Comparison of Carbon-13 Nuclear Magnetic Resonance Shifts and Relative Charge Delocalization in Para-Substituted Phenyl, Alkyl, and Cyclopropylcarbinyl Cations[1a]

George A. Olah,*[1b] G. K. Surya Prakash, and Gao Liang[1c]

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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A comprehensive series of para-substituted phenyl, alkyl, and cyclopropylcarbinyl cations have been prepared and their ^{13}C NMR spectra studied. The relative charge delocalizing abilities are discussed with regard to the observed ^{13}C NMR shifts. The relative order of positive charge delocalizing ability in the studied ions is found to be phenyl ≈ cyclopropyl ≫ alkyl. The effect of *p*-phenyl substituents was demonstrated by correlating the carbenium center ^{13}C NMR shifts with σ^+ substituent constants. A linear dependence was observed in each series of closely related ions with the exception of the *p*-CF_3 substituent. A similar correlation with σ_R^+ values indicates a linear relationship only in symmetrically substituted ions (with limited dependence on σ_I values). This demonstrates that the cyclopropyl group exhibits a leveling effect depending on the electron demand of the carbenium center and/or steric effects predominate in asymmetrically substituted ions.

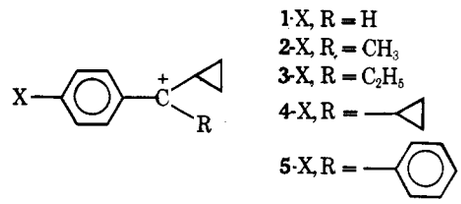
The delocalizing ability of a cyclopropyl group adjacent to a carbocationic center is well documented.[2-4] From our previous studies,[5a] it was concluded that no single uniform sequence of delocalizing ability of neighboring groups such as phenyl and cyclopropyl can be predicted for structurally widely different ions, although among closely related tertiary carbenium ions phenyl and cyclopropyl groups exhibit similar delocalizing ability. The difference, as also seen in a study[5b] on substituted alkenyl cations, between neighboring cyclopropyl and phenyl group is small. Rate enhancements observed in cyclopropyl substituted systems in solvolytic reactions might be caused by conjugative effects and by release of strain in the carbocationic intermediate.

Timberlake, Thomson, and Taft[6] have correlated the ^{19}F NMR chemical shift difference for the *p*-fluoro atom in *p*-fluorophenylcarbenium ions with the calculated positive charge character of the carbenium carbon. Ray, Kurland, and Colter[7] have investigated a comprehensive series of triarylcarbenium ions and shown good correlation of the carbocationic center carbon shifts with σ^+ substituent constants with the calculated charge densities (by the CNDO method). We have reported in our preceding work a study of the relationship between ^{13}C NMR shifts and substituent effect in substituded benzyl cations.[8] A better correlation, however, can be obtained for Colter's data as well as for our previous data with σ_R^+ values (with limited dependence on σ_I values, see subsequent discussion).

In continuation of our studies, we wish to report now the preparation and ^{13}C NMR studies of a series of para-substituted phenyl, alkyl, and cyclopropylcarbinyl cations in superacidic, low nucleophilicity media at low temperatures. The effect of *p*-phenyl substituent is demonstrated by correlating the carbenium center shift with σ^+ substituent constants as well as with the dual substituent parameter (σ_R^+ and σ_I values).

Results

A series of para-substituted phenyl, alkyl and cyclopropylcarbinyl cations were prepared from their corresponding alcohol precursors in FSO_3H/SbF_5 (1:1) or FSO_3H/SO_2ClF solution at −78 °C. The proton decoupled ^{13}C NMR spectra were obtained by the Fourier-transform method. The assignment of shifts was made with now customary methods,[9] including "off-resonance", decoupling experiments. The data are summarized in Table I. Ions 1-H, 2-H, 4-H, 5-H, 2-F, and 4-F listed for comparison have been prepared earlier and their ^{13}C NMR characteristics reported.[2,5a,10]



1-X, R = H
2-X, R = CH_3
3-X, R = C_2H_5
4-X, R =
5-X, R =

X = H, F, Cl, Br, OCH_3, CH_3, C_2H_5, and CF_3

Discussion

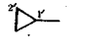
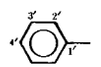
Charge Delocalizing Ability. ^{13}C NMR chemical shifts cannot be quantitatively correlated to charge densities, but they do qualitatively reflect the charge densities at carbons of similar hybridization and substitution.[11]

Despite many uncertainties in the present state of ^{13}C NMR chemical shift theory, there is considerable experimental evidence[7,11,12] indicating that the chemical shifts for carbon atoms of similar hybridization and substitution in hydrocarbon molecules significantly reflect electron densities.[13] As pointed out by Farnum,[14] steric constraints imposed by the substituents can influence the shielding and deshielding of a tertiary cationic center.

Alkyl, cyclopropyl, and phenyl groups stabilize an adjacent carbocationic center by their inductive and/or conjugative effects.[3a,b,15-17] The degree of conjugation between π bonds in phenyl or σ bonds in cyclopropyl rings, respectively, with an adjacent empty p orbital of a carbocationic center depends upon the orientation of these substituents.

Considering the 1-X series of ions where the α substituent is hydrogen (i.e., the parent secondary cations), the phenyl and cyclopropyl groups effectively share the positive charge by their conjugative abilities. The degree of delocalization of the positive charge into the phenyl ring is dependent upon the nature of the para substituent. The carbocationic center is most deshielded for X = H and CF_3, about equally deshielded for X = F, Cl, Br, and CH_3, and most deshielded for X = OCH_3. The stabilizing effect of the *p*-OCH_3 substituent in 1-OCH_3 is reflected by shielding of C_α and C_β carbons of the cyclopropyl group as compared to the parent ion 1-H ($\Delta\delta^{13}C_\alpha$ 14.4 ppm, $\Delta\delta^{13}C_\beta$ 16.0 ppm). An opposite effect is observed with regard to *p*-CF_3 substituent 1-CF_3. The C_α and C_β carbons of the cyclopropyl group are largely deshielded ($\Delta\delta^{13}C_\alpha$ 11.8 ppm, $\Delta\delta^{13}C_\beta$ 11.3 ppm), though the carbenium center shift is comparable to the shift in the parent ion 1-H. One can also see from the cyclopropyl carbon shifts in 1-CH_3 that the *p*-CH_3 substituent is better charge delocalizing than F, Cl, and

Table I. ^{13}C NMR Shifts[a] of Ions from 1-X–5-X Series in FSO_3H/SbF_5 (1:1) in SO_2ClF at −70 or −90 °C

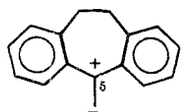
Registry no.	No.	R	X	C^+	C_1	$C_2'C_6$		$C_3'C_5$		C_4		Others			
												C_1'	C_2'		
15810-26-1	1-X	H	H	226.3	137.8	145.2	J_{C-F}	132.2	J_{C-F}	149.0	J_{C-F}	45.1	45.1		
15810-31-8			F	222.2	134.5	141.1	(14.2)	120.7	(23.9)	175.6	(282.6)	43.4	43.0		
						149.0	(14.7)	119.4	(21.7)						
			Cl	223.1	134.6	145.0		132.7		156.8		45.2	45.0		
						137.3		132.0							
15810-33-0			Br	223.6	135.9	144.9		135.9		144.4		45.7	45.3		
						136.7		135.3							
15810-27-2			OCH_3	208.6	132.8	150.4		120.6		179.1		30.7	29.1	OCH_3, 58.30	
						141.4		117.0							
			CH_3	221.6	135.9	145.5		133.4		166.3		40.0	39.2	CH_3, 23.6	
						137.1		132.5							
			CF_3	225.9								54.3	53.8		
												CH_3	C_1'	C_2'	
41912-19-0	2-X	CH_3	H	246.2	139.8	134.8	J_{C-F}	131.2	J_{C-F}	145.5	J_{C-F}	23.4	45.8	45.0	
56519-31-4			F	243.2	136.4	139.1	(12.6)	118.9	(22.5)	173.9	(277.3)	21.6	43.0	41.9	
15876-04-7			Cl	244.8	137.8	135.6		131.4		153.4		21.8	44.7	43.9	
62586-65-6			Br	245.3	137.7	135.0		134.4		143.0		21.7	45.4	44.7	
15810-35-2			OCH_3	227.1	133.5	140.5		117.6		176.7		19.0	32.7	29.5	OCH_3, 57.8
15810-34-1			CH_3	241.9	137.6	135.5		132.1		162.5		20.9	40.2	38.4	CH_3, 22.8
15876-01-4			CH_2CH_3	241.0	137.9	135.7		130.0		168.0		20.9	40.1	38.5	CH_2:30.5, CH_3:13.9
62586-66-7			CF_3	250.0	141.3	133.2		127.0		153.0	(33.5)	23.3	51.8	51.7	CF_3:134.6 (274.0)
												CH_2	CH_3	C_1'	C_2'
62586-67-8	3-X	CH_2CH_3	H	251.6	138.2	134.8	J_{C-F}	131.2	J_{C-F}	145.5	J_{C-F}	28.2	18.3	43.5	43.5
62586-68-9			F	247.8	135.3	139.6	(12.9)	119.4	(22.1)	174.1	(277.7)	28.3	18.5	41.8	41.8
62586-69-0			Cl	249.4	136.3	135.7		131.3		152.1		28.3	18.3	44.6	44.6
62586-70-3			Br	250.6	136.6	135.2		134.7		143.7		28.1	18.2	44.0	44.0
62586-71-4			OCH_3	231.0	132.3	140.9		117.9		176.8		25.4	18.7	31.0	31.0 OCH_3, 57.9
62586-72-5			CH_3	246.1	136.1	135.8		132.3		162.5		27.3	18.7	38.8	38.3 CH_3:22.7
62586-73-6			CH_2CH_3	246.3	136.8	134.4		131.2		168.5		26.6	18.7	38.7	38.1
												30.6	13.8 (ring)		
62586-74-7			CF_3	254.8	140.1	133.3		127.3		152.1	(J_{C-C-F}, 68.1)	29.4	17.2	56.8	51.9
														CF_3:134.2(251.9)	
												C_1'	C_2'		
41912-21-4	4-X		H	261.0	135.3	129.6	J_{C-F}	128.0	J_{C-F}	136.5	J_{C-F}	42.7	37.0		
56531-75-0			F	258.0	132.2	132.3	(10.9)	117.3	(22.9)	168.0	(262.0)	39.9	34.9		
62586-75-8			Cl	259.8	133.5	129.8		129.8		143.1		41.3	36.1		
62586-76-9			Br	260.0	131.6	132.9		129.5		133.5		41.5	36.3		
62586-77-0			OCH_3	248.7	132.0	135.3		115.9		169.6		34.8	30.1	OCH_3, 57.1	
41912-27-0			CH_3	257.0	134.1	130.5		130.1		151.4		38.0	32.9	CH_3, 21.4	
62586-78-1			CF_3	264.6	139.8	127.9		126.3		132.8	(38.7)	47.3	38.9	CF_3;134.2(272.2)	
												C_1'	C_2'		
38252-94-7	5-X		H	235.0	141.9	139.0		131.4		150.2		40.9	35.9		
					137.3	134.7		129.9	J_{C-F}	145.2	J_{C-F}				
62586-79-2			F	232.5				119.0	(19.4)	176.9	(282.1)	39.8	34.9		
41912-39-4			Cl	233.4						145.5		40.4	35.7		
62586-80-5			Br	233.5						148.0		40.7	36.0		
62586-81-6			OCH_3	219.8	136.3	130.9		117.9		177.6		31.4	27.1	OCH_3, 58.1	
				1′ 134.4	2′ 129.6	3′ 116.5		4′ 144.0							
41912-35-0			CH_3	231.5	138.5	133.7		131.9		163.8		37.3	32.4	CH_3, 22.7	
				1′ 13.7	2′ 131.1	3′ 129.4				4′ 139.7					
62586-82-7			CH_2CH_3	231.4						175.5		37.2	32.0	CH_2:30.4,CH_3:14.1	
62586-83-8			CF_3	235.3								43.9	42.1		

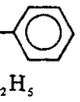
[a] Shifts from external capillary Me_4Si in parts per million.

Br substituents, which is, however, not indicated in the carbenium center shift. The comparative ability of cyclopropyl and phenyl groups to delocalize charge is thus affected to a significant degree by the nature of the para substituents. It is rather difficult to decide exactly the relative charge delocalizing ability based on the study of 1-X series alone. Comparing ions 2-X to 5-X a pronounced para-substituent effect is seen in each series of related ions. In the case of electron-releasing substituents such as $-OCH_3$ (and to a lesser degree $-CH_3$, $-C_2H_5$) substantial charge is dispersed into the phenyl ring, as evidenced by the significant shielding pattern of the α and β carbons of the cyclopropyl group and also by the large shielding of the carbenium center with regard to the parent, i.e., para hydrogen substituted ion. An opposite effect is observed for an electron-withdrawing substituent such as $-CF_3$, although the carbenium center is less deshielded as compared to the parent ion.

In the 1-X series where X = F, Cl, Br, CH_3, H, and CF_3, the difference between $\delta^{13}C_2$ and $\delta^{13}C_6$ ($\delta^{13}C_3$ and $\delta^{13}C_5$) is caused by the differing H and c-C_3H_5 neighbors and should, therefore, be constant. This is found in all cases except X = H. The similar behavior in the latter case, therefore, reflects the lower rotational barrior of the phenyl ring (i.e., H substituent less stabilizing). The case X = OCH_3 must be excluded from these considerations, since the difference between $\delta^{13}C_2$ and $\delta^{13}C_6$ is increased or decreased by the different conformations of the $-OCH_3$ group. In all other series where R $\neq$ H one finds that C_2, C_6 and C_3, C_5 carbons are equivalent. This is reasonable, since the barrier of the phenyl rotation should be lowered due to two reasons: (a) steric repulsions in the planar conformation; (b) decreased interaction between the carbenium center and the phenyl ring due to smaller positive charge on the carbenium center.

Comparing the 2-X to 5-X series of ions with the 1-X series (involving ions with the same para substituents) the carbenium center shows the following deshielding: 2-X $\simeq \Delta\delta^{13}C^+ \approx$20–25 ppm; 3-X, $\Delta\delta^{13}C^+ \approx$25–30 ppm; 4-X, $\Delta\delta^{13}C^+ \approx$35–40 ppm; and 5-X, $\Delta\delta^{13}C^+$ 10 ppm. The explanation for these results can be found in the relative α-substituent deshielding effects. Similar effects were found for dibenzocycloheptadienyl cations,[18] where it was shown that the α-substituent effect of a methyl, ethyl, or cyclopropyl group at the carbenium center causes deshielding by about 22–25 ppm relative to hydrogen, while a phenyl group causes deshielding by about 10 ppm. Results of ions of series 2-X, 3-X, and 5-X are in complete agreement with these observations, whereas the ions of series 4-X show an additional deshielding of the carbenium centers by about 10 ppm. This was attributed in our earlier work[5b] to an unusual neighboring group deshielding effect by the cyclopropyl group adjacent to a carbenium center.



6a, $\delta_{C_5}{}^{13}$ 195.6, R = H
6b, $\delta_{C_5}{}^{13}$ 218.3, R = CH_3
6c, $\delta_{C_5}{}^{13}$ 217.0, R = 
6d, $\delta_{C_5}{}^{13}$ 205.1, R = 
6e, $\delta_{C_5}{}^{13}$ 221.2, R = C_2H_5

Replacement of the $-CH_3$ and $-C_2H_5$ groups in the 2-X and 3-X series of ions by a cyclopropyl group (i.e., a transition to the 4-X series) brings about a deshielding of the carbenium center by 15–17 and 10–11 ppm, respectively, which can be largely attributed to the neighboring group deshielding effect[5b] by the additional cyclopropyl group. A decrease in conjugation of the phenyl ring with the carbocationic center is also evident from the shielding trend observed for the ortho- and para-carbon shifts (3.5–4.5 ppm for ortho carbons, 8–9 ppm for para-carbon shifts). Interestingly, C_α and C_β of the cyclopropyl group are also shielded. This may be due to sharing of the positive charge by two cyclopropyl groups rather than by one as evident from the magnetic equivalence of the cyclopropyl groups. The extent of charge delocalization in the phenyl ring is decreased considerably by the replacement of $-CH_3$ and $-C_2H_5$ groups at the carbenium center by a cyclopropyl group. In similar replacement of $-CH_3$ and $-C_2H_5$ groups in 2-X and 3-X series of ions by a phenyl group (transition to the 5-X series) the charge distribution in the cyclopropyl group is altered as seen by the shielding of the α and β carbons of the cyclopropyl group (2-X to 5-X $\Delta\delta^{13}C_\alpha \approx$3–5 ppm, $\Delta\delta^{13}C_\beta$ 4–6 ppm; 3-X to 5-X $\Delta\delta^{13}C_\alpha$ 2.5–4, $\Delta\delta^{13}C_\beta$ 5–7 ppm). Such direct comparison shown can often be misleading as change from the 2-X and 5-X series of ions to the 4-X series causes steric factors to favor the bisected conformation for the cyclopropyl groups which effectively interact with the neighboring carbenium center. However, in the 5-X series the two phenyl rings bump into each other due to steric hindrance and hence the coplanarity of the two phenyl rings with the empty p orbital of the carbenium center is not possible, resulting in decreased delocalization of the charge. However, comparison of the 2-X and 5-X series with the 4-X and 5-X series shows that both phenyl and cyclopropyl groups are much better in their ability to delocalize the positive charge than the $-CH_3$ and $-C_2H_5$ groups. Steric factors seem to be of major importance in competitive charge delocalization in tertiary carbenium ions by phenyl and cyclopropyl groups. σ electrons of saturated bonds (i.e., C–H in methyl, C–C in ethyl, and bent C–C cyclopropyl) delocalize charge from adjacent carbenium center through σ–p conjugation to various degrees. This ability is weaker for C–H bonds than for C–C bonds (C–H hyperconjugation is less significant than C–C hyperconjugation). The bent σ bond of cyclopropyl can delocalize charge effectively if the cyclopropyl group adapts a bisected conformation with the carbenium center.[19] Delocalization of charge into the phenyl ring is favored because of the large conjugated π system involved, but the phenyl group is more sensitive to steric effects than the cyclopropyl group.

Considering ions in series 4-X and 5-X the para carbons are substantially deshielded in the latter series as compared to the former, whereas the α and β carbons are not correspondingly shielded. The shift difference between the α and β carbon shifts remains around $\Delta\delta^{13}C_{\alpha-\beta}$ 4.5–5.5 ppm in both series. This may be due to the fact that in the 4-X series of ions the positive charge is delocalized into two magnetically equivalent cyclopropyl groups and hence direct comparison between 4-X and 5-X is not possible. Substitution of a cyclopropyl by a phenyl group brings about insignificant changes in the α and β carbon shifts of the cyclopropyl group, whereas substitution of phenyl by cyclopropyl brings about significant shielding of the ortho and para carbons of the phenyl ring (one can also argue it the other way based on the ortho- and para-carbon deshielding in the 5-X series). Hence, from the presently studied series of ions one can conclude that the phenyl and cyclopropyl group have comparable delocalizing abilities. However, in tertiary carbenium ions (like the ones we studied) steric constraint can play a major role in deciding their de facto relative delocalizing abilities.

It is difficult to divide the total effect of substituents at carbenium centers into the corresponding inductive and conjugative components. When one attempts to directly compare cyclopropyl and phenyl groups, steric effects are more significant for phenyl substituents than for cyclopropyl substituents. When conjugation between the phenyl group and the empty 2p orbital of the carbenium center is possible,

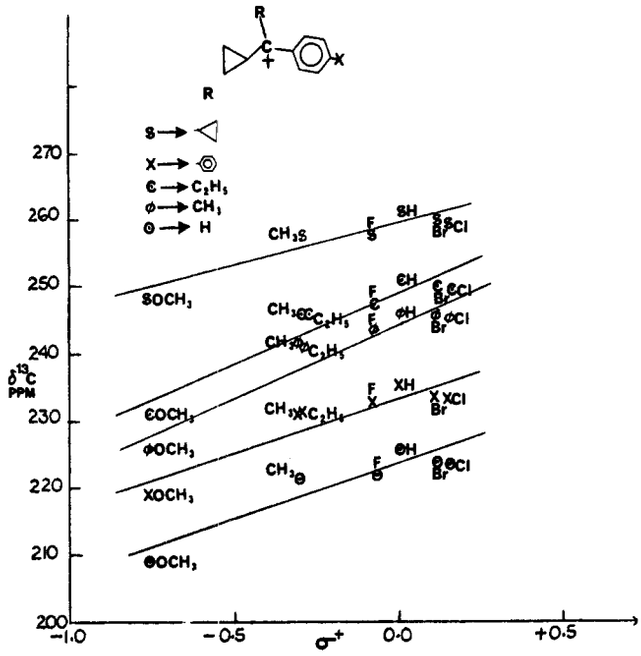


Figure 1. A plot of carbenium center shifts of ions from 1-X to 5-X series vs. σ^+ substituent constants.

positive charge is nearly equally distributed among the ortho and para carbons of the phenyl ring. However, ortho shifts are easily affected by the steric effects of the substituents.[19] Para shifts which are not similarly affected can be more safely employed as reliable indicators for the extent of charge delocalization. The β-carbon shifts of the cyclopropyl rings can also be used as an indicator of charge delocalization into these rings in cyclopropylcarbenium ions, although obviously our present understanding of charge effects on overall chemical shifts and in particular that of cyclopropyl rings is still inadequate.[20]

The neighboring group deshielding effect of the cyclopropyl group is not observed in neutral compounds;[5b] hence the effect should be strongly dependent upon the orientation of the cyclopropyl group, since it is apparently only observed concurrent with conjugative electron donation and dependent on the total charge at the carbenium center which is being stabilized. This was not fully realized in the earlier studies on tertiary carbocations. Since no strict additivity of neighboring group (or substituent effects) can be assumed it is difficult to obtain a quantitative comparison concerning the relative delocalizing abilities of phenyl vs. cyclopropyl groups. However, in the presently studied systems, we observe the relative positive charge delocalizing ability order to be phenyl ≈ cyclopropyl ≫ alkyl, though the trend may vary depending upon the system under consideration.

Para-Substituent Effects. As discussed earlier, charge densities can be well correlated to ^{13}C NMR shifts in closely related systems having similar geometry and hybridization.[11] Brown and his co-workers[21] have demonstrated by carrying out solvolytic studies on several para- and meta-substituted benzylic systems that a Hammett-type relationship is generally observed. They expressed the effect of aromatic ring substituents by the σ^+ substituent constants which correlated well with the relative rates of solvolysis of these systems. Brown's σ^+ relationship reflects the ability of a particular aromatic substituent to lower or increase the energy of the intermediate benzylic cation relative to the parent unsubstituted ion by inductive and resonance effects.[22] ^{13}C NMR chemical shifts of the carbocationic center of several types of benzyl cations have been reasonably correlated with Brown's σ^+ values.[7,8]

Table II. Slopes and Correlation Coefficients for the Plot of Carbenium Center ^{13}C NMR Shifts vs. σ^+ Values for the Series of Ions 1-X–5-X (Excluding Ions with p-CF_3 Group)

Series	$\Delta\sigma^+/\Delta^{13}C^+$	Corr coeff
1-X	0.06033	0.9102
2-X	0.05186	0.9338
3-X	0.04878	0.9329
4-X	0.07944	0.9568
5-X	0.06849	0.9090

Reynolds and co-workers[23] from an all-valence molecular orbital calculation on 4-substituted phenylacetylenes and styrenes have shown that the effect of para substituents on ^{13}C NMR shifts mainly arises from π-electron delocalization effects rather than π-inductive effects. Similar studies extended to ^1H and ^{19}F shifts have been recently reviewed by Hehre, Taft, and Topsom.[24] σ^+ values do not reflect such composition. Hence in Colter's study on trityl cations, the shifts are fitted to σ^+ values with a standard deviation (SD) of 7.2 ppm. On the other hand, these data are fitted rather satisfactorily (SD 1.6 ppm) by σ_R^+ parameters (with a very minor dependence on σ_I parameters).[25] Our previously reported data on substituted cumyl cations are also fitted better by this approach than by correlation with σ^+ values (Table III).

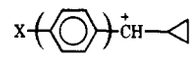
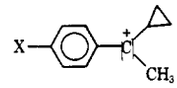
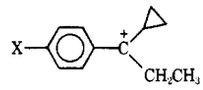
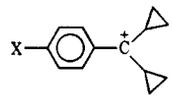
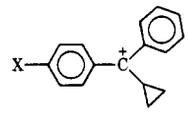
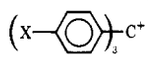
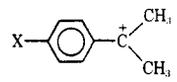
Applying this approach[25,26] to our data on series of ions 1-X to 5-X a satisfactory fit is observed only for the 3-X series which are symmetrically substituted ions (f = SD/rms = 0.105). The other asymmetrically substituted ions fail to give a reasonable fit (see Table III). In the case of similar correlation of the ^{13}C NMR shifts of the carbenium center with σ^+ values for the series of ions 1-X to 5-X (Figure 1, Table II), a reasonable linearity is apparent only if one excludes the p-CF_3 substituted ions. The best correlation is obtained for the 3-X series which are symmetrical. These observations are, however, not unexpected in view of the fact that the cyclopropyl group tends to share the charge developed on the carbenium center (as indicated by the deshielding of the C_α and C_β carbons of the cyclopropyl group in Table I).

There is a leveling effect exhibited by the adjacent cyclopropyl group in stabilizing the carbenium center depending upon the nature of the para substituent on the phenyl ring. The effect of cyclopropyl group is enhanced in the case of electron-withdrawing substituents (of which the strongest studied is the p-CF_3 group). One can also conclude from the trend in the correlation coefficients that the correlation should be better as more charge has to be stabilized on the carbenium center. Tables II and III therefore suggest that H is stabilizing the charge less than CH_3 and C_2H_5, while the cyclopropyl group is stabilizing best and the phenyl group is less stabilizing, which is largely due to a steric effect. This raises the question whether an additional phenyl group in the system has any stabilizing effect. It has already been demonstrated by Taft, Hehre, et al.[27] that a substantial reversal is noted in the relative stabilizing ability of the phenyl and cyclopropyl groups going from primary to tertiary carbocations. The deviation in slopes can be attributed to the steric constraints imposed by the α-substituent groups as well as their respective inductive and delocalizing abilities.

Conclusions

Alkyl, cyclopropyl, and phenyl are different kinds of neighboring groups capable of charge delocalization from a neighboring carbocationic center by different interactions (σ–p, bent σ–p, and π–p, respectively). Phenyl and cyclopropyl groups show comparable ability to delocalize the positive

Table III. Dual Substituent Parameter Analysis[a] of Carbenium Carbon ^{13}C NMR Shifts vs. p-Phenyl Substituent Effects

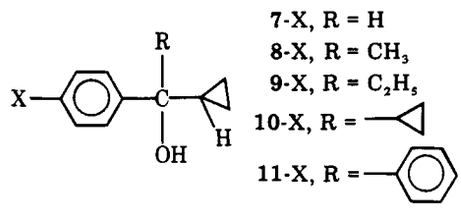
Series	Ions	ρ_I	ρ_R	$\lambda = \rho_R/\rho_I$	SD	f^d = SD/rms
1-X		0.5	−7.8	−16.5	1.2	0.277
2-X		−6.3	−11.0	1.8	0.6	0.129
3-X		−10.1	−20.5	2.0	2.0	0.223
4-X		−7.4	−13.5	1.8	0.6	0.105
5-X		−4.7	−13.7	2.9	2.2	0.337
6-X[b]		−1.5	−19.4	12.7	1.6	0.096
7-X[c]		−26.1	−41.1	1.6	1.9	0.105

[a] The results were compiled and kindly commented on by Professor R. W. Taft. [b] Based on data from ref 7. X = $N(CH_3)_2$, OCH_3, CH_3, F, Cl, NO_2. [c] Based on data from ref 8. X = OCH_3, CH_3, F, Br, CF_3. [d] $f \leq 0.1$ acceptable correlation: ref 25.

charge in the studied system; however, steric interactions are more severe for a phenyl group than for a cyclopropyl group, which was observed in the 5-X series of ions. The relative ability to delocalize positive charge is determined by the series of substituent effects, steric constraints, and the nature of the system under consideration.

Experimental Section

Precursor alcohols were either commercially available or prepared by the standard Grignard reactions on the corresponding ketones. p-Trifluoromethylphenyl cyclopropyl ketone (12) was prepared by the reaction of p-trifluoromethylphenylmagnesium bromide with cyclopropyl cyanide. The secondary alcohol 7-CF_3 was prepared by the borohydride reduction of the ketone 12. The physical constants and ^1H NMR data of newly synthesized alcohols are the following:



X = H, F, Cl, Br, OCH_3, CH_3, C_2H_5, and CF_3

p-Trifluoromethylphenyl Cyclopropyl Ketone (12): bp 72 °C (0.5 mm); ^1H NMR ($CDCl_3$) δ 9.1–8.2 (AB quartet, 4 H, aromatic), 3.45–3.15 (m, 1 H, CH of Cpr), and 2.0–1.6 (m, 4 H, CH_2 of Cpr).

α-Cyclopropyl-p-trifluoromethylbenzyl Alcohol (7-CF_3): bp 74 °C (0.4 mm); ^1H NMR ($CDCl_3$) δ 8.3 (singlet, 4 H, aromatic), 4.9 (doublet, 1 H, J_{CH} = 8 Hz, >CH–), 3.2 (s, 1 H, –OH), 2.1–1.5 (m, 1 H, CH of Cpr), 1.5–1.1 (m, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-methyl-p-chlorobenzyl Alcohol (8-Cl): bp 131–132 °C (13 mm); ^1H NMR ($CDCl_3$) δ 7.4–7.9 (AB quartet, 4 H, aromatic), 2.1 (broad singlet, 1 H, OH), 1.9 (s, 3 H, CH_3), 1.3–1.5 (m, 1 H, CH of Cpr), and 0.6–1.0 (m, 4H, CH_2 of cyclopropyl).

α-Cyclopropyl-α-methyl-p-bromobenzyl Alcohol (8-Br): bp 142—143 °C (13 mm); ^1H NMR ($CDCl_3$) δ 7.7 (s, 4 H; aromatic), 1.8 (s, 4 H, OH and CH_3), 1.5–1.6 (m, 1 H, CH of Cpr), and 0.6–0.8 (m, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-methyl-p-methoxybenzyl Alcohol (8-CH_3O): bp 142 °C (13 mm); ^1H NMR ($CDCl_3$) δ 7.0–7.8 (AB quartet, 4 H, aromatic), 4.2 (s, 3 H, CH_3O), 1.9 (s, 1 H, OH), 1.7 (s, 3 H, CH_3), 1.2–1.6 (m, 1 H, CH of Cpr), and 0.6–0.9 (m, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-methyl-p-ethylbenzyl Alcohol (8-C_2H_5): bp 140 °C (12 mm); ^1H NMR ($CDCl_3$) δ 7.3–7.9 (AB quartet, 4 H, aromatic), 2.6–3.0 (q, 2 H, CH_2), 2.9 (s, 1 H, OH), 1.8 (s, 3 H, CH_3), 1.3–1.7 (t, 3H, CH_3), 1.2–1.3 (b, 1 H, CH of Cpr), and 0.5–0.8 (m, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-methyl-p-trifluoromethylbenzyl Alcohol (8-CF_3): bp 147 °C (11.0 mm); ^1H NMR ($CDCl_3$) δ 8.0 (s, 4 H, aromatic), 2.3 (s, 1 H, –OH), 1.8 (s, 3 H, CH_3), 1.7–1.3 (m, 1 H, CH of Cpr), 1.0–0.7 (m, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-ethyl-p-fluorobenzyl Alcohol (9-F): bp 58 °C (0.1 mm); ^1H NMR ($CDCl_3$) δ 7.1–7.9 (m, 4 H, aromatic), 2.7 (s, 1 H, OH), 1.9–2.2 (q, 2 H, CH_2), 1.3–1.7 (m, 1 H, CH of Cpr), 0.9–1.3 (t, 3 H, CH_3), and 0.5–0.9 (b, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-ethyl-p-chlorobenzyl Alcohol (9-Cl): bp 62–64 °C (0.1 mm); ^1H NMR ($CDCl_3$) δ 7.5–7.9 (b, 4 H, aromatic), 2.5 (s, 1 H, OH), 1.9–2.4 (q, 2 H, CH_2), 1.4–1.7 (b, 1 H, CH of Cpr), 0.9–1.3 (t, 3 H, CH_3), and 0.6–0.9 (b, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-ethyl-p-bromobenzyl Alcohol (9-Br): bp 74–76 °C (0.1 mm); ^1H NMR ($CDCl_3$) δ 7.5–7.8 (b, 4 H, aromatic), 2.4 (s, 1 H, OH), 1.9–2.4 (q, 2 H, CH_2), 1.3–1.6 (b, 1 H, CH of Cpr), 0.9–1.2 (t, 3 H, CH_3), and 0.4–0.8 (b, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-ethyl-p-methoxybenzyl Alcohol (9-CH_3O): bp 69–71 °C (0.1 mm); ^1H NMR ($CDCl_3$) δ 7.0–7.8 (AB quartet, 4 H, aromatic), 3.9 (s, 3 H, CH_3O), 1.9–2.4 (m, 3 H, OH and CH_2), 0.9–1.5 (m, 4 H, CH of Cpr and CH_3), and 0.6–0.9 (m, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-ethyl-p-methylbenzyl Alcohol (9-CH_3): bp 68–70 °C (0.15 mm); ^1H NMR ($CDCl_3$) δ 7.3–7.8 (AB quartet, 4 H, aromatic), 2.6 (s, 3 H, CH_3), 2.0–2.3 (m, 3 H, OH and CH_2), 1.3–1.5 (b, 1 H, CH of Cpr), 0.9–1.4 (t, 3 H, CH_3), and 0.5–0.9 (m, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-ethyl-p-ethylbenzyl Alcohol (9-C_2H_5): bp 74 °C (0.15 mm); ^1H NMR ($CDCl_3$) δ 7.4–7.9 (AB quartet, 4 H, aromatic), 2.7–3.1 (q, 2 H, benzylic CH_2), 2.5 (s, 1 H, OH), 2.0–2.4 (q, 2 H, CH_2), 1.4–1.7 (m, 4 H, CH of Cpr and CH_3 attached to benzylic CH_2), 0.9–1.1 (t, 3 H, CH_3), and 0.5–0.9 (m, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-ethylbenzyl Alcohol (9-H): bp 57 °C (0.1 mm); ^1H NMR ($CDCl_3$) δ 7.1–7.8 (b, 5 H, aromatic), 2.2 (s, 1 H, OH), 1.8–2.2 (q, 2 H, CH_2), 1.2–1.6 (b, 1 H, CH of Cpr), 0.8–1.2 (t, 3 H, CH_3), and 0.4–0.8 (b, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-ethyl-p-trifluoromethylbenzyl Alcohol (9-CF_3): bp 145 °C (8.0 mm); ^1H NMR ($CDCl_3$) δ 8.3 (s, 4 H, aromatic), 2.6 (q, 2 H, CH_2 of ethyl), 2.3 (s, 1 H, –OH), 2.1–1.8 (m, 1 H, CH of Cpr), 1.7 (t, 3 H, CH_3 of ethyl), 1.4–1.0 (m, 4 H, CH_2 of Cpr).

α,α-Dicyclopropyl-p-fluorobenzyl Alcohol (10-F): bp 100–101 °C (0.15 mm); ^1H NMR ($CDCl_3$) δ 7.2–8.2 (m, 4 H, aromatic), 2.5 (s, 1 H, OH), 1.5–1.9 (m, 2 H, CH of Cpr) and 0.7–1.0 (b, 8 H, CH_2 of Cpr).

α,α-Dicyclopropyl-p-chlorobenzyl Alcohol (10-Cl): bp 104–105 °C (0.15 mm); ^{1}H NMR ($CDCl_3$) δ 7.6–8.1 (AB quartet, 4 H, aromatic), 2.8 (s, 1 H, OH), 1.5–1.8 (m, 2 H, CH of Cpr), and 0.6–1.1 (b, 8 H, CH_2 of Cpr).

α,α-Dicyclopropyl-p-bromobenzyl Alcohol (10-Br): bp 110–112 °C (0.1 mm); ^{1}H NMR ($CDCl_3$) δ 7.8–8.0 (s, 4 H, aromatic), 2.7 (b, 1 H, OH), 1.4–1.8 (m, 2 H, CH of Cpr) and 0.6–1.1 (b, 8 H, CH_2 of Cpr).

α,α-Dicyclopropyl-p-methoxybenzyl Alcohol (10-CH_3O): bp 114–115 °C (0.15 mm); ^{1}H NMR ($CDCl_3$) δ 7.1–7.9 (AB quartet, 4 H, aromatic), 4.1 (s, 3 H, OCH_3), 2.3 (b, 1 H, OH), 1.4–1.7 (m, 2 H, CH of Cpr), and 0.6–1.0 (m, 8 H, CH_2 of Cpr).

α,α-Dicyclopropyl-p-trifluoromethylbenzyl Alcohol (10-CF_3): bp 74 °C (0.1 mm); ^{1}H NMR ($CDCl_3$) δ 8.3 (s, 4 H, aromatic), 2.4 (s, 1 H, -OH), 2.2–1.5 (m, 2 H, CH of cyclopropyls), 1.4–1.0 (m, 8 H, CH_2 of cyclopropyls).

α-Cyclopropyl-α-phenyl-p-fluorobenzyl Alcohol (11-F): bp 142–143 °C (0.1 mm); ^{1}H NMR ($CDCl_3$) δ 6.9–7.6 (m, 9 H, aromatic), 2.0 (s, 1 H, OH), 1.4–1.6 (b, 1 H, CH of Cpr), and 0.4–0.6 (m, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-phenyl-p-chlorobenzyl Alcohol (11-Cl): bp 149–151 °C; ^{1}H NMR ($CDCl_3$) δ 7.3–7.8 (b, 9 H, aromatic), 2.5 (s, 1 H, OH), 1.5–1.8 (b, 1 H, CH of Cpr), and 0.5–0.9 (b, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-phenyl-p-bromobenzyl Alcohol (11-Br): bp 159–160 °C (0.15 mm); ^{1}H NMR ($CDCl_3$) δ 7.1–7.6 (b, 9 H, aromatic) 2.0 (s, 1 H, OH), 1.1–1.4 (b, 1 H, CH of Cpr) and 0.4–0.6 (b, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-phenyl-p-methoxybenzyl Alcohol (11-CH_3O): bp 156 °C (0.1 mm); ^{1}H NMR ($CDCl_3$) δ 6.8–7.6 (m, 9 H, aromatic), 3.7 (s, 3 H, CH_3O), 2.2 (s, 1 H, OH), 0.9–1.3 (b, 1 H, CH of Cpr), and 0.4–0.6 (b, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-phenyl-p-methylbenzyl Alcohol (11-CH_3): bp 148–150 °C (0.10 mm); ^{1}H NMR ($CDCl_3$) δ 7.2–7.6 (m, 9 H, aromatic), 2.3 (s, 4 H, OH and CH_3), 1.7–2.1 (b, 1 H, CH of Cpr), and 0.5–0.7 (b, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-phenyl-p-ethylbenzyl Alcohol (11-C_2H_5): bp 156–158 °C (0.15 mm); ^{1}H NMR ($CDCl_3$) δ 7.1–7.6 (b, 9 H, aromatic), 2.4–2.7 (q, 2 H, CH_2), 2.0 (s, 1 H, OH), 1.1–1.6 (m, 4 H, CH of Cpr and CH_3), and 0.5–0.7 (b, 4 H, CH_2 of Cpr).

α-Cyclopropyl-α-phenyl-p-trifluoromethylbenzyl Alcohol (11-CF_3): bp 127 °C (0.4 mm); ^{1}H NMR ($CDCl_3$) δ 8.3–7.8 (m, 9 H, aromatic), 2.8 (s, 1 H, -OH), 2.5–2.2 (m, 1 H, CH of Cpr), 1.6–1.2 (m, 4 H, CH_2 of Cpr).

Preparation of Carbocations. Freshly distilled FSO_3H or FSO_3H/SbF_5 (1:1) was dissolved in about twofold amount of SO_2ClF at dry ice–acetone temperature (ca. −78 °C). To this was slowly added with vigorous stirring a cooled solution of the appropriate precursor dissolved in SO_2ClF, to give an approximately 15–20% solution of the ion.

Proton Magnetic Resonance Spectra. ^{1}H NMR spectra were obtained on a Varian Associates Model A56/60A spectrometer. External (capillary) Me_4Si was used as the reference for the precursor alcohols.

Carbon-13 Magnetic Resonance Spectra. The spectrometer used was a Varian Associates Model XL-100 equipped with a broad band decoupler and variable temperature probe. The instrument and techniques used are described in ref 24. Chemical shifts were measured from external (capillary) Me_4Si.

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Registry No.—7-CF_3, 62586-84-9; 8-Cl, 62586-85-0; 8-Br, 56041-75-9; 8-CH_3O, 62586-86-1; 8-C_2H_5, 62586-87-2; 8-CF_3, 61971-67-3; 9-F, 62586-88-3; 9-Cl, 62586-89-4; 9-Br, 62586-90-7; 9-CH_3O, 62586-91-8; 9-CH_3, 62586-92-9; 9-C_2H_5, 62586-93-0; 9-H, 62586-94-1; 9-CF_3, 62586-95-2; 10-F, 62586-96-3; 10-Cl, 62586-97-4; 10-Br, 62586-98-5; 10-CH_3O, 62586-99-6; 10-CF_3, 62587-00-2; 11-F, 62587-01-3; 11-Cl, 62609-09-0; 11-Br, 62587-02-4; 11-CH_3O, 62587-03-5; 11-CH_3, 62587-04-6; 11-C_2H_5, 62587-05-7; 11-CF_3, 62587-06-8; 12, 62587-07-9; p-trifluoromethylphenyl bromide, 402-43-7; cyclopropyl cyanide, 5500-21-0.

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