Structural Effects in Solvolytic Reactions. 43. Effect of Increasing Electron Demand on the ¹³C NMR Shifts for 2-Arvl-3-methyl-2-butyl Cations. A Static System Becoming an Equilibrating System with **Electron-Withdrawing Substituents**

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Abstract: A series of 2-aryl-3-methyl-2-butyl cations was prepared in SbF₅/FSO₃H/SO₂ClF at -78 °C and their ¹³C NMR shifts were measured at -80 °C. A plot of the observed $\Delta\delta C^+$ values against the σ^{C^+} constants gives a straight line for substituents over the range p-OCH₃ to m-Cl (slope $\rho^{C^+} = -18.2$, correlation coefficient r = 0.999). However, the data points for the strongly electron-withdrawing substituents, m-CF₃, 3,5-Cl₂, and p-CF₃, deviate upward from this straight line. The $\Delta\delta C_{\alpha}/\sigma^{\alpha C^+}$ plot for the α -methine (CH) carbon atom exhibits a linear correlation of the data points for derivatives with substituents p-OCH₃ to m-Cl, with a downward deviation of the data points for derivatives containing strongly electron-withdrawing substituents. These results are in accord with a rapid 2,3-hydride shift in derivatives containing benzylic cations with higher energies. An increase in temperature from -80 °C to -30 °C causes enhanced deviations, in accord with a rapid equilibration that forms more of the less stable cations at the higher temperatures. In the case of 2-aryl-2-norbornyl cations, similar upward deviations are observed in the $\Delta\delta C^+/\sigma^{C^+}$ plot. However, the spectra of these cations reveal no temperature dependence over the same temperature range. This indicates that equilibration is not the factor responsible for the deviations observed in the $\Delta\delta C^+/\sigma^{C^+}$ plot for the substituted 2-aryl-2-norbornyl cations.

The ¹³C NMR shifts for the carbocationic centers of many substituted benzylic cations are nicely correlated by the σ^{C} constants.²⁻⁶ However, the C⁺ shifts for several other systems (1-6) fail to correlate against these constants.^{7,8}



Three different explanations have been proposed to account for the anomalous C⁺ shifts observed in these cases. Olah and coworkers,⁹ as well as Farnum and co-workers,¹⁰ attributed the

- (1) Postdoctoral research associate on a grant provided by the Exxon
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deviations observed in the correlation of the C⁺ shifts for the 2-aryl-2-norbornyl system 1 to the "onset of nonclassical σ bridging". Similar deviations observed for the nortricyclyl system (5) were attributed to the "onset of increased cyclopropyl conjugation" by Olah and co-workers.¹¹ Farnum and co-workers suggested steric inhibition to coplanarity as the factor responsible for such deviations in the benzhydryl system (6, $R = CH_3$).¹⁰

Recently, we pointed out that the behavior of the C_1 and C_6 carbon atoms in the 2-aryl-2-norbornyl cations is not consistent with that for the σ -bridging proposal.⁷ We are exploring four possible explanations: (1) steric inhibition to coplanarity; (2) rapid equilibration (tert \Rightarrow sec) in some systems; (3) enhanced electron supply from certain moieties; and (4) inductive π -polarization, as suggested by Brownlee and co-workers.¹² The results observed with the substituted o-methyl tert-cumyl cations (no deviation)¹³ and substituted 9-methyl-9-anthracenium cations 7 (deviation in the $\Delta\delta C^+/\sigma^{C^+}$ plot)⁸ appear to rule out the steric origin. The present study was undertaken to test rapid equilibration in certain cations as a possible cause for such deviations in the $\Delta\delta C^+/\sigma^{C^+}$ plots and the utility of temperature effects on such deviations as a basis for assigning or ruling out this origin.

Olah and co-workers have reported that in the 2-aryl-3methyl-2-butyl system (8) the *p*-MeO, *p*-Me, and *p*-H derivatives exist as the static benzylic cations.¹⁴ However, the p-CF₃ derivative undergoes a rapid 2,3-hydride shift $(9 \rightleftharpoons 10)$.¹⁴ We selected this system to test the effect of such equilibration on the ¹³C NMR shift correlation. For this correlation, we required a much wider range of substituents than was available in the earlier study.14

Results and Discussion

The ¹³C Shifts for the 2-Aryl-3-methyl-2-butyl Cations. The 2-aryl-3-methyl-2-butanols (11) were prepared by the addition

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- Soc. 1972, 94, 2044.

⁽¹⁰⁾ Farnum, D. G.; Botto, R. E.; Chambers, W. T.; Lam, B. J. Am. Chem. Soc. 1978, 100, 3847.



of 3-methyl-2-butanone to the Grignard reagent prepared from the corresponding bromo- or iodobenzenes.



The 2-aryl-3-methyl-2-butyl cations 8 were prepared by the slow addition of the alcohols as a solution in SO₂ClF at -78 °C to a cooled solution of SbF₅/FSO₃H/SO₂ClF at -78 °C. The ¹³C NMR spectra were recorded at -80 °C and -30 °C. The data are summarized in Tables I and II.

The shifts for the derivatives Z = p-OCH₃ to *m*-Cl are not significantly affected by increasing the temperature from -80 °C to -30 °C. On the other hand, the C⁺ shifts observed for the *m*-CF₃, 3,5-Cl₂, and *p*-CF₃ derivatives undergo an upfield shift by increasing the temperature from -80 °C to -30 °C. At the same time, the methine carbon (CH) shifts undergo a downfield shift at the higher temperature. This observation is consistent with the proposed equilibration, $9 \Rightarrow 10$, with an increased population of 10 at the higher temperature. In the case of 3,5-(CF₃)₂, the C⁺ and the α -CH signals are not observed at -80 °C, indicating more concentration of the higher-energy component as well as a more rapid equilibration between the two cations. These cations decompose into unidentified products at -30 °C.

Deviations in the $\Delta\delta C^+/\sigma^{C^+}$ **Plots for the 2-Aryl-3-methyl-2-butyl Cations.** The $\Delta\delta C^+$ values are plotted against the σ^{C^+} constants in Figure 1. The data points for the derivatives, Z = p-OCH₃ to *m*-Cl, nicely correlate against the σ^{C^+} values with a slope (ρ^{C^+}) of -18.2 and a correlation coefficient (*r*) of 0.999. A significant upward deviation is observed for the 3,5-Cl₂ and *p*-CF₃ derivatives.

The C⁺ signals for the derivatives Z = m-CF₃, 3,5-Cl₂, and p-CF₃ of the 2-aryl-3-methyl-2-butyl cations appear relatively upfield at -30 °C (Tables I and II). The deviation in the $\Delta\delta C^+/\sigma^{C^+}$ plot is also greater at -30 °C (Figure 1). For example, the deviation from the correlation line is 4.0 ppm for p-CF₃ at -80 °C and 5.6 ppm at -30 °C. Similarly, the deviation for 3,5-Cl₂ is 7.1 ppm at -80 °C and 9.9 ppm at -30 °C. This difference in the magnitude of the deviations can be accounted for on the basis of a greater population of 10 at the higher temperature, -30 °C, in the equilibrium $9 \implies 10$.

Deviations in the $\Delta\delta C^+/\sigma^{C^+}$ Plots for the 2-Aryl-2-norbornyl Cations. The ¹³C shifts for the 2-aryl-2-norbornyl cations have been determined previously at -70 °C and -40 °C.⁷ However, we wished to compare the shifts over the same wider temperature range used for the 2-aryl-3-methyl-2-butyl cations in this study. Accordingly, we redetermined the ¹³C shifts for the 2-aryl-2-norbornyl cations at -80 °C and -30 °C. Since we did not observe any significant difference in the shifts over those reported earlier,⁷ we are not reporting the individual data but are using these values for the correlations shown in Figure 2.

In the case of the 2-aryl-2-norbornyl cations, no such temperature dependence is observed in the range -80 °C to -30 °C (Figure 2). That is, the deviations from the correlation line at -80 °C and -30 °C are not significantly different. For example, the deviation from the correlation line for p-CF₃ is 6.4 ppm at -80 °C and 6.5 ppm at -30 °C. Accordingly, it seems unlikely that the deviation observed in the 2-aryl-2-norbornyl is due to any



Figure 1. Plots of σ^{C^+} against the $\Delta\delta C^+$ values for the 2-aryl-3methyl-2-butyl cations: slope $\rho^{C^+} = -18.2$ (-80 °C), -18.1 (-30 °C); correlation coefficient r = 0.9999 (-80 °C), 0.9998 (-30 °C) (for the derivatives *p*-OCH₃ to *m*-Cl only).

such equilibration. (It should be pointed out that Farnum had previously argued against such equilibration on the basis of energy considerations.¹⁰)

Comparison of ¹³C Shifts of the Methine (CH) Carbon Atom in the 2-Aryl-3-methyl-2-butyl Cations with the Shifts for the C₁ and C₆ Carbon Atom in the 2-Aryl-2-norbornyl Cations. Another interesting feature is the behavior of the α -methine (CH) carbon atom in the 2-aryl-3-methyl-2-butyl cations (8). The $\Delta\delta C_{\alpha}$ values observed for the α -methine (CH) carbon atom are plotted against the $\sigma^{\alpha C^+}$ constants¹⁵ in Figure 3. Here, as expected, the deviation occurs in the opposite direction (downfield), supporting the existence of the proposed equilibrium 9 = 10, with a greater population of 10 at the higher temperature.

In the case of the 2-aryl-2-norbornyl system (1), any 6,2-hydride shift ($12 \rightleftharpoons 13$) or Wagner-Meerwein shift ($10 \rightleftharpoons 15$) should cause similar deviations in the correlation of chemical shifts observed for the C₁ and C₆ carbon atoms.



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Table I. ¹³C NMR Shifts of 2-Aryl-3-methyl-2-butyl Cations (8) in SbF₅/FSO₃H/SO₂ClF at -80 °C

	chemical shift ^a											
substituent (Z)	C+	$C_{\alpha(CH)}$	$C_{\alpha'(CH_3)}$	C _β	C _Z	C ₁	C ₂	C3	C4	C,	C ₆	
p-OCH ₃	227.8	38.9	21.9	21.9	59.8	133.1	146.3 ^b	120.1	182.7	120.1	144.0 ^b	
<i>p</i> -CH ₃	252.7	42.3	25.9	22.9	24.9	137.6	142.7 ^b	134.3 ^c	174.5	134.2 ^c	140.1 ^b	
<i>p</i> -F	257.3	43.8	27.0	23.3		136.8	147.9 ^b	121.8	180.9	121.8	145.4 ^b	
	(5)						(17)	(22)	(293.7)	(22)	(17)	
p-C1	260.6	44.4	27.6	23.5		138.0	143.3 ^b	133.9	165.6	133.9	140.7	
m-CH ₃	262.6	44.1, 43.9	27.7	23.3	20.7	140.0	144.3, 142.2 ^b	140.4 ^c	157.0	132.9 ^c	139.7.	
											137.8 ^b	
Н	264.9	44.4	28.1	23.5		139.7	142.6 ^b	133.1	155.7	133.1	140.0 ^b	
m-F	271.0	46.6	29.8	24.1		135.1	125.0	164.3	142.2	134.7	138.2	
	(3)						(22)	(256)	(22)			
m-Cl	271.0	46.6	29.8	24.1		140.9	140.0	140.9	153.7	134.3	140.0	
m-CF ₃ d	274.2	47.7	30.5	24.2	123.0							
					(272)							
3,5-Cl ₂	269.8	57.9	30.9	25.2		141.1	137.1	140.0	150.7	140.0	137.1	
p-CF ₃	275.3	52.4	31.3	24.8	122.8	141.4	140.8	129.4	150.0	129.4	140.8	
-					(266)							
$3,5-(CF_3)_2^{e}$	f	f	35.5	27.0	123.2							
					(273)							

^a Chemical shifts are downfield from external Me₄Si (capillary). ^b Assignments may be interchanged. ^c Assignments may be interchanged. ^d Aromatic signals are not assigned because of ambiguities due to the presence of rotomers. ^e Aromatic signals are too weak to measure. ^f Not observed because of rapid hydride shift.



Figure 2. Plots of σ^{C^+} against the $\Delta\delta C^+$ values for the 2-aryl-2-norbornyl cations: slope $\rho^{C^+} = -13.6 \ (-80 \ ^\circ\text{C}), -13.7 \ (-30 \ ^\circ\text{C})$; correlation coefficient $r = 0.999 \ (-80 \ ^\circ\text{C}), 0.999 \ (-30 \ ^\circ\text{C})$ (for the electron-donating derivatives only).

However, no such deviation is observed in the correlations of the ¹³C NMR chemical shifts for these carbon atoms (see Figures 2^7 and 3^7). Accordingly, equilibrations $12 \Rightarrow 13$ or $14 \Rightarrow 15$ cannot be the factors responsible for the deviations in the $\Delta\delta C^+/\sigma C^+$ plot for the 2-arylnorbornyl system. However, the proposed "onset of σ -bridging" also cannot be the cause because the behavior of the C_1 and C_6 carbon atoms is not consistent with this proposal. In a σ -bridged cation, the C_6 carbon atom would be pentacoordinated. Such pentacoordinated carbon atoms are proposed to appear at extremely high field—even above Me₄Si.¹⁶



Figure 3. Plots of $\sigma^{\alpha C^+}$ against the $\Delta \delta C_{\alpha}$ values of the methine (CH) carbon atom in the 2-aryl-3-methyl-2-butyl cations: slope $\rho^{\alpha C^+} = -4.8$ (-80 °C), -4.9 (-30 °C); correlation coefficient r = 0.994 (-80 °C), 0.992 (-30 °C) (for the derivatives p-OCH₃ to m-Cl only).

However, the C_6 carbon shift in the 2-aryl-2-norbornyl cations (1) nicely correlates against the C_β shifts of the classical 1-aryl-1-cyclohexyl cations.

Accordingly, we have now ruled out both the onset of σ -bridging and equilibration as the responsible factor in the deviations ob-

⁽¹⁶⁾ Hogeveen, H.; Kwant, P. W. Acc. Chem. Res. 1975, 8, 413.

Table II. ¹³C NMR Shifts of 2-Aryl-3-methyl-2-butyl Cations (8) in SbF₅/FSO₃H/SO₂ClF at -30 °C

	chemical shift ^a												
substituent (Z)	C+	C _{a(CH)}	C _{α'(CH₃)}	C _β	CZ	C ₁	C ₂	C3	C4	C,	C ₆		
p-OCH,	227.8	39.0	22.0	22.0	59.8	133.3	146.3 ^b	120.2 ^c	183.0	119.9 ^c	144.1 ^b		
<i>p</i> -СН,	252.7	42.5	25.0	23.1	25.8	137.9	142.7 ^b	134.4 ^c	174.9	134.3 ^c	142.2 ^b		
p-F	257.2	44.0	27.0	23.4		137.1	147.8 ^b	121.9	181.1	121.9	145.4 ^b		
	(4)						(17)	(22)	(294)	(22)	(17)		
<i>p-</i> C1	260.3	44.5	27.4	23.6		138.3	141.9	134.1	166.2	134.1	141.9		
m-CH	262.5	44.2	27.6	23.5	20.7	140.4	144.6 ^b	140.4	157.2	133.1	140.4 ^b		
Н	264.9	44.6	28.0	23.6		139.9	141.4	133.2	155.8	133.2	141.4		
m-F	270.7	47.0	29.7	24.2		135.2	125.1	164.2	142.2	134.8	138.2		
	(2)						(22)	(256)	(22)				
<i>m</i> -Cl	270.7	47.0	29.6	24.2		139.9	139.7	141.2	153.9	134.4	139.0		
m -CF $_{3}^{d}$	273.7	48.6	30.4	24.4	123.2								
5					(272)								
3,5-Cl,	267.0	61.0	30.7	25.5		141.2	137.0	140.3	150.7	140.3	137.0		
p-CF	273.6	54.5	31.1	25.1	123.0	141.6	140.8	129.6	150.1	129.6	140.8		
					(270)			(3)	(34)	(3)			
$3,5-(CF_3)_2^e$									-	-			

^a Chemical shifts are in parts per million downfield from external Me₄Si (capillary). ^b Assignments may be interchanged. ^c Assignments may be interchanged. ^d Aromatic signals are too weak to assign. ^e This ion decomposes to unidentified products.

served in the ¹³C shifts for the 2-aryl-2-norbornyl cations and steric inhibition of coplanarity as the responsible factor in the deviations observed in the ¹³C shifts for the benzhydryl cations.⁸

We are left with two factors to consider: enhanced electron supply in some systems and inductive π -polarization, as suggested by Brownlee and co-workers.¹² These two phenomena could be related since enhanced electron supply by conjugation (or hyperconjugation) would provide some double bond character to the bond between the C⁺ carbon atom and the conjugating (or hyperconjugating) carbon atom. This will result in inductive π polarization similar to that suggested by Brownlee and co-workers to explain the upfield shifts observed for the carbonyl carbon atom in substituted acetophenones containing electron-withdrawing substituents.¹²



We are currently exploring the utility of this interpretation for the observed deviations.

Estimation of Equilibrium Concentrations of 9 and 10. It is of interest to see whether the data can be used to estimate the concentrations of the equilibrating cations, 9 and 10. The C⁺ shifts observed for the derivatives Z = p-OCH₃ to m-Cl do not vary with temperature. The $\Delta\delta C^+$ values for these derivatives correlate nicely against the σ^{C^+} constants (Figure 1). Accordingly, it is possible to estimate the C⁺ shift for the static ion 9. The following equation can be written with use of the observed C⁺ shift, the estimated shift of C⁺ in 9, and the shift of the methine (CH) carbon atom in 10, where x is the mole fraction of the component 9.

$$\delta_{C^+}(obsd) = x\delta_{C^+}(est) + (1-x)\delta_{CH}$$

The value of the CH carbon shift in 10 can be assumed to be 70 ppm by adding a value of ~15 ppm to the -CH carbon atom shift in 8 (Z = m-CF₃) for the substituent effect in replacing a methyl group by an aryl group.¹⁷ The concentrations of 9 and 10 estimated by using the above equation are summarized in Table III. These entries in Table III show that the concentration of 10 is more when Z = 3,5-Cl₂ than when Z = p-CF₃. This is contrary to expectation on the basis of the σ^{C^+} values, since p-CF₃

 Table III.
 Equilibrium Concentrations of Cations 9 and 10

substituent	temp	obsd &C+	est 5 C+	concn, %		
(Z)	°C	(ppm)	(ppm)	9	10	
m-CF ₃	-80	274.2	275.1	99.6	0.4	
5	-30	273.7	275.0	99.4	0.6	
3,5-Cl,	-80	269.8	276.9	96.6	3.4	
•	-30	267.0	276.9	95.2	4.8	
p-CF,	80	275.3	279.3	98.1	1.9	
	-30	273.6	279.2	97.3	2.7	

 $(\sigma^{C^+} = 0.79)$ is more an electron-withdrawing substituent than 3,5-Cl₂ ($\sigma^{C^+} = 0.66$). On the other hand, the σ^+ scale indicates that the 3,5-Cl₂ ($\sigma^+ = 0.798$) substituent is more electron withdrawing than p-CF₃ ($\sigma^+ = 0.612$). This indicates that the σ^+ constants may be more suitable for estimating the position for equilibration or the relative stabilities of benzylic cations than the σ^{C^+} values, which may be complicated by contributions from factors other than the stabilizing effect of the substituent.

Conclusion

The substituted 2-aryl-3-methyl-2-butyl cations provide an example of a system that is static (tertiary benzylic) over a wide range of substituents (p-OCH₃ to m-Cl) but rapidly equilibrating with strongly electron-withdrawing substituents (m-CF₃, p-CF₃, 3,5-Cl₂). A plot of the ¹³C shifts for the cationic carbon against the substituent constants, σ^{C^+} , gives an excellent linear correlation from p-OCH₃ through m-Cl, with upward deviations revealed for m-CF₃, p-CF₃, and 3,5-Cl₂. The plots are quite similar to those produced by the data for 2-aryl-2-norbornyl cations. However, the deviations for the substituted 2-aryl-3-methyl-2-butyl cations increase with increasing temperature (-80 °C \rightarrow -30 °C), in agreement with the predicted effect of the increasing temperature to increase the equilibrium concentration of the minor component of the equilibrium system. On the other hand, the deviations in the 2-aryl-2-norbornyl system do not vary over the same temperature range. Similar differences are observed for ¹³C shifts of the methine (CH) carbons in the 2-aryl-3-methyl-2-butyl cations and the ${}^{13}C$ shifts of C_1 and C_6 in the 2-aryl-2-norbornyl system. It is concluded that the observed deviations in the 2-aryl-2-norbornyl cations cannot be the result of equilibration, either 6,2hydride shift or Wagner-Meerwein shift. Consequently, we have now ruled out both steric inhibition to coplanarity and equilibration as factors in those systems 1-7 that exhibit such deviations in their $\Delta \delta C^+ / \sigma^{C^+}$ plots.

Experimental Section

Precursors. The 2-aryl-3-methyl-2-butanols were prepared by the addition of 3-methyl-2-butanone to the Grignard reagent prepared from the corresponding substituted bromo- or iodobenzenes. The boiling point data are as follows, substituent, bp in °C (mmHg): p-CH₃, 56 (0.1) [lit.¹⁴

⁽¹⁷⁾ Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972.

bp 84-85 (3.0)]; p-F, 56 (0.2); p-Cl, 70 (0.1); m-CH₃, 60 (0.2); m-F, 54 (0.1); m-Cl, 66 (0.1); m-CF₃, 58 (0.2); 3,5-Cl₂, 84 (0.1). The p-OCH₃, H, p-CF₃, and 3,5-(CF₃)₂ derivatives were available from earlier work in our laboratories.¹⁸ Satisfactory analytical data (C \pm 0.2, H \pm 0.2, F \pm 0.1, and Cl \pm 0.2) were obtained for all of the new compounds. All of these precursors gave ¹³C NMR spectral data in accordance with their structures.

Carbocations. The ions were prepared by slow addition of a solution of the precursor in SO₂ClF at -78 °C to a solution of SbF₅/FSO₃H/SO₂ClF at -78 °C with rapid vortex mixing. The acid (SbF₅/FSO₃H 1:1 M) concentration in the solution was 3 M. The concentration of the ion based on the precursor added was ~0.5 M. Transfer of the solution under nitrogen to an 8-mm NMR tube was achieved via a cooled double-ended syringe, as described previously.¹⁹

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NMR Spectra. ¹³C NMR spectra were recorded at -80 °C or at -30 °C on a Varian CFT-20 spectrometer with 8-mm tubes containing a concentric 3-mm (o.d.) capillary tube of acetone- d_6 and Me₄Si, 8192 data points, a spectral width of 6500 Hz, and a pulse angle of 45°. Chemical shifts are in parts per million downfield from external Me₄Si.

Registry No. 1 (Z = p-OCH₃), 53600-66-1; 1 (Z = p-CH₃), 53600-69-4; 1 (Z = p-F), 51823-56-4; 1 (Z = p-Cl), 53600-70-7; 1 (Z = m-CH₃), 64618-83-3; 1 (Z = H), 18026-67-0; 1 (Z = m-F), 81390-38-7; 1 (Z = m-Cl), 53600-74-1; 1 (Z = m-CF₃), 81390-39-8; 1 (Z = 3,5-Cl₂), 81390-40-1; 1 (Z = p-CF₃), 53600-75-2; 1 (Z = 3,5-(CF₃)₂), 53600-76-3; 8 (Z = p-OCH₃), 35144-47-9; 8 (Z = p-CH₃), 36043-28-4; 8 (Z = p-F), 51804-42-3; 8 (Z = p-Cl), 41912-30-5; 8 (Z = m-CH₃), 84074-03-3; 8 (Z = m-CH₃), 84074-05-5; 8 (Z = m-CF₃), 84074-06-6; 8 (Z = 3,5-Cl₂), 84074-07-7; 8 (Z = p-CF₃), 84074-08-8; 8 (Z = 3,5-(CF₃)₂), 84074-09-9; 10, 84074-10-2.

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Carbocationic Rearrangements Originating from the 2-tert-Butyl-2-adamantyl System¹

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Abstract: The nature of carbocationic species ($C_{14}H_{23}^+$) related to the 2-*tert*-butyl-2-adamantyl cation (3) has been explored by trapping and isotope-labeling experiments and by spectroscopic studies under stable ion conditions. Treatment of either 2-*tert*-butyl-2-adamantanol (1) or 2-isopropenyl-2-methyladamantane (2) with acid in the presence of a reducing agent (HI or tri-*n*-hexylsilane) yielded 2-*tert*-butyladamantane (5) as the major or exclusive product. Deuterium exchange experiments established the rapid interconversion of the 2-(2-methyl-2-adamantyl)-2-propyl cation (4) with ion 3 under these conditions. In hydrogen chloride saturated media ($E_{12}O$, CH_2Cl_2 , or $CHCl_3$) at 100 °C, alkene 2 formed within 4 h a mixture containing 5% of the isomeric compound 2,2-dimethylspiro[cyclopropane-1,2'-tricyclo[3.3.1.1^{3,7}]decane] (7). Each of the compounds 1, 2, and 7 gave a single carbocationic species in the temperature range of -78 to -20 °C in FSO₃H-SbF₅-SO₂ClF that was identified by ¹H and ¹³C NMR spectroscopy as ion 3. At extended times or temperatures of 150-200 °C, 2 and 7 in HCl-saturated CHCl₃ solution were consumed and replaced by a mixture of products consisting of 2-isobutylideneadamantane (8, 30-40%), 1-(2-adamantyl)-2-methylprop-1-ene (9, 60-70%), and methyleneadamantane (10, 0-10%). Pure 8 and 9 formed a 40:60 equilibrium mixture in the presence of acid at 150 °C. Deuterium labeling established a single 1,3-hydride shift connecting isomeric carbocations as the pathway between 8 and 9. The formation of 10 is suggested to arise from the α expulsion of dimethylcarbene from ion 4.

2-tert-Butyl-2-adamantanol (1) and its derivatives undergo carbocation-forming reactions extremely rapidly.² For example, 2-tert-butyl-2-adamantyl p-nitrobenzoate quickly reacts in aqueous solvolytic media to give the methyl-shifted alkene 2-isopropenyl-2-methyladamantane (2) as the major product along with minor amounts of the unrearranged parent alcohol $1.^{2,3}$ Treatment of alcohol 1 with traces of acid causes a fast conversion to alkene $2.^{2,4}$ These results have been understood in terms depicted in Scheme I.

The driving force for the dehydration of 1 as well as the solvolytic behavior of its ester derivative is believed to be the formation of the relatively unstrained 2-*tert*-butyl-2-adamantyl cation (3) from sterically strained $1.^{2-4}$ Since direct loss of a β proton from ion 3 would result in the formation of an extremely strained

Scheme I



bridgehead alkene, a methyl rearrangement to produce ion 4 which can then undergo proton loss to yield the observed alkene 2 seems to be a more favorable reaction pathway. That ion 3 is a discrete precursor to the methyl-shifted ion 4 was indicated by the disparity of the deuterium kinetic isotope effects on the overall rate of solvolysis (1.11) vs. methyl migration (1.25) during the solvolysis of the *p*-nitrobenzoate ester which was deuterated at all *tert*-butyl methyl groups.³

⁽¹⁾ Portions of this work have been communicated in preliminary form: Fry, J. L.; Saba, J. A. *Tetrahedron Lett.* **1982**, *23*, 1743; "Abstracts of Papers", 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 28-April 2, 1982; American Chemical Society: Washington, D.C, 1982; ORGN 56.

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