MULTINUCLEAR NMR STUDY ON THE
HIGHLY BRIDGED ARYL SUBSTITUTED
COATES CATION

AND

SIMILAR STUDIES ON THE
CLASSICAL ARYL SUBSTITUTED
2-ADAMANTYL AND 7-NORBORNYL CATIONS

By

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ABSTRACT

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Following the work of Botto and Chambers, three series of aryl substituted carbocations were prepared and their NMR spectra taken. The first series studied was the 9-aryl-9-pentacyclo$[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]$nonyl cation; the only system that all in the field agree to be bridged. The results from the study of it are twofold:

1) The NMR of aryl substituted bridged ions is in sharp contrast to those of classical ions. The degree of contrast is difficult to predict but qualitative trends are readily apparent.
2) The perturbation of placing an aryl substituent on a bridged system tends to stabilize the "classical" structure much more than the bridged structure. Thus weakly bridged systems may easily become classical by the placement of even very electron demanding aryl groups.

The second system studied was the 2-aryl-2-adamantyl cation. It was found that the perturbation of placing an aryl group on the weakly bridged 2-adamantyl cation produces a classical cation. Hence a

lower limit for the amount of bridging that is detectable by this probe has been established.

The third system studied was the 7-aryl-7-norbornyl cation with the hope of inferring some unusual behavior for the parent cation. No such behavior was found, however, and hence, if the geometry of the 7-norbornyl cation is deformed, then the energy difference between it and its classical structure must be too small to measure by the probe used.

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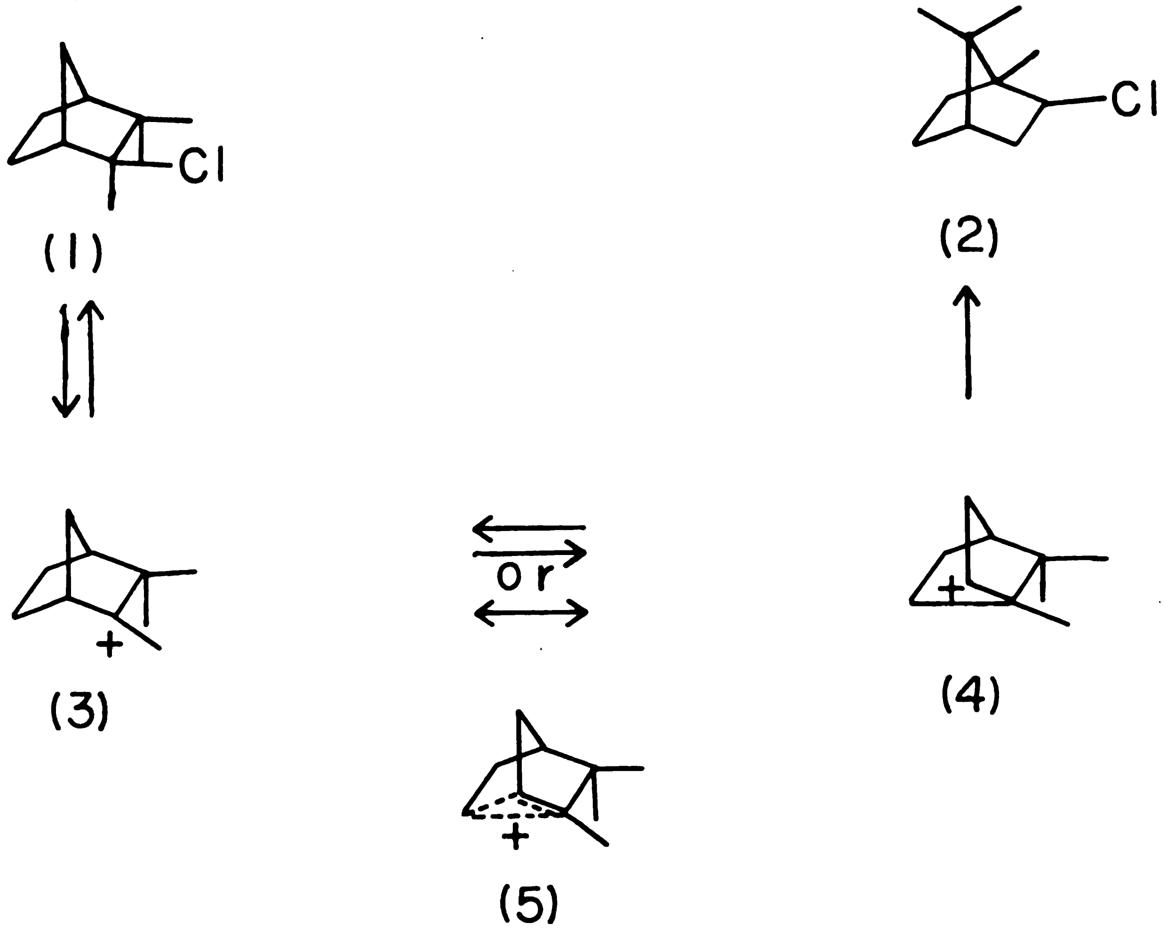
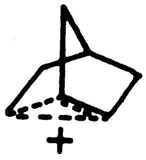
INTRODUCTION

In 1939, Wilson[1] made the suggestion that the proposed intermediates (3) and (4) in the solvolysis of camphene hydrochloride (1) might exist as a resonance hybrid (5) rather than separate entities. In the early 1960's, structures of other cations showing similar delocalization to that of (5) were proposed, the most famous being the 2-norbornyl (6)[2] and the cyclopropylcarbinyl (7)[3] cations. Soon, practically every carbocation known was reevaluated in terms of delocalized sigma bonds and was given the designation of a "nonclassical cation". It was not until the late 1970's, however, when the term "nonclassical cation" was defined.[4a]





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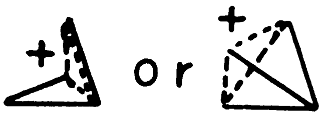

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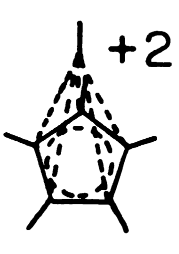
In the early 1960's, when H.C. Brown[5] and others challenged the issue of nonclassical cations, an immense amount of extremely valuable work was undertaken to prove or disprove the existence of these ions. Possibly no other area of organic chemistry has had the time and scrutiny of so many chemists as this question concerning the carbocation geometry. Although even after a quarter of a century, many of the early questions raised are still the objects of enthusiastic debate (the 2-norbornyl and cyclopropylcarbinyl cationic structures for instance), there is no doubt that these questions have inspired a great deal of advancement in organic chemistry.

At present there can be no doubt as to the possibility of nonclassical cations existing. The three-center, two-electron bonds found in many boranes strongly indicate that carbocations (which are isoelectronic with the boranes) may also enjoy the same type of bonding. Recently, structures (8) - (11) have gained wide approval over their classical counter-parts.[6-9] Still, however, the approval of structures (8) - (11) is more than balanced by the rejection of a great many proposed nonclassical structures[4b] such as (12) - (14).



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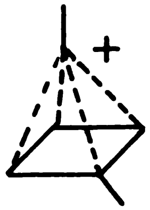

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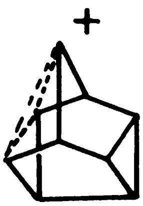

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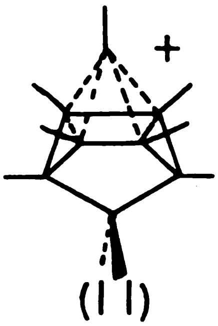

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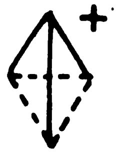

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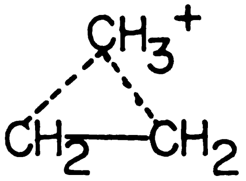


(14)

There remains, however, a large number of carbocations whose structures have yet to be established as classical or nonclassical. Of the many methods used to prove the structure of carbocations, NMR seems to have been the most used. The main disadvantage of NMR studies has been the lack of suitable model compounds. Thanks to the efforts of Olah and others,[10] we now have a workable supply of NMR data on proven classical cations. The limited number of cations known to be bridged, however, offers us little in the way of what is "normal" for the NMR of nonclassical cations. The major theme of this thesis is to enhance our knowledge of what is normal for classical and nonclassical cations.

The method used to examine cations in this project was to correlate chemical shifts of various α-aryl cations with those of known classical cations as a function of electron demand. Olah has shown that a plot of the chemical shift of the cationic center of cations (15) - (17) correlates in a somewhat linear fashion with σ^+ (see figures 1-3).[11] From the large standard deviations, however, it became clear that the effect of different aryl groups on the chemical shifts was not just a function of electron demand, and that a new set of σC^+ values might be established for NMR studies in super acid media.[12]

Upon reexamination of Olah's results, it was found that excellent correlations could be obtained by plotting the chemical shift of one cationic center with that of the cationic center in another system.[13] An example of such a correlation is given in figure 4. In all cases, a

Figure 1. Correlation of the chemical shift of (15) with σ^+

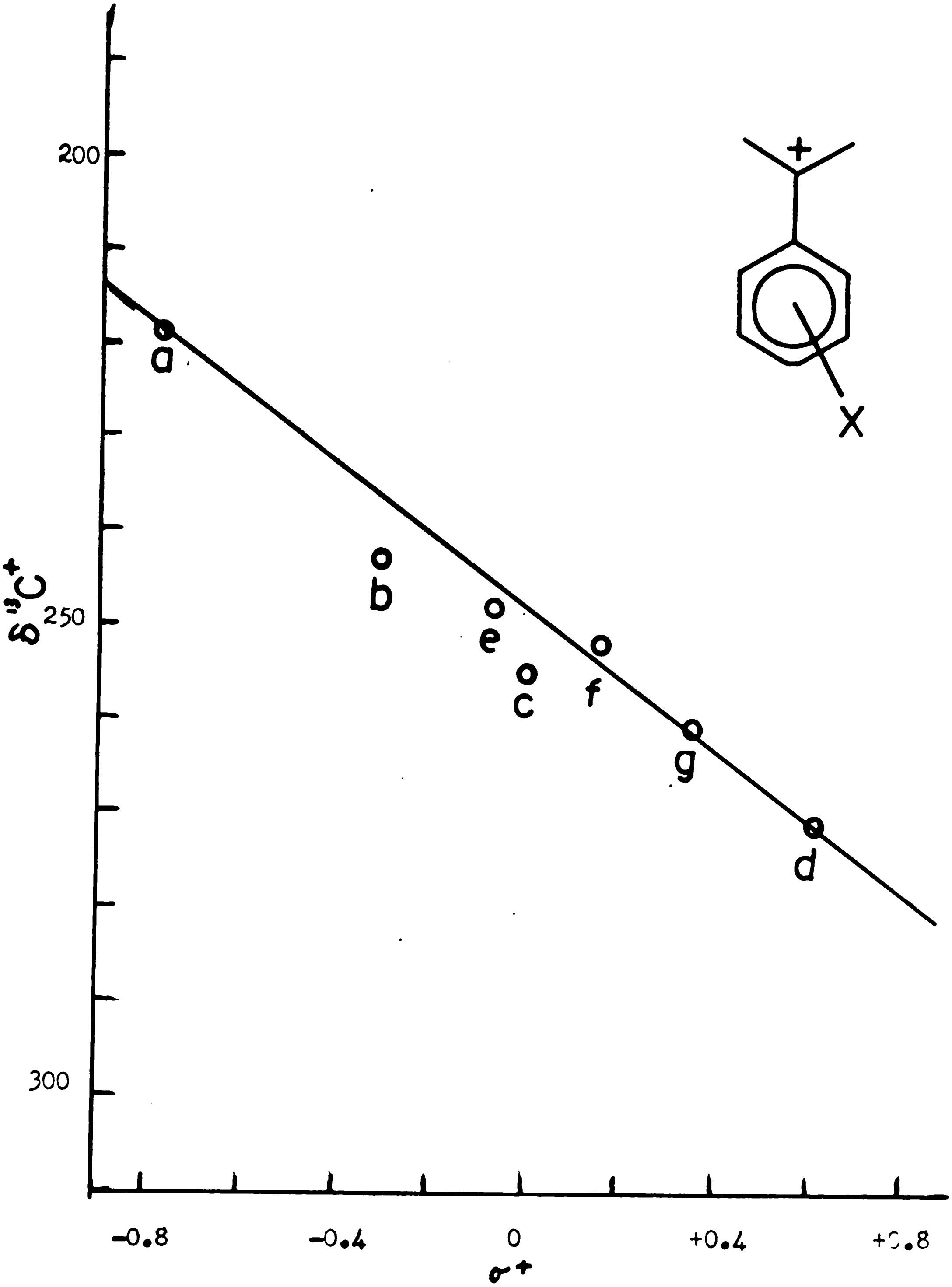


Figure 2. Correlation of the chemical shift of (16) with σ^+

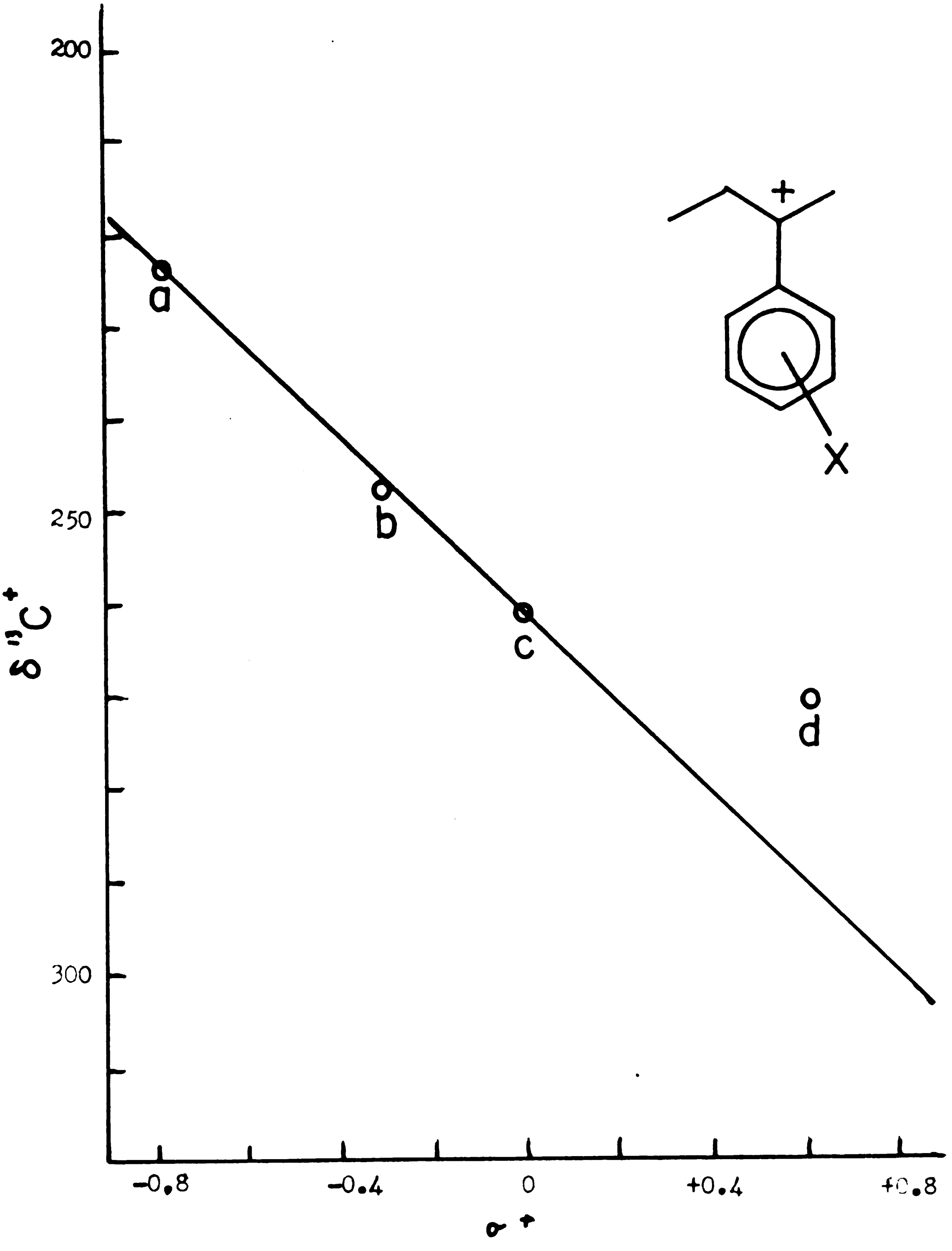


Figure 3. Correlation of the chemical shift of (17) with σ^+

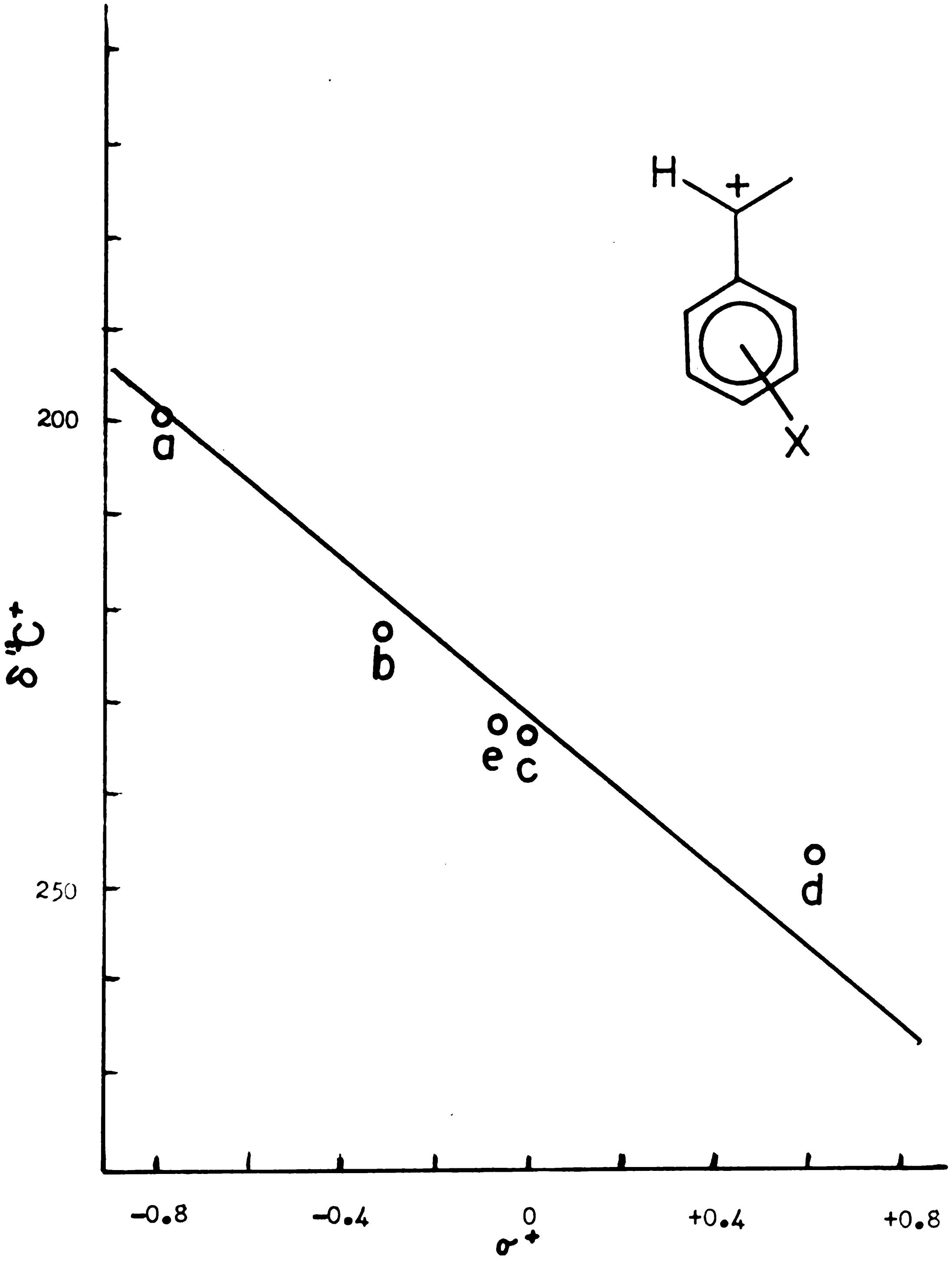
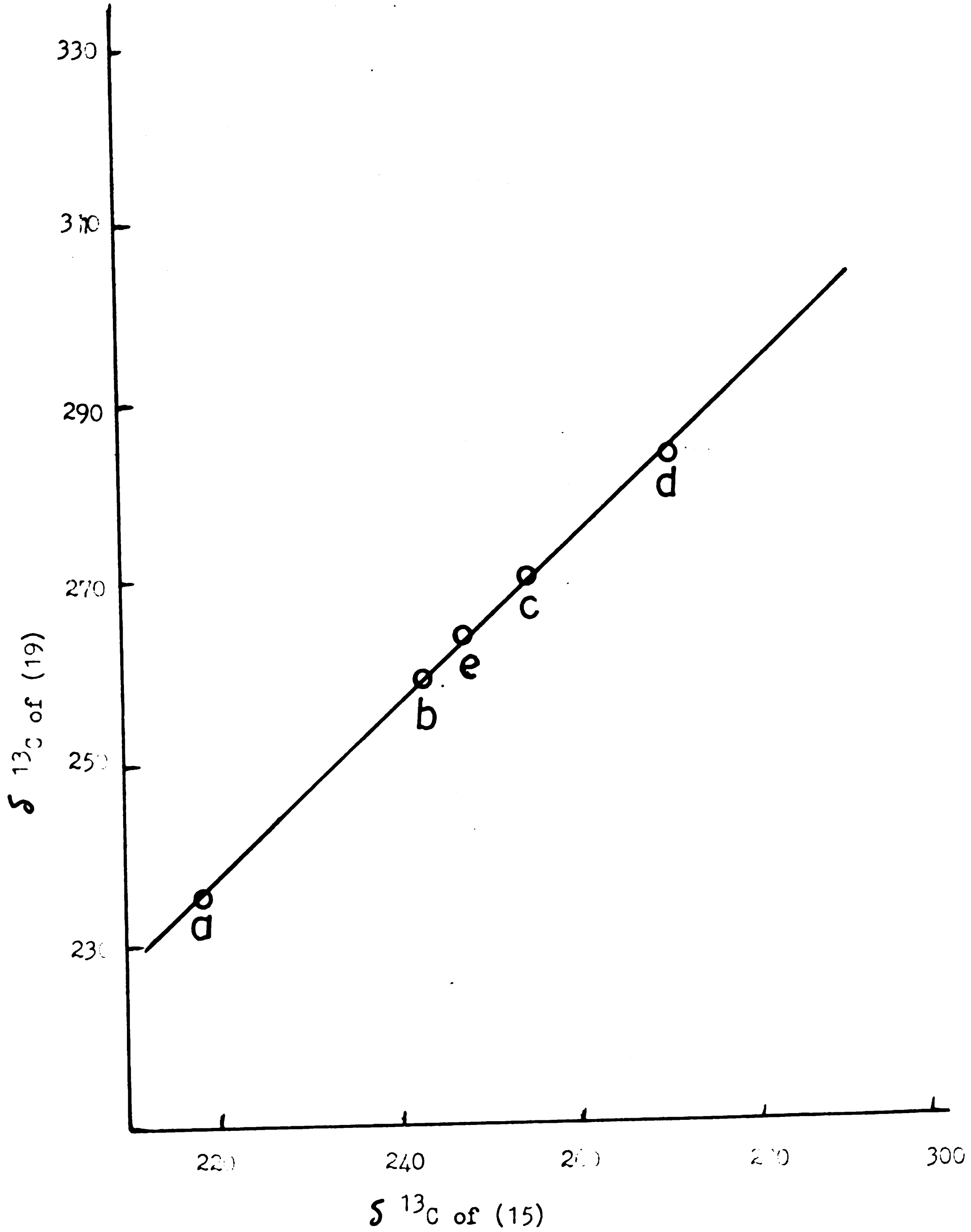
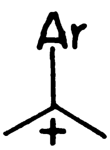
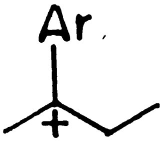


Figure 4. Plot of the chemical shifts of the cationic center of (15) vs. (19)

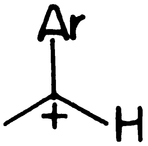




(15a–g)



(16a–d)



(17a–e)

a) 4-OCH_3

b) 4-CH_3

c) phenyl

d) 4-CF_3

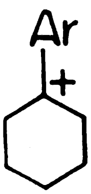
e) 4-F

f) 4-Br

g) 3-F

straight line with a negligible standard deviation was obtained with close to a unit slope. It appears that the factors leading to the deviations of the correlation of chemical shifts versus electron demand could be cancelled in this manner.

Botto[14] and Chambers[13] continued this line of reasoning and found similar linear relationships with the chemical shifts of compounds (18) - (21). Compounds (15) - (17) also showed linear relationships with compounds (18) - (21) and in all cases it was surprising to find slopes very near unity. It appeared then, that some measure for detecting "normal" cations was available. The prime question was whether this approach would yield sufficiently different results for "unusual" cations.



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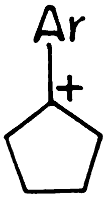

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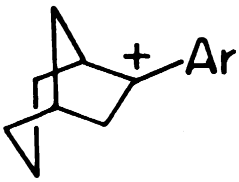

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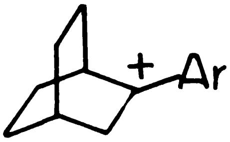
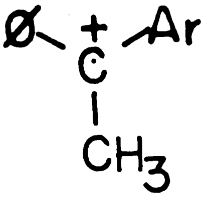


(21)

The first attempt to find unusual behavior in cations with increasing electron demand (via NMR correlations of chemical shifts) was done by Chambers[13] with the 1-aryl-1-phenyl-1-ethyl cation, (22a-k). When plotting the chemical shift of the cationic center in (22) with the cationic center of any of the compounds (15) - (21), two straight lines were obtained which intersected when the aryl group was phenyl (figure 5). The rationale for this behavior rests on the fact that only one aromatic ring may be conjugated with the cationic center at any given time due to steric effects. Thus it is reasonable for the aryl group to be conjugated with the cationic center for those cases where it is less electron demanding than phenyl (cases 22a-f). When the phenyl is more electron donating than the aryl group, the aryl group would be twisted out of conjugation (cases 22h-k). It was thus established that by examining the chemical shifts of a series of aryl substituted cations, changes in geometry may be detected.



(22a-k)

a) p-OCH_3
b) 3,4-$(CH_3)_2$
c) p-CH_3
d) p-F
e) p-Cl
f) p-Br

g) phenyl
h) m-F
i) m-Cl
j) p-CF_3
k) 3,5-$(CF_3)_2$

Botto[14] found breaks in the plots of the chemical shifts of compounds (23) - (25) when plotted against any of the classical compounds (15) - (21) (see figure 6 for a superb example). These breaks were inter-

Figure 5. Plot of the chemical shifts of the cationic center of (19) vs. (22)

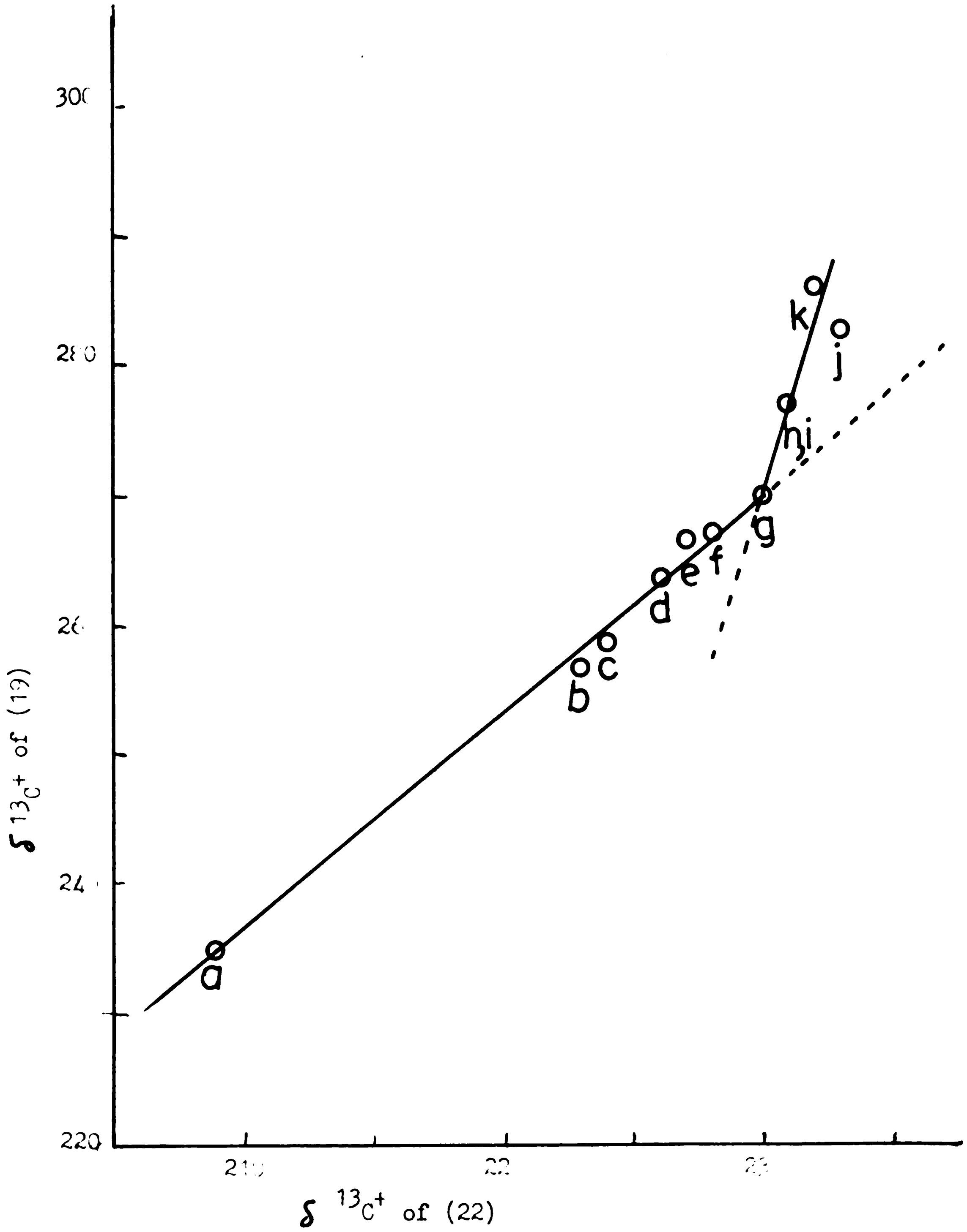
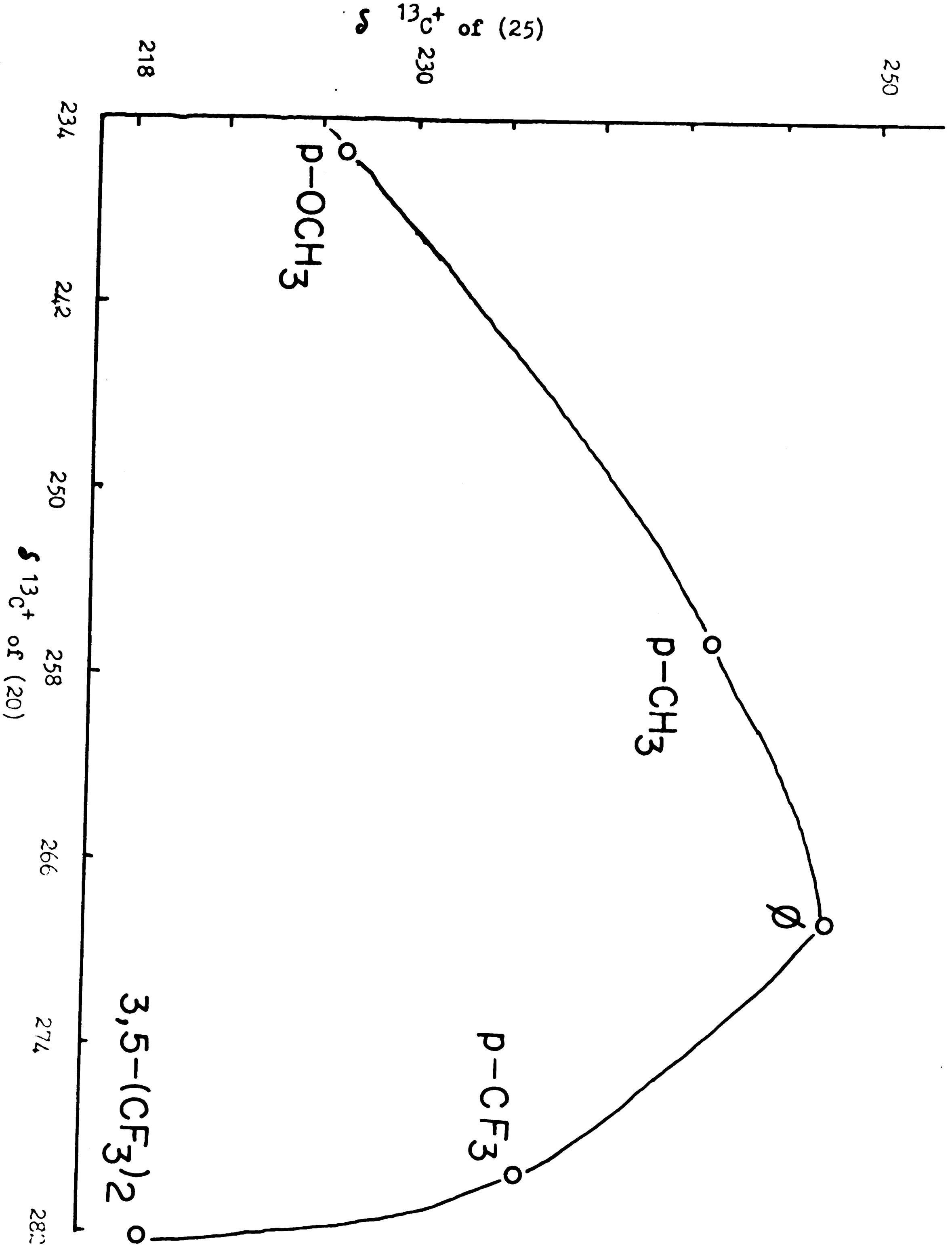
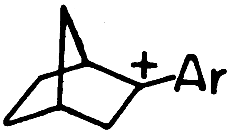


Figure 6.[14] Plots of the chemical shifts of the cationic center of (25) vs. (20).





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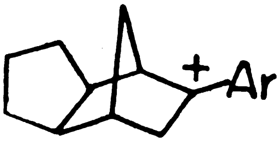

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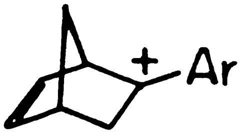
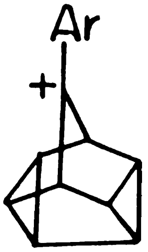


(25)

preted in the case of (22), as an abrupt change in their geometries. With the highly stabilizing aryl groups, it was assumed that the systems need no further stabilization from other portions of the molecule, while with the electron withdrawing aryl groups, the systems would begin seeking further stabilization elsewhere. The change in the resultant electronic state would likely leave the aryl group in a less optimum position to stabilize the cation by conjugation, thus requiring the system to seek out still further stabilization. This feedback effect would continue until a new optimized geometry resulted. Thus the abrupt change in slope for these plots seems reasonable.

The work in this dissertation is a continuation of the work done by Botto and Chambers. The three series studied are the aryl substituted 9-pentacyclo$[4.3.0.0.^{2,4}0.^{3,8}0.^{5,7}]$nonyl (26), the 2-adamantyl (27) and the 7-norbornyl (28) cations.



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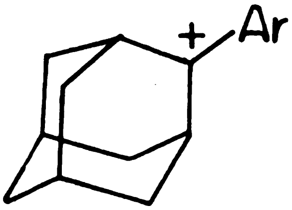

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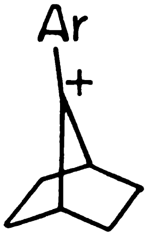
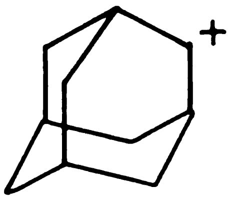


(28)

These systems were chosen for the following reasons:

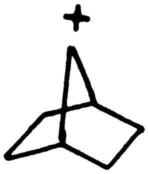
1) Although Botto's work suggests that the systems (23)-(25) are nonclassical, the arguments proposed have not been accepted by all in the field. Chemical shifts of cations known to be bridged are required in order to extrapolate into the more questionable systems such as the 2-norbornyl cation (6). The only cation that is accepted as being bridged by all in the field[15] is the 9-pentacyclo $[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]$nonyl cation (10)[8] which would thus seem a logical start for the characterization of nonclassical cations.
2) The 2-adamantyl cation (29) has been postulated to possess a barely detectable amount of bridging.[16,17] It is hoped that by correlating the chemical shift of the cationic carbons of the 2-aryl-2-adamantyl cations (27) with the chemical shifts of established classical cations, a qualitative measure of how sensitive this probe is can be determined. Also, any abnormal deviations observed would lend support to the proposed bridged nature of (29).



(29)

3) No studies on the 7-norbornyl cation (30) concerning its structure in stable ion conditions have appeared in the literature.

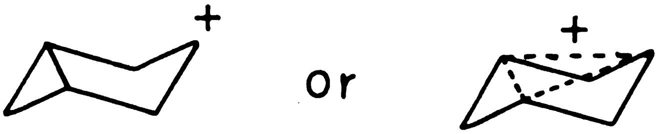
It is hoped that the 7-aryl-7-norbornyl cations (28) will be stable enough to be observed under super acid conditions. If such is the case, perhaps some direct evidence concerning the electronic structure of the 7-norbornyl cation can be obtained.



(30)

9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl cation. (10)

Perhaps the cation most accepted as being nonclassical is the 9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl cation, better known as the Coates cation.[15] Other cations have been made which resemble the Coates cation. Most notable are the 3-bicylo[3.1.0.]hexyl (31)[18] and the endo-8-tricyclo[3.2.1.0^{2,4}]octyl (32)[19] cations. Although both of these systems have been proposed to be nonclassical,[18,19] such proposals have met resistance.[20]



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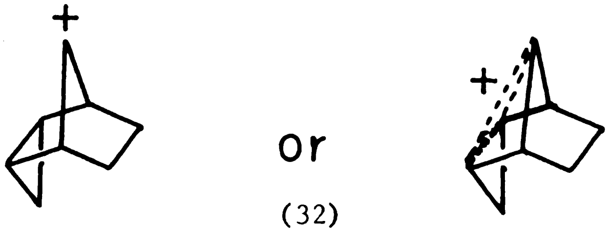
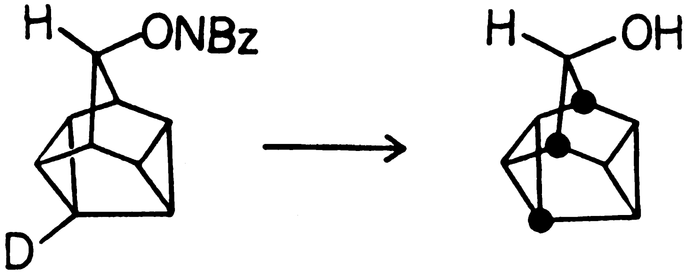


(32)

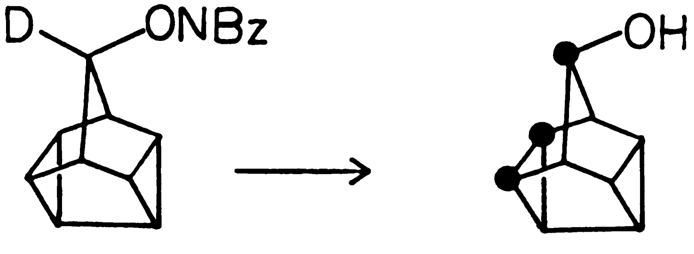
The Coates cation on the other hand, offers a geometry which is not subject to the classical interpretations imposed on (31)[20]

Both its ^1H NMR and ^{13}C NMR show a system possessing a three fold symmetry.[8a,b] Rapid equilibration does not explain this symmetry because such equilibration would cause all NMR signals to coalesce.

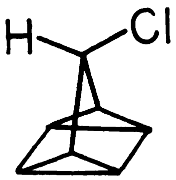
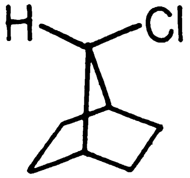
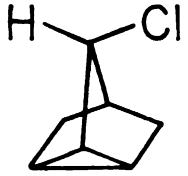
Deuterium labeling studies in the solvolysis of 9-pentacyclo$[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]$nonyl-p-nitrobenzoates, (33) and (35), are only consistent with the formation of the nonclassical intermediate (10).[8a] These studies further substantiate that only one cyclopropane ring may bridge with the cationic center at any given time (notably the ring *anti* to the nitrobenzoate). This observation is precedented in that other systems are known that allow participation with only one functionality at a time.[21,22] The most noteworthy examples are found in the solvolysis[21a-c] of 7-chloronortricyclane (37) and 7-chloronorbornadiene (41).[22,21c] In both of these systems, the relative rate of solvolysis is about the same with two functionalities present as is with only one functionality, but these rates are much larger than those systems with no functionality.



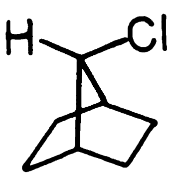
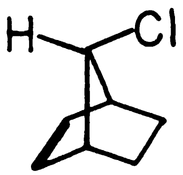
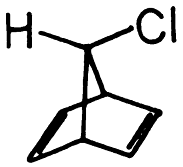
(33) (34)



(35) (36)

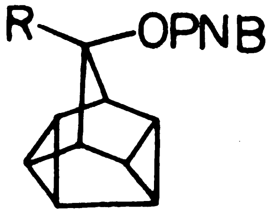




	(38)	(39)	(37)
Relative Rate of Solvolysis	(30-40)10^{10}	1	10^{10}

	(39)	(40)	(41)
Relative Rate of Solvolysis	1	10^{11}	10^{14}

A nonclassical structure for (10) is also supported by comparison of the relative rate of solvolysis of its 9-substituted nitrobenzoate (42), with that of the corresponding 7-substituted norbornane (43) as a function of electron demand.[8d] (42) was found to be as high as 10^{14} times as reactive as (43). This large rate enhancement of (42) is best explained by invoking bridging in the transition state of the solvolysis. It was further noted[8d] that these rate differences were much less when the comparison was made with 7-substituted norbornenes (44) (where participation is significant). Although no "break" was found in the Hammett[8d] plot for (42), the ρ^+ value of -2.05 is so low in magnitude when compared to -5.27 for (43), that some charge delocalization seems unavoidable.



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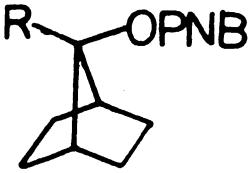
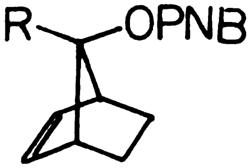


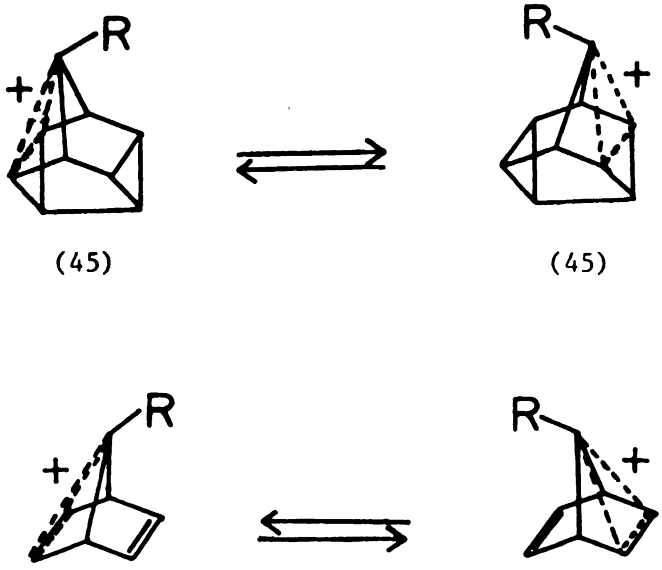
(43)



(44)

The stability of the trishomocyclopropylium ion in (10) was estimated by obtaining the activation energy required to effect a bridge flip as shown in the following scheme.[8b]

Scheme I



(45) (45)

(46) (46)

With R = H, the activation energy was sufficiently high so as to be unmeasurable (an experimental value of ΔG was not cited). With R = methyl, however, $\Delta G_{-8^\circ C}$ = 13.0 Kcal/mole in contrast to the unsubstituted cation; when R = phenyl, the bridge flipping occurs rapidly even at -75°C (ΔG is less than 9.6 Kcal/mole). These results are in agreement with those of the 7-substituted norbornadienyl cation, (46).[23] Here, with R again being hydrogen, methyl and phenyl, the ΔG values are greater than 19.6 Kcal/mole (0°C), equal to 12.4 Kcal/mole (-14°C) and less than 7.6

Kcal/mole (-100°C) respectively.

Finally, Jorgenson[8e] has used MINDO/3 calculations to substantiate, on theoretical grounds, the presence of the trishomocyclopropylium ion in (10). His calculations substantiate the presence of C_{3v} symmetry in (10), which is consistent with its NMR spectrum. Also, his calculations confirmed the activation energies found for the bridge flipping of (45). With R = hydrogen, a calculated ΔG of 22.1 Kcal/mole was obtained, while for R = methyl, ΔG_{calc} = 8.8 Kcal/mole. No calculation was done, however, for R = phenyl.

2-adamantyl cation (29)

The studies of the 2-adamantyl cations can be subdivided into two major areas of investigation:

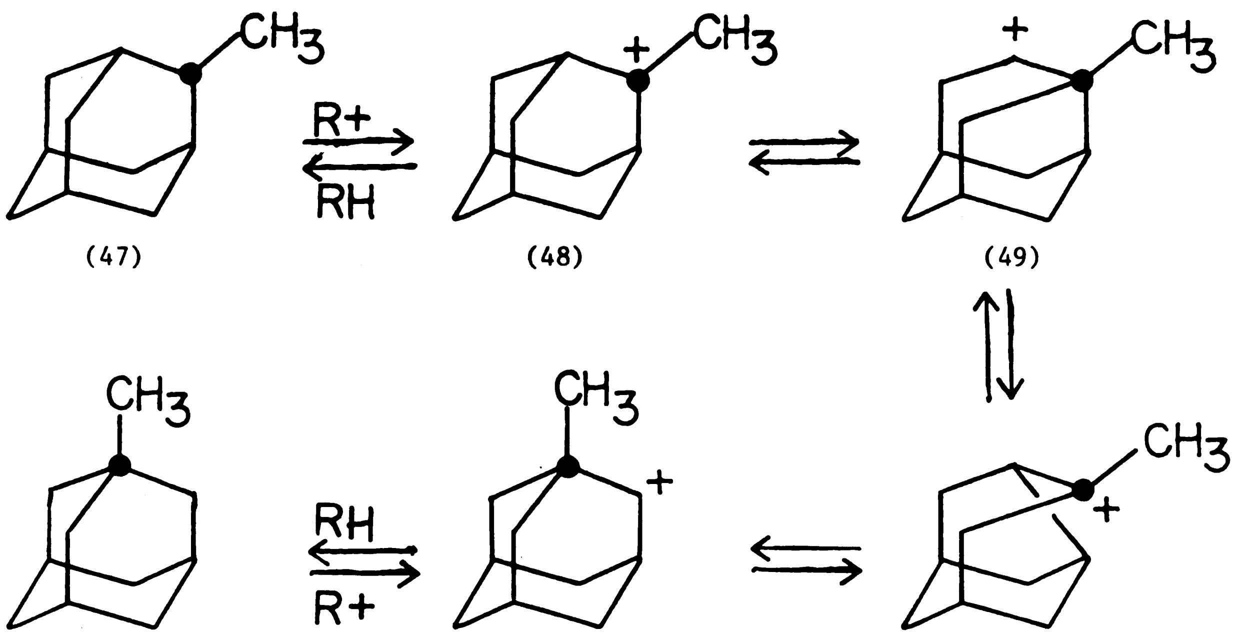
1) Rearrangements of the 2-adamantyl cations.
2) The possibility of the 2-adamantyl cations existing as bridged species.

Rearrangements of the 2-adamantyl cation

Unfortunately, observations of the 2-adamantyl cation (29) under stable ion conditions have not been achieved due to decomposition.[24,25] Nonetheless, theory concerning its rearrangements agrees with a vast amount of indirect evidence that requires its existence as a fleeting intermediate during solvolysis reactions.[26,27]

Perhaps one of the most striking properties of the 2-adamantyl cation is the lack of 1,2 hydride shifts which are common to most cationic species.[28,29] This is expected and is readily explained by the orthogonality between the migrating hydrogen and the "empty p orbital" on the cationic center. Indeed, the equilibration of the 2-adamantyl cation (29) to its more stable isomer, the 1-adamantyl cation,[29] has been shown to involve intermolecular hydride shifts,[28,30] or in some 3° 2-adamantyl cases,[29,31] a series of Wagner-Meerwein shifts. 2-Methyladamantane (47) is an example of the latter case and rearranges cleanly to 1-methyladamantane (52) under Lewis acid conditions.[29,31] A mechanism is given in scheme II and is consistent with labeling studies in which 2-^{14}C-2-methyladamantane (47) is treated with a Lewis acid. The ^{14}C label was found on the C-1 position bearing the methyl as predicted by the mechansim.

Scheme II



(47) (48) (49)

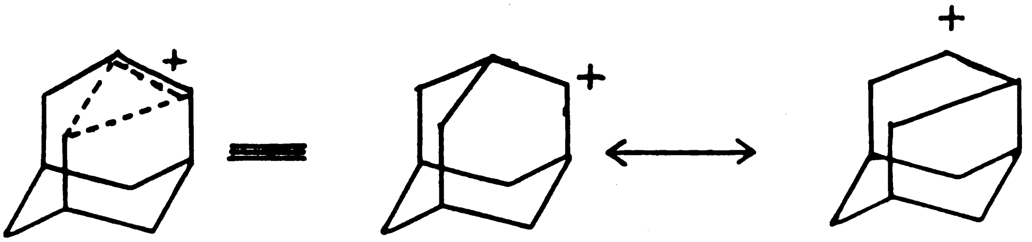
(52) (51) (50)

Although 2-adamantyl cations do not undergo 1,2-hydride shifts, 1,3-hydride shifts appear to be facile.[32] Such shifts are well documented in cyclohexane derivatives.[33] Only one system, however, has clearly demonstrated 1,3-hydride shifts in the 2-adamantyl series in preference to intermolecular hydride shifts.[34]

Further rearrangements of 2-adamantyl cations will be discussed with regard to possible nonclassical intermediates.

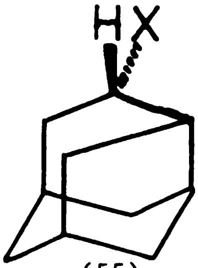
Nonclassical behavior of the 2-Adamantyl cation

The 2-adamantyl cation possesses a rigid geometry that may show some observable bridging. Such bridging (53), if it exists, would be unsymmetrical and would thus be expected to favor the less strained contributing structure (29):

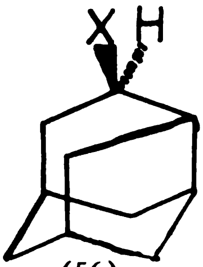


(53) (29) Major (54) Minor

The major studies which attempt to determine whether the 2-adamantyl cation is classical or not involve solvolysis of 4-substituted-protoadamantanes, (55) and (56).[16,17]



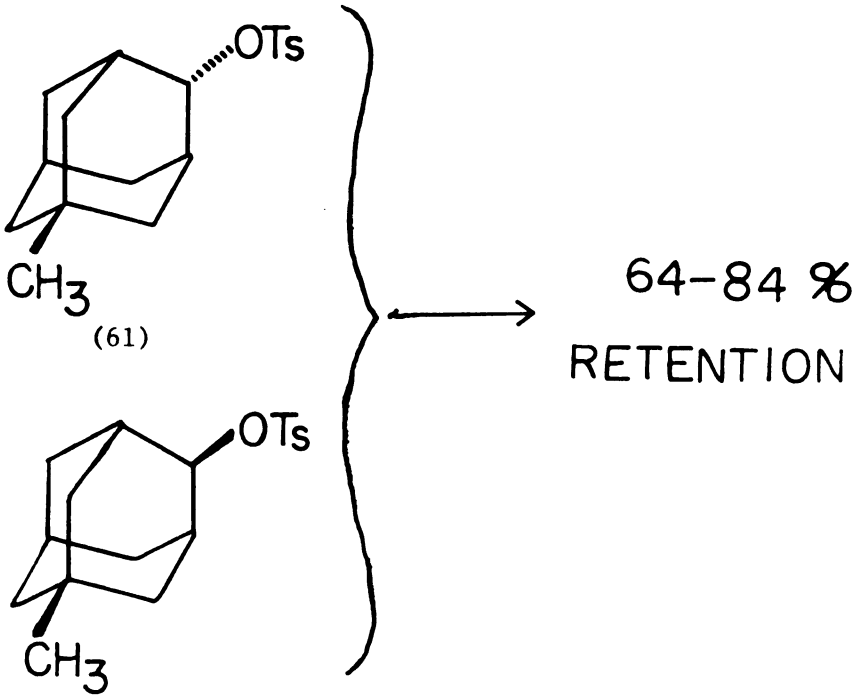
(55)
Exo



(56)
Endo

In solvolysis reactions, (55) was found to be about 10^4 times more reactive than its endo isomer (56).[16] The high reactivity of the exo isomer is indicative of anchimeric assistance. Further insight into the solvolysis of 4-substituted-protoadamantanes was found by labeling the 4-position with deuterium.[16] With endo-4-substituted-4-d-protoadamantane (59) solvolysis gives the 2-substituted adamantane (60), with deuterium completely scrambled in the 1 and 2 positions. This suggests a rapid degenerate 4-protoadamantyl---➤ 2-protoadamantyl cation rearrangement followed by a slower capture by solvent (see scheme III). The exo isomer, however, yields only 1-d-2-substituted adamantane (58) implying that the above degenerate rearrangement is slow compared to solvent capture of the cation. These results are best interpreted by anchimeric assistance in the transition state in going from (57) to (58), but say little of the nature of the intermediate involved.

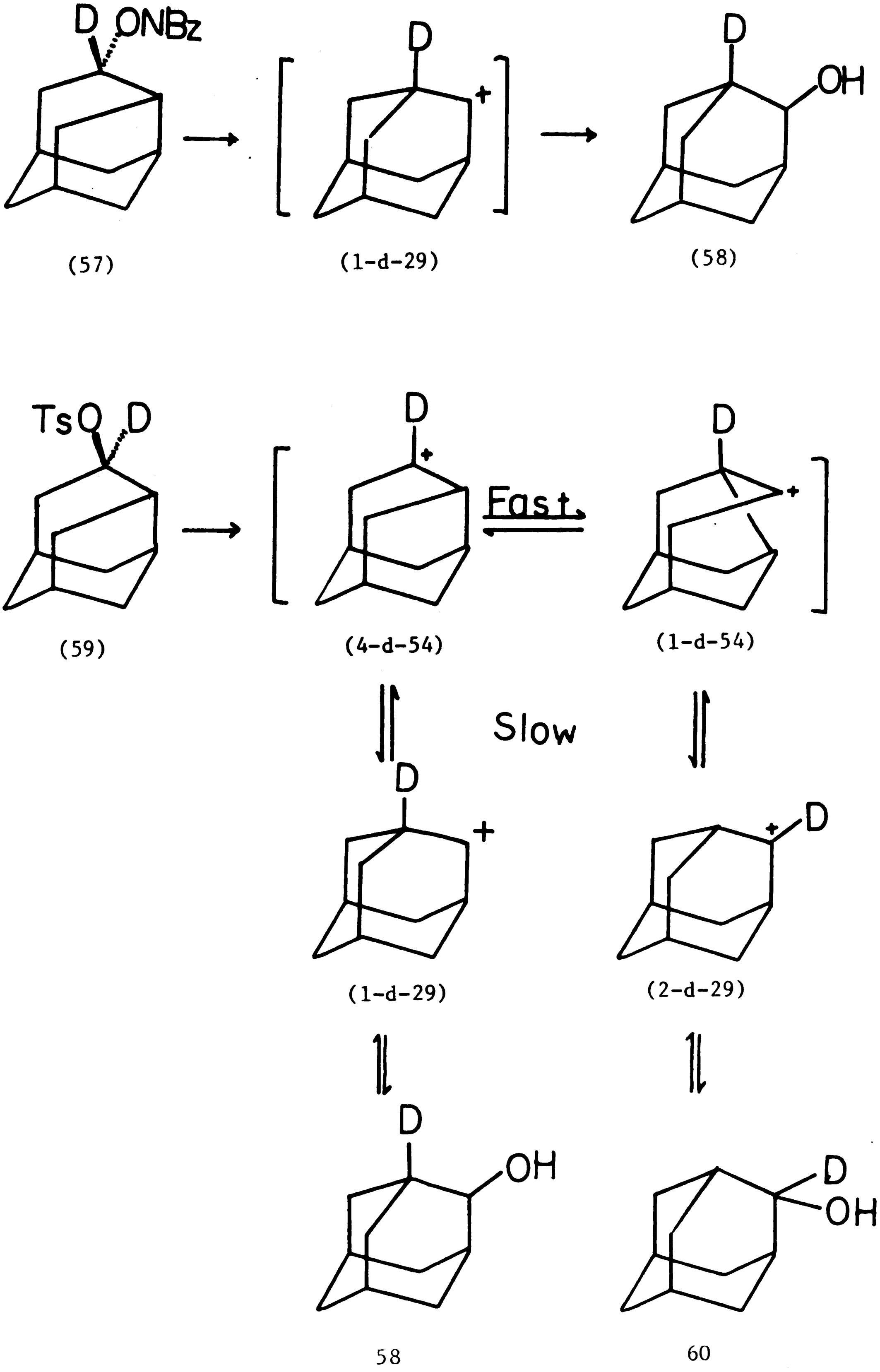
Evidence for bridging in the intermediates formed from the solvolysis of 2-adamantyl or 4-protoadamantyl systems exists, but it is not conclusive. Solvolysis of optically active 2-adamantyl derivatives (61) and (62), for instance, have yielded as high as 84% retention of configuration in the products.[35]



(61)

(62)

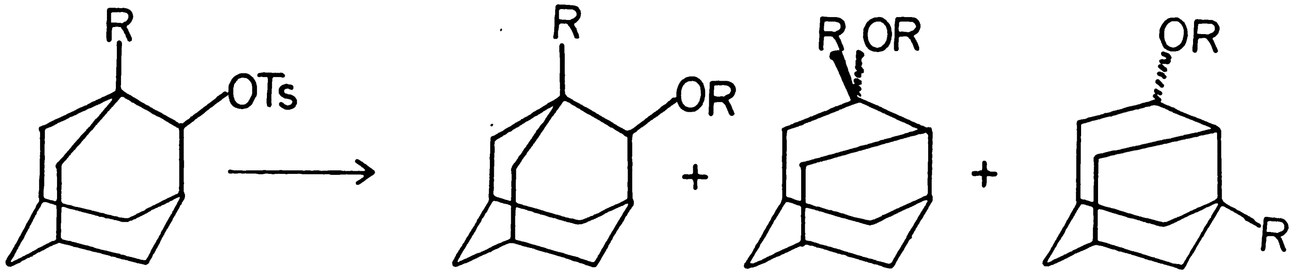
Scheme III.


D
ONBz
(57)
D
+
(1-d-29)
D
OH
(58)
TsO
D
(59)
D
+
(4-d-54)
Fast
D
+
(1-d-54)
Slow
D
+
(1-d-29)
+
D
(2-d-29)
D
OH
58
D
OH
60

The amount of retention as well as the product distribution in the solvolysis of 2-adamantyl derivatives may be made more pronounced by adding substituents that would either stabilize the minor resonance form (54) or destabilize the major resonance form (29) thereby increasing the amount of bridging. The results of studies on such systems are shown on the following page and are in accord with a bridged intermediate.[17a,26,27]

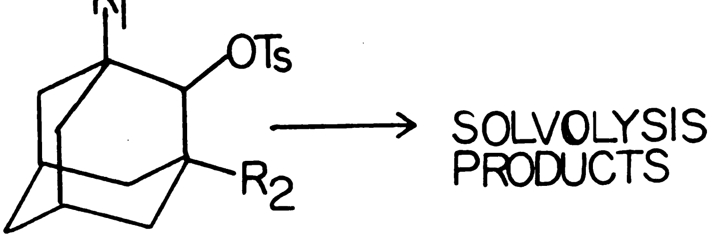
In a related study,[17b] it was found that adding successive methyl groups adjacent to the 2-position of 2-adamantyl tosylates produces an additive rather than a multiplicative effect towards the rate of solvolysis. Again, the data are given on the following page and are in accord with a bridged system.

Although, as mentioned earlier, the 2-adamantyl cation has not been observed under stable ion conditions, the tetramethyl-2-adamantyl cation (68) is stable enough to be analyzed by NMR.[36,37] Presumably this is a consequence of the inability of (68) to undergo the intermolecular hydride shifts that are facile in the 2-adamantyl cation. The ^{13}C NMR spectrum of (68) is striking when compared to that of the similar 3° cation (69) (see table 1).[36] The higher field shift of the cationic carbon in (68), and the lower field shifts for carbons 1 and 3 relative to those of (69), suggest extensive charge dispersal from C-2 to C-1 and C-3. These discrepancies cannot be reconciled by invoking a rapid equilibration of (68) with its 4-protoadamantyl isomer (70) if "reasonable" chemical shifts for (70) are assumed.[36,37] Furthermore, the ^{1}H NMR of (68) shows the H-2 absorption at 5.10 ppm, a value over 8 ppm upfield from what is expected from model compounds.[37] These results strongly favor a set of bridged structures (71) that are in rapid equilibration, which allows for the observed symmetry of (68). (see scheme IV).[36,37]



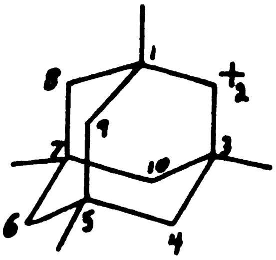
(63) (64) (65) (66)

SUBSTRATE	% 64	% 65	% 66
H	99.6	.4	0
CH_3	73	27	0
CO_2CH_3	94	0	6
CN	62	0	38

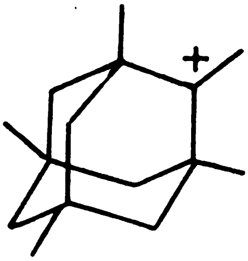


(67)

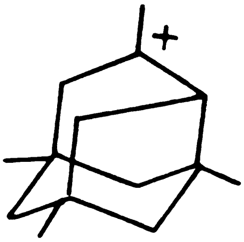
SUBSTRATE	RELATIVE RATE
$R_1 = R_2 = H$	1
$R_1 = H$, $R_2 = CH_3$	14–21
$R_1 = R_2 = CH_3$	38–70



(68)



(69)

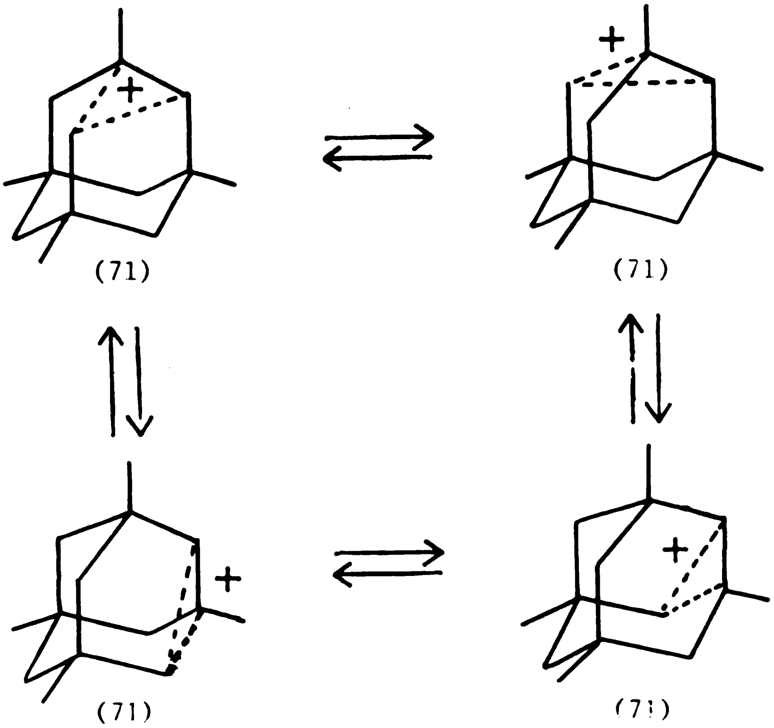


(70)

Table 1 NMR chemical shifts (PPM from TMS) of (68) and (69).

Cation		$C_{1,3}$	C_2	$C_{4,8,9,10}$	$C_{5,7}$	C_6
(68)	^{13}C	138.6	92.3	51.0	26.2	45.7
	^1H		5.10	2.53		1.68
(69)	^{13}C	68.3	329.7	63.7	33.2	48.4
	^1H			2.68		2.08

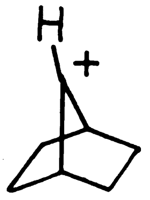
Scheme IV



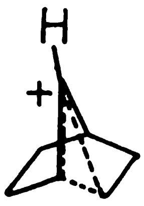
All of the evidence presented strongly suggests a bridged structure for 2° 2-adamantyl cations. However, it is prudent to reemphasize that if such bridging is in fact present, it is unsymmetrical, and hence, probably weak. For instance, the excellent correlation of 2-adamantyl tosylate with regard to the Foote-Schleyer equation[38] is consistent with little or no bridging of the 2-adamantyl cation during solvolysis.

7-norbornyl cation (30)

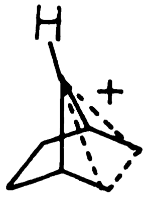
As a result of the instability of the 7-norbornyl cation, studies associated with it and its precursors have been meager. In addition to the scant amount of data concerning it, interpretations of such data have been widely divergent, leading to three structures, (30),[38] (72)[39,40-42] and (73),[43] proposed for this elusive cation. The arguments which support these structures will be briefly discussed below.



(30)



(72)



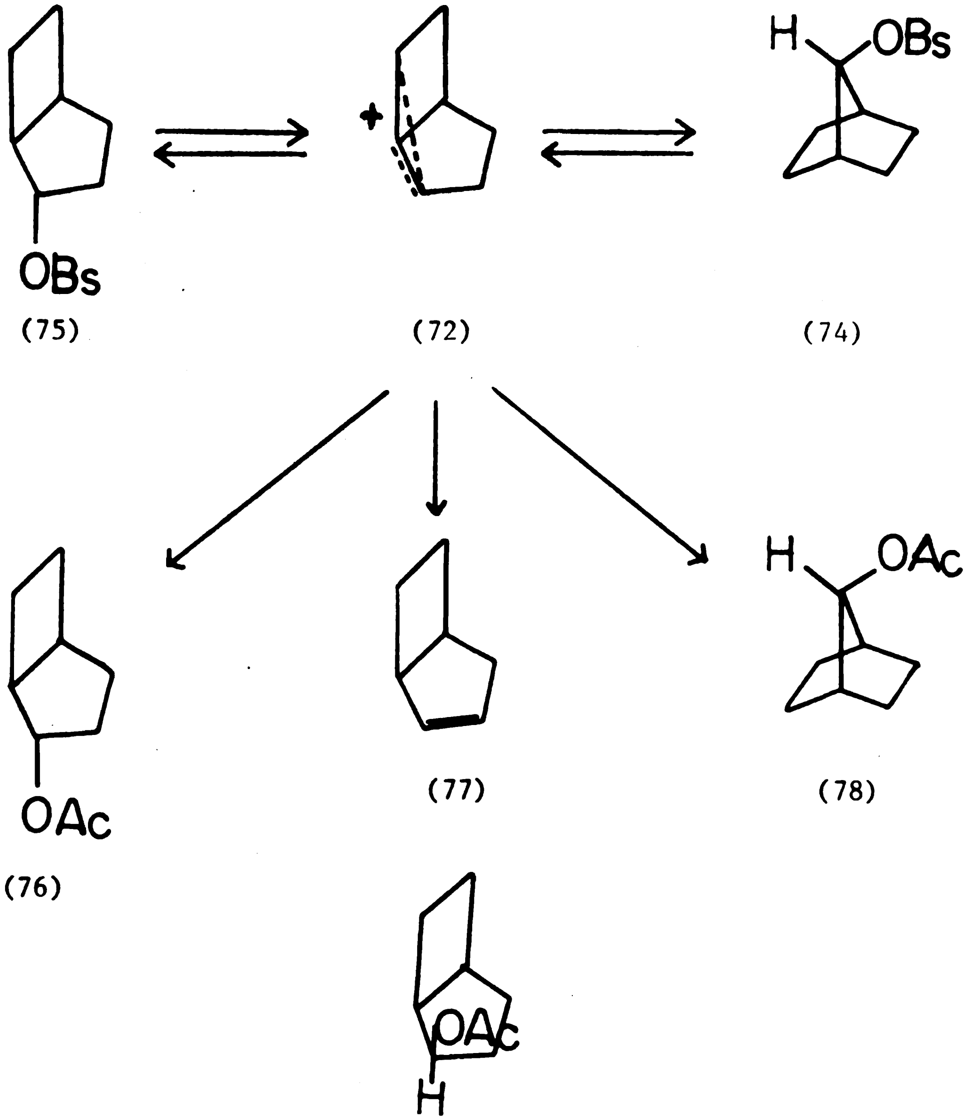
(73)

The first representation of the 7-norbornyl cation is that shown by (30); i.e., a classical cation. Correlation with the Foote-Schleyer equation[38] (log k_{rel}^{obs} = -7.00; log k_{rel}^{calc} = -7.04) is the only direct evidence suggesting such a structure. However, from the scattering of data points about the Foote-Schleyer equation, a rate enhancement by a factor of ten could be easily undetected implying the possibility of a small amount of anchimeric assistance in the solvolysis of 7-norbornyl tosylates. Furthermore, as stated earlier, the absence of any anchimeric assistance in the transition state of such a solvolysis implies little about the nature of the intermediate.

Perhaps the strongest case for (30) is the lack of sufficient evidence to prove the existence of the more controversial structures, (72) and (73). Nonetheless, evidence does exist for (72) and (73) and is given below along with some classical interpretations.

Structure (72) was first postulated by Winstein and co-workers[39] in 1958. Winstein's conclusions were based primarily on the products obtained from the acetolysis of 7-norbornyl brosylate (74) and its isomer, 2-bicyclo[3.2.0]heptyl brosylate (75). The mechanism proposed invoked the intermediate (72) to account for the absence of any of the endo isomer of (76); i.e., (79). Similar arguments have been forwarded for the exclusive formation of exo-2-norbornyl products in the solvolysis of endo and exo-2-norbornyl derivatives.[44] Since this work, however, Brown[45] has refuted the need to impose nonclassical intermediates on the basis of the exo/endo ratio of product distributions. To be explicit, regardless of whether or not the intermediate is bridged, the exo face is the less hindered and hence should capture the solvent preferentially.

Later, Gassman and others found additional evidence supporting Winstein's proposed intermediate.[40-42] Gassman found that the acetolysis of exo, exo-2,3-dideuterio-anti-tosyloxynorbornane (80) and the syn isomer, yields the corresponding acetate (82) with about 90% retention. From this, it is clear that the free 7-norbornyl cation (30) plays, at best, a minor role in the solvolysis. Two possibilities were considered or the intermediate, one being a nonclassical intermediate such as (d_2-72) and the other being a tight ion pair (81) that rapidly collapses to (82).

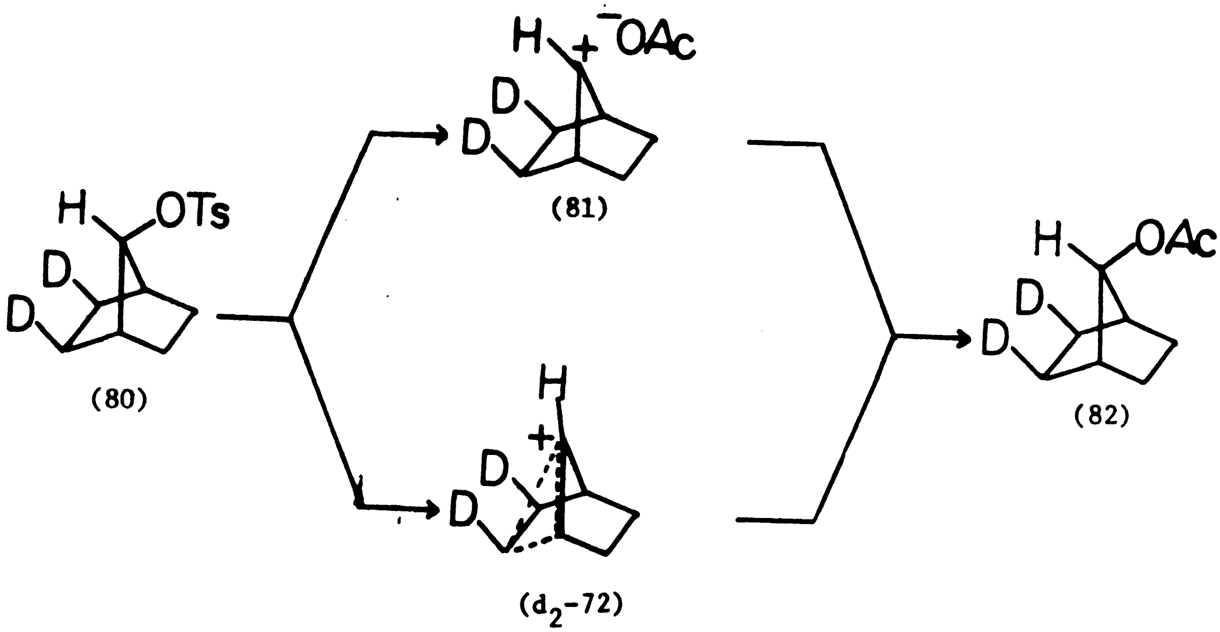


(75) (72) (74)

(76) (77) (78)

(79)

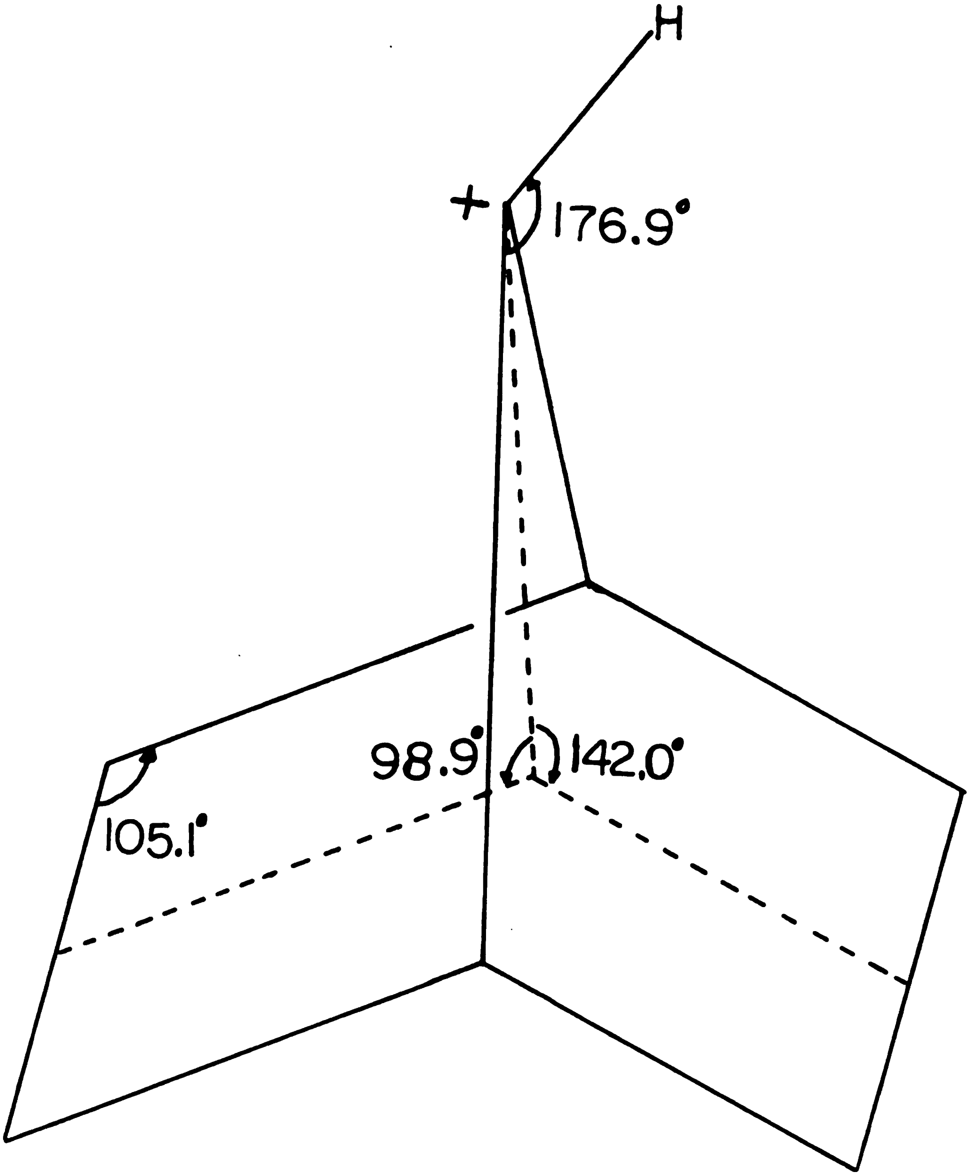
The presence of about 10% inversion in the product is most readily explained by conversion of either (d_2-72) or (81) to the free classical cation (31) followed by solvent capture. An SN_2 type mechanism is unlikely because the addition of acetate ion has no observable effect on the percent retention of configuration found in the product.[41] The possibility of sulfur-oxygen bond breakage instead of carbon-oxygen bond cleavage of (80) to explain the amount of retention was excluded by an ^{18}O-labeling experiment.[46]



Although structure (73) could also be used to explain Gassman's observations, it was not considered. The only mention of (73) was in a paper by Dewar[43] describing a MINDO/2 calculation to obtain an optimum geometry for the 7-norbornyl cation. His calculations assumed a plane of symmetry passing through atom 7 and bisecting the 2,3 and 5,6 bonds (thereby excluding the possibility of (72)). The results of his calculations clearly favor an unsymmetrical cation as diagrammed on the following page.

It is evident that very little can be conclusively stated concerning the exact geometry of the 7-norbornyl cation. Perhaps Brown's arguments should be applied here and the classical structure (30) accepted until more convincing evidence for (72) and (73) can be forwarded.

Figure 7 Calculated geometry of the 7-norbornyl cation

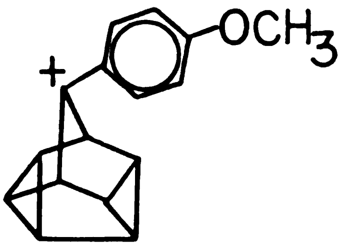


RESULTS

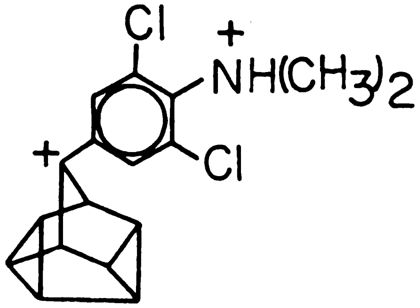
The details for the generation and observation of the carbocations are given in the experimental section. The results of these observations are briefly stated below.

The ^{1}H NMR chemical shifts of the α-aryl Coates cations (26a-e) are presented in tables 2 and 3 respectively. The spectra were unaffected from -100°C to about -50°C at which time decomposition occurred. The chemical shifts of the 9-phenyl Coates cation (26b) have been reported earlier[8b] and are included in the tables.

Several unsuccessful attempts were made to generate the 9-(p-anisyl) Coates cation (26f) and the 9-(3,5-dichloro-4-N,N-dimethylammoniophenyl) Coates cation (26g). In the case of the electron rich cation (26f), the complexity of the spectra observed suggested decomposition. For (26g), however, rearrangement to two species predominated even at -100°C. No attempts were made to elucidate the structures of the rearranged products.



(26f)



(26g)

The ^{1}H NMR and ^{13}C NMR spectra of the α-aryl adamantyl cations (27a-i) are given in tables 4 and 5 respectively. Except for (27i), all of these systems were stable up towards the boiling point of the solvent (+10°C).

Table 2 ^1H NMR chemical shifts (PPM from TMS) of (26).

Compound	Aryl group	C1,C8	C2,3 C6,7	C4 C5	Misc.
(26a)	4-CH_3-C_6H_4	5.003	3.840	2.917	CH_3-2.626 Ar-8.130 (d;J=7.5 Hz) -7.875 (d;J=7.5 Hz)
(26b)[a]	C_6H_5	4.695 (4.60)	3.537 (3.43)	2.346 (2.25)	Ar-7.792-7.630 (m) -(7.63)
(26c)	3-F-C_6H_4	5.013	3.915	2.758	Ar-7.985 (t;J=6.7 Hz) -7.763-7.895 (3H;m)
(26d)	4-CF_3-C_6H_4	4.720	2.457	3.580	Ar-7.903 (d;J=8.7 Hz) -7.804 (d;J=8.7 Hz)
(26e)	3,5-$(CF_3)_2$-C_6H_3	4.238	2.096	3.022	Ar-7.921 (1H;s) -7.809 (2H;s)

[a] Numbers in parenthesis are taken from reference 8b.

Table 3 ^{13}C NMR chemical shifts (PPM from TMS) of (26).

Compound	Aryl group	C9	C1,8	C2,3 6,7	C4 C5	Misc.
(26a)	4-CH_3-C_6H_4	107.80	38.27	36.33	40.47	CH_3-22.49
(26b)[a]	C_6H_5	89.08 (87.62)	37.45 (37.03)	37.59 (37.32)	40.47 (40.14)	
(26c)	3-F-C_6H_4	76.86	36.91	38.58	40.40	
(26d)	4-CF_3-C_6H_4	70.88	36.71	39.30	40.49	
(26e)	3,5-$(CF_3)_2$-C_6H_3	65.11	36.69	40.04	40.63	

[a] Numbers in parenthesis are taken from reference 8b.

Table 4 ^{1}H NMR chemical shifts (PPM from TMS) of (27)

Compound	Aryl group	C1,3	C4,8, 9,10[a]	C5,7 & C6	Misc.
(27a)	$4\text{-}CH_3O\text{-}C_6H_4$	4.220	2.700 2.363	2.288	CH_3- 4.372 Ar-8.740(2H;d;j=9.5Hz) -7.424(2H;d;j=9.5hz)
(27b)	$4\text{-}CH_3\text{-}C_6H_4$	4.438	2.811 2.469	2.311	CH_3-2.842 Ar-8.698(2H;d;J=7.25Hz) -7.838(2H;d;J=7.25hz)
(27c)	$4\text{-}F\text{-}C_6H_4$	4.459	2.888 2.546	2.333	Ar-7.680(2H;t;J=8.5hz) -8.912-8.970(2H;m)
(27d)	C_6H_5	4.571	2.939 2.590	2.355	Ar-8.811(2H;d;J=8.3Hz) -8.668(1H;t;J=8.3Hz) -8.022(2H;t;J=8.3Hz)
(27e)	$3\text{-}Br\text{-}C_6H_4$	4.576[b] 4.528	3.001 2.643	2.365	Ar-8.879(1H;s) -8.748(1H;d;J=7.8Hz) -8.646(1H;d;J=7.8Hz) -7.914(1H;t;J=8.0Hz)
(27f)	$4\text{-}CF_3\text{-}C_6H_4$	4.685	3.099 2.726	2.390	Ar-8.876(2H;d;J=8.3Hz) -8.221(2H;d;J=8.3Hz)
(27g)	$3,5\text{-}(CF_3)_2\text{-}C_6H_3$	4.745	3.202 2.827	2.430	Ar-9.132(1H;s) 8.988(2H;s)
(27h)	$3,5\text{-}Cl_2\text{-}4\text{-}$ $N(CH_3)_2\text{-}C_6H_2$	4.681	3.286 2.917	2.427	CH_3-3.774(d;J=4.5Hz) Ar-8.773(2H;s)
(27i)	$3,5\text{-}Cl_2\text{-}4\text{-}$ $CN\text{-}C_6H_2$	4.819	3.482 3.061	2.496 2.459	Ar-8.610(2H;s)

---

[a] All of these peaks appeared as doublet with a coupling constant varying between 11.0 and 13.0 hz.

[b] The unsymmetrical aryl group causes these two hydrogens to become non-equivalent.

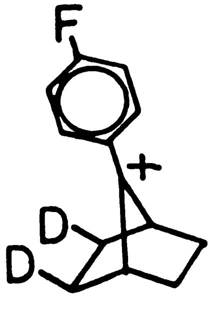
Table 5 ^{13}C NMR chemical shifts (PPM from TMS) of (27).

Compound	Aryl group	C2	C1,3	C4,8,9,10	C5,7	C6	Misc.
(27a)	4-CH_3O-C_6H_4	237.9	44.8	45.3	36.3	28.9	CH_3-59.6
(27b)	4-CH_3-C_6H_4	260.8	49.3	48.3	36.8	29.8	CH_3-24.9
(27c)	4-F-C_6H_4	265.2	51.2	49.4	37.0	30.0	
(27d)	C_6H_5	271.8	51.9	49.8	36.8	30.1	
(27e)	3-Br-C_6H_4	277.1	54.1	51.3	36.8	30.3	
(27f)	4-CF_3-C_6H_4	283.6	56.8	52.9	37.1	30.8	
(27g)	3,5-$(CF_3)_2$-C_6H_3	286.2	58.5	54.2	37.0	30.9	
(27h)	3,5-Cl_2-4-$N(CH_3)_2$-C_6H_2	290.4	62.4	56.9	37.5	31.9	

The latter system, however, rearranged and consequently, no ^{13}C NMR could be obtained for it even at -110°C. To determine if this rearrangement was unique for the adamantyl system, the corresponding cyclopentyl cation (19) was generated and was found to be a complex mixture of products. No definitive spectra could be obtained for it.

The 2-(p-anisyl)adamantyl cation showed a peculiarity in its ^{13}C NMR. All peaks showed a dependence on the concentration of acid used. This dependence is shown semiquatitatively in table 6.

Tables 7 and 8 show the ^{1}H NMR and ^{13}C NMR results respectively for the 7-aryl-7-norbornyl cations (28a-f). Olah[47] has obtained chemical shifts for several of these systems and his results are included in table 8. The peak assignments for the exo and endo hydrogens were deduced by generating the 7-(p-fluorophenyl)norbornyl cation (28c) with deuterium placed on the _exo_ face of the 2 and 3 positions.



(exo,exo-2,3-D$_2$-28c)

The 7-(3,5-dichloro-4-N,N-dimethylammoniophenyl)-7-norbornyl cation (28g) could not be generated. All attempts to make it resulted in the formation of a system showing less than the expected symmetry of the classical cation. Furthermore, quenching the sample with sodium methoxide dissolved in methanol (five fold excess) at -80°C yielded the starting alcohol and not the expected methyl ether. To insure that the methyl ether was not cleaved to the alcohol under the work-up conditions, the

Table 6 Dependence of ^{13}C NMR chemical shifts (PPM from TMS) of (27a) with respect to acid concentration.

Approximate amount of acid used	C2	C1,3	C4,5,9,10	C5,7	C6	CH_3
1 equivalent	237.9	44.8	45.3	36.2	28.9	59.6
2 equivalents	243.4	46.2	46.2	36.5	29.1	61.2
4 equivalents[a]	266.8[a]	52.8	50.7	37.0	30.3	68.4
6 equivalents	280.4	56.7	53.0	37.1	30.8	73.0

---

[a] The C2 chemical shift is approximate because of the broadness of the peak.

Table 7 ^1H NMR chemical shifts (PPM from TMS) of (28) and (83).

Compound	Aryl group	C1,4	C2,3,5,6(exo)[a]	C2,3,5,6(endo)[a]	Misc.
(28a)	4-CH_3O-C_6H_4	3.616	2.103	2.103	CH_3-4.394 Ar-8.535(2H;d;J=8.3Hz) -7.470(2H;d;J=9.0Hz)
(28c)[b]	4-F-C_6H_4	3.809	2.218	2.279	Ar-8.882(2H;m) -7.797(2H;t;J=8.5Hz)
(28d)	C_6H_5	3.900	2.242	2.326	Ar-8.779(3H;d;J=7.5Hz) -8.152(2H;t;J=8.0Hz)
(28e)	4-CF_3-C_6H_4	3.998	2.326	2.450	Ar-8.964(2H;d;J=8.0Hz) -8.363(2H;d;J=8.3Hz)
(28f)	3,5-$(CF_3)_2$-C_6H_3	4.047	2.368	2.523	Ar-9.221(2H;s) -9.160(1H;s)
(83)[c]	3,5-Cl_2-4-$N(CH_3)_2C_6H_2$	3.141		2.257 (d;J=7.8Hz) 1.953 (d;J=7.8Hz) 1.731 (d;J=8.3Hz) 1.590 (d;J=8.3Hz)	CH_3-3.707(d;J=3.8Hz) Ar-7.994(s)

---

[a] All of these peaks appeared as doublets with a coupling constant varying between 7.8 and 9.3 Hz.

[b] These chemical shifts were inferred from the spectra of the exo,exo-2,3-dideutero derivative.

[c] No attempt is made to assign the methylene protons to the exo and endo positions.

Table 8 ^{13}C NMR chemical shifts (PPM from TMS) of (28) and (83).

Compound	Aryl group	C7	C1,4	C2,3,5,6	Misc.
(28a)[a]	4-CH_3-C_6H_4	229.4 (229.9)	41.3 (41.7)	27.0 (27.3)	CH_3-60.0 (60.3)
(28b)[a]	4-CH_3-C_6H_4	(252.6)	(43.2)	(26.9)	CH_3(25.7)
(28c)	4-F-C_6H_4	257.5	44.7	27.4	
(28d)[a]	C_6H_5	264.3 (263.9)	44.6 (44.2)	27.2 (26.9)	
(28e)[a]	4-CF_3-C_6H_4	278.1 (277.8)	46.6 (46.3)	27.4 (27.1)	
(28f)[a]	3,5-$(CF_3)_2$- C_6H_3	282.9 (283.1)	47.3 (47.4)	27.0 (27.2)	
(83)[b]	3,5-Cl_2-4-$N(CH_3)_2$-C_6H_2	108.5	42.7	28.0 24.6	CH_3-46.3

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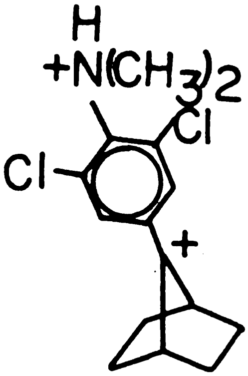
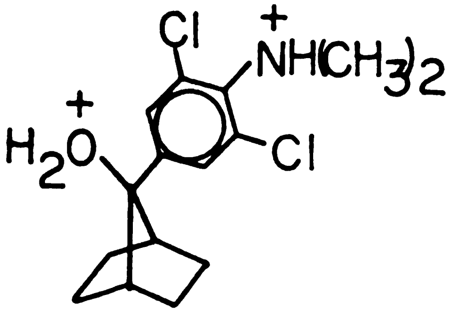
[a] Numbers in parenthesis are taken from reference 47.

[b] No attempt is made to assign the methylene carbons as *syn* or *anti* to the aromatic ring.

crude product was analyzed by mass spectrometry and showed the molecular ion peak for the alcohol. No peak was observed for the methyl ether. It was thus determined that the species observed was the protonated alcohol (83). Upon warming of the solution containing (83) to about -80°C, the system slowly ionized to cations whose structures could not be elucidated. The NMR spectra of (83) are included in tables 7 and 8.



(28g)



(83)

DISCUSSION

Coates system (26)

Figure 8 is a plot of the ^{13}C NMR chemical shifts of the cationic centers of (26a-e) (taken from table 3) versus the ^{13}C NMR chemical shifts of the corresponding α-arylcyclopentyl cations (19).[13] The striking feature of this plot is the overall negative slope which is in sharp contrast to the corresponding plots of classical cations (refer to figure 4). This negative slope is best explained as a result of an increase in bridging with the substitution of increasingly electron demanding aryl groups. It has been observed for bridged systems that the apical carbon has dramatic high field chemical shifts. Compounds (8)[6], (9)[7], (10)[8], and (11)[9] have the respective $^{13}C^+$ chemical shifts of 22.5, -23.04, 29.55 and 1.5 ppm from TMS. These shifts are well over 200 ppm upfield from what would be expected for the corresponding classical structures. Hence, it is expected, that by increasing the degree of bridging in (26) by the placement of electron demanding aryl substituents on the bridged carbon, an upfield shift of the cationic center would result, thus causing a negative slope when plotted against that of a classical system.

Recently, Olah[47] has reported the ^{13}C NMR spectra of a variety of 7-aryl-7-norbornenyl cations (84). Figure 9 is a plot of the $^{13}C^+$ chemical shifts of (84) against those of (19). The similarity between figures 8 and 9 is readily apparent, indicating a general behavior for α-aryl substituted bridged cations.

It is tempting to interpret the nonlinearity of figures 8 and 9 in

Figure 8 ^{13}C NMR chemical shifts of the cationic carbon of (26) versus (19).

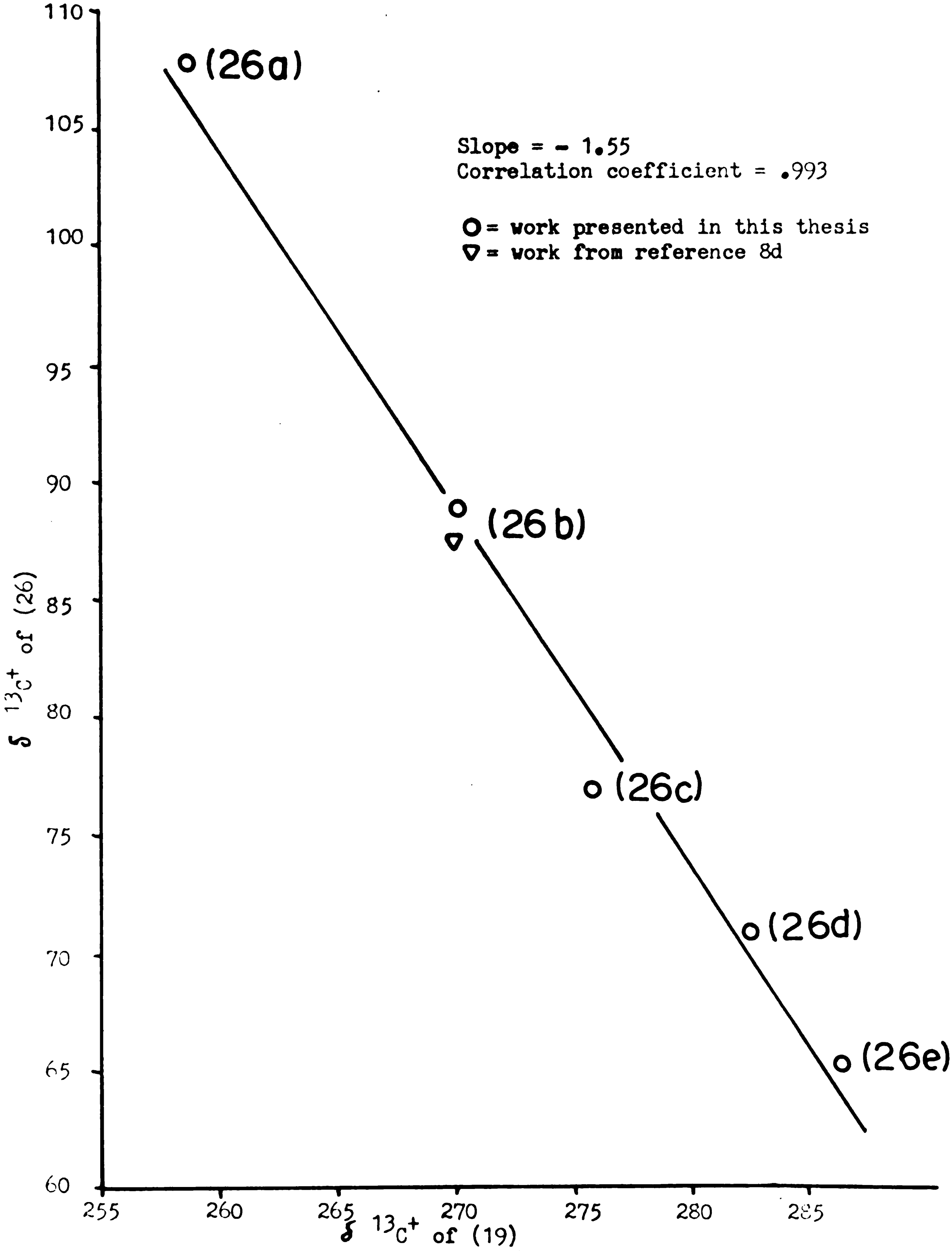
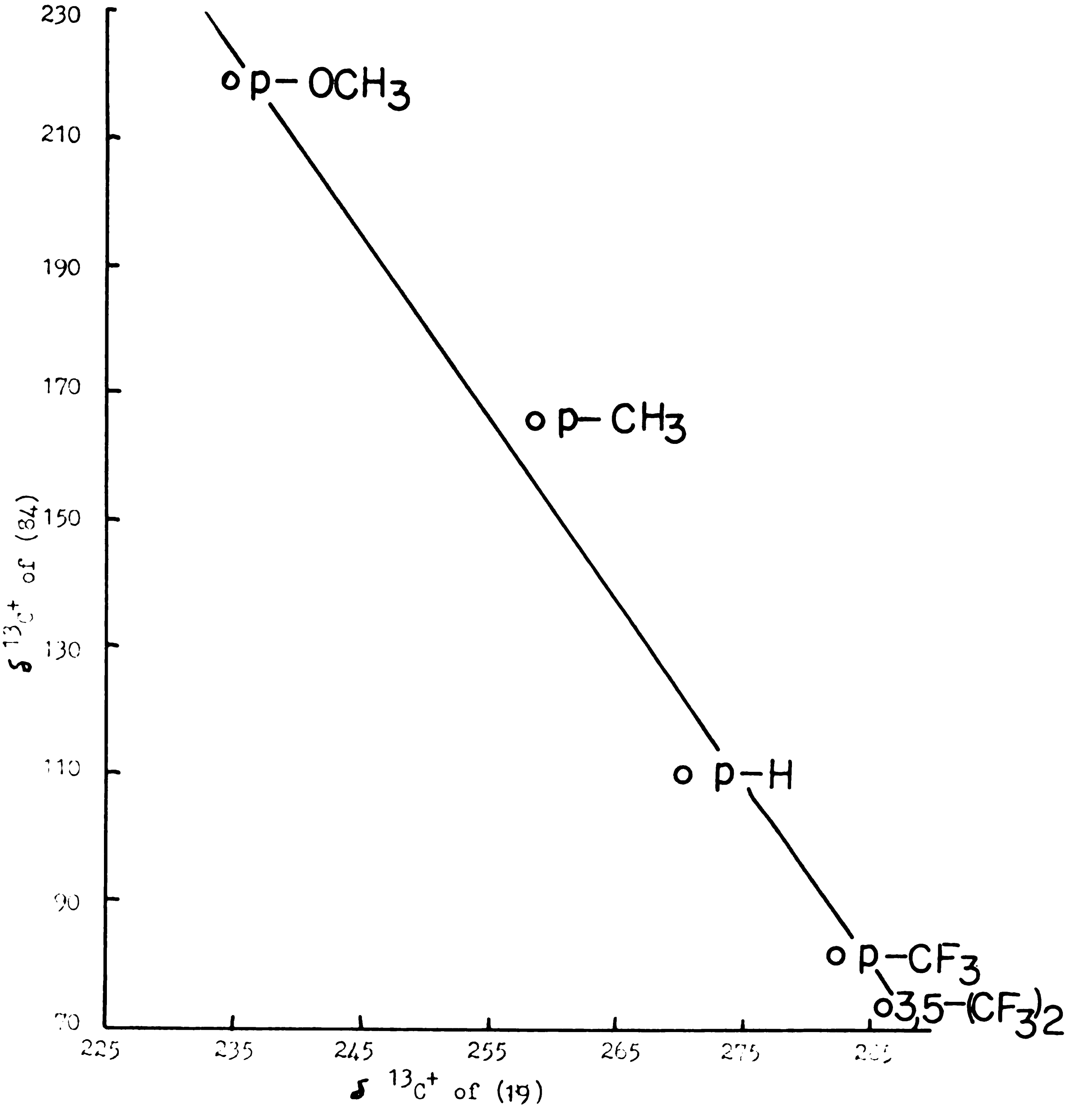


Figure 9 ^{13}C NMR chemical shifts of the cationic carbon of (84) versus (19).*



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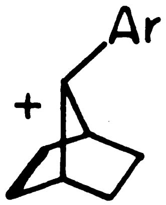
* Taken from reference 47.



(84)

terms of "saturation of bridging"[48] or in terms of the "onset of classical behavior".[48] However, there is no reason why such plots between classical and nonclassical systems must be linear and thus the small deviations are not sufficient to interpret with any confidence. Perhaps if more data could be obtained to extend the plots, further interpretations could be forwarded. Unfortunately, attempts to do so for (26) failed.

An unexpected result from table 3 is the almost negligible effect of the aryl substituents on the ^{13}C chemical shifts of the other bridging carbons. Over the range of substituents studied, these sites showed a steady downfield shift of less than 4 ppm with increasing electron demand. Perhaps the chemical shift dependence on the degree of bridging for these positions is cancelled by their dependence on the amount of charge developed. Such a cancellation appears less fortuitous, however, when compared to Olah's[47] results on (84). In this system, the ^{13}C chemical shifts of the vinyl carbons vary only about 4 ppm but with an upfield trend with increasing electron demand. Whether this is a general property of bridged α-aryl substituted cations cannot be decided until more data are obtained. Nonetheless, this result does warn that little can be deduced concerning the classical versus nonclassical nature of aryl substituted cations by observing sites removed from the aryl group.

The chemical shifts of the aryl protons shown in table 4 deserve some comment. Comparison of these chemical shifts to those of cations (27) and (28) reveal that they are significantly upfield from what at first is expected (see table 9). Furthermore, this upfield trend is most pronounced for the more electron demanding aryl substituents, which suggest some relationship with the degree of bridging present. The most reasonable explanation is that, as the system becomes more bridged, more charge is placed on sites away from the aryl group. This would result in less than the normal amount of charge delocalized onto the aromatic ring causing an upfield shift of the aromatic protons.

Table 9 Comparison of the ^{1}H NMR of the ortho hydrogens between (26), (27) and (28)

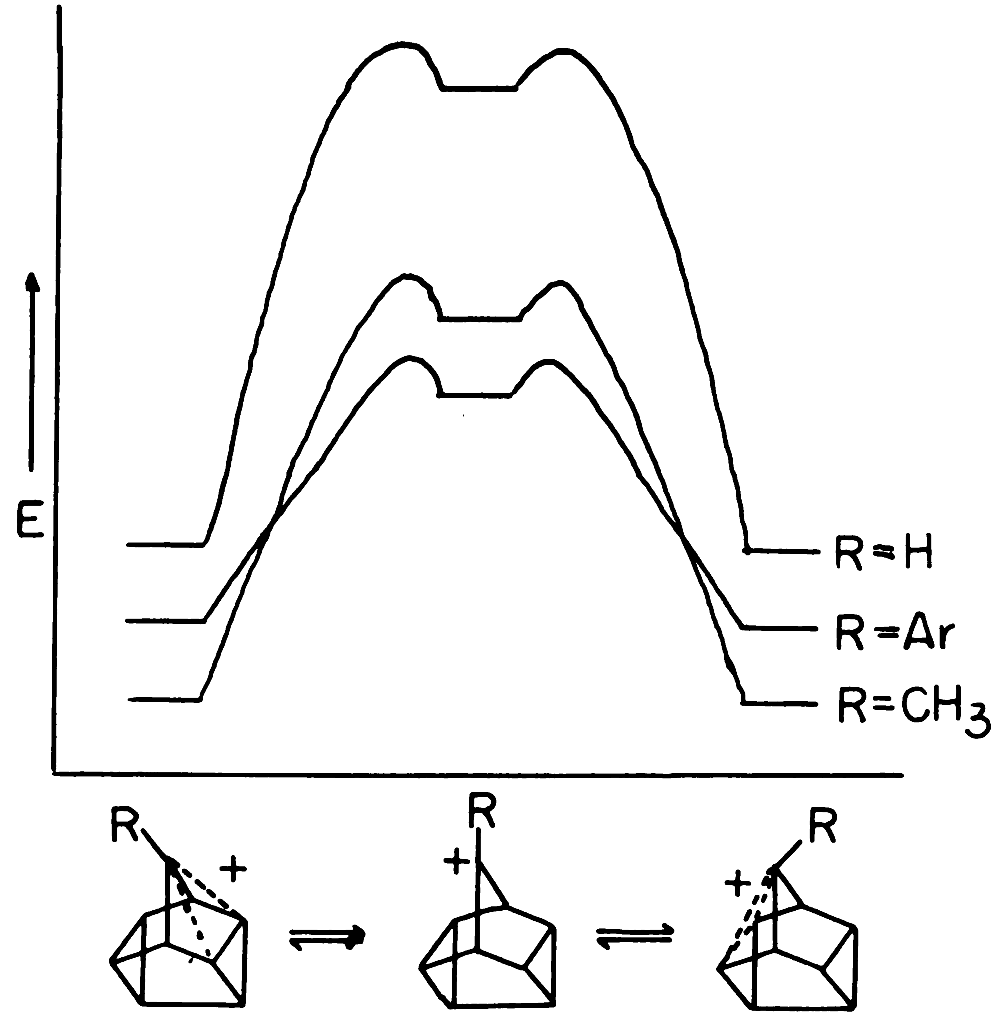
Aryl group	$^1H_{ortho}$ of (26)	$^1H_{ortho}$ of (27)	$^1H_{ortho}$ of (28)
4-CH_3-C_6H_4	8.130	8.698	——
C_6H_5	7.790	8.811	8.779
4-CF_3-C_6H_4	7.903	8.876	8.964
3,5-$(CF_3)_2$-C_6H_3	7.809	8.988	9.221

The symmetry shown by the spectra of (26) implies a rapid bridge flipping process described earlier in scheme I.[8b] It was hoped that with the strongly electron withdrawing aryl substituent, (26) would become sufficiently bridged to enable the observation of its "frozen out" form rather than its averaged spectrum. Unfortunately, the spectra obtained were unchanged over the temperature range studied. Even at -110° C, the NMR spectra of the highly bridged (26e) gave no indication of freezing out. In contrast to this observation, the NMR spectra of the methyl substituted Coates cation (45; R=CH_3) and the parent Coates cation (10) coalesce at

-5°C and over $+10^\circ$C respectively[8b] (decomposition commences before complete averaging is observed). Thus the activation energies for bridge flipping are in the order: $E_a^H > E_a^{CH_3} \gg E_a^{Ar}$.

The relative rates of solvolysis of substituted nitrobenzoates of (42) are $1:1.3(10)^2:1.3(10)^1$ for R = H, CH_3 and 3,5-$(CF_3)_2C_6H_3$ respectively.[8d] Assuming similar ground state energies for the nitrobenzoates and that the transition states resemble the intermediates formed, then the Hammond postulate requires the ground state energies of (45) to decrease in the order of R = H, Ar, CH_3. The above results are represented in figure 10 as an energy diagram for the bridge flipping of (45; R=H, CH_3, Ar).

Figure 10 A qualitative energy diagram for the bridge flipping of (45)

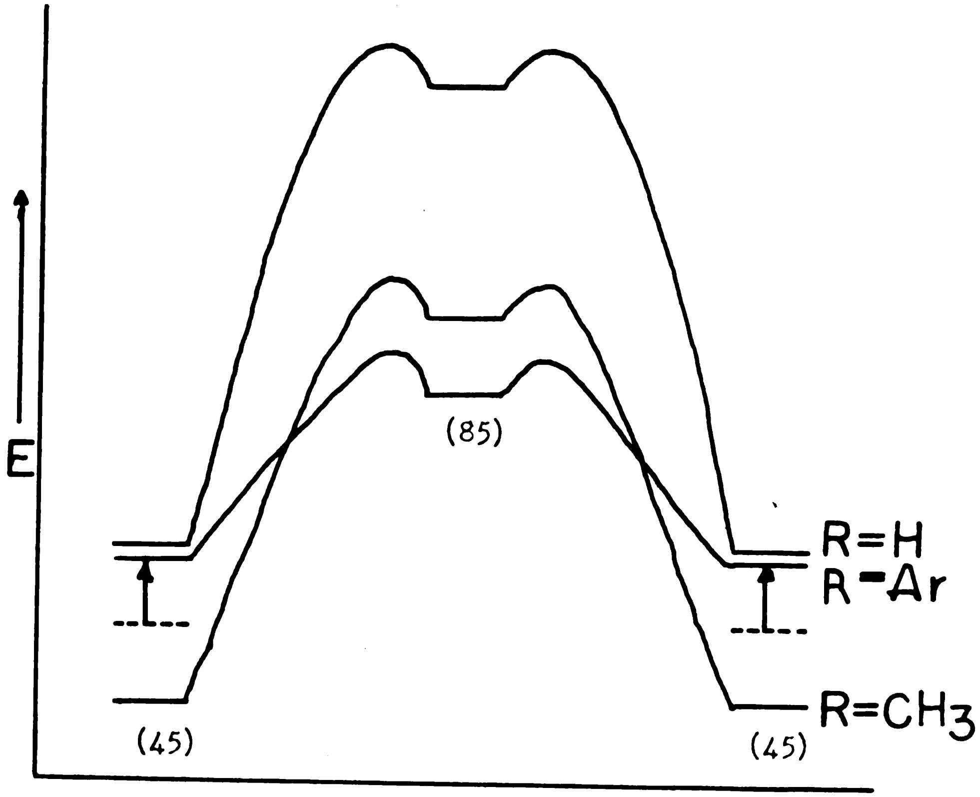


(45) (85) (45)

To accomodate the relative energies of the substituted Coates cations and the activation energies for bridge flipping, an important consequence can be deduced; i.e., aryl groups stabilize nonclassical cations far less than classical cations whereas alkyl groups stabilize nonclassical cations comparably (but still less) than classical cations.

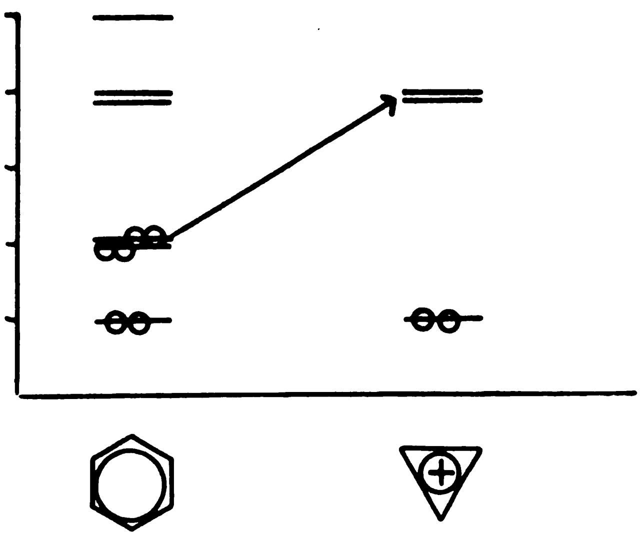
If one assumes in the solvolysis of (42) that an appreciable amount of classical character is developed in the transition state, then by the previous statement, the transition state will be greatly stabilized by the aryl substituent when compared to a totally bridged transition state. This in turn will modify the energy diagram in figure 10 to make the energy level of the aryl substituted bridged species much higher in energy as shown in figure 11. The net effect may be that electron withdrawing aryl groups may actually destabilize nonclassical cations while they stabilize classical cations.

Figure 11 A modification of figure 10 stressing the higher energy of aryl substituted bridged cations compared to classical cations.



An explanation for the smaller stabilizing influence of aryl groups on bridged systems may be inferred from a molecular orbital diagram showing the interaction between a cyclopropenium cation (a model for bridged cations) and benzene (see figure 12). It is apparent that for benzene to donate electrons via conjugation with the cyclopropenium ion, a bonding orbital of benzene must interact with an antibonding orbital of the cyclopropenium cation (shown by the arrow in figure 12). This interaction must be minimal and its stabilizing effect therefore must be small when compared to the interaction of benzene with an "empty" nonbonding orbital of a classical cation.

Figure 12 Molecular orbital diagram showing the interaction of aryl groups with a bridged system.



In summary, the aryl substituted Coates system (26) as a model for nonclassical cations shows an inverse relationship of the chemical shifts of the cationic carbons when plotted against classical systems. Other positions, however, are much less sensitive toward the aryl group due most probably to a cancellation of the effects of charge and hybridization on the ^{13}CNMR chemical shifts. Whether this is fortuitous remains to be determined.

The inability to slow down the bridge flipping of the aryl substituted Coates cations sufficiently to observe the "frozen out" form is most readily explained by the lowering of the energies of the classical intermediates much more so than the bridged cations. This explanation is supported both by theory (figure 12) and by experiment (figures 10 and 11).

The direct observation of the aryl substituted Coates system now allows a more rigorous examination of other aryl substituted cations with regard to their classical or nonclassical structures.

Adamantyl system (27)

Figure 13 is a plot of the $^{13}C^+$ chemical shifts of the adamantyl system (27a-h) versus the $^{13}C^+$ chemical shifts of the α-arylcyclopentyl cations (19). That an excellent correlation is obtained is obvious. It must be concluded, therefore, that, over the range of substituents studied, the adamantyl system is classical. An attempt to extend the plot by including the powerfully electron withdrawing group, 3,5-dichloro-4-cyanophenyl, gave only a ^1H NMR spectrum of (27i). The interpretation of the spectrum of (27i) was complicated by the vast amount of rearranged isomers present. Only after several attempts at generating (27i) could a reliable ^1H NMR for it be obtained. Because of the time required to observe ^{13}C NMR spectra, no ^{13}C chemical shifts could be obtained on unrearranged (27i). Indeed, this is the first report of a cation with such a powerfully electron withdrawing group attached to the cationic carbon, presumably due to the resistance of 3° adamantyl cations to rearrange.

In order to make use of the ^1H NMR of (27i), the nonequivalent methylene protons are plotted against each other in figure 14. Again, a well defined correlation is obtained, suggesting that even the highly electron deficient adamantyl system (27i) is classical.

Figure 13 ^{13}C NMR chemical shifts of the cationic carbon of (27) versus (19)

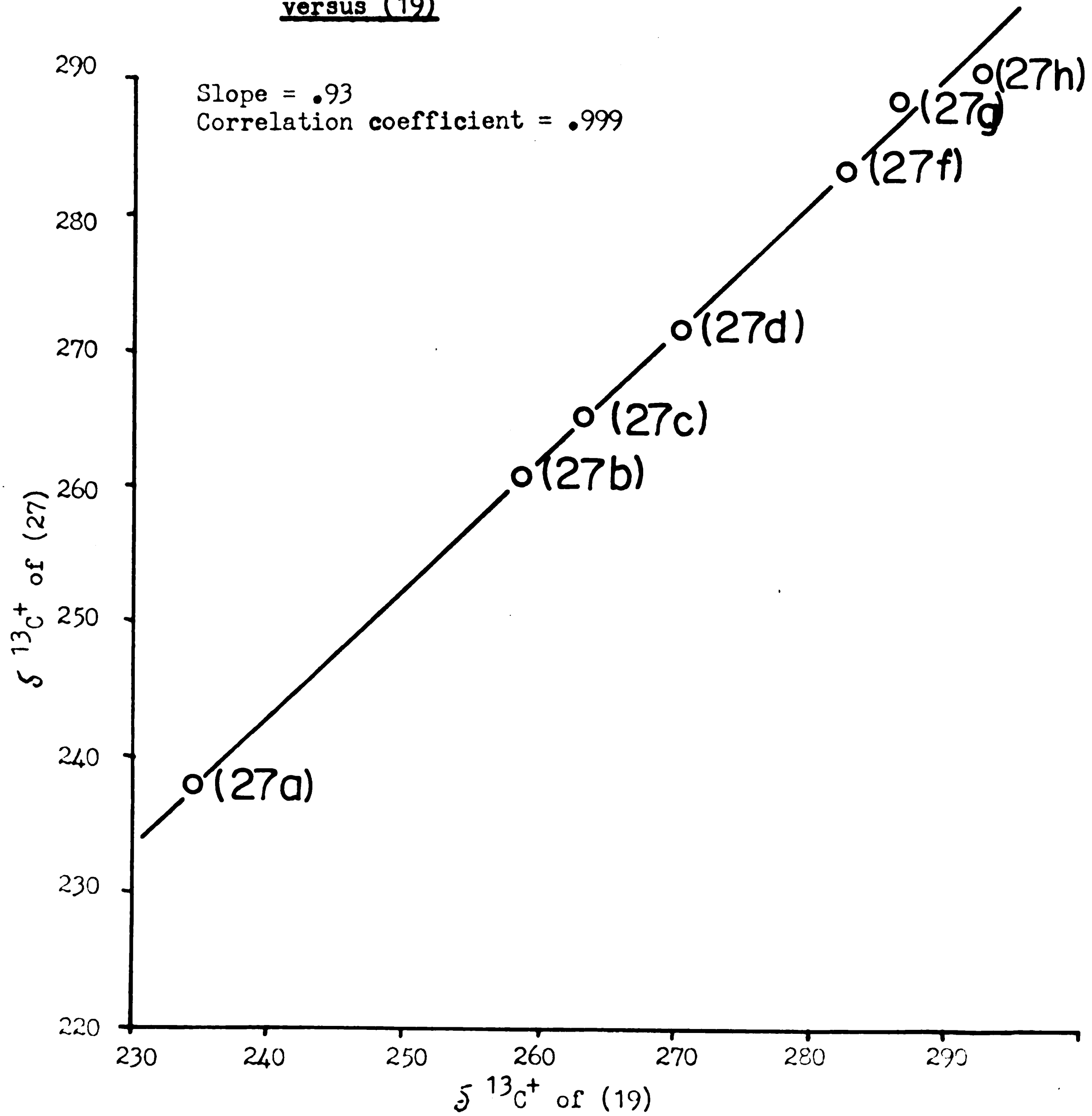
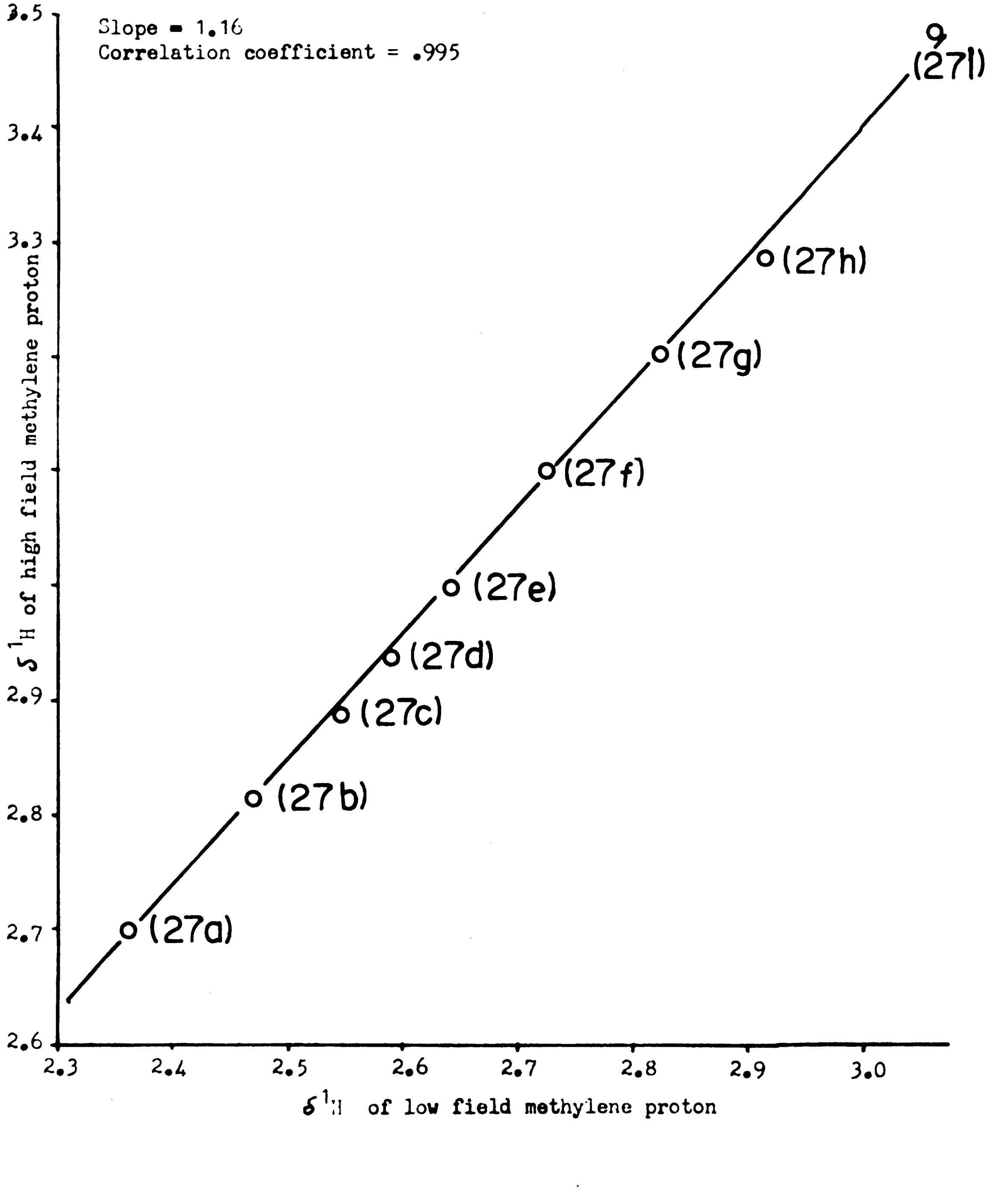


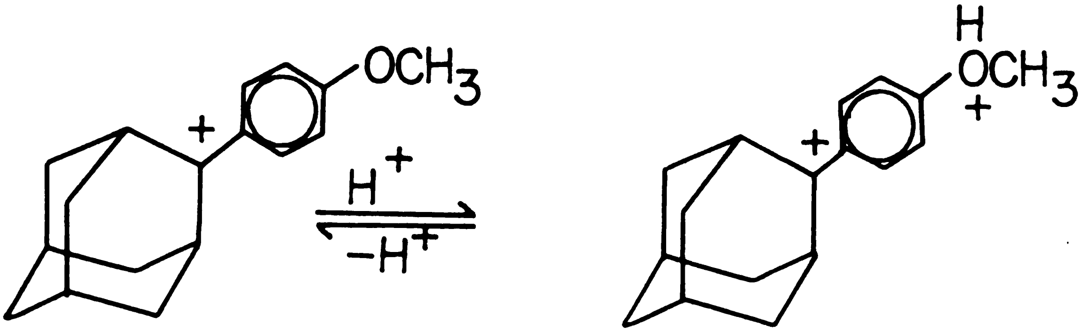
Figure 14 ^{1}H NMR chemical shifts of the nonequivalent geminal protons in (27) plotted against each other.



If the parent 2-adamantyl cation (29) is indeed bridged, then it must be assumed that our probe is too coarse to detect the presence of bridging in ions (27a-i). It may be argued that even the powerfully electron withdrawing aryl groups can still stabilize cations by delocalization of charge into the aromatic ring. This in turn may cause an unsubstituted nonclassical cation to become classical when substituted with an aryl group. Thus it is likely for a system such as the 2-adamantyl cation (29), which is at best weakly bridged, to become classical upon substitution with an aryl group.

Perhaps the most significant result in this study is the effect of acid concentration on the ^{13}C NMR of the 2-(p-anisyl)-2-adamantyl cation (27a) (table 6). Workers in the past have reported difficulties in reproducing NMR spectra of methoxy substituted cations.[12] This is the first direct observation of a α-(p-anisyl)cation which adequately explains the irreproducible spectra. The most feasible interpretation of the NMR dependence on acid concentration is that a rapid equilibration shown in scheme V is in progress.

Scheme V Equilibration of (27a) and (86) in the presence of acid



(27a)

(86)

As the acid concentration is increased, the equilibrium is shifted from the electron rich cation (27a) to the electron deficient cation (86). The net effect of downfield shifts in the NMR spectra of (27a) as the acid concentration is increased is in accord with such a mechanism.

In conclusion, the study presented on the aryl substituted adamantyl cations (27a-i) warns of two pitfalls. The first is that the probe of increasing electron demand can be used to detect only highly bridged cations. What degree of bridging is detectable is still uncertain, but it must be maintained that this probe is rather coarse and should not be used to prove that any given system is classical. The second pitfall is that any data concerning the p-anisyl group under strongly acidic media should not be weighted heavily unless precautions are taken to insure no O-protonation.

7-norbornyl system (28)

Figure 15 is a plot of the $^{13}C^{+}$ chemical shifts of the 7-norbornyl system (28) against the corresponding $^{13}C^{+}$ chemical shifts of (19). As in the adamantyl system (27), an excellent correlation is obtained indicating that at best, the 7-norbornyl cation (30) is too weakly bridged to be detected by this probe. All attempts to extend the plot beyond the bistriflouromethylphenyl substituent found in (28f) failed due to decomposition of the cation.

It is interesting to note that the endo hydrogens of (28) are at lower field in the ^{1}H NMR than the exo hydrogens. That this observation becomes more pronounced as the aryl group becomes more electron demanding is consistent with a through space bond polarization of the endo hydrogens by the cationic center. This is shown in figure 16.

Figure 15 ^{13}C NMR chemical shifts of the cationic carbon of (28) versus (19).

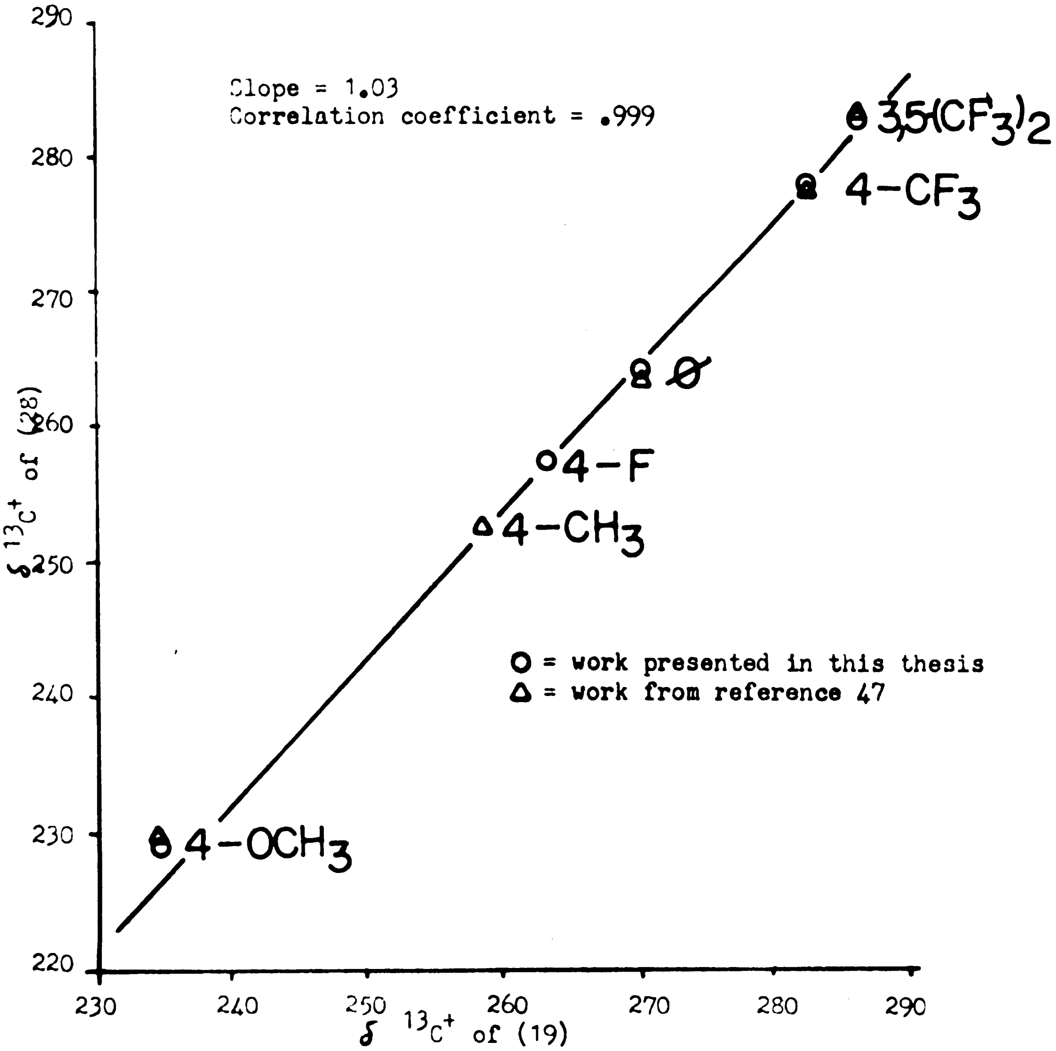
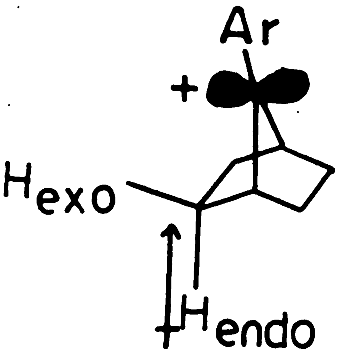


Figure 16 Bond polarization of the endo hydrogens of (28) by through space interaction with the cationic center.



EXPERIMENTAL

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

Mass spectra were obtained using a Finnigan 4000 mass spectrometer with an INCOS data system. In all cases, the correct molecular ion peak was obtained.

Infrared spectra are uncorrected and were taken on a Perkin Elmer sodium chloride spectrometer, model 137.

^1H NMR spectra of the carbocation precursors were done on a Varian T-60 spectrometer using deuterochloroform ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as an internal standard.

^{13}C NMR spectra of the carbocation precursors were taken on a Varian CFT-20 spectrometer using deuteriochloroform as the solvent and internal standard (79.00 ppm relative to TMS). All spectra were decoupled.

All NMR spectra of the carbocations (26) and (28) were taken on a Bruker WM-250 spectrometer equipped with a variable temperature controller. ^{13}C NMR of the adamantyl cations (27) were obtained on a Varian CFT-20 spectrometer equipped with a Varian V-6040 N-M-R variable temperature controller. Peaks were referenced to internal dideuteriomethylene chloride (CD_2Cl_2) for all spectra (54.5 ppm for ^{13}C NMR and 5.374 ppm for ^1H NMR from TMS) with the exception of the ^{13}C NMR of the adamantyl cations (27) which were referenced against external d_6-acetone (204.5 ppm from TMS; corrected).

Carbocation precursors

All of the carbocation precursors are alcohols obtained by reacting the corresponding ketone with 1.1 equivalents of the appropriate Grignard reagent. 7-Norbornanone[49] and 9-pentacyclo$[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]$nonanone[50] were made by literature procedures. 2-Adamantanone was purchased from Aldrich and was used as is. Yields of the Grignard reactions ranged from 40-85%. A description of the procedure used is given below.

In a flame-dried 100-mL, round-bottomed, three-necked flask equipped with a stir bar, condenser, addition funnel and a nitrogen bubbler, was placed 20 mL of dry ether and 0.23 grams of finely cut magnesium ribbon. Stirring was started and 0.011 moles of the appropriate aryl bromide was added. Occasional heating and/or a crystal of iodine was needed to start the reaction. When the reaction was under way, more ether was added (20-50 mL) and the mixture was stirred until the reaction stopped (one half hour after refluxing ends).

0.01 Moles of the corresponding ketone, dissolved in about 20 mL of dry ether was added dropwise and the mixture then stirred for an additional hour. The reaction was quenched with a saturated aqueous ammonium chloride solution and the layers separated. The ether layer was washed with a saturated sodium chloride solution, dried (sodium sulfate) and the ether removed. The resulting crystalline compound was recrystallized from pentane repeatedly until a constant melting point was obtained.

The important physical and spectral data for the precursors are given at the end of this section.

Carbocation formation

All carbocations were generated in a 10mm NMR tube. Three procedures were used:

1) For the ^{13}C NMR samples of the adamantyl systems (27), about 0.10 g of precursor was placed in the nmr tube which was equipped with

a 2mm insert filled with d_6-acetone. Approximately 2 mL of sulfuryl flouride chloride was condensed in the tube and the mixture was mixed by bubbling a slow steady stream of argon through it until all the precursor was dissolved. The flow of argon was continued while the tube was cooled in a dry ice-acetone bath (-78°C) followed by the rapid addition of about 0.5 mL of 100% magic acid (obtained from Aldrich Chemical Co.). The argon flow was continued until complete mixing was accomplished. Spectra were taken immediately afterwards.

2) All carbocations, except for those of the adamantyl series intended for ^{13}C NMR and the highly unstable cations (see procedure 3), were prepared similarly to that shown in procedure 1 with the following exceptions.

a) The 10mm NMR tube was not equipped with a 2mm insert.

b) The precursor was initially dissolved in about 0.5 mL of d_2-methylene chloride, followed by the introduction of the sulfuryl fluoride chloride.

c) In the case of the Coates system (26), flourosulfonic acid was preferred over magic acid.[8d]

3) This procedure was used for the highly unstable and difficult-to-make cations ((26f), (26g), (27i) and (28g)). In a 10mm NMR tube was placed 0.5 mL of 100% magic acid followed by about 2 mL of sulfuryl flouride chloride. The contents were mixed by bubbling argon and cooled to -130°C (liquid N_2-pentane bath). A slow introduction of the precursor (0.10 g) dissolved in 0.5 mL of d_2-methylene chloride was accomplished while the mixture was mixed with the argon flow. The temperature was slowly raised until a homogeneous solution resulted and then the temperature was again lowered to -130°C. Spectra were recorded immediately after carbocation formation.

Quench study on (83).

About 15 mL of sulfuryl fluoride chloride was condensed in an apparatus described by Hart.[51] To this solution was added 1.0 mL of 100% magic acid and the apparatus was cooled to -80°C (dry ice-acetone bath). The contents were mixed by the passage of a steady stream of argon through the mixture. 0.20 g of the precursor, dissolved in 0.5 mL of methylene chloride, was added slowly and the mixture was mixed for about 15 minutes.

The above acid solution was rapidly added to a rapidly stirred solution of 75 grams of sodium methoxide dissolved in 1.0 liter of methanol held at -80°C. Extraction of the resultant solution with ether, followed by drying (Na_2SO_4) and removal of the ether yielded a colorless oil. NMR and mass spectral analysis confirmed that the oil was the starting alcohol. No evidence could be found for the presence of the methyl ether.

Measurement of the dependence of the ^{13}C NMR of (27a) on acid concentration.

(27a) was generated as described by procedure 1 using about 0.25 mL of 100% magic acid (about 1 equivalent) and the ^{13}C NMR of this sample was recorded. More acid was measured into the NMR tube and the NMR was recorded again. This procedure was repeated until no change was observed in the NMR spectra. The results are recorded in table 6.

Physical and spectral data of the carbocation precursors 9-aryl-9-pentacyclo$[4.3.0.0^{2,4}0^{3,8}0^{5,7}]$nonanols

$4\text{-}N(CH_3)_2\text{-}3,5\text{-}Cl_2\text{-}C_6H_2$: mp 156-157°C; ^{1}H NMR ($CDCl_3$) 7.16 (2H, s), 2.76 (6H, s), 2.73 (2H, m), 2.23 (5H, m), 1.63 (2H, m); ^{13}C NMR ($CDCl_3$) 145.3, 141.1, 134.8, 128.7, 105.8, 50.0, 42.1, 39.3, 36.6, 35.7, 35.0; ir (nujol)μ 2.90, 6.45, 11.32; m/e = 321, 323, 325.

$3,5\text{-}(CF_3)_2\text{-}C_6H_3$: mp 79-80°C; ^{1}H NMR ($CDCl_3$) 7.77 (2H, s), 7.65 (1H, s), 3.18 (1H, s), 2.55-2.95 (2H, m), 2.50-1.83 (4H, m), 1.77-1.37 (2H, m); ^{13}C NMR ($CDCl_3$) 145.3, 133.7, 132.0, 128.1, 121.2, 105.8, 50.2, 39.5, 36.5, 35.6, 34.8; ir (nujol)μ 2.94, 6.12, 11.13; m/e = 346.

$4\text{-}CF_3\text{-}C_6H_4$: mp 73-74°C; ^{1}H NMR ($CDCl_3$) 7.43 (4H, s), 2.83 (3H, br s), 2.48-2.17 (4H, m), 1.70-1.43 (2H, m); ^{13}C NMR ($CDCl_3$) 146.7, 128.2, 124.9, 124.8, 106.2, 49.9, 39.2, 36.4, 35.2, 34.9; ir (nujol)μ 2.50, 11.00, 11.90, 12.50; m/e = 278.

$3\text{-}F\text{-}C_6H_4$: mp 69-69.5°C; ^{1}H NMR ($CDCl_3$) 7.50-6.65 (4H, m), 3.14-2.70 (2H, m), 2.66 (1H, s), 2.48-1.93 (4H, m), 1.81-1.47 (2H, m); ^{13}C NMR ($CDCl_3$) 1.68.5, 156.3, 145.6, 145.2, 129.6, 129.1, 123.3, 115.4, 114.5, 114.3, 113.5, 106.2, 49.9, 39.1, 36.4, 35.1, 35.0; ir (nujol)μ2.93, 6.30, 11.70, 12.55; m/e = 228.

C_6H_5: mp 83-84°C; ^{1}H NMR ($CDCl_3$) 7.6-7.0 (5H, m), 2.85 (2H, br s), 2.65 (1H, s), 2.95-1.92 (4H, m), 1.75-1.42 (2H, m); ^{13}C NMR (CDCl) 142.9, 127.9, 127.7, 127.1, 106.8, 49.1, 39.0, 36.5, 35.0; ir (nujol)μ 2.95, 13.12, 14.43; m/e = 210.

4-CH_3-C_6H_4: mp 77-78°C; ^1H NMR($CDCl_3$) 7.0 (4H, 9, J=8Hz), 2.93-2.66 (2H, m), 2.52 (1H, s), 2.36-2.28 (7H, m), 1.77-1.50 (2H, m); ^{13}C NMR($CDCl_3$) 140.0, 136.4, 128.4, 127.4, 106.4, 49.6, 38.8, 36.5, 34.9, 20.8; ir (nujol)μ 2.90, 12.2; m/e = 224.

4-OCH_3-C_6H_4: mp 66-68°C; ^1H NMR($CDCl_3$) 7.50 (2H, d, J=6Hz), 6.63 (2H, , J=6Hz), 3.65 (3H, s), 2.78 (3H, br s), 2.33-1.87 (4H, m), 1.67-1.37 (2H, m); ^{13}C NMR($CDCl_3$) 158.5, 135.3, 128.7, 113.2, 106.4, 55.0, 49.9, 39.0, 36.6, 35.0; ir (nujol)μ 2.89, 2.96, 6.21, 12.00; m/e = 240.

2-Aryl-2-adamatanols

4-CN-3,5-Cl_2-C_6H_2: mp 199-201°C: ^1H NMR ($CDCl_3$) 7.45 (2H, s), 2.44-2.28 (4H, m), 1.82-1.75 (11H, m); ^{13}C NMR($CDCl_3$) 154.7, 140.2, 217.4, 114.9, 77.0, 38.8, 37.1, 36.2, 34.2, 28.6, 28.1; ir (nujol) μ2.88, 4.50, 6.31, 6.16, 11.45, 12.25; m/e = 321, 323, 325.

4-$N(CH_3)_2$-3,5-Cl_2-C_6H_2: mp 125-127°C; ^1H NMR ($CDCl_3$) 7.20 (2H, s), 2.80 (6H, s), 2.40-1.60 (15H, m); ^{13}C NMR($CDCl_3$) 145.1, 143.6, 135.3, 126.5, 75.0, 42.0, 37.4, 35.5, 34.6, 32.7, 27.2, 26.6; ir (nujol)μ 3.00, 6.87, 11.44, 12.56; m/e = 339, 341, 343.

3,5-$(CF_3)_2$-C_6H_3: mp 89-89.5°C; ^1H NMR ($CDCL_3$) 7.79 (2H, s), 7.60 (1H, s), 2.47 (2H, br s), 2.27 (1H, br s), 1.80-1.67 (12H, m); ^{13}C NMR($CDCl_3$) 151.2, 136.6, 134.9, 130.0, 129.9, 125.0, 120.5, 79.2, 41.1, 39.5, 38.4, 36.4, 31.1, 30.4; ir (nujol)μ 2.93, 6.82, 7.28, 11.08; m/e = 364.

4-(CF_3)-C_6H_4: mp 86-87°C; ^{1}H NMR ($CDCl_3$) 7.45 (4H, s), 2.42 (2H, br s), 2.22 (1H, br s), 1.73-1.68 (12H, m); ^{13}C NMR ($CDCl_3$) 149.2, 125.8, 125.3, 125.1, 75.1, 37.3, 35.4, 34.4, 32.5, 27.2, 26.6; ir (nujol) μ 2.94, 6.12, 11.93; m/e = 296.

3-Br-C_6H_4: mp 74-76°C; ^{1}H NMR ($CDCl_3$) 7.67 (1H, s), 7.48-7.40 (3H, m), 2.58-2.37 (4H, m), 1.91-1.54 (9H, m); ^{13}C NMR ($CDCl_3$) 147.9, 141.5, 130.2, 128.9, 124.1, 122.9, 75.7, 37.5, 35.6, 34.7, 32.9, 27.3, 26.8, ir (nujol) μ 3.06, 3.52, 6.31, 12.80, 14.40; m/e = 306, 308.

C_6H_5: mp 79-80°C; ^{1}H NMR ($CDCl_3$) 7.48-7.00 (5H, m), 2.44 (2H, br s), 2.27 (1H, br s), 1.65 (12H, br s); ^{13}C NMR ($CDCl_3$) 145.2, 128.5, 127.0, 125.3, 75.4, 37.5, 35.5, 34.7, 32.8, 27.3, 26.8; ir (nujol) μ 2.96, 6.20, 12.96, 14.30; m/e = 228.

4-F-C_6H_4: mp 79-80°C; ^{1}H NMR ($CDCl_3$) 7.50 (2H dd, J=9Hz, 5.5H_2), 7.041 (2H t, J=9Hz), 2.52 (1H, 6s), 1.51-1.90 (12H, m); ^{13}C NMR ($CDCl_3$) 167.1, 155.5, 141.3, 141.1, 127.4, 127.0, 115.7, 114.7, 75.1, 37.6, 35.8, 34.7, 32.8, 27.4, 26.8; ir (nujol) μ 2.95, 3.50, 6.26, 12.0; m/e = 246.

4-CH_3-C_6H_4: mp 77-78.5°C: ^{1}H NMR ($CDCl_3$) 7.30 (2H, d, J=8Hz), 7.04 (2H, d, J=8Hz), 2.46 (2H, br s), 2.26 (4H, br s), 1.95 (2H, m), 1.66 (9H, br s), 1.47 (2H, s); ^{13}C NMR ($CDCl_3$) 144.1, 138.4, 130.4, 126.9, 77.0, 39.3, 37.3, 36.5, 34.6, 29.1, 28.6, 22.5; ir (nujol) μ 2.86, 2.91, 6.62, 12.25; m/e = 242.

4-OCH_3-C_6H_4: mp 96-98°C; ^1H NMR ($CDCl_3$) 7.25 (2H, d, J=9Hz), 6.70 (2H, d, J=8Hz), 3.70 (3H, s), 2.45 (2H, br s), 2.28 (1H, br s), 1.68-1.50 (12H, m); m/e = 258.

7-Aryl-7-norbornanols

4-N-$(CH_3)_2$-3,5-Cl_2-C_6H_2: mp (oil); ^1H NMR ($CDCl_3$) 7.15 (2H, s), 2.83 (6H, s), 2.25 (4H, m), 1.93 (1H, s), 1.42 (6H, m); ^{13}C NMR ($CDCl_3$) 145.5, 140.7, 135.2, 127.9, 87.0, 42.1, 28.3, 27.2; ir (neat)μ 3.0, 3.49, 3.55, 6.90, 12.55, 13.65; m/e = 399, 401, 403.

3,5-$(CF_3)_2$-C_6H_3: mp 65-66°C; ^1H NMR ($CDCl_3$) 7.70 (2H, s), 7.60 (1H, s), 2.33 (2H, br s), 2.22-1.88 (2H, m), 1.62-1.26 (7H, m); ^{13}C NMR ($CDCl_3$) 145.0, 132.0, 130.2, 127.5, 121.4, 87.4, 42.4, 28.3, 27.2; ir (nujol)μ 3.03, 3.48, 3.53, 6.89, 11.10, 11.81; m/e = 324.

4-(CF_3)-C_6H_4: mp 79-80°C; ^1H NMR ($CDCl_3$) 7.61 (4H, s), 2.407 (2H, s), 2.155 (2H, d, J=7.25Hz), 1.80 (1H, s), 1.48-1.24 (6H, m); ^{13}C NMR ($CDCl_3$) 146.4, 127.6, 125.5, 87.5, 42.1, 28.3, 27.2; ir (nujol) μ3.09, 3.48, 3.55, 6.18, 6.90, 11.90; m/e = 256.

C_6H_5: mp 46-47°C; ^1H NMR ($CDCl_3$) 7.35-7.00 (5H, m), 2.32 (2H, br s), 2.28-1.83 (3H, m), 1.53-1.17 (6H, m); ^{13}C NMR ($CDCl_3$) 142.5, 128.4, 127.4, 127.0, 87.7, 41.9, 28.4, 27.3; ir (nujol)μ 3.05, 3.47, 3.54, 6.86, 13.05, 14.36; m/e = 188.

exo,exo-2,3-d_2-P-F-C_6H_4: mp (oil); ^1H NMR ($CDCl_3$) 7.42-7.13 (2H, m), 6.85 (2H, t, J=8.5Hz), 2.35-1.60 (5H, m), 1.60-.97 (4H, m), ^{13}C NMR ($CDCl_3$) 132.6, 129.06, 128.64, 115.88, 114.82, 87.29, 42.22, 28.44, 27.29; ir (neat)μ 3.00, 3.45, 3.51, 4.60, 6.25, 6.67, 11.95, 12.31; m/e = 208.

P-CH_3O-C_6H_4: mp 50-51°C; ^{1}H NMR ($CDCl_3$) 7.30 (2H, d, J=8Hz), 6.75 (2H, d, J=8Hz), 3.73 (3H, s), 2.28-1.17 (11H, m); ^{13}C NMR ($CDCL_3$) 1.58.9, 128.3, 127.7, 113.9, 87.5, 55.2, 42.2, 28.6, 27.5; ir (nujol)μ 2.95, 3.46, 3.52, 6.21, 6.62, 12.02; m/e = 218.

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