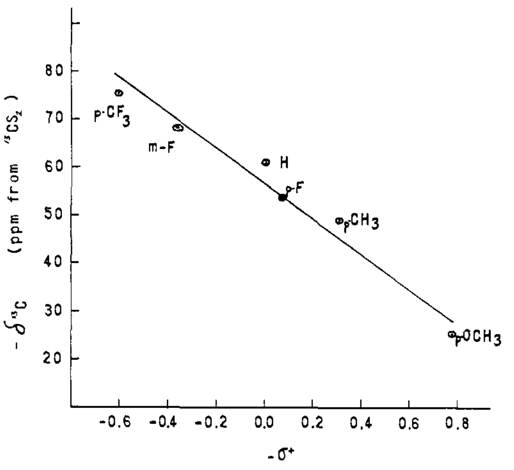
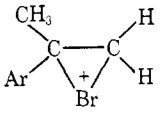


Figure 1. Correlation of ^{13}C chemical shifts of substituted phenyldimethylcarbonium ions in SbF_5–SO_2 solutions at −60° with Brown σ^+ constants.

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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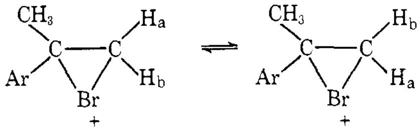
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An additional aspect of our work results from consideration of the ^{13}C shifts of the cumyl cations themselves. This series has been extended to include the *p*-fluoro (**2**-F, X = F), *m*-fluoro, and *p*-methoxy (**2**-OCH_3, X = OCH_3) derivatives. 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 σ^+ 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.

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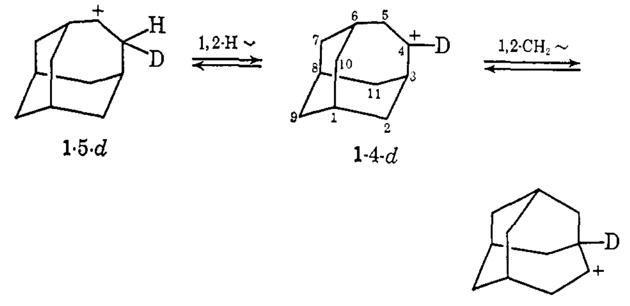
Acetolysis of 4-Homoadamantyl Tosylate

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.

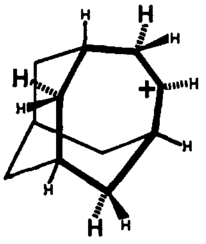


1·5-*d*

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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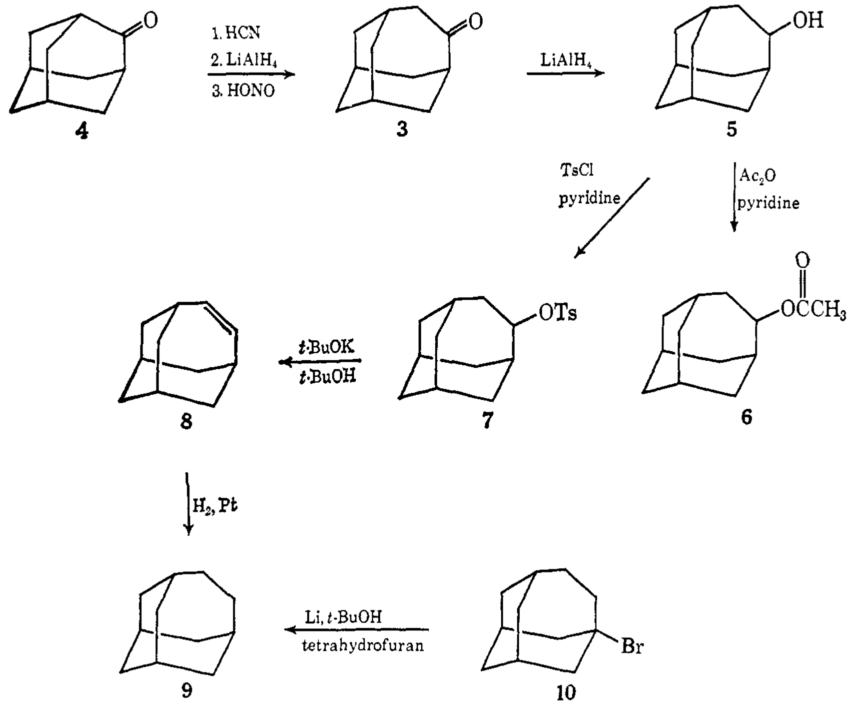
[2] (a) P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 5679 (1964); (b) M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964); (c) F. R. Jensen and B. H. Beck, *Tetrahedron Letters*, 4287 (1966); (d) G. A. Olah and J. Lukas, *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).

Scheme I



consequences of this restriction are presented in structure **2**, in which the tosylate counterion is understood to be paired at the front side of the carbonium charge site. Peregrination of the charge under these conditions is limited to one seven-membered face. Additionally, only the large hydrogens in **2** may undergo migration while only the small hydrogens may become located at the charge site.

Further interest in the 4-homoadamantyl system was provided by models of 4-homoadamantanone (**3**), which indicate the CC(=)C bond angle to be strained substantially beyond its normal value, of unusual interest with respect to the Foote[4] and Schleyer[5] correlations of secondary tosylate acetolysis reactivities with corresponding ketone stretching frequencies and other geometric parameters.[5]

4-Homoadamantanone[6] (**3**), mp 269.0–270.0°, was synthesized by Tiffeneau-Demjanov homologation[7] of adamantanone[8] **4**. Lithium aluminum hydride reduction of the ketone gave 4-homoadamantanol[6] (**5**), mp 267.0–268.0°, from which the acetate[6] **6** and tosylate[6] **7**, mp 71.5–72.5°, were prepared as usual. Treatment of the tosylate **7** with potassium *t*-butoxide in *t*-butyl alcohol furnished homoadamantene[6] (**8**), mp 237.5–238.5°. Catalytic hydrogenation of the latter produced the known[9] homoadamantane (**9**), also obtained by reductive debromination[10] of 3-bromohomoadamantane[11] (**10**) (see Scheme I).

As anticipated, the ketone stretching frequency for **3** was abnormally low, 1698 cm^{-1} (dilute CCl_4 solution), corresponding in the Foote correlation[4] to a predicted acetolysis rate of $10^{2.90}$ for tosylate **7** relative to cyclohexyl tosylate at 25°. Application of the ketone frequency and torsional terms of the Schleyer relationship[5] with the aid of molecular models led to a calculated relative rate for **7** of from $10^{3.94}$ (ϕ_i = 28,46°) to $10^{4.76}$ (ϕ_i = 60,0°; *i.e.*, an untwisted two-carbon bridge). Schleyer and coworkers have obtained theoretical[12a] and experimental[12b] support for the latter conformation for homoadamantane and *cis*-4,5-homoadamantanediol, respectively.

The observed first-order rate data for the acetolysis of 4-homoadamantyl tosylate (**7**) are given in Table I. At 25.0° **7** solvolyzes $10^{2.44}$ times as fast as cyclohexyl tosylate, a factor *smaller* than the predicted values above by $10^{1.50}$ and $10^{2.32}$, respectively.

Table I. Rate Data for Acetolysis[a] of 4-Homoadamantyl Tosylate (**7**)

Temp, °C	10^5k_1, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_1 (4-homoAd-OTs) / k_1 (cyclohexyl-OTs)[b]
55.0	49.7			
40.0	8.17	22.7	−4.9	
25.0	1.35[c]			275
24.9	1.34			

[a] Glacial acetic acid containing 1 wt % acetic anhydride. [b] k_1 (cyclohexyl-OTs) = $4.88 \times 10^{-8}\ \mathrm{sec}^{-1}$ at 25.0° (S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1127 (1952)). [c] Interpolated.

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(4) C. S. Foote, *J. Am. Chem. Soc.*, **86**, 1853 (1964).

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(6) C, H (and S) analyses within 0.30% of theoretical were obtained for all new compounds.

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(8) H. W. Geluk and J. L. M. A. Schlatmann, *Chem. Commun.*, 426 (1967).

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(10) (a) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind.* (London), 405 (1960); (b) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

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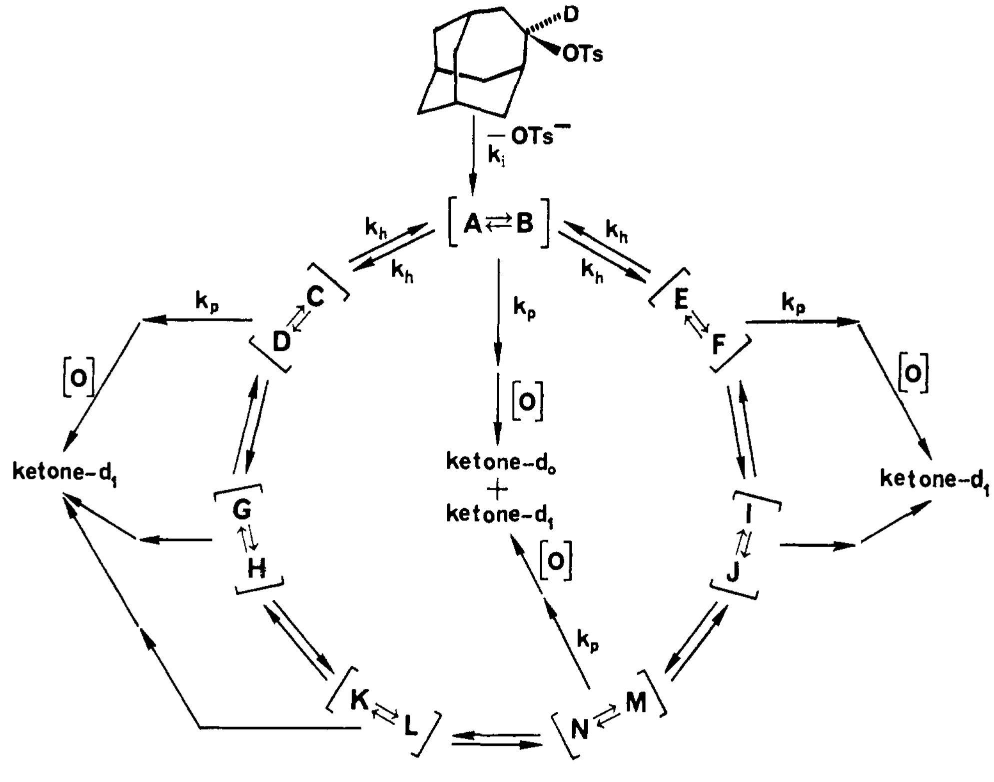
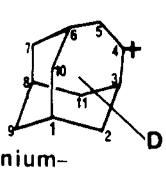
Scheme II





Carbonium-Ion Structures

(Enantiomeric Pairs)	Deuterium Position
A,N	4
B,M	3
C,L	5
D,K	2
E,J	6
F,I	1
G,H	10

While sizeable negative deviations from the Foote–Schleyer correlation are not unprecedented,[13] they are rare. Steric hindrance to ionization[14] has been a suggested explanation for such cases.[13a] In any event, the present results serve as evidence against bridged ion formation.

The products (88% yield, 0.014-mole scale) of sodium acetate buffered acetolysis of tosylate **7** at 40° were readily identified[15] as 25% homoadamantene (**8**) and 75% 4-homoadamantyl acetate (**6**); kinetic control was demonstrated separately. Repetition of the reaction with tosylate deuterium labeled at the ionization site, **7**-4-*d*, gave olefin **8**-*d* and acetate **6**-*d*, each with 100% retention of the deuterium label, as determined mass spectrometrically. Saponification of the acetate to alcohol **5**-*d* and oxidation of the latter with chromium trioxide in acidic aqueous acetone[16,17] gave homoadamantanone **3**, 62.0 ± 0.1% d_1 and 38.0 ± 0.1% d_0.[18]

By either Wagner–Meerwein or vicinal hydride-shift equilibration alone, equal amounts of ketone **3**-d_1 and **3**-d_0 would have been produced. The experimental results require a combination of the two degenerate processes. The generally evident greater facility o degenerate Wagner–Meerwein than vicinal hydride shifts in related systems[1a,h,2a-c,h,3,19] supports interpretation of the acetate **6** label-distribution results most simply as outlined in Scheme II.[20] Methylene and hydride shifts are postulated to occur with backside stereospecificity within 14 possible degenerate ion pairs (seven enantiomeric couples), the former rearrangement being much faster than both the latter and solvent capture. Steady-state treatment of this scheme provides the relationship of eq 1 between the derived homoadamantanone-d_1 and -d_0 composition and the competitive first-order rate constants for hydride shift,

$$\frac{[3\text{-}d_0]}{[3\text{-}d_1]} = \frac{4k_p{}^3 + 10k_hk_p{}^2 + 6k_h{}^2k_p + k_h{}^3}{4k_p{}^3 + 18k_hk_p{}^2 + 22k_h{}^2k_p + 6k_h{}^3} \quad (1)$$

k_h, and acetate product formation, k_p. The experimental results correspond to $k_h/k_p = 0.37$ and $100\% \times k_h/(k_h + k_p) = 27\%$.

Experiments to provide additional mechanistic information are in progress.

Acknowledgment. We are appreciative of experimental assistance by Miss Susan Bronczyk. Support of this work by National Science Foundation Grants GP-6074 and GP-8421 is gratefully acknowledged.

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(14) See also (a) H. C. Brown and W. J. Hammar, *ibid.*, **89**, 6378 (1967); (b) H. C. Brown, I. Rothberg, and D. L. Vander Jagt, *ibid.*, **89**, 6380 (1967); (c) H. C. Brown and S. Ikegami, *ibid.*, **90**, 7122 (1968); (d) S. Ikegami, D. L. Vander Jagt, and H. C. Brown, *ibid.*, **90**, 7124 (1968).

(15) 3-Homoadamantyl acetate,[11] the product of possible hydride shift from the bridgehead, was specifically not detected in the reaction mixture.

(16) (a) R. G. Curtis, I. Heilbron, E. R. H. Jones, and G. F. Woods, *J. Chem. Soc.*, 457 (1953); (b) J. Meinwald, J. Crandall, and W. E. Hymans, *Org. Syn.*, **45**, 77 (1965).

(17) Control experiments established the absence of measurable β-hydrogen exchange during the oxidation.

(18) Relative to reactant tosylate **7** normalized to 100.0% d_1.

(19) 1,2-Hydride shifts play at best minor roles in the cycloalkyl cations during acetolysis: A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.* (London), **20**, 119 (1966).

(20) This scheme is consonant also with the observed formation of homoadamantene **8** with complete retention of the deuterium label from tosylate **7**-4-*d*.

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