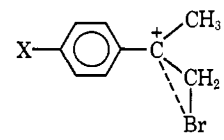
# Stable Carbonium Ions. XCII.[1] Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study of Neighboring Halogen Participation and Substituent Effects in Carbonium Ions. Comparison of Substituted Cumyl and β-Bromocumyl Cations

*Sir:*

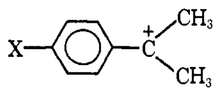
We recently demonstrated that $^{13}C$ nmr spectroscopy is a powerful tool to differentiate between symmetrically bridged ions and unsymmetrically bridged or equilibrating species.[1] In continuation of our studies of long-lived halonium ions,[2] we now report results of $^{13}C$ nmr studies which, we believe, furnish evidence for varying degrees of neighboring halogen participation in carbonium ions.

In principle, there should be a range of structures varying between open-chain β-halocarbonium ions and symmetrically bridged halonium ions. Unsymmetrically bridged halonium ions (**1**) have structures intermediate between the above two extremes.[3] Alternatively, an equilibrium between open and bridged structures may be considered. In either case, partial bridging or equilibration, one would expect that the degree or amount of bridging should be governed by the ability of the phenyl ring to disperse the positive charge and the ability of neighboring halogen to bear positive charge.

We compared the $^{13}C$ chemical shifts of a series of *p*-X-substituted cumyl cations (phenyldimethylcarbonium ions) **2**, used as model, open-chain cations, with their β-bromo analogs **3**. In Table I are summarized the $^{13}C$ chemical shifts of a series of cumyl and related β-bromocumyl cations.



**1**



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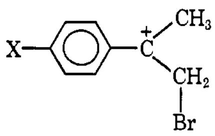
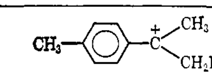
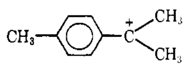
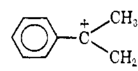
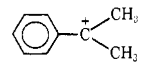
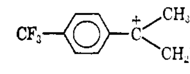
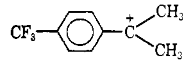


**3**

X = H, $CH_3$, $CF_3$

In order to compare the effect of a bromomethyl group with a methyl group on the $^{13}C$ chemical shifts of an $sp^2$-hybridized carbon, we also measured the shift of the central carbon atom of allyl bromide and that of propene. These values are included in Table I. From the allyl bromide–propene comparison, it might be expected in the absence of other effects that the shift of **3-H** would be about 2 ppm to lower field of **2-H**. We attribute the large upfield shift observed (23.3 ppm) for **3-H** (*cf.* **2-H**) to participation of the bromine atom with the carbonium ion carbon atom. In the last column of Table I are listed chemical shift differences between the β-bromo ions and related cumyl cations. The observed trend in these values is as anticipated on the basis of a progressive decrease in conjugative stabilization by the phenyl ring from *p*-$CH_3$ to *p*-H to *p*-$CF_3$, accompanied by an increased interaction of bromine with the carbonium ion center. That is, for the β-bromocarbonium ions **3**, bridging becomes most important for the *p*-$CF_3$ derivative **3-CF₃** (*cf.* **3-CH₃** and **3-H**) for which stabilization from the phenyl ring is least.

Table I. $^{13}C$ Chemical Shifts[a] of *p*-X-β-Bromocumyl Cations and Related Cumyl Ions

| | β-Bromocumyl cation[b] | $\delta_{^{13}C}$ | | Cumyl cation[c] | $\delta_{^{13}C}$ | $\Delta\delta_{^{13}C}$[d] |
|---|---|---|---|---|---|---|
| **3-CH₃** |  | −28.0 | **2-CH₃** |  | −49.1 | 21.1 |
| **3-H** |  | −37.9 | **2-H** |  | −61.2 | 23.3 |
| **3-CF₃** |  | −44.4 | **2-CF₃** |  | −75.4 | 31.0 |
| | $CH_2{=}^{13}CH{-}CH_2Br$[e] | 59.4 | | $CH_2{=}^{13}CHCH_3$[f] | 61.4 | −2.0 |

[a] $^{13}C$ nmr spectra were obtained using the INDOR method. For details see part LXXIX: G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **91**, 2943 (1969). Shifts (in parts per million from $^{13}CS_2$) are for carbons which bear positive charge as shown. Spectra were recorded at low temperature (*ca.* −60°). [b] β-Bromocumyl cations were prepared by ionization of 1,2-dibromo-2-(*p*-X-phenyl)propanes in $SbF_5$–$SO_2$ solutions at −78°). [c] Cumyl cations were prepared by ionization of *p*-X-phenyldimethylcarbinyl derivatives (alcohols or chlorides). [d] $\Delta\delta^{13}C = (\delta^{13}C)_3 - (\delta^{13}C)_2$. [e] Spectrum was run at room temperature on the neat liquid. [f] Spectrum was run at −60° on the neat liquid.

Based on the data obtained it is not possible to distinguish between the two possibilities: a single, weakly bridged ion **1** or equilibration between open and bridged ions (**3** $\rightleftarrows$ **4** [or **1**]).

That any of the β-bromocarbonium ions examined can be described by symmetrically bridged species (either a static ion **4** or an equilibrating pair **5**) is unlikely since the position of the $^{13}C$ shift of each ion is distinctly different from that expected for a three-membered ring structure. Comparison of the $^{13}C$ shifts of the β-bromocumyl cations with that of the symmetrically

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[1] Part XCI: G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, in press.

[2] (a) G. A. Olah and J. M. Bollinger, *ibid.*, **89**, 4744 (1967); (b) G. A. Olah and J. M. Bollinger, *ibid.*, **90**, 947 (1968); (c) G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 2587 (1968); (d) G. A. Olah and P. E. Peterson, *ibid.*, **90**, 4675 (1968); (e) G. A. Olah, J. M. Bollinger, and J. Brinich, *ibid.*, **90**, 6988 (1968).

[3] The intermediacy of unsymmetrically bridged species has been considered for bromine additions to phenyl-substituted olefins: 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. Thurmaier, *J. Org. Chem.*, **27**, 4523 (1962); R. E. Buckles, J. L. Miller, and R. J. Thurmaier, *ibid.*, **32**, 888 (1967); G. Heublin, *J. Prakt. Chem.*, **31**, 84 (1966).

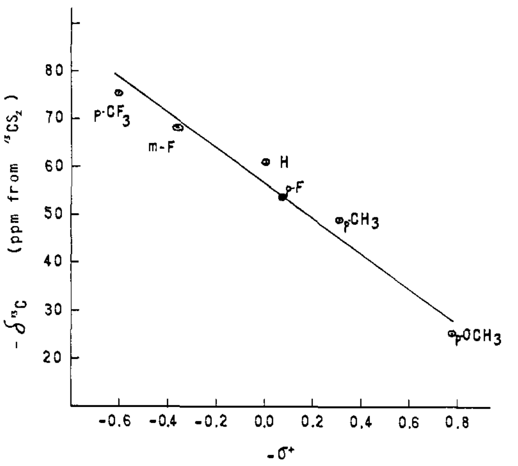
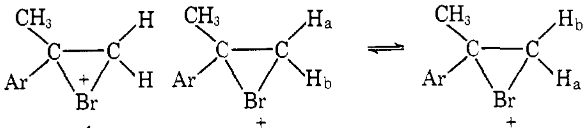


Figure 1. Correlation of $^{13}C$ chemical shifts of substituted phenyldimethylcarbonium ions in $SbF_5$–$SO_2$ solutions at −60° with Brown $\sigma^+$ constants.

bridged ethylenebromonium ion (120.8 ppm)[1] reveals that bromine participation in the β-bromocumyl ions is a weak interaction. The unlikelihood of static symmetrically bridged ions is corroborated by the proton magnetic resonance spectrum[4,5] of each β-bromocarbonium ion, which indicates the equivalence of the methylene protons.



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An additional aspect of our work results from consideration of the $^{13}C$ shifts of the cumyl cations themselves. This series has been extended to include the *p*-fluoro (**2**-F, X = F), *m*-fluoro, and *p*-methoxy (**2**-$OCH_3$, X = $OCH_3$) derivatives. The $^{13}C$ shifts of these ions are −53.9 ppm for **2**-F, −67.6 ppm for *m*-fluorophenyldimethylcarbonium ion, and −25.2 ppm for **2**-$OCH_3$.

For the cumyl cations studied, the shifts cover a range of 50 ppm. As shown in Figure 1 a plot of $\delta_{^{13}C}$ values *vs.* the Brown $\sigma^+$ constants derived from solvolysis of cumyl chlorides in 90% aqueous acetone at 25°[5] gives a reasonably linear relationship. This indicates that the electronic requirements of the solvolysis transition states are similar to those of the corresponding long-lived intermediate ions.

**Acknowledgment.** Support by the U. S. Army Research Office (Durham) and the National Science Foundation is gratefully acknowledged.

[4] Details of the pmr spectroscopic studies will be reported in a full paper.

[5] L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, 1, 89 (1963).

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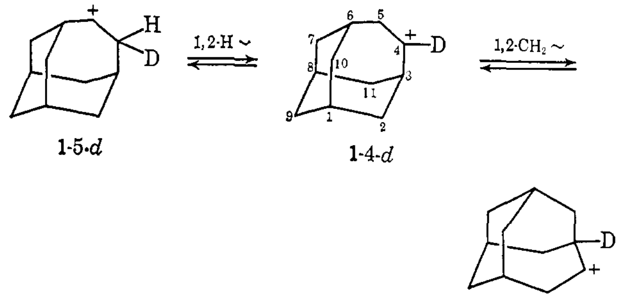
## Acetolysis of 4-Homoadamantyl Tosylate

*Sir:*

Increasing attention has been directed recently to a variety of carbonium ions, as solvolysis intermediates[1] or stable species,[2] in which multiple degenerate rearrangements may take place. In this regard we have undertaken a solvolytic study of the 4-homoadamantyl (4-tricyclo[4.3.1.1$^{3,8}$]undecyl) cation (**1**), which is degenerate with respect both to Wagner–Meerwein rearrangement and to vicinal hydride shift. The two processes are distinguishable on the basis of deuterium label redistribution.

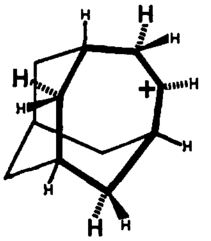


1-5-*d*

1-4-*d*

1-3-*d*

The potential degeneracy of **1** in terms of open carbonium ions alone may be expressed as 11-fold; by combined methylene and hydride shifts the charge may be transposed to each of the carbon atoms. Limitations may be imposed,[1j,3] however, by ion pairing or by bridged carbonium ion formation. Within localized carbonium tosylate ion pairs backside stereospecificity for both rearrangements would be anticipated. The



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[1] (a) J. A. Berson in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 3; (b) S. Winstein, P. Bruck, P. Radlick, and R. Baker, *J. Am. Chem. Soc.*, **86**, 1867 (1964), and references therein; (c) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *ibid.*, **87**, 1613 (1965); (d) S. Masamune, K. Fukumoto, U. Yasunari, and D. Darwish, *Tetrahedron Letters*, 193 (1966); (e) P. K. Freeman and D. M. Balls, *ibid.*, 437 (1967); (f) P. von R. Schleyer, J. J. Harper, G. L. Dunn, V. J. DiPasquo, and J. R. E. Hoover, *J. Am. Chem. Soc.*, **89**, 698 (1967); (g) R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *ibid.*, **89**, 880 (1967); (h) J. A. Berson, J. H. Hammons, A. W. McRowe, R. G. Bergman, A. Remanick, and D. Houston, *ibid.*, **89**, 2590 (1967), preceding papers in this series, and references therein; (i) A. Nickon, G. D. Pandit, and R. O. Williams, *Tetrahedron Letters*, 2851 (1967); (j) J. C. Barborak and R. Pettit, *J. Am. Chem. Soc.*, **89**, 3080 (1967); (k) M. J. Goldstein and B. G. Odell, *ibid.*, **89**, 6356 (1967); (l) A. Nickon and G. D. Pandit, *Tetrahedron Letters*, 3663 (1968); (m) R. M. Coates and J. L. Kirkpatrick, *J. Am. Chem. Soc.*, **90**, 4162 (1968); (n) P. von R. Schleyer and R. E. Leone, *ibid.*, **90**, 4164 (1968).

[2] (a) P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 5679 (1964); (b) M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964); (c) F. R. Jensen and B. H. Beck, *Tetrahedron Letters*, 4287 (1966); (d) G. A. Olah and J. Lukas, *J. Am. Chem. Soc.*, **89**, 4739 (1967); (e) M. Brookhart, R. K. Lustgarten, and S. Winstein, *ibid.*, **89**, 6352, 6354 (1967); (f) R. K. Lustgarten, M. Brookhart, and S. Winstein, *ibid.*, **89**, 6350 (1967); **90**, 7364 (1968); (g) G. A. Olah and J. Lukas, *ibid.*, **90**, 933 (1968); (h) G. A. Olah, A. Commeyras, and C. Y. Lui, *ibid.*, **90**, 3882 (1968); (i) M. Saunders and E. L. Hagen, *ibid.*, **90**, 2436, 6881 (1968); (j) M. Saunders, E. L. Hagen, and J. Rosenfeld, *ibid.*, **90**, 6882 (1968); (k) R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968); (l) B. G. Derendyaev, V. I. Mamatyuk, and V. A. Koptyug, *Tetrahedron Letters*, 5 (1969); (m) B. G. Ramsey and J. Cook, *ibid.*, 535 (1969).

[3] For example, H. L. Goering and G. N. Fickes, *J. Am. Chem. Soc.*, **90**, 2848, 2856, 2862 (1968).