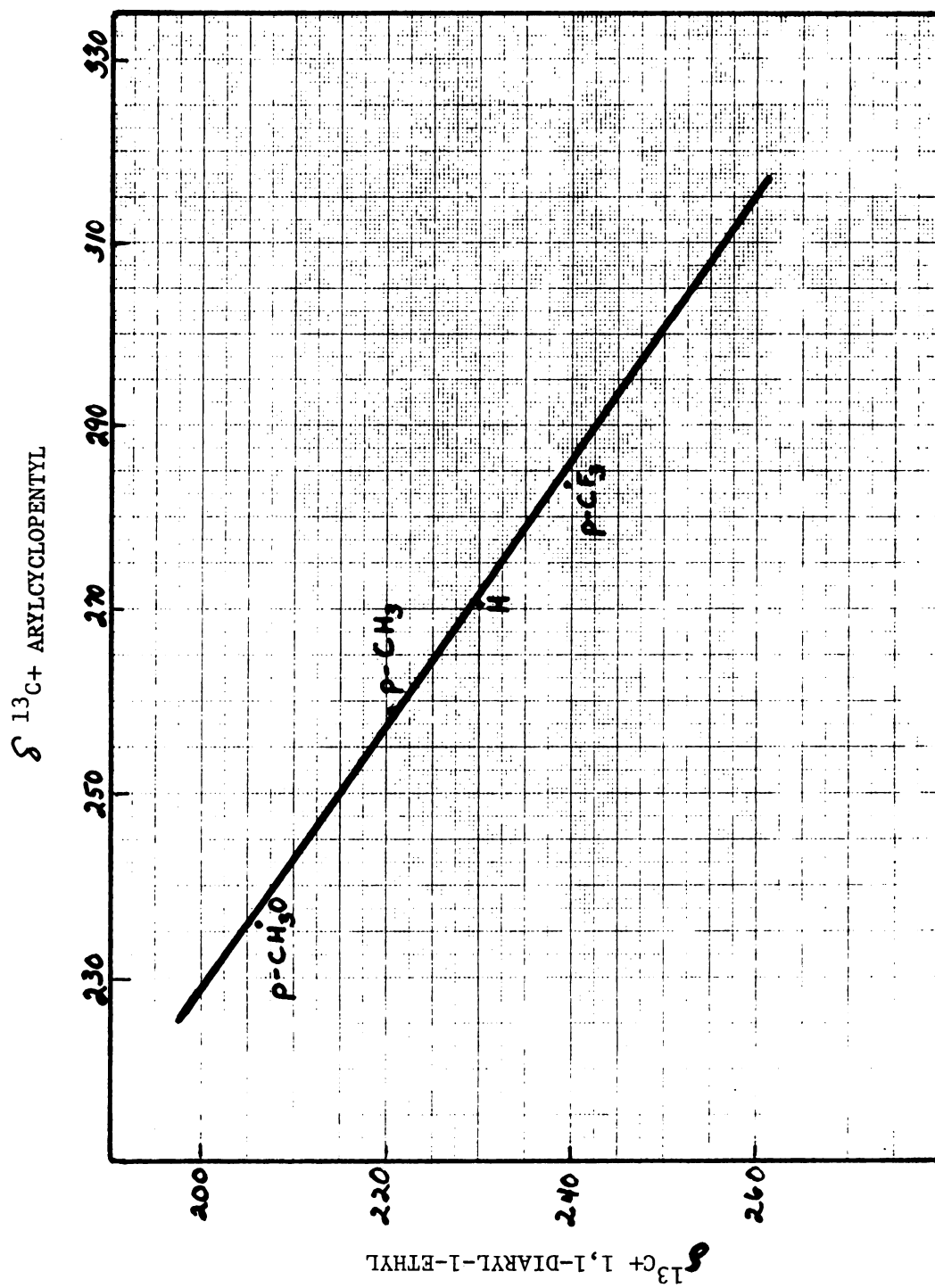


Figure 11. Graph of substituted aryl cyclopentyl vs. substituted 1,1-diaryl-1-ethyl cationic center chemical shifts.

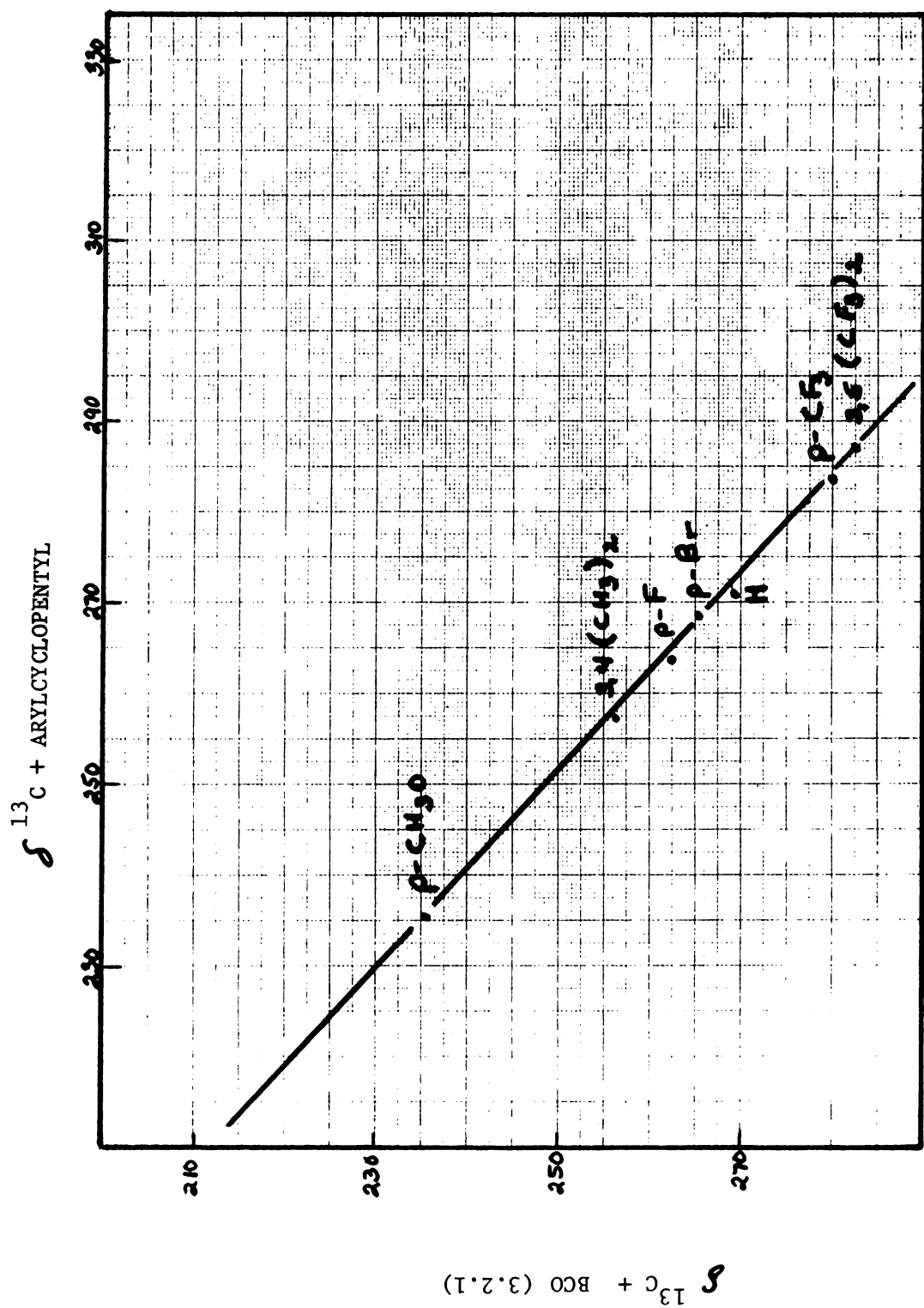
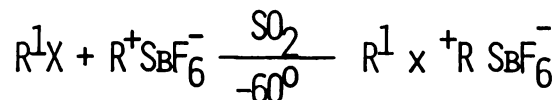


Figure 12. Graph of substituted arylcyclopentyl vs. substituted 6-aryl-6 bicyclo (3.2.1) octyl carbocationic center chemical shifts.

Olah¹⁷ has shown that formation of tertiary dialkyl halonium ions is at least difficult, when he tried to prepare the unsymmetrical dialkyl halonium ions by the procedure:



He was able to prepare unsymmetrical dialkyl halonium ions by alkylation of primary alkyl fluoroantimonates with primary and secondary alkyl halides. Attempts to alkylate alkyl fluorantimonates with tertiary alkyl halides led only to tertiary alkyl carbocation formation and symmetrical dialkyl halonium ion formation. Perhaps tertiary carbocations are too hindered or too stable to allow halonium ion formation to take place or be detected.

Perhaps halonium ion formation could be more readily detected in secondary carbocations such as the substituted 1-aryl-1-ethyl cations, which are expected to be "hotter" species. A plot of the carbon-13 carbocationic center chemical shifts vs. those of our own model systems should be linear with the exception of the p-halogen if halonium ion formation is taking place. Olah¹³ has done some preliminary work in forming 1-aryl+ethyl cations. However, he has only obtained C-13 spectra for one p-halogen substituent, para-fluoro, in this series. Figure 13 contains the graph of these cations versus our model system. A good linear correlation is observed for all substituents, both electron donating and withdrawing, except for the p-fluoro substituent which deviates from the line by approximately 5 ppm. This preliminary result indicates that halonium ion formation may even be taking place

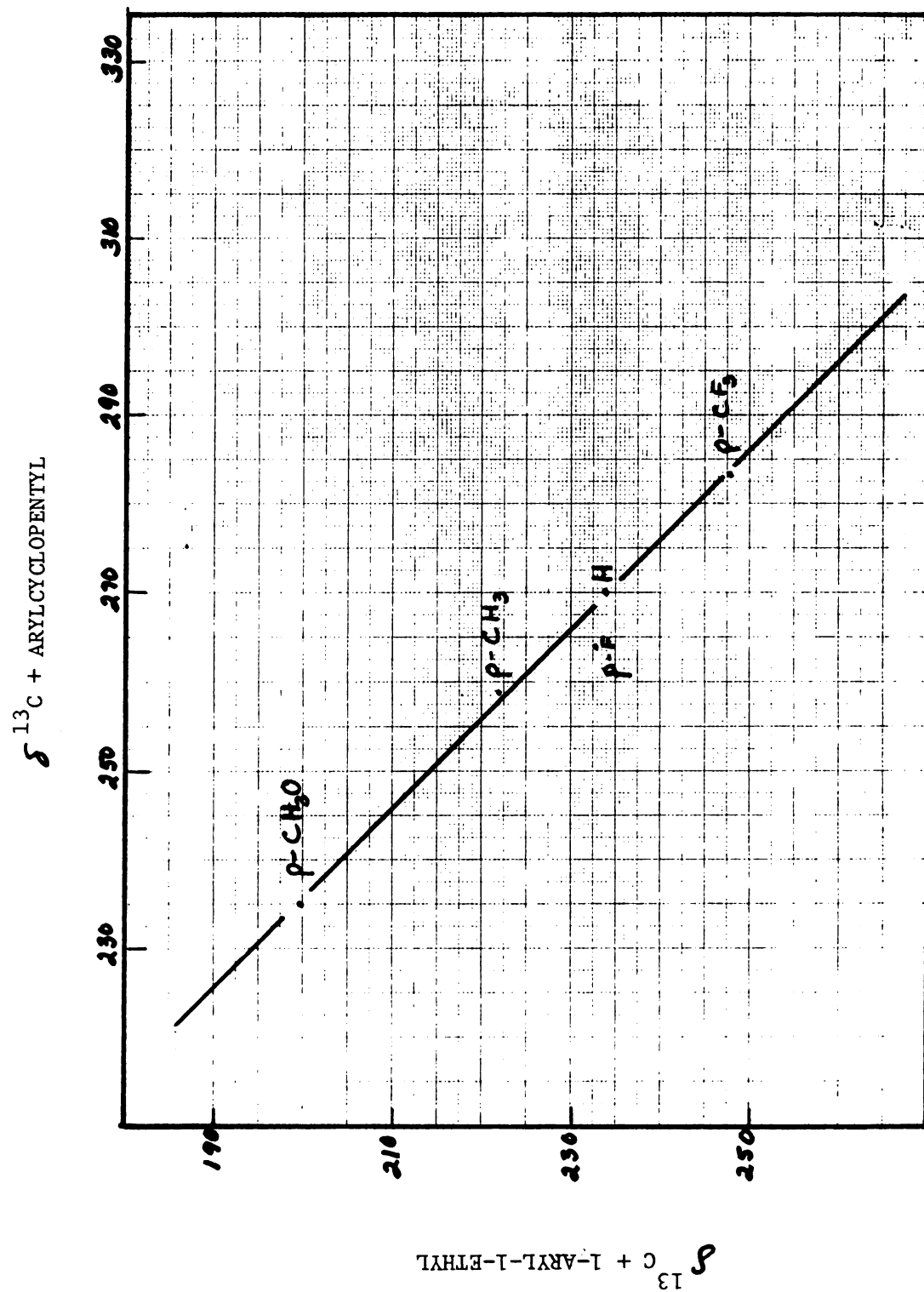


Figure 13. Graph of substituted arylcyclopentyl vs. substituted 1-aryl-1-ethyl carbocationic center chemical shifts.

in the p-fluoro substituted 1-aryl-1-ethyl cation. These results suggest that further experiments in these cation systems would provide theoretically interesting and fruitful results. It is possible that other para-halogen substituents would show larger deviations as a result of dimeric halonium ion formation.

Having already established that the substituted arylcyclopentyl cation is a good model for a number of acyclic, cyclic, and bicyclic systems where no changes in bonding are occurring at the carbocationic center, we thought that it would be theoretically interesting to plot the carbon-13 chemical shifts of our model systems against several series of substituted aryl cations where changes in bonding at the carbocationic center were expected to take place. Any change in bonding at the cation center should lead to deviation from linearity in the plots.

We first chose to look at substituted 1-aryl-1-phenyl-1-ethyl cations (see Figure 14). This graph shows a reasonable linear correlation for all substituents showing electron donating ability greater than or equal to para-hydrogen. For more electron withdrawing substituents, large deviations from linearity are observed. We believe that these results indicate that the substituted 1-aryl-1-phenyl-1-ethyl cations exist in an unsymmetrically twisted propeller conformation, most easily pictured by the plane propeller conformations 7 and 8, where the twisting of the more planar aryl ring is not considered.

The top portion of the graph reflects the conformation 7 in which the more electron donating group is more nearly coplanar with the cationic center than the phenyl.

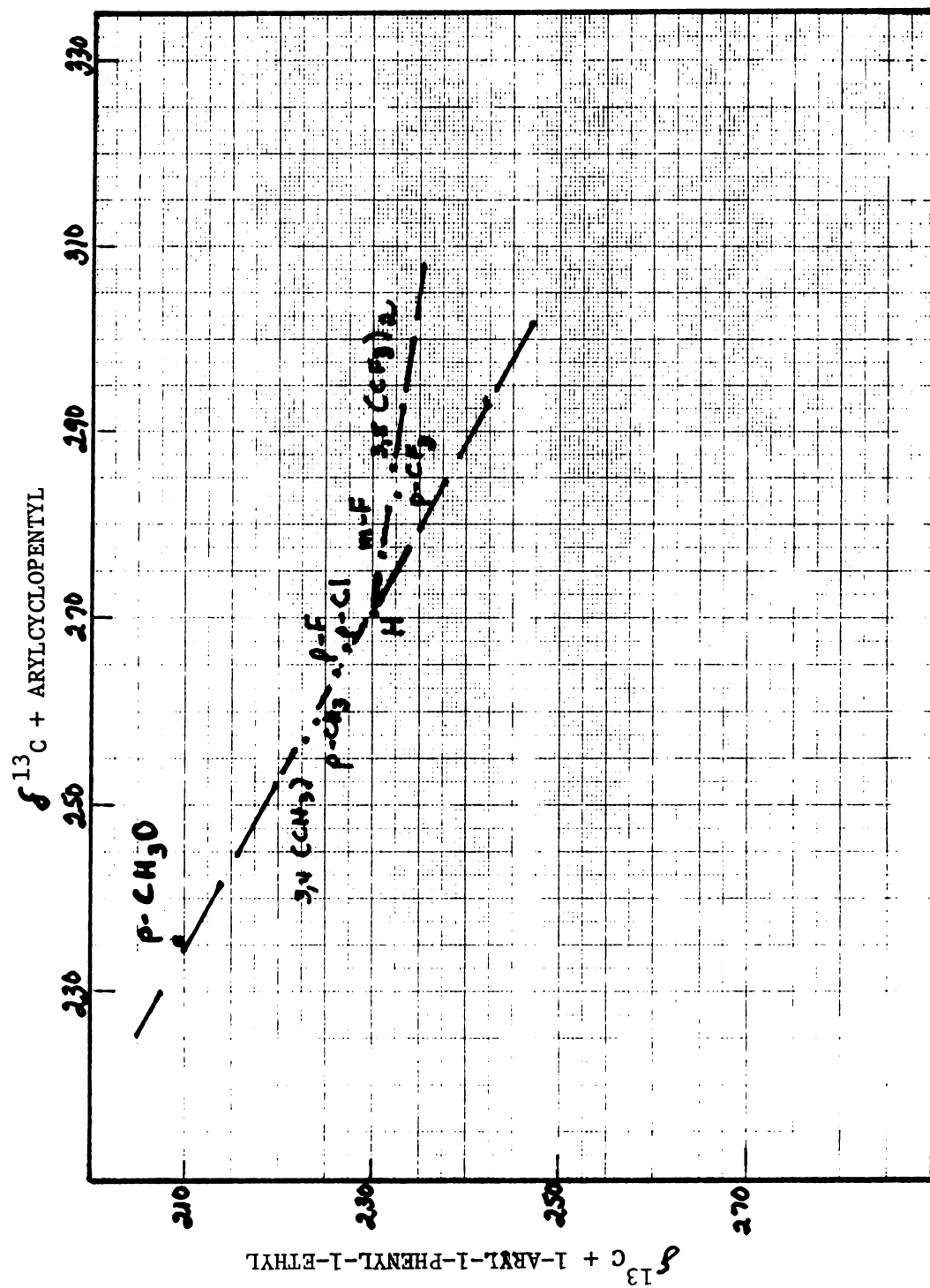
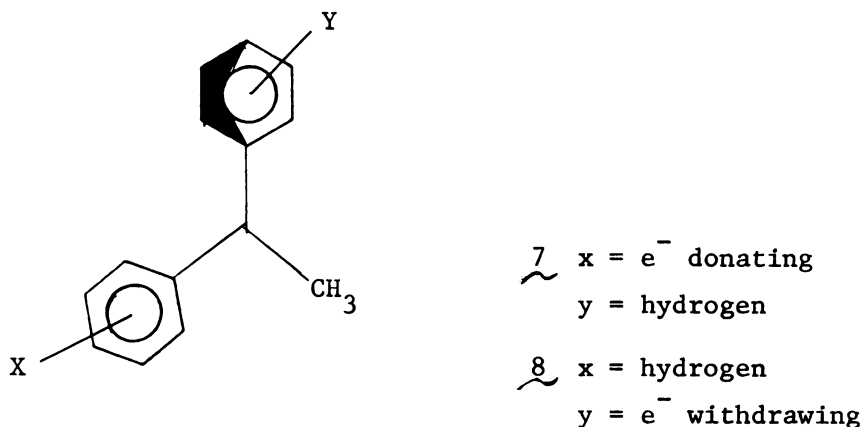


Figure 14. Graph of substituted arylcyclopentyl vs. substituted 1-aryl-1-phenyl-1-ethyl carbocationic center chemical shifts.



The bottom portion of the graph reflects the conformation 8 in which the phenyl is more nearly coplanar with the carbocationic center, and the less coplanar ring has an electron withdrawing substituent.

Thus we see two reasonably linear portions to our graph in which the carbocationic center chemical shift is dominated by the aryl ring more nearly coplanar with it. The other aryl ring; i.e., the ring less coplanar with the carbocationic center, acts similar to another alkyl substituent. We have shown above that the carbon-13 chemical shifts of carbocationic centers of monoaryl carbocations correlate with our model systems where electron demand is thought to be qualitatively the same. The top portion of our graph effectively represents a series of substituted monoaryl carbocations with two substituents, a nonplanar phenyl ring and a methyl group. The bottom portion of the graph effectively represents a series of monophenyl carbocations in which the electron donating ability of one of the other substituents, i.e., the less planar aryl ring, is varied.

The entire graph can be interpreted to represent a very subtle change in bonding at the carbocationic center; i.e., it represents a simple conformational change in which one ring becomes more nearly coplanar with the carbocationic center.

To support our hypothesis we have prepared a few of the substituted diaryl ethyl cations using a wide range of substituents and plotted their C-13 carbocationic center chemical shifts against our model systems (Figure 11). Since one ring is now restricted to be more or less coplanar with the trigonal carbocationic center. Thus, a plot should be linear with our model systems; e.g., the substituted aryl-cyclopentyl. This plot has already been shown in Figure 11 and a good linear correlation is observed. We believe these results in conjunction with those given in Figure 14, are consistent with the interpretation that the substituted 1-aryl-1-phenyl-1-ethyl cations do exist in the unsymmetrically twisted "propeller" conformation and exhibit a simple geometry change; i.e., the conformational change discussed above.

Botto¹⁸ has used our results to help interpret the result he obtained in several series of bicyclic cations which are known to have a propensity for rearrangement. One such system is the substituted 2-aryl-2-bicyclo(2.2.1)heptyl carbocation. He has plotted the carbon-13 chemical shifts of this carbocationic system vs. that of the substituted 6-aryl-6-bicyclo(3.2.1)octyl carbocationic system as shown in Figure 15. These results show a good linear correlation for electron donating substituents. A breaking in the plot at para-hydrogen indicates that a change in bonding at the carbocationic center is taking

Figure 15. Graph of 2-Aryl-2-Norbornyl vs. 6-Aryl-6-Bicyclo (3.2.1) octyl Carbocation Chemical Shifts.

place. One hypothesis consistent with these results is that the onset of nonclassical participation is occurring in substituted 2-aryl-2-bicyclo(2.2.1)heptyl cations for substituents more electron demanding than para-H.

In summary, we believe we have established that a good linear correlation is observed between the carbon-13 carbocationic center chemical shifts of several series of acyclic, cyclic, and bicyclic aryl substituted carbocations where electron demands are thought to be qualitatively the same. In addition, our results indicate that changes in bonding or geometry at the carbocationic center can be detected by deviations from linearity.

EXPERIMENTAL

All melting points are uncorrected and were taken on a Thomas Hoover capillary melting point apparatus.

Infrared spectra were recorded on a Perkin Elmer Grating Infrared Spectrophotometer, Model 327 B.

Mass spectra analysis were performed using a Hitachi Mass Spectrometer, Model RMU-6.

NMR spectra of the carbocationic precursors were obtained using a T-60 Spectrometer with tetramethylsilane (TMS) as an internal standard.

A Varian CFT-20 Spectrometer equipped with a Varian V-6040 N-M-R Variable Temperature Controller was used to obtain carbon-13 Magnetic Resonance spectra. The temperatures at which the CMR spectra were obtained were calibrated from the probe, not from the sample. Accuracy is within $\pm 3^{\circ}$.

Table 6. Preparation of substituted arylcyclopentanol.

Derivative	Molecular Formula	bp	mp	Mass Spectra	
				m/e (Calc.)	m/e (Found)
p-CH ₃ O-C ₆ H ₄ *	C ₁₂ H ₁₄ O	---	78-80°	174	174
3,4(CH ₃) ₂ C ₆ H ₃	C ₁₃ H ₁₈ O	103° at 0.5 mm	---	190	190 175 (p-15) 172 (p-18)
p-CH ₃ -C ₆ H ₄ **	C ₁₂ H ₁₆ O	---	---	176	176 158 (p-18)
p-F-C ₆ H ₄	C ₁₁ H ₁₃ FO	82° at 0.3 mm	---	180	180 162 (p-18)
p-Cl-C ₆ H ₄	C ₁₁ H ₁₃ ClO	---	59-60°	198,196	198,196 180,178 (p-18)
p-Br-C ₆ H ₄	C ₁₁ H ₁₃ BrO	130° at 0.15 mm	---	242,240	242,240 224,222 (p-18)
C ₆ H ₅	C ₁₁ H ₁₄ O	72° at 0.25 mm	---	162	162 144 (p-18)
m-F-C ₆ H ₄	C ₁₁ H ₁₃ FO	95° at 0.75 mm	---	180	180 162 (p-18)
				continued	

Table 6--continued

Derivative	Molecular Formula	bp	mp	Mass Spectra	
				m/e (Calc.)	m/e (Found)
m-Cl-C ₆ H ₄	C ₁₁ H ₁₀ ClO	110° at mm	----	198, 196	198, 196 180, 178 (p-18)
p-CF ₃ -C ₆ H ₅	C ₁₂ H ₁₀ F ₃ O	75° at mm	37-40°	230	230 212 (p-18) 211 (p-19)
3,5(CF ₃) ₂ C ₆ H ₃	C ₁₃ H ₁₂ F ₆ O	----	79-81°	298	298 280 (p-18) 279 (p-19)

* Olefin.

** Chromatographed on neutral Al₂O₃ (Activity II), with ether hexane (1:5).

Table 7. Preparation of substituted arylcyclohexanols.

Derivative	Molecular Formula	bp	mp	Mass Spectra	
				m/e (Calc.)	m/e (Found)
p-CH ₃ O-C ₆ H ₄	C ₁₃ H ₁₈ O ₂	---	36-38°	206	206
3,4(CH ₃) ₂ C ₆ H ₃	C ₁₄ H ₂₀ O	110° at 0.1 mm	---	204	204
					189 (p-15)
					186 (p-18)
p-CH ₃ -C ₆ H ₄ **	C ₁₃ H ₁₈ O	---	55-57°	190	190
					172 (p-18)
p-F-C ₆ H ₄	C ₁₂ H ₁₅ FO	---	73-75°	194	194
					176 (p-18)
p-Cl-C ₆ H ₄	C ₁₂ H ₁₅ ClO	---	77-79°	212, 210	212, 210
					194, 192 (p-18)
p-Br-C ₆ H ₄	p-C ₁₂ H ₁₅ BrO	---	92-94°	256, 254	256, 254
					238, 236 (p-18)
C ₆ H ₅	C ₁₂ H ₁₆ O	---	66-67°	176	176
					158 (p-18)
m-F-C ₆ H ₄	C ₁₂ H ₁₅ FO	---	52-54°	194	194
					176 (p-18)
					continued

Table 7---continued

Derivative	Molecular Formula	bp at 1 mm	mp	Mass Spectra	
				m/e (Calc.)	m/e (Found)
m-Cl-C ₆ H ₄	C ₁₂ H ₉ ClO	125°	---	212, 210	212, 210
					194, 192 (p-18)
p-CF ₃ -C ₆ H ₅	C ₁₃ H ₉ F ₃ O	---	56-58°	244	244
					226 (p-18)
					225 (p-19)
3,5(CF ₃) ₂ C ₆ H ₃	C ₁₄ H ₆ F ₆ O	---	102-104°	312	312
					294 (p-18)
					293 (p-19)

** Chromatographed on neutral Al₂O₃ (Activity II) eluted with hexane/ether.

Table 8. Preparation of substituted 1-aryl-1-phenylethyl alcohols.

Derivative	Molecular Formula	bp	mp	Mass Spectra	
				m/e (Calc.)	m/e (Found)
$\text{p-CH}_3\text{O-C}_6\text{H}_4^*$	$\text{C}_{15}\text{H}_{14}\text{O}$	---	74-75°	210	210
$3,4(\text{CH}_3)_2\text{C}_6\text{H}_3$	$\text{C}_{16}\text{H}_{18}\text{O}$	140° at 0.1 mm	---	226	226 211 (p-15) 208 (p-18)
$\text{p-CH}_3\text{-C}_6\text{H}_4$	$\text{C}_{15}\text{H}_{16}\text{O}$	112° at 0.5 mm	---	212	212 197 (p-15) 194 (p-18)
$\text{p-F-C}_6\text{H}_4$	$\text{C}_{14}\text{H}_{13}\text{FO}$	112° at 0.1 mm	---	216	216 201 (p-15) 198 (p-18)
$\text{p-Cl-C}_6\text{H}_4$	$\text{C}_{14}\text{H}_{13}\text{ClO}$	127° at 0.1 mm	---	234, 232	234, 232
C_6H_5	$\text{C}_{14}\text{H}_{14}\text{O}$	---	79-81°	198	198 183 (p-15) 180 (p-18)
$\text{m-F-C}_6\text{H}_4$	$\text{C}_{14}\text{H}_{13}\text{FO}$	---	72-73°	216	216 201 (p-15) 198 (p-18)
					continued

Table 8---continued

Derivative	Molecular Formula	bp	mp	Mass Spectra	
				m/e (calc.)	m/e (Found)
m-Cl-C ₆ H ₄	C ₁₄ H ₉ ClO	127° at 0.1 mm	---	234, 232	234, 232
p-CF ₃ -C ₆ H ₄	C ₁₅ H ₉ F ₃ O	110° at 0.1 mm	---	266	266 251 (p-15) 248 (p-18)
3,5(CF ₃) ₂ C ₆ H ₃	C ₁₆ H ₁₂ F ₆ O	---	62-64°	334	334 319 (p-15) 316 (p-18) 315 (p-19)

* Olefin.

Table 9. Preparation of substituted diarylmethyl carbinols.

Derivative	Molecular Formula	bp or sp	mp	Mass Spectra	
				m/e (Calc.)	m/e (Found)
$\text{p-CH}_3\text{O-C}_6\text{H}_4^*$	$\text{C}_{16}\text{H}_{18}\text{O}_3$	---	---	258	258 243 (p-15) 240 (p-18)
$\text{p-CH}_3\text{-C}_6\text{H}_4^*$	$\text{C}_{16}\text{H}_{18}\text{O}$	---	---	226	226 211 (p-15) 208 (p-18)
C_6H_5	$\text{C}_{14}\text{H}_{14}\text{O}$	---	79-81°	198	198 183 (p-15) 180 (p-18)
$\text{P-CF}_3\text{-C}_6\text{H}_4$	$\text{C}_{16}\text{H}_{12}\text{F}_6\text{O}$	112° at 0.5 mm	---	334	334 319 (p-15) 316 (p-18) 315 (p-19)

* Chromatographed on aluminum (Activity II), and eluted with hexane/ether (5:1).

Carbocation Precursors

The alcohols were prepared by reacting 1.1 moles of the appropriate Grignard reagent with 1 mole of the corresponding ketone; cyclopentanone, cyclohexanone, and substituted aryl methylketones or by reacting 2.2 equivalent of the Grignard reagent with 1 mole of ethyl acetate.

In all cases a 20% molar excess, with respect to the carbonyl compound, of magnesium was used. Yields of the appropriate alcohol range from 45% to 90% based on the ketone.

The important physical constants for the compounds are summarized in Tables 6 through 9.

Carbocation Formation

In order to facilitate complete ionization, one of the following methods was chosen to form the carbocations:

1) Approximately 8×10^{-4} moles of precursor was placed in a jacketed dropping funnel at 0 to -20° in the apparatus described by Hart.¹⁹ Enough Freon II was added to dissolve the precursor. The resulting solution was added over approximately a twenty minute period to 1.57 ml of rapidly stirred FSO_3H at -78° under a N_2 blanket. The resulting colored, nonhomogenous solution was allowed to stir for fifteen minutes at -78° and was then blown with N_2 into a CNMR tube cooled at -78° . The Freon II was allowed to separate and was removed with a micropipette.

2) The precursor was added in small amounts to 1.57 of the acidic media, FSO_3H or $\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ (1/3) with a trace of SbF_5 at the

appropriate temperature (-78° to -110°). A homogenous solution was obtained by intermitant vibra stirring and cooling.

IR and NMR Spectra

Arylcyclopentanols

$\text{CH}_3\text{O}-\text{C}_6\text{H}_4$ (olefin): nmr (CCl_4) δ 6.85 (4H, AA'BB' $\Delta\nu = 30$ Hz, $J = 9$ Hz) 5.83 (1H, t, $J = 2$ Hz), 3.67 (3H,s) 2.80-1.77 (6H, m); ir (nujol) μ 6.15, 9.67.

3,4(CH_3) $_2\text{C}_6\text{H}_3$: nmr (CCl_4) δ 7.17-6.63 (3H, m), 2.3 (1H, s) 2.13 (6H, br. s.), 1.77 (8H, br. s.); ir (neat) μ 2.93, 6.05, 9.91.

p- $\text{CH}_3-\text{C}_6\text{H}_4$: nmr (CCl_4) δ 6.90 (4H, AA'BB' $\Delta\nu = 17$ Hz, $J = 7$ Hz), 2.12 (3H,s), 1.77 (9H, br. s.); ir (neat) μ 2.90, 6.20, 9,35.

p-F- C_6H_4 : nmr (CCl_4) δ 7.20 (2H, distorted quartet, $J = 5$ Hz, $J = 8$ Hz), 6.75 (2H, distorted triplet, $J^1 = J = 8$ Hz), 2.73 (1H, br. s.), 1.80 (8H, br. s.); ir (neat) μ 2.95, 6.18, 9.95.

p-Cl- C_6H_4 : nmr (CCl_4) δ 7.20 (4H, AA'BB' $\Delta\nu \cong 0$, $J = 10$ Hz), 1.90 (9H, br. s.), ir (nujol) μ 3.01, 6.21, 9.88.

p-Br- C_6H_4 : nmr (CCl_4) δ 7.17 (4H, AA'BB' $\Delta\nu \cong 0$, $J = 10$ Hz), 1.83 (8H, br. s.), 1.43 (1H, s); ir (neat) μ 2.95, 6.08, 9.90.

C_6H_4 : nmr (CCl_4) δ 7.4-6.90 (5H, m), 2.15 (1H, s), 1.33 (8H br. s.); ir (neat) μ 2.92, 6.20, 9.90.

m-Cl- C_6H_4 : nmr (CCl_4) δ 7.73-6.90 (4H, m), 2.40 (1H, br. s.), 1.80 (8H, br. s.); ir (neat) μ 2.95, 6.23, 9.92.

m-F- C_6H_4 : nmr (CCl_4) δ 7.20-6.49 (4H, m), 1.80 (8H, br. s.), 1.53 (1H, br. s.); ir (neat) μ 2.99, 6.18, 6.28, 9.89.

$p\text{-CF}_3\text{-C}_6\text{H}_4$: nmr (CCl_4) δ 7.48 (4H, s), 1.93 (9H, br. s.); ir (nujol) μ 2.95, 6.17, 9.82.

$3,5(\text{CF}_3)_2\text{C}_6\text{H}_3$: nmr (CCl_4) δ 7.80 (2H, br. s.), 7.63 (1H, br. s.), 1.97 (1H, s), 1.73 (1H, s); ir (nujol) μ 2.98, 6.10, 8.80.

Arylcyclohexanols

$p\text{-CH}_3\text{O-C}_6\text{H}_4$: nmr (CCl_4) δ 6.83 (4H, AA'BB' $\Delta\nu = 34$ Hz, $J = 8$) 3.70 (3H, s), 1.66 (10H, br. s.), 1.20 (1H, s); ir (nujol) μ 2.90, 6.19, 9.60.

$3,4(\text{CH}_3)_2\text{C}_6\text{H}_3$: nmr (CCl_4) δ 6.87 (3H, m), 3.33 (1H, s), 2.23 (6H, br. s.), 1.67 (10H, br. s.); ir (neat) μ 2.87, 6.60, 9.60.

$p\text{-F-C}_6\text{H}_4$: nmr (CCl_4) δ 7.23 (2H, distorted quartet, $J = 8$ Hz, $J = 5$ Hz), 6.77 (2H, distorted triplet, $J = 8$ Hz), 1.63 (11H, br. s.); ir (nujol) μ 2.99, 6.19, 9.60.

C_6H_5 : nmr (CCl_4) δ 7.37-6.93 (5H, m), 1.70 (10H, br. s.), 1.37 (1H, s.); ir (nujol) μ 3.05, 6.22, 9.68.

$p\text{-CH}_3\text{-C}_6\text{H}_4$: nmr (CCl_4) δ 7.0 (4H, AA'BB', $\Delta\nu = 16$ Hz, $J = 8$ Hz), 2.25 (3H, s.), 1.63 (10H, br. s.), 1.45 (1H, s); ir (nujol) μ 2.95, 6.60, 9.60.

$m\text{-F-C}_6\text{H}_5$: nmr (CCl_4) δ 7.2-6.53 (4H, m), 1.67 (11H, br. s.); ir (nujol) μ 3.00, 6.19, 6.29, 9.59.

$p\text{-Cl-C}_6\text{H}_5$: nmr (CCl_4) δ 7.13 (4H, AA'BB', $\Delta\nu \approx 0$, $J = 8$ Hz), 1.67 (10H, br. s.), 1.43 (1H, br. s.); ir (neat) μ 3.00, 6.25, 9.89.

$\text{CF}_3\text{-C}_6\text{H}_4$: nmr (CCl_4) δ 7.43 (4H, s.), 2.67 (1H, s.), 1.63 (10H, br. s.); ir (neat) μ 2.90, 6.13, 8.85.

3,5(CF₃)₂-C₆H₃: nmr (CCl₄) δ7.73 (2H, br. s.), 7.57 (1H, br. s.),
1.67 (10H, br. s.), 1.60 (1H, s.); ir (nujol) μ 3.00, 6.15, 8.75.
p-Br-C₆H₄: nmr (CCl₄) δ7.20 (4H, AA'BB', Δν ≈ 0, J = 8 Hz), 1.67
(11H, br. s.); ir (nujol) μ 2.92, 6.23, 9.91.

Diarylmethyl carbinols

p-CH₃O-C₆H₄: nmr (CCl₄) δ6.77 (8H, AA'BB';, Δν = 32 Hz, J = 9 Hz), 2.53
(6H, s.), 2.67 (1H, br. s.), 1.70 (3H, s.); ir (neat) μ 2.95, 6.19,
9.70.
p-CH₃-C₆H₄: nmr (CCl₄) δ6.90 (8H, AA'BB', Δν = 14 Hz, J = 8 Hz), 2.23
(1H, br. s.), 1.70 (3H, s.); ir (neat) μ 2.90, 6.19, 9.15.
p-CF₃-C₆H₄: nmr (CCl₄) δ7.40 (8H, s.), 2.73 (1H, s.), 1.87 (3H, s.);
ir (neat) μ 2.88, 6.10, 9.80.

1-Aryl-1-phenylethanols

3,4(CH₃)₂-C₆H₄: nmr (CCl₄) δ7.27-6.73 (8H, m), 2.10 (6H, br. s.), 2.0
(1H, br. s.), 1.73 (3H, s.); ir (neat) μ 2.85, 6.18, 9.68.
p-CH₃-C₆H₄: nmr (CCl₄) δ6.67-7.27 (9H, m), 2.23 (3H, s.), 2.07
(1H, br. s.), 1.73 (3H, s.); ir (neat) μ 2.90, 6.20, 9.35.
p-F-C₆H₄: nmr (CCl₄) δ7.30-6.50 (9H, m), 2.67 (1H, s.), 1.73 (3H, s.);
ir (neat) μ 2.91, 6.21, 9.35.
p-Cl-C₆H₄: nmr (CCl₄) δ7.00 (9H, distorted br. s.), 2.67 (1H, s.),
1.70 (3H, s.); ir (neat) μ 2.89, 6.19, 9.12.
C₆H₅: nmr (CCl₄) δ7.33-6.87 (10H, m), 2.53 (1H, br. s.), 1.73 (3H, s.);
ir (nujol) μ 2.95, 6.25, 9.40.

m-F-C₆H₄: nmr (CCl₄) δ7.26-6.50 (9H, m), 2.00 (1H, s.), 1.80 (3H, s.);

ir (neat) μ 2 99, 6.12, 9.45.

m-Cl-C₆H₄: nmr (CCl₄) δ7.30-6.80 (9H, basically 3 broad peaks with

maxima 7.22, 7.07 and 6.97), 2.67 (1H, br. s.), 1.70 (3H, s.);

ir (nujol) μ 2.92, 6.22, 6.35, 9.35.

p-CF₃-C₆H₄: nmr (CCl₄) δ7.33 (5H, s.); 7.12 (4H, AA'BB' Δν = 0,

J = 10 Hz), 2.80 (1H, s.), 1.90 (3H, s.); ir (neat) μ 2.90, 6.15,

8.90 (br.).

3,5(CF₃)₂-C₆H₃: nmr (CCl₄) δ7.67 (2H, br. s.), 7.60 (1H, br. s.),

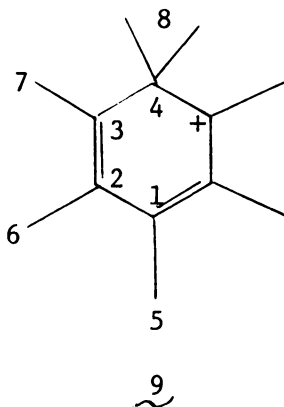
7.20 (5H, br. s.), 2.03 (1H, s.), 1.93 (3H, s.); ir (nujol)

μ 2.78, 6.10, 8.80.

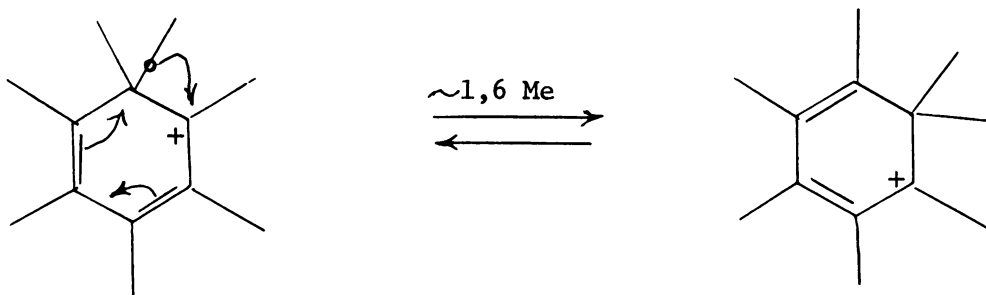
MISCELLANEOUS

Determination of the Spin Lattice Relaxation Times of the Heptamethylbenzenonium ion using CNMR

The heptamethylbenzenonium ion has long been a system of interest.



Proton NMR has shown it to undergo a very rapid 1,6-methyl migration at $+70^{\circ}$.²⁰



The availability of more routine instrumentation has made carbon-¹³ nuclear magnetic resonance spectroscopy, CNMR, another important

tool for structure elucidation. Although the literature involving CNMR is rapidly expanding, very few spin lattice relaxation, (T_1), studies have been undertaken. We have obtained the CNMR spectrum and determined the spin lattice relaxation time for the carbons of the heptamethylbenzenonium ion at probe temperature. We have undertaken this preliminary study for two reasons; first, to familiarize ourselves with the technique for determining spin lattice relaxation time; and second, to see if the spin lattice relaxation time can give an indication as to whether a species might be either rapidly equilibrating or a bridged species.

The solution of the heptamethylbenzenonium ion was prepared by gradual addition, with intermittent vibra-stirring and cooling, of 200 mg of 4 methylene-1,1,2,3,5,6-hexamethyl-2,5-cyclohexadiene to approximately 1 ml of a mixture of 4.8 parts $\text{CF}_3\text{CO}_2\text{H}$ and 5.2 parts H_2SO_4 at -30° . The solution was then diluted to 1.57 ml with the acid mixture. The resulting solution gave proton spectra for the heptamethylbenzenonium ion nearly identical with those reported in the literature.²⁴

The CNMR spectra was run on a Varian CFT-20 with lock being obtained on an external capillary of d_6 -DMSO. The resulting probe temperature spectrum showed absorption at -37.50, -31.04, +20.94, +113.52, +136.22, +138.59, +115.06 relative to the carbonyl carbon in $\text{CF}_3\text{CO}_2\text{H}$. These chemical shifts are assigned C_1 , C_3 , C_2 , C_4 , C_5 , and C_7 , C_6 , and C_8 respectively as in 9. It should be noted that there should be four high field absorptions for the methyl carbons; however, there are only three. We believe that if our assignments for C_1 and C_3

are correct, then the methyl carbons most likely to be coincidentally equivalent are those attached to C_1 and C_3 ; i.e., C_5 and C_7 .

The spin lattice relaxation times were obtained using the inversion recovery method with a pulse delay of 70 seconds and are recorded below:

Carbon	T_1
C_1	11.8 sec.
C_2	9.60 sec.
C_3	9.88 sec.
C_4	14.0 sec.
$C_{5,7}$	1.7 sec.
C_6	2.0 sec.
C_8	2.7 sec.

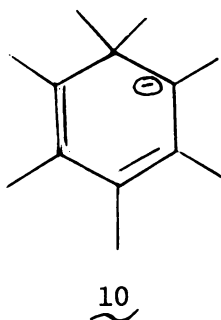
Finding appropriate models for relaxation times for these carbons is difficult since few ^{13}C relaxation studies have been done on uncharged species, and, to our knowledge, none have been done on carbocations.

Levy³ has reported the T_1 for the quaternary ring carbon of toluene (C_1) to be 51 sec. for an undegassed sample. The T_1 values obtained for the ring carbons of the heptamethylbenzenonium ion, ~ 10 sec., indicate something unusual about these carbons.

One factor which could possibly influence the rate of relaxation is the fluctuating positive charge in the molecule. Further experiments are needed.

Synthesis of Some Potential Precursors to the Heptamethylcyclohexadienyl Anion

The heptamethylbenzenonium ion 9 has been shown to undergo a rapid methyl migration at 70°. The heptamethylcyclohexadienyl anion 10, unlike the heptamethylbenzenonium ion, is not expected to undergo the rapid rearrangement thermally; however, it can be predicted that it would undergo the rearrangement photochemically.



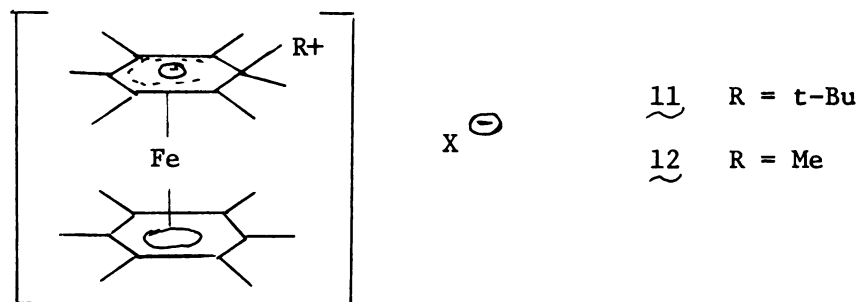
For reasons of comparison with the heptamethylbenzenonium ion, we have synthesized some potential precursors to the anion and have attempted a few experiments in order to generate the anion itself.

Our first approach was patterned after that of two groups of workers: 1.) Braitsch and Helling^{23,24} and 2) Nesmayanov²⁵.

Braitsch and Helling^{23,24} have reported the synthesis of π -hexamethylbenzene- π -exo-t-butylhexamethyl cyclohexadienyl iron (II) hexafluorophosphate, 11.

We have prepared and isolated the methyl analogue π -hexamethylbenzene- π -heptamethylcyclohexadienyl iron (II) hexafluorophosphate, 12, by reacting bis (hexamethylbenzene) iron (II) hexafluorophosphate dihydrate, 13, with three equivalents of methyl lithium in ether.

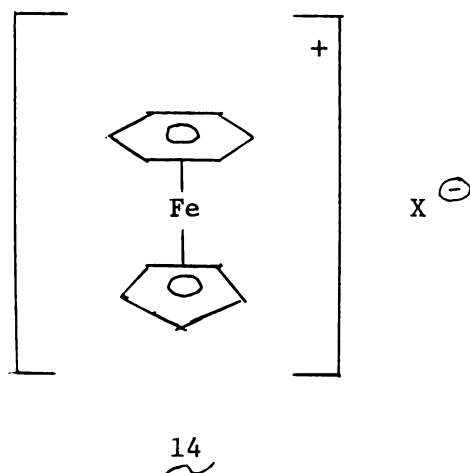
The PNMR spectrum showed absorption at τ 7.48 (3H, s.), 7.70 (18H, s.), 8.17 (6H, s.), 8.73 (3H, s.), 8.80 (6H, s.), and 10.16 (3H, s.). This spectrum compares very favorably with that of the exo-t-butyl compound 11 made by Helling and Braitsch^{22,23} where resonances at τ 7.63 (3H, s.), 7.79 (18H, s.), 8.20 (6H, s.), 8.32 (3H, s.), 8.73 (6H, s.), 9.73 (9H, s.) are reported. The only resonance which has any appreciable chemical shift difference is the exo-t-butyl and the exo-methyl, in compound 11 and 12 respectively.



If one compares these resonances with those of π -mesitylene- π -exo-alkyl-1,3,5-trimethyl cyclohexadienyl iron II hexafluorophosphates 14 and 15 where the alkyl substituents are t-butyl and methyl one finds resonances of τ 9.53 and 9.84 respectively for the exo substituents. If this 9.31 ppm chemical shift difference were to hold in the hexafluorophosphate salts 11 and 12, then the chemical shift of the exo methyl in 12 should come at 10.04. The value of 10.16 is in reasonable agreement.

We had then hoped to remove the heptamethylcyclohexadienyl anion from the metal by one of two methods:

1) Exchanging it with sodium cyclopentadienide²⁵. This method of exchange was known to work for complexes of the type 14, to give the free arene and ferrocene.



Our hope was not only that the arene would be exchanged off, but also, the cyclohexadienyl anion. We have found that reaction of 12 with sodium cyclopentadienide gave no ferrocene type products; i.e., neither the arene ring nor the heptamethyl cyclohexadienyl ring is exchanged off the metal.

2) Reducing the anion off the metal. It was known that complexes of the type 14 were converted into ferrocene and the free arene by the action of reducing agents as Na/Hg amalgam. We hoped that the complex 12 could be converted either to the bis-(π -heptamethylcyclohexadienyl)-iron (II) from which we could attempt to remove the metal by some similar process or the free heptamethylcyclohexadienyl anion and/or arene would be liberated from the metal. Attempted reduction of 12 led only to recovery of starting material and isolation of small amounts of hexamethylbenzene.

Our second approach involved the synthesis of 1,2,3,3,4,5,6-heptamethyl-1,4-cyclohexadiene by reduction of 1,1,2,3,5,6-hexamethyl-4-methylene-2,5-cyclohexadiene with Na/NH₃(l). The PNMR of the product shows resonance at δ 2.17 (1H, q, J = 6Hz), 1.58 (12H, s.), 1.0 (3H, s.), and 9.95 (3H, d, J = 6Hz). Irradiation of the signal at 2.17 collapsed the signal at 0.95 to a singlet. This signal at 2.17 is unusually high for a doubly allylic methine hydrogen. However, the doubly allylic protons in 1,4-cyclohexadiene and 1,4-dimethyl-1,4-cyclohexadiene came at 2.63 and 2.45 respectively. If this shift to higher field by about 0.2 ppm per set of methyl groups located 1,4 on the diene system were to continue, then the value of 2.17 is reasonable. The mass spectrum with a parent peak of 178 and fragments at 163, 148, and 133, is consistent with the assigned structure. This does not, however, exclude the conjugated isomer, 1,2,3,4,5,5,6-heptamethyl-1,3-cyclohexadiene, which might have a similar PNMR spectrum if some of the signals were accidentally coincidental. The UV spectrum and the CNMR spectra ruled out the conjugated diene. No UV maximum is observed above 200 nm. The CNMR shows only nine absorptions as expected for the nonconjugated diene while the conjugated diene should show thirteen.

Bates²⁶ has described a procedure for generating anions from 1,4-dienes. Attempts at generating the anion by this method are described in the experimental.

Experimental

Preparation of π -Hexamethylbenzene- π -Heptamethylcyclohexadienyl Iron (II) Hexafluorophosphate

In a flame dried three necked round bottom flask equipped with stopper, nitrogen inlet, a serum cap and magnetic stirrer, was placed 1.0 gm of bis-(hexamethylbenzene) iron (II) hexafluorophosphate under a blanket of N_2 . Ether (3.0 ml), dried over sodium was added using a syringe. The resulting suspension was stirred and cooled to -78° . Methyl lithium, 3.2 ml (1.24 M), was added to the reaction flask all at once. The reaction mixture was allowed to stir for one minute and was allowed to warm slowly to room temperature. As the vessel warmed the reaction mixture turned a dark purple, almost black, color. The reaction flask was allowed to stir for two hours at room temperature. Ether (10 ml), saturated with H_2O was added to react with the excess methyl lithium. The resulting mixture was filtered through a fritted funnel. The solid was placed in a beaker and extracted three times with metnylene chloride (10 ml). The resulting red solution was gravity filtered. Ether was added to precipitate the light brown product (0.59 gm, 51%) NMR ($CDCl_3$): τ 7.40 (3H, s.), 7.70 (18 H, s.), 8.17 (6H, s.), 8.73 (3H, s.), 8.80 (6H, s.), 10.16 (9H, s.); ir (KBr): 2950, 1437, 1005, 845 cm^{-1} ; mp (sealed evacuated capillary): gradual decomposition as temperature raised above 100° .

Preparation of Bis-(hexamethylbenzene) iron (II) hexafluorophosphate

A flame dried three necked round bottom flask, equipped with stoppers, magnetic stirrer, and a condenser with a nitrogen inlet on

the top, was purged with nitrogen. Hexamethylbenzene (6.85 gm), ferrous chloride (2.15 gm), and cyclohexane (2.5 ml) were placed in the flask and stirred. Aluminum chloride (5.40 gm, freshly sublimed) was added to the stirred suspension. The suspension was refluxed for twenty-four hours under a blanket of nitrogen. The reaction mixture was allowed to cool to room temperature and then cooled to 0° in an ice bath. Hydrolysis was accomplished by adding 30 ml of iced water. The organic layer was discarded. The aqueous layer was extracted with two 25 ml portions of petroleum ether and filtered. To the aqueous solution was added an aqueous solution of 13.88 gm of sodium hexafluorophosphate to precipitate the product which was collected by filtration. The crude product was dissolved in 95% aqueous acetone and precipitated by adding ether. Yield: 7.68 (64%) light orange solid; mp: gradual decomposition on heating; NMR (d_6 -acetone): τ 7.18 (3.6H, s.), 7.5 (36H, s.); ir (KBr) 3450, 3000, 1470, 1445, 1300, 1010, 850 cm^{-1} .

Attempted preparation of bis(π -heptamethylcyclohexadienyl)-iron (II)

The procedure used here was basically the same as that used for the preparation of π -hexamethylbenzene- π -heptamethylcyclohexadienyl iron(II)hexafluorophosphate. All experiments started with 1.0 gm of bis(hexamethylbenzene) iron (II) hexafluorophosphate. The following modifications were made:

1) Five equivalents of methyl lithium were added at -78° and then allowed to warm to room temperature and kept there for two hours with constant stirring. Work-up followed.

2) Five equivalents of methyl lithium were added at -78° and then the reaction mixture was refluxed overnight. Work-up followed.

3) Reaction was run in di-n-butyl ether as a solvent. The reaction mixture was cooled to -0° before adding the methyl lithium (eight equivalents). It was allowed to warm to room temperature. The ether was distilled out. The reaction mixture was refluxed overnight. Work-up followed.

The work-up procedure was also a little different from that used in the π -hexamethylbenzene- π -heptamethylcyclohexadienyl iron (II) hexafluorophosphate preparation. It was as follows: After the reaction with methyl lithium was thought to be complete, the reaction mixture was cooled to 0° . Fifty ml of ether saturated with water followed by 10 ml of water were added to quench any unreacted methyl lithium. The reaction mixture was filtered. The solid was collected and extracted with 2 x 25 ml of Et_2O and then saved for recrystallization. The ether was combined with the mother liquor from the reaction. The combined two phase water-ether mixture was put in a separatory funnel and the two layers were separated. The ether solution was again extracted with 10 ml of H_2O . The ether layer, which should contain any bis(π -heptamethylcyclohexadienyl) iron (II) was dried over MgSO_4 , filtered, and rotovap distilled. None of the desired product was obtained in any of the cases mentioned above.

The solid obtained from these reactions was recrystallized by dissolving it in CH_2Cl_2 and reprecipitating it with ether. The solid had an NMR identical to that of π -hexamethylbenzene- π -heptamethylcyclohexadienyl iron (II) hexafluorophosphate. The yield of

π -hexamethylbenzene- π -heptamethylcyclohexadienyl iron (II) hexafluorophosphate was 41-68% based on the bis arene iron complex.

Attempted exchanges of π -hexamethylbenzene- π -heptamethylcyclohexadienyl iron II hexafluorophosphate with sodium cyclopentadienide

In a one necked flame dried flask with a Teflon stopcock in a side arm, equipped with a magnetic stirrer, and condenser, was placed 0.51 gm π -hexamethylbenzene- π -heptamethylcyclohexadienyl iron (II) hexafluorophosphate (0.51 gm) and 3 ml of THF (dried by distilling from LAH) under argon. The reaction mixture was also purged of oxygen by bubbling the argon through the solution, and then kept under a blanket of argon. The side arm of the flask was equipped with a serum cap and the reaction was cooled to -78° . Sodium cyclopentadienide (2 ml of a 2.5 M solution in THF) was added all at once. The reaction mixture was stirred at -78° for five minutes and allowed to warm to room temperature where it was then stirred for twenty hours before 2 ml of H_2O were added to quench the reaction mixture at 0° . Most of the THF was rotovap distilled, leaving a wet brown solid. Ten ml of H_2O were added and then the mixture was extracted with petroleum ether to attempt to remove any ferrocene type products. The brown solid was filtered from the mother liquor and saved for recrystallization. The two phase mother liquor was separated in a separatory funnel and the petroleum ether layer was dried and rotovap distilled. No observable products were found. The solid and aqueous layer was then extracted with methylene chloride giving a red brown solution. Et_2O was added to precipitate a

a light brown solid (0.38 gm). The NMR of the solid was identical with that of the starting material.

Other attempts to exchange were made using 2 to 15 equivalents of sodium cyclopentadienide. Temperatures ranged from room temperature to refluxing THF for times up to twelve hours. In all cases neither ferrocene type products nor any hydrocarbon type products, with the exception of small amounts of hexamethylbenzene were observed. In all cases, recovery of starting material was observed (70-95%).

Attempted reduction of π -heptamethylbenzene- π -heptamethylcyclohexadienyl iron (II) hexafluorophosphate

π -hexamethylbenzene- π -heptamethylcyclohexadienyl iron (II) hexafluorophosphate (0.805 gm) was placed in a dried flask containing approximately 80 ml of dried THF, degassed with argon. In a second flame dried flask was placed 1 ml of mercury. Sodium (0.15 gm) was added to the mercury to make Na/Hg amalgam under an argon blanket. The solution of the iron complex was added to the vessel containing the amalgam. The reaction mixture turned from its initial red color to a dark brown. The reaction was allowed to stir for three hours at room temperature. If an aliquot was removed and exposed to the air, the solution immediately turned back to the red color. The reaction mixture was then either allowed to stir for three more hours at room temperature or sodium cyclopentadienide (4 ml of 2.5 M in THF) was added and then allowed to stir for three hours more. The reaction was then quenched with water. The starting material was precipitated by adding ether and isolated by filtration (0.6 gm and 0.49 gm recovered



respectively). The mother liquor was evaporated at room temperature under vacuum. The residue was chromatographed on silica gel with hexane as the eluant. The only insoluble materials were mineral oil (250 mg) when the sodium cyclopentadienide was added and hexamethylbenzene (~ 40 mg).

Reduction of 1,2,4,5,6,6-hexamethyl-3-methylene-1,4-cyclohexadiene with sodium

The entire system consisting of a 100 ml, three necked round bottom flask with N_2 inlet, Dry Ice condenser with a soda lime drying tube, ammonia inlet, and magnetic stirrer was flamed while being flushed with N_2 . 1,2,4,5,6,6 hexamethyl-3-methylene-1,4-cyclohexadiene (0.176 gm) was then placed in the flask and approximately 10 ml of NH_3 was condensed into the apparatus. Half of the sodium (0.046 gm) was added and a blue solution resulted. The rest of the sodium was added and 20 ml more of NH_3 were condensed into the apparatus. When the solution lost its blue color, 1 gm of ammonium chloride was added slowly. Water (10 ml) was added and the NH_3 was allowed to evaporate. Et_2O (20 ml) was added and the two layers were separated in a separatory funnel. The ether layer was dried over $MgSO_4$, filtered, and rotovap distilled. A light yellow liquid (9.150 gm) was obtained. Chromatography on a 6 ft., 20% SE-30 column at 150° showed two peaks (ret. ratio 5/3) of an unknown compound and starting material. T.L.C. on 20% $AgNO_3$ impregnated silica with hexane ether, (10/1 eluent showed two spots ($R_f = 0.87$, $R_f^1 = 0.55$). The second spot had an R_f identical to that of the starting material.

Chromatography on 20% silver nitrate impregnated silica gel (70-135 mesh) lead to the isolation of 102 mg of compound whose spectra were consistent with the structure 1,2,3,3,4,5,6 heptamethyl-1,4-cyclohexadiene ^1H NMR (CCl_4): 2.17 (1H, q, $J = 6\text{Hz}$), 1.57 (12H, s.), 1.0 (3H, s.), 0.95 (1H, d, $J = 6\text{Hz}$); irradiation of the signal at 2.17 collapsed the signal at 0.95 to a singlet; no UV max above 200 nm; ^{13}C NMR (CDCl_3) 14.34, 18.06, 19.96, 24.77, 39.99, 43.31, 75.45, 128.46, 131.49; mass spectra (m/e) 178, 153, 148, 133 and 0.23 gm of starting material. The 1,2,3,3,4,5,6 heptamethyl-1,4-cyclohexadiene must be stored in a freezer (below -30°) under an inert atmosphere. Attempts at obtaining a satisfactory microanalysis were unsuccessful.

Attempted generation of the heptamethylcyclohexadienyl anion

A) In a flame dried NMR tube with a serum cap was placed 1,2,3,3,4,5,6-heptamethylcyclohexadiene (0.356 gm) and 0.6 ml of THF. The solution was degassed by bubbling through argon. The mixture was cooled to -78° and 1.2 ml of a 1.67 M solution of $n\text{-BuLi}$ in hexane was added. The mixture was allowed to warm to room temperature. A faint yellow color appeared but no layer separation occurred as expected. Quenching with water at 0° followed by extraction with hexane led to the recovery of 0.327 gm of starting material after chromatography on 20% AgNO_3 impregnated silica gel with hexane ether (10/1) eluent.

B) The reaction was run identically as in A only with 2.4 ml of $n\text{-BuLi}$ in hexane. Again no layer separation occurred. Quenching with D_2O , followed by extraction with hexane led to the recovery of 0.313 gm

of starting material. Mass spectra of the crude recovered starting material showed no deuterium incorporation.

C) The reaction was run as in either A or B with one or two equivalents of a BuLi in hexane with one and two equivalents, relative to the butyl lithium, of either dry tetramethylethylene diamine or dry HMPA. The reaction was quenched with water (either H_2O or D_2O), at 0° .

In those experiments where tetramethylethylene diamine was used, the quenched reaction mixture was diluted with water (3 ml) (H_2O or D_2O) and then extracted with three 5 ml portions of hexane. The hexane solution was then extracted with two 5 ml portions of 1% HCl, and then with one 5 ml portion of H_2O . The hexane solution was dried over MgSO_4 , filtered and rotovap distilled. The crude recovered starting material (~ 100 mg), showed no deuterium incorporation.

In those cases where HMPA was used, a fleeting red color was observed on addition of the butyl lithium. After quenching with water at 0° , the reaction mixture was diluted with 3 ml of water and then the mixture was extracted with five 2 ml portions of hexane. The hexane extracts were dried with MgSO_4 , filtered and rotovap distilled. Attempted chromatography on silica gel or AgNO_3 impregnated silica gel led to no insoluble product. As material was eluted down the column with hexane/ether (10/1), the column turned every color of the rainbow.

REFERENCES

1. a) J. F. Norris, Am. Chem. J., 25, 117 (1901); Chem. Zentr. 1901 (I) 699.
 b) J. F. Norris and W. W. Saunders, Am. Chem. J., 25, 54 (1901); through Chem. Zentr. 1901 (I) 463.
2. F. Tehrmann and F. Wentzel, Chem. Ber., 34, 3815 (1901).
3. M. Gomberg and L. H. Cone, Ann. Chem., 370, 142, 193 (1909); 376, 183 (1910).
4. K. A. Hofmann, and H. Kirmreuther, Chem. Ber., 42, 4856 (1909).
5. G. A. Olah et al., J. Am. Chem. Soc., 86, 1360 (1964).
6. G. A. Olah et al., J. Am. Chem. Soc., 86, 2198 (1964).
7. "Carbonium Ions", Vol. I-IV, G. A. Olah and P. V. R. Schleyer, Eds. John Wiley and Sons, New York, London, and Sidney (Especially Chapters 7 and 28).
8. D. G. Farnum and A. D. Wolf, J. Am. Chem. Soc., 96, 5166 (1974).
9. N. G. Deno and W. L. Evans, J. Am. Chem. Soc., 79, 5804 (1951).
10. McKenzie, J. Chem. Soc., 101, 1196 (1912).
11. a) W. G. Young et al., J. Am. Chem. Soc., 51, 2528 (1929).
 b) S. Winstein and H. J. Lucas, J. Am. Chem. Soc., 61, 1576 (1939).
 c) H. O. House and R. S. Ro, J. Am. Chem. Soc., 80, 182 (1958).
 d) J. H. Rolston and K. Yates, ibid., 91, 1496, 1477, 1483 (1969).
12. a) G. A. Olah and J. M. Bollinger, J. Am. Chem. Soc., 90, 947 (1969).
 b) G. A. Olah and Yoke K. Mo, ibid., 96, 3560 (1972).
 c) G. A. Olah et al., ibid., 96, 3565 (1972)
 d) G. A. Olah et al., ibid., 680 (1975) and reference cited in the above.

13. a) G. A. Olah et al., ibid., 94, 2044 (1972).
b) G. A. Olah et al., ibid., 93, 464 (1971).
14. a) D. C. Farnum, ibid., 89, 2970 (1967).
b) D. C. Farnum and C. F. Wilcox, ibid., 5379 (1967).
15. D. C. Farnum and Goverdhan Mehta, ibid., 91, 3256 (1969).
16. G. A. Olah and Gao Lang, ibid., 96, 195 (1974).
17. G. A. Olah et al., ibid., 92, 2112 (1970), 94, 156 (1972).
18. R. Botto, Ph.D. Thesis, Michigan State University, 1975.
19. Harold Hart and Masayuki Kuzuya, J. Amer. Chem. Soc., 96, 6436 (1974).
20. M. Saunders, Magnetic Resonance in Biological Systems, A. Ehrenberg, B. G. Malmstrom, and T. Vanngerd (editors), 90 (1967).
21. Harold Hart et al., J. Am. Chem. Soc., 88, 1005 (1966).
22. C. C. Levy and I. R. Prat, J. Magnetic Resonance, 18, 500-521 (1975).
23. J. F. Helling and D. M. Braitsch, J. Amer. Chem. Soc., 92, 7209 (1970).
24. D. M. Braitsch, Ph.D. Thesis, University of Florida, 1971.
25. A. N. Mesmeyanov et al., Akademi Nauk, SSR Vol. 190 No. 2, pp. 354 (1970).
26. R. B. Bates et al., Tetrahedron Letters, No. 3, 199 (1967).

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