Stable Carbocations. CXXV.[1a] Proton and Carbon-13 Magnetic Resonance Studies of Phenylcarbenium Ions (Benzyl Cations). The Effect of Substituents on the Stability of Carbocations[1b]

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Abstract: Several homologous series of phenylcarbenium ions (benzyl cations) have been studied and characterized by proton (pmr) and carbon-13 (cmr) magnetic resonance spectroscopy. Effects of ring as well as carbenium carbon substituents on magnetic resonance parameters for these carbenium ions have been examined, including the effect of β-bromine, β-methyl, and β-deuterium substituents on *tert*-cumyl cations. Stability of carbenium ions, as inferred by kinetic solvolytic studies, has been shown to correlate with the ability of substituents to delocalize positive charge from the carbenium center. Relative effects can be estimated, keeping structural geometry at the carbenium ion center constant, by the cmr chemical shifts of the carbenium carbons in homologous series of phenylcarbenium ions. Near-linear relationships with Brown's σ^+ substituent constants of such cmr shifts are demonstrated. The first complete cmr characterization of a primary cation is made using a combination of Fourier transform and indor spectroscopy of the only known monosubstituted (p-methoxy) benzyl cation. Competition between bromonium ion formation (β-bromine participation) and benzylic stabilization in *tert*-cumyl cations at the carbenium carbon centers is studied. The magnitude of such β-n-electron donation is observed to be minimal even for the case of the relatively destabilized p-trifluoromethyl benzylic system. Rearrangements of stable benzylic cations are observed where aromatic stabilization is small, and only observed where the benzylic ions rearrange *via* tertiary carbenium ion intermediates.

Much of the recent effort in stable carbocation chemistry has been directed toward the object of elucidating structures of various ions by nmr spectroscopy using the proven assumptions that: (a) electron density and nmr chemical shifts are related, and (b) structural features such as carbon geometry lend themselves to assignments by nuclear magnetic resonance studies.[2] Much information in these studies has been obtained from comparison with known model compounds. The correlation of cmr chemical shifts with electron density was first studied in depth by Spiesecke and Schneider,[3] but more recently the application of such a relationship to carbocations has been shown by correlations of molecular orbital calculations of charge density to cmr chemical shifts.[4] The use of model compounds to infer structural geometry and electronic characteristics to carbocations has been employed in our laboratories for a wide range of representative ions. Recently, in studies of norbornonium,[5] ethylenearenium,[6] and cyclopropyl carbonium[7] ions this method has been used especially effectively in demonstrating carbenium *vs.* carbonium ion characteristics of the particular ions. In these studies a key class of model compounds was benzylic cations. These were used because of their fixed and well-defined geometry and the extensive study to which they have been subjected under a variety of reaction conditions.[8]

We have recently reported carbon-13 and proton magnetic resonance studies of secondary arylmethylcarbenium (styryl) cations,[9] including the parent styryl cation itself. Until now attempts were mostly made to correlate spectral parameters of precursors or model compounds for the intermediates[10] to solvolytic kinetic data.

Timberlake, Thompson, and Taft[11] have demonstrated the great sensitivity of fluorine-19 chemical shifts of the p-fluoro atom in p-fluorophenylcarbenium ions to the anticipated positive charge character of the carbenium carbon. They found dependence on isotopic deuterium substitution of the methyl group in the p-fluorophenyldimethylcarbenium ion to be significant (12.5 ± 0.5 Hz at 54.6 MHz). As the electron deficiency of the carbenium carbon atom is obviously much larger than that of any other nucleus in benzylic ions,[12] we felt the sensitivity of this nucleus toward charge delocalizing effects should be an excellent probe for substituent effects in these ions. Our initial studies have shown this assumption to be qualitatively accurate while varying ring substituents. Therefore we decided to carry out a comprehensive study, the results of which are reported in this paper. Although obvious deficiencies in a study

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(1) (a) Stable Carbocations. CXXIV: G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 2034 (1972); (b) submitted in part in preliminary form: G. A. Olah, C. L. Jeuell, and A. M. White, *ibid.*, **91**, 3961 (1969); (c) postdoctoral research investigators.

(2) For a survey of cmr as used in characterizing structures of a variety of stable carbocations, along with discussion of assignments derived in equilibrating systems, see: G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

(3) H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961).

(4) (a) G. J. Ray, R. J. Kurland, and A. K. Coulter, *Chem. Phys. Lett.*, **2** (5), 324 (1968); (b) V. Koptyug, A. Rezvukhin, E. Lippmaa, and T. Pehk, *Tetrahedron Lett.*, 4009 (1968); (c) G. A. Olah and Gh. D. Mateescu, *J. Amer. Chem. Soc.*, **92**, 1430 (1970).

(5) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *ibid.*, **92**, 4627 (1970).

(6) G. A. Olah and R. D. Porter, *ibid.*, **93**, 6877 (1971).

(7) G. A. Olah, C. L. Jeuell, D. P. Kelly, and R. D. Porter, *ibid.*, **94**, 146 (1972).

(8) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

(9) G. A. Olah, R. D. Porter, and D. P. Kelly, *J. Amer. Chem. Soc.*, **93**, 464 (1971).

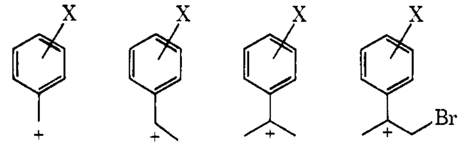
(10) C. S. Foote, *ibid.*, **86**, 1853 (1964); P. v. R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

(11) J. W. Timberlake, J. A. Thompson, and R. W. Taft, *ibid.*, **93**, 274 (1971).

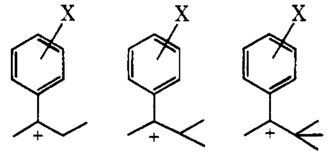
(12) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York N. Y., 1967, p 360.

of this nature are likely, they should be of lesser importance than conclusions made exclusively from model compounds of the intermediates or those derived from precursors. Ray, Kurland, and Coulter[4a] have investigated a comprehensive series of para-substituted triarylcarbenium ions and shown good σ^+ substituent constant correlations with carbenium carbon cmr shifts.

We have investigated in our work the effect of β-bromine substituents on *tert*-cumyl systems (particularly the 2-aryl-1-bromo-2-propyl cations) with a view toward determining the effect of stabilization of positive charge of the benzylic carbenium center by n-electron delocalization (from partial n-electron bridging on one hand to near symmetrical bromonium ion formation on the other). The series of ions **3-X** to **7-X** as well as some **1-X** ions were examined in this study. In these laboratories we have investigated previously the effect of β-bromine substituents on a number of alkyl systems.[6,13] Bromonium ion formation in the bromination of styrenes has been considered by several workers.[14] Pmr as well as selected cmr parameters for the series of ions **1-X** through **7-X** were compared. This series of carbocations should demonstrate the importance of effects of aryl ring and carbenium carbon substituents on the charge density at the carbenium carbon and hence the ability of these substituents to stabilize carbocation intermediates. Kinetic solvolytic data obtained by other investigators on the same systems are compared with the results of the study of stable ions.



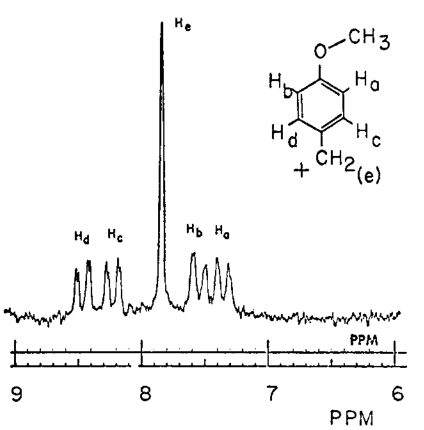
1-X 2-X 3-X 4-X



5-X 6-X 7-X

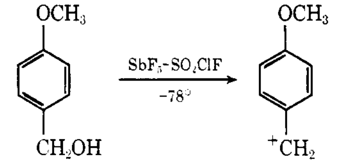
Results

A. Primary Phenylcarbenium Ions (Benzyl Cations) 1-X. The complete cmr and pmr spectra of the first stable monosubstituted primary benzyl cation, the *p*-methoxybenzyl ion **1**-*p*-OCH_3, were obtained. Resonance structures for the ion make probable high $C_{aromatic}$–O and $C_{aromatic}$–$C_{carbenium}$ bond rotational barriers (*vide infra*). Temperature-dependence studies show the C–O rotation to be "frozen out" on the nmr time scale below −25° while the C–C rotation appears to "freeze out" at −130°. Ion **1**-*p*-OCH_3 was prepared by ionizing *p*-methoxybenzyl alcohol, **8**-*p*-OCH_3, in SbF_5–SO_2ClF solution at −78°. The methoxy absorption appears as a singlet at δ 4.25. The aromatic and carbenium proton absorptions are shown at 100 MHz at −70° in Figure 1. Complete proton–proton decoupling has been carried out and the assignments are given in Figure 1. The pmr spectrum shows, in addition to the extensive coupling, unusual shielding effects due to orientation of the O–CH_3 bond as the $C_{aromatic}$–O bond rotation is "frozen out." Syn (H_a) and anti (H_b) assignments are based on the anticipated shielding effect of the methyl group on H_a relative to H_b. The spectrum displays nonequivalence of meta protons which is less than that for ortho protons. The low-temperature (−130°) spectrum indicates as well the "freezing out" of the rotation of the C–C$^+$ bond to be observable by nonequivalence of the carbenium protons due as well to the orientation of the *p*-OCH_3 substituent. Upon warming to −25°, the aromatic region becomes an apparent AB system, indicative of rapid C–O bond rotation.[15]



J_{ab} = 1.5 Hz δ_a = 7.48 δ_d = 8.56
J_{ac} = 9.5–9.8 Hz δ_b = 7.66 δ_e = 7.82
J_{bd} = 9.7–10.0 Hz δ_c = 8.36 δ_{CH_3} = 4.68
J_{cd} = 1.0 Hz

Figure 1. 100-MHz proton nmr spectrum of the *p*-methoxybenzyl cation **1**-*p*-OCH_3 in SbF_5–SO_2ClF at −70°.



8-*p*-OCH_3 1-*p*-OCH_3

The carbon-13 nmr spectrum was obtained for the ion by fast Fourier transform (FFT) spectroscopy.[16] Assignments were made with the aid of indor ^{13}C nmr spectroscopy[17] on the same ion. The indor method

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[13] G. A. Olah and J. M. Bollinger, *J. Amer. Chem. Soc.*, **89**, 4744 (1967); G. A. Olah and J. M. Bollinger, *ibid.*, **90**, 947 (1968); G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 2587 (1968); G. A. Olah and P. E. Peterson, *ibid.*, **90**, 4675 (1968); G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 6988 (1968).

[14] K. Yates and W. V. Wright, *Can. J. Chem.*, **45**, 167 (1967); J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1469, 1477, 1483 (1969); K. Yates and W. V. Wright, *Tetrahedron Lett.*, 1927 (1965); J. E. DuBois and A. Schwarcz, *ibid.*, 2167 (1964); J. E. DuBois and W. V. Wright, *ibid.*, 3101 (1967); R. C. Fahey and H. J. Schneider, *J. Amer. Chem. Soc.*, **90**, 4429 (1968); R. E. Buckles, J. M. Bader, and R. J. Thurmeier, *J. Org. Chem.*, **27**, 4523 (1962); R. E. Buckles, J. L. Miller, and R. J. Thurmeier, *ibid.*, **32**, 888 (1967); G. Hueblin, *J. Prakt. Chem.*, **31**, 84 (1966).

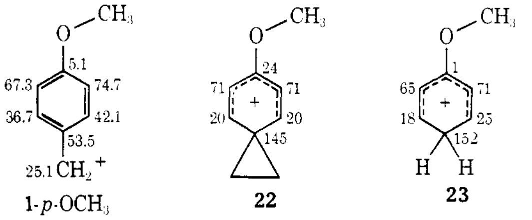
[15] As the temperatures of "freezing out" of the C–O and C–C$^+$ bond rotation were quite different (105°) the rotational barriers as well may be implied to be substantially lower in the C–C$^+$ case. The observation of the freezing out of the C–C$^+$ bond rotation occurred at a temperature of high viscosity broadening and was marked by loss of the $^+CH_2$ absorption, the aromatic region being then characterized by broad absorptions on either side, due presumably to the nonequivalent benzylic proton absorptions as well as those for the ortho and para protons. Unfortunately, the viscosity effects at this low temperature precluded estimation of the relative rotational barriers.

[16] R. R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, **37**, 93 (1966).

[17] (a) E. B. Baker, *J. Chem. Phys.*, **37**, 911 (1962); (b) G. A. Olah

of ^{12}C–H main peak enhancement was used to obtain cmr shifts of C_{ortho} carbons, as well as the C_{para} absorption. Carbon-13 chemical shifts are shown at −70° to display the nonequivalence conferred by orientation of methoxy substituent as was observed for the ring protons (Chart I). The cmr shift of the benzylic carbons is included in Table I for comparison with other benzylic chemical shifts obtained in this study.

Chart I. Cmr Chemical-Shift Values[a] for Aryl (Arenium) Ring Carbons in Anisenium-Like Cations



1-*p*-OCH$_3$ **22** **23**

[a] Parts per million relative to ^{13}CS$_2$.

Table I. Carbon-13 Chemical Shifts[a] for Carbenium Carbons in Benzylic Ions **1**-X, **2**-X, **3**-X, **5**-X, **6**-X, and **7**-X

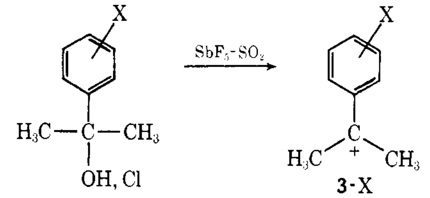
X	1-X	2-X	3-X	5-X	6-X	7-X
p-OCH$_3$	+25	−5[b]	−25	−30	−33	−44
p-CH$_3$		−28[b]	−49	−54	−57	
p-F		−39	−54			
p-H		−40[b]	−61	−67	−72	
p-Br			−58[c]			
m-F			−67			
p-CF$_3$		−53[b]	−75	−82	−77	

[a] Parts per million relative to external ^{13}CS$_2$ (negative values are indicative of deshielding relative to reference). [b] Reference 9. [c] Reference 6.

The cmr shifts of benzylic carbenium carbon atoms were obtained for the pentamethylbenzyl cation **9** at $\delta_{^{13}C}$ +23 as well as for the 2,6-dimethyl-4-*tert*-butylbenzyl cation **10** at $\delta_{^{13}C}$ +19.5. Both of these highly substituted primary benzylic ions were known from previous work. The cmr shifts were obtained by monitoring the ^{13}C–H satellite for ion **10** where the ^{13}C–H coupling constant was known from previous studies to be J = 169 Hz. The ^{13}C–H satellite for ion **9** could not be directly observed, but the coupling constant was obtained by estimating $J_{^{13}C-H}$ values close to the known J = 169 Hz value for ion **10** and monitoring the appropriate position relative to the main pmr ^{12}C–H absorption of the benzylic proton singlet. Indor satellite decoupling was then attempted by sweeping the proper ($\delta_{^{13}C}$ = +40 to +10 ppm) frequency range with the decoupling irradiation at that point on the apparent base line. After several attempts at accumulating indor spectra at different points, the satellite was found (J = 168 Hz) as indicated by negative absorption in the accumulated indor spectra at $\delta_{^{13}C}$ +23.

B. Secondary Phenylmethylcarbenium Ions (α-Phenylethyl (Styryl) Cations) 2-X. We have previously reported pmr and some cmr parameters for these ions.[9] We include the carbenium carbon cmr chemical shifts for these ions in Table I for comparison with other benzylic ions studied in the present work. The *p*-fluorostyryl ion **2**-*p*-F was prepared by ionizing 1-*p*-fluorophenylethyl alcohol in SbF$_5$–SO$_2$ at −78°. The pmr spectrum of this ion is reported in the Experimental Section; the cmr carbenium carbon chemical shift is included as well in Table I. Extensive H–F coupling was found as evidenced in the proton spectrum of this ion. Fluorine–proton coupling to all protons in the ion is quite large and an unusual seven-bond H–F coupling of 2.7 Hz to the methyl protons through the carbenium carbon center is also observed. The ^{19}F nmr data for ion **2**-*p*-F have been reported by Taft.[11]

C. Aryldimethylcarbenium Ions (Cumyl Cations) 3-X. A series of aryldimethylcarbenium ions (cumyl cations) **3**-X was generated from the precursor *tert*-cumyl chlorides or alcohols **11**-X in SbF$_5$–SO$_2$ solution at −78°.

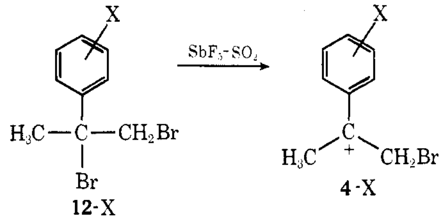


11-X **3**-X

Pmr spectra for several of these **3**-X ions where X = H,[18] *p*-CF$_3$,[18] *p*-Br,[6] *p*-CH$_3$,[18] and *p*-OCH$_3$[18] have been reported. These are included for comparison in Table II along with those for ions **3**-*p*-F and **3**-*m*-F examined in this study as well as ions **4**-X through **7**-X. Cmr chemical shifts for the carbenium carbon atoms of the ions were obtained *via* the indor method of enhancement of the main ^{12}C–H methyl singlet by decoupling the ^{13}C–C–H long-range satellites. The cmr data are summarized in Table I.

As was the case for ion **2**-*p*-F, long-range seven-bond methyl to *p*-fluorine H–F coupling (1.2 Hz) is observed for ion **3**-*p*-F. Ion **3**-*m*-F shows no such effect. Proton–proton and proton–fluorine coupling constants given for **3**-*m*-F are tentative as the aromatic absorption region was complex making double irradiation experiments difficult.

D. β-Bromocumyl Cations 4-X. The β-bromocumyl cations **4**-X where X = *p*-CF$_3$, H, and *p*-CH$_3$ were prepared by addition of SO$_2$ solutions of the dibromo **12**-X precursors at −70° to an SbF$_5$–SO$_2$ solution. Ions



12-X **4**-X

4-X are compared with analogous ions **3**-X to determine the extent of positive charge delocalization from the tertiary carbenium center due to the β-bromine substituent. Cmr shifts of carbenium carbons were obtained *via* the indor method of main ^{12}C–H peak enhancement of the carbenium methyl singlet as for the **3**-X ions and are shown in Table III. They vary over the range from the substantially deshielded value of $\delta_{^{13}C}$ −44 for ion **4**-*p*-CF$_3$ to that of $\delta_{^{13}C}$ −28 for **4**-*p*-

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and A. M. White, *J. Amer. Chem. Soc.*, **89**, 7072 (1967); (c) A. M. White and G. A. Olah, *ibid.*, **91**, 2943 (1969); (d) W. H. Horsley and H. Sternlicht, *ibid.*, **90**, 3738 (1968).

(18) G. A. Olah, M. B. Comisarow, and C. J. Kim, *ibid.*, **91**, 1458 (1969).

Table II. Pmr Chemical Shifts[a] of Tertiary Benzylic Ions

X	CH_3C^+	$(CH_3)_2CHC^+$ $(CH_3)CH_2C^+$	$BrCH_2C^+$	$(CH_3)_xCH_{3-x}C^+$	Aromatic Ortho	Aromatic Meta	Aromatic Para
3-X							
p-OCH_3[d]	3.12				8.72	7.40	4.37
p-CH_3[d]	3.45				8.75	7.86	2.84
p-F	3.38, d				8.88	7.50	
H[d]	3.48				8.73	7.82	8.42
m-F	3.61				8.68, 8.37	7.91, F	8.18
p-CF_3[d]	3.71				8.90	8.08	
5-X							
p-OCH_3	2.95	3.22, q		1.30, t	8.54	7.20	4.18
p-CH_3	3.27	3.52, q		1.37, t	8.47	7.62	2.60
H	3.46	3.75, q		1.51, t	8.72	7.84	8.44
p-CF_3	3.70	3.98, q		1.55, t	8.88	8.06	
6-X							
p-OCH_3	2.86	4.05, s		1.29, d	8.56	7.21	4.18
p-CH_3	3.45	4.51, s		1.73, d	8.73	8.11	3.15
H	3.67	4.78, s		1.82, d	9.05	8.22	8.78
p-CF_3[b]	3.60	4.72, s		1.68, d	8.84	8.06	
7-X							
p-OCH_3[d]	2.98			1.50	8.62	7.18	4.11
p-CH_3[c]	3.49			1.80	8.80	7.94	2.78
4-X							
p-CH_3	3.37		5.10		8.70, 8.90	7.90	2.79
p-H	3.55		5.25		8.70, 8.90	7.94	8.60
p-CF_3	2.76		5.48		9.11	8.28	

[a] Parts per million relative to TMS: d, doublet; t, triplet; q, quartet; s, septet. In SbF_5–SO_2 or SbF_5–SO_2ClF at −70°. [b] Solvent HSO_3F–SbF_5–SO_2. [c] Solvent SbF_5–SO_2ClF at −125°. [d] See ref 18.

Table III. Comparison of Carbenium Carbon Cmr Chemical Shifts[a] of Cumyl (**3**-X), β-Bromocumyl (**4**-X), and Neutral Model Compounds

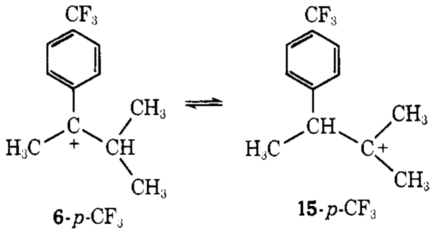
X	Cumyl ion (**3**-X)	β-Bromocumyl ion (**4**-X)	$\Delta\delta_{^{13}C}$ (**3**-X − **4**-X)
p-CH_3	−49	−28	−21
P-H	−61	−38	−23
p-CF_3	−75	−44	−31
Propene (C_2)	+61[b]	+59[b] (3-bromopropene)	+2

[a] Parts per million relative to $^{13}CS_2$. [b] C_2 of neutral molecule for bromine substituent effect comparison.

CH_3. Comparing this range of values with those observed for the analogous ions **3**-X shows that the differences of cmr shift between ions **3**-X and **4**-X does not remain constant. Table III makes the comparison between the cmr shifts of the ions showing differences $\Delta\delta$(**3**-X − **4**-X). The decrease in $\Delta\delta$ is presumably due to neighboring group participation (delocalization) by the β-bromine atom into the carbenium carbon center *via* bridging or partial bridging. Effect of a β-bromine atom on the cmr shift of a neutral sp^2 carbon atom was measured *via* the indor method, by determining the $\delta_{^{13}C_2}$ in propylene and 3-bromopropene-1. These values are included as well in Table III, and the effect is shown to be small relative to that observed for carbocation analogs and was opposite in direction.

Pmr spectral parameters for ion **4**-X are given in Table II. For all ions the methylene protons are observed to be equivalent, which is not expected for a stable bridged species. For ions **4**-H and **4**-*p*-CH_3, nonequivalence of the ortho protons is observed indicating that the rotation of the C–C+ bond is "frozen out" on the pmr time scale. In ion **4**-*p*-CF_3, the aromatic absorptions show an apparent simple AB quartet indicating that rotation of the C–C+ bond is faster in this case. Differences in chemical shifts of the ortho and meta absorptions, as well as the deshielded values for the ortho chemical shifts, indicate that positive charge delocalization into the aromatic ring is substantial. In all **4**-X ions the methylene absorptions appear as sharp singlets. Magnetic resonance parameters for precursors **12**-X are given in the Experimental Section.

E. Phenylmethylalkyl Carbenium Ions 5-X, 6-X, and 7-X. These ions were studied to establish the effect of replacement of a β-hydrogen atom in aryldimethylcarbenium ions **3**-X by a methyl substituent. Ions **5**-X, **6**-X, and **7**-X were compared to demonstrate the effect of replacement of one, two, and three protons, respectively, by methyl groups. The resultant changes in carbon-13 chemical shift of the carbenium carbon centers are shown in Table I. Ions **5**-X and **6**-X (where X = *p*-OCH_3, *p*-CH_3, H, and *p*-CF_3) were prepared by ionizing precursor alcohols or chlorides **13**-X and **14**-X in SbF_5–SO_2 or SbF_5–SO_2ClF solution (with the exception of **6**-*p*-CF_3) at low temperature (−78°). The ions were stable over the range −30 to −80°. Ion **6**-*p*-CF_3 was prepared by ionization of alcohol **14**-*p*-CF_3 in 1:1 molar HSO_3F-SbF_5 in SO_2 at −60°. Ionization proceeded slowly over a 3-hr period at that temperature. Figure 2 shows the resultant temperature-dependent pmr spectrum of the solution. Coalescence of the methyl absorptions at −25° is shown in the lower trace. Coalescence is presumably due to a **6**-*p*-CF_3 ⇌ **15**-*p*-CF_3 equilibrium. Unfortunately, at



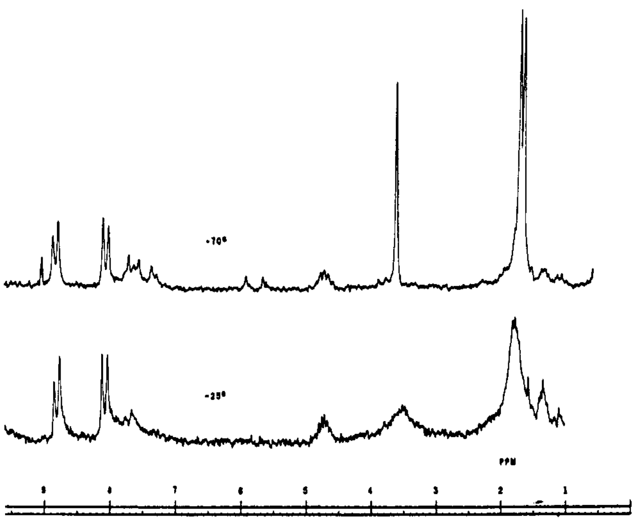
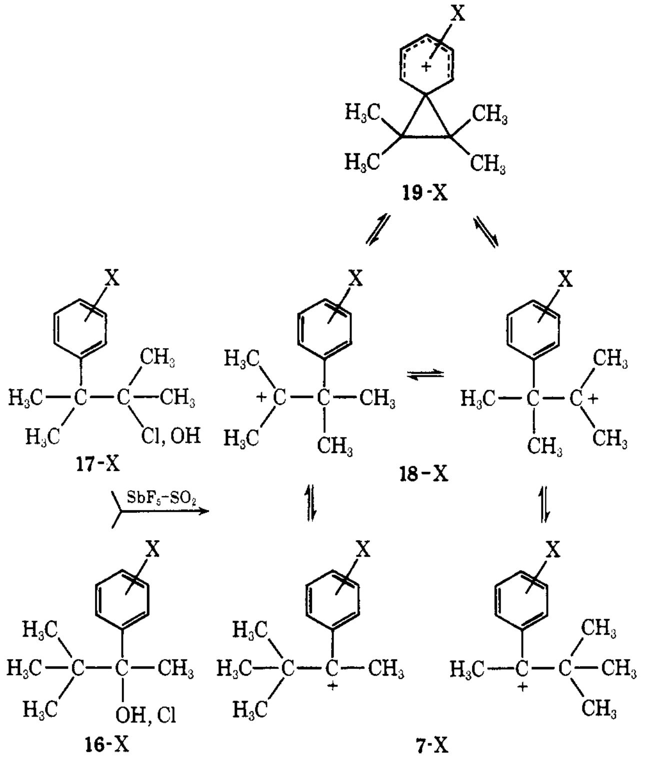


Figure 2. Temperature-dependent spectra of 2-(*p*-trifluoromethylphenyl)-3-methyl-2-butyl cation (**6**-*p*-CF_3) equilibrium in HSO_3F–SbF_5–SO_2.

higher temperatures side reactions occur and the completely time-averaged spectrum could not be obtained.

Ions **7**-X have been reported previously.[18] Scheme I shows the ions which can be obtained *via* ionization

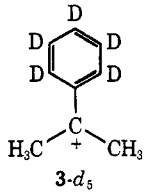
Scheme I



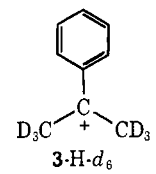
of **16**-X or **17**-X under stable ion conditions. From the ions obtained from the precursors **16**-X (**17**-X) where X = H, *p*-Br, and *p*-CF_3, **19**-X is the most stable as shown by our previous studies.[6] For the case where X = *p*-OCH_3, the proton magnetic resonance spectrum is consistent with **7**-*p*-OCH_3, which is frozen out as the most stable species below −40°.[18] Ion **7**-*p*-CH_3 was obtained from **16**-*p*-CH_3 and was shown at −120° in the solvent system SbF_5–SO_2ClF–SO_2F_2 to be consistent with ion **7**-*p*-CH_3 as the stable frozen-out species on the pmr time scale. Upon raising the temperature, the time-averaged spectrum is shown to be within 1 Hz of the expected weighted average of α-methyl and *tert*-butyl protons in **7**-*p*-CH_3 ions. Presumably **18**-X must be an intermediate in any **7**-X equilibrium as shown. Attempts to obtain the carbenium carbon cmr shift of **7**-*p*-CH_3 were not successful.

Pmr shifts of ions **5**-X and **6**-X where X = *p*-OCH_3, *p*-CH_3, H, and *p*-CF_3 as well as ion **7**-X, where X = *p*-OCH_3 and *p*-CH_3, are given in Table II and the cmr shifts of the carbenium carbon atoms of the same ions except **7**-*p*-CH_3 are given in Table I. Pmr parameters for the ions show the expected characteristics. Carbenium atom cmr chemical shifts for ions **5**-X and **6**-X were obtained *via* the indor method of enhancement of the β-methyl singlet main ^{12}C–H absorption. Carbenium carbon cmr shifts obtained for these ions as well as those for ions **2**-X and **3**-X show a trend of deshielding as aromatic substituents become more electron withdrawing, *i.e.*, shielded $\delta_{^{13}C^+}$ for *p*-OCH_3-substituted ions, and deshielded values for *p*-CF_3-substituted ions, the range between them being about 50 ppm. Carbenium carbons show a deshielding trend as β-hydrogens are replaced by methyl substituents. Within each series (X being identical) the cmr shifts follow the order of deshielding **3**-X > **5**-X > **6**-X > **7**-X.

F. Deuterium Substitution of Ion 3-H. The pentadeuteriophenyldimethylcarbenium ion **3**-d_5 was prepared by ionizing the corresponding *tert*-cumyl-d_5 alcohol in SbF_5–SO_2. The spectrum of the ion **3**-d_5



3-d_5



3-H-d_6

consists of a singlet at nearly identical pmr shift with that for ion **3**-H (2 Hz deshielded as shown by mixtures of ions). Indor ^{12}C–H mainline enhancement was carried out to obtain an accurate carbenium carbon cmr shift. For comparison, immediately beforehand the indor spectrum was run on the **3**-H ion under identical conditions. Between the two samples, no changes in instrumentation other than slight homogeneity adjustments were made. Indor-obtained cmr shifts of carbenium carbons were practically identical (less than 0.1-ppm difference) due to small ring-d_5 deuterium isotope effect.

An identical experiment was carried out on phenyldi(deuteriomethyl)carbenium ion **3**-H-d_6, again prepared from the corresponding d_6 alcohol in SbF_5–SO_2. The largest aromatic ortho proton ^{12}C–H absorption was monitored, indor spectra being taken consecutively as above and comparisons made between **3**-H-d_6 and **3**-H for slight deuterium isotope effects. The indor spectra again were identical although the observed absorptions in both **3**-H and **3**-H-d_6 were broad, presumably due to the combination of a lower signal/noise ratio of the proton spectrum, making homogeneity tuning difficult, and weaker $J_{^{13}C-H}$ coupling. Pmr and cmr parameters for these ions are not tabulated as they were, with the exception of the undetected absorptions at the deuterated sites, the same as those observed for ion **3**-H.

Discussion

Recent studies on stable carbocations have led to a substantial extension of the validity of a general charge density to cmr chemical-shift relationship, first presented by Spiesecke and Schneider.[3] This relationship is contingent upon closely related structures having essentially the same geometry. Ions **3**-X and other related ions studied have the advantage that their solvolytic reactions were studied by many investigators. It has been shown that large rate differences can be effected at the benzylic reaction site by remote (meta or para), sterically fixed substituents. Hammett-type relationships in solvolyses of tertiary benzylic systems were initially demonstrated by Brown and coworkers,[8] expressing effects of aromatic ring substituents by σ^+ substituent constants in the relative rate expressions. The Brown σ^+ relationship reflects the ability of the particular aromatic substituent to lower the energy of the intermediate benzylic cation relative to the standard unsubstituted ion by inductive and resonance stabilization. This treatment is subject to the assumption that under nucleophilic conditions a late transition state approximates in character the carbenium ion intermediate.[19]

Cmr carbenium carbon chemical shifts of ions **3**-X are plotted against Brown's σ^+ substituent constants in Figure 3.[20] Also included are similar plots of ions **2**-X, **5**-X, and **6**-X. In all cases the approximate linearity of the relationship is apparent, especially in the highly resonance stabilized ions where X = p-OCH$_3$, p-CH$_3$, and H. The given lines were calculated by the method of least squares and their slopes ($\Delta\sigma^+/\Delta\delta_{^{13}C}$) are -0.02715 (**2**-X), -0.02744 (**3**-X), -0.02597 (**5**-X), and -0.02752 (**6**-X). Standard deviations (parts per million) of the points from the calculated lines were 4.7 (**2**-X), 3.7 (**3**-X), 5.8 (**5**-X), and 7.1 (**6**-X). Okamoto and Brown measured relationships for solvolysis of 1-arylethyl chlorides and found the Brown σ^+ relationship to hold well in these secondary benzylic systems. The parallel between carbenium carbon cmr shifts for ions **2**-X and **3**-X can be shown now in the form of constant methyl substituent effect on the carbenium carbon atoms.

The continued relationship of ions **5**-X and **6**-X to σ^+ is not surprising, as positive charge delocalization into the aromatic ring for ions **5**-X and **6**-X is probably intermediate between that for **2**-X and **3**-X. The deshielding trend at the carbenium carbon throughout the series **3**-X, **5**-X, **6**-X (as X remains constant), insofar as it is indicative of greater positive charge localization at the carbenium center, indicates the effect of β-H delocalization by the carbenium carbon and is decreasing through the series with increasing methyl substitution. This effect can be extended through ions **7**-X to the **7**-p-OCH$_3$ ion. Comparison of the effect of substitution at the analogous β-carbon on cmr shifts of sp^2-hybridized carbon has been made, for example, by Friedel and Retcofsky,[21] who showed the effect of methyl, ethyl, isopropyl, and *tert*-butyl substitution on α-carbon in alkylbenzenes. Stothers and Lauterbur[22] made a similar study of the same substituents at carbonyl carbon in alkyl methyl ketones. In Table IV, the pertinent values obtained for analogs **3**-p-OCH$_3$, **5**-p-OCH$_3$, **6**-p-OCH$_3$, and **7**-p-OCH$_3$ are compared to those values of carbonyl carbon of methyl alkyl ketones **20**-R and alkylbenzenes **21**-R. In all cases, increasing branching at the β-carbon has a deshielding effect. The difference of 11 ppm for carbenium carbon cmr shifts between ions **6**-p-OCH$_3$ and **7**-p-OCH$_3$ is large, but surprising differences in magnitude in **20**-R from that in **21**-R suggest that no unequivocal interpretation of the cmr results for the benzyl cation systems can be made.

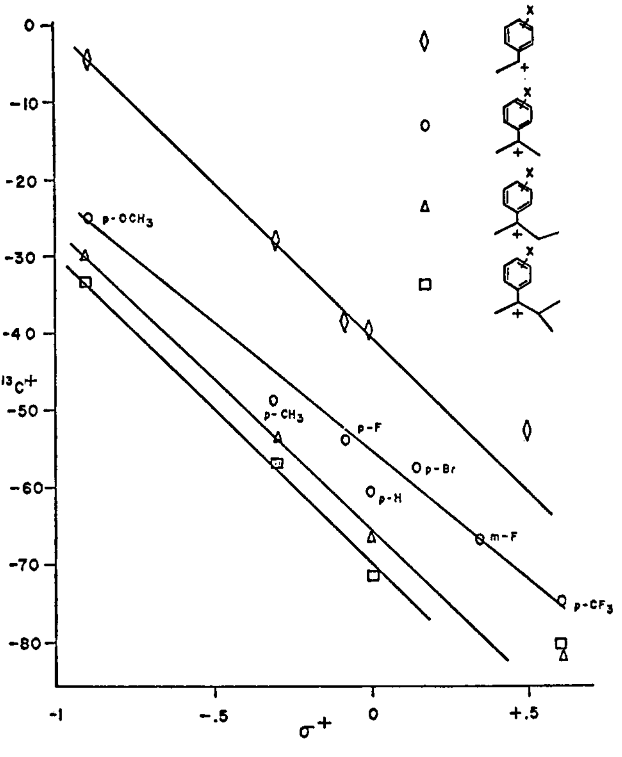
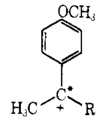
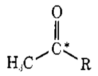
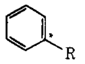


Figure 3. Relationships of carbenium carbon cmr chemical shifts to Brown σ^+ substituent constants for ions **2**-X, **3**-X, **5**-X, and **6**-X.

Table IV. Comparison of Substituted sp^2-Hybridized Carbon Cmr Shifts[a]

R		 **20**–R[c]	 **21**–R[b]
CH$_3$	−25	−12	+56
C$_2$H$_5$	−30	−14	+50
i-C$_3$H$_7$	−33	−17	+46
tert-C$_4$H$_9$	−44	−18	+42

[a] Parts per million relative to ^{13}CS$_2$. The asterisk denotes carbon tabulated. [b] Reference 21. [c] Reference 22.

The case of equilibrating ions **7**-X $\rightleftharpoons$ **18**-X $\rightleftharpoons$ **19**-X and the comparable case of **6**-p-CF$_3$ $\rightleftharpoons$ **15**-p-CF$_3$ reflects the ability of the aromatic ring to stabilize the

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(19) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).

(20) Carbenium ^{13}C chemical shifts for estimated values of primary benzyl ions projected from these data have been correlated with r and σ^+ parameters making use of the Yukawa–Tsuno relationship as well ($\delta_{^{13}C} = k[\sigma + r(\sigma^+ - \sigma)]$). The r value obtained was 0.80; see G. A. Olah, S. Kobayashi, and M. Tashiro, *ibid.*, in press.

(21) R. A. Friedel and H. L. Retcofsky, *ibid.*, **85**, 1300 (1963).

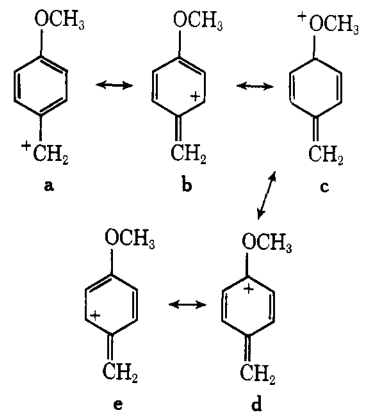
(22) J. B. Stothers and P. C. Lauterbur, *Can. J. Chem.*, **42**, 1563 (1964).

benzylic ion in relation to the competing tertiary dimethylbenzylcarbenium ions, and by analogy suggests that the cmr shifts reflect the stability of the ions in relation to the X substituent. Unfortunately this cannot be used in estimating the relative ion destabilizing effects of *tert*-butyl, isopropyl, ethyl, and methyl substituents. The reasons for this are the following: (1) The competing ions resulting from a 1,2 shift in the equilibria, *e.g.*, the tertiary ions in the equilibria of ions **6**-X and **17**-X, and for ions **5**-X, the competing secondary ions, are different in stability. (2) Proton migration in ions **6**-X is compared here to methyl migration in ions **7**-X. Anticipated differences in strain between ions **7**-X and **6**-X make reliable estimates of migratory aptitudes difficult.

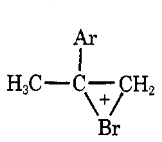
Ion **1**-*p*-OCH$_3$ (Figure 1) shows extensive positive charge delocalization into the aromatic ring in comparison to the analogous secondary ion **2**-*p*-OCH$_3$[23] and tertiary ion **3**-*p*-OCH$_3$ (Table II). This is indicated not only by pmr chemical shifts relative to these analogs but also by the facility with which the rotation of the $C_{aromatic}$–O bond is "frozen out." For ions **2**-*p*-OCH$_3$ and **3**-*p*-OCH$_3$ the aromatic absorptions show an apparent AB quartet with no differences in H_{meta} pmr shifts being observed. Other known stable *p*-methoxy substituted arenium ions are the ethylene-*p*-anisenium ion **22**[24] for which the rotation of the $C_{aromatic}$–O bond is not "frozen out," and C-protonated anisole **23**[25] for which it is. Comparison of these three ions in Chart I shows their obvious similarities in positive charge distribution in their aromatic rings, although in ion **1**-*p*-OCH$_3$ relative to **23** there is significant charge at the carbenium carbon atom much as the spirocyclopropane ring bears positive charge in ion **22**. In ion **1**-*p*-OCH$_3$, there is significant charge at the carbenium carbon atom as indicated by the shielding of the ortho and para cmr shifts relative to their analogs in **23**. The same argument indicates the spirocyclopropane ring bears positive charge in ion **22** relative to its **23** analog.

The extrapolation of carbenium carbon cmr shift values is not linear through the tertiary (**3**-*p*-OCH$_3$), secondary (**2**-*p*-OCH$_3$), primary (**1**-*p*-OCH$_3$) series of ions, as $\Delta\delta_{C^+}$ (**3**-*p*-OCH − **2**-*p*-OCH$_3$) = −20, while $\Delta\delta_{C^+}$ (**2**-*p*-OCH$_3$ − **1**-*p*-OCH$_3$) = −30. This is perhaps due to flexibility of the *p*-anisyl system in responding to increased demand for carbenium carbon stabilization. Possible valence bond structures for ion **1**-*p*-OCH$_3$ are shown. The high barrier for rotation of the $C_{aromatic}$–O bond indicates structure **c** to be important, while the observable $C_{aromatic}$–C^+ barrier, along with charge distribution (as estimated from Chart I), indicates structures **b**–**e** to all be of substantial importance.

Table III shows comparison of ions **4**-X to **3**-X. Differences in carbenium carbon chemical shifts, *i.e.*, Δδ (**3**-X − **4**-X), become smaller as X becomes more electron withdrawing. The cmr shifts are predominantly characteristic of carbenium carbons as indicated by their deshielded values. Bromine-bridged ions, *e.g.*, **24**, should show much more shielded cmr shifts from about δ +121 (ethylenebromonium) to +55 (tetramethylethylenebromonium ion).[2,6]



1-*p*-OCH$_3$



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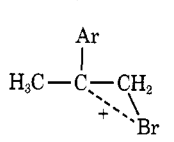

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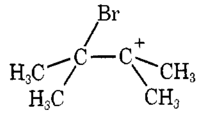
A weak *n*-donor interaction as in ion **25** is more likely. The strength of the interaction is, however, insufficient even in the ions showing the strongest bromine–carbenium carbon interaction (*e.g.*, **4**-*p*-CF$_3$) to slow down rotation of the C^+–CH$_2$Br bond on the pmr time scale and thereby cause nonequivalence of methylene protons. We therefore conclude that bromine bridging plays only a minor contributory role in stabilizing benzylic systems even in the case of the *p*-CF$_3$-substituted species. In the tertiary alkyl system **26**, the adjacent bromine atom is known to participate, thereby forming the full bridged tetramethylethylenebromonium ion **27**.



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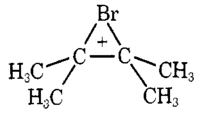

27

The large shielding effect of C–Br *vs.* C–H substitution in methyl groups adjacent to carbenium centers is puzzling, especially when considering the deshielding effect observed on the C$_2$ carbon of 1-bromo-2-propene (Table III). We have seen, however, many long-range effects in carbocations (*cf.* ions **1**-*p*-OCH$_3$, **2**-*p*-F, **3**-*p*-F, long-range coupling *tert*-amyl[26]) which are difficult to explain. The cmr shift data as well as general pmr characteristics in all the ions **4**-X indicate that these ions should be assigned as carbenium ions as depicted (**25**).

The lack of sensitivity of carbenium carbon cmr shifts to deuterium substitution in attached methyl groups or in adjacent aromatic rings is not surprising. Taft,[11] using ^{19}F nmr data on aromatic para fluorine substituents, noted a 0.22-ppm deuterium isotope effect for substitution of CD$_3$ for CH$_3$ in ion **3**-*p*-F. The problem with a fluorine probe of this kind is the ability of the probe itself to participate in stabilization of the

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[23] See ref 9. For ion 2-*p*-OCH$_3$ the pmr spectrum shows the following parameters: C^+H, δ 8.86; CH_3C^+, 2.98; CH_3O, 4.50; $H_{o\text{-}Ar}$ 9.40; and $H_{m\text{-}Ar}$ 8.86.

[24] G. A. Olah, M. B. Comisarow, E. Namanworth, and B. Ramsey, *J. Amer. Chem. Soc.*, **89**, 5259 (1967).

[25] G. A. Olah and Y. K. Mo, in press, and references given therein.

[26] G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. MacIntyre, and I. J. Bastien, *J. Amer. Chem. Soc.*, **86**, 1360 (1964).

Table V. Pmr Parameters[a] and Physical Characteristics for **13**-X and **14**-X Alcohols

Alcohol	$\text{C}\mathit{H}_3\overset{\text{OH}}{\text{C}}$	$(\text{CH}_3)_x\text{C}\mathit{H}_{(3-x)}\overset{\text{OH}}{\text{C}}$	$(\text{C}\mathit{H}_3)_x\text{CH}_{(3-x)}\overset{\text{OH}}{\text{C}}$	Ortho	Meta	X	Bp, °C (mm)
13-*p*-OCH_3	1.41, s	1.72, q (6.4)	0.73, t	6.69	7.19 7.25	3.67	99–107 (2.0)
13-*p*-CH_3	1.43, s	1.70, q (7.3)	0.72, t	6.95	7.20	2.28	78–81 (3.0)
13-H	1.45, s	1.75, q (7.1)	0.75, t		(7.05–7.50, m)		82 (3.9)
13-*p*-CF_3	1.49, s	1.78, q (7.4)	0.77, t		(7.50, s)		80 (4.0)
14-*p*-OCH_3	1.41, s	1.90 (7.0)	0.76[b] 0.81	6.72	7.24	3.69	108–111 (3.0)
14-*p*-CH_3	1.40, s	1.92 (7.0)	0.74[b] 0.83	6.98	7.21	2.27	84–85 (3.0)
14-H	1.38, s	1.85 (6.7)	0.80[b] 0.84		(7.00–7.56, m)		74–80 (4.0)
14-*p*-CF_3	1.48, s	1.98 (6.9)	0.85[b] 0.90		(7.49, s)		79–82 (4.0)

[a] Parts per million relative to TMS; coupling constants (hertz) in parentheses; room temperature; CCl_4 solvent; s = singlet, t = triplet, q = quartet, m = multiplet. [b] Two doublets, probably asymmetric induction.

ion.[27] Spectroscopic data obtained on ions **2**-*p*-F and **3**-*p*-F show interactions which are unusual in nature (seven-bond long-range coupling) to occur in the case of a para fluorine substituent. Data on β-deuterium isotope effects in solvolyses of cumyl systems[28] show rate enhancements not likely detected in terms of ion stability in present stable ion systems.

Conclusions

Cmr spectroscopic studies of benzylic carbocations show that essentially the cmr shifts reflect the positive charge density at carbenium carbons indicating the stability of the ions. The results obtained parallel those observed in solvolytic rate studies of the same systems. Relationships of this nature with aromatic substituents hold most closely for resonance stabilizing groups. Not only cmr shifts but competing rearrangements in ions **6**-X and **7**-X are indicative of the expected relative benzylic stabilization conferred by aromatic substituents of various σ^+ character.

Tertiary benzyl stabilization is shown to be favored over β-bromine n-electron donation, even when the destabilizing *p*-CF_3 group is present on the aromatic ring (*i.e.*, **4**-*p*-CF_3). Stabilization by β-hydrogen, *i.e.*, "hyperconjugation" of tertiary benzylic ions, may not be inferred from cmr shifts at this time due to lack of consistent comparative data on model compounds, although the trend is in the expected direction for hyperconjugative stabilization. The cmr studies were carried out directly on the ions themselves, without recourse to measurements on structurally similar models or the use of chemical probes, like fluorine substitution, thereby changing the species itself being studied. Cmr spectroscopy thus is considered the best method presently available for the study of the substituent effect on carbocation stabilities.[29]

Experimental Section

Precursor Alcohols. Dimethylarylcarbinols **11**-X, ethylmethylarylcarbinols **13**-X, and isopropylmethylarylcarbinols **14**-X were prepared either by reaction of the appropriate arylmagnesium bromide with alkyl ketones or alkylmagnesium bromide with acetophenone, by standard procedures. Preparations and physical properties of **11**-X are given by Brown, Okamoto, and Ham[30] for X = halide. For other **11**-X precursors both physical properties and nmr data have been given in previous work.[18] Pmr parameters for **11**-*p*-F and **11**-*m*-F are: for **11**-*p*-F, δ 1.53 (s, 6 H); δ_o 7.42 (2 H, $J_{\text{H-H}}$ = 9.0 Hz, $J_{\text{H}_o\text{-F}}$ = 5.5 Hz); δ_m 6.98 (2 H, $J_{\text{H-H}}$ = 9.0 Hz, $J_{\text{H}_m\text{-F}}$ = 8.5 Hz); for **11**-*m*-F, δ 1.47 (s, 6 H), 6.6–7.3 (m, 4 H). Pmr parameters as well as boiling points for alcohols **13**-X and **14**-X are given in Table V. The *p*-fluorostyryl ion was prepared from *p*-fluoro-α-methylbenzyl alcohol (Aldrich). The preparation of **7**-*p*-CH_3 was from **16**-*p*-CH_3, and **17**-*p*-OCH_3 was used to prepare ions **7**-*p*-OCH_3: the preparations and spectral properties of these precursors have been described.[18] Precursor chlorides for the two primary polyalkylbenzyl cations were those from a previous study.[31]

Deuterium-Labeled Alcohols. Dimethyl-d_6-phenylcarbinol was prepared by addition of acetone-d_6 (Merck, Sharpe, and Dohme) to phenylmagnesium bromide as above. Phenyl-d_5-dimethylcarbinol was prepared from phenyl-d_5-magnesium bromide and acetone. Phenyl-d_5-magnesium bromide was prepared from the reaction of magnesium with bromobenzene-d_5 in diethyl ether. Bromobenzene-d_5 was prepared by the reaction of bromine with benzene-d_6 (Merck Sharp and Dohme) in dry pyridine as described by Vogel.[32] Ions **3**-H and **3**-d_6-H appear identical by pmr (with the exception of the missing singlet in the latter). Ions 3-H and **3**-H-d_5 when mixed show two proton singlets, the pentadeuterated aromatic system showing 2-Hz deshielding of the methyl singlet, due to the isotope effect.

1,2-Dibromo-2-(*p*-X-phenyl)propanes (12-X). These **12**-X compounds were all prepared by adding bromine in $CHCl_3$ to a solution of the α-methylstyryl precursor in $CHCl_3$ at −78°. The solutions were warmed to 0° and stirred 1–2 hr, warmed to room temperature, and worked up by standard methods. **12**-*p*-CH_3 was prepared in 77% yield: pmr (CCl_4) δ 2.28 (s, 3 H, carbinyl methyl), 4.18 (q, 2 H, methylene), 7.47 (d, 2 H, ortho), 7.14 (d, 2 H, meta, J = 8 Hz), 2.34 (s, 3 H, ring methyl). **12**-H was prepared in 93% yield: pmr (CCl_4) δ 2.22 (s, 3 H, carbinyl methyl), 4.13 (q, 2 H, methylene), 7.34 (m, 5 H, aromatic). **12**-*p*-CF_3 was obtained in 81% yield: pmr (CCl_4) δ 2.31 (s, 3 H, methyl), 4.21 (q, 2 H, methylene), 7.71 (s, 4 H, aromatic).

α-Methylstyrenes. α,*p*-Dimethylstyrene and α-methylstyrene were obtained from Aldrich. *p*-Trifluoromethyl-α-methylstyrene was prepared by the procedure of Bachman and Lewis[33] by de-

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(27) R. T. C. Brownlee and R. W. Taft, *J. Amer. Chem. Soc.*, **92**, 7007 (1970).

(28) E. S. Lewis and C. E. Boozer, *ibid.*, **74**, 6306 (1952); V. J. Shiner, *ibid.*, **75**, 2925 (1953).

(29) Hopefully ESCA spectroscopy, which directly provides binding energies, will find use as well in the study of substituent effects. Recently this technique has been applied to stable carbocation systems. See G. A. Olah, G. D. Mateescu, L. A. Wilson, and M. H. Gross, *J. Amer. Chem. Soc.*, **92**, 7231 (1970). The sensitivity of the technique, however, at this stage of development precludes the study of effect of the magnitude anticipated for hyperconjugation.

(30) H. C. Brown, Y. Okamoto, and G. Ham, *ibid.*, **79**, 1906 (1957).

(31) J. M. Bollinger, M. B. Comisarow, C. A. Cupas, and G. A. Olah, *ibid.*, **89**, 5687 (1967).

(32) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Wiley, New York, N. Y., 1948, p 535.

(33) G. B. Bachman and L. L. Lewis, *J. Amer. Chem. Soc.*, **69**, 2022 (1947).

hydrating 12.4 g of **11**-p-CF_3 alcohol at 150–160° with potassium hydrogen sulfate (yield 8.3 g, 74%): pmr δ 2.12 (d, 3 H), 5.18 (q, 1 H), 5.41 (s, 1 H), 7.56 (s, 4 H).

Preparation of the Ions. Ion **1**-p-OCH_3 was prepared from p-methoxybenzyl alcohol (Aldrich) at −78° by freezing 0.1 g on the wall of a cold test tube containing about 2.0 ml of 30% by volume SbF_5 in SO_2ClF. The frozen alcohol was slowly washed off the wall with the ionizing solvent by careful swirling of the tube while in the cold bath. All other ions reported in this study were prepared by the usual addition of alcohol or chloride in SO_2 or SO_2ClF solution to a solution of acid (SbF_5–SO_2, SbF_5–SO_2ClF, or HSO_3F–SbF_5–SO_2) at −78°.

Nuclear Magnetic Resonance Measurements. Spectra were obtained on Varian A56/60A or HA-100 spectrometers. Fourier transform spectroscopy was carried out on a Bruker HFX-90 spectrometer equipped with a low-temperature probe and broad-band decoupler for irradiating the proton region. The sample was contained in a 15-mm tube with the lock to a coaxially contained 5-mm nmr tube containing ethylidene fluoride for the lock. Fourier transformations were made directly in a PDP-8 computer. Indor spectra were obtained by methods described in detail previously.[9,17c]

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α Effect. V. Kinetic and Thermodynamic Nature of the α Effect for Amine Nucleophiles

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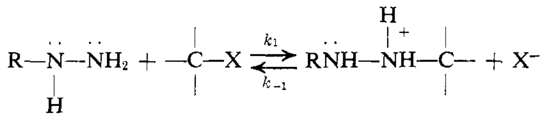
Abstract: The α effect for amine nucleophiles, as expressed by the ratio of $k_{\text{hydrazine}}/k_{\text{glygly}}$, is established to be directly related to the Brønsted β constant for the reaction of amines with 17 substrates of vastly different structure. The origin of the correlation is discussed.

Edwards and Pearson[3] coined the term α effect to describe the unusual reactivity of nucleophiles possessing an unshared pair of electrons α to the nucleophilic atom (eq 1). Several previous papers from this



$$R\text{—}\underset{H}{\underset{|}{\ddot{N}}}\text{—}\ddot{N}H_2 + \text{—}\overset{|}{\underset{|}{C}}\text{—}X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RNH\text{—}\overset{H}{\overset{|+}{\ddot{N}H}}\text{—}\overset{|}{\underset{|}{C}}\text{—} + X^- \quad (1)$$

laboratory[4] and others[5] have shown that the reaction of α-effect nucleophiles (*i.e.*, hydrazine as in eq 1) are associated with larger equilibrium constants (k_1/k_{-1}) than anticipated for nucleophiles of the same pK_a. A number of rationales have been advanced to explain the origin of the enhanced reactivity;[4,6] however, it is quite probable that the α effect is not associated with a single factor, but may well be associated with several factors depending upon the various nucleophiles in question.[7]

The kinetic appearance of the α effect (positive deviation from the Brønsted equation) has been noted to be present with activated phenyl esters,[8] phosphonate esters,[9] and nitriles,[10] and to be absent in the aminolysis of certain other substrates such as methyl iodide[11] and p-nitrophenyl sulfate.[12] It has been noted previously[11,12] that the α effect is associated with reactions exhibiting a large degree of sensitivity to the basicity of the attacking nucleophile. In this study it is established that a direct relationship exists between the Brønsted β constant[13] and the α effect for a series of 17 substrates of widely divergent nature.

Experimental Section

Materials. Hydrazine (City Chemical Co.) and trifluoroethylamine hydrochlorides (Pierce) were recrystallized before use. Glycine (Fisher), n-butylamine (Matheson Coleman and Bell), and glycylglycine (Aldrich) were reagent grade and used without further purification. The 2,4-dinitrofluorobenzene, 2,4-dinitrochlorobenzene, and 2,4-dinitroiodobenzene employed were from a previous study.[4] The 2,4,6-trinitrochlorobenzene (K & K) was obtained as a 20% aqueous solution.

Apparatus. Kinetic measurements were made with a Gilford Model 2000 spectrophotometer equipped with dual thermospacers through which water circulated at 30 ± 0.1°.

The pH of a kinetic solution was determined both prior to and at the completion of the reaction, using a Radiometer Model 22 pH meter with a PHA 630 scale expander, and a combined glass calomel electrode (Radiometer CK 2021 C) thermostated at 30 ± 0.1°. When a drift in pH in excess of 0.03 unit occurred, that kinetic run was discarded.

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