rate ratio in this system is the result of π-participation (times 120) in the exo isomer[13] and steric hindrance to ionization (times 890) in the endo isomer.

The effect of increasing electron demand in the related three systems subjected to study is revealed in Figure 1. In the 2-norbornenyl system, significant increase in the exo:endo rate ratio, reflecting π-participation, is observed only with the secondary derivative. In the 5-methyl-2-norbornenyl system, such increase in the exo:endo rate ratio is observed with much smaller electron demand, after the 2-*p*-anisyl derivative. In 2-norbornyl, no significant change in the exo:endo rate ratio is observed over the full range of electron demand explored.

References and Notes

(1) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **95**, 2398 (1973).
(2) S. Winstein, H. Walborsky, and K. C. Schreiber, *J. Am. Chem. Soc.*, **72**, 5795 (1950).
(3) Later the synthesis was successfully achieved and we realized an exo:endo rate ratio of 447 (Figure 1).
(4) R. A. Sneen, *J. Am. Chem. Soc.*, **80**, 3982 (1958).
(5) P. D. Bartlett and G. D. Sargent, *J. Am. Chem. Soc.*, **87**, 1297 (1965).
(6) P. G. Gassman and D. S. Patton, *J. Am. Chem. Soc.*, **91**, 2160 (1969).
(7) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).
(8) We adopted the rates of solvolysis of the *endo*-norbornyl derivatives as a measure of the electron demand. In the case of the 2-aryl derivatives, this is equivalent to using σ^+, but the procedure adopted permits the inclusion of the 2-Me and 2-H derivatives in the same plot (Figure 1).
(9) R. S. Bly, C. M. Du Bose, Jr., and G. B. Konizer, *J. Org. Chem.*, **33**, 2188 (1968).
(10) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).
(11) If it is assumed that the 5-methyl group does not alter the rate of the endo isomer in the secondary derivative, the exo:endo rate ratio in that derivative is 22,000,000 (private communication from C. F. Wilcox); see Figure 1.
(12) J.D. Roberts, W. Bennett, and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3329 (1950).
(13) E. N. Peters and H. C. Brown, *J. Am. Chem. Soc.*, **94**, 5899 (1972).
(14) Postdoctoral Research Associate, 1972–1973, on a grant (GP 31385) provided by the National Science Foundation.
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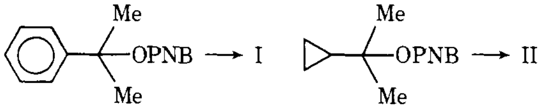
Substituent Effects on the Stability of Carbocations. The Anomalous Case of Phenyl vs. Cyclopropyl Substitution

Sir:

There have been numerous attempts made in the past decade to establish linear correlations between proton[1] and ^{19}F NMR[2] shielding constants of carbocation species and their thermodynamic stabilities in solution. That such direct relationships should indeed exist is reasonable enough.[2a] Thus, one speaks of electron donation into a carbonium center, leading to increased local shielding, as being of benefit energetically. Certainly the opposite process, withdrawal of electrons from a center which already has been largely divested of its charge, can be of little merit. Although no systematic attempt to relate ^{13}C shieldings to solution phase thermodynamic stabilities has as yet appeared in the literature, the existence of at least limited correlations here are strongly implied, by linear relationships between shieldings of different nuclei.[3]

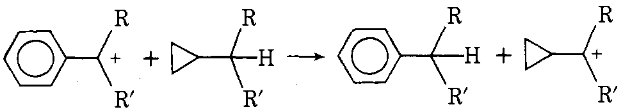
It has become increasingly evident, though, that NMR chemical shift-energy correlations are not general. For example, Olah has reported the ^{13}C shielding at the carbonium center in the *tert*-butyl cation to be shifted some 10 ppm *downfield* from that of the analogous carbon in the isopropyl system,[4] thus suggesting that the additional methyl substituent increases, not diminishes, the local positive charge. The normal relationship with energy would thus indicate an ordering of stabilities, *isopropyl* > *tert*-butyl, clearly at variance with gas phase measurements[5] and with theoretical ab initio molecular orbital calculations.[6]

There is also evidence for disparity in the electron donating and stabilizing effects of phenyl and cyclopropyl groups directly attached to a carbonium center. Olah has prepared a variety of phenyl and cyclopropyl substituted carbocations and has concluded from ^{13}C shielding measurements that the aromatic grouping is far superior to the small ring in displacing positive charge from the carbonium center.[7] For example, the observed ^{13}C shielding at the carbonium center in the dimethylbenzyl cation (I) occurs some 26 ppm upfield from that in the corresponding position in the dimethylcyclopropylcarbinyl system (II). It is more than tempting then, to suggest that the phenyl ring should be, energetically speaking, the better substituent. This stipulation is, however, at odds with Brown's measured rates of solvolysis of tertiary 2-propyl *p*-nitrobenzoate esters.[8] There are several reasonable causes for the inconsistency here. Possibly it stems from an incorrect association of NMR shielding constants and degree of charge displacement, or of thermodynamic stability and rates of solvolysis reactions. Perhaps instead, we are witnessing a breakdown in our notions of charge delocalization leading to (or accompanying) stabilization.



In this communication we describe the preliminary results of our combined experimental and theoretical efforts aimed at detailing the mechanisms by which phenyl and cyclopropyl substituents stabilize a carbonium center. Employed has been pulsed ion cyclotron resonance spectroscopy,[9] and ab initio molecular orbital theory,[10] both of which provide information on the ionic species in gas phase. Comparison of our data with those of Olah and of Brown taken in solution should provide insight into the importance of solvation.[13]

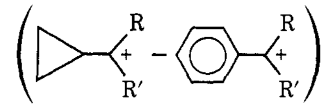
We have considered the energy of the *isodesmic*[14] hydride exchange reaction (eq 1) as a measure of the relative abilities of phenyl and cyclopropyl groups to stabilize a carbonium center. More familar processes which involve loss of a halide anion instead of H^- would lead to qualitatively similar results. Experimental values of $\Delta G°$ for processes 1a and 1b have been obtained from the relative gas phase basicities α-methylstyrene–isopropenylcyclopropane (1a) and of styrene–vinylcyclopropane (1b). Low pressure ion cyclotron resonance techniques have been utilized as described previously.[15] ΔE theoretically for (eq 1) is based upon STO-3G optimized geometries for the parent benzyl and cyclopropylcarbinyl cations.[16] Details will be presented in an upcoming full report. Our data are presented in Table I, along with the NMR shift measurements of Olah and coworkers[7] and Brown's solvolysis rates.[8]



(1)

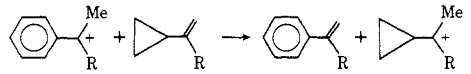
a, R = R' = Me
b, R = Me; R' = H
c, R = R' = H

Table I. Substituent Effects on Properties of Carbocations



Rel property	Tertiary R = R' = Me	Secondary R = Me, R' = H	Primary R = R' = H
^{13}C shift at C^+ (ppm)[a]	−26.2	−19.1	
STO-3G π charge at C^+[b]	+0.092	+0.115	+0.137
Log rate of solvolysis of *tert*-2-propyl *p*-nitrobenzoate esters[c]	2.7		
$\Delta G°_{icr}(1)$[b]	−0.8	+4.8	
$\Delta E_{STO\text{-}3G}(1)$[b]	+2.4	+6.6[d]	17.0[d]

[a] Reference 7. [b] This work. Experimentally what is actually measured is $\Delta G°$ for the proton transfer reactions.



R = Me, $\Delta G° = -2.2$ kcal/mol; R = H, $\Delta G° = +3.6$ kcal/mol

[c] Reference 8. [d] Values for the energies of reactions 1b and 1c have been obtained by correcting for the error in the theoretical determination of the tertiary system (reaction 1a).

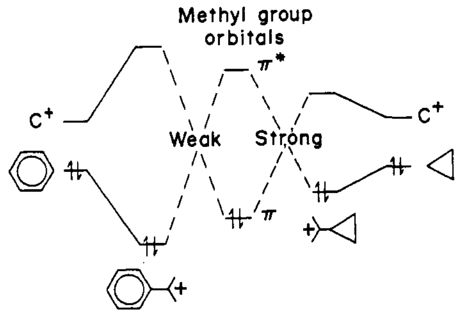


Figure 1. Interaction of the phenyl π system with the vacant p orbital on a carbonium center is more effective than that involving the Walsh functions on cyclopropane. The enhanced orbital splitting which results reduces the ability of the attached methyl groups to further stabilize the cation center. See text for discussion.

The following conclusions deserve special note.

Calculated STO-3G π charges at C^+ in the dimethylbenzyl and dimethylcyclopropylcarbinyl cations parallel the corresponding ^{13}C shielding constants for the species in superacid media. In general, we have found that the correlation between calculated π charges and ^{13}C shielding constants for a variety of tertiary ions, $R\text{-}C^+(Me)_2$, is excellent, the overall slope being 246 ppm per unit charge.[17]

Neither the calculated π charge densities nor the NMR shielding properly reflect the relative stabilizing effects of the phenyl and cyclopropyl groups on the tertiary ions in the gas phase. Our ICR data indicate the *isodesmic* process (1a) to be nearly thermoneutral, with a cyclopropyl substituent just slightly superior (0.8 kcal/mol) to phenyl in stabilizing a tertiary carbonium center. The theoretical STO-3G calculations, although showing a reverse stabilization pattern, are in essential agreement with the experiment regarding the closeness in stabilizing ability of phenyl and cyclopropyl groups in the tertiary cations.

The gas phase result has conclusive significance for solution behavior. Consideration of the various reasonable influences of solvent on reaction (1a)—or on the corresponding halide exchange processes—indicates that the reaction will be more spontaneous (certainly not less) in solution. These solvent effects include: the greater polarizability of phenyl than cyclopropyl, which might be more important in stabilizing the gaseous than the solvated ions;[18] the smaller effective Born radius of the cyclopropylcarbinyl cation, which would lead to a greater solvation energy for it;[18c] greater specific (e.g., solvent encumbered ion formation[19]) for the cyclopropyl system; lesser steric hindrance to solvation[20] would also be expected to favor the cyclopropylcarbinyl cation.

A substantial reversal is noted in the relative stabilizing of the phenyl and cyclopropyl groups in going to a secondary carbocation center. Our theoretical studies of the primary and secondary benzyl and cyclopropylcarbinyl systems do indeed anticipate this fact and clearly depict the phenyl group as the more effective substituent, by some 20 kcal/mol when it is the only recourse open to the carbonium center and roughly half that amount when it is in competition with a single methyl.[21] Rationalization of this behavior—that of diminishing energetic preference for phenyl over cyclopropyl substitution in progressing from primary to secondary to tertiary systems—is straightforward and is detailed in Figure 1. As evidenced by the energy of reaction (1c) the phenyl π system is more able to stabilize an unsubstituted carbonium center than are the Walsh orbitals of cyclopropane.[22,23] In effect, the highest occupied molecular orbital of the resultant benzyl cation has been pushed to a lower energy than that on cyclopropylcarbinyl, making it less available for interaction with the valence functions on a methyl group.[24] Thus, the diminishment of methyl substituent effect which we observe in the benzyl system (relative to cyclopropylcarbinyl) simply reflects the greater stabilizing ability of phenyl in the parent ion.

Acknowledgment. This research was generously supported by grants from the National Science Foundation and from the Research Corporation.

References and Notes

(1) D. G. Farnum and G. Metha, *J. Am. Chem. Soc.*, **91**, 3256 (1969), and references therein.
(2) (a) R. W. Taft and L. D. McKeever, *J. Am. Chem. Soc.*, **87**, 2489 (1965); (b) D. G. Farnum and D. S. Patton, *ibid.*, **95**, 7728 (1973).
(3) (a) P. C. Lauterbur, *Tetrahedron Lett.*, **8**, 274 (1961); (b) H. Spiesecke and W. G. Schneider, *ibid.*, **14**, 468 (1961); (c) G. E. Maciel and J. S. Notterstad, *J. Chem. Phys.*, **42**, 2427 (1965).
(4) (a) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **91**, 5801 (1969); for a discussion see (b) G. A. Olah and D. A. Forsyth, *ibid.*, in press.
(5) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).
(6) L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 5593 (1972).
(7) (a) G. A. Olah and P. W. Westerman, *J. Am. Chem. Soc.*, **95**, 7530 (1973); (b) G. A. Olah, P. W. Westerman, and J. Nishimura, *ibid.*, **96**, 3548 (1974). For further discussion of the relative charge delocalization afforded by phenyl and cyclopropyl groups see (c) G. A. Olah and R. J. Spear, *ibid.*, in press.
(8) H. C. Brown and E. N. Peters, *J. Am. Chem. Soc.*, **95**, 2400 (1973).
(9) (a) R. T. McIver, Jr., *Rev. Sci. Instrum.*, **41**, 555 (1970); (b) J. D. Baldeschwieler and S. S. Woodgate, *Acc. Chem. Res.*, **4**, 114 (1971); (c) R. T. McIver, Jr., and R. C. Dunbar, *Int. J. Mass. Spectrom. Ion Phys.*, **7**, 471 (1971).
(10) Computations have been carried out at the minimal basis STO-3G level,[11] and using the GAUSSIAN 70 series of computer programs.[12]

(11) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

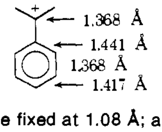
(12) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, program no. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

(13) For our earlier work on the effects of solvent on the stabilities of carbocations see W. J. Hehre, R. T. McIver, Jr., J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96,** 7162 (1974).

(14) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **92,** 4796 (1970).

(15) (a) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **93,** 4314 (1971); (b) R. T. McIver, Jr., and J. R. Eyler, *ibid.*, **93,** 6334 (1971); (c) R. T. McIver, Jr., and J. H. Silvers, *ibid.*, **95,** 8462 (1973); (d) W. G. Henderson, M. Taagepera, D. Holtz, R. . McIver, Jr., J. L. Beauchamp, and R. W. Taft, *ibid.*, **94,** 4728 (1972).

(16) (a) Benzyl cation:



All C–H bond lengths are fixed at 1.08 Å; all CCC and CCH bond angles are fixed at 120°. (b) Cyclopropylcarbinyl cations: W. J. Hehre and P. C. Hiberty, *J. Am. Chem. Soc.*, **96,** 302 (1974).

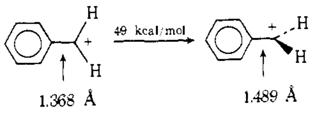
(17) W. J. Hehre and R. W. Taft, unpublished. For a detailed discussion of related correlations see G. A. Olah, P. W. Westerman, and D. A. Forsyth, *J. Am. Chem. Soc.*, in press.

(18) (a) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **90,** 5636, 6501 (1968); (b) E. M. Arnett, F. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. W. Holtz, and R. W. Taft, *ibid.*, **94,** 4724 (1972); (c) D. H. Aue, H. M. Webb, and M. T. Bowers, *ibid.*, **94,** 4726 (1972); (d) R. W. Taft, M. Taagepera, K. D. Summerhays, and J. Mitsky, *ibid.*, **95,** 3811 (1973); (e) J. F. Wolf, P. G. Harch, and R. W. Taft, *ibid.*, **97,** following paper in this issue.

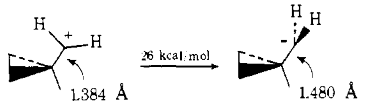
(19) See, for example, R. H. Boyd, R. W. Taft, A. P. Wolf, and D. R. Christman, *J. Am. Chem. Soc.*, **82,** 4729 (1960).

(20) E. M. Arnett and J. M. Abboud, *J. Am. Chem. Soc.*, in press.

(21) Differences in rotational barriers and changes in geometry accompanying torsion about the carbonium center-substituent linkage provide further evidence that a phenyl ring interacts more effectively with an unsubstituted cation center than does cyclopropyl. Thus, torsion of CH_2^+ in the benzyl cation from a planar to an orthogonal arrangement requires 49 kcal/mol, and leads to a lengthening of the phenyl ring–carbonium center linkage of 0.121 Å.



Rotation in cyclopropylcarbinyl is less costly and leads to a smaller lengthening in connecting bond length.[16b]



(22) This conclusion has also been reached independently by Dr. L. Radom (Australian National University) and Professor J. A. Pople (Carnegie-Mellon University). We thank them for communication of their results prior to publication.

(23) For a discussion of the cyclopropane Walsh orbitals see R. Hoffmann and R. B. Davidson, *J. Am. Chem. Soc.*, **93,** 5699 (1971).

(24) For a discussion see R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **94,** 6221 (1972).

(25) Alfred P. Sloan Fellow, 1974–1976.

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Concerning Negligible Aqueous Solvent Effects on Proton Transfer Equilibria of Aryl Carbocations[1]

Sir:

Utilizing pulsed ion cyclotron resonance spectroscopy,[2] accurate determinations of equilibrium constants, $K_{(g)}$, for reaction 1 in the gas phase have become available.[3] Comparison with corresponding equilibrium constants in aqueous solution $K_{(aq)}$, provides a quantitative evaluation of the medium effect of water on the proton transfer equilibrium (1), i.e., $K_{(g)}/K_{(aq)}$. For simple alkyl and aryl substituted amines, medium effects 5–17 powers of ten are found.[3,4] These very large medium effects for proton transfer *between neutral molecules* are primarily associated with differential cation solvation.[3,4] With careful balance achieved in cation solvation,[4] the medium effects of water (and of acetonitrile)[4b] may be reduced to less than one power of ten.

$$NH_4^+ + :B \rightleftharpoons HB^+ + :NH_3 \qquad (1)$$

We wish to report the observation of extremely large medium effects of water ($K_{(g)}/K_{(aq)} \simeq 10^{25}$) for reaction 1 with carbon base precursors of aryl carbocations. Such ions as a class are apparently poorly solvated (the hydration energy may be estimated[3,4] at about 50 kcal) due to the absence of exposed atomic sites with appreciable positive charge. The very extensive delocalization of the cationic charge throughout such relatively large cations has been thought to assure this condition and in particular to maintain the poor proton donating ability of C–H bonds.[5] This picture of cation solvation[6] has been associated with the basis for the Deno-Long-Boyd (DLB) H_0 acidity function for carbon bases.[6f]

The standard free energies for reaction 1 in the gas phase, $\delta_R\Delta G^\circ{}_{i(g)}$, have been obtained by the method reported previously using standards developed in prior work.[4b] The results are listed in Table I together with the corresponding aqueous standard free energies, $\delta_R\Delta G^\circ{}_{i(aq)}$. The values of $\delta_R\Delta G^\circ{}_{i(aq)}$ are based upon measurements in acids ranging from dilute aqueous to about 90% (wt) H_2SO_4. The latter have been extrapolated to the former condition by use of the DLB H_0 function.[7] It will be noted that there is a nearly constant difference (Δ) of ~35 ± 1 kcal (i.e., $K_{(g)}/K_{(aq)} \simeq 10^{25}$) between the corresponding free energy changes. Although pyridinium ions in general give very much smaller solvent effects for reaction 1, a special one, 2,6-di-*tert*-pyridinium,[8] is found to give the same solvent effect as for the aryl carbocations. Since it is expected that the *tert*-butyl groups will completely hinder aqueous hydrogen-bonding to the N: and the NH^+ groups, this conjugate acid-base pair meet the same criteria for poor solvation of the acid-base pair as for the aryl carbocations.[8c]

The following points may be singled out for specific comment.

(1) A plot of the $-\delta_R\Delta G^\circ{}_{i(g)}$ vs. corresponding $-\delta_R\Delta G^\circ{}_{i(aq)}$ values from Table I is linear with approximately *unit* slope and intercept, $\Delta = 35$ kcal. Thus, for

$$C_6H_5CHMe^+ + R_c \rightleftharpoons R_cH^+ + C_6H_5CH{=}CH_2 \qquad (2)$$
$$(R_c = \text{carbon base})$$

reaction 2, a range of structural effects of ~23 kcal is accompanied by essentially no solvent effect ($K_{2(g)}/K_{2(aq)} \simeq 1$). Although $\delta_R\Delta G^\circ{}_{i(aq)}$ values are unavailable for nonaryl and less stable aryl carbocations, we believe it is unlikely that this striking result applies to them (cf. point 5 below).

(2) The DLB acidity function has been confirmed by our measurements in the absence of solvent as a valid measure of intrinsic effects of molecular structure on protonation of carbon bases leading to aryl carbocations. In view of the large medium effects observed[3,10] for proton transfer equilibria with other classes of bases, B, this result appears limited to the DLB acidity function.

(3) The present results are analogous to the findings of Chandhuri, Jagur-Grodzinski, and Swarc[11] that the free energies of formation of free aryl carboanion radicals by reduction of polynuclear aromatic hydrocarbons are essentially the same in the gas phase and in solutions of tetrahydro-