ARYL SUBSTITUTED POLYCYCLIC CATIONS. DEPENDENCE OF C-13 NUCLEAR MAGNETIC RESONANCE PARAMETERS ON ELECTRON DEMAND

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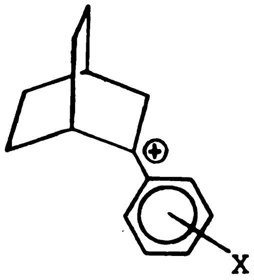
ABSTRACT

Aryl Substituted Polycyclic Cations. Dependence of C-13 Nuclear Magnetic Resonance Parameters on Electron Demand

By

Robert Ernest Botto

The charge dependence of both β-carbon chemical shifts for a series of 2-aryl-2-bicyclo [2.2.2]- or 6-aryl-6-bicyclo [3.2.1] octyl cations, **32a-f** or **33a-g**, respectively, is very closely the same throughout the range of aryl groups studied. Plots of the carbocation chemical shifts of these cations against those of classical models (*e.g.* arylcyclopentyl) exhibit ideal linear behavior. By contrast similar plots of chemical shifts of C(1) *vs.* C(3) for a series of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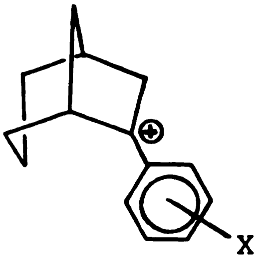
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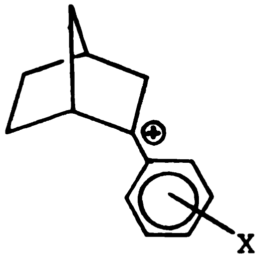
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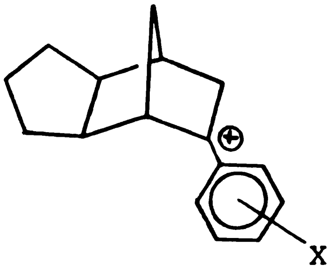
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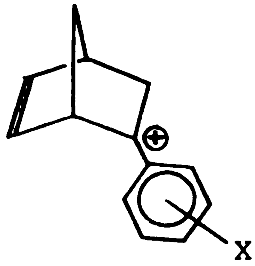
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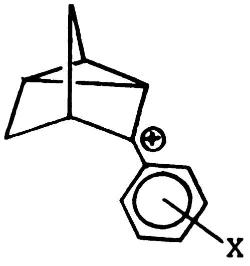
38a-f

2-aryl-2-norbornyl cations **34a**-**g** and 2-aryl-*exo*-5,6-trimethylene-2-norbornyl cations **35a**-**g** show substantial deviation from linearity for substituents (X) on the aryl group more electron demanding than *m*-chloro. A plot of the α-carbon chemical shifts of either series *versus* those of our bicyclo [3.2.1] octyl model reveals a dramatic reversal in slope in the same region. The results are consistent with the onset of C(1)-C(6) bond participation in those norbornyl or *exo*-5,6-trimethylenenorbornyl cations with substituents more electron demanding than *m*-chlorophenyl.

A plot of the olefinic cmr parameters of a series of 2-arylnorbornen-2-yl cations **36a**-**e** against Brown σ^+ substituent constants is consistent with the onset of π-participation in those cations more electron demanding than 2-phenylnorbornenyl cation. The impressive turnabout in the α-carbon chemical shifts implicates a rehybridization of the carbocation center on electron demand.

Free-energy relationships of the C-13 chemical shifts for a series of 3-aryl-3-nortricylyl cations **38a**-**f** suggest that there is extensive charge delocalization into the cyclopropyl moiety without extensive rehybridization at the carbocation center.

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By

Robert Ernest Botto

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DOCTOR OF PHILOSOPHY

Department of Chemistry

1975

Dr. Farnum

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PERSPECTIVE

The existence of carbocationic species has been proposed since the turn of the century when Norris[1,2] and Kehrman[3] independently observed that colorless derivatives of triphenylmethane give striking yellow solutions in concentrated sulfuric acid and form orange complexes with aluminum and tin halides. The intense colors of these extraordinary compounds in solution and their sensitivity to hydrolysis were the only properties remarked upon in these early papers. Less than one year after these perplexing observations von Baeyer recognized[4] the salt-like character of the compounds formed in the solutions of triphenylcarbinol and sulfuric acid. He supposed a correlation between the formation of salt and the appearance of color - termed "halochromy". Such salts were named carbonium salts.

In 1902 Gomberg pointed out the inconsistency of von Baeyer's nomenclature. He wrote:[5] "In my opinion, the name 'carbonium' should be applied to salts in which an increase of the number of valences of the carbon takes place, just as in the case of the ammonium, sulfonium, iodonium, and oxonium salts." Gomberg coined the term "carbyl salt" which never quite caught on. Later Dilthey and Wizinger suggested the name of carbenium salts[6] for such species in accord with their theory of coordinately unsaturated chromophores.

Interestingly this controversy still remains with us. With the discovery of pentavalent cations of carbon in highly protic media, Olah[7] suggested replacement of the term "carbonium ion" with "carbenium ion" for the trivalent cationic species. Farnum[8], arguing that the "onium" suffix has not been exclusively reserved for the highest valence state, feels such change inappropriate. Both authors surprisingly agree on the perfectly adequate term "carbocation", which (this author feels) can be justified by its analogy with "carbanion" and for the sake of simplicity, could easily replace both incongruous nomenclatures for positive charged species of carbon currently in use.

The existence of carbocationic salts was finally confirmed in 1909 by independent discoveries of Hofmann[9] and Gomberg[10] when both men isolated crystalline, colored anhydrous perchlorates from triarylcarbinols. The identity of these colored species in solution was later confirmed by their very characteristic absorption spectrum by Hantzsch[11]. Conductimetric measurements[12] as well as molal freezing point depression studies[13] further substantiated the ionic nature of these species - an electron deficient, trivalent carbon species had become reality.

During the period that followed, 1920-1940, the nature of the chemical bond had become better understood and electronic theory matured from a sapling to bear many conceptual fruits. It was an age of exploration and an age of refinement - physical-organic chemistry was born. One of the most daring as well as important concepts visualized during this period concerned the intermediacy of carbocation species in the course of reactions involving non-ionic reactants and leading to non-ionic products. Most of the research provided evidence in favor or against the intervention of transient cationic intermediates in specific chemical reactions.

Carbocations were considered intermediates in skeletal rearrangements. Wagner's discovered rearrangement of camphene hydrochloride in 1899 was rediscovered by Meerwein in 1922[14]. His kinetic study of these reactions led him to conclude that: ". . . the rearrangement takes place only after a preceding ionization" and involves the rearrangement of the cation. Meerwein's rearrangement theory was later generalized by Whitmore in 1948 in a then comprehensive review on carbocations[15].

The kinetic approach proved to be invaluable in the years to come. Substituent effects were noted and reaction types were classified by Oliver[16]. Hughes and Ingold[17] undertook an extensive research effort during 1933-5 which placed reaction types in one of two categories: unimolecular or bimolecular. Their theory on the duality of reaction mechanism in solvolytic reactions dissipated the quandry concerning Walden inversion.[18] The increasing stability of carbocations with branching was realized as well as the importance of solvent interactions during the course of a solvolytic reaction.

Although many of the experimental techniques remained the same after 1940, a higher level of sophistication was attained partially by the development of new instrumental and analytical methods. The advancement of theoretical chemistry had great impact on the understanding of reaction processes. The transition state theory[19] allowed the construction of a graphical representation of reacting systems - a reaction coordinate. From the fields of thermodynamics and statistical mechanics emerged extrathermodynamic relationships which permitted investigation of the actual mechanisms of substituent or medium effects and which provided a view of the ordering effects present in the transition state[20]. Increasingly accurate representations of the structures of the fundamental states of the reactants also allowed a better understanding of their transition states. Stable carbocations have been prepared in strongly acidic media and their properties determined spectroscopically. Indeed, after 1940 investigators aspired to far more ambitious experimentation than ever before.

Perhaps a climax was reached when it was observed that some unimolecular processes proceed with participation by neighboring carbon atoms. Winstein[21] suggested the term "anchimeric assistance" while "synartetic acceleration" was proposed by Ingold[22] for this general phenomenon. Electronic delocalization of a saturated carbon-carbon bond was first suggested in a paper by Nevell, deSalas, and Wilson[23] in 1939. Supporting evidence did not appear in the literature until some ten years later. Winstein and Trifan[24] revealed their studies of the chemical behavior of the norbornyl cation and postulated a symmetrically-bridged, delocalized cationic intermediate. Bridged cationic intermediates were considered in the solvolyses of unsaturated systems and small ring compounds (i.e. three and four membered rings) as well. The dialectic which followed concerning nonclassical behavior stimulated an enormous quantity of chemical research spanning the last twenty-five years. During this period a number of thorough reviews on the subjects of $\underline{\sigma}$- and $\underline{\pi}$-participation representative of both sides of the controversy have appeared in the literature[25].

Thus dawned the era of nonclassical cations only two decades after the concept that classical cations are discrete reaction intermediates was placed on a firm experimental foundation. Perhaps an age of enlightenment, it brought us closer to physical reality than ever before. The ideological confrontations found in the voluminous literature on the subject serve to illustrate that we ourselves limit our interpretations, yet that all interpretations serve us. Max Planck writes: "The ideal aim before the mind (of the scientist) is to understand the external world of reality. But the means . . . to attain this end are what are known in physical science as measurements, and these give no direct information about external phenomena. As such they contain no explicit information and have to be interpreted."

INTRODUCTION

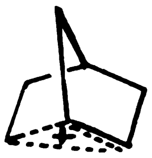
Within the past twenty-five years an extensive research effort has been undertaken to evaluate the viability of the concept of bridged, nonclassical ions. Until the early sixties the nonclassical formulation was based upon evidence derived from kinetic, stereochemical and isotope tracer studies. Yet all the experimental observations supporting the intervention of bridged ions could be explained in terms of rapidly equilibrating, classical ions. Subsequent methods to generate stable, long-lived carbocations in low nucleophilicity solvents have since allowed direct spectroscopic measurements to be made. These spectroscopic studies provide the chemist with an invaluable tool for the structure elucidation of carbocationic species. If one assumes that cations formed in poorly solvating media are structurally equivalent with those cationic intermediates produced along the reaction coordinate during solvolysis, then the conclusions drawn from the study of cations in super acid are relevant to the nonclassical ion problem.

A nonclassical cation has been defined by Sargent as "a positively charged organic moiety, representing a free energy minimum with respect to internuclear distortions, which is capable of delocalizing positive charge density by means of a multicentre molecular orbital formed, at least in part, by sigma overlap of atomic orbitals." The charge dispersal seemingly apparent in the 2-norbornyl, cyclopropylcarbinyl and unsymmetrical homoallylic cations has been ascribed to this phenomenon: either inferred from the solvolysis data of the parent systems or concluded from the spectral parameters obtained for stable cations in highly acidic media.

We shall discuss each purported nonclassical system individually; and, in view of the voluminous literature already available on this subject we shall select those experiments and hypotheses which seem relevant to our results.

The Norbornyl Cation

In 1949 Winstein and Trifan[26] proposed the symmetrically bridged cation **1** (suggesting the contribution from three canonical forms (**1a**, **1b**, **1c**) to account for their observations found in the solvolysis reactions of exo- and endo-2-norbornyl p-bromobenzenesulphonates. Since that time the



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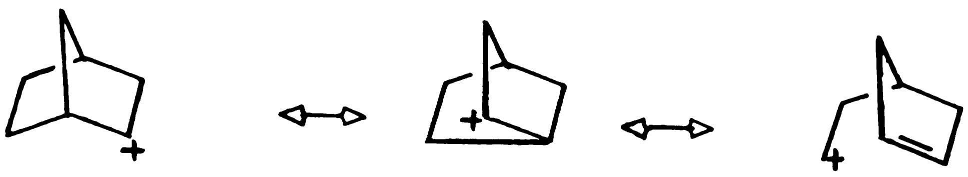
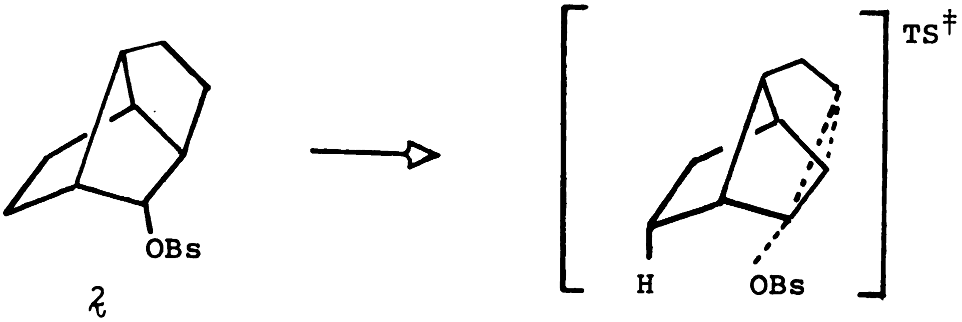


1a **1b** **1c**

proposal that nonclassical ions are involved in the solvolysis of 2-norbornyl derivatives has rested on three major foundations: (1) unusually fast rates of solvolysis for the exo derivatives, (2) high exo/endo rate ratios, (3) and stereoselective formation of solvolysis products.

Whereas proponents of nonclassical participation explain the rate ratio of the 2-norbornyl epimers in terms of stereoelectronic factors, Brown argues that the endo-norbornyl transition state is destabilized on the basis of steric grounds[27]. Schleyer suggests[28] that tortional and nonbonded interactions in the endo derivatives leading to the transition state may well account for the observed exo/endo rate ratio. Brown also argues that one need not invoke nonclassical participation to account for the high stereoselectivity of the solvolysis products. He has demonstrated the strong preference for exo orientation in reactions of U-shaped systems, including norbornyl, not involving cationic intermediates[29]. Other studies which lend support to Brown's views are: (1) the enhanced rates of solvolysis of highly branched tertiary derivatives with increasing steric strain[30]. As model compounds, they strongly support the contention that relief of steric strain is the major contributing factor in the solvolysis of tertiary norbornyl derivatives, (2) the failure of appropriate substitution to enhance solvolysis rates of norbornyl derivatives[31], (3) considerable retention of optical activity in the deamination of optically active norbornyl amines[32], (4) the incomplete deuterium scrambling observed in the ionic addition of DCI to norbornene[33].

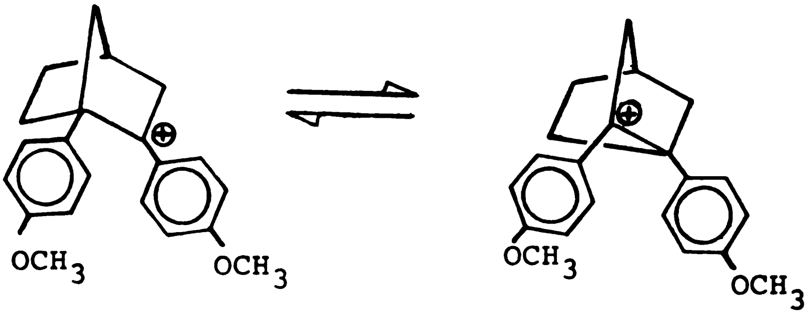
One of the difficulties in the interpretation of data in the area of norbornyl cation chemistry has been the unavailability of suitable model compounds for direct comparison. However, the 2-tricyclo $[4.3.0.0^{3,7}]$ nonyl derivative **2** studied by Nickon and Swartz[34] is unique in that the substituent at C-2 occupies both an exo and an endo bonding relationship to a norbornyl ring system. The importance of steric and torsional effects in the presence



2

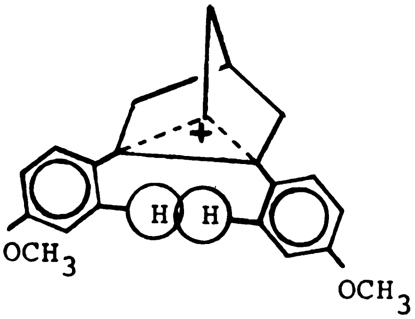
of a favorable stereoelectronic environment for participation can be evaluated. Solvolysis of compound **2** is 225 times faster than endo-2-norbornyl brosylate, nearly two-thirds the rate of solvolysis of exo-2-norbornyl brosylate. It is apparent that steric hindrance to ionization and torsional effects play a minor role. The solvolysis of **2** is the most convincing evidence to date asserting the intervention of σ-participation in the solvolysis of secondary norbornyl derivatives.

Schleyer's observation[35] of a rapidly equilibrating pair of classical 1,2 dianisylnorbornyl cations **3a** and **3b** support Brown's model. The interconversion of **3a** and **3b** is rapid on a pmr time scale even at -70°C. The absence



3a **3b**

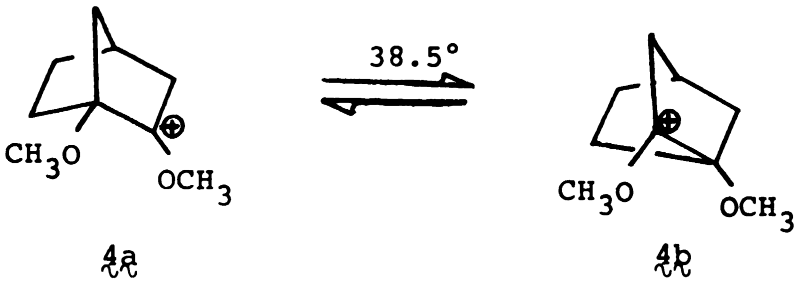
of bridging was rationalized in terms of unfavorable non-bonding interactions which may exist in the bridged species



3c

3c when one or both the aryl groups are oriented to allow overlap with the electron deficient center. In addition, Winstein contends that the cationic center is substantially stabilized by the p-anisyl moiety and need not require additional stabilization.[36]

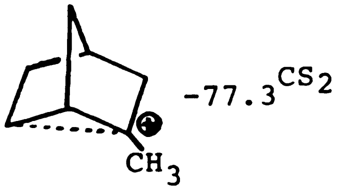
The 1,2-dimethoxy-2-norbornyl cation studied by Nickon[37] (in which the nonbonded repulsions should be absent or at least far less severe than in cation 3) similarly exhibits a temperature dependent pmr spectrum consistent with rapidly equilibrating, classical structures 4a and 4b. The cmr spectrum of the 2-methoxy-2-norbornyl cation has been discussed by Olah[38]. That the positive charge rests primarily on the oxygen atom suggests Nickon's disubstituted cation to be a poor model for comparison with the norbornyl cation, in which charge is concentrated on the carbons directly.



Olah has demonstrated that the 1,2 diphenyl-2-norbornyl cation is classical, undergoing rapid dengenate 1,2 Wagner-

Meerwein shift and with very little charge delocalization into the phenyl rings[39]. Out of plane π-p distortion of the phenyl substituents implicate unfavorable nonbonded interactions between them as is the case in the dianisyl derivative (vide supra).

In contrast the 2-methyl-2-norbornyl cation **5** appears to be a partially σ-delocalized ion[40]. A nearly 70 ppm C-13 chemical shift difference of the carbocation centers is observed when **5** is compared with classical models such



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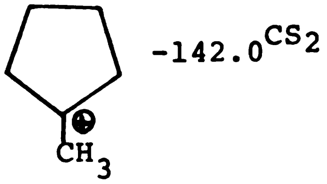

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as methylcyclopentyl cation **6**. Olah later employs average cmr chemical shifts to distinguish among rapidly equilibrating, symmetrically delocalized and partially delocalized structures (Table 1)[38] of substituted norbornyl cations.

Cmr and pmr studies of the parent norbornyl cation are best accommodated by a nonclassical model[41]. Its Raman spectrum at -78°C is consistent with nortricyclene-like rather than norbornane-like skeletal symmetry[41]. The photoelectron spectrum (ESCA) of the norbornyl cation further supports this conclusion[42] although the quantitative accuracy involved is recently viewed with suspicion[43].

Table 1. CMR Average Chemical Shift (C_1,C_2) in Substituted Norbornyl Carbocations[*]

Ion	Classification	^{13}C Average Chemical Shift	Adjusted Average Chemical Shift
1,2-Dimethylnorbornyl Cation	Rapidly Equilibrating Partially σ- Delocalized	+26	+26
2-*t*-Butylpropyl Cation	Rapidly Equilibrating	-11	-17
2-Norbornyl Cation	Symmetrically σ- Delocalized	+70	+50
2-Methylnorbornyl Cation	Partially σ- Delocalized	+21	+20

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[*] Chemical shifts relative to external CS_2.

Lastly, although Brown and Takeuchi[44] find a linear dependence of log k for the solvolysis of a number of 2-aryl-2-norbornyl derivatives with σ^+ values, Farnum and Wolf[45] observe nonlinear free energy behavior of 2-aryl-2-norbornyl cations in FSO_3H. A plot of the pmr chemical shifts of H(1) versus H(3) shows nonlinearity for substituents on the aryl group more electron withdrawing than hydrogen and which is not consistent with a pair of rapidly equilibrating, classical ions.

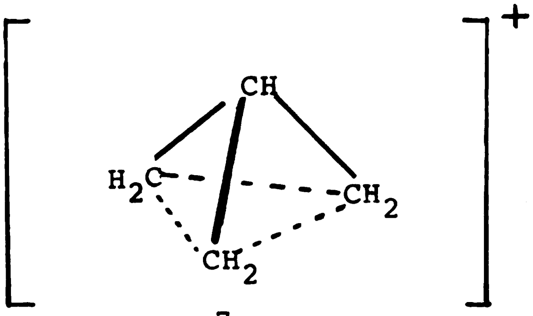
Cyclopropylcarbinyl Cations

The ability of cyclopropane rings to conjugate with adjacent π-orbitals has been realized for some time. In 1917 Kohler and Conant[46] concluded that a cyclopropyl moiety in the proper position can form a conjugated system similar in properties with those found for conjugated olefinic compounds. Their conclusions were based on chemical reactivity. Later, as evidence amassed from solvolysis studies a true appreciation of the stability of cyclopropylcarbinyl cations was realized.

Roberts and Mazur have demonstrated the unusually fast reactivity of cyclopropylcarbinyl halides in solvolysis reactions. In fact they are considerably more reactive than analogously constituted allyic halides[47].

Although the intense conjugation in cyclopropylcarbinyl cations is widely accepted, the mode of such interaction is still the subject of serious debate.

Roberts initially proposed an attractive "nonclassical" (coined by Roberts[48]) cationic intermediate of structure **7**[48,49] to account for the abnormally large solvolytic reactivities of cyclopropylcarbinyl, cyclobutyl and allylcarbinyl derivatives and the striking ease of interconversion among them. Subsequent isotopic scrambling studies revealed that ^{14}C-distribution in the products from cyclopropylcarbinyl solvolysis is extensive but not completely random[50]. (The symmetry of structure **7** is incompatible with the data; nor does it receive theoretical support[51].) Roberts posed the intermediacy of σ-participating, unsymmetrical bicyclobutyl cations **8a**, **8b** and **8c**, which equilibrate rapidly, to explain the results.



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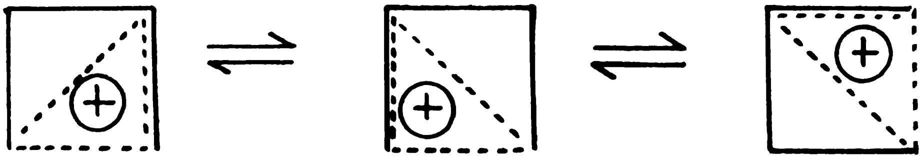
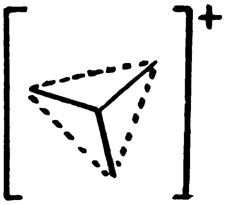


8a **8b** **8c**

Indeed many structures for the cyclopropylcarbinyl cation have been considered (7-15)[47-59].



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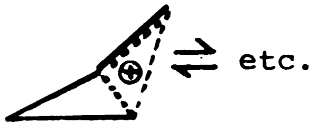

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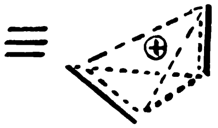

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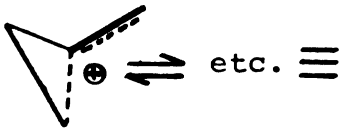

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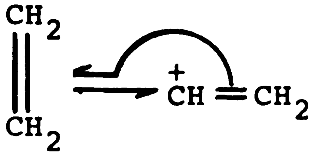

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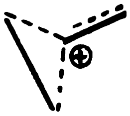

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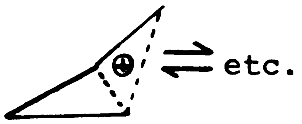

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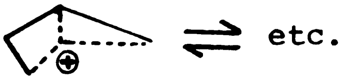

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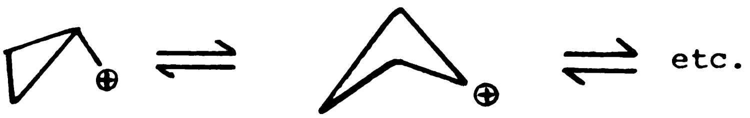

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The profusion of these dashed structures tends to complicate matters.

Simply two modes of stabilization of strained cyclopropyl bonds are worthy of consideration on the basis of experimental evidence and theoretical considerations: σ-bond participation and hyperconjugative interaction. The first requires atomic movement so as to allow maximum σ-p overlap of atomic orbitals (Figure 2) irrespective of which dashed representation (8, 9, 14, 15) is chosen.

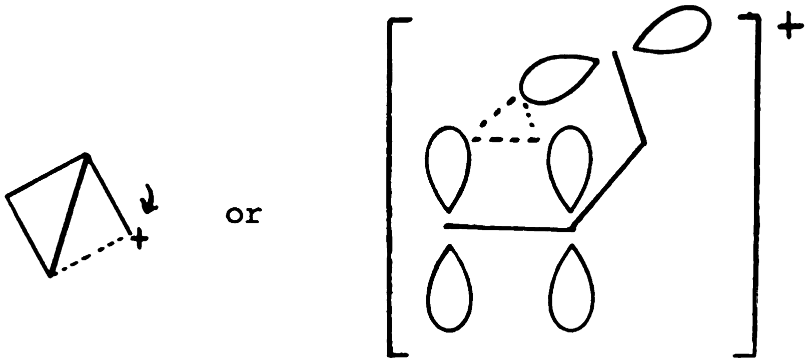


Figure 2

The hyperconjugative mode of interaction is available without changing the spatial arrangement of atoms. It can be represented by partial p-π overlap and partial p-σ overlap of orbitals without distortion of the carbon framework (Figure 3, structures 10 and 11)[53] or as a vertical process in the Frank-Condon sense (Figure 4)[59]. Hyperconjugative interaction requires one of the bisected structures indicated in Figure 4.

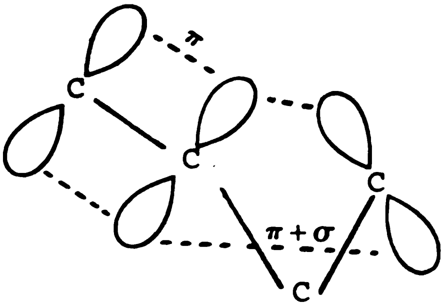


Figure 3

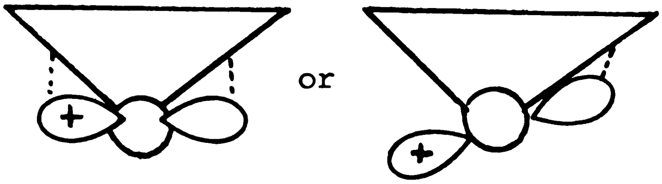


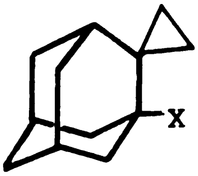
Figure 4

The bisected structure has been strongly indicated by the discovery that cyclopropanecarboxaldehyde[60] and cyclopropyl methyl ketone[61] exist in a cis and trans isomer, both of which have bisected conformations. The bisected conformation presumably permits maximum overlap of the p-orbital of the adjacent carbonyl carbon with the cyclopropane "bent bonds".

Hart and coworkers have shown that successive replacement of isopropyl by cyclopropyl groups lead to large solvolysis rate enhancements by nearly constant increments per cyclopropyl moiety introduced[62]. That similar modes of conjugation are present in the mono-, di- and tricyclopropyl carbocation implicates the bisected structure.

Methyl substituent effects on the rates of cyclopropylcarbinyl solvolysis are evidence for symmetrical transition states.[63]

The rigid conformation of the adamantane nucleus allows quantitative evaluation of the stereoelectronic requirements of cyclopropylcarbinyl cations. Adamantyl derivatives 17 which incorporate the cyclopropylcarbinyl system in the perpendicular conformation exhibit rates of solvolysis retarded by inductive interaction[64]. Solvolysis rates for those derivatives 18 which incorporate a bisected cyclopropyl interaction are predictably fast.



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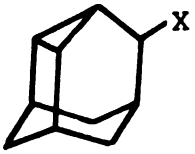

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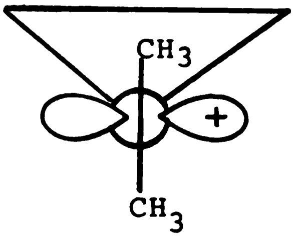
Pittman and Olah[66] have shown that the two methyl groups in the 2-cyclopropyl-2-propyl cation 19 are not equivalent. The result is consistent with the bisected structure.



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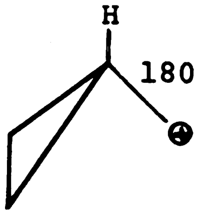
Although nmr examination of methyl- and dimethylcyclopropyl carbocations has established their preferred bisected geometry[66-68], Olah suggests a bridged structure for the parent system[67,68] based on a discrepancy between observed and calculated (estimated from a classical model) ^{13}C chemical shifts. The methylene carbon shift calculated for a set of rapidly equilibrating classical ions is 115 ppm (TMS) as compared to the observed value of 57.6 ppm (TMS).

Brown and Kelly have measured the ^{13}C-'H coupling constants for cyclopropyl, methylcyclopropyl and dimethylcyclopropyl carbocations. The methine coupling constant for the parent compound 20 is in accord with the formulation



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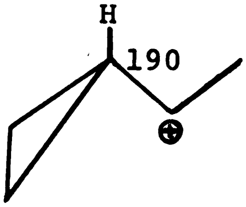

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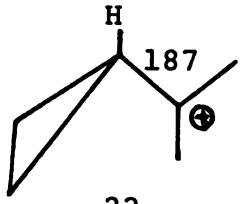

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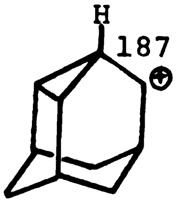

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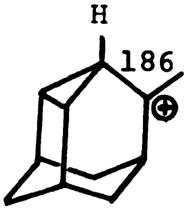

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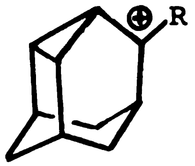
as an equilibrating set of ions with the bisected arrangement. An increase in the ^{13}C-^{1}H coupling constant postulated[70] to accompany an increase in angle strain (arising from σ-bridging) is not observed.

Examination of the pmr and cmr parameters of 8,9-dehydro-2-adamantyl cations **25a** and **25b** by Olah and coworkers[70]

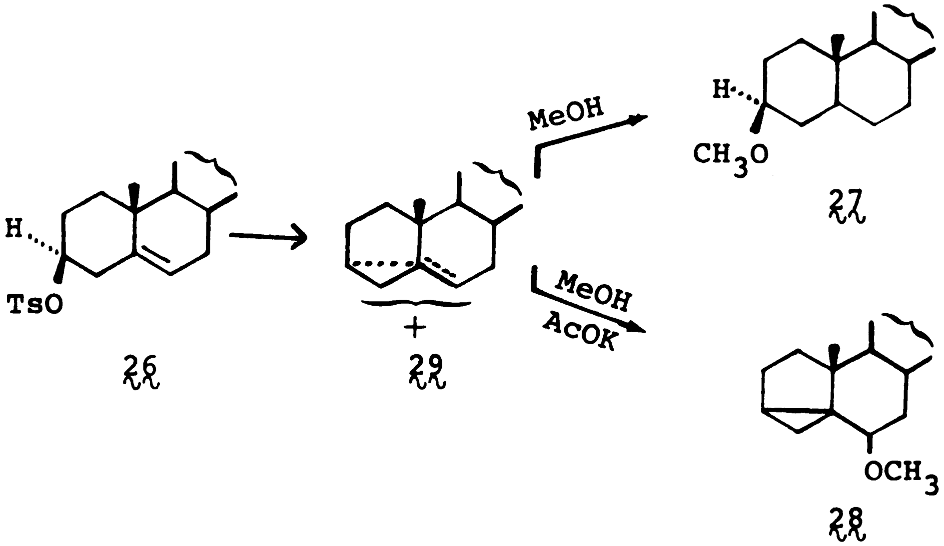


25a: R = H
25b: R = CH_3

suggests the absence of nonclassical participation in these compounds.

Allyl Carbocations

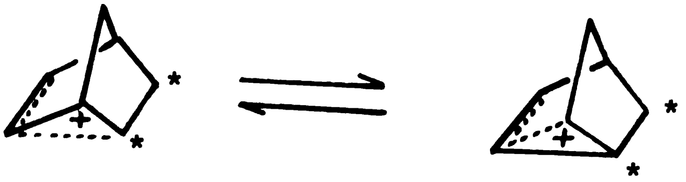
In 1946 Shoppee[71] had demonstrated that cholesteryl chloride undergoes nucleophilic substitution with complete retention of configuration while cholestanyl chloride reacted with inversion as expected. To explain these results he invoked the participation of the adjacent double bond. Later Winstein and Adams[72] found that solvolysis of cholesteryl tosylate 26 in pure methanol leads to the formation of methyl ether 27 with retention of configuration while



the same reaction buffered with potassium acetate yields cyclopropylcarbinyl ether 28. The formation of the two products and the stereochemical outcome was explained in terms of nonclassical ion 29 as an intermediate in the reaction.

Solvolysis of exo or endo-5-norbornenyl halides or sulfonates and deamination 5-norbornenyl-amines with nitrous acid yield nortricyclic derivatives[73]. Roberts postulates a hyperconjugative, homoallylic interaction to account for the products and/or the rates of solvolysis.

The relatively incomplete scrambling of ^{14}C- labeled dehydronorbornyl derivatives during solvolysis leads Roberts to pose the intermediacy of a pair of slowly equilibrating enantiomorphic cations **30** and **31**[74].



30 **31**

However, Roberts explains the formolysis of allylcarbinyl tosylate (in 1964), which formylizes 3.7 times faster than *n*-butyl tosylate, in terms of the formation of "bicyclobutonium ion" intermediates[75].

The most dramatic example of homoallylic assistance is found in the acetolysis of *anti*-7-norbornenyl tosylate. This compound reacts faster than its saturated analog by a factor of 10^{11} and reacts with complete retention of configuration[76,77].

The occurence of a sharp break in the ρ-σ^+ plot for a series of 7-aryl-7-norbornenyl *p*-nitrobenzoates indicates a dramatic change in the mechanism of solvolysis[78]. A similar plot of aryl-substituted saturated analogues is linear over the same range of σ^+ values. The results are consistent with the onset of neighboring group participation by the π-electrons of the norbornenyl double bond. Furthermore it provides evidence that participation can be a linear function of electron demand.

A plot of the pmr parameters reported by Winstein[79] versus σ^+ constants (Figure 5) shows similar results for 7-aryl-7-norbornenyl cations with the exception that the break occurs at a different value of σ^+. Thus solvolysis rates and nmr parameters of carbocations in super acid correlate qualitatively with Brown σ^+ constants although not quantitatively.

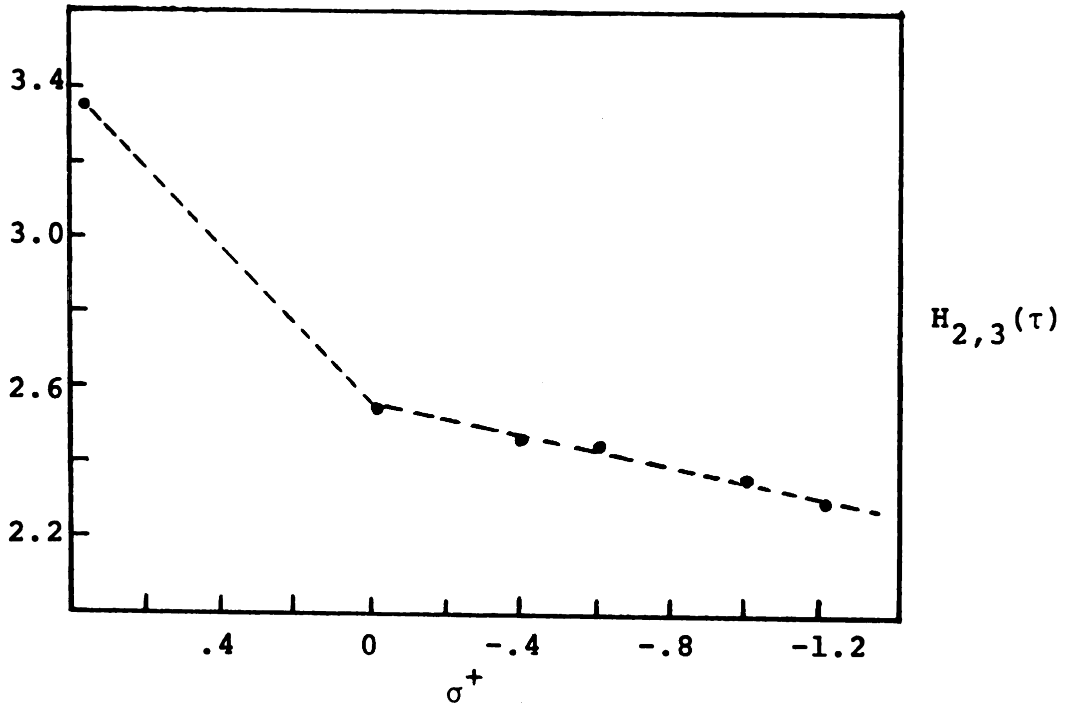


Figure 5. Graph of H(2),(3) Chemical Shift in 7-Aryl-7-Norbornenyl Cations vs. σ^+ Constants[78].

The nature of participation in a homoallyl system is much like that apparent in cyclopropylcarbinyl. In fact ab initio molecular orbital calculations indicate that all forms of the homoallyl cation collapse without activation energy to a bisected cyclopropylcarbinyl cation[80].

Much effort has been directed toward structure elucidation of various carbocations by means of nmr spectroscopy. Many of the structural conclusions drawn from these studies have rested on chemical shift comparisons to known models.

The recent development of Fourier transform (FT) nuclear magnetic resonance spectroscopy has made cmr studies both practical and routine. Extension of this spectroscopic method to the area of stable carbocation chemistry has led to a better understanding of the structural geometry and electronic characteristics or organic ions. Spiesecke and Schneider[81] were the first to show the validity of a charge density to cmr chemical shift relationship which is contingent upon related structures having the same geometry. Cmr spectroscopic studies of classical benzylic cations[82] also reveal that cmr parameters reflect the positive charge density. Hammett-type relationships of these cmr parameters (to Brown σ^+ constants) roughly parallel those observed in solvolytic rate studies of the same systems.

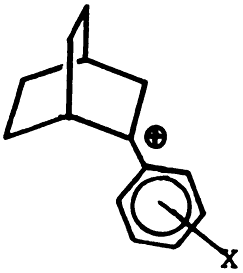
Thus, it seems reasonable that our extension of the extrathermodynamic relationship of cmr parameters of stable carbocations to the area of nonclassical cations may reveal changes in geometry and charge distribution in these ions with increasing electronic demand. Moreover, comparing our data to those observed in solvolytic studies of the same systems could provide information concerning the nature of those transition states involving stabilization from distant π- and σ- electrons. We have prepared several series of aryl-substituted polycyclic cations to explore these possibilities.

RESULTS

Experimental procedures for the preparation of the cations for this study are described in the experimental section. The carbon-13 nmr spectra were obtained by Fourier transform (FT) spectroscopy. Coupled spectra were obtained by the off-resonance decoupling technique.

That ^{13}C parameters are invariable with temperature is essential to the interpretation of our data. In temperature studies involving equilibria among aryllbicyclooctyl cations (vide infra), we find that the cmr chemical shifts of cations **32a**, **b** and **33a**, **b** are constant over an 85 degree temperature range (-60° to +25°), and that those of cations **32c**-**e** and **33c**-**e** are constant over 60 degrees (-60° to 0°).

A series of 2-aryl-2-bicyclo [2.2.2] octyl cations **32a**-**e** were generated from the precursor 2-aryl-2-bicyclo-[2.2.2] octanols in FSO_3H at -78°.



32a-**f**

The C-13 chemical shifts for these cations are reported at -30°. Cation **32f** (X = CF_3) was prepared from the corresponding alcohol in FSO_3H-SbF_5-SO_2ClF at -110° and its spectrum determined at -90°. Viscosity line broadening and coincidental interference from the $^{13}CD_3$ resonance lines of the d_6-acetone lock preclude accurate evaluation of the $C_{6,8}$ chemical shift of **32f**. The cmr data are summarized in Table 2. The five carbon-13 resonance lines assigned to the bicyclo [2.2.2] octyl skeletal carbons not including C_2 reflect the symmetry present in these cations.

We have been unsuccessful in our attempts to prepare 2-(<u>bis</u>-3,5-trifluoromethyl) phenyl-2-bicyclo [2.2.2] octyl cation **32g**. Careful ionization of alcohol **34** in FSO_3H-SbF_5-SO_2ClF at -120° provided a spectrum, recorded at -100°, which is consistent with skeletal rearrangement to the 6-aryl-6-bicyclo [3.2.1] octyl cation **33g**. Wolf has

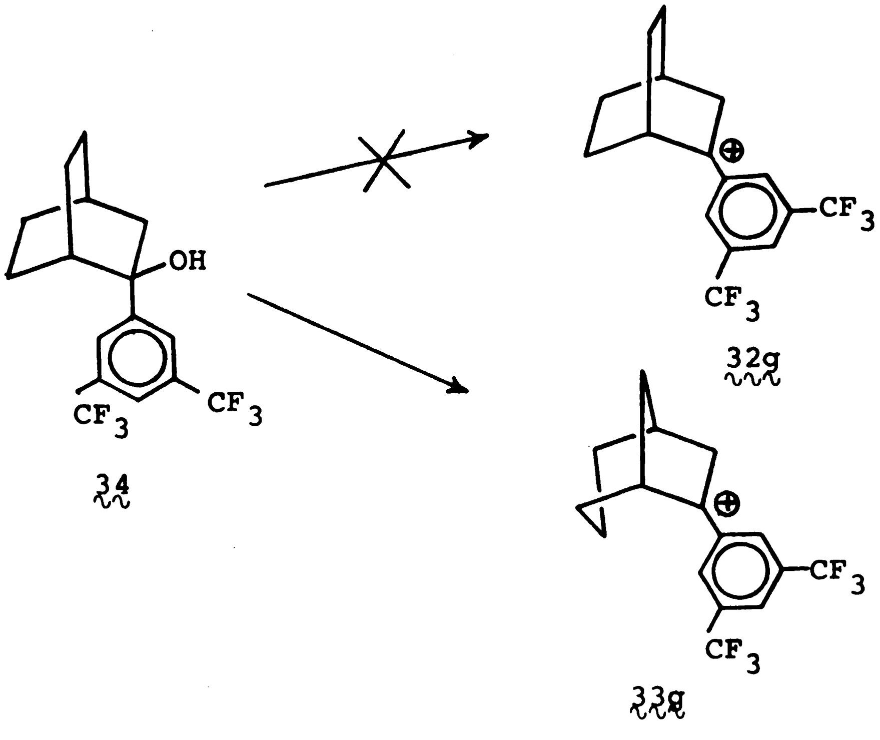


Table 2. ^{13}C Chemical Shifts for 2-Aryl-2-Bicyclo [2.2.2] octyl Cations (33a-f)[a]

Derivative	$C^+(s)^b$	$C_1(d)$	$C_3(t)$	$C_4(d)$	$C_{5,7}(t)$	$C_{6,8}(t)$
a) p-$C_6H_4OCH_3$	237.7	42.9	41.0	28.9	24.7	26.9
b) 3,4-$C_6H_3(CH_3)_2$	259.7	46.1	45.1	30.5	24.8	28.2
c) p-C_6H_4F	266.4	47.4	47.0	30.9	24.9	28.5
d) C_6H_5	272.9	48.3	47.7	31.3	24.6	28.9
e) p-C_6H_4Br	270.2	48.2	48.1	31.5	24.8	29.0
f) p-$C_6H_4CF_3$	285.4	52.5	51.5	33.3	24.6	∿29

a) Parts per million relative to external TMS.

b) Multiplicity.

previously reported that careful ionization of 34 or its olefin analog gives a mixture of cations at -100°, 32g being the minor component[82]. Perhaps the length of time required to perform the cmr experiment coupled with poor resolution of the spectra at these low temperatures prevented our detecting cation 32g.

The propensity for rearrangement of the bicyclo [2.2.2]-octyl skeleton allowed spectral determination of 6-aryl-6 bicyclo [3.2.1] octyl cations 33c-g to be made. The ease of this skeletal reorganization was heavily dependent on the electron withdrawing ability of the aryl substituent. The extent of rearrangement is summarized in Table 3. Warming cations 32a and 32b in the nmr probe to +25° failed to induce rearrangement. At temperatures above +25° decomposition precluded rearrangement.

Consequently, cations 33a and 33b were prepared from their alcohol precursors in FSO_3H at -78°. Their spectra were recorded at -30°. The ^{13}C nmr parameters of the cationic center, C_5 and C_7 for these ions are presented in Table 4.

We cannot assign ^{13}C chemical shifts for all the bicyclo-[3.2.1] octyl skeletal carbons with assurance since appropriate models are not available for comparison. Nonequivalence of the *ortho* and *meta* carbons of the aryl group for ions 33-*p*-OCH_3 and 33-di-CH_3 suggests that rotation about the C-C^+ bond is slow on the cmr time scale. This is true for the other *p*-OCH_3 and di-CH_3 phenyl, and some aryl substituted

Table 3. Extent of Rearrangement to 6-Aryl-6-Bicyclo [3.2.1] octyl Cations 33a-g.

	Derivative	Percent Conversion	Temperature (°C)
a)	$\underline{p}$-$C_6H_4OCH_3$	0%	+25°
b)	3,4-$C_6H_3(CH_3)_2$	0%	+25°
c)	$\underline{p}$-C_6H_4F	50%	0°
d)	C_6H_5	60%	0°
e)	$\underline{p}$-C_6H_4Br	70%	0°
f)	$\underline{p}$-$C_6H_4CF_3$	∿100%	-61°
g)	3,5-$C_6H_3(CF_3)_2$	∿100%	-90°

Table 4. Selected ^{13}C Chemical Shifts for 6-Aryl-6-Bicyclo [3.2.1] octyl Cations (**33a**-**g**)^{a}.

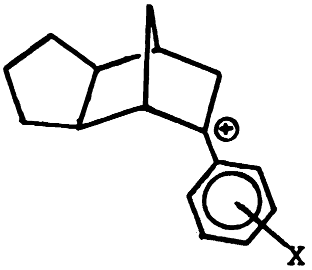
	Derivative	C^+	C_5	C_7
a)	*p*-$C_6H_4OCH_3$	235.5	49.8	44.5
b)	3,4-$C_6H_3(CH_3)_2$	256.4	53.1	47.5
c)	*p*-C_6H_4F	262.3	55.2	49.1
d)	C_6H_5	268.6	55.7	49.6
e)	*p*-C_6H_4Br	265.4	55.9	49.6
f)	*p*-$C_6H_4CF_3$	279.5	59.1	52.5
g)	3,5-$C_6H_3(CF_3)_2$	282.2	60.8	53.6

a) Parts per million relative to external TMS.

polycyclic cations in this study as well.

2-Arylnorbornyl cations 34b-g were prepared from their corresponding alcohols in FSO_3H at -78°. Their spectra were taken at -30°. Pmr spectra for these ions 34a-g have previously been reported by Wolf and Farnum[45]. The cmr spectrum for 34a has been obtained by Lam[83]. The ^{13}C parameters for the skeletal norbornyl carbons are listed in Table 5. Assignments of chemical shifts were made by comparison with those found for 2-norboranone and with the aid of coupled spectra.

A series of 8-aryl-8-tricyclo [$5.2.1.0^{2,6}$] decyl cations 35b-g were generated from their alcohol precursors in FSO_3H at -78°. Cation 35a was prepared under identical conditions via ionization of its precursor olefin. It is not possible to assign ^{13}C chemical shifts to all the skeletal carbons with assurance (particularly C_3, C_4, C_5 on the trimethylene bridge) in these cations. However, those ^{13}C parameters which are pertinent to this study are unambiguously assigned (Table 6).



35a-g

Solutions of 2-arylnorbornen-2-yl cations 36c-e, generated by dissolving "Freon-11" solutions of the corresponding

Table 5. ^{13}C Chemical Shifts for 2-Aryl-2-Bicyclo [2.2.1] heptyl Cations (**34a-g**)[a]

	Derivative	C^+(s)	C_1(d)	C_3(t)	C_4(d)	C_6(t)	C_7(t)	C_5(t)
a)	*p*-$C_6H_4OCH_3$[b]	232	53.5	47.2	----	----	----	----
b)	3,4-$C_6H_3(CH_3)_2$	251.5	56.6	49.1	39.0	33.1	41.4	26.0
c)	*p*-C_6H_4F	255.8	58.9	50.4	39.8	33.9	41.8	25.8
d)	C_6H_5	260.8	59.6	50.8	39.9	34.4	41.7	25.7
e)	*p*-C_6H_4Br	258.5	59.8	50.9	40.1	34.4	41.9	25.8
f)	*p*-$C_6H_4CF_3$	265.3	64.4	52.7	41.8	37.1	42.1	25.4
g)	3,5-$C_6H_3(CF_3)_2$	263.3	67.2	53.2	42.3	38.8	42.3	25.4

a) Part per million relative to external TMS.

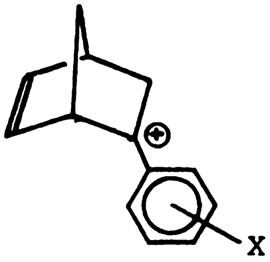
b) Data from Bing Lam, M.S. Thesis, Michigan State University.

Table 6. Selected ^{13}C Chemical Shifts for 2-Aryl-*exo*-5,6-Trimethylene-2-Norbornyl Cations (**35a-g**)[a].

Derivative	$C^+(s)$	$C_1(d)$	$C_3(t)$	$C_6(d)$
p-$C_6H_4OCH_3$	231.9	56.3	45.4	48.8
3,4-$C_6H_4(CH_3)_2$	250.4	60.2	48.6	50.9
p-C_6H_4F	255.0	62.4	49.9	52.0
C_6H_5	260.4	63.2	50.6	52.7
p-C_6H_4Br	258.2	63.6	50.9	52.9
p-$C_6H_4CF_3$	268.0	67.6	53.2	55.8
3,5-$C_6H_3(CF_3)_2$	268.4	69.5	54.1	57.2

a) Parts per million relative to external TMS.

alcohols in FSO_3H at -78°, are stable at low temperatures. The spectra of cations 36c, 36d and 36e were recorded at



36a-e

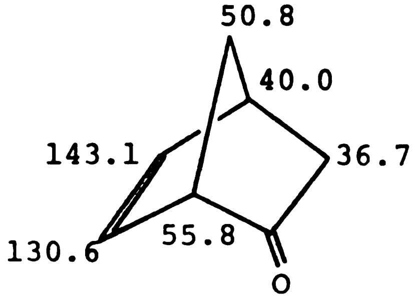
-30°, -60° and -80°, respectively. However, solutions prepared from alcohol precursors (36-p-OCH_3) and (36-di-CH_3) under identical conditions furnished spectra with a different pattern of absorptions. The spectra are devoid of any olefinic carbon atoms. An absorption appearing at δ ^{13}C 88.0 in both spectra, and which appears as a doublet in the proton-coupled cmr spectra, is consistent with addition of FSO_3H across the double bond. Perhaps conjugation of the olefinic moiety in cations 36c-e is sufficient to preclude addition of FSO_3H, where it is not in 36a,b.

Cations 36a and 36b were instead prepared at -78° employing a limited amount of FSO_3H diluted with SO_2ClF. Their spectra are reported at -30°. The cmr data for cations 36a-e are summarized in Table 7. Chemical shift assignments were made by comparison with those found for the parent ketone 37[86] and with the aid of off-resonance FT spectra.

Table 7. ^{13}C Chemical Shifts for 2-Arylnorbornen-2-yl Cations (**36a-e**)[a].

Derivative	C^+(s)	C_1(d)	C_7(t)	C_4(d)	C_5(d)	C_6(d)	C_3(t)
p-$C_6H_4OCH_3$	226.8	56.5	54.2	42.8	150.8	128.6	43.4
3,4-$C_6H_3(CH_3)_2$	242.6	59.7	55.1	43.3	156.8	126.5	46.4
C_6H_5	247.4	62.2	55.5	43.7	163.3	124.2	48.0
p-$C_6H_4(CF_3)$	234.4	65.8	54.7	44.0	180.4	117.8	48.5
3,5-$C_6H_4(CF_3)_2$	218.1	67.3	53.8	44.1	193.4	113.0	48.1

a) Parts per million relative to external TMS.



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3-Aryl-3-nortricyclyl cations 38a-f were prepared in the usual manner in FSO_3H at -78°. Cations 38a and 38b are reported at -30° while cations 38c-f are reported at -50°. The cmr data for these ions are compiled in Table 8.

Relatively minor differences in like-aryl carbon chemical shifts indicate that the extent of charge delocalization into the aromatic systems are similar within the series of polycyclic cations investigated. Typical aryl carbon chemical shifts are given in Table 9. In the case of the p-fluorophenyl derivatives long range ^{13}C-^{19}F coupling (4.3 Hz) to the cationic center is observed.

Table 8. ^{13}C Chemical Shifts for 3-Aryl-3-Nortricyclyl Cations (**38a**-**f**)^{a}.

Derivative	C^+(s)	$C_{1,6}$(d)	C_2(d)	C_4(d)	$C_{5,7}$(t)
p-$C_6H_4OCH_3$	234.8	43.2	33.7	38.8	38.5
p-$C_6H_4CH_3$	250.7	54.3	41.8	40.0	40.0
C_6H_5	257.1	61.3	47.0	40.5	40.8
m-C_6H_4Cl	258.3	68.1	52.1	41.2	41.7
p-$C_6H_4CF_3$	260.0	73.5	56.2	41.3	42.3
3,5-$C_6H_3(CF_3)_2$	258.5	80.5	61.2	41.9	43.1

a) Parts per million relative to external TMS.

Table 9. Typical Aryl Carbon Chemical Shifts in Aryl-Substituted Polycyclic Cations[a].

X	C_{para}	C_{ortho}	C_{meta}	C_{β}
p-OCH_3	181.9	143.7, 143.4	120.2, 118.8	131.8
p-CH_3	167.6	140.4, 140.2	134.0, 133.2	132.4
p-H	152.4	141.9, 141.1	132.6, 132.5	133.8
p-F	177.6 (288 Hz)[b]	146.9, 146.2 (14.9 Hz)	121.6, 120.5 (4.2 Hz)	131.1
p-Br	152.9	141.8, 141.1	136.5	132.5
p-CF_3	146.6	140.9 (br)	134.7	128.8 (br)

a) Parts per million relative to external TMS.

b) ^{13}C-F Coupling.

DISCUSSION

Graphs (Figures 6-11) correlating cmr chemical shifts are constructed from selected parameters found in Tables 2, 4-8. The following symbols will represent the various polycyclic cations in the figures below:

BCO [2.2.2] = 2-aryl-2-bicyclo [2.2.2] octyl cations.
BCO [3.2.1] = 6-aryl-6-bicyclo [3.2.1] octyl cations.
N = 2-aryl-2-norbornyl cations = 2-aryl-2-bicyclo [2.2.1] heptyl cations.
XTN = 2-aryl-5,6-*exo*-trimethylene-2-norbornyl cations.
NE = 2-arylnorbornen-2-yl cations.
NTC = 3-aryl-3-nortricyclyl cations = 3-aryl-3-tricyclo $[2.2.1.0^{2,6}]$ heptyl cations.

In their extensive pmr study revealing the nonlinear free energy behavior of 2-aryl-2-norbornyl cations, Wolf and Farnum[45] chose as their classical model the bicyclo-[2.2.2] octyl system. Indeed this system was known to have less tendency to exhibit those properties usually associated with σ-participation. Their study, however, was limited by rearrangement of the more electron demanding aryl-substituted cations ($\underline{p}$-CF_3, $\underline{m},\underline{m}'$-$(CF_3)_2$) in superacid media *via* successive Wagner-Meerwein and 7,2 hydride shifts.

Our cmr study of 2-aryl-2-bicyclo [2.2.2] octyl cations is limited by this same factor. The equilibrium among

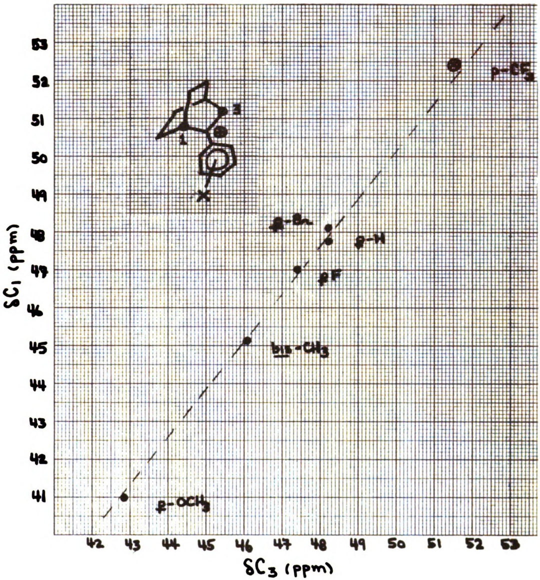


Figure 6. Graph of C(1) vs. C(3) Chemical Shifts in 2-Aryl-2-Bicyclo[2.2.2]octyl Cations 32a-f.

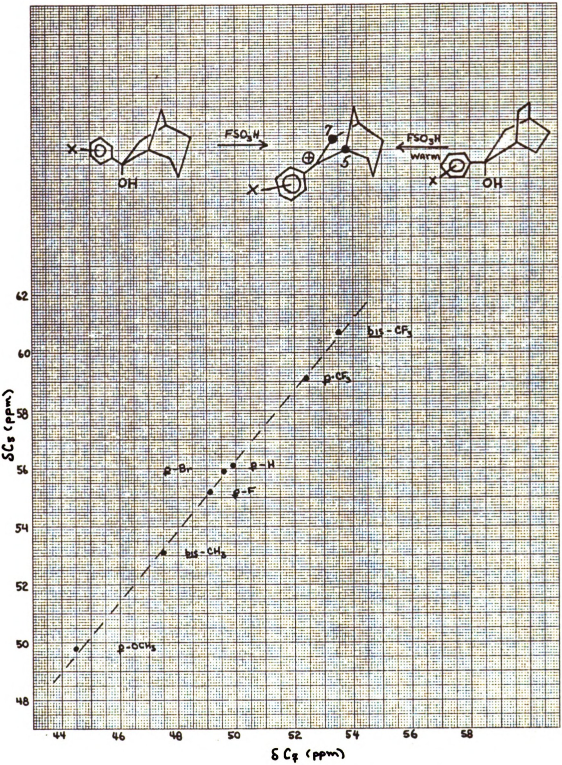


Figure 7. Graph of C(5) vs. C(7) Chemical Shifts in 6-Aryl-6-Bicyclo[3.2.1]octyl Cations 33a-g.

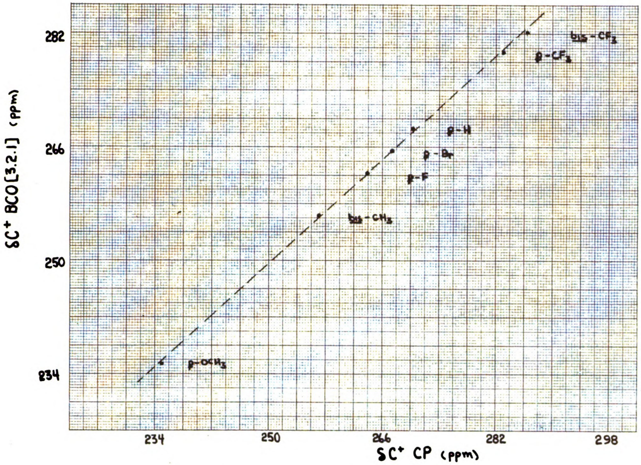


Figure 8. Correlation of 6-Aryl-6-Bicyclo[3.2.1]octyl and Arylcyclopentyl Carbocation Chemical Shifts.

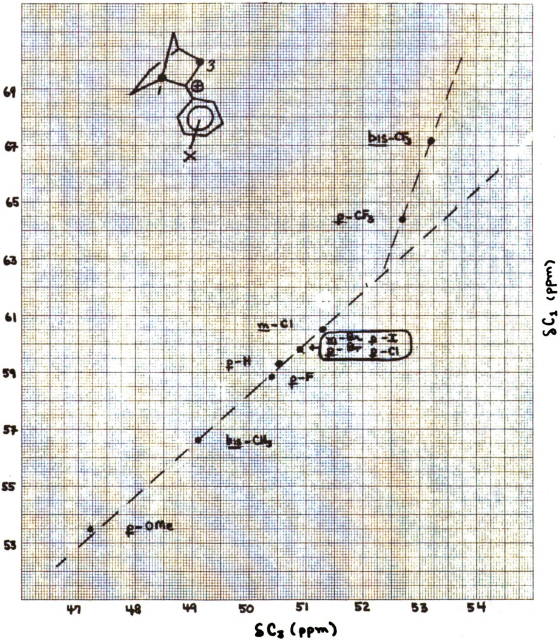


Figure 9. Graph of C(1) vs. C(3) Chemical Shifts in 2-Aryl-2-Norbornyl Cations 34a-g.

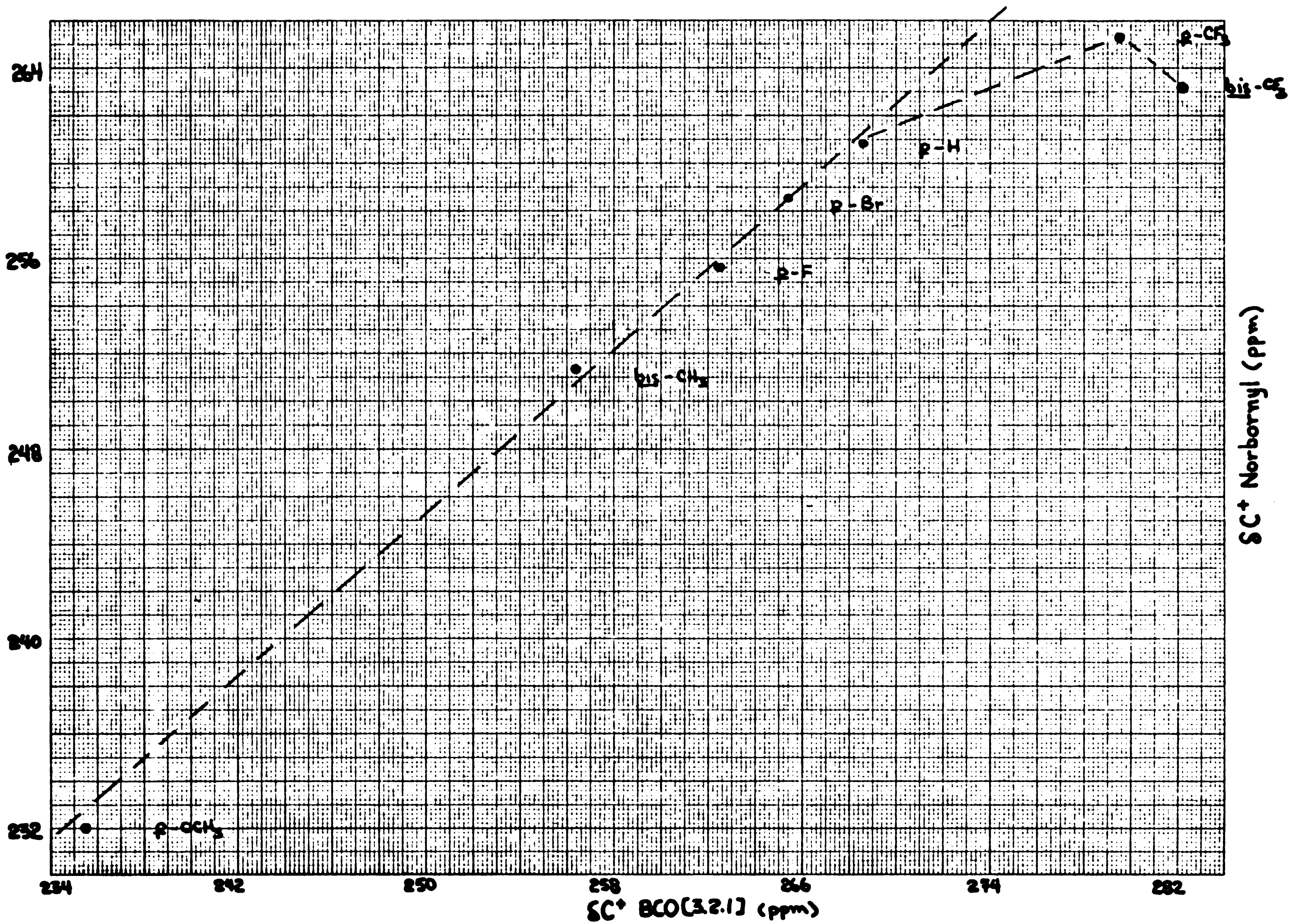


Figure 10. Correlation of 2-Aryl-2-Norbornyl and 6-Aryl-6-Bicyclo[3.2.1]octyl Carbocation Chemical Shifts.

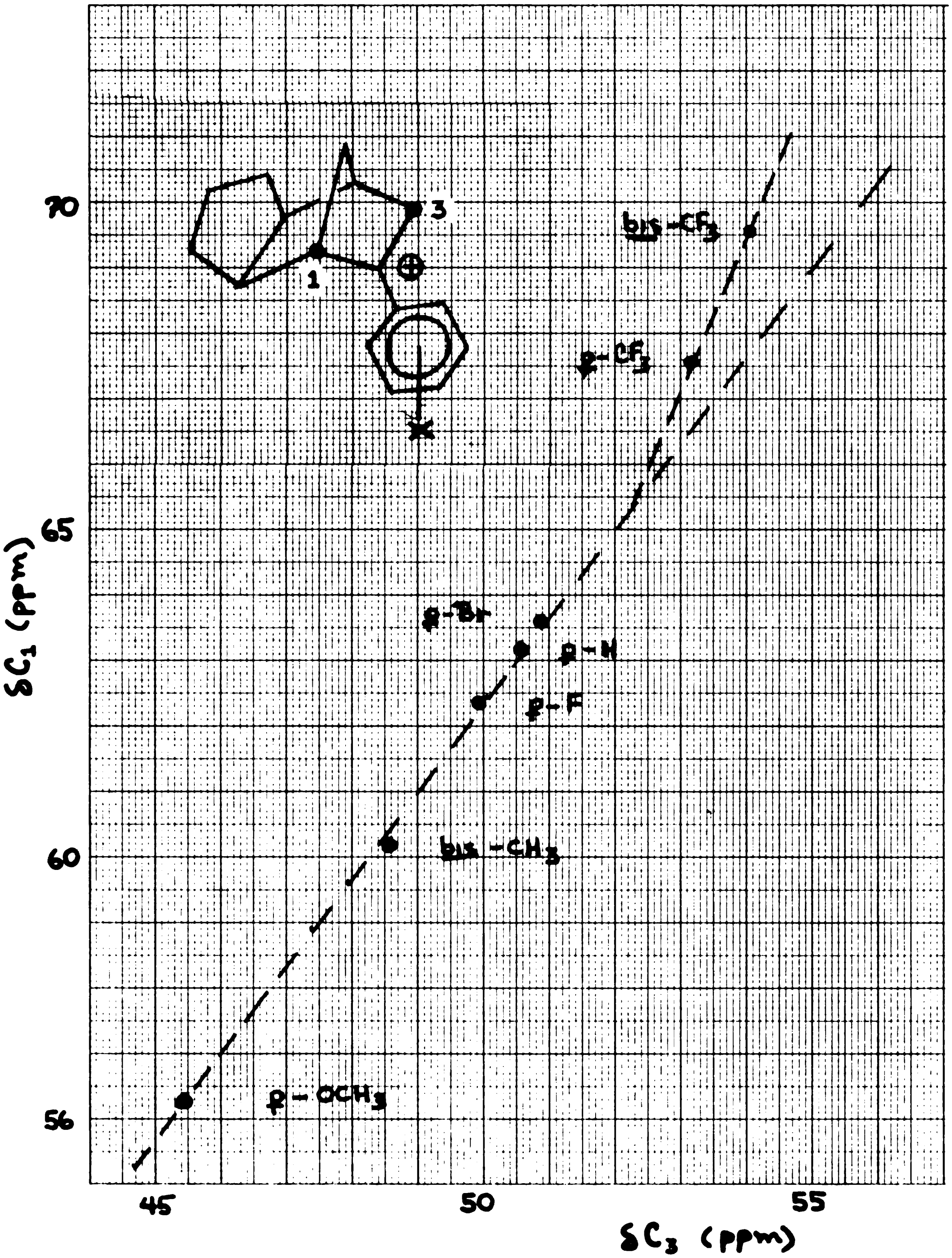


Figure 11. Graph of C(1) *vs.* C(3) Chemical Shifts in 2-Aryl-*exo*-5,6-Trimethylene-2-Norbornyl Cations **35a-g**.

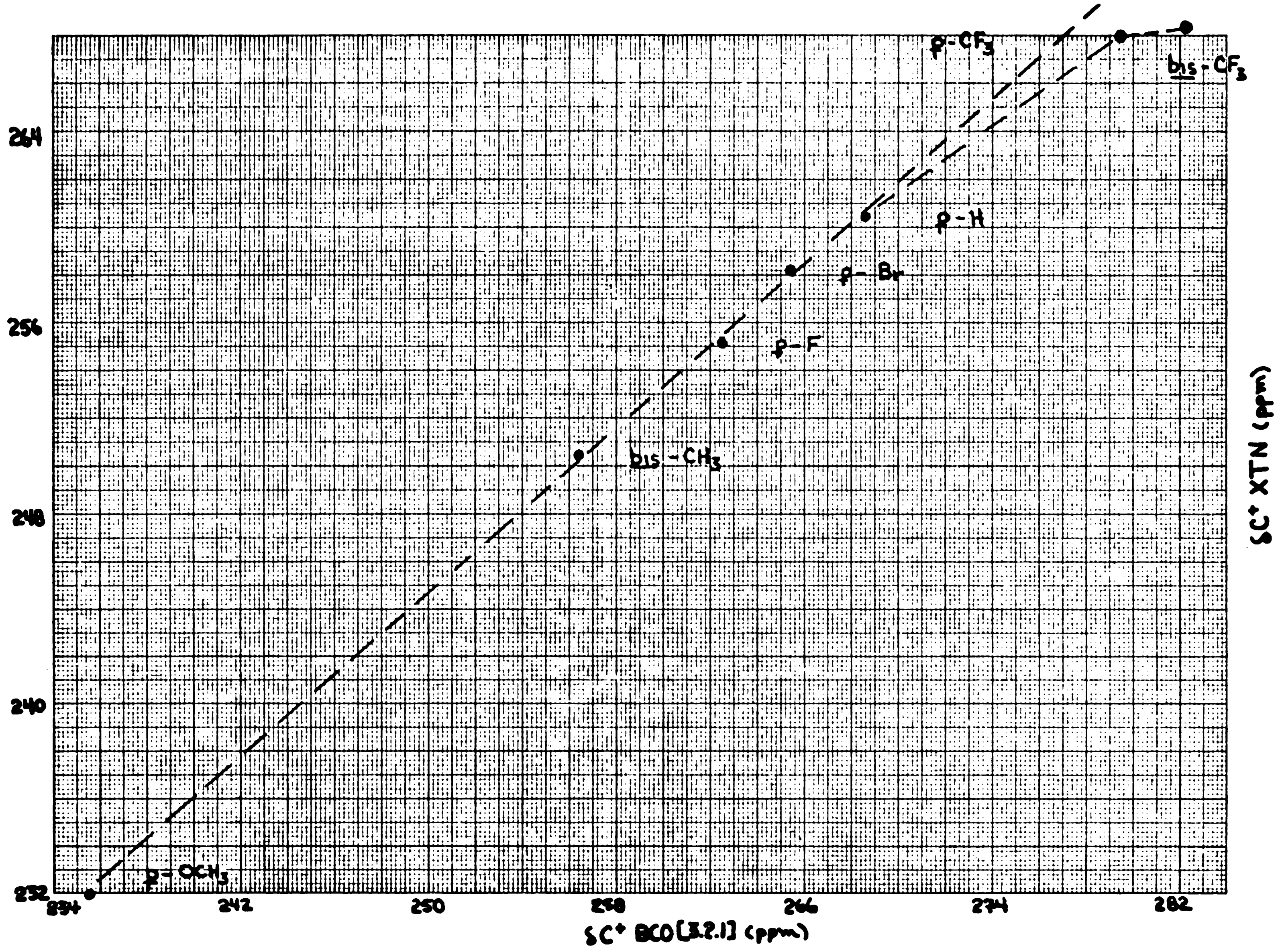


Figure 12. Correlation of 2-Aryl-exo-5,6-Trimethylene-2-Norbornyl and 6-Aryl-6-Bicyclo[3.2.1]octyl Carbocation Chemical Shifts.

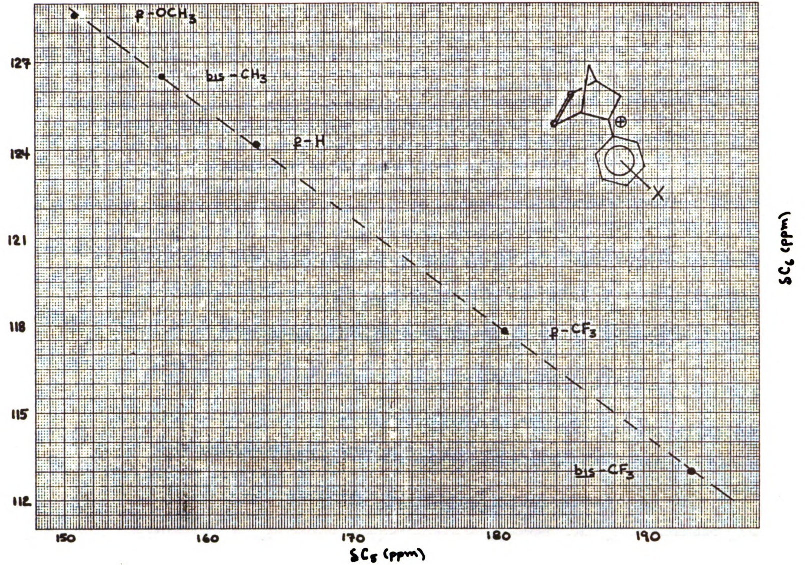


Figure 13. Graph of C(5) vs. C(6) Chemical Shifts in 2-Arylnorbornen-2-yl Cations 36a-e.

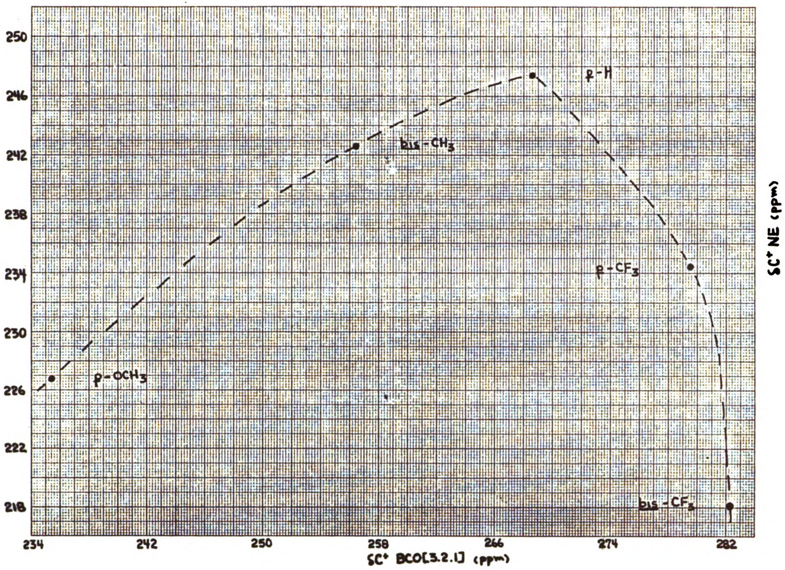


Figure 14. Correlation of 2-Arylnorbornen-2-yl and 6-Aryl-6-Bicyclo[3.2.1] Carbocation Chemical Shifts.

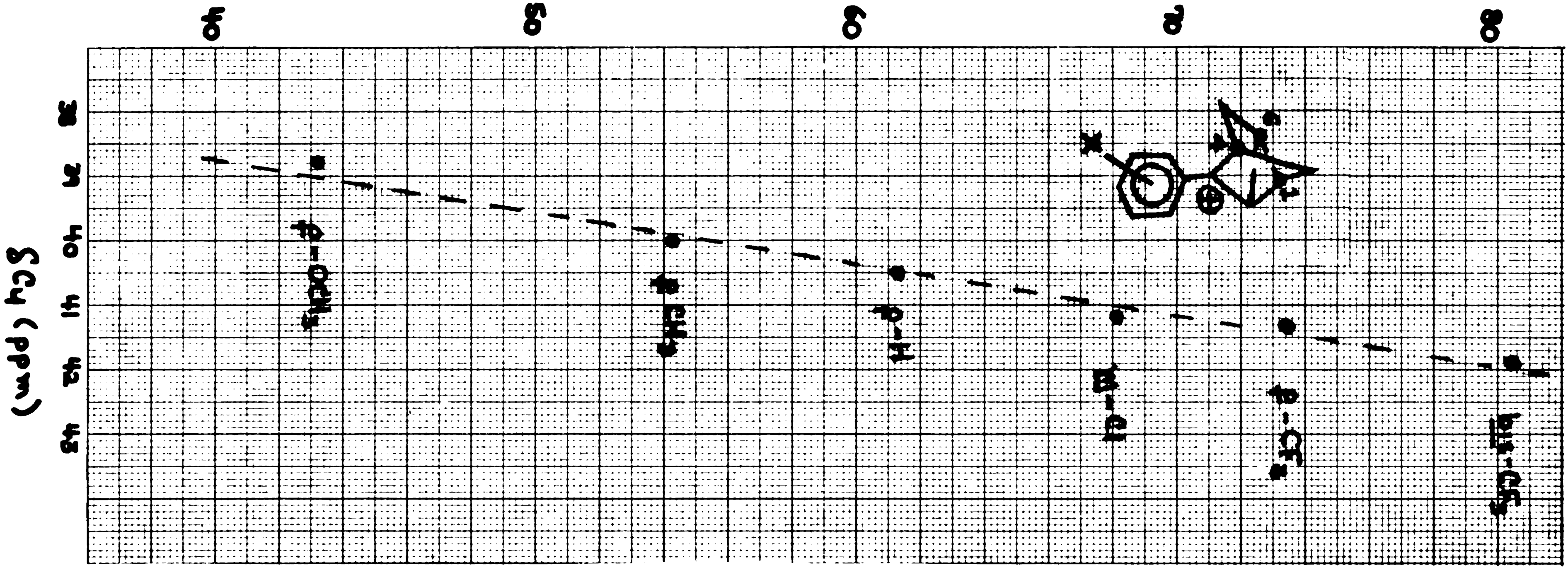


Figure 15. Graph of C(1), (6) *vs.* C(4) Chemical Shifts in 3-Aryl-3-Tricyclo $[2.2.1.0^{2,6}]$heptyl Cations 38a-f.

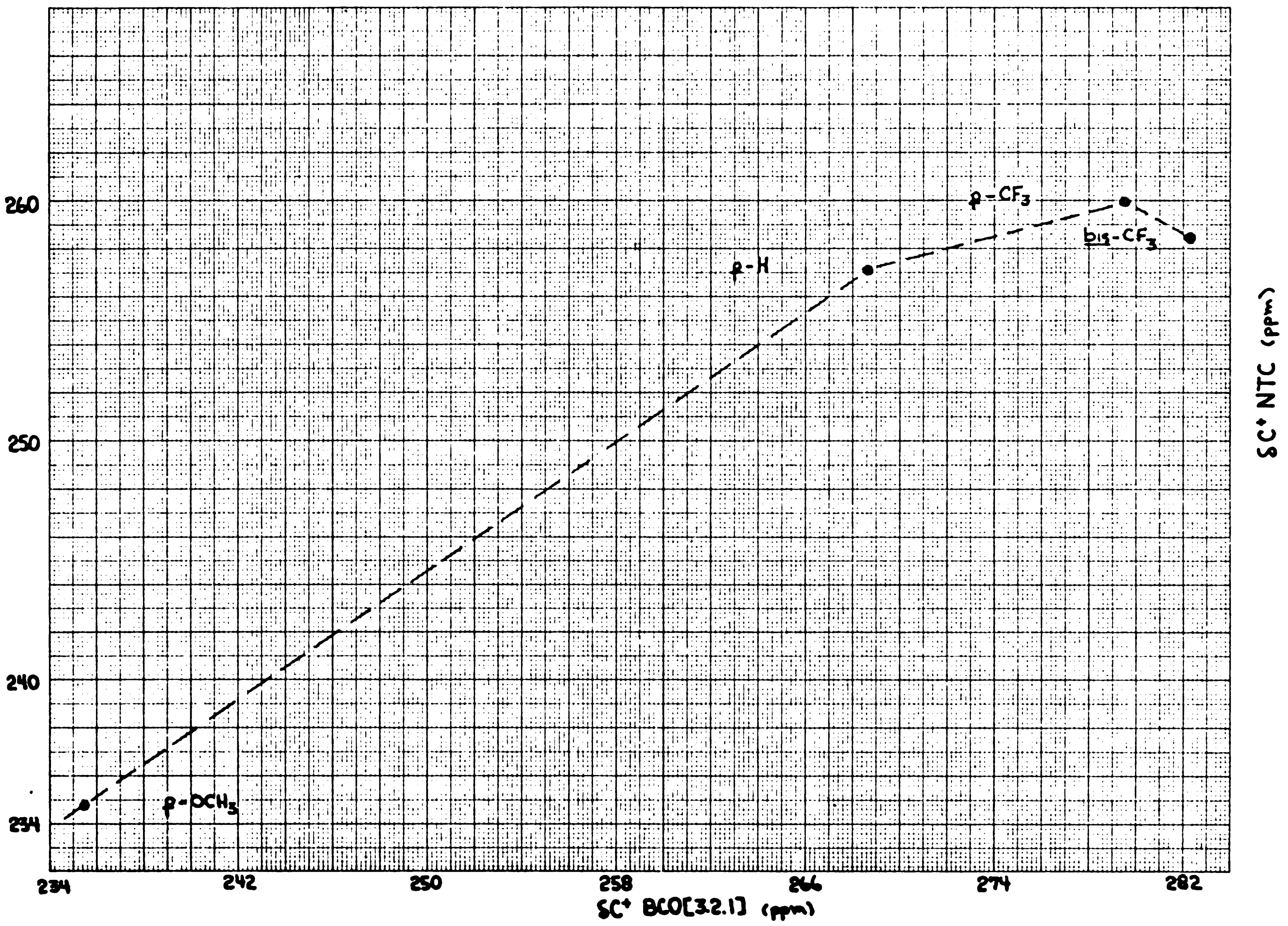
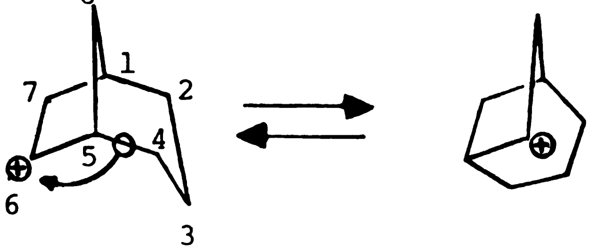


Figure 16. Correlation of 3-Aryl-3-Tricyclo[$2.2.1.0^{2,6}$] heptyl and 6-Aryl-6-Bicyclo[3.2.1]octyl Carbocation Chemical Shifts.

arylbicyclooctyl cations lies strongly in favor of the more stable 6-aryl-6-bicyclo [3.2.1] octyl cations. Rearrangement precludes our observing the *m*,*m*'-$(CF_3)_2$-phenyl substituted cation even at extremely low temperature. Even more disheartening, we find the cmr spectrum of cation 32f (*p*-CF_3) poorly resolved. Although a plot of C(1) versus C(3) chemical shifts is very closely linear throughout the limited range of aryl groups studied (Figure 6), our confidence in these data leaves much to be desired.

A study of 6-aryl-6-bicyclo [3.2.1] octyl cations 33a-g has distinct advantages: (1) They are by far the most stable among the equilibrating arylbicyclooctyl cations in superacid media[83] and thus are easily obtained. (2) Geometry about the carbocation center is similar to that of norbornyl. (3) Participation or 1,2-alkyl migration in the parent cation is degenerate as in the norbornyl cation.



A plot of the cmr chemical shifts of C(5) versus C(7) for cations 33a-g is linear throughout the range of aryl substituents studied (Figure 7). The ordering of points corresponds qualitatively to Brown σ^+ constants which reflect the ability of a particular aromatic substituent to lower the energy of the cation by inductive and resonance stabilization. Specifically, a decrease in the electron releasing capacity of an aryl substituent should result in a corresponding increase in charge density at C(6). Thus a deshielding of the C(5) and C(7) resonances derives from the increase in positive charge at C(6). For classical ions in which only α-inductive effects are transmitted along the chemical bonds one would expect to obtain a linear expression from a plot of the β-carbon parameters with increasing charge at C_α. Indeed this is precisely what we observe.

In Figure 8 the carbon-13 shifts for the carbocation center in the bicyclo [3.2.1] octyl cations are plotted against those in a series of arylcyclopentyl cations as determined by Chambers[88]. That a reasonably linear correlation is observed with such a well-established classical model confirms the classical nature of these bicyclic cations throughout the free-energy range studied.

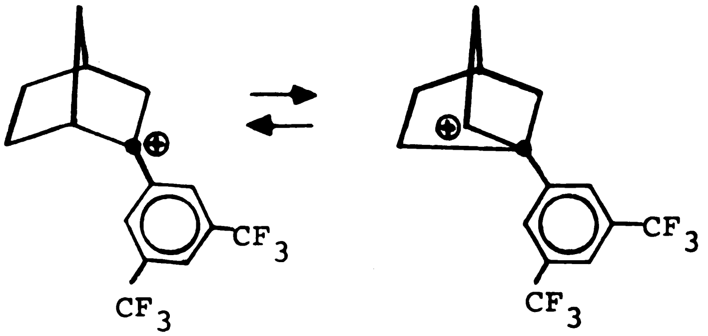
In contrast a nonlinear behavior in a graph of C(1) versus C(3) chemical shifts is observed in a corresponding series of 2-aryl-2-norbornyl cations (Figure 9). This plot shows marked deviation from linearity between the m-chloro- and p-trifluoromethylphenyl cations, i.e. σ^+ = 0.373-0.61.

It has been our assumption that an increase in positive charge at C(1) relative to C(3) would lead to a break in the plot. Thus we would expect the change in slope to arise from additional deshielding of C(1) with little change in C(3) chemical shifts. A comparison with the plot for the arylbicyclooctyl cations verifies that the deviation is caused primarily by a displacement of the chemical shift of C(1) rather than that of C(3).

Assuming that the C(3) chemical shifts of cations **34f** and **34g** are very similar to those expected if no break occurred, then the C(1) chemical shifts are off the line by 1.4 and 3.2 ppm, respectively. The abrupt deviation in our plot suggests that a change in the mechanism for charge transmission to C(1) has taken place. Furthermore, a dramatic reversal of slope to higher field is encountered when one plots the arylnorbornyl α-carbon chemical shifts against those of arylbicyclooctyl (Figure 10). The chemical shift of cation **34g** is shielded by 10 ppm relative to that assumed for linear behavior of the plot.

As we have already stated in the Introduction, the experimental observations supporting the intervention of a bridged-norbornyl cation have also been explained in terms of rapidly equilibrating, classical ions. Do rapidly equilibrating, classical norbornyl cations account for our results?

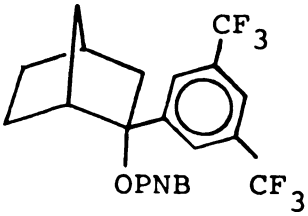
For systems undergoing rapid interconversion such as 34g ⇄ 34g', the central carbon (•C) will give rise to a single signal whose position is some average of the shieldings for the nonequivalent carbons in the individual ions. The value of this average signal will depend on the relative concentrations of the ions present at equilibrium. A σ-bridged species will exhibit a single signal for these carbons also, but its position may be expected to differ from that of the corresponding equilibrating system since the hybridization of these carbons will be altered[38]. We can determine the expected value of the average signal for



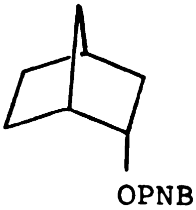
34g (•C = δ274) 34g' (•C ∿δ74)

•C for equilibrating ions 34g and 34g' by simply estimating their relative concentrations at equilibrium.

Assuming that the aryl group would not significantly alter the rate of a 3,2 hydride shift in 34g' relative to the known rate for norbornyl cation, Wolf was able to estimate that the ratio of 34g'/34g at +70° could not possibly be larger than 10^{-4}. Alternatively, a similar value can be derived from the solvolysis rate data obtained for the *m*,*m*'-$(CF_3)_2$-phenyl- and secondary-*endo*-norbornyl-*p*-nitrobenzoates, **39** and **40**, respectively[44]. One must, however, assume: (1) that the electronic demands in a developing cationic center during solvolysis are less than those in a fully developed cation, (2) that both compounds solvolyze



39



40

relative rates: 1 $\cong 10^{-4}$

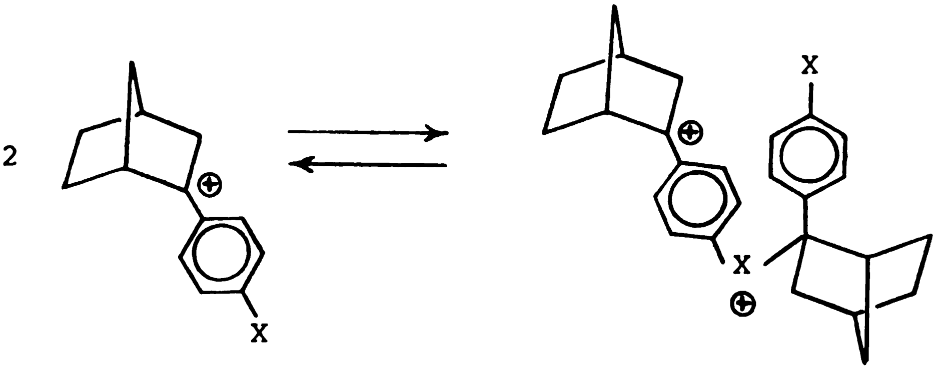
via classical transition states, (3) that **39** and **40** experience similar steric factors leading to their respective transition states during solvolysis, and (4) that introduction of an aryl substituent at C(1) does not drastically alter the stability (energy) of a classical 2-norbornyl cation. Considering these factors, then it seems intuitively reasonable that the difference in log k for solvolysis of compounds **39** and **40** is proportional to the energy difference between their classical transition-states, which should define the minimum energy between their respective classical ions. As models they provide a reasonable estimate (consider assumption (4)) for the maximum ratio of 34g'/34g present at equilibrium, *i.e.* $\lesssim 10^{-4}$.

Returning to Figure 10, we can estimate a •C(2) chemical shift of δ274 for classical ion 34g by merely extending the line which includes those well-behaved, aryl-substituted cations. We have intentionally underestimated the value for the •C(1) chemical shift expected for classical ion 34g', ∿δ74. Thus a 10^{-4} molar concentration present at equilibrium would lead to an upfield shift of approximately 0.02 ppm (200×10^{-4}) for the α-carbon in cation 34g. We, however, observe a 10 ppm shift to higher field. We therefore conclude that equilibrating classical cations cannot account for our data.

Our results seem consistent with the onset of C(1)-C(6) bond participation in those norbornyl cations more electron demanding than 2-*m*-chlorophenyl-2-norbornyl cation.

The pmr study of the arylnorbornyl and arylbicyclo-[2.2.2] octyl series revealed that an unusual effect was present in the *p*-halogen substituted cations causing their points to fall off the line. Farnum posed an equilibrium mixture of monomeric and dimeric cationic species (Figure 17) to account for their anomalous behavior, since large changes in the anisotropic environment associated with the proximity of an additional aryl moiety in dimeric species 34d should have a profound effect on the H(1) and H(3) chemical shifts. However, our dilution study[45] over a

50-fold change in concentration did not reveal any significant changes in the pmr spectrum (specifically in the H(1) and H(3) chemical shifts) of the p-iodophenylnorbornyl derivative.

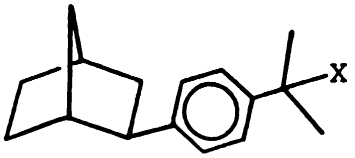


34d

Figure 17

Inspection of Figures 6, 7 and 9 reveals that the ^{13}C chemical shifts of the p-halogen derivatives are remarkably well-behaved. These results support the original hypothesis that a dimeric species is present, since magnetic anisotropy in the dimer would be expected to affect the ^{13}C chemical shifts proportionately much less than the ^{1}H shifts. Thus, although the relative magnitude of the magnetic effects is the same, the total range of ^{13}C chemical shifts caused by electronic factors is 30 times greater than that of protons[89]. Therefore large changes in anisotropy associated with the presence of 34d is expected to have relatively little effect on the chemical shifts of the β-carbons to the cation center.

In addition to σ-participation there is another mode of stabilization that is worthy of consideration. Traylor has proposed a hyperconjugative interaction of the C(1)-C(6) bond to account for the solvolytic behavior of the norbornyl system. Such "vertical stabilization"[59] of neighboring σ-bonds is available without changing the reactant geometry. In an attempt to demonstrate hyperconjugation Brown[90] observed a normal solvolysis rate for the *p-exo*-2-norbornylcumyl derivative **41** compared with those for appropriate models, *i.e.* *p*-isopropyl, *etc*.



41

However, the strained C(1) orbital which is predisposed to hyperconjugation with a vacant *p*-orbital at C(2) is insulated from the aryl *p*-orbitals by C(2) in compound **41**. Brown's study seems poorly designed.

Nonclassical participation results in a rehybridization about C(2) to allow σ-overlap with the C(6) orbital. The increase in C(2)-C(6) overlap should occur only at the expense of C(2) overlap with the aryl substituent. We feel that obstruction of aryl conjugation by σ-participation of the C(1)-C(6) bond is the source of the break in our plot of the arylnorbornyl β-carbon chemical shifts. On the other hand, hyperconjugation of the C(1)-C(6) bond does not require rehybridization at C(2) to be effective and should not interfere with aryl conjugation. If two independently stabilizing influences within the molecule operate harmoniously with one another, then we are convinced that a plot of C(1) versus C(3) chemical shifts would be a sum of two independent linear plots and thus would be linear over the entire free-energy range.

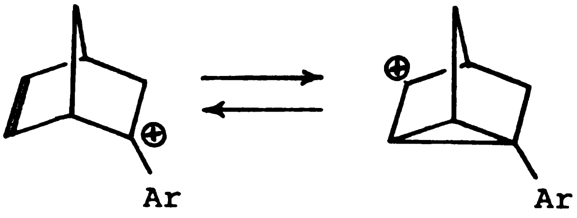
To explore the possibility of vertical stabilization we have prepared a series of 2-aryl-*exo*-5,6-trimethylene-2-norbornyl cations **35a-g**. In this tricyclic norbornyl analog the structural reorganization which accompanies nonclassical participation would force the trimethylene bridge into a pseudo-*endo* bonding relationship to the norbornyl skeleton. The five-membered ring formed by the trimethylene bridge must become distorted causing an increase in the free-energy of the system. The ratio of *exo*- and *endo*-5,6-trimethylene-2-norbornyl formate esters produced by the addition of formic acid to dicyclopentadiene under equilibrating conditions suggests that the *exo*-5,6-trimethylene derivative is ∼4.2 kcal more stable[100]. Hyperconjugative stabilization should not suffer from severe steric interactions, and consequently, should be a lower energy process.

Figures 11 and 12 contain in graphic form the pertinent information for the 2-aryl-5,6-trimethylene-2-norbornyl cations **35a-g**. The nonlinear behavior of the C(1) and

C(3) chemical shifts with increasing electron demand clearly demonstrates that we are observing the onset of charge leakage to C(1). Appreciable deviation from linearity occurs at a σ^+ value similar to that observed in a similar plot for the arylnorbornyl cations. Moreover, a change of slope to higher field occurs in the C_α chemical shift correlation with our bicyclooctyl standard. The qualitative similarity of both plots to those found for the arylnorbornyl cations leaves little room for doubt that we are indeed observing the onset of nonclassical participation, although quantitatively the change in slope is not nearly so dramatic in this case as in the norbornyl system. In the aryltricyclic cations the free-energy decrease associated with electron delocalization more than compensates for the small free-energy increase associated with minimal atomic movement causing steric interactions, although the overall free-energy associated with σ-participation is somewhat greater than that of the parent system. Our data suggest that with sufficient electron demand norbornyl-like systems require participation with atomic movement even in those cases in which an unfavorable energy change is associated with the movement of atoms.

Figures 13 and 14 provide in graphic form chemical shift correlations of C(5) <u>versus</u> C(6) and C_α <u>versus</u> those of our bicyclooctyl model, respectively, for a series of 2-arylnorbornen-2-yl cations **36a-e**. It is evident that the shielding of the C(6) resonance relates linearly to the deshielding effect found for C(5). The correlation implies that charge distribution placing charge at C(5) involves rehybridization of C(6) from sp^2 toward sp^3. Furthermore, the sharp break in the C(5) chemical shift-σ^+ plot (Figure 18) indicates that a dramatic change in the mechanism of charge transmission to C(5) occurs at the phenyl derivative ($\sigma^+ \sim 0$). The impressive turnabout in the C_α chemical shifts to higher field reflect this change, and at the same time, implicate rehybridization of the carbocation center with increasing electron demand.

The results are consistent with the formulation that minimal charge delocalization involving little structural and hybridizational change is followed by substantial electron supply involving dramatic changes in structure and hybridization under the increasing demand of the cationic center. These data, however, do not distinguish between nonclassical π-participation and rapidly equilibrating, classical ions 42 and 43, since it is most difficult to



42 43

determine the relative energies for these structurally different ions with certainty.

Brown points to the need for caution in extrapolating data from superacid media to solvolytic media[91]. We agree. However, to conclude that qualitative comparisons are therefore invalid seems unreasonable. A graph of the exo:endo rate ratio for a series of 2-arylnorbornen-2-yl p-nitrobenzoates as determined by Brown (Figure 19)[92] stands beside our plot of the C(5) chemical shifts of the 2-arylnorbornen-2-yl cations *versus* σ^+ constants (Figure 18). A plot of the olefinic pmr parameters of the 7-arylnorbornen-7-yl cations reported by Gassman and Ritchie[79] *versus* σ^+ constants is superimposed on a Hammett plot for a series of 7-arylnorbornen-7-yl p-nitrobenzoates[78] in Figure 20. At first glance our plot appears significantly different from that for the 7-norbornenyl cations.

Let us construct a hypothetical curve which depicts the change in the nmr parameters of a π-participating moiety over an extremely broad free-energy range (Figure 21). From left to right, initially the change in chemical shift is some linear function of electron demand. That a drastic change in slope occurs indicates the onset of participation involving the π-electrons causing a deshielding of the olefinic resonances. This portion of the curve should again be linear with respect to free-energy. Eventually electron donation saturates. Whereas Figure 20 is

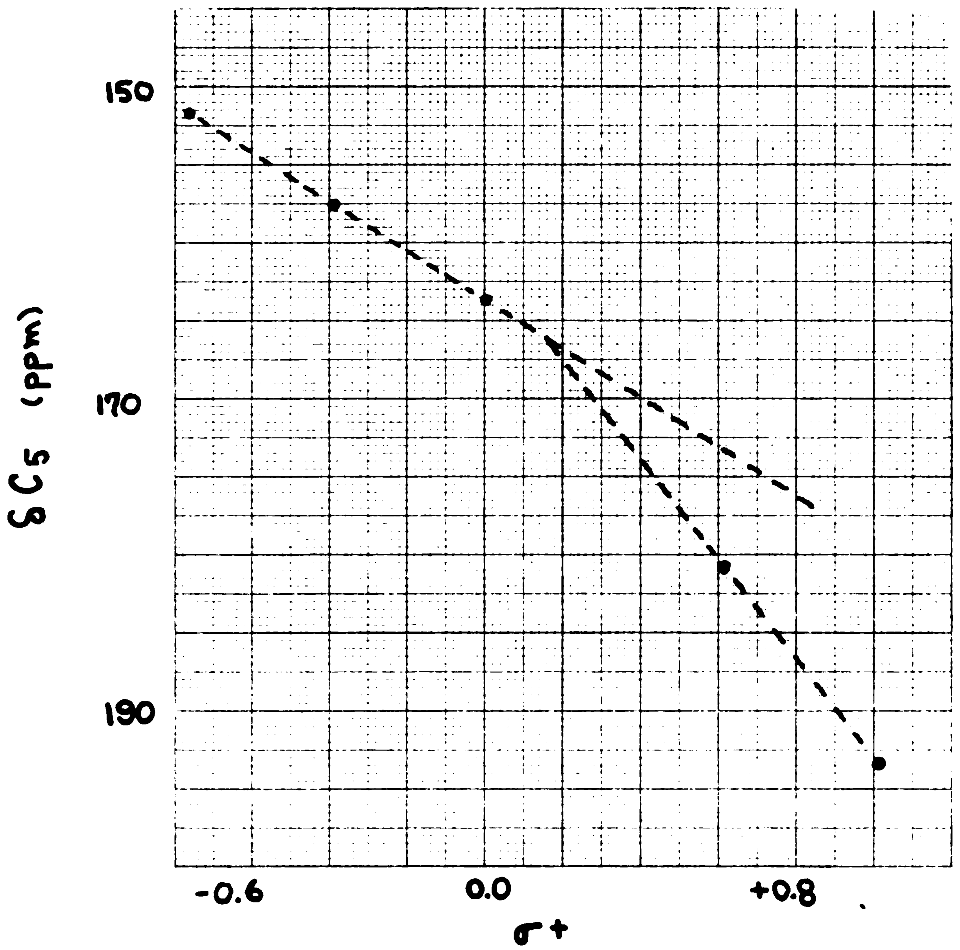


Figure 18. Graph of C(5) Chemical Shift in 2-Arylnorbornen-2-yl Cations <u>vs</u>. σ^+ Constants.

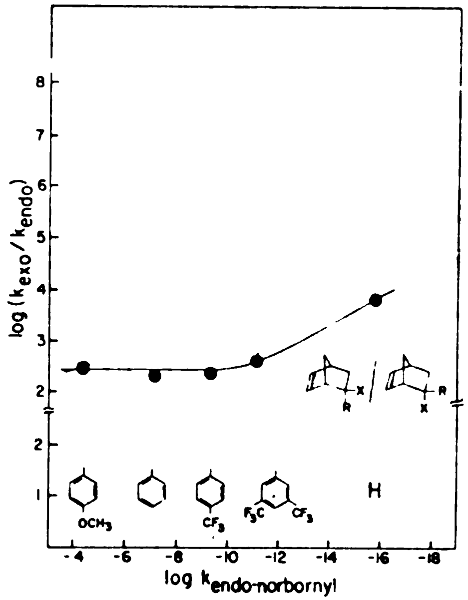


Figure 19. Effect of Increasing Electron Demand on Exo: Endo Rate Ratio in 2-Arylnorbornen-2-yl p-Nitrobenzoates[92].

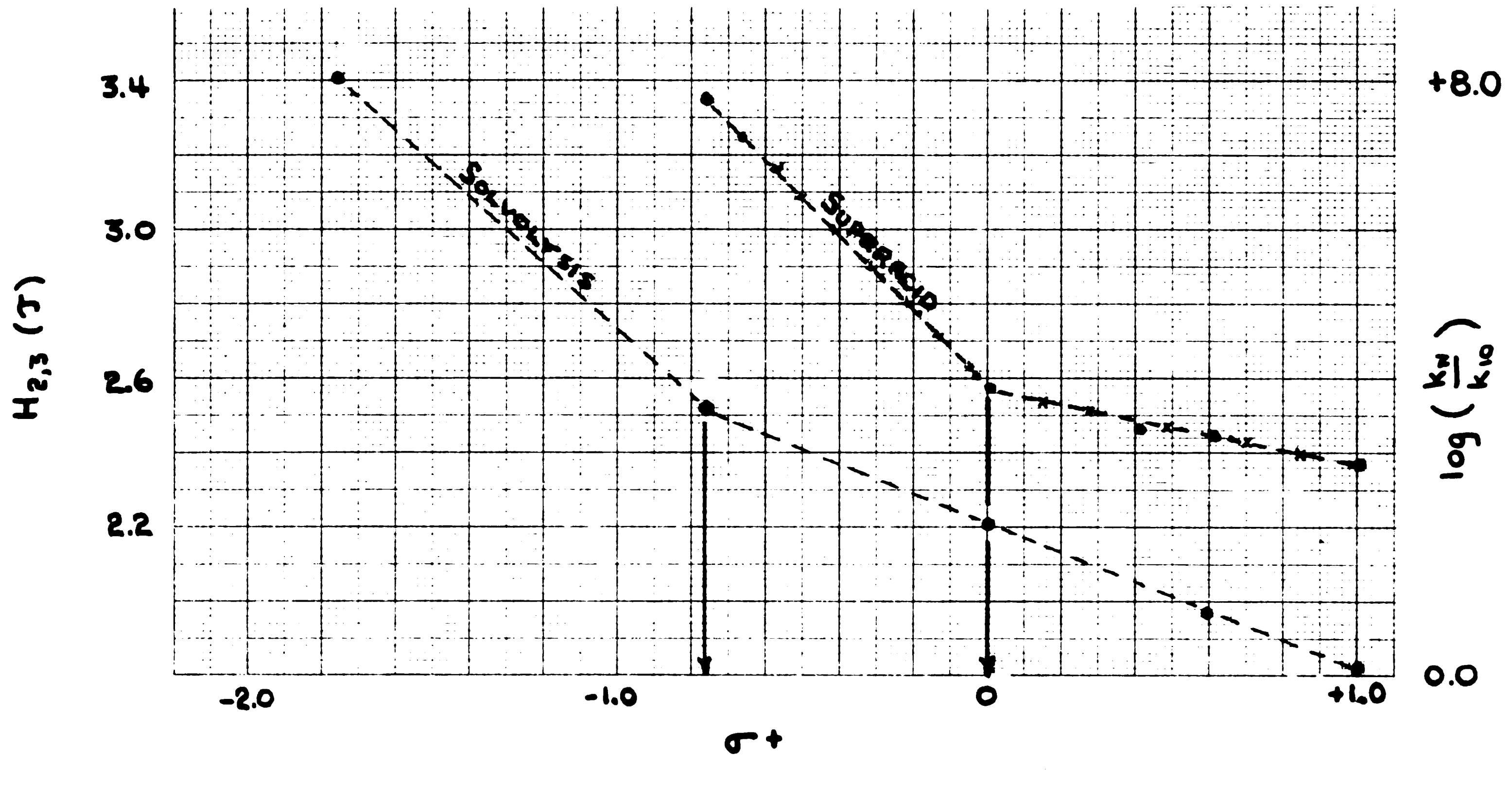


Figure 20. Graph of H(2),(3) Chemical Shift in 7-Arylnorbornen-7-yl Cations[79] and Log [Rate Constant] for a Series of 7-Arylnorbornen-7-yl p-Nitrobenzoates[78] vs. σ^+ Constants.

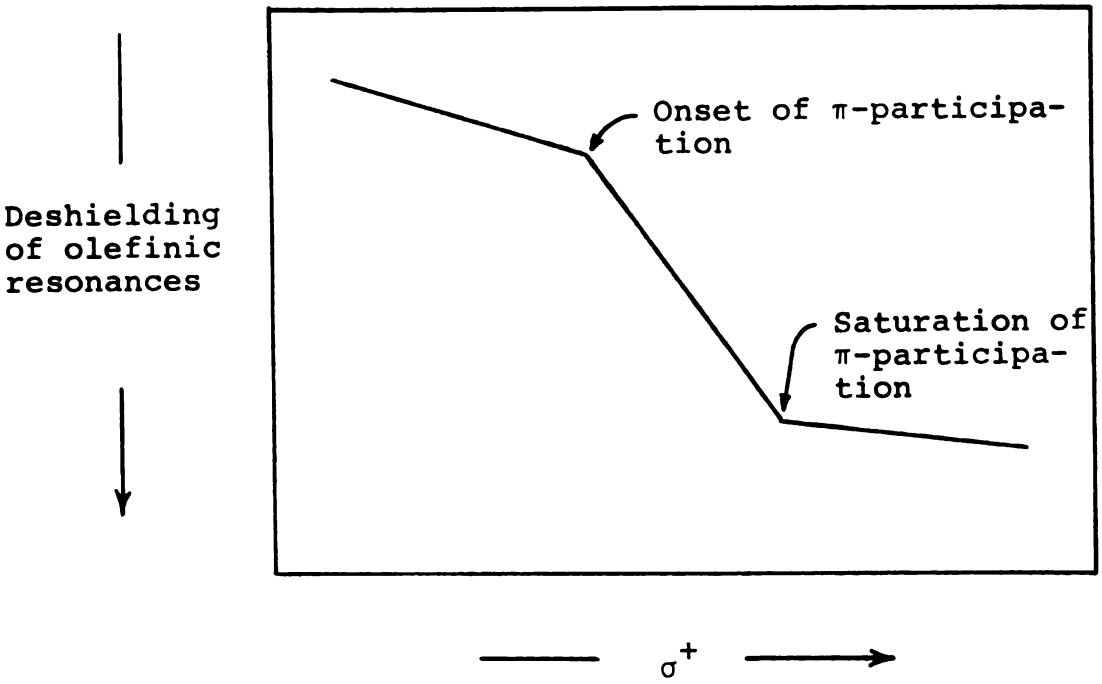


Figure 21. Dependence of nmr Parameters in the Presence of π-Participation With Increasing Electron Demand.

best described by the lower half of our hypothetical graph where saturation of π-participation occurs, Figure 18 is best represented by the upper half which reflects the onset of participation. Both figures, however, reveal the same general phenomenon, i.e. π-participation.

Compare Figures 18 and 19. The onset of participation is observed in the cations generated in FSO_3H before it is observed in solvolysis (σ^+ 0 vs. + 1.04). It seems reasonable that the more electron demanding cations would benefit more from electron donation from nearby π- and σ-bonds than their corresponding solvated transition states.

From the data presented in Figure 20, Gassman and Richey conclude that the 7-aryl group eliminates double bond involvement somewhat more readily in the cations than in the transition states for solvolysis, <u>i.e.</u> the onset of π-participation occurs much earlier in the solvolysis of the 7-norbornenyl derivatives than it does in the corresponding cations in superacid. However, if we now replot their data as a function of π-participation (Figure 22), it then becomes evident that their interpretation is incorrect. While the solvolysis results are indeed consistent with the onset of π-participation, their nmr observations are consistent with our aforementioned formulation that the break in the plot reflects a saturation phenomenon. The small changes in the H(2) and H(3) chemical shifts to aryl substitution in the region σ^+ 0.0 - 1.04 are consistent with a pair of classical cyclopropyl carbocation structures or their resonance hybrid having most of the positive charge concentrated at C(2) and C(3) and with little charge at C(7), since in these classical structures the pmr parameters should be affected insignificantly by long range inductive effects of the 7-aryl substituent. Furthermore, the pmr spectrum of the <u>p</u>-methoxyphenyl derivative suggests that it <u>approximates</u> a classical structure; therefore, the onset of π-participation must occur before (at a σ^+ value more negative than -0.78) the 7-<u>p</u>-methoxyphenylnorbornenyl cation.

In view of these findings let us re-examine both the

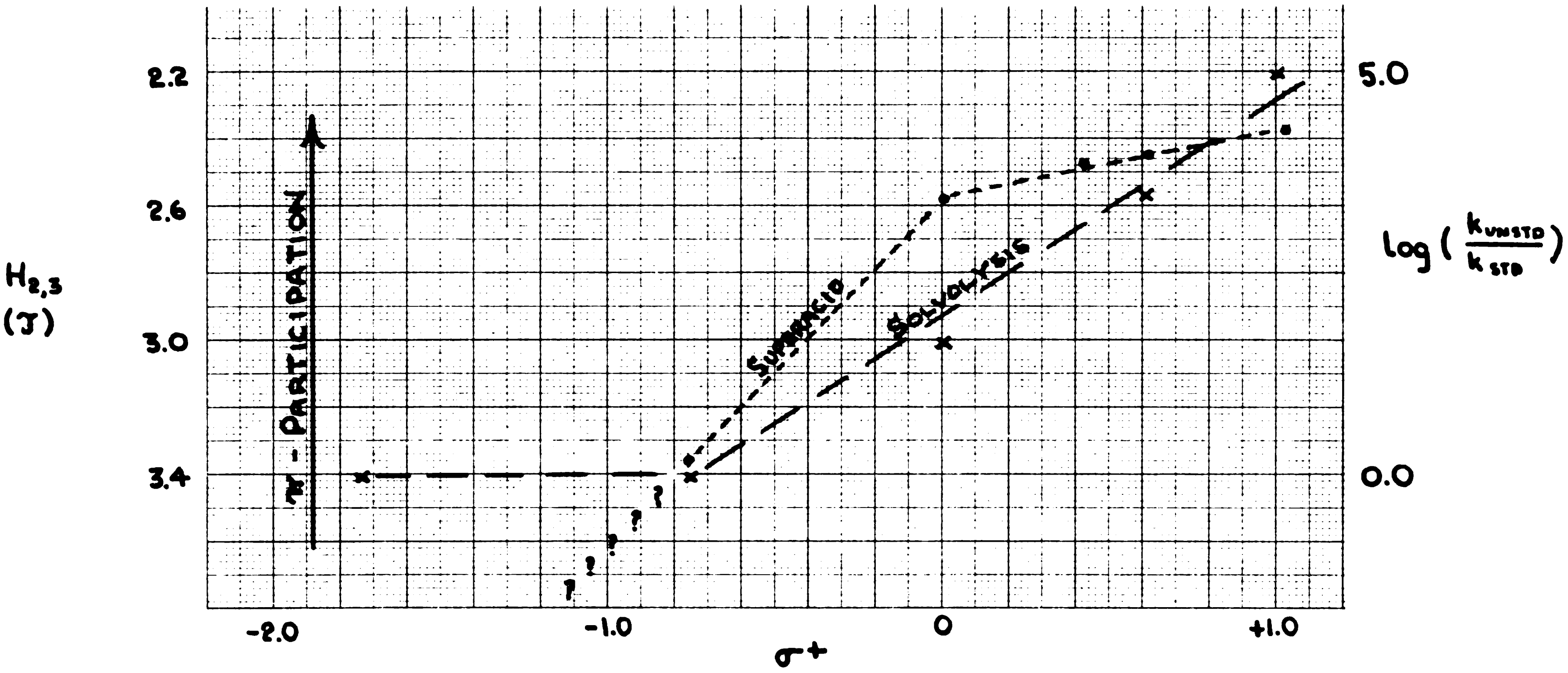


Figure 22. Figure 20 Replotted as a Function of π-Participation.

solvolysis and our carbocation studies of the arylnorbornyl derivatives. From his investigation of the solvolysis of arylnorbornyl derivatives, Brown has concluded that there is no evidence for nonclassical participation in the transition states[91]. Thus, a plot of the exo:endo rate ratio delineates a linear free-energy relationship over a range of aryl substituents from p-methoxyphenyl to m,m'-trifluoromethylphenyl, approximately 75% of the difference in activation energy between 2-p-methoxyphenylnorbornyl and norbornyl derivatives. In our plot of C(1) versus C(3) chemical shifts we find a deviation from linearity for the arylnorbornyl cations: The break in our plot occurs between the m-chloro- and p-trifluoromethylphenyl derivatives.

We have shown that for the cations we have studied the onset of participation in solvolysis lags behind that observed in the study of the cations in powerful acids. Indeed, we have shown that this observation finds a reasonable interpretation in the relative electron demands of the solvolysis transition state and the cation in weakly solvating media. Comparing the solvolysis and stable carbocation studies for the norbornyl and norbornenyl derivatives, we would expect the break in Brown's plot of the norbornyl derivatives to occur for those aryl substituents more electron withdrawing than the m,m'-trifluoromethylphenyl derivative. Therefore, we conclude that Brown's investigation is incomplete.

Our investigation of a series of 3-aryl-3-nortricyclyl cations 38a-f reveals that there is extensive charge delocalization into the cyclopropyl ring (Figure 15). While there is very little deshielding of the C(4) resonance, the C(1) and C(6) chemical shifts concurrently move to lower field with increasing electron demand.

A break in the C(1), (6) chemical shift - σ^+ relationship (Figure 23) occurs for those derivatives more electron demanding than the 3-phenyl-3-nortricyclyl cation. The change in slope reflects the inability of this cyclopropyl moiety to stabilize the more electron demanding cations as efficiently. Furthermore, the reversal in slope to higher field in a plot of the C_α chemical shifts versus

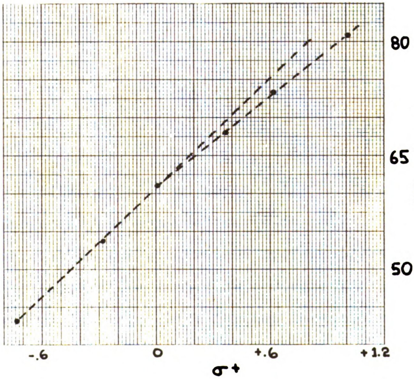
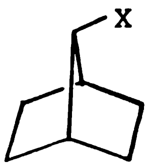
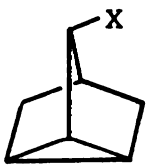


Figure 23. Graph of C(1),(6) Chemical Shift in 3-Aryl-3-Nortricyclyl Cations vs. σ^+ Constants.

those of our bicyclooctyl model (Figure 16) implies a changing geometry about the carbocation center. Are these results consistent with the presence of nonclassical participation involving a cyclopropyl ring in which atomic movement is repressed by the rigid nortricyclic skeleton?

Comparison of the relative rates of solvolysis for compounds 44 and 45 reveals a major contribution of the cyclopropylcarbinyl moiety[93]. However, the ability of a cyclopropyl ring to stabilize an incipient secondary carbocation by neighboring group participation can be demonstrated





	44	45
Relative Rate	1	$\sim 10^8$

by a rate difference of up to 10^{14}.[65,94-96] Again, can this discrepancy in enhanced rates of solvolysis reflect the inability of the constrained cyclopropylcarbinyl moiety to participate with atomic movement? The answer to this question must await further investigation.

EXPERIMENTAL

Melting points were taken on a Thomas Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Grating Infrared Spectrophotometer, Model 327B. They were calibrated with the 6.23 μ band of a polystyrene film reference. Mass spectral analysis were performed by Mrs. R. L. Guile at Michigan State University using a Hitachi Mass Spectrometer, Model RMU-6. Nuclear Magnetic Resonance (nmr) spectra were obtained using a Varian T-60 Spectrometer. The nmr data are presented in the following manner: δ 6.00 (2H, d, J=4). All spectra are recorded in delta (δ) units relative to tetramethylsilane (TMS). The multiplicities are s=singlet, d=doublet, t=triplet, q=quartet and m=multiplet; br=broad.

Carbon-13 Magnetic Resonance (cmr) spectra were obtained using a Varian CFT-20 Spectrometer equipped with a Varian V-6040 N-M-R Variable Temperature Controller. All chemical shifts are expressed in parts per million (ppm) downfield from external capillary TMS and d_6-acetone. Primary carbon-hydrogen coupling multiplicities were determined by the off-resonance decoupling (spin-tickling) procedure which does not allow determination of the size of coupling. The temperatures at which the various cmr spectra were recorded are accurate within ±3°C. Temperatures were calibrated for the probe, not for the sample.

Carbonium Ion Formation

The acidic medium was chosen to try to ensure complete ionization of the carbonium ion precursor yet to avoid unwanted side reactions. The carbonium ions were formed using either of the following methods:

(1) When FSO_3H was used the carbonium ion precursor was dissolved in $CFCl_3$ (Freon 11) and slowly added dropwise to the rapidly stirred acid at -78°C and maintained under a blanket of nitrogen.

(2) When a limited amount of FSO_3H was necessary, SbF_5 was added, or low temperatures were desired, SO_2ClF (50-85%) was employed as a cosolvent. The carbonium ion was prepared directly in the sample tube. Neat carbonium ion precursor was introduced to the ionizing medium (maintained at -78° or -110°) and carefully mixed with a glass rod until a uniform mush was produced. The sample was allowed to warm to the desired temperature. Additional SO_2ClF was added and the sample vibro-stirred until a homogeneous mixture resulted.

Carbonium Ion Precursors

The alcohols used in this study were prepared from the appropriate Grignard reagent and ketone; <u>i.e.</u> 2-norbornanone[97], bicyclo [2.2.2]-octan-2-one[98], tricyclo [2.2.1.$0^{2.6}$] hepta-3-one[99], tricyclo [5.2.1.$0^{2,6}$] deca-8-one[100], 2-norbornenone[97]. In every case a 10% molar excess of aryl bromide and a 20% molar excess of Magnesium metal was used with respect to ketone. Yields of aryl alcohols ranged from 60% to 95% based on ketone.

Tables 10-13 summarize the important physical and spectral data obtained for the compounds prepared.

IR and NMR Spectra

A. 2-Aryl-*exo*-5,6-Trimethylene-*endo*-2-Norbornanols.

p-$C_6H_4OCH_3$ (olefin): nmr (CCl_4) δ 6.70 (4H, AA'BB', $\Delta\nu$ = 31 Hz, J = 8.5 Hz) 5.91 (1H, d, J=3 Hz) 3.61 (3H, s) 2.77 (1H, m) 2.48 (1H, m) 2.20-.68 (10H, m); ir (neat) μ 6.20, 9.62.

3,4-$C_6H_3(CH_3)_2$: nmr (CCl_4) δ 6.90 (3H, m) 0.60-2.80 (15H, m) 2.12 (6H, br s); ir (neat) μ 3.04, 6.17, 9.59.

p-C_6H_4F: nmr (CCl_4) δ 7.17 (2H, m) 6.77 (2H, distorted t, J=9 Hz) 2.62 (2H, m) 2.10 (2H, d, J=4.5 Hz) 0.60-2.0 (11H, m); ir (nujol) μ 2.98, 6.17, 9.58.

p-C_6H_4Br: nmr (CCl_4) δ 7.24 (4H, AA'BB', $\Delta\nu$ ∿0 Hz, J=9 Hz) 0.60-2.86 (15H, m); ir (neat) μ 3.04, 6.24, 9.89.

p-$C_6H_4CF_3$ nmr (CCl_4) δ 7.23 (5H, s) 0.60-3.0 (15H, m); ir (KBr) μ 2.98, 6.14, 8.92.

3,5-$C_6H_4(CF_3)_2$: nmr (10% $CDCl_3/CCl_4$) δ 7.80 (2H, br s) 7.61 (1H br s) 0.60-3.0 (15H, m); ir (KBr) μ 3.02, 6.14, 8.88.

Table 10. Preparation of 2-Aryl-*exo*-5,6-Trimethylene-*endo*-2-Norbornanols.

Derivative	Molecular Formula	bp or sp*	mp	Mass Spectra	
				m/e (Calc.)	m/e (Found)
p-$C_6H_4OCH_3$**	$C_{17}H_{20}O$	100° at 0.1 mm	----	240	240
3,4-$C_6H_3(CH_3)_2$	$C_{18}H_{24}O$	180° at 0.1 mm	----	256	256 241 (P-15) 238 (P-18)
p-C_6H_4F	$C_{16}H_{19}FO$	150° at 0.1 mm	58-60°	246	246 228 (P-18)
p-C_6H_4Br	$C_{16}H_{19}BrO$	170° at 0.1 mm	----	306,308	306,308 288,290 (P-18)
C_6H_5	$C_{16}H_{20}O$	75° at 2 mm	69-70°	228	228 210 (P-18)
p-$C_6H_4CF_3$	$C_{17}H_{19}F_3O$	----	79.5-80.5°	296	296 278 (P-18) 277 (P-19)
3,5-$C_6H_3(CF_3)_2$	$C_{18}H_{18}F_6O$	----	121.5-122°	364	364 346 (P-18) 345 (P-19)

*Sublimation point **Olefin

Table 11. Preparation of 2-Arylnorbornen-2-ols.

Derivative	Molecular Formula	bp or sp*	mp	Mass Spectra	
				m/e (Calc.)	m/e (Found)
p-$C_6H_4OCH_3$	$C_{14}H_{16}O_2$	121° at 0.1 mm	35-38°	216	216 198 (P-18)
3,4-$C_6H_3(CH_3)_2$	$C_{15}H_{18}O$	120° at 0.1 mm	-----	214	214 196 (P-18)
C_6H_5	$C_{13}H_{14}O$	92° at 0.1 mm	-----	186	186 120 (P-66)
p-$C_6H_4CF_3$	$C_{14}H_{13}F_3O$	98° at 0.1 mm	56-57°	254	254 188 (P-66)
3,5-$C_6H_3(CF_3)_2$	$C_{15}H_{12}F_6O$	82° at 0.1 mm	58-60°	322	322 303 (P-19)

*Sublimation point.

Table 12. Preparation of 3-Aryl-3-Tricyclo [2.2.1.0^{2,6}] heptanols.

Derivative	Molecular Formula	bp or sp*	Mass Spectra		
			mp	m/e (Calc.)	m/e (Found)
$\underline{p}$-$C_6H_4OCH_3$	$C_{14}H_{16}O_2$	110° at 0.1 mm	83-84°	216	216 215 (P-1)
$\underline{p}$-$C_6H_4CH_3$	$C_{14}H_{16}O$	111° at 0.1 mm	61-62.5°	200	200 185 (P-15)
C_6H_5	$C_{13}H_{14}O$	100° at 0.1 mm	-----	186	186 185 (P-1)
$\underline{m}$-C_6H_4Cl	$C_{13}H_{13}ClO$	90° at 0.1 mm	94.5-95°	220,220	220,222 185,187 (P-35) 183,185 (P-37)
$\underline{p}$-$C_6H_4CF_3$	$C_{14}H_{13}F_3O$	122° at 2 mm	84-85°	254	254
3,5-$C_6H_3(CF_3)_2$	$C_{15}H_{12}F_6O$	131° at 0.1 mm	102-103.5°	322	322 303 (P-19)

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*Sublimation point.

Table 13. Preparation of 6-Aryl-6-Bicyclo [3.2.1] octanols.

Derivative	Molecular Formula	bp or sp*	mp	Mass Spectra m/e (Calc.)	Mass Spectra m/e (Found)
p-$C_6H_4OCH_3$	$C_{15}H_{20}O_2$	138° at 0.1 mm	38-40°	232	232
3,4-$C_6H_3(CH_3)_2$	$C_{16}H_{22}O$	130° at 0.1 mm	-----	230	230 215 (P-15)

*Sublimation point.

C_6H_5: nmr (CCl_4) δ 6.90-7.45 (5H, m) 2.47-3.02 (1H, br m) 2.24 (1H, m) 0.90-2.10 (13H, complex); ir (nujol) μ 3.97, 6.23, 8.87.

B. 3-Aryl-3-Tricyclo [2.2.1.$0^{2,6}$] heptanols.

p-$C_6H_4OCH_3$: nmr (CCl_4) δ 6.85 (4H, AA'BB', Δν = 34 Hz, J = 9 Hz) 3.68 (3H, s) 2.11 (1H, dd, J = 10, 1.5 Hz) 1.82 (1H, s) 1.76 (1H, m) 0.90-1.40 (5H, m); ir (nujol) μ 2.99, 6.16, 9.68.

p-$C_6H_4CH_3$: nmr (CCl_4) δ 7.00 (4H, AA'BB', Δν 17 Hz, J = 7 Hz) 2.26 (3H, s) 2.13 (1H, br d, J ∿ 10 Hz) 1.78 (2H, m) 1.0-1.42 (5H, m); ir (neat) μ 2.93, 6.15 6.60, 9.34.

C_6H_5: nmr (CCl_4) δ 7.16 (5H, m) 2.15 (1H br d, J = 10 Hz) 1.77 (2H, m) 1.01-1.46 (5H, m); ir (neat) μ 2.95, 6.19, 9.38.

m-C_6H_4Cl: nmr (20% $CDCl_3/CCl_4$) 7.28 (1H, m) 7.10 (3H, m) 1.70-2.12 (3H, m) 1.00-1.45 (5H, m); ir (nujol) μ 2.97, 6.21, 6.32, 9.33.

p-$C_6H_4CF_3$: nmr (CCl_4) δ 7.41 (4H, s) 2.18 (1H, d, J = 10 Hz) 1.78 (2H, m) 1.05-1.55 (5H, m); ir (nujol) μ 3.03, 6.16, 9.38.

3,5-$C_6H_3(CF_3)_2$: nmr (CCl_4) δ 7.78 (2H, br s) 7.63 (1H, br s) 1.78-2.32 (3H, m) 1.10-1.64 (5H, m); ir (nujol) μ 2.95, 6.08, 8.78.

C. 2-Aryl-endo-Norbornen-2-ols

$\underline{p}$-$C_6H_4OCH_3$: nmr (CCl_4) δ 6.89 (4H, AA'BB', Δν = 37 Hz, J = 8.5) 6.25 (1H, d of d's, J = 3, 6 Hz) 6.02 (1H, d of d's J = 3, 6 Hz) 3.65 (3H, s) 2.98 (1H, m) 2.81 (1H, m) 2.24 (1H, d of d's, J = 4, 12 Hz) 1.83 (1H, br s) 1.09-1.56 (3H, m); ir (neat) μ 2.90, 6.20 9.63 (br).

3,4-$C_6H_3(CH_3)_2$: nmr (CCl_4) δ 6.91 (4H, m) 6.26 (1H, d of d's, J = 3, 6 Hz) 6.01 (1H, d of d's, J = 3, 6 Hz) 2.95 (1H, m) 2.78 (1H, m) 2.20 (6H, br s) 2.10-2.42 (1H, hidden m) 1.07-1.78 (4H, m); ir (neat) μ 2.90, 6.16, 6.30, 9.58.

C_6H_5: nmr (CCl_4) δ 7.27 (2H, m) 7.05 (3H, m) 6.22 and 6.00 (1H, d of d's, J = 3, 6 Hz), 2.93 (1H, m) 2.75 (1H, m) 2.24 (1H, d of d's, J = 4, 12 Hz) 1.72 (1H, br s) 1.09 - 1.53 (3H, m); ir (neat) μ 2.90, 6.20, 6.29, 9.56.

$\underline{p}$-$C_6H_4CF_3$: nmr (CCl_4) δ 7.43 (4H, AA'BB', Δν ∿ 0, J = 9 Hz) 6.35 (1H, d of d's, J = 2.5, 5 Hz) 6.08 (1H, d of d's, J = 2.5, 5 Hz) 2.89 (2H, m) 2.28 (1H, d of d's, J = 4, 12 Hz) 1.77 (1H, s) 1.14-1.63 (3H, m) ir (nujol) μ 2.99, 6.14, 6.30, 9.34.

3,5-$C_6H_3(CF_3)_2$: nmr (CCl_4) δ 7.90 (2H, br s) 9.65 (1H, br s) 6.47 (1H, d of d's, J = 2.5, 5 Hz) 6.20 (1H, d of d's, J = 2.5, 5 Hz) 3.00 (2H, m) 2.37 (1H, d of d's, J = 4, 12 Hz) 1.90 (1H, br s) 1.20-1.72 (3H, m); ir (neat) μ 2.89, 6.10, 8.70 (br).

D. 6-Aryl-6-*endo*-Bicyclo [3.2.1] octanols.

p-$C_6H_4OCH_3$: nmr (CCl_4) δ 6.89 (4H, AA'BB', Δν = 32.4 Hz, J = 8.8 Hz) 3.65 (3H, s) 1.10-2.65 (13H, complex); ir (nujol) μ 3.18, 6.19, 9.68.

3,4-$C_6H_3(CH_3)_2$: nmr (CCl_4) δ 6.72-7.18 (3H, m) 2.27 (3H, s) 2.22 (3H, s) 1.00-2.61 (13H, complex); ir (neat) μ 3.20, 6.15, 9.29.

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