

Structural Effects in Solvolytic Reactions. 37. Effect of Increasing Electron Demand on Carbon-13 Nuclear Magnetic Resonance Shifts in the 9-Aryl-*exo*-5,6-trimethylene- and 9-Aryl-*endo*-5,6-trimethylene-9-norbornyl Carbocations. Effect of the Cationic Carbon Center on Remote Carbon Atoms in the Skeleton As Revealed by Increasing Electron Demand

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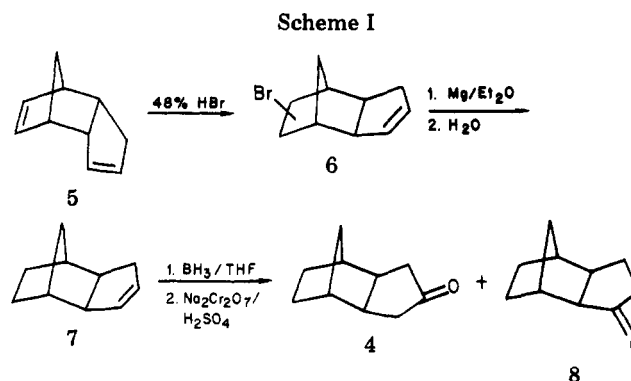
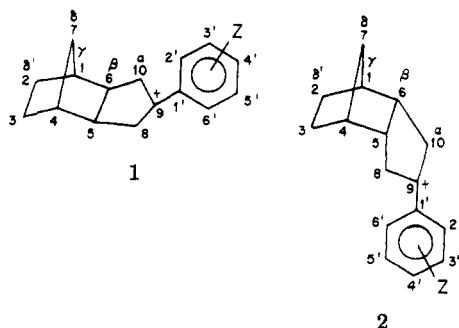
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The ¹³C NMR shifts of a series of meta- and para-substituted 9-phenyl-*exo*-5,6-trimethylene-9-norbornyl and 9-phenyl-*endo*-5,6-trimethylene-9-norbornyl carbocations were measured in SbF₅/FSO₃H/SO₂ClF at -80 °C. Excellent linear correlations were realized in the plots of Δδ^{C+} against the σ^{C+} constants. The 9-aryl-*exo*-5,6-trimethylene-9-norbornyl system yields a ρ^{C+} value of -16.3 with a correlation coefficient of 0.999. The 9-aryl-*endo*-5,6-trimethylene-9-norbornyl system gives a ρ^{C+} value of -15.9 with a correlation coefficient of 0.999. In addition, the data reveal some unusual effects of the cationic center on the remote carbon atoms in the skeleton. For example, the C^β carbon in the 9-aryl-*endo*-5,6-trimethylene-9-norbornyl system undergoes an upfield shift of 1.5 ppm from the *p*-OCH₃ to the *p*-CF₃ substituent, as compared to the downfield shifts (or no shifts) observed for the C^α, C^β, and C^γ carbons in simple arylalkyl carbocations. Possible reasons for such upfield shifts with electron demand are discussed.

Although several attempts to correlate the ¹³C NMR shifts of carbocationic centers against the electrophilic substituent constants, σ⁺, have been reported,^{2,3} no systematic study has been made to test the precision and utility of such correlations.

Recently, we established that new enhanced substituent constants are necessary to achieve precise correlations of such shifts.⁴ Thus we introduced a new set of substituent constants, σ^{C+}, to provide for the greater electron demand at the cationic centers of carbocations in superacid media, using the procedures previously applied in developing the σ⁺ constants. We then tested the ability of these σ^{C+} constants to correlate the C⁺ shifts in representative acyclic⁵ and cyclic carbocations.⁶ It was gratifying to observe that the data are correlated very nicely by these σ^{C+} values.

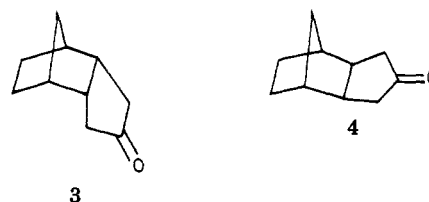
It appeared desirable to test the ability of these σ^{C+} constants to correlate the C⁺ shifts in relatively more complex (polycyclic) systems. Accordingly, we decided to examine the 9-aryl-*exo*-5,6-trimethylene-9-norbornyl (1) and 9-aryl-*endo*-5,6-trimethylene-9-norbornyl (2) carbocations.



In addition to providing a further test of the range of applicability of the σ^{C+} constants, the data would reveal the effect of the cationic center on the remote carbons in a rigid skeleton.

Results

endo-5,6-Trimethylene-9-norbornanone (3) was synthesized by following the procedure previously developed in our laboratories.⁷ *exo*-5,6-Trimethylene-9-norbornanone (4) was prepared by the route outlined in Scheme I.



The desired 9-ketone (4) was separated quantitatively from the 8-isomer (8) by forming the more stable bisulfite adduct of 4.⁷

The 9-aryl-*exo*-5,6-trimethylene-9-norbornanols (9) and 9-aryl-*endo*-5,6-trimethylene-9-norbornanols (10) were prepared by addition of the corresponding ketone to the

(1) Postdoctoral research associate on a grant provided by Exxon Research and Engineering Co.

(2) Olah, G. A.; Jeuell, C. L.; White, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 3961.

(3) Olah, G. A.; Porter, A. D.; Jeuell, C. L.; White, A. M. *J. Am. Chem. Soc.* **1972**, *94*, 2044.

(4) Brown, H. C.; Kelly, D. P.; Periasamy, M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6956.

(5) Brown, H. C.; Periasamy, M.; Liu, K.-T. *J. Org. Chem.* **1981**, *46*, 1646.

(6) Part 36: Brown, H. C.; Periasamy, M. *J. Org. Chem.*, previous paper in this issue.

(7) Brown, H. C.; Rothberg, I.; Vander Jagt, D. L. *J. Org. Chem.* **1972**, *37*, 4098.

Table I. ^{13}C NMR Shifts^a for the 9-Aryl-*exo*-5,6-trimethylene-9-norbornyl Cations in $\text{SbF}_5/\text{FSO}_3\text{H}/\text{SO}_2\text{ClF}$ at -80°C

substituent (Z)	chemical shift												
	C_9^+	$\text{C}_{8,10}^\alpha$	$\text{C}_{5,6}^\beta$	$\text{C}_{1,4}^\gamma$	C_7^δ	$\text{C}_{3,3}^{\delta'}$	C_Z	$\text{C}_{1'}$	$\text{C}_{2'}$	$\text{C}_{3'}$	$\text{C}_{4'}$	$\text{C}_{5'}$	$\text{C}_{6'}$
<i>p</i> -OCH ₃	235.1	46.2	47.7	43.9	32.8	28.7	59.5	129.9	146.3	119.4	181.8	119.4	146.3
<i>p</i> -CH ₃	258.2	49.5	48.0	43.9	32.8	28.8	25.1	134.2	142.6	133.9	173.4	133.9	142.6
<i>p</i> -F	262.5 (4.8)	50.7	48.2	43.8	32.8	28.7		133.1	147.7 (16.3)	121.2 (22.5)	179.7 (292)	121.2 (22.5)	147.7 (16.3)
<i>p</i> -Cl	265.5	51.2	48.2	43.7	32.7	28.7		134.2	143.2	133.3	164.0	133.3	143.2
H	269.3	51.3	48.2	43.8	32.8	28.8		136.0	142.7	132.8	154.9	132.8	142.7
<i>m</i> -Cl	274.7	52.9	48.3	43.7	32.7	28.7		138.8	141.0 ^b	136.9	152.9	133.8	140.2 ^b
<i>m</i> -CF ₃ ^c	277.8	53.6	48.4	43.7	32.7	28.7		139.4	138.9	137.2	150.8	137.2	138.9
3,5-Cl ₂	279.7	54.4	48.5	43.7	32.7	28.7							
<i>p</i> -CF ₃ ^c	281.5	54.4	48.5	43.6	32.6	28.7							
3,5-(CF ₃) ₂ ^c	284.7	55.9	48.8	43.8	32.7	28.8							

^a In parts per million downfield from Me₄Si (capillary). Assignments for aliphatic carbon signals are based on SFOR experiments and comparison of peak intensities. The aromatic carbon signals are assigned by comparison with the previously reported values for other systems.⁴⁻⁶ ¹³C-F coupling constants (in hertz) are in parentheses. ^b Assignments may be interchanged. ^c The ions slowly decompose in the probe (new small peaks start appearing). The CF₃ and some of the aromatic carbon signals are comparatively weak and were not assigned.

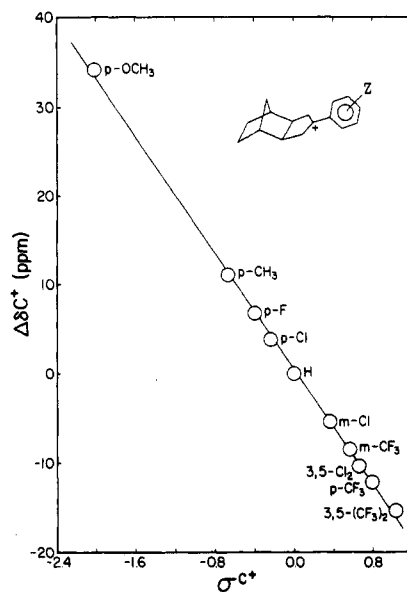


Figure 1. Plot of $\Delta\delta^{\text{C}^+}$ against σ^{C^+} values for 9-aryl-*exo*-5,6-trimethylene-9-norbornyl cations: correlation coefficient, $r = 0.999$; slope, $\rho^{\text{C}^+} = -16.3$; standard deviation, $\text{SD}(\rho^{\text{C}^+}) = 0.2$; standard deviation, $\text{SD}(\Delta\delta^{\text{C}^+}) = 0.5$.

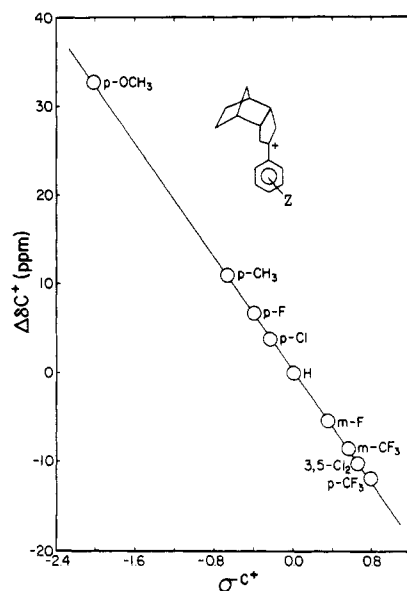
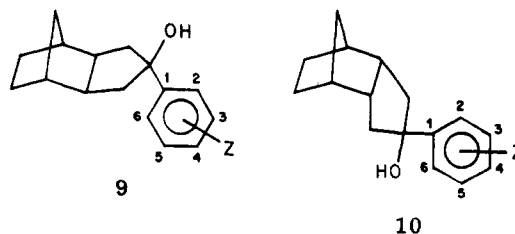


Figure 2. Plot of $\Delta\delta^{\text{C}^+}$ against σ^{C^+} values for 9-aryl-*endo*-5,6-trimethylene-9-norbornyl cations: correlation coefficient, $r = 0.999$; slope, $\rho^{\text{C}^+} = -15.9$; standard deviation, $\text{SD}(\rho^{\text{C}^+}) = 0.1$; standard deviation, $\text{SD}(\Delta\delta^{\text{C}^+}) = 0.2$.

appropriate Grignard reagents prepared from the corresponding substituted bromo- or iodobenzenes.



These alcohols were ionized by solution in "magic acid", 1:1 $\text{FSO}_3\text{H}/\text{SbF}_5$, diluted with SO_2ClF at -78°C , with care taken to ensure the presence of a fourfold excess of acid. The ^{13}C NMR shifts of the resulting solutions of the corresponding cations were then measured at -80°C . The data are summarized in Tables I and II.

Table II. ^{13}C NMR Shifts^a for the 9-Aryl-endo-5,6-trimethylene-9-norbornyl Cations in $\text{SbF}_5/\text{FSO}_3\text{H}/\text{SO}_2\text{Cl}_2$ at -80°C

substituent (Z)	chemical shift												
	C_9^+	$\text{C}_{8,10}^\alpha$	$\text{C}_{5,6}^\beta$	$\text{C}_{1,4}^\gamma$	C_7^δ	$\text{C}_{2,3}^{\delta'}$	C_Z	$\text{C}_{1'}$	$\text{C}_{2'}$	$\text{C}_{3'}$	$\text{C}_{4'}$	$\text{C}_{5'}$	$\text{C}_{6'}$
<i>p</i> -OCH ₃	233.9	41.9	43.9	41.9	39.8	23.3	59.8	130.3	146.3	119.8	181.8	119.8	146.3
<i>p</i> -CH ₃	255.6	45.0	44.2	41.7	39.2	23.5	25.1	134.4	142.8	134.3	174.0	134.3	142.8
<i>p</i> -F	259.9 (5.6)	46.4	44.6	41.6	39.0	23.4		133.5	147.9 (16.1)	121.7 (22.3)	180.2 (292.2)	121.7 (22.3)	147.9 (16.1)
<i>p</i> -Cl	262.8	46.9	44.7	41.7	38.9	23.5		134.8	143.4	133.9	164.9	133.9	143.4
H	266.6	47.0	44.5	41.6	38.8	23.5		136.4	142.8	133.2	155.3	133.2	142.8
<i>m</i> -F ^b	272.0	48.8	44.7	41.4	38.5	23.5							
<i>m</i> -CF ₃ ^b	275.1	49.6	44.9	41.4	38.5	23.6		139.1	139.9	137.6	151.4	137.6	139.9
3,5-Cl ₂	276.8	50.4	45.1	41.4	38.2	23.6							
<i>p</i> -CF ₃ ^b	278.5	50.4	45.1	41.4	38.3	23.5							

^a In parts per million downfield from Me₄Si (capillary). Assignments for aliphatic carbon signals are based on SFOR experiments and comparison of peak intensities. The aromatic carbon signals are assigned by comparison with the previously reported values for other systems.⁴⁻⁶ ^{13}C -F coupling constants (in hertz) are in parentheses. Attempts to prepare the 3,5-(CF₃)₂ ion were unsuccessful. ^b The ions decompose in the probe (i.e., new, small peaks start appearing). The CF₃ and some of the aromatic carbon signals are comparatively weak and were not assigned.

Table III. Variations in ^{13}C NMR Shifts with Electron Demand

carbon	substituents compared, <i>p</i> -OCH ₃ to <i>p</i> -CF ₃	
	ion 1	ion 2
$\text{C}_{8,10}^\alpha$	8.2 ^a	8.5 ^a
$\text{C}_{5,6}^\beta$	1.1 ^a	1.2 ^a
$\text{C}_{1,4}^\gamma$	~ 0.0	-0.5 ^b
C_7^δ	~ 0.0	-1.5 ^b
$\text{C}_{2,3}^{\delta'}$	~ 0.0	~ 0.0

^a Downfield shift in parts per million. ^b Upfield shift in parts per million.

Discussion

σ^{C^+} - $\Delta\delta^{\text{C}^+}$ Plots and ρ^{C^+} Values. A plot of the ^{13}C shifts, $\Delta\delta^{\text{C}^+}$, against the σ^{C^+} values for the 9-aryl-*exo*-5,6-trimethylene-9-norbornyl (1) system reveals an excellent correlation (Figure 1). The correlation yields a ρ^{C^+} value of -16.3, with a correlation coefficient of 0.999. Similar treatment for the 9-aryl-*endo*-5,6-trimethylene-9-norbornyl system (2) gives a ρ^{C^+} value of -15.9, with a correlation coefficient of 0.999 (Figure 2).

The ρ^{C^+} values for the systems 1 and 2 compare with the value of ρ^{C^+} of -16.8 for the 1-aryl-1-cyclopentyl system.⁴ The slightly less negative ρ^{C^+} values for the tricyclic systems 1 and 2 compared to the cyclopentyl system could be accounted for on the basis of the additional inductive effects of the norbornyl moiety fused to the cyclopentyl ring system in 1 and 2.

Comparison of the Effect of Increasing Electron Demand on ^{13}C NMR Shifts of Other Carbons in 1 and 2. Variations in the $\text{C}_{8,10}^\alpha$, $\text{C}_{5,6}^\beta$, $\text{C}_{1,4}^\gamma$, C_7^δ , and $\text{C}_{2,3}^{\delta'}$ carbon shifts for systems 1 and 2 are summarized in Table III.

The $\text{C}_{8,10}^\alpha$ carbons undergo a downfield shift with increasing electron demand (*p*-OCH₃ to *p*-CF₃) at the cationic center in essentially the same order of magnitude for both systems 1 and 2. Such downfield shifts were also observed for the 1-aryl-1-cyclopentyl system⁴ and could be accounted for on the basis of inductive and hyperconjugative transfer of the positive charge to the $\text{C}_{8,10}^\alpha$ carbon atoms.

The $\text{C}_{5,6}^\beta$ carbons also undergo a downfield shift with increasing electron demand, but of considerably smaller magnitude. This could be accounted for also on the basis of similar considerations.

The $\text{C}_{5,6}^\delta$ carbon shift is essentially not affected by increasing electron demand for both systems 1 and 2. This is not unexpected because the inductive effect would tend to fall off sharply as the distance between the positive charge and the carbon atoms of the structure increases.

Whereas the $\text{C}_{1,4}^\gamma$ carbon shift for system 1 is essentially constant from *p*-OCH₃ to *p*-CF₃, a slight upfield shift (0.5 ppm) is observed for the $\text{C}_{1,4}^\gamma$ carbon in system 2.

The difference between the systems 1 and 2 with respect to the variation in the C_7^δ carbon shift is more significant. In the case of system 1, the C_7^δ carbon shift is essentially not affected from *p*-OCH₃ to *p*-CF₃. On the other hand, the C_7^δ carbon shift in system 2 undergoes a regular upfield shift (1.5 ppm from *p*-OCH₃ to *p*-CF₃), approximately in the same order as the variation in the σ^{C^+} constants. This trend is unusual. This observation indicates that the cationic center not only causes downfield shifts with increasing electron demand but could also cause upfield shifts for certain remote carbon atoms.

The difference between the systems 1 and 2 with respect to the upfield shift of the C_7^δ carbon indicates that the interaction which causes the upfield shift depends pri-

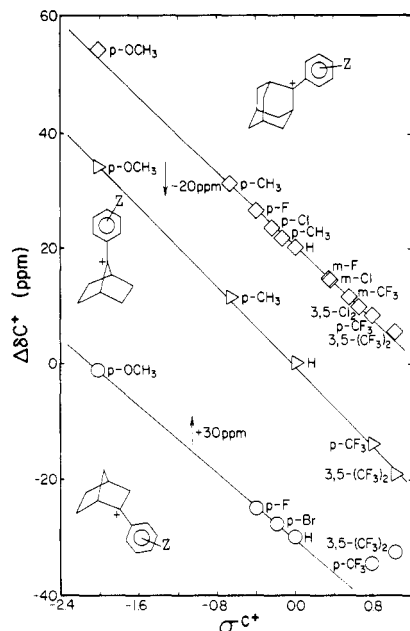
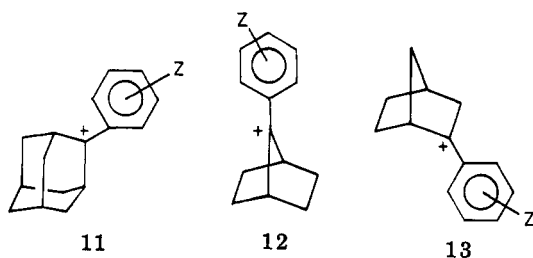


Figure 3. $\Delta\delta^{C^+}-\sigma^{C^+}$ plots for 2-aryl-2-adamantyl, 7-aryl-7-norbornyl, and 2-aryl-2-norbornyl carbocations.

marily on the orientation of the C_7^δ carbon with respect to the C^+ carbon.

We cannot come to a definite conclusion as to the cause of the upfield shift with increasing electron demand observed for the C_7^δ carbon atoms because it has been observed for but one of the systems thus far studied. However, a possible explanation might be the field effect of the cationic center on the C_7^δ carbon. Such field effects are reported to cause upfield shifts in protonated amines and are proposed to be dependent on the distance between the positive charge and the ^{13}C site, the electric field, and the orbital orientations.⁸

$\sigma^{C^+}-\Delta\delta^{C^+}$ Plots for Some Polycyclic Systems. ^{13}C NMR data have been reported for some other polycyclic systems (11–13). It may be of interest to examine these data against the σ^{C^+} values.



Kelly and co-workers⁹ reported that the $\Delta\delta^{C^+}$ values for the 2-aryl-2-adamantyl (11) system are nicely correlated by the σ^{C^+} constants with a ρ^{C^+} of -16.1 and an r of 0.9987 (Figure 3).

The data for several 7-aryl-7-norbornyl cations (12) have been reported by Olah and co-workers.¹⁰ These $\Delta\delta^{C^+}$ values also correlate nicely against the σ^{C^+} constants ($\rho^{C^+} = -17.3$, $r = 0.999$, Figure 3).

^{13}C NMR data for some 2-aryl-2-norbornyl derivatives have been reported by both Olah and his co-workers¹¹ and

Table IV. Physical Constant Data^a for 9-Aryl-*exo*-5,6-trimethylene-9-norbornanols (9) and 9-Aryl-*endo*-5,6-trimethylene-9-norbornanols (10)

substituent (Z)	mp, °C	
	9	10
<i>p</i> -OCH ₃	110–111	84–86
<i>p</i> -CH ₃	127–128	115–116
<i>p</i> -F	127–128	94–95
<i>p</i> -Cl	122–123	102–103
H	135–136	93–94 ^b
<i>m</i> -F		61–62
<i>m</i> -Cl	143–144	
<i>m</i> -CF ₃	103–104	73–74
3,5-Cl ₂	193–194	96–97
<i>p</i> -CF ₃	130–131	92–93
3,5-(CF ₃) ₂	104–105	121–122

^a Satisfactory analytical data ($\pm 0.3\%$ for C, H, Cl, and F) were obtained for all of the new compounds. ^b Lit.¹⁷ mp 93.5–94.5 °C.

Farnum and his co-workers.¹² Comparison of these data reveals certain discrepancies. Accordingly, we decided to restrict our examination to one set. Figure 3 shows the plot of the data of Farnum and his co-workers against σ^{C^+} . The plot reveals that the data for the electron-donating substituents are nicely correlated against the σ^{C^+} values ($\rho^{C^+} = -14.4$ and $r = 0.999$). However, the correlation breaks down for the *p*-CF₃ and 3,5-(CF₃)₂ derivatives. Farnum and co-workers¹² (as well as Olah and his co-workers¹¹) concluded that such deviations are the result of the onset of σ -bridging in these derivatives. However, Kelly and Spear¹³ have pointed out that the C_1 carbon shifts observed in these 2-aryl-2-norbornyl cations are nicely correlated against the α -CH₃ carbon shifts of the substituted *tert*-cumyl cations. Kelly's observation suggests that the unusual behavior of the C^+ shifts of the 2-aryl-2-norbornyl cations may not be due to σ bridging.

The present program of developing σ^{C^+} constants, as well as σ^{ac} constants,¹⁴ was undertaken to test the conclusion of Olah¹¹ and of Farnum¹² that the unusual behavior of the ^{13}C NMR shifts for the C^+ atom in the 2-aryl-2-norbornyl cations (Figure 3) is the result of the inception of σ bridging in the derivatives containing the more electron-demanding substituents. Before we examine this topic in detail, it is desirable to examine the α - C^+ shifts to see if such shifts can be correlated by a set of constants, either σ^{C^+} or some other set.¹⁴

Experimental Section

Synthesis of *exo*-5,6-Trimethylene-9-norbornanone (Scheme I). The bromo compounds 6, prepared by the addition of 48% aqueous hydrobromic acid to dicyclopentadiene,¹⁵ were converted to the Grignard reagent and the latter decomposed with water to give the olefin 7.¹⁶ The olefin 7 (40.2 g, 300 mmol) in ethyl ether (100 mL) was hydroborated with BH₃·THF (160 mL of 1 M BH₃, 160 mmol) and oxidized with sodium dichromate dihydrate (67 g, 225 mmol) in dilute sulfuric acid (50 mL of 96% sulfuric acid and 250 mL of water), following the conditions similar to the procedure reported for the preparation of *endo*-5,6-tri-

(11) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Am. Chem. Soc.* **1977**, *99*, 5683.

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

(13) Kelly, D. P.; Spear, R. *J. Aust. J. Chem.* **1978**, *31*, 1209.

(14) Part 38: Brown, H. C.; Kelly, D. P.; Periasamy, M. *J. Org. Chem.*, following paper in this issue.

(15) Bruson, H. A.; Reiner, T. W. *J. Am. Chem. Soc.* **1946**, *68*, 8.

(16) Bartlett, P. D.; Sneider, A. *J. Am. Chem. Soc.* **1946**, *68*, 6.

(17) Brown, H. C.; Vander Jagt, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 6850.

(8) Batchelor, J. G. *J. Am. Chem. Soc.* **1975**, *97*, 3410.

(9) Kelly, D. P.; Jenkins, M. J.; Mantello, R. A. *J. Org. Chem.*, **1981**, *46*, 1650.

(10) Olah, G. A.; Berrier, A. L.; Arvanaghi, M.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1981**, *103*, 1122. We are grateful to Professor G. A. Olah for communicating these results prior to publication.

methylene-9-norbornanone.⁷ The *exo*-5,6-trimethylene-9-norbornanone (4) was quantitatively separated from the *exo*-5,6-trimethylene-8-norbornanone (8) by bisulfite addition.⁷ After workup,⁷ the *exo*-5,6-trimethylene-9-norbornanone (4) was obtained in 27% yield [bp 102–104 °C (15 mm)], and the *exo*-5,6-trimethylene-8-norbornanone was obtained in 40% yield [bp 102–104 °C (15 mm)]. These ketones gave satisfactory analytical data (C, $\pm 0.3\%$; H, $\pm 0.2\%$). The ¹³C NMR data were in accordance with the assigned structures.

Precursors. 9-Aryl-*exo*-5,6-trimethylene-9-norbornanols (9) and 9-aryl-*endo*-5,6-trimethylene-9-norbornanols (10) were prepared by addition of the corresponding ketone to the Grignard reagent prepared from the corresponding substituted bromo- or iodobenzenes. The physical constant data for these precursors are summarized in Table IV. All of these compounds gave ¹³C NMR data in accordance with the assigned structures. Satisfactory elemental analyses were obtained for all of the new compounds ($\pm 0.3\%$ for C, H, Cl, and F).

Carbocations. The ions were prepared by slow addition of the appropriate precursor to a solution of FSO₃H/SbF₅ (1:1 M)/SO₂ClF cooled to -78 °C with rapid vortex mixing. The "magic acid", SbF₅/FSO₃H (1:1 M), concentration in the solution was 3 M. The concentration of the ion based on the alcohol 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.¹⁸

NMR Spectra. ¹³C 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 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), 77826-81-4; 1 (Z = *p*-CH₃), 77826-82-5; 1 (Z = *p*-F), 77826-83-6; 1 (Z = *p*-Cl), 77826-84-7; 1 (Z = H), 77826-85-8; 1 (Z = *m*-Cl), 77845-74-0; 1 (Z = *m*-CF₃), 77826-86-9; 1 (Z = 3,5-Cl₂), 77826-87-0; 1 (Z = *p*-CF₃), 77826-88-1; 1 (Z = 3,5-(CF₃)₂), 77845-75-1; 2 (Z = *p*-OCH₃), 77826-72-3; 2 (Z = *p*-CH₃), 77826-73-4; 2 (Z = *p*-F), 77826-74-5; 2 (Z = *p*-Cl), 77845-63-7; 2 (Z = H), 77826-75-6; 2 (Z = *m*-F), 77845-76-2; 2 (Z = *m*-CF₃), 77826-77-8; 2 (Z = 3,5-Cl₂), 77826-78-9; 2 (Z = *p*-CF₃), 77826-79-0; 3, 19138-60-4; 4, 77845-77-3; 9 (Z = *p*-OCH₃), 77845-78-4; 9 (Z = *p*-CH₃), 77845-79-5; 9 (Z = *p*-F), 77845-80-8; 9 (Z = *p*-Cl), 77845-81-9; 9 (Z = H), 77845-82-0; 9 (Z = *m*-Cl), 77845-83-1; 9 (Z = *m*-CF₃), 77845-84-2; 9 (Z = 3,5-Cl₂), 77845-85-3; 9 (Z = *p*-CF₃), 77845-86-4; 9 (Z = 3,5-(CF₃)₂), 77845-87-5; 10 (Z = *p*-OCH₃), 77845-88-6; 10 (Z = *p*-CH₃), 77845-89-7; 10 (Z = *p*-F), 77845-90-0; 10 (Z = *p*-Cl), 77845-91-1; 10 (Z = Ph), 27409-21-8; 10 (Z = *m*-F), 77845-92-2; 10 (Z = *m*-CF₃), 77845-93-3; 10 (Z = 3,5-Cl₂), 77845-94-4; 10 (Z = *p*-CF₃), 77845-95-5; 10 (Z = 3,5-(CF₃)₂), 77845-96-6.

(18) Kelly, D. P.; Brown, H. C. *Aust. J. Chem.* 1976, 29, 957.

Structural Effects in Solvolytic Reactions. 38. Carbon-13 Nuclear Magnetic Resonance Studies of Carbocations. 6.¹ Effect of Increasing Electron Demand on the Chemical Shifts of the α -Carbon Atoms in Substituted Aryldialkyl Carbocations. Correlation of the Data with a New Set of Substituent Constants, $\sigma^{\alpha C^+}$

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With increasing electron demand, the ¹³C NMR shifts of the α -carbons, the carbon atoms adjacent to the cationic center (C⁺), undergo significant downfield shifts. However, the substituent chemical shifts, $\Delta\delta^{C^+}$, for the α -carbon atoms (CH₃) of substituted *tert*-cumyl cations are not correlated either by the σ^+ or the σ^{C^+} constants. Plots of $\Delta\delta^{C^+}$ against σ^+ and of $\Delta\delta^{C^+}$ against σ^{C^+} reveal that the points for the para derivatives deviate systematically from the lines defined by the data for the meta derivatives. These deviations indicate that a new set of para substituent constants, one intermediate in value between the σ_p^+ and $\sigma_p^{C^+}$ constants, is needed to correlate satisfactorily the α -carbon chemical shifts for the para derivatives. Accordingly, such a set of substituent constants, $\sigma^{\alpha C^+}$, was estimated by using the slope (-4.1) of the line defined by a plot of $\Delta\delta^{C^+}$ for the meta derivatives vs. σ_m^+ to satisfy the Hammett-type equation $\Delta\delta^{C^+} = \rho^{\alpha C^+} \sigma^{\alpha C^+}$. The utility of these new $\sigma^{\alpha C^+}$ constants to correlate chemical shift data for the α positions of substituted benzylic cations was tested with the data for ten different systems. Indeed, very good correlations were observed when the chemical shifts for these systems are plotted against these $\sigma^{\alpha C^+}$ values: 2-aryl-2-butyl, $r = 0.997$, $\rho(\text{CH}_2)^{\alpha C^+} = -4.1$, $r = 0.998$, $\rho(\text{CH}_3)^{\alpha C^+} = -4.0$; 3-aryl-3-pentyl, $r = 0.999$, $\rho^{\alpha C^+} = -3.9$; 4-aryl-4-heptyl, $r = 0.994$, $\rho^{\alpha C^+} = -3.6$; 1-aryl-1-cyclopentyl, $r = 0.999$, $\rho^{\alpha C^+} = -4.9$; 1-aryl-1-cyclohexyl, $r = 0.998$, $\rho^{\alpha C^+} = -4.9$; 1-aryl-1-cycloheptyl, $r = 0.999$, $\rho^{\alpha C^+} = -4.7$; 9-aryl-*exo*-5,6-trimethylene-9-norbornyl, $r = 0.999$, $\rho^{C^+} = -4.1$; 9-aryl-*endo*-5,6-trimethylene-9-norbornyl, $r = 0.998$, $\rho^{\alpha C^+} = -4.4$; 2-aryl-2-adamantyl, $r = 0.993$, $\rho^{\alpha C^+} = -5.9$. The trend in the $\rho^{\alpha C^+}$ values in these cations is discussed.

Although isolated attempts to correlate the α -carbon shifts in substituted benzylic cations against σ^+ constants have been reported,^{3,4} no systematic examination has been made to test the practicality and validity of such correlations.

Recently we undertook a systematic investigation of the effect of increasing electron demand on the ¹³C NMR shifts of aryldialkyl carbocations. We established that new enhanced substituent constants are needed to correlate the chemical shifts of the cationic center in these cations.⁵ We determined these σ^{C^+} constants as follows. The data for the meta derivatives were correlated satisfactorily by σ_m^+ . The para derivatives deviated seriously, indicating much greater resonance interactions with the cationic center than

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(3) Olah, G. A.; Prakash, G. K. S.; Liang, G. *J. Am. Chem. Soc.* 1977, 99, 5683.

(4) Kelly, D. P.; Spear, R. *J. Aust. J. Chem.* 1978, 31, 1209.

(5) Brown, H. C.; Kelly, D. P.; Periasamy, M. *Proc. Natl. Acad. Sci. U.S.A.* 1980, 77, 6956.