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

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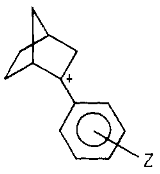
Abstract: A series of 2-aryl-3-methyl-2-butyl cations was prepared in $SbF_5/FSO_3H/SO_2ClF$ at −78 °C and their ^{13}C NMR shifts were measured at −80 °C. A plot of the observed $\Delta\delta C^+$ values against the σ^{C^+} constants gives a straight line for substituents over the range p-OCH_3 to m-Cl (slope $\rho^{C^+} = -18.2$, correlation coefficient $r = 0.999$). However, the data points for the strongly electron-withdrawing substituents, m-CF_3, 3,5-Cl_2, and p-CF_3, 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-OCH_3 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 ^{13}C 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]



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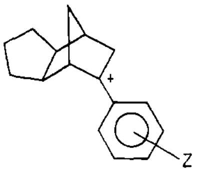

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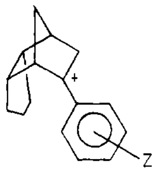

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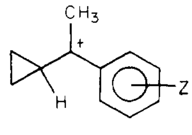

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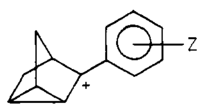

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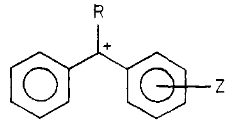
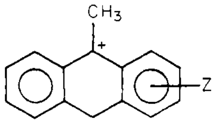


6, R = H, CH_3



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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 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 $\rightleftharpoons$ 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-3-methyl-2-butyl system (**8**) the p-MeO, p-Me, and p-H derivatives exist as the static benzylic cations.[14] However, the p-CF_3 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 ^{13}C 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 ^{13}C 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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[1] Postdoctoral research associate on a grant provided by the Exxon Research and Engineering Company.

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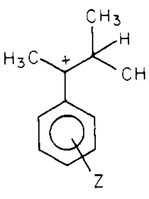
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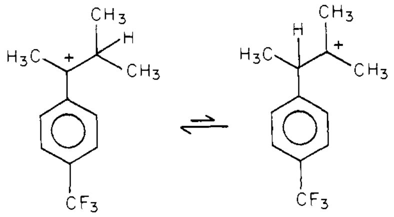
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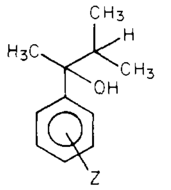
of 3-methyl-2-butanone to the Grignard reagent prepared from the corresponding bromo- or iodobenzenes.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The 2-aryl-3-methyl-2-butyl cations **8** were prepared by the slow addition of the alcohols as a solution in SO_2ClF at −78 °C to a cooled solution of $SbF_5/FSO_3H/SO_2ClF$ at −78 °C. The ^{13}C 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-OCH_3 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-CF_3, 3,5-Cl_2, and p-CF_3 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** ⇌ **10**, with an increased population of **10** at the higher temperature. In the case of 3,5-$(CF_3)_2$, 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-OCH_3 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-Cl_2 and p-CF_3 derivatives.

The C^+ signals for the derivatives Z = m-CF_3, 3,5-Cl_2, and p-CF_3 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-CF_3 at −80 °C and 5.6 ppm at −30 °C. Similarly, the deviation for 3,5-Cl_2 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** ⇌ **10**.

Deviations in the $\Delta\delta C^+/\sigma^{C^+}$ Plots for the 2-Aryl-2-norbornyl Cations. The ^{13}C 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 ^{13}C 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-CF_3 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 such equilibration. (It should be pointed out that Farnum had previously argued against such equilibration on the basis of energy considerations.[10])

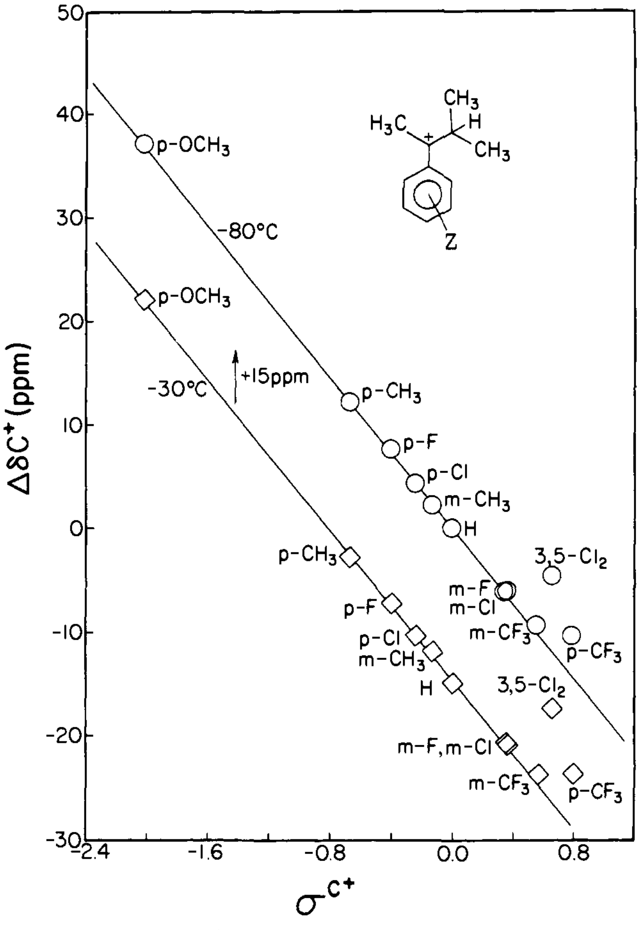

Figure 1. Plots of σ^{C^+} against the $\Delta\delta C^+$ values for the 2-aryl-3-methyl-2-butyl cations: slope $\rho^{C^+} = -18.2$ (−80 °C), −18.1 (−30 °C); correlation coefficient r = 0.9999 (−80 °C), 0.9998 (−30 °C) (for the derivatives p-OCH_3 to m-Cl only).

Comparison of ^{13}C Shifts of the Methine (CH) Carbon Atom in the 2-Aryl-3-methyl-2-butyl Cations with the Shifts for the C_1 and C_6 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 $\sigma^{\alpha C^+}$ constants[15] 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** ⇌ **13**) or Wagner–Meerwein shift (**10** ⇌ **15**) should cause similar deviations in the correlation of chemical shifts observed for the C_1 and C_6 carbon atoms.

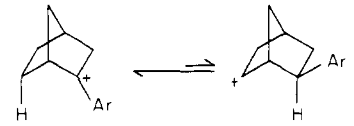
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Table I. ^{13}C NMR Shifts of 2-Aryl-3-methyl-2-butyl Cations (8) in $SbF_5/FSO_3H/SO_2ClF$ at −80 °C

	chemical shift[a]										
substituent (Z)	C^+	$C_{\alpha(CH)}$	$C_{\alpha'(CH_3)}$	C_β	C_Z	C_1	C_2	C_3	C_4	C_5	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]
p-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]
p-F	257.3 (5)	43.8	27.0	23.3		136.8	147.9[b] (17)	121.8 (22)	180.9 (293.7)	121.8 (22)	145.4[b] (17)
p-Cl	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]
H	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 (3)	46.6	29.8	24.1		135.1	125.0 (22)	164.3 (256)	142.2 (22)	134.7	138.2
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 (266)	141.4	140.8	129.4	150.0	129.4	140.8
3,5-$(CF_3)_2$[e]	f	f	35.5	27.0	123.2 (273)						

[a] Chemical shifts are downfield from external Me_4Si (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.

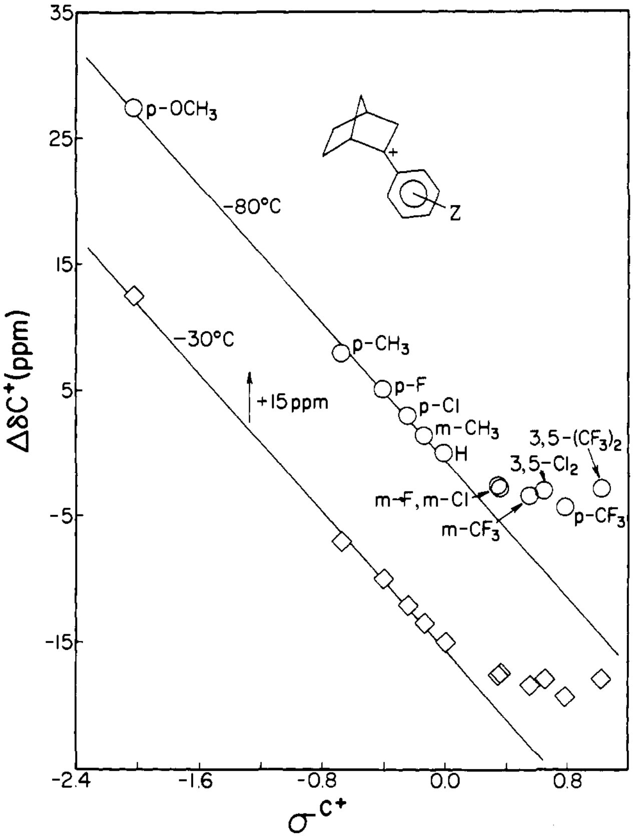

Figure 2. Plots of σ^{C^+} against the $\Delta\delta C^+$ values for the 2-aryl-2-norbornyl cations: slope $\rho^{C^+} = -13.6$ (−80 °C), −13.7 (−30 °C); correlation coefficient $r = 0.999$ (−80 °C), 0.999 (−30 °C) (for the electron-donating derivatives only).

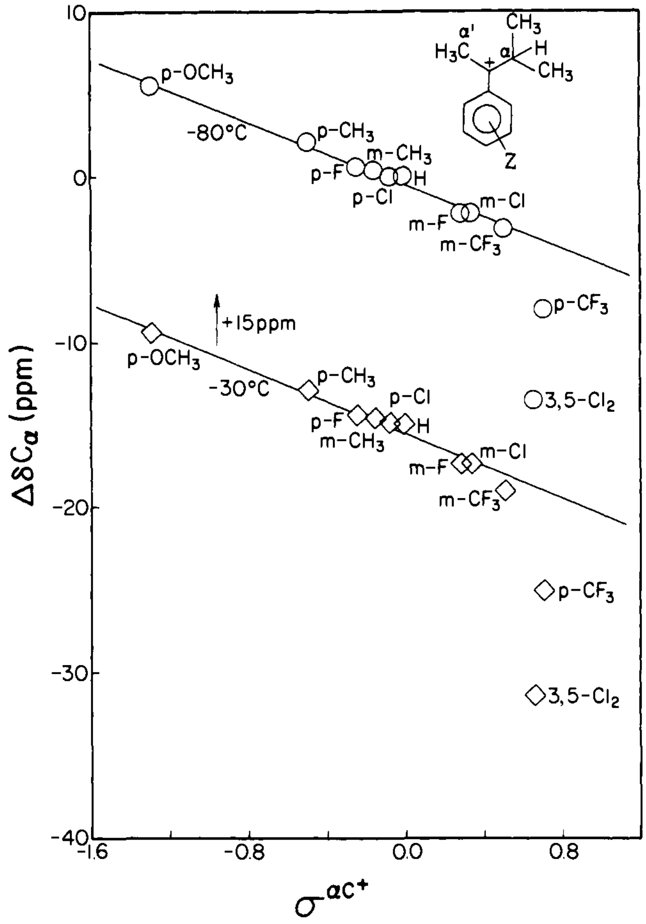

Figure 3. Plots of $\sigma^{\alpha C^+}$ against the $\Delta\delta C_\alpha$ values of the methine (CH) carbon atom in the 2-aryl-3-methyl-2-butyl cations: slope $\rho^{\alpha C^+} = -4.8$ (−80 °C), −4.9 (−30 °C); correlation coefficient $r = 0.994$ (−80 °C), 0.992 (−30 °C) (for the derivatives p-OCH_3 to m-Cl only).

However, no such deviation is observed in the correlations of the ^{13}C NMR chemical shifts for these carbon atoms (see Figures 2[7] and 3[7]). Accordingly, equilibrations **12** $\rightleftharpoons$ **13** or **14** $\rightleftharpoons$ **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 Me_4Si.[16]

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-

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

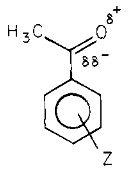
Table II. ^{13}C NMR Shifts of 2-Aryl-3-methyl-2-butyl Cations (8) in $SbF_5/FSO_3H/SO_2ClF$ at −30 °C

	chemical shift^a										
substituent (Z)	C^+	C_{α}(CH)	$C_{\alpha'}(CH_3)$	C_β	C_Z	C_1	C_2	C_3	C_4	C_5	C_6
p-OCH_3	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
p-CH_3	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)
p-Cl	260.3	44.5	27.4	23.6		138.3	141.9	134.1	166.2	134.1	141.9
m-CH_3	262.5	44.2	27.6	23.5	20.7	140.4	144.6^b	140.4	157.2	133.1	140.4^b
H	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)		
m-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						
					(272)						
3,5-Cl_2	267.0	61.0	30.7	25.5		141.2	137.0	140.3	150.7	140.3	137.0
p-CF_3	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 Me_4Si (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 ^{13}C shifts for the 2-aryl-2-norbornyl cations and steric inhibition of coplanarity as the responsible factor in the deviations observed in the ^{13}C 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]



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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-OCH_3 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**.

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

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-CF_3) 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-Cl_2 than when Z = p-CF_3. This is contrary to expectation on the basis of the σ^{C^+} values, since p-CF_3 (σ^{C^+} = 0.79) is more an electron-withdrawing substituent than 3,5-Cl_2 (σ^{C^+} = 0.66). On the other hand, the σ^+ scale indicates that the 3,5-Cl_2 (σ^+ = 0.798) substituent is more electron withdrawing than p-CF_3 (σ^+ = 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.

Table III. Equilibrium Concentrations of Cations 9 and 10

substituent (Z)	temp, °C	obsd δC^+ (ppm)	est δC^+ (ppm)	concn, %	
				9	10
m-CF_3	−80	274.2	275.1	99.6	0.4
	−30	273.7	275.0	99.4	0.6
3,5-Cl_2	−80	269.8	276.9	96.6	3.4
	−30	267.0	276.9	95.2	4.8
p-CF_3	−80	275.3	279.3	98.1	1.9
	−30	273.6	279.2	97.3	2.7

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-OCH_3 to m-Cl) but rapidly equilibrating with strongly electron-withdrawing substituents (m-CF_3, p-CF_3, 3,5-Cl_2). A plot of the ^{13}C shifts for the cationic carbon against the substituent constants, σ^{C^+}, gives an excellent linear correlation from p-OCH_3 through m-Cl, with upward deviations revealed for m-CF_3, p-CF_3, and 3,5-Cl_2. 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 → −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 ^{13}C 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 6,2-hydride 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-CH_3, 56 (0.1) [lit.[14]

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bp 84–85 (3.0)]; *p*-F, 56 (0.2); *p*-Cl, 70 (0.1); *m*-CH_3, 60 (0.2); *m*-F, 54 (0.1); *m*-Cl, 66 (0.1); *m*-CF_3, 58 (0.2); 3,5-Cl_2, 84 (0.1). The *p*-OCH_3, H, *p*-CF_3, and 3,5-$(CF_3)_2$ derivatives were available from earlier work in our laboratories.[18] Satisfactory analytical data (C ± 0.2, H ± 0.2, F ± 0.1, and Cl ± 0.2) were obtained for all of the new compounds. All of these precursors gave ^{13}C NMR spectral data in accordance with their structures.

Carbocations. The ions were prepared by slow addition of a solution of the precursor in SO_2ClF at −78 °C to a solution of $SbF_5/FSO_3H/SO_2ClF$ at −78 °C with rapid vortex mixing. The acid (SbF_5/FSO_3H 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]

NMR Spectra. ^{13}C 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 Me_4Si, 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 Me_4Si.

Registry No. 1 (Z = *p*-OCH_3), 53600-66-1; **1** (Z = *p*-CH_3), 53600-69-4; **1** (Z = *p*-F), 51823-56-4; **1** (Z = *p*-Cl), 53600-70-7; **1** (Z = *m*-CH_3), 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*-CF_3), 81390-39-8; **1** (Z = 3,5-Cl_2), 81390-40-1; **1** (Z = *p*-CF_3), 53600-75-2; **1** (Z = 3,5-$(CF_3)_2$), 53600-76-3; **8** (Z = *p*-OCH_3), 35144-47-9; **8** (Z = *p*-CH_3), 36043-28-4; **8** (Z = *p*-F), 51804-42-3; **8** (Z = *p*-Cl), 41912-30-5; **8** (Z = *m*-CH_3), 84074-03-3; **8** (Z = H), 36043-29-5; **8** (Z = *m*-F), 84074-04-4; **8** (Z = *m*-Cl), 84074-05-5; **8** (Z = *m*-CF_3), 84074-06-6; 8 (Z = 3,5-Cl_2), 84074-07-7; **8** (Z = *p*-CF_3), 84074-08-8; **8** (Z = 3,5-$(CF_3)_2$), 84074-09-9; **10**, 84074-10-2.

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Carbocationic Rearrangements Originating from the 2-*tert*-Butyl-2-adamantyl System[1]

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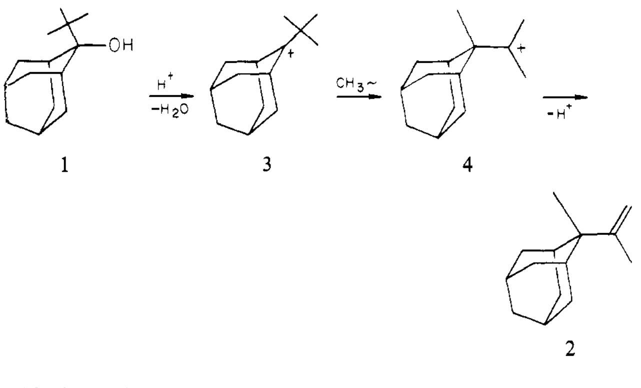
Abstract: The nature of carbocationic species ($C_{14}H_{23}^+$) related to the 2-*tert*-butyl-2-adamantyl cation (**3**) has been explored by trapping and isotope-labeling experiments and by spectroscopic studies under stable ion conditions. Treatment of either 2-*tert*-butyl-2-adamantanol (**1**) or 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 (Et_2O, 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 FSO_3H–SbF_5–SO_2ClF that was identified by ^1H and ^{13}C NMR spectroscopy as ion **3**. At extended times or temperatures of 150–200 °C, **2** and **7** in HCl-saturated $CHCl_3$ 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 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]

Scheme I



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