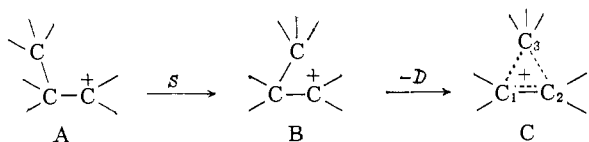


positive^{2d} (not negative) even in the bicyclo[2.2.1]-heptyl cases. However, *S* is very probably less than in the open-chain analogs.



The question of charge distribution in a bridged ion such as VI or C, especially as regards the amount of positive charge on the bridging atom, C-6 in VI or C-3 in C, has been commented on in recent discussions of norbornyl cations.^{4,7b,9c} While we prefer a symbol like C for three-center ions^{8a} of the norbornyl type because of its generality,^{8b} there is intended no implication regarding the fraction of the charge on each of the three electron-deficient carbon atoms. Actually, the charge on C-3 is apt to be fairly small^{8c} in such ions. As we point out elsewhere,^{8c} C-3 will tend toward sp³-hybridization. Such hybridization corresponds to a larger Coulomb integral and better C-3-C-1 and C-3-C-2 orbital overlap, thus leading to stabilization of the bridged ion. These very features of sp³-hybridization on C-3 tend to diminish^{8c} the charge on C-3.

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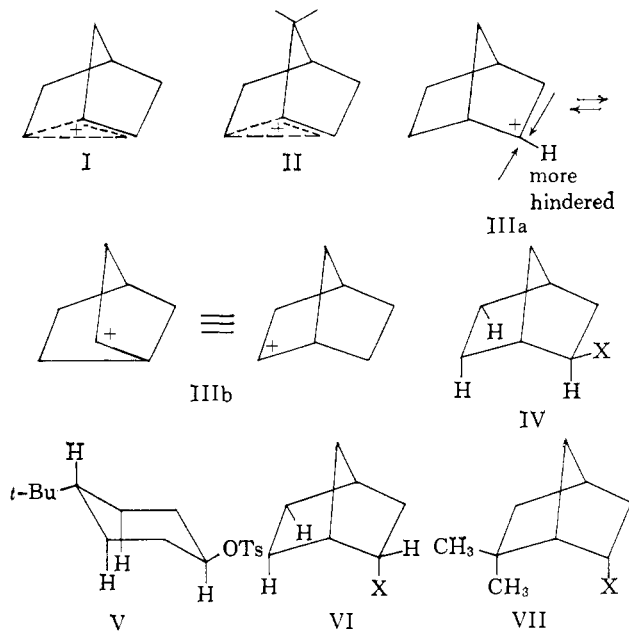
On Brown's Classical Norbornyl Cation

Sir:

As discussed elsewhere,¹ the available evidence on reactivity and stereochemistry in solvolysis of *exo*-norbornyl bromobenzenesulfonate (IV-OBs) and related secondary systems, such as apoisobornyl,² shows that the carbonium ion intermediates have a decided preference for a bridged or nonclassical structure (I and II). Brown³ has advocated another interpretation of the facts involving only classical carbonium ions, *e.g.*, III, and we here consider his proposals more explicitly.

Regarding reactivity, Brown³ proposes that the *exo*-norbornyl rate is not anchimerically accelerated. Instead he regards it as "normal" and that of the *endo* epimer VI-OBs as retarded due to "steric hindrance to ionization" involving the steric effect of the *endo*-hydrogen atoms. However, we know of no *bona fide* example where steric congestion geometrically similar to that in VI-OBs leads to a net retarding factor as large as is required to account for the *exo/endo* acetolysis rate ratio (>10³). To our knowledge, the largest retarding factor which might be cited as an example of Brown's "steric hindrance to ionization" is the factor of 19 observed by Schleyer^{4a} for the methyl groups in the

6,6-dimethyl-2-norbornyl system VII. Extrapolation from this case back to *endo*-norbornyl (VI), which has an *endo*-hydrogen atom instead of the *endo*-methyl group in VII, suggests that Brown's "steric hindrance



to ionization" in *endo*-norbornyl would in fact be quite small. Further, with a method of estimating anchimerically unassisted acetolysis rates which attempts to take account of angle strain,^{4c} eclipsing strain, and steric compressions, and which is quite successful in a number of cases, Schleyer^{4b} finds the *endo*-norbornyl rate to be quite normal, while the *exo* rate is indeed very accelerated.

Regarding stereochemistry of solvolysis of IV-OBs, Brown³ explains the very predominant *exo* nature of the product by a "steric hindrance to *endo* substitution" argument on the classical norbornyl cation IIIa. The racemic character of the *exo* product is not as explicitly treated by Brown, but he apparently feels that this can be accounted for with equilibrating classical ions IIIa,b. On the basis of classical hydrolysis of IV-OBs, we would find it inexplicable that this system leads to >99.98% retention¹ of epimeric configuration while typical simple secondary systems lead to very predominant inversion. For example, *trans*-4-*t*-butylcyclohexyl *p*-toluenesulfonate (V), a system with considerable steric resemblance to IV-OBs, acetolyzes⁵ with 98% inversion of configuration, the retention/inversion ratio differing by a factor >10⁵ from the one observed with *exo*-norbornyl *p*-bromobenzenesulfonate! The >99.98% apparent retention¹ in hydrolysis of IV-OBs would mean in Brown's explanation that a $\Delta\Delta F^*$ >5000 cal./mole obtains between *endo* and *exo* substitution on the classical ion IIIa. We would find it hard to believe that even the *endo* substitution on a simple secondary classical ion IIIa is associated with a ΔF^* as large as 5000 cal./mole, let alone that the $\Delta\Delta F^*$ between *endo* and *exo* substitution is this large.⁶

(1) S. Winstein, *et al.*: (a) *J. Am. Chem. Soc.*, **71**, 2953 (1949); (b) *ibid.*, **74**, 1154 (1952); (c) *ibid.*, **87**, 376 (1965), and intervening papers.

(2) S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **87**, 378, 379 (1965), and references cited there.

(3) (a) H. C. Brown, Special Publication No. 16, The Chemical Society, London, 1962, pp. 140-157, 176-178; (b) H. C. Brown, *et al.*, *J. Am. Chem. Soc.*, **86**, 1246 (1964); **86**, 5008 (1964), and intervening communications.

(4) (a) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, **87**, 375 (1965); (b) P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964); (c) C. S. Foote, *ibid.*, **86**, 1853 (1964).

(5) (a) S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955); M. Whiting, private communication.

(6) With the apoisobornyl system, the "steric hindrance to substitution" argument with a classical cation even fails to predict the correct predominant product epimer² by a factor >2 × 10³.

If equilibration of a classical norbornyl cation IIIa with its enantiomorph IIIb is to account for the >99.95% racemic character¹ of the solvolysis product from IV-OBs, the equilibration rate would need to exceed the rate of collapse of IIIa to solvolysis product by a factor greater than 2×10^3 . The rate constant for collapse of the norbornyl cation to product can be estimated in several ways to be at least in the 10^9 – 10^{10} sec.⁻¹ range.⁷ This brings the equilibration rate IIIa \rightarrow IIIb into the 2×10^{12} – 2×10^{13} sec.⁻¹ range. This is becoming greater than kT/h in absolute rate theory, namely 6×10^{12} sec.⁻¹ at 25°, the rate constant predicted for zero ΔF^* . An additional argument, which may be dubbed the “windshield wiper,” has been employed by Brown^{3a} in accounting for the *exo* nature of the solvolysis product from norbornyl derivatives. Quoting him, “These bicyclic carbonium ions are unusual in that they cannot be fully solvated from both directions. . . . The very rapid movement of the ethylene bridge between the two adjacent positions of the cyclopentyl ring system will prevent an accumulation of solvent in the *endo* direction and thereby favor substitution in the *exo* direction.” It is rather an astonishing suggestion that a cation, which allegedly prefers a classical structure, nevertheless equilibrates so rapidly that solvent is effectively excluded from the *endo* side. Such “desolvation” should inevitably be associated with a corresponding destabilization, so that the proposal is thermodynamically unsound.

Brown apparently ignores available evidence that a classical norbornyl cation does not uniformly have the properties he attributes to it. From deamination⁹ of the norbornyl amines, where it is more likely that a classical cation is produced, the product contains appreciable *endo* epimer and displays considerable optical activity. Further, in solvolysis¹ of *endo*-norbornyl *p*-bromobenzenesulfonate, which leads first to a classical cationic species, the *exo* solvolysis product also displays appreciable optical activity. Thus, Brown needs two varieties of equilibrating classical cations, the one from IV-OBs, very rapidly equilibrating with zero ΔF^* , and another type, *e.g.*, from VI-OBs, not so rapidly equilibrating.

We ourselves have visualized the possible importance of equilibrating classical ions in certain neighboring group situations,¹⁰ and good examples of such are now known.^{8b} However, it seems clear to us that equilibrating classical ions III do not and the nonclassical bridged ion I does provide the explanation for *exo*-norbornyl solvolysis. We certainly do not regard a “classical ion” equilibrating with zero ΔF^* , or the “windshield wiper,” as a “reasonable alternative to the nonclassical structure.”^{3a}

Brown has employed a great deal of indirect “evi-

(7) For example, ion collapse in aqueous acetone is faster than 6,2-hydrogen shift.² The rate constant for the latter process may be estimated as 10^9 sec.⁻¹ at 25° from the data of Olah, *et al.*, on the direct observation of the norbornyl cation.^{8a} The fact that rate of collapse of classical secondary ions to products is quite competitive with rate of rotation about C–C single bonds^{8b,c} also leads to a minimal estimate of 10^9 – 10^{10} sec.⁻¹ for rate of collapse.

(8) (a) G. Olah, *et al.*, *J. Am. Chem. Soc.*, **86**, 5679, 5680, 5682 (1964); (b) C. J. Collins and B. M. Benjamin, *ibid.*, **85**, 2519 (1963); (c) P. S. Skell, Special Publication No. 16, The Chemical Society, London, 1962, p. 173.

(9) J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, **86**, 1749 (1964), and cited references.

(10) S. Winstein, *et al.*, *ibid.*, **70**, 835 (1948); **74**, 1134 (1952); **77**, 1738 (1955).

“ence” in favor of equilibrating norbornyl classical ions in solvolysis of IV-OBs, based on the behavior of 1- and 2-substituted 2-norbornyl systems as compared to cyclopentyl analogs or unsubstituted norbornyl itself. However, we disagree with most of his treatment of the data.¹¹ Brown rather assumes, and gives the impression that it is generally agreed, that tertiary norbornyl cations are classical. In his series of communications Brown reports the behavior of a series of tertiary norbornyl systems to be qualitatively similar to the symmetrical secondary ones as regards *exo/endo* rate ratios¹² and even stereochemistry. The general conclusion he reaches is that the secondary and tertiary norbornyl cations are either both nonclassical or both classical. He chooses the latter alternative, having already assumed it for the tertiary cations. We have felt for some time^{1b} that the older evidence for typical tertiary norbornyl cations is in line with preferred bridged structures. So is Brown’s recent evidence and other recent observations on the camphenhydro^{13a,b} and 2-phenyl-2-norbornyl types.^{13c} Except for possible extreme tertiary norbornyl systems, the available evidence seems to us to favor preferred bridged structures for typical secondary and tertiary norbornyl cations.

(11) For example, Brown incorrectly employs Hammond’s postulate [G. S. Hammond, *ibid.*, **77**, 334 (1955)] to argue that the transition state for ionization of a substrate to a bridged ion should closely resemble the latter. However, there are good reasons to expect carbon bridging to lag behind C–X ionization at the transition state.

(12) The apparent quantitative similarity in these ratios for tertiary and secondary systems is not to be trusted because the necessary corrections have either not been applied or are unknown for the disturbances from *exo-endo* ground state free-energy differences, ion-pair return, and nucleophilic solvent participation (for *endo* secondary substrates in a nucleophilic solvent).

(13) (a) P. Beltrame, *et al.*, *J. Chem. Soc.*, 658 (1964); C. A. Bunton, private communication; (b) W. F. Erman, *J. Am. Chem. Soc.*, **86**, 2887 (1964); (c) C. J. Collins, *et al.*, Paper at International Symposium on Organic Reaction Mechanisms, Cork, Ireland, July 20–25, 1964, p. 38 of Abstracts; *J. Am. Chem. Soc.*, **86**, 4913 (1964).

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The Acidities of Weak Acids in Dimethyl Sulfoxide. II. The Hammett Acidity Function

Sir:

We reported earlier¹ that the apparent acidity of alcohols in dimethyl sulfoxide (DMSO) or tetrahydrofuran is comparable to that of triphenylmethane when alcohol concentrations are low. Further study of this unexpected result led us to extend one Hammett² acidity scale into regions of high basicity in the solvent systems DMSO, water–DMSO, methanol–DMSO. The acidity scale is expressed in terms of the acidity function, $H_- = -\log (a_H \cdot \gamma_I / \gamma_{IH}) = pK_{IH} + \log [I^-]/[IH]$, which is measured through the use of indicator acids (IH). The function is useful when there are available a series of overlapping indicators of known relative acidities which have activity coefficient ratios, $\gamma_I / \gamma_{IH} = \Gamma$, which are essentially constant from me-

(1) E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, **85**, 3054 (1963).

(2) L. P. Hammett, “Physical Organic Chemistry,” McGraw-Hill Book Company, Inc., New York, N. Y., 1940, p. 269.