85973-82-6; **2h**, 85973-84-8; **2i**, 85973-83-7; **2j**, 72284-73-2; **3a**, 503-17-3; **3b**, 928-49-4; **3c**, 501-65-5; **3d**, 693-02-7; **3e**, 628-71-7; **3f**, 536-74-3; **3g**, 1066-54-2; **3h**, 6224-91-5; **3j**, 78-80-8; **4f**, 52784-31-3; **4g**, 62012-20-8; **5f**, 13866-28-9; **5g**, 85973-87-1; **6e**, 86853-62-5; **6f**, 86853-63-6; **6g**, 86853-64-7; (*E*)-**7a**, 86853-65-8; (*E*)-**7b**, 86853-66-9; (*E*)-**7c**, 86853-67-0; (*Z*)-**7c**, 86853-68-1; **7f**, 86853-69-2; **7f'**, 86853-70-5; **10**, 754-05-2; **13**, 86853-71-6; **14**, 38425-47-7; trichloroacetyl chloride, 76-02-8.

Structural Effects in Solvolytic Reactions. 44. Effect of Increasing Electron Demand on the Carbon-13 NMR Shifts in 1-Aryl-1-hydroxyethyl Carbocations. Deviations in the σ^{C^+}-$\Delta\delta C^+$ Plot for These Protonated Acetophenones Containing Strongly Electron-Withdrawing Substituents

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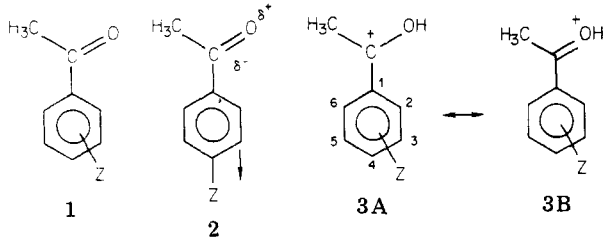
A series of meta- and para-substituted 1-aryl-1-hydroxyethyl carbocations were prepared by protonation of the corresponding acetophenones in $SbF_5/FSO_3H/SO_2ClF$ at −78 °C and the carbon-13 NMR shifts were measured at −70 °C. A plot of $\Delta\delta C^+$ shifts against the σ^{C^+} constants exhibits deviations from linearity for electron-demanding substituents. The deviation is attributed to more shielding of the cationic carbon center than that estimated by the σ^{C^+} constants. Previously, such shielding effects were observed for side-chain conjugated benzene derivatives containing electron-demanding substituents. For example, the carbonyl carbon atom in substituted acetophenones becomes more shielded on substitution with electron-demanding substituents. This was attributed to inductive π-polarization of the conjugating side chain. Accordingly, the present study establishes that the deviations observed for the ^{13}C shifts of the carbonyl carbon atom in acetophenones with electron-demanding substituents persist in the protonated acetophenones (1-aryl-1-hydroxyethyl carbocations).

It was recently reported that the inductive (field) effect contribution to the chemical shift of the first atom in a conjugating side chain was negative, leading to reverse substituent chemical shifts.[1] For example, in meta- and para-substituted acetophenones **1**, the carbonyl carbon atom becomes more shielded with electron-withdrawing substituents. This is contrary to the expectation that the electron-withdrawing substituents should withdraw electron density, decrease the shielding, and cause an increased chemical shift.



Brownlee and co-workers suggested that these reverse chemical shifts result from the interaction of the substituent dipole with the side-chain π-system.[1] This interaction is suggested to operate through the space of the molecular cavity, resulting in the polarization shown in **2**. The net result is that the inductive withdrawing substituent increases the electron density around the carbonyl carbon atom and hence increases the shielding to cause a reduced chemical shift. Brownlee and co-workers also reported that in the case of 1-aryl-1-hydroxyethyl carbocations normal chemical shifts (deshielding) are observed for electron-withdrawing substituents.[1] They suggested that the normal behavior [i.e., increased shifts (deshielding) for inductive withdrawing substituents] is observed for the C^+ carbon atom in 1-aryl-1hydroxyethyl cations **3** because of the absence of the conjugate double bond in the side chain. In that case, we would expect the $\Delta\delta C^+$ values observed for **3** to correlate linearly with the σ^{C^+} constants similar to the correlations observed for simple benzylic carbocations.[2-7] Accordingly, we decided to run the carbon-13 NMR spectra for the entire range of the 1-aryl-1-hydroxyethyl carbocations **3** [Z = *p*-OCH_3 to Z = 3,5-$(CF_3)_2$].

Table I. Comparison of the $\Delta\delta C^+$ Shifts[a] of 1-Aryl-1-hydroxyethyl Carbocations

substit	$\Delta\delta C^+$ [a] concn H_2SO_4 (25 °C)	$\Delta\delta C^+$ [a] $SbF_5/FSO_3H/SO_2ClF$ [c] (−70 °C)
m-Br	−0.8 [b]	−1.1
m-CF_3	−1.6 [b]	−2.0
p-CF_3	−2.3 [b]	−3.1
3,5-Cl_2	−0.30 [c]	−2.2
3,5-$(CF_3)_2$	+0.9 [c]	−3.4

[a] $\Delta\delta C^+ = \delta C^+(Z = H) - \delta C^+(Z \neq H)$. [b] Data taken from ref 1. [c] Present work.

Results and Discussion

Several 1-aryl-1-hydroxyethyl cations **3** were studied by Olah and co-workers.[8] These authors prepared these ions by protonation of the corresponding acetophenones in

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Table II. ^{13}C NMR Shifts for the 1-Aryl-1-hydroxyethyl Carbocations 3 in $SbF_5/FSO_3H/SO_2ClF$ at −70 °C

substit (Z)	chemical shift[a]								
	C^+	C_{CH_3}	C_Z	C_1	C_2	C_3	C_4	C_5	C_6
p-OCH_3	209.1	23.3	57.7	122.1	142.9[b]	118.2[c]	174.8	116.8[c]	137.5[b]
p-CH_3	216.4	24.9	23.4	126.9	139.7[b]	132.7[c]	162.3	132.6[c]	134.2[b]
p-F	217.3	25.3		126.3	143.4[b] (13)	119.9[c] (23)	174.4 (276)	119.5[c] (23)	138.3[b] (13)
p-Cl	218.7	25.5		127.8	140.2[b]	132.2[c]	154.6	135.1[c]	132.2[b]
H	220.0	25.5		129.4	139.4[b]	131.8[c]	146.7	131.8[c]	134.0[b]
m-Br	221.1	26.1		125.3	140.7	131.1	148.5	133.2	136.7
m-CF_3	222.0	26.3	123.6 (273)	130.0	132.7	134.0 (34)	141.8	130.0	132.7
3,5-Cl_2	222.2	26.6		131.8	132.8	138.7	144.4	138.7	132.8
p-CF_3	223.1	26.6	123.4 (273)	132.1	137.0	128.5	144.6 (34)	128.3	136.7
3,5-$(CF_3)_2$	223.4	27.0	122.9 (272)	131.0	136.0	135.1 (34)	137.8	135.1 (34)	136.0

[a] Chemical shift in parts per million downfield from external Me_4Si. [b] Assignment may be interchanged. [c] Assignment may be interchanged.

$SbF_5/FSO_3H/SO_2ClF$. Unfortunately, the authors did not study the shifts for derivatives containing electron-withdrawing substituents.

Brownlee and co-workers prepared several of the 1-aryl-1-hydroxyethyl cations in concentrated H_2SO_4 and reported the substituent chemical shifts ($\Delta\delta C^+$) for the C^+ center.[1] The values reported for the electron-donating substituents in concentrated sulfuric acid by these authors[1] are essentially the same as those values reported for the corresponding cations in $SbF_5/FSO_3H/SO_2ClF$ by Olah and co-workers.[2] However, we have observed that the $\Delta\delta C^+$ values observed for the electron-withdrawing derivatives in concentrated sulfuric acid are significantly different from those observed in $SbF_5/FSO_3H/SO_2ClF$ (Table I). The C^+ shifts observed in concentrated sulfuric acid are more shielded compared to the shifts observed in $SbF_5/FSO_3H/SO_2ClF$. This may be attributed to incomplete protonation in concentrated sulfuric acid, leading to an equilibrium between the protonated and parent acetophenones. In strongly acidic "magic acid" ($SbF_5/FSO_3H/SO_2ClF$), such complications may be less significant. Accordingly, we protonated the meta- and para-substituted acetophenones in $SbF_5/FSO_3H/SO_2ClF$ at −78 °C. The ^{13}C NMR spectra of the resulting ions **3** were measured at −70 °C. The data are summarized in Table II.

A plot of the $\Delta\delta C^+$ values against σ^{C^+} is shown in Figure 1. The figure shows that a linear correlation exists for the derivatives Z = p-OCH_3 to Z = H. The points for the electron-withdrawing derivatives [Z = m-Br to Z = 3,5-$(CF_3)_2$] drift upward corresponding to shielding at the C^+ center. It is of interest to note that the deviation observed in this case is similar (albeit smaller) to the deviation observed for the 2-aryl-2-nobornyl cations.[9]

Brownlee and co-workers observed that the first atom in conjugated systems, such as the carbonyl atom in substituted acetophenones **1**, becomes shielded with inductive withdrawing substituents.[1] They attributed this observation to the inductive effect of the substituent causing the inductive π-polarization shown in **2**. They suggested that such polarization would vanish when the carbonyl double bond is removed. However, the deviation (Figure 1) observed in the σ^{C^+}–$\Delta\delta C^+$ plot for the 1-aryl-1-hydroxyethyl cations indicates that such polarization causing shielding of the C^+ center has not completely vanished. Possibly the structure **3B**, with a C–O double bond, makes a significant contribution to the ground state-structure of the ion.

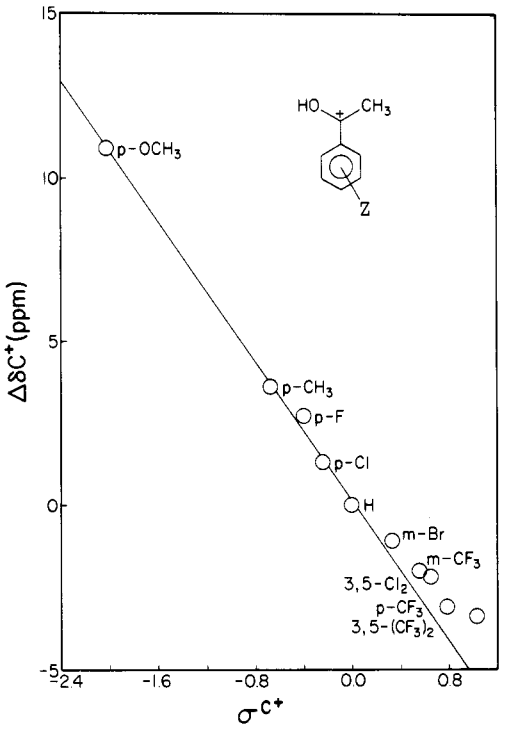
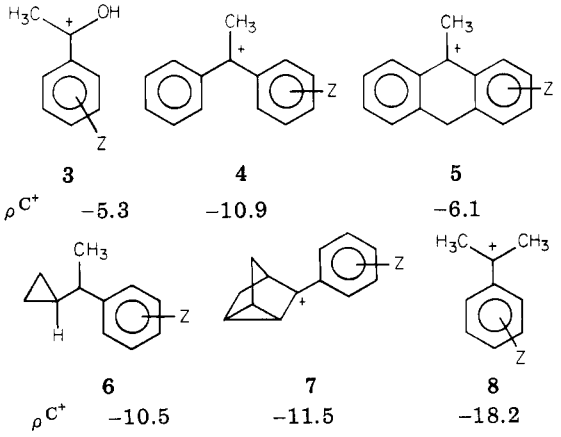


Figure 1. A plot of σ^{C^+} values against $\Delta\delta C^+$ shifts for the 1-aryl-1-hydroxyethyl carbocations **3** (slope ρ^{C^+} = −5.3, correlation coefficient = 0.998, for electron-donating substituents only).

Chart I



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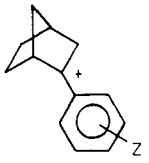
σ^{C^+}–$\Delta\delta C^+$ Plots for Systems Containing a Stabilizing Group. Deviations similar to those observed for the 1-aryl-1-hydroxyethyl system (**3**, Chart I) have also been observed for other systems containing stabilizing groups such as phenyl or cyclopropyl (**4–7**).[9–12] The ρ^{C^+} values observed for the linear portion of the curves (i.e., data points for the electron-donating substituents) in these systems are relatively less negative than the value observed in the case of substituted *tert*-cumyl cations used to define the σ^{C^+} constants.[2] This can be accounted for on the basis of lesser electron demand from the substituted phenyl ring because of greater electron supply by the hydroxyl (**3**), phenyl (**4**, **5**), and cyclopropyl (**6**, **7**) groups.

In the case of substituted *tert*-cumyl cations **8**, the electron supply from the methyl group increases with increasing electron demand, as indicated by the deshielding of the methyl carbon with increasing electron demand at the cationic center.[2] Similarly, in the systems **3–7**, the electron supply from the hydroxy, phenyl, or cyclopropyl group would be expected to increase with increasing electron demand. Accordingly, one would expect a linear σ^{C^+}–$\Delta\delta C^+$ plot for both electron-donating and electron-demanding substituents (unless the greater electron supply from these groups introduces difficulties into the quantitative correlation).

The data observed for these systems do give linear plots for the electron-donating substituents. However, the data points for the electron-demanding substituents deviate upward from the correlation line for the data points of the electron-donating substituents. This deviation corresponds to more shielding of the C^+ center than that estimated by the σ^{C^+} constants. Clearly, some phenomenon causing shielding at the C^+ center enters into the picture for those derivatives that contain electron-demanding substituents.

Comparison of the deviations in the σ^{C^+}–$\Delta\delta C^+$ plots observed for the systems **4–7** with that observed for the system **3** suggests that the phenomenon that causes shielding at the C^+ center may be inductive π-polarization similar to that proposed[1] for **2**. It is not unreasonable for these systems to have such π-polarization because conjugation by the phenyl or the cyclopropyl group would give partial π-bond character to the bond between the C^+ center and the conjugating group in these systems. The presence of such a partial π-bond would lead to inductive π-polarization in the derivatives containing electron-withdrawing substituents, as shown in **2**. This would lead to shielding at the C^+ center, resulting in the observed deviations in the σ^{C^+}–$\Delta\delta C^+$ plots.

Similar deviations have been also observed in the case of 2-aryl-2-norbornyl cations (**9**) containing electron-de-



9

ρ^{C^+} −14.0

manding substituents.[9] Previously, such deviations were attributed to the onset of nonclassical σ-bridging in these derivatives.[11,13,14] Recently, we pointed out that such deviations cannot be considered as evidence for the onset of nonclassical σ-bridging on the basis of the following observations: (1) the lack of any anomalous shifts for the C_1 and C_6 carbon atoms involved in such σ-bridging,[15] (2) lack of deviations in other systems for which σ-bridging has been proposed on the basis of other studies.[9]

Comparison of the deviation observed in the case of 2-aryl-2-norbornyl cations with those observed for the systems **3–7** indicates that all such deviations may have the same origin. The deviations observed for the systems **3–6** can be rationalized on the basis of inductive π-polarization of the C^+-conjugating group bond that could attain partial π-bond character because of the greater electron-releasing ability of these groups. If the relatively less negative ρ^{C^+} value (−14.0) observed in the correlation of the data points of electron-donating substituents is due to the greater electron-donating ability of the norbornyl moiety, the upward deviation observed in the σ^{C^+}–$\Delta\delta C^+$ plot for the electron-demanding substituents could be well due to the inductive π-polarization of the partial π-bond between the C^+ and C_1 carbon atoms.

A problem with this interpretation is its qualitative nature. At this stage, we see no way of predicting with confidence which structures will exhibit a good correlation in the $\Delta\delta C^+/\sigma^{C^+}$ plot and which will not. Until we can achieve predictive capability, we must consider inductive π-polarization as a tentative interpretation to be explored, but applied with caution.

The dependence of the deviations on the electron-donating ability of different aryl groups in substituted benzhydryl cations has been examined and will soon be reported.

Experimental Section

Carbocations. The substituted acetophenones **1**, Z = 3,5-Cl_2,[16] bp 68–70 °C (0.2 mm), and Z = 3,5-$(CF_3)_2$,[17] bp 88–90 °C (20 mm), were prepared by following a literature procedure.[18] All other derivatives are commercially available. The ions were prepared by slow addition of the appropriate precursor to a solution of FSO_3H/SbF_5 (1:1 mol/mol)/SO_2ClF cooled to −78 °C with rapid vortex mixing. The "magic acid", SbF_5/FSO_3H (1:1 mol/mol), concentration in the solution was 3 M. The concentration of the ion based on the ketone 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.[19] The ions (~0.5 M) in concentrated sulfuric acid (96%) were prepared by dissolving the required amount of substituted acetophenone in 1.2 mL of concentrated sulfuric acid in an 8-mm NMR tube at 0 °C. The contents were slowly warmed to 25 °C with stirring.

NMR Spectra. ^{13}C NMR spectra were recorded at −70 or 25 °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 6000 Hz, and a pulse angle of 45°. Chemical shifts are in parts per million downfield from external Me_4Si.

Acknowledgment. This work was supported by a grant from Exxon Research and Engineering Co.

Registry No. **3** (Z = *p*-OCH_3), 70205-59-3; **3** (Z = *p*-CH_3), 56485-33-7; **3** (Z = *p*-F), 70205-60-6; **3** (Z = *p*-Cl), 70205-61-7; **3** (Z = H), 39922-13-9; **3** (Z = *m*-Br), 86803-09-0; **3** (Z = *m*-CF_3), 86822-02-8; **3** (Z = 3,5-Cl_2), 86803-10-3; **3** (Z = *p*-CF_3), 70205-64-0; **3** (Z = 3,5-$(CF_3)_2$), 86803-11-4.

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