forms C_7, *S*; C_{14}, *S*; N_1, *R*; N_4, *S*; N_8, *R*; and N_{11}, *S*.[10]

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[10] The financial support of the National Science Foundation is gratefully acknowledged.

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Stable Carbocations. CLX.[1] The Relative Order of Charge Delocalization by Phenyl, Cyclopropyl, and Methyl Groups in Carbenium Ions Based on ^{13}C Nuclear Magnetic Resonance Studies

Sir:

In our continued study of carbocation intermediates we reported, on the basis of the ^{13}C chemical shifts of the carbenium ion centers in the phenyldimethylcarbenium ion, the cyclopropyldimethylcarbenium ion, and the trimethylcarbenium ion, that the relative effectiveness of the phenyl, methyl, and cyclopropyl groups to delocalize charge shows the order[2] $C_6H_5 >$ c-$C_3H_5 > CH_3$. Brown and Peters[3] took exception with our conclusion and suggested that ^{13}C nmr shifts of carbocations do not correlate with "stabilities of solvolytic transition states and the corresponding cationic intermediates." They based their contention mainly on the fact that our observed order of deshielding of chemical shifts in ions $R(CH_3)_2C^+$ (where R = C_6H_5, c-C_3H_5, and CH_3) is different from the rate order c-$C_3H_5 > C_6H_5 > CH_3$ observed in their solvolytic rate studies, as well as the stabilities of these ions deduced from equilibrium studies of the ions and their related alcohol (or olefin) precursors.

We now present extensive additional experimental evidence to show, based on ^{13}C nmr data, the trend in delocalization in related phenyl-, cyclopropyl-, and methyl-substituted ions is consistently indicated in our preceding studies. Brown and Peters[3] further did not consider the difference between spectroscopic (nmr) structural studies of carbocations which measure directly properties of the ions and conclusions based on kinetic and equilibrium data which relate only the relative stabilities, *i.e.*, energy differences between covalent precursors and carbenium ion like transition states and intermediates, respectively (in the involved tertiary systems).

Using methods developed in our laboratories the complete ^{13}C nmr spectra of several related series of phenyl-, cyclopropyl-, and methylcarbenium ions were obtained using fast Fourier transform nmr spectroscopy. Data are tabulated in Table I. ^{13}C chemical shifts cannot be directly equated with, although they obviously do reflect, the charge densities at carbons of similar hybridization and substitution.[4] The shielding constant (σ) for a particular atom is generally assumed to be composed of a paramagnetic term (σ_p) reflecting charge polarization, variation in bond order, and average excitation energy, a diamagnetic term (σ_d), and a term reflecting neighboring group effects ($\sigma' = \sigma - (\sigma_p + \sigma_d)$). The latter two terms for carbon-13 are considered to be much less significant than the paramagnetic term.[5] The chemical-shift differences between the carbenium centers of closely related ions (*i.e.*, comparing related secondary or tertiary systems) in Table I are too large to be accounted for solely by changes in σ_d and σ' terms. The differences in the carbon shifts on substituents in comparable ions, however, are much smaller, and may only reflect changes in the σ_d and σ' terms rather than different electron densities.[6] The ^{13}C chemical shifts of the carbenium centers in closely related series of carbocations thus clearly indicate the trend of charge delocalization by neighboring methyl, phenyl, and cyclopropyl groups.

In all systems studied the trend is that phenyl delocalizes charge from neighboring carbenium centers more than cyclopropyl, which in turn is much more effective than methyl. We feel that this order is, indeed, the expected one considering the nature of charge delocalization by these neighboring groups. The π-electron system of a phenyl group, when not hindered by steric effects, can conjugatively (*i.e.*, *via* p–π interaction) delocalize charge more effectively than hyperconjugation with the bent σ C–C bonds of the cyclopropane system, which in turn is more effective than C–H bond hyperconjugation by the methyl group.

We further feel, in contrast to Brown and Peters,[3] that there is no discrepancy at all with data of solvolytic rates and other observations, such as Deno's study of equilibrium constants of the related ions and their alcohol or olefin precursors in acid media.[8]

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[1] Part CLIX: G. A. Olah, G. Liang, P. W. Westerman, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, in press.

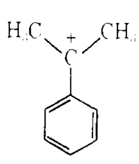
[2] G. A. Olah, R. D. Porter, and D. P. Kelly, *J. Amer. Chem. Soc.*, **93**, 464 (1971).

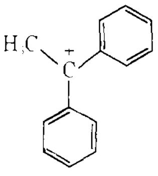
[3] H. C. Brown and E. N. Peters, *J. Amer. Chem. Soc.*, **95**, 2400 (1973). We thank Professor Brown for a copy of his manuscript prior to publication.

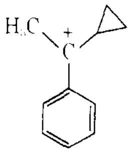
[4] H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, **468** (1961).

[5] M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

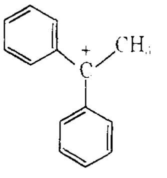
[6] In simple monosubstituted benzenes particular success has been achieved in correlating para carbon shifts with calculated charge densities.[7] Professor H. C. Brown, refereeing our communication, has noted *inter alia* that the para carbon shifts in the following ions seem to suggest that the ability of the cyclopropyl ring to delocalize charge is greater than the phenyl ring. We feel, however, that such comparison

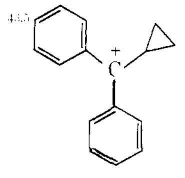

37.8

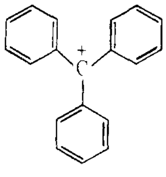

45.6


48.2

would neglect the effect that a cyclopropyl ring may have on the phenyl ring shifts. When considering, for example, the para carbon shifts in the subsequently shown series of ions, one would arrive at the opposite conclusion. Significantly, the difference of 5 ppm in the para carbon shifts of the diphenylcyclopropylcarbenium ion, in which one phenyl ring lies in the face of the cyclopropyl ring, clearly shows substituent group effects (σ') to be important even at the distant para position.


45.6


48.5


49.7

For similar reasons, in the cyclopropylmethylphenylcarbenium ion, the substituent group effects could cause the para shift to be more shielded than that expected from a consideration of the paramagnetic term alone.

[7] (a) H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961); (b) G. L. Nelson, G. C. Levy, and J. D. Cargioli, *J. Amer. Chem. Soc.*, **94**, 3089 (1972).

Table I. ^{13}C Nmr Shifts of Phenyl, Cyclopropyl, and Methylcarbenium Ions[a]

Ion	C^+	α-CH	β-CH_2	CH_3	Phenyl C_i	C_o	C_m	C_p
$(CH_3)_2CH^+$	−125.0[b]			132.8				
$(c\text{-}C_3H_5)_2C^+H$	−59.9	148.1	155.1					
$(C_6H_5)_2CH^+$	−6.9				55.4	44.6 50.3	60.0	42.8
$c\text{-}C_3H_5CH^+C_6H_5$	−32.6	148.6	148.6		56.1	48.5 57.3	61.5	44.7
$c\text{-}C_3H_5CH^+CH_3$	−59.1	126.5	136.3	160				
$C_6H_5\overset{+}{C}HCH_3$	−40							
$(CH_3)_3C^+$	−135.4[b]			145.3				
$(c\text{-}C_3H_5)_3C^+$	−77.8	161.2	162.9					
$(C_6H_5)_3C^+$	−18.1[c]				52.9	49.5	62.5	49.7
$(c\text{-}C_3H_5)_2C^+CH_3$	−81.6	148.6	155.4	155.4				
$(C_6H_5)_2C^+CH_3$	−35.5			162.5	52.2	52.5	62.2	45.6
$C_6H_5(c\text{-}C_3H_5)\overset{+}{C}CH_3$	−52.5	147.9	148.7	170.3	53.9	58.9	62.5	48.2
$(C_6H_5)_2\text{-}c\text{-}C_3H_5\overset{+}{C}$	−41.3	152.8	157.8		51.8 56.4	54.7 59.0	62.3 63.8	43.5 48.5
$C_6H_5(c\text{-}C_3H_5)_2\overset{+}{C}$	−67.3	151.0	156.7		58.4	64.1	65.7	57.2
$C_6H_5\overset{+}{C}(CH_3)_2$	−60.6			158.8	53.7	51.3	60.4	37.8
$c\text{-}C_3H_5\overset{+}{C}(CH_3)_2$	−86.8	133.8	140.4	153.9 162.7				
$(CH_3)_2C^+OH$	−55.7			162.0 163.3				
$(c\text{-}C_3H_5)_2C^+OH$	−43.6	174.0 164.7	166.8 167.4					
Ph_2C^+OH	−15.4				62.3 63.2	53.6 57.1	61.3	48.3 50.4

[a] Recorded in $SO_2ClF\text{–}SbF_5$ or $SO_2ClF\text{–}FSO_3H\text{–}SbF_5$ at −60 to −90°. Chemical shifts are in parts per million from $^{13}CS_2$. A positive sign indicates shielding from the reference. [b] G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969). [c] G. A. Olah, E. B. Baker, and M. B. Comisarow, *ibid.*, **86**, 1265 (1964); G. J. Ray, R. J. Kurland, and A. K. Colter, *Tetrahedron*, **27**, 735 (1971).

The fact that cyclopropylcarbin esteylrs solvolyze faster than the related phenyl esters clearly shows that cyclopropyl is a better participating group in solvolysis than phenyl. A contributing factor can be that the significant strain in the bent, electron-rich cyclopropyl groups bound to a tetrahedral carbon in covalent cyclopropylcarbinyl esters is partially relieved upon reaching the carbenium ion like transition state, thus greatly facilitating the reaction. The fact that cyclopropyl is a better participating group than phenyl in these reactions does not necessarily mean that it also delocalizes charge better in the intermediate ion. In other words, phenyl can remove charge further, spreading it out over a larger system without necessarily meaning that the stability of phenylcarbenium ions is greater than that of cyclopropylcarbenium ions. Similar considerations explain the equilibrium data between ions and their alcoholic or olefin precursors. pK_{R^+} values show only the stabilities of the ions relative to their covalent precursors, with which they are in equilibrium. If, for example, cyclopropylcarbinyl esters release more strain upon ionization than related phenylcarbinyl esters this could affect the solvolysis and pK_{R^+} data. Spectroscopic data, particularly the ^{13}C nmr study of related long-lived ions, give information on the structure of the carbenium ion intermediates, but cannot directly indicate their stabilities.

We cannot recollect, in contrast to Brown, any suggestion that ^{13}C nmr shifts could be used to predict solvolytic rates and stabilities of carbocations or any reason why they should. We maintain our position that ^{13}C nmr shifts, if used with proper consideration of all factors involved, are a very powerful tool in studying the structure of carbocations, including the trend of charge distribution.

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[8] N. C. Deno and A. Schriesheim, *J. Amer. Chem. Soc.*, **77**, 3051 (1955); N. C. Deno, N. C. J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954).

Extended Hückel Calculations on the Electrophilic Ring Opening of Substituted Cyclopropanes. Hyperconjugative Stabilization for a Face-Protonated Cyclopropane

Sir:

The electrophilic ring-opening reactions of cyclopropanes provide the mechanistic challenge of an unusual reaction type (potentially S_E2) and the synthetic possibility of simultaneous stereochemical control at three asymmetric carbons.[1] Simple orbital symmetry theory predicts an even number of inversions to be the stereochemical consequence of such a $[_{\sigma}2_s + {}_{\omega}0_s]$ cycloreaction.[2] Thus, for proton addition, retention of configuration is indicated at the carbon atom receiving the electrophile in a direct one-step reaction;[3]

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(1) For a comprehensive review, see C. H. DePuy, *Fortsch. Chem. Forsch.*, **40**, 74 (1973), and references therein.

(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969); R. R. Schmidt, *ibid.*, **12**, 212 (1973).

(3) This prediction assumes retention of configuration at the departing carbon atom as in the $[_{\sigma}2_a + {}_{\omega}2_s]$, or S_N2, reaction.