Structural Changes in 2-Arylnorbornyl and Other Aryl Carbocations with Increasing Electron Demand. 13C Nuclear Magnetic Resonance as a Probe

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Abstract: The 13C NMR chemical shifts of the cationic carbons for the following carbocations in fluorosulfonic acid have been determined: 1-arylcyclopentyl, 1-arylcyclohexyl, 6-aryl-6-bicyclo[3.2.1]octyl, 1,1-diarylethyl, 1-aryl-1-phenylethyl, 2-aryl-norbornenyl, 2-arylnorbornyl, and 5,6-*exo*-trimethylene-2-arylnorbornyl. The aryl group has been varied in electron demand from *p*-methoxyphenyl to 3,5-bis(trifluoromethyl)phenyl. The chemical shifts for the first four cations show linear relationships with one another and with those reported for the 2-arylpropyl cations, as expected for "ordinary" behavior. The chemical shifts for the remaining cations show deviations from linearity when plotted against those of the "ordinary" cations. Their "extraordinary" behavior can be interpreted in terms of reasonable changes in structure for the cations with the more electron-demanding aryl groups: for the 1-aryl-1-phenylethyl cations, a change from a planar aryl carbocation to a twisted aryl carbocation; for the 2-arylnorbornenyl, the onset of π bridging; for the 2-arylnorbornyl and 5,6-*exo*-trimethylene-2-arylnorbornyl, the onset of σ bridging. The data for the last two cations are not quantitatively consistent with the hypothesis that they are each a pair of rapidly equilibrating unbridged cations. The deviation from linearity has been shown to occur with less electron-demanding aryl groups for the chemical shifts of the cations than for the solvolysis rate constants of the appropriate precursors, where data are available for comparison. Therefore, we conclude that the onset of π or σ bridging occurs with less electron-demanding aryl groups in the cations than in the transition states presumed to lead to them. The earlier reported results for the 7-arylnorbornenyl system are shown to be consistent with this conclusion upon reinterpretation.

Introduction

In an earlier paper[1] we reported the results of a 1H NMR study of several 2-aryl-2-norbornyl cations (1, R = Ar), from

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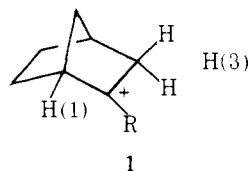
which we concluded that the abrupt increase in slope of a plot of the chemical shift of H(1) vs. that of H(3) for substituents more electron demanding than R = phenyl was best interpreted in terms of a change in structure of the cation from "classical" to "nonclassical" or "σ-bridged" at the point of intersection, with a resultant increased dispersal of positive charge to C(1). The method used in that work, based on a classical principle,[2] was used by Gassman, Richey, and Winstein[3] to examine the solvolysis and NMR spectra of 7-aryl-7-norbornenyl derivatives, and has been used extensively by Brown, as the "tool of increasing electron demand", to examine the solvolysis of norbornyl and other systems.[4]

During the course of these investigations, the following questions have been in our minds and those of others about our use of the combined tools of increasing electron demand and NMR spectroscopy as probes into carbocation structure: (1) Since the 1H NMR shift differences were small, was not the percentage error in the determinations too large to permit reliable conclusions? (2) Since the only model system examined (the bicyclo[2.2.2]octyl cations) showed a change in slope similar to though less pronounced than that of the norbornyl cations, how could we be sure that the phenomenon we observed did not originate in some other characteristic of carbocations having nothing to do with σ bridging? (3) Why would σ bridging result in an abrupt change in slope, rather than a gradual curvature?[5] (4) Could we be sure that a pair of rapidly equilibrating classical cations could not explain our data?[6] (5) Would the structure of the stable cations in fluorosulfonic acid solvent systems have any relationship to the structure of the transition state or cation under solvolytic

conditions? It is our purpose in this paper to report the results of a 13C NMR study of a number of carbocations, including the 2-aryl-2-norbornyl derivatives, which further support the conclusions from our earlier 1H NMR study, and to attempt to provide some answers to the above questions.

Results and Discussion

13C NMR Chemical Shifts in Model Carbocations. The use of 13C NMR rather than 1H NMR as a probe offered advantages because of the larger magnitude of the shifts and the opportunity to look directly at the tertiary, cationic carbon, where the effect of a structural change would be maximized. However, it also presented hazards because of the newness of the tool, the attendant lack of a foundational theory of the chemical shift, and the recurring doubts about the reliability of empirical charge–chemical shift correlations in cations.[8] Therefore, we thought it desirable to test 13C NMR shift correlations with a number of "ordinary" tertiary aryl substituted cations in order to determine what constituted "ordinary" behavior. The 13C NMR chemical shifts for the cationic carbon for a series of arylcyclopentyl, arylcyclohexyl, and 6-aryl-6-bicyclo[3.2.1]octyl cations in fluorosulfonic acid mixtures are given in Table 1, and plotted in sundry combinations against each other and against some known values for the 2-aryl-2-propyl cations[9] in Figures 1–3. From the plots it is apparent that over the range of substituents studied (*p*-methoxyphenyl to 3,5-bis(trifluoromethyl)phenyl) the 13C NMR chemical shifts are linearly related with nearly unit slopes. Although these results surely surprise no one, they do provide us with a set of cations of confirmed "ordinariness" to use as standards to discover "extraordinariness".

The 1,1-Diarylethyl Cation. A Simple Test of the Probe. We next turned to a system which we expected to show a predictable, easily understood deviation from ordinary behavior—the 1,1-diarylethyl cation. Kinetic linear free energy relationships had already been explored for cations of this type by Dubois,[10] who investigated the bromination of 1,1-diarylethylenes, and by Nishida,[11] who examined the solvolysis of subsituted benzhydryl derivatives. Although the symmetrically disubstituted diaryl derivatives showed normal, linear Hammett plots, in

Table I. ^{13}C NMR Chemical Shifts[a] for 1-Arylcyclopentyl, 1-Arylcyclohexyl, and 6-Aryl-6-bicyclo[3.2.1]octyl Cations

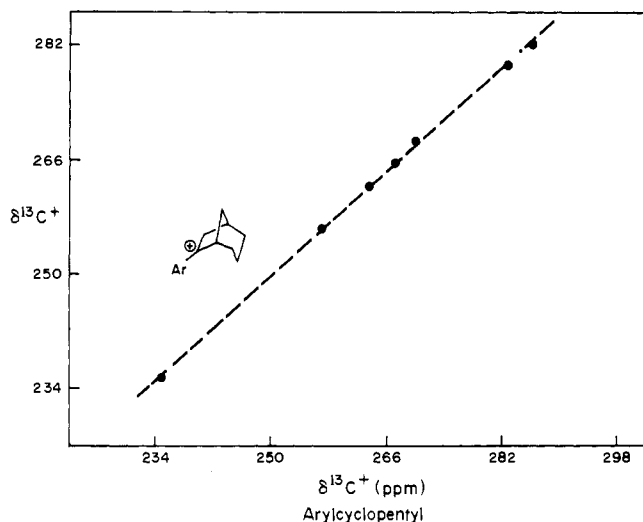| Aryl substituent	Cyclopentyl C[+]	Cyclohexyl C[+]	Bicyclo[3.2.1]octyl		
			C[+]	C(5)	C(7)
p-CH$_3$O	235	227	235.5	49.8	44.5
3,4-(CH$_3$)$_2$	257	249	256.4	53.1	47.5
p-CH$_3$	259	251			
p-F	264	256	262.3	55.2	49.1
p-Cl	267	259			
p-Br	267	260	265.4	55.9	49.6
H	270	263	268.6	55.7	49.6
m-F	277	267			
m-Cl	277				
p-CF$_3$	283	276	279.5	59.1	52.5
3,5-(CF$_3$)$_2$	286	279	282.2	60.8	53.6

[a] In parts per million downfield from capillary Me$_4$Si.
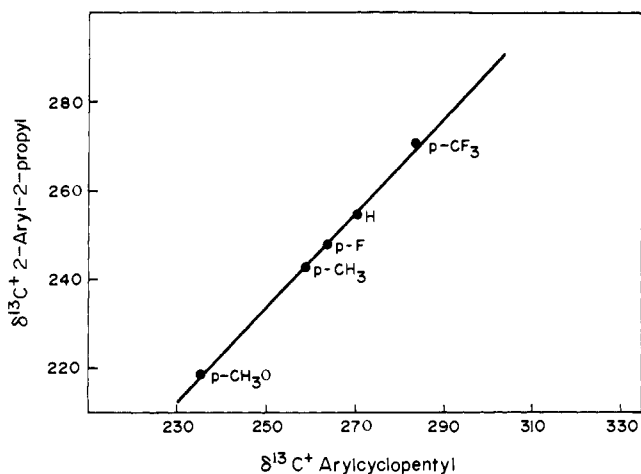
Figure 1. Correlation of the ^{13}C chemical shifts at the carbocationic center of the 2-aryl-2-propyl cations with those of the 1-arylcyclopentyl cations.
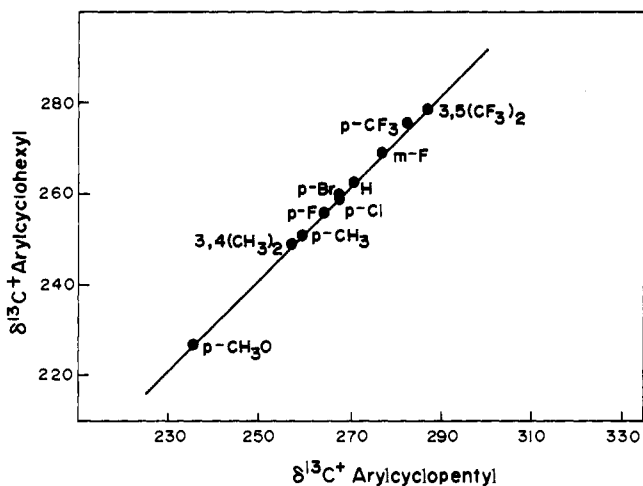
Figure 2. Correlation of the ^{13}C chemical shifts at the carbocationic center of the 1-arylcyclohexyl cations with those of the 1-arylcyclopentyl cations. Slope = 1.01, root mean square (rms) error = 0.64, *r* = 0.998.

Figure 3. Correlation of the ^{13}C chemical shifts at the carbocationic center of the 6-aryl-6-bicyclo[3.2.1]octyl cations with those of the 1-arylcyclopentyl cations. Slope = 0.915, rms error = 0.31, *r* = 0.9996.

neither case were the rate constants for the monosubstituted (i.e., the arylphenyl) derivatives correlated well by a simple Hammett relationship with either σ or σ^+ constants. Rather they were correlated with σ^+ constants for electron-donating substituents and σ constants (with a different ρ value) for electron-withdrawing substituents. These results could be very reasonably interpreted in terms of an abrupt change in structure of the cationic intermediate from one in which the substituted aryl group is planar with the cationic carbon and the

phenyl group is twisted for electron-donating groups (hence the σ^+ correlation) to one in which the substituted aryl group is twisted and the phenyl is planar for electron-withdrawing groups (hence the σ correlation). We therefore expected similar behavior for the ^{13}C NMR chemical shifts of the cations.

We first checked to ensure that the symmetrically substituted 1,1-diarylethyl cation showed an ordinary ^{13}C NMR correlation, as in the solvolysis studies. Figure 4 shows the linear correlation of the chemical shifts with those of 1-arylcyclopentyl cations with a slope considerably less than unity, as expected if the charge is dispersed more in the diaryl cation, resulting in less charge at the para position of each aryl group, and less influence of the substituents. We then compared the correlation of the chemical shifts of the 1-aryl-1-phenylethyl cations with those of the 1-arylcyclopentyl cations, as shown in Figure 5. As can be seen our expectations were fully realized, with the appearance of two linear correlations, intersecting at aryl = phenyl, the one of steeper slope corresponding to the electron-releasing substituents.

In order to appreciate our use of this method with other cations, it is important to appreciate the "metastable" position occupied by the diphenylethyl cation in the series. This cation is quite reasonably considered to have the two like phenyl groups twisted equally some 25-30° out of the plane of the trigonal cationic carbon.[12] Destruction of the symmetry of the cation by placing an electron-withdrawing group on one phenyl will make more electron demands on the other phenyl, causing it to become more coplanar with the cationic carbon. The
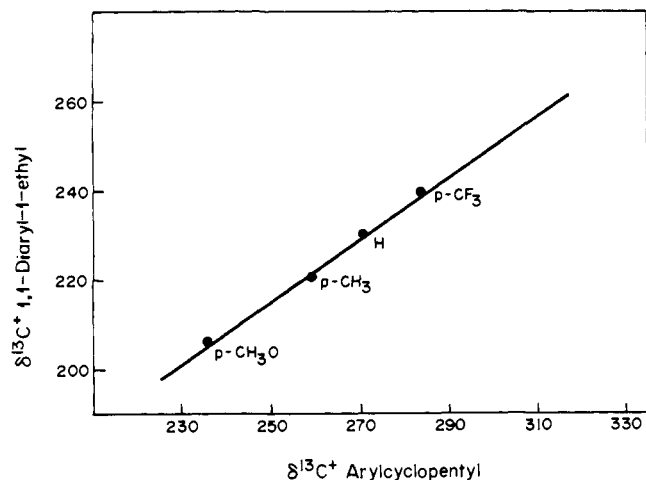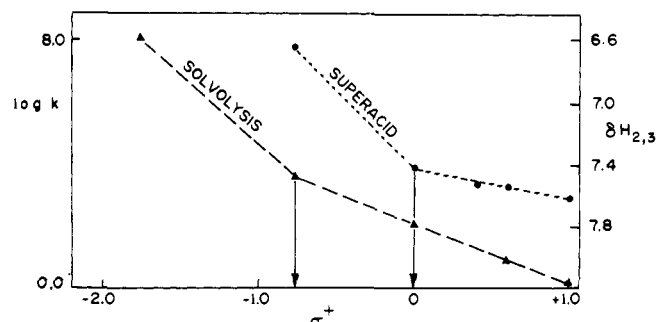
Figure 4. Correlation of the ^{13}C chemical shifts at the carbocationic center of the 1,1-diaryl-1-ethyl cations with those of the 1-arylcyclopentyl cations. Slope = 0.71, rms error = 0.77, r = 0.998.
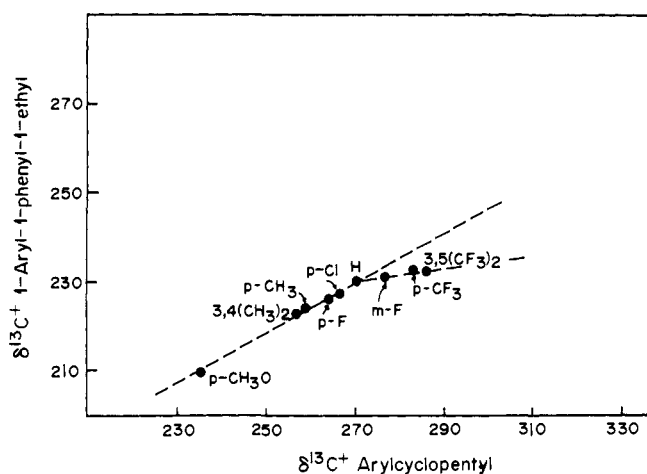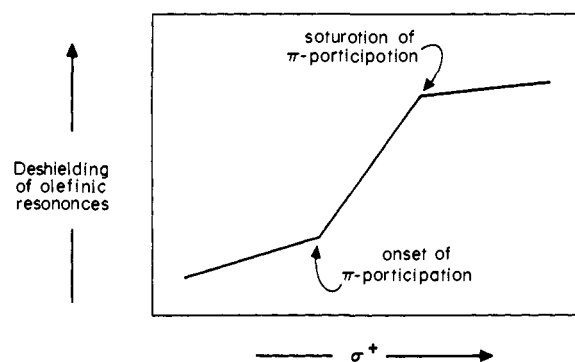

Figure 5. Correlation of the ^{13}C chemical shifts at the carbocationic center of the 1-aryl-1-phenyl-1-ethyl cations with those of the 1-arylcyclopentyl cations. If only points to the left of and including "H" are considered, then the slope = 0.58, rms error = 0.54, r = 0.996. If all points are included, then the slope = 0.46, rms error = 1.56, and r = 0.967.

Figure 6. Correlation of the ^1H chemical shifts at H(2) and H(3) (δH2,3) in the 7-aryl-7-norbornenyl cations (superacid) and the logarithm of the solvolysis rate constants (log k) for the 7-aryl-7-norbornenyl p-nitrobenzoates (solvolysis) with σ^+ constants.


Figure 7. Expected dependence of NMR parameters on increasing electron demand (increasing σ^+) in the presence of π participation.

substituted phenyl will, therefore, be forced further out of the plane, resulting in a still more electron-demanding cation, thus reinforcing the driving force for coplanarity of the phenyl, and so on. Hence the geometry of the cation will change from a symmetrically twisted one to one in which the phenyl is close to coplanar with the trigonal cationic carbon, and the aryl group is largely twisted out of the plane. More electron-demanding substituents will have little effect on this structure, but will influence the ^{13}C NMR shift of the cationic carbon by transmission of their electron demand through the nonplanar benzene ring. Similarly, destruction of the symmetry of the cation by placing an electron-donating group on one phenyl will drive the substituted phenyl into a more nearly coplanar arrangement, forcing the unsubstituted phenyl to twist more, and setting up the same unstable cycle. Hence, the geometry of the cation will change to one in which the substituted phenyl is close to coplanarity, and the unsubstituted one is largely twisted out of the plane. More powerfully electron-releasing substituents will have little effect on this structure, but will transmit their electron-releasing influence through the planar benzene ring. The probe has thus detected a subtle, but abrupt, change in cation structure by detecting an abrupt change in the way in which the influence of the aryl substituents is transmitted to the cationic carbon in the two structures.

We now turn to the use of the probe to search for the onset of participation in a number of bicyclic systems of current interest.

The 7-Arylnorbornenyl Cation. A Reinterpretation. Gassman, Richey, and Winstein[3] looked for the onset of π participation in the well-known 7-arylnorbornenyl cations both in solvolysis [3b](by a Hammett treatment) and in the stable cations in fluorosulfonic acid[3c] (by qualitative observations). They concluded that, since the Hammett plot of the rate constants showed a marked increase in slope for aryl groups less electron releasing than p-methoxyphenyl, only 7-p-methoxyphenyl and 7-p-dimethylaminophenylnorbornenyl cations were solvolyzing without π participation, with the methoxyphenyl derivative in fact at the point of intersection of the two correlations (see Figure 6). They also stated that the ^1H NMR spectrum of the p-methoxyphenyl derivative in fluorosulfonic acid was qualitatively different from that of the others (the p-dimethylaminophenyl derivative was not reported, because of N-protonation) indicating that it was a classical cation, while the others showed π participation. We were quite satisfied with their interpretation until we replotted both their solvolysis rate constants and their ^1H NMR chemical shifts for the vinyl protons against σ^+ on the same graph (Figure 6). We then became concerned that the onset of π participation in the *cation* in fluorosulfonic acid appeared to be with the p-tolyl derivative, while the onset of π participation in the *transition state* for solvolysis, which we expected to require a *more* electron-demanding aryl group than in the cation, appeared with the *less* electron-demanding p-methoxyphenyl substituent.

We now believe that their results are better interpreted in terms of Figures 7 and 8. In Figure 7 we have shown what we would expect for the behavior of the vinyl hydrogen chemical shift in the 7-arylnorbornenyl cations as the aryl group becomes more electron demanding. In the classical cation, with very
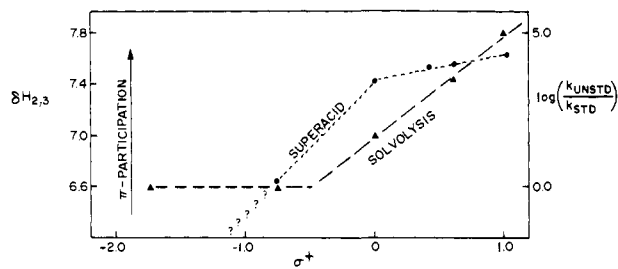
Figure 8. The effect of increasing electron demand (increasing σ^+) on π participation in the 7-aryl-7-norbornenyl cations as measured by the ratio of the rate constant (k_{unstd}) to that of the corresponding 7-aryl-7-nor-bornyl-p-nitrobenzoate (k_{std}).

powerful electron-releasing aryl groups (large negative σ^+), the vinyl hydrogen chemical shift would be relatively insensitive to the nature of the substituent, since there would be little transmission of charge to the double bond. At some point, labeled "onset of π participation" on Figure 7, the electron demand of the cation would result in π participation with transmission of charge to the vinyl hydrogens and a marked downfield shift of their NMR signal, steeply dependent on the electron demand of the aryl group. Eventually a point might be reached, labeled "saturation of π participation" in Figure 7, where the double bond had given all it could give (i.e., the cation was best represented by the pair of structures **2a** and **2b**,
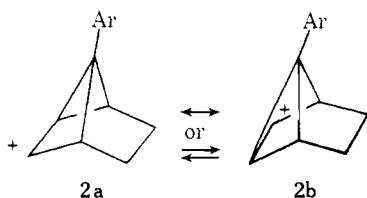
either as a pair of resonance contributors or an equilibrating pair[13]), and further electron withdrawal would have little effect on the vinyl proton chemical shifts.

In Figure 8 we have replotted the literature data for the cation to emphasize the conformity with the expectations of Figure 7. The *rate* data are plotted against σ^+ as the ratio of the rate for the unsaturated compound to that of the the saturated model compound, and show the onset of π participation with the p-methoxyphenyl derivative, as already noted by the earlier authors. However, the ^{1}H NMR shifts show a steep dependence on σ^+ from p-methoxyphenyl to phenyl, then a leveling out consistent with the saturation of π participation. Significantly, the saturation phenomenon appears in the more electron-demanding *cation,* but is not detected in the less electron-demanding *solvolysis transition state.* Clearly, then, the region between p-methoxyphenyl and phenyl represents π participation in the cation. It is tempting to guess that π participation in the cation occurs for even less electron-demanding groups than in the solvolysis, and therefore extends to even more electron-releasing groups than p-methoxyphenyl (Figure 8, dotted line), especially since the vinyl proton chemical shift (δ 6.65) in this cation is already considerably downfield from its position in the neutral molecule (δ 6.0). However, the data are not yet available, nor have we determined any ^{13}C NMR data on these ions. Nonetheless, we believe that the above reinterpretation provides a necessary and consistent prelude to the other bicyclic systems now to be discussed.

The 2-Arylnorbornenyl Cation (3). A Comparison of Participation in Solvolysis with Bridging in the Stable Cation. In his application of the tool of increasing electron demand to solvolysis of bicyclic systems Brown concluded that the 2-arylnorbornenyl-2-tosylates exhibited π participation in solvolysis only when the aryl group was the very electron de-
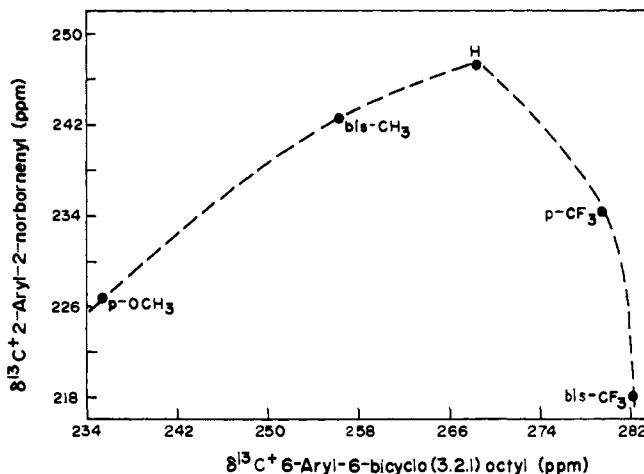

Figure 9. Correlation of the ^{13}C chemical shifts at the carbocationic center of the 2-aryl-2-norbornenyl cations with those of the 6-aryl-6-bicyclo[3.2.1]octyl cations.

manding 3,5-bis(trifluoromethyl)phenyl group.[4] This conclusion was based on an increase in the exo/endo rate ratio for this derivative compared with the others. We chose to examine the ^{13}C NMR spectra for the corresponding 2-arylnorbornenyl cations (**3**) in order to see if we could demonstrate π partici-

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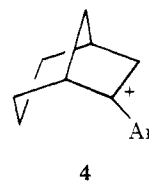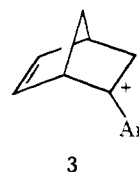
pation in the cations with less electron-demanding aryl groups, as anticipated.[14] Chemical shifts for the carbons in the limited number of cations of type **3** examined are given in Table II. The assignments were made on the basis of peak multiplicities and comparison with the known carbon chemical shifts for the ketone[15] (also given in the table for comparison). In Figure 9, the chemical shifts of the cationic carbon, C(2), for ions of type **3** are plotted against those of C(6) for the model 6-aryl-6-bicyclo[3.2.1]octyl cations (**4**). In contrast to the strictly linear

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relationship observed with ordinary cations, the plot shows a dramatic curvature, consistent with a significant structural change for cations more electron demanding than **3**, Ar = C_6H_5. In this case, we cannot rigorously distinguish between the onset of π bridging or increased contribution of the rearranged **3a** to an equilibrium, because we cannot estimate the expected concentrations of **3** and **3a** at equilibrium. For ex-

| **3** | **3a** |
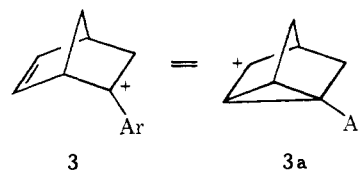
ample, if we assume that the chemical shift at the cationic carbon of **3**, Ar = 3,5-bis(trifluoromethyl)phenyl, is the same as that for the model bicyclo[3.2.1]octyl system (282.2 ppm), and we assume that the chemical shift for the same carbon in **3a** is 100 ppm,[16] then an equilibrium ratio **3:3a** of 65:35 will

**Table II.** ^{13}C NMR Chemical Shifts[a] for 2-Aryl-5-norbornen-2-yl Cations

Aryl substituent	C[+] (s)[b]	C$_1$ (d)	C$_3$ (t)	C$_4$ (d)	C$_5$ (d)	C$_6$ (d)	C$_7$ (t)
p-CH$_3$O	226.8	56.5	43.4	42.8	150.8	128.6	54.2
3,4-(CH$_3$)$_2$	242.6	59.7	46.4	43.3	156.8	126.5	55.1
H	247.4	62.2	48.0	43.7	163.3	124.2	55.5
p-CF$_3$	234.4	65.8	48.5	44.0	180.4	117.8	54.7
3,5-(CF$_3$)$_2$	218.1	67.3	48.1	44.1	193.4	113.0	53.8

[a] Given in parts per million downfield from capillary Me$_4$Si. [b] Multiplicities are given in parentheses as s = singlet, d = doublet, t = triplet as determined by off-resonance decoupling.

Table III. Calculated Equilibrium Constants and Chemical Shifts[a] for the 2-Aryl-5-norbornen-2-yl Cations Assuming a Rapidly Equilibrating Pair **3** $\rightleftharpoons$ **3a**[b]
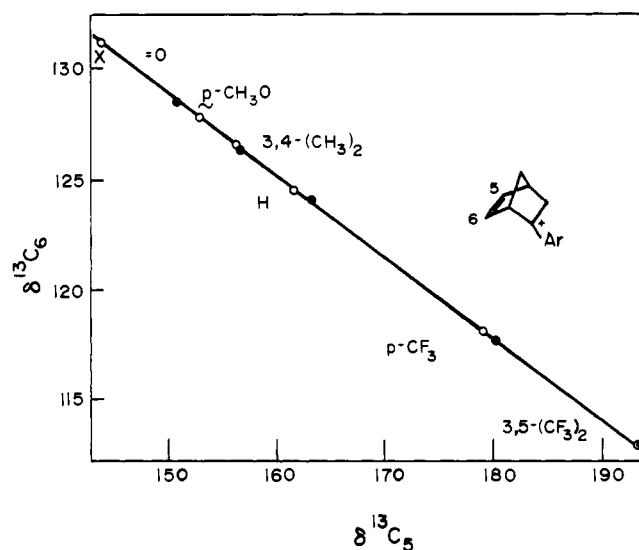
Aryl substituent	Chemical shift at C$_2$ = cationic carbon Obsd	Expected for **3**[c]	Calcd mole fraction of **3** in equilibrium with **3a**[d]	K_{eq} **3** $\rightleftharpoons$ **3a**	Chemical shift at C$_5$ and C$_6$ for equilibrating pair[b] C$_5$ (calcd)	C$_5$ (obsd)	C$_6$ (calcd)	C$_6$ (obsd)
p-CH$_3$O	226.8	235.5	0.936	14.6	153.0	150.9	127.9	128.6
3,4-(CH$_3$)$_2$	242.6	256.4	0.912	10.4	156.4	156.8	126.7	126.5
H	247.4	268.6	0.874	6.94	161.7	163.3	124.7	124.2
p-CF$_3$	234.4	279.5	0.749	2.98	179.2	180.4	118.2	117.8
3,5-(CF$_3$)$_2$	218.1	282.2	0.648	1.84	193.4	193.4	113.0	113.0

[a] In parts per million downfield from capillary Me$_4$Si. [b] See text for further explanation. [c] Taken as values for 6-aryl-6-bicyclo[3.2.1]octyl cations. [d] Assuming a chemical shift for the aryl substituted carbon in **3a** of 100 ppm. See text for further discussion.
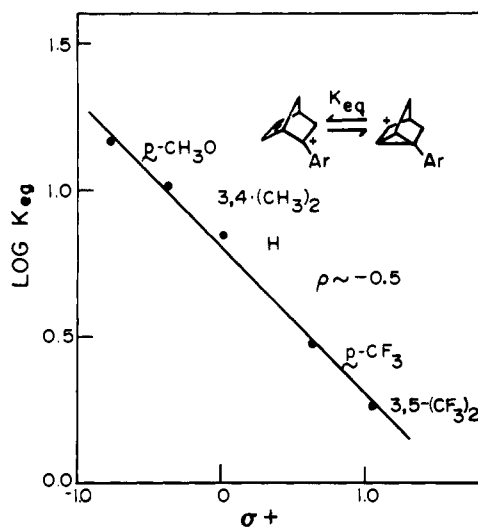
Figure 10. Linear free energy relationship for the equilibrium constant if the 2-aryl-2-norbornenyl cation is represented as a pair of equilibrating cations (See Table III for data and text for discussion.)

Figure 11. Correlation of the vinyl hydrogen chemical shifts (H$_5$ and H$_6$) of the 2-aryl-2-norbornenyl cations with one another: ● .., observed; O .., calculated from the equilibrium constants in Table I (see Table I and text).

reproduce the observed chemical shift (218.1 ppm). However, we have no way of knowing if a 65:35 ratio is reasonable for these two cations. We can, in fact, calculate an apparent equilibrium constant for each of the cation pairs **3** $\rightleftharpoons$ **3a**, as given in Table III, column 5, and from these, plotted against σ^+,[17] obtain a reasonable linear free energy relationship as shown in Figure 10, although the small negative ρ value ($\sim$−0.5)[16] does not really seem consistent with substituent effects on a carbonium ion equilibrium.

The variation in the chemical shifts of the vinyl carbons in **3**, C(5) and C(6), can similarly be interpreted in terms of an equilibrium between **3** and **3a**. They are linearly related to each other as shown in Figure 11 (black spots). In fact, even the point for C(5) and C(6) of the related ketone[15] (marked with an "X") is not far from the correlation line, even though the solvent is quite different. The data can be very nearly duplicated, as also shown in Table III and Figure 11 (open circles), by using the equilibrium constants from Table III and as-

signing to rearranged structure **3a** reasonable chemical shift values of C(2) 100 ppm, C(5) 284.4 ppm, and C(6) 50.5 ppm.[18]

In spite of the easy accommodation of the data by the mobile equilibrium **3** $\rightleftharpoons$ **3a**, we want to emphasize that π bridging in the cation or, indeed, any combination of π bridging and equilibration would probably not differ qualitatively in accommodating the data, but only quantitatively in ways that we are unable to predict. We are, therefore, unable to distinguish between π bridging and a mobile equilibrium **3** $\rightleftharpoons$ **3a** as explanations for our data in this case.[19] Perhaps the most important point to be emphasized is that whatever the structural change that takes place, it is significantly manifest in the cation when Ar = p-trifluoromethylphenyl (σ^+ = 0.61), but is not evident in the transition state for solvolysis until Ar = 3,5-bis(trifluoromethyl)phenyl (σ^+ = 1.04).[4] That the transition

Table IV. ^{13}C Chemical Shifts for 2-Aryl-2-norbornyl Cations[a]

Aryl substituent	C^+ (s)[b]	C_1 (d)	C_3 (t)	C_4 (d)	C_6 (t)	C_7 (t)	C_5 (t)
p-CH$_3$O	232	53.5	47.2				
3,4-(CH$_3$)$_2$	251.5	56.6	49.1	39.0	33.1	41.4	26.0
p-F	255.8	58.9	50.4	39.8	33.9	41.8	25.8
p-Br	258.5	59.8	50.9	40.1	34.4	41.9	25.8
H	260.8	59.6	50.8	39.9	34.4	41.7	25.7
p-CF$_3$	265.3	64.4	52.7	41.8	37.1	42.1	25.4
3,5-(CF$_3$)$_2$	263.3	67.2	53.2	42.3	38.8	42.3	25.4

[a] In parts per million downfield from capillary Me$_4$Si. [b] Multiplicities determined by off-resonance decoupling and reported in parentheses as s = singlet, d = doublet, t = triplet.
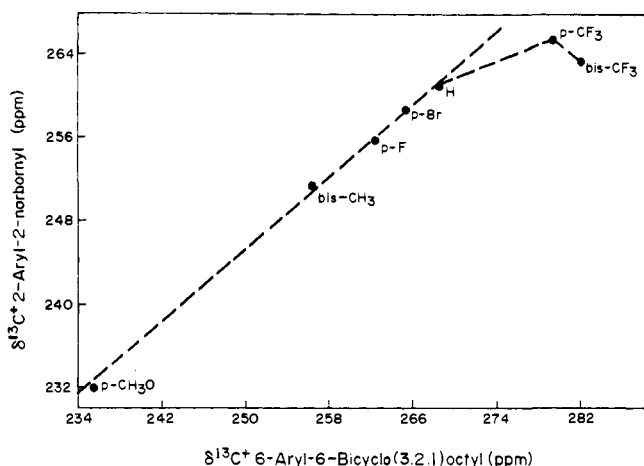
Figure 12. Correlation of the ^{13}C chemical shifts of the carbocationic center of the 2-aryl-2-norbornyl cations with those of the 6-aryl-6-bicyclo[3.2.1]octyl cations. If only points to the left of and including "H" are considered, then the slope = 0.877, rms error = 0.40, r = 0.999. If all points are considered, then the slope = 0.71, rms error = 2.35, and r = 0.967.

state for solvolysis appears to be less electron demanding than the cation is no dramatic revelation, but the smallness of the difference ($\Delta\sigma^+$ = 0.43) may be surprising, and provides support for comparing conclusions from solvolysis data with those from stable carbocation data.

The 2-Arylnorbornyl Cation (1, R = Ar). Brown has also searched vainly for evidence of σ bridging in the solvolysis of 2-arylnorbornyl tosylates.[4] The constancy of the exo/endo rate ratio for a variety of derivatives from p-methoxyphenyl to 3,5-bis(trifluoromethyl)phenyl led him to conclude that there was no participation by bridging in any of the transition states, in contrast to our earlier conclusion,[1] based on ^1H NMR data, that σ bridging was manifested in the p-trifluoromethylphenyl and 3,5-bis(trifluoromethyl)phenyl cations in fluorosulfonic acid. We have, therefore, compiled and analyzed ^{13}C NMR data for this series of ions which confirm the onset of σ bridging. Taken in concert with the above analysis of the 2-aryl-norbornenyl system, our results suggest that more powerfully electron-demanding aryl groups than bis(trifluoromethyl)-phenyl will be required before σ bridging will be manifest in the solvolysis data.

The ^{13}C NMR data for a number of 2-arylnorbornyl cations are given in Table IV. Chemical shift assignments were made on the basis of peak multiplicities (given in the table) determined from undecoupled spectra, and comparison with the known chemical shifts for norbornanone.[20] A plot of the chemical shifts at the cationic carbon against those for the model bicyclo[3.2.1]octyl derivatives (Figure 12) again reveals the deviation of the cations with the electron-demanding trifluoromethyl substituents, which we have taken as evidence of a structure change.

Further confirmation that there is charge dispersal to C(1)

in the trifluoromethyl substituted cations is found in a plot of the chemical shifts of C(1) vs. C(3). In an ordinary cation a linear relationship might be expected in the response of these α carbon chemical shifts to increasing electron demand at C(2). This, indeed, was the basis of our earlier ^1H NMR study. Figure 13 shows the expected linear relationship in the ^{13}C NMR shifts for the bicyclo[3.2.1]octyl model cations. However, Figure 14 shows the deviation from linearity in the norbornyl cations, implicating a change in structure resulting in more charge dispersal to C(1) than C(3) for the trifluoromethyl substituted derivatives.

The phenomena revealed in Figures 13 and 14 are consistent with the onset of σ bridging with the trifluoromethyl substituted 2-arylnorbornyl cations resulting in delocalization of charge to C(1), rehydridization at C(2), and a consequent reversal of the tendency of the ^{13}C chemical shift at C(2) to move downfield with increasing positive charge.[8] Are they consistent with an equilibrating pair of classical ions? Several lines of evidence rule out the equilibrating classical ion explanation conclusively in this case. (1) The model bicyclo[3.2.1]octyl cations provide a very closely similar pair of equilibrating cations for comparison. If equilibrating cations
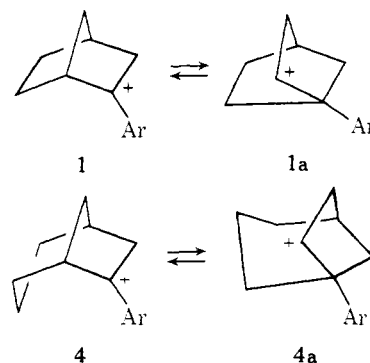
resulted in the deviation from linearity observed with the norbornyl cations, they should also result in a deviation from linearity with the bicyclo[3.2.1]octyl cations, which is not observed. (2) If one chooses to argue that some unrecognized steric factor is altering the positions of equilibrium in the bicyclo[3.2.1]octyl system, then we can turn to estimates of the maximum concentration of **1a** that could be present at equilibrium. In our earlier work[1] we estimated a maximum ratio **1a:1** (Ar = 3,5-bis(trifluoromethyl)phenyl) of 10^{-4} based on the absence of hydrogen scrambling in the ^1H NMR.[21] We can also estimate the ratio **1a:1** necessary to account for the ^{13}C NMR chemical shifts in several different ways. If we assume that the p-methoxyphenyl derivative is entirely in the form **1**, and assign a value of 100 ppm to the bridgehead carbon in **1a** (independent of the aryl substituent), then the ratio **1a:1** necessary to give the observed cationic carbon chemical shift for the 3,5-bis(trifluoromethyl)phenyl derivative is about 10^{-1},[22] a factor of 10^3 more than the maximum estimated. If we choose to explain the excess dispersal of charge to C(1) revealed in Figure 14 by a contribution of **1a** to the equilibrium, then a
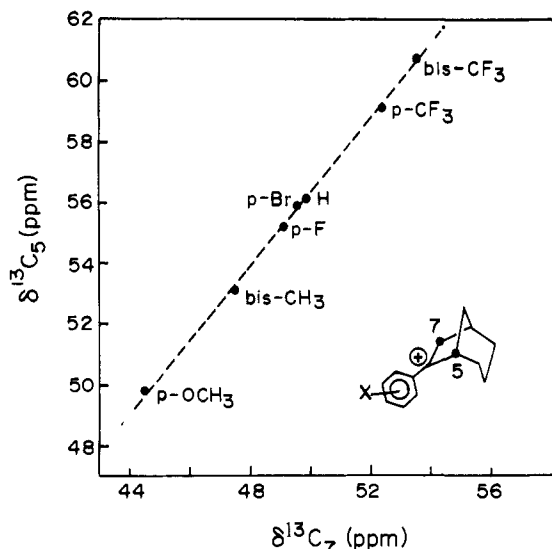
Figure 13. Correlation of the ^{13}C chemical shifts for the α carbons (C_5 and C_7) of the 6-aryl-6-bicyclo[3.2.1]octyl cations with one another.

Table V. Selected ^{13}C Chemical Shifts for 2-Aryl-*exo*-5,6-trimethylene-2-norbornyl Cations[a]

Aryl substituent	C^+ (s)[b]	C_1 (d)	C_3 (t)	C_6 (d)
p-CH$_3$O	231.9	56.3	45.4	48.8
3,4-(CH$_3$)$_2$	250.4	60.2	48.6	50.9
p-F	255.0	62.4	49.9	52.0
p-Br	258.2	63.6	50.9	52.9
H	260.4	63.2	50.6	52.7
p-CF$_3$	268.0	67.6	53.2	55.8
3,5-(CF$_3$)$_2$	268.4	69.5	54.1	57.2

[a] In parts per million downfield from capillary Me$_4$Si. [b] Multiplicities determined by off-resonance decoupling and reported in parentheses as s = singlet, d = doublet, t = triplet.

concentration ratio **1a**:1 of $>10^{-2}$ is required to account for the 3 ppm deviation of the C(1) chemical shift of the 3,5-bis-(trifluoromethyl)phenyl derivative from the extrapolated line.[23] In either case the required ratio is prohibitively greater than the 10^{-4} maximum estimated from ^{1}H NMR. (3) The maximum concentration of **1a** that could be present at equilibrium has been estimated quantitatively by Sorensen, who has determined the activation energies for the following rearrangement of these ions[24] by observing the ^{1}H NMR equivalencing of H(1) and H(N).[25] Reference to Figure 15 shows

that the activation energy for this reaction exceeds the energy difference between the assumed classical ions 1 and **1a** by the activation energy for the 6,2-hydride shift, known to be about 5.9 kcal/mol in the norbornyl cation.[26] Sorensen finds an activation energy for rearrangement in the 3,5-bis(trifluoromethyl)phenyl derivative of 12.3 ± 0.2 kcal/mol at −20 °C corresponding to an equilibrium energy difference **1a** ⇌ 1 of 6.4 kcal/mol or an equilibrium ratio of ca. 10^{-4}–10^{-5}. Again
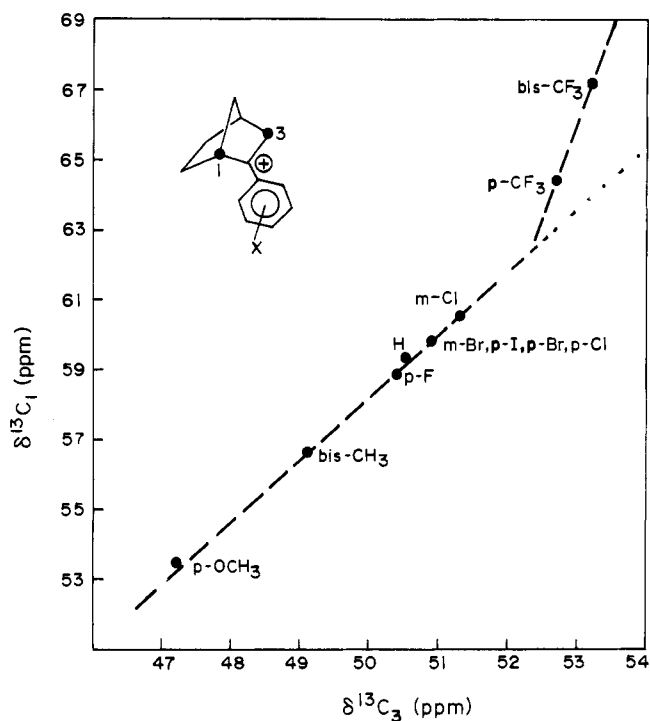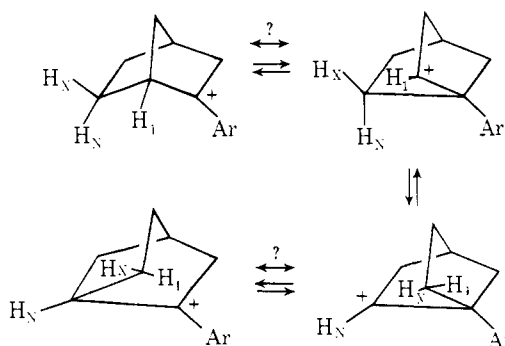

Figure 14. Correlation of the ^{13}C chemical shifts for the α carbons (C_1 and C_3) of the 2-aryl-2-norbornyl cations with one another.
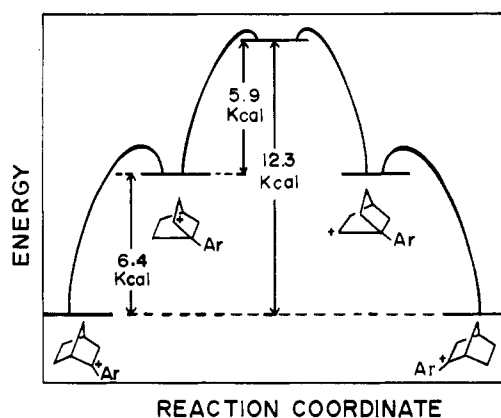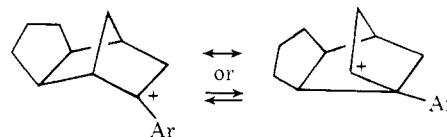

REACTION COORDINATE

Figure 15. Goering–Schewene diagram for the Wagner–Meerwein shift-6,2-hydride shift–Wagner–Meerwein shift sequence in the 2-[3,5-bis(trifluoromethyl)phenyl]-2-norbornyl cation assuming equilibrating classical cations.

this is far less than the 10^{-1}–10^{-2} ratio required to account for the observed chemical shifts. We are thus left with σ bridging as an entirely satisfactory explanation for our results.

The 5,6-*exo*-Trimethylenenorbornyl Cation 5. Cation **5** was chosen for examination because the system exhibited less evidence for σ bridging in solvoly. is than norbornyl, presumably because of steric hindrance to bridging of C(6).[27] The pertinent

5

^{13}C NMR data for aryl derivatives of this ion are given in Table V and plotted as for the norbornyl derivatives in Figures 16 and 17. Although the results are qualitatively the same as those for the norbornyl cation, the deviations are quantitatively less, as expected for an ion in which σ bridging, though initially
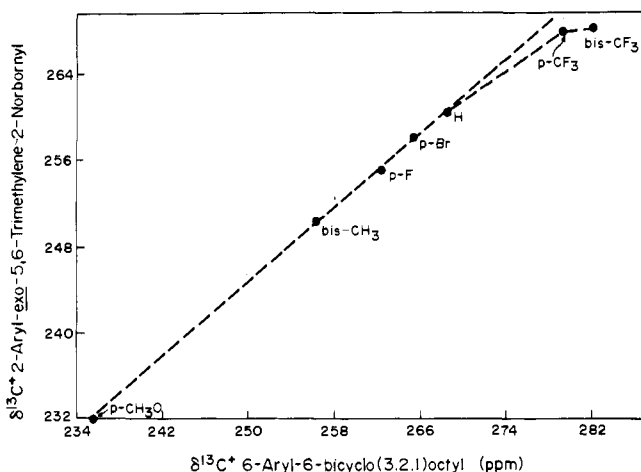
Figure 16. Correlation of the ^{13}C chemical shifts at the carbocationic center of the 2-aryl-*exo*-5,6-trimethylene-2-norbornyl cations with those of the 6-aryl-6-bicyclo[3.2.1]octyl cations.

allowed, becomes more difficult as it progresses because of increasing steric hindrance.

Conclusions

The tool of increasing electron demand, combined with ^{13}C NMR as a probe, has revealed subtle changes in the structure of a number of organic carbocations of contemporary interest. The data for the 2-arylnorbornyl cations cannot be interpreted in terms of equilibrating classical cations, but are readily interpreted in terms of σ bridging in the more electron-demanding cations. Comparison of these results with related solvolysis studies allows a comparison of the electron demands of transition states with those of the carbocations to which they are presumed to lead.

Experimental Section

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 analyses were performed by Mrs. R. L. Guile at Michigan State University using a Hitachi mass spectrometer, Model RMU-6. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained using a Varian T-60 spectrometer. The data are presented in the following manner: δ 6.00 (2 H, d, J = 4 Hz). All spectra are recorded in δ units relative to internal tetramethylsilane. The multiplicities are s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet; br = broad. Carbon-13 magnetic resonance (^{13}C NMR) spectra were obtained using a Varian CFT-20 spectrometer equipped with a Varian V-6040 NMR variable temperature controller. All chemical shifts are expressed in parts per million (ppm) downfield from external capillary Me$_4$Si in acetone-d_6. 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 spectra were recorded are accurate within ±3 °C. Temperatures were calibrated for the probe, not the sample.

Carbocation Formation. The acidic medium was chosen to try to ensure complete ionization of the carbocation precursor yet to avoid unwanted side reactions. The carbocations were formed using either of the following methods.

(1) When FSO$_3$H was used the carbocation precursor was dissolved in CFCl$_3$ (Freon 11) and slowly added dropwise to the rapidly stirred acid at −78 °C, maintained under a blanket of nitrogen.

(2) When a limited amount of FSO$_3$H was necessary, SbF$_5$ was added, or low temperatures were desired, SO$_2$ClF (50–85%) was employed as a cosolvent. The carbocation was prepared directly in the sample tube. Neat carbocation precursor was introduced to the ionizing medium (maintained at −78 or −110 °C) 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$_2$ClF was
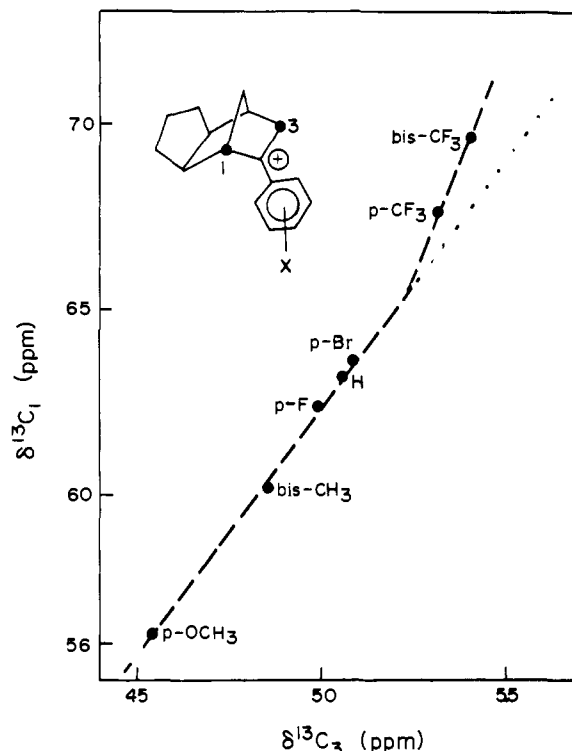
Figure 17. Correlation of the ^{13}C chemical shifts of the α carbons (C$_1$ and C$_3$) of the 2-aryl-*exo*-5,6-trimethylene-2-norbornyl cations with one another.

added and the sample vibro-stirred until a homogeneous mixture resulted.

Carbocation Precursors. The alcohols used in this study were prepared from the appropriate Grignard reagent and carbonyl compound; i.e., cyclopentanone, cyclohexanone, aryl methyl ketone, ethyl acetate, bicyclo[3.2.1]octan-6-one,[28] tricyclo[5.2.1.0$^{2.6}$]decan-8-one,[27] and 2-norbornenone.[29] 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 45 to 95% on ketone.

References and Notes

(1) D. G. Farnum and A. D. Wolf, *J. Am. Chem. Soc.*, **96**, 5166 (1974).
(2) Possibly the earliest reference to the perturbation method used here to confirm an extraordinary phenomenon is in the Old Testament, Judges 6: 36–40. The method might therefore be called the "Gideon's fleece method".
(3) (a) P. G. Gassman, J. Zeller, and J. T. Lumb, *Chem. Commun.*, 69 (1968); (b) P. G. Gassman and A. F. Fentiman, Jr., *J. Am. Chem. Soc.*, **91**, 1545 (1969); **92**, 2549 (1970); (c) H. G. Richey, Jr., D. Nichols, P. G. Gassman, A. F. Fentiman, Jr., S. Winstein, M. Brookhart, and R. K. Lustgarten, *ibid.*, **92**, 3783 (1970).
(4) H. C. Brown, K. Takeuchi, and M. Ravindranathan, *J. Am. Chem.* Soc., **99**, 2684 (1977). For a thorough and entertaining review, see H. C. Brown and P. von R. Schleyer, "The Nonclassical Ion Problem", Plenum Press, New YORK= N.Y., 1977.
(5) A discussion of this point can be found in our earlier paper.[1] The key assumptions are (1) that the ρ value for a Hammett correlation in an aryl substituted σ-bridged cation would be different from that for a nonbridged ion, and (2) that σ bridging inhibits π delocalization from the aryl group and vice versa.
(6) This point was also discussed in our earlier paper.[1] However, the assumptions required and the possible error in the determinations left us and others uneasy with the conclusions.
(7) Olah has independently studied and reported the ^{13}C NMR of the 2-aryl-2-norbornyl cations: G. A. Olah, G. K. Surya Prakash, and G. Liang, *J. Am. Chem. Soc.*, **99**, 5683 (1977). We thank Professor Olah for keeping us informed of the progress of his work and providing a prepublication account of his results.
(8) D. G. Farnum, *Adv. Phys. Org. Chem.*, **11**, 123 (1975).
(9) G. A. Olah, R. D. Porter, C. L. Jeuell, and A. M. White, *J. Am. Chem. Soc.*, **94**, 2044 (1972).
(10) A. F. Hegarty, J. S. Lomas, W. V. Wright, E. D. Bergmann, and J-E. Dubois, *J. Org. Chem.*, **37**, 2222 (1972).
(11) S. Nishida, *J. Org. Chem.*, **32**, 2697 (1967).

(12) B. Ancian, J.-P. Doucet, and J-E. Dubois, *J. Am. Chem. Soc.*, **98**, 4764 (1976).
(13) Our data do not distinguish between these alternatives if the cyclopropyl group in **2a** and **2b** is considered to be donating electrons to the cationic center.
(14) A preliminary report of some of our results on this cation has already appeared: D. G. Farnum and R. E. Botto, *Tetrahedron Lett.*, 4013 (1975).
(15) E. Lippmaa, T. Pehk, J. Paasivirta, N. Belikova, and A. Plate, *Org. Magn. Reson.*, **2**, 581 (1970).
(16) The calculated ratio **3:3a** is relatively independent of the chemical shift assigned. For example, a choice of 40 ppm gives a ratio of 74:26. Neither is the *p* value for the Hammett correlation affected.
(17) H. C. Brown and Y. Okamoto, *J. Org. Chem.*, **22**, 485 (1957).
(18) The values of C(5) and C(6) were chosen to give the correct slope and the correct value for the bis(trifluoromethyl) substituted derivative.
(19) Note, however, the small *p* value if an equilibrium is assumed.
(20) J. B. Stothers, J. R. Swenson, and C. T. Tan, *Can. J. Chem.*, **53**, 581 (1975).

(21) The argument, given in detail in our earlier paper,[1] is not reproduced here, since other arguments to be given are simpler.
(22) This concentration is relatively independent of the chemical shift chosen for the bridgehead carbon. We have chosen 100 ppm as an upper limit, which is least favorable to our case.
(23) Estimates of the ^{13}C chemical shift per unit positive charge vary from 150 to 300 ppm.[8] We have chosen 300 ppm as an upper limit, which is least favorable to our case.
(24) We have also reported these rearrangements,[1] though we did not study them quantitatively.
(25) T. Sorenson, personal communication.
(26) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Am. Chem. Soc.*, **92**, 4627 (1970).
(27) S. Cristol, W. Siefert, and B. Soloway, *J. Am. Chem. Soc.*, **82**, 2351 (1960).
(28) K. B. Wiberg and B. A. Hess, Jr., *J. Org. Chem.*, **31**, 2250 (1966).
(29) P. K. Freeman, D. M. Balls, and D. J. Brown, *J. Org. Chem.*, **33**, 2211 (1968).

A Test for "Wrong-Bond" Rupture in the Thermal Structural Isomerization of Phenylcyclopropane and a Confirmation of the Two-Center Epimerization Mechanism in Its Stereomutation[1]

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Abstract: The major products of the thermal structural isomerization of phenylcyclopropane at 340–360 °C are *trans-* and *cis-*β-methylstyrene and allylbenzene. A small amount of *n*-propylbenzene also is found, but the product distribution is quite different from that in the literature, where *n*-propylbenzene and α-methylstyrene were reported to be the major products. Synthesis of the three isomers of 1-phenylcyclopropane-*2,3-d$_2$* can be achieved by routes terminating in a stereospecific Haller–Bauer cleavage. The trans isomer, $[\alpha]_D$ +0.519° (neat, 0.5 dm), loses optical activity at 309.5 °C in a first-order reaction. By combining the rate constant for this reaction with that for the trans–cis isomerization of *trans-*1-phenylcyclopropane-*2-d*, it is possible to conclude that the stereomutation at C_1, the phenyl-bearing carbon, occurs in synchrony with stereomutations at C_2 and C_3.

Thermal stereomutations of cyclopropane-*1,2-d$_2$* (**1**) and 1-phenylcyclopropane-*2-d* (**2**) employ a two-center epimerization mechanism, in agreement with the theoretically predicted synchronous pairwise rotation of ring members.[2–4] In **1**, the molecular symmetry requires that each of the C–C bonds

1-*1.2-d$_2$*   2-*2-d*

must participate in the stereomutation at the same rate, except for a small secondary isotope effect.[2] In **2**, however, the 1,2 and 1,3 bonds are equivalent, but the 2,3 bond is unique. This has prevented a complete kinetic analysis, and it has been possible to say only that the rotation of C_1 is strongly coupled to that of C_2 (and by symmetry C_3) (>96% double rotation).[3] The rotation of C_2 in synchrony with that of C_1 constitutes about 80% of the total C_2 stereomutation, the remainder being made up of C_2–C_3 double rotation and C_2 single rotation in a ratio that cannot be determined at the monodeuterio level of substitution.[3]

The mechanistic assignment of this last 20% of C_2 stereomutation has significance for the general problem of reaction at sites other than the most substituted one in cyclopropane stereomutations. Should the mechanism prove to have a substantial component of reaction at the "wrong" bond (C_2–C_3

double rotation), the interpretation of many previous studies would be in jeopardy, since analysis of the kinetic data in the majority of the cases[4] has depended on the assumption that reaction occurs only at the most substituted bond.

Although intuitive arguments, bond energy considerations,[5,6] and quantum mechanical calculations of the reaction pathways[7] all suggest that C_1–C_2 cleavage should predominate strongly over C_2–C_3 in the stereomutation of phenylcyclopropane, it nevertheless would be comforting to have some experimental assurance. We were particularly drawn to investigate the phenylcyclopropane system by the intriguing report of Leermakers and Ross[8] that pyrolysis of this hydrocarbon gave α-methylsytrene (**3**) as a major product of the *structural* isomerization. Although this finding is not necessarily relevant to the stereomutation, and although a radical chain mechanism[8] via **4** could rationalize the result, the ex-