J. Org. Chem. 1982, 47, 4740–4742

Structural Effects in Solvolytic Reactions. 41. The Effect of Coplanarity on the Carbon-13 Nuclear Magnetic Resonance Shifts of Substituted *o*-Methyl-*tert*-cumyl Cations

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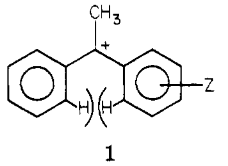
Received April 13, 1982

The effect of steric inhibition on coplanarity was examined by preparing a series of 4/5-substituted *o*-methyl-*tert*-cumyl carbocations in $SbF_5/FSO_3H/SO_2ClF$ at −78 °C and measuring their ^{13}C NMR shifts at −80 °C. The $\Delta\delta C^+$ shifts correlate linearly against the σ^{C^+} constants with a ρ^{C^+} value of −18.3 and a correlation coefficient of 0.9995. The excellent correlation observed for this system indicates that the deviations in the σ^{C^+}–$\Delta\delta C^+$ plots observed for certain systems of benzylic carbocations are probably not the result of steric hindrance to coplanarity in these systems. The ρ^{C^+} value of −18.3 is essentially the same as the value of −18.2 observed for the substituted *tert*-cumyl cations. This indicates that the fully developed dimethylcarbinyl cationic center must be able to overcome the steric difficulties in achieving coplanarity with the aromatic ring with only minor costs in energy, in contrast to the situation in the solvolysis of related derivatives.

A systematic study of the effect of substituents upon the ^{13}C NMR shifts of carbocations was undertaken to provide a fuller understanding of the mechanisms for stabilization of the cations.[1-6] Thus we developed a set of σ^{C^+} constants to correlate the C^+ shifts of representative substituted benzylic carbocations.[1] These constants nicely correlated the $\Delta\delta C^+$ ($\Delta\delta C^+ = \delta C^+_H - \delta C^+_Z$) observed for some 10 different systems of representative aryldialkyl carbocations.[1-4,6] However, the $\Delta\delta C^+$ shifts observed for several other systems failed to correlate against these constants.[7] For example, in the case of 1-aryl-1-phenyl-1-ethyl cations (1), the data points of the electron-withdrawing derivatives deviate upward from the straight line defined by the electron-donating derivatives.



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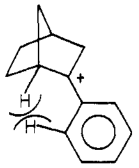

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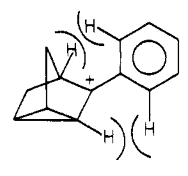

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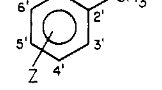
Farnum and co-workers previously observed such deviation in the plot of the C^+ shifts of 1-aryl-1-phenyl-1-ethyl cations 1 against the C^+ shifts of 1-aryl-1-cyclopentyl cations.[8] They suggested that in this system the more stabilizing aryl group would become more coplanar and would force the other aryl group out of coplanarity, leading to the observed deviations. Presumably steric effects operate to prevent both aryl groups from assuming a coplanar arrangement simultaneously.

Olah and Liang previously invoked the steric hindrance to the coplanarity phenomenon to explain the difference in the C^+ shifts between the 2-phenyl-2-norbornyl cation 2 and the 3-phenyl-3-nortricyclyl cation 3 that they had observed.[9] Incidentally, in these cases (2 and 3) also the σ^{C^+}–$\Delta\delta C^+$ plots exhibit upward deviations for the electron-withdrawing derivatives.[7] Accordingly, it appeared desirable to study the effect of steric hindrance to coplanarity on the C^+ shifts in a simple system. We selected the 4′/5′-substituted *o*-methyl-*tert*-cumyl cations 4.



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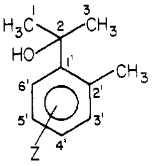
Results and Discussion

The tertiary alcohol precursors 5 were synthesized by the reaction of acetone with the Grignard reagent prepared from the corresponding 4/5-substituted *o*-bromotoluenes 6.



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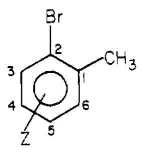

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The carbocations 4 were prepared by dissolution of these alcohols in $SbF_5/FSO_3H/SO_2ClF$ at −78 °C. The ^{13}C NMR spectra were recorded at −80 °C. The data are summarized in Table I. The assignments of all of the signals except those observed for the α-CH_3 signals are straightforward. The α-CH_3 carbon atoms give two signals for all of the derivatives except Z = 5′-CF_3. The signal that appears at high field was assigned to the α-methyl carbon atom closer to the ortho methyl group because the steric interactions between these groups would cause an upfield shift for the α-CH_3 carbon atom.[10] The α-CH_3 carbon atom signals are separated by ≥1.6 ppm for the derivatives Z = 4′-OCH_3 to Z = 5′-F. In the case of Z = 5′-CF_3 derivative, a broad signal is observed for both of these carbon atoms. Pre-

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0022-3263/82/1947-4740$01.25/0

Table I. ^{13}C NMR Shifts[a] of Substituted 2′-Methylphenyl-2-propyl Carbocations 4 in $SbF_5/FSO_3H/SO_2ClF$ at −80 °C

substituent (Z)	chemical shift[b]										
	C^+	$C_{1(CH_3)}$	$C_{3(CH_3)}$	2′-CH_3	C_Z	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{5'}$	$C_{6'}$
4-OCH_3	217.7	33.3	32.1	27.9	59.4	136.0	162.6	118.0	180.5	122.4	147.4
4-CH_3	241.8	36.7	34.9	27.6	24.4	140.7	159.3	131.6	172.0	138.2	143.7
4-F	246.8	37.6	36.0	27.9		140.0	165.3	119.1	178.6	124.8	149.1
	(5)						(17)	(22)	(292)	(22)	(17)
4-H	254.2	38.6	36.5	27.5		143.2	159.3	130.3	153.6	137.2	143.4
5-F	260.3	39.9	38.0	27.3		143.7	156.6	139.0	140.3	162.2	126.4
						(8)		(7)	(22)	(253)	(22)
5-CF_3	265.5	40.1	39.8[c]	39.8[c]	123.3	142.9	162.3	138.1	147.0	132.1	138.5
					(273)					(35)	(3)

[a] In parts per million downfield from Me_4Si (capillary). [b] The signals were assigned on the basis of off-resonance experiments and comparison with the reported values for the substituted *tert*-cumyl cations.[1] ^{13}C–F coupling constants (in hertz) are in parentheses. [c] Appears as a broad signal (40.6–38.9 ppm).

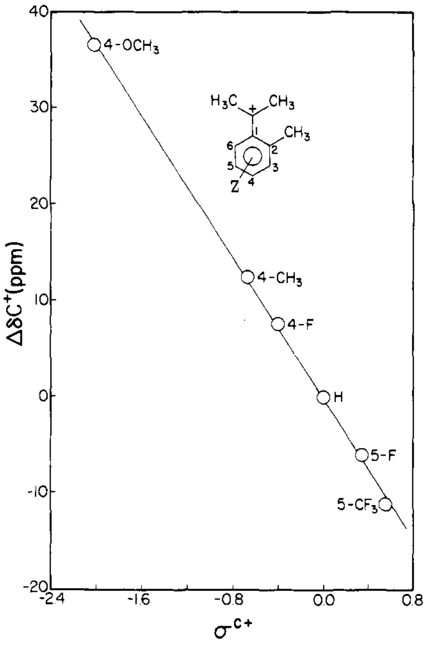
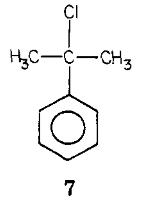


Figure 1. A plot of σ^{C^+} against $\Delta\delta C^+$ shifts for the 4- or 5-substituted *o*-methylphenyl-2-propyl cations 4: slope (ρ^{C^+}) = −18.3 and correlation coefficient (r) = 0.9995.

sumably, the α-CH_3 carbon atoms become equivalent because of faster rotation of the C^+–C_{ipso} bond as the single bond character of this bond increases.

A plot of the $\Delta\delta C^+$ shifts against the σ^{C^+} constants gives a good straight line with a slope (ρ^{C^+}) of −18.3 and a correlation coefficient of 0.9995 (Figure 1). This ρ^{C^+} value is essentially the same as the ρ^{C^+} value (−18.2) observed for the substituted *tert*-cumyl cations.[1] This indicates that the cationic center must be able to accommodate the difficulties in achieving coplanarity with only minor costs in energy.

In solvolysis, the *p*-methyl substituent (**8**) markedly enhances the rate of the parent compound (**7**). This rate enhancement is attributed to stabilization of the incipient carbonium ion in the transition state by hyperconjugative interactions of the *p*-methyl substituent with the developing cationic center.



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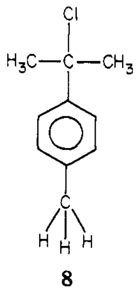

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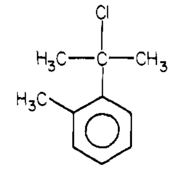
rel rate at 25 °C 1.00 26.0

The effect of an *o*-methyl substituent is much less (**9**).[11]



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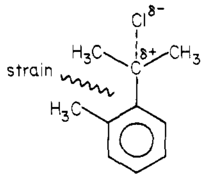
rel rate at 25 °C 3.63

This decreased effect was attributed to the difficulties encountered in the developing cationic center to become coplanar with the aromatic ring (**10**).[11] Delocalization of



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the charge of the developing cationic center into the aromatic ring and into the methyl substituent would be most favored by a coplanar arrangement.

How, then, can we account for the failure to observe any significant effect of the *o*-methyl substituent in the fully developed *tert*-cumyl carbocations examined in the present study? We can only conclude that in the fully developed cations the stabilization provided by the aryl group overcomes the modest steric inhibition of resonance afforded by the *o*-methyl substituent. The decreased rate of solvolysis observed for the *o*-methyl-*tert*-cumyl chloride **9** indicates that in solvolysis the steric effect of the *o*-methyl group resists the stabilization provided by the aryl ring. An additional factor to be considered in the case of solvolysis may be steric hindrance to solvation which contributes to decreased rate of solvolysis for the *o*-methyl-*tert*-cumyl chloride.[12]

If the steric effects were much larger, the system would encounter much greater difficulties in overcoming such a steric barrier. Indeed, this has been observed recently.[13]

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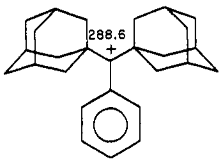
These authors observed that 1,1′-diadamantylphenylmethyl cation (**11**) exhibits a ^{13}C NMR shift at the carbonium carbon that is considerably downfield from the shift in the *tert*-cumyl cation (**12**).



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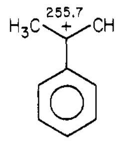

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However, the *tert*-cumyl system is clearly capable of overcoming the steric barrier to coplanarity in the fully developed ions.[14] The steric barrier in 1,1-diarylethyl cations (**1**), 2-aryl-2-norbornyl cations (**2**), and 3-aryl-3-nortricyclyl cations (**3**) should be correspondingly small. Consequently, it does not appear that such barriers can be responsible for the observed deviations in the ^{13}C plots for electron-withdrawing substituents. This conclusion has been tested further in the accompanying publication.[15]

We have considered four possible origins for the observed deviations in the $\Delta\delta C^+/\delta^{C^+}$ plots for certain benzylic systems containing strongly electron-withdrawing substituents: (1) steric inhibition to coplanarity,[8,9] (2) rapid equilibration (tert $\rightleftharpoons$ sec),[16] (3) enhanced electron supply from certain moieties,[7] and (4) inductive π polarization, as suggested by Brownlee and co-workers.[17] The studies reported in this and the accompanying publication[15] appear to rule out the steric origin. We are now testing the other explanations experimentally.

Experimental Section

Precursors. The 4′- or 5′-substituted *o*-methylphenyl-2-propyl alcohols **5** were synthesized by the reaction of acetone with the Grignard reagent prepared from the corresponding bromotoluenes **6**. All of these bromotoluenes **6** are commercially available except the 4′-OCH$_3$ and 5′-CF$_3$ derivatives. The 4′-OCH$_3$ (**6**) derivative was prepared by bromination of *m*-cresylmethyl ether with *N*-bromosuccinimide following a literature procedure.[18] The 5′-CF$_3$ (**6**) derivative was synthesized by bromination of *p*-(trifluoromethyl)toluene with bromine following a literature method.[19] The alcohol **5** derivatives Z = 4′-OCH$_3$ (mp 68 °C) and Z = H [bp 108 °C (20 mm)] have been reported previously from our laboratories.[10,20] The boiling point data for other derivatives are as follows: Z = 4′-CH$_3$, 117 °C (20 mm); Z = 4′-F, 56 °C (0.1 mm); Z = 5′-F, 59 °C (0.1 mm); and Z = 5′-CF$_3$, 67 °C (0.1 mm). All of these compounds gave ^{13}C NMR data in accordance with their structures. Satisfactory analytical data (<±0.3% for C, H, and F) were obtained for all of the new compounds.

Carbocations. The cations **4** were prepared by slow addition of the appropriate precursor as a solution in SO$_2$ClF at −78 °C to a solution of FSO$_3$H/SbF$_5$(1:1 M)/SO$_2$ClF cooled to −78 °C with rapid vortex mixing. The acid concentration in the solution was 3 M. The concentration of the ion based on the precursor added was ~0.5 M. Transfer of the solutions under nitrogen to an 8-mm NMR tube was achieved via a cooled double-ended syringe, as described previously.[21]

NMR Spectra. ^{13}C NMR spectra were recorded at −80 °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$_4$Si, 8192 data points, a spectral width of 6000 Hz, and a pulse angle of 45°. Chemical shifts are in parts per millon downfield from external Me$_4$Si.

Registry No. 4 (Z = 4′-OCH$_3$), 83208-01-9; 4 (Z = 4′-CH$_3$), 83208-02-0; 4 (Z = 4′-F), 83208-03-1; 4 (Z = 4′-H), 20615-38-7; 4 (Z = 5′-F), 83208-04-2; 4 (Z = 5′-CF$_3$), 83208-05-3; 5 (Z = 4′-CH$_3$), 83208-06-4; 5 (Z = 4′-F), 51788-85-3; 5 (Z = 5′-F), 83208-07-5; 5 (Z = 5′-CF$_3$), 83208-08-6.

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[14] For a fuller understanding of the effect of steric inhibition of resonance on the ^{13}C NMR shifts of carbocations, it may be desirable to run systems in which steric effects can be larger than in the present system, as in *o-tert*-butylcumyl cations. Very large effects of such *tert*-butyl substituents have been observed in a number of systems (see Harff, G. A.; Sinnema, A.; Wepster, B. M. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 71 and references cited therein, as well as Tanida, H.; Matsumura, H. *J. Am. Chem. Soc.* **1973**, *95*, 1586).

[15] Accompanying paper in this issue.

[16] We have observed similar deviations in the plot of the equilibrating 2-aryl-3-methyl-2-butyl cations. These results will be reported shortly.

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Structural Effects in Solvolytic Reactions. 42. Effect of Increasing Electron Demand on the Carbon-13 Nuclear Magnetic Resonance Shifts for Substituted 9-Methyl-9-anthracenium Cations. Evidence for the Unimportance of Steric Hindrance to Coplanarity in Causing Anomalous Carbon-13 Nuclear Magnetic Resonance Shifts

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Received April 13, 1982

A series of substituted 9-methyl-9-anthracenium cations were prepared in FSO$_3$H/SO$_2$ClF at −78 °C and their ^{13}C NMR shifts were measured at −80 °C. The $\Delta\delta C^+$ shifts observed for the electron-donating substituents correlate linearly against the σ^{C^+} constants. However, the data observed for the electron-withdrawing substituents deviate upward from the straight line defined by the data of electron-donating substituents, similar to the deviation observed for the 1-aryl-1-phenyl-1-ethyl carbocations. The deviation observed in the latter case was previously attributed to steric inhibition of coplanarity. However, comparison of the behavior of this system with that of the 9-methyl-9-anthracenium system casts doubt upon this explanation.

Recently, we proposed new σ^{C^+} constants to correlate the C$^+$ shifts of benzylic carbocations.[1] The C$^+$ shifts of several simple aryldialkyl carbocations, such as 1-aryl-1-cyclopentyl cations, correlate linearly against these σ^{C^+}

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