

endo solvolysis products (<0.5%) were observed and this evidence in favor of bridged or nonclassical cations is especially compelling in the apoisobornyl case where one would predict^{2b} predominantly *endo* product from a classical apoisobornyl species IV. The solvolysis products from apo-OBs and *endo*-cam-OBs tend to be nearly identical with those from their *exo* epimers, indicating efficient leakage from the original classical ions to the nonclassical species V.

Table II. Summary of Solvolysis Product Percentages

ROBs	apoisol	<i>exo</i> -cam	β -fenchol
AcOH, 0.049 N NaOAc			
25° { Apoiso	47.0	4.5	48.5
{ <i>exo</i> -Cam	47.0	4.0	49.0
75° { Apoiso	43.0	6.0	51.0
{ Apo	43.0	6.0	51.0
72.4% Dioxane, 25°			
Apoiso	(70.9) ^a	(11.3) ^a	(18.5) ^a
<i>exo</i> -Cam	71.5	10.5	18.0
β -Fenchol	12.5	2.0	85.5
70% Me ₂ CO			
25° { Apoiso	72.0	10.5	17.5
{ Apoiso	64.0	11.5	24.5
75° { Apo	63.5	11.5	25.0
{ <i>exo</i> -Cam	62.5	12.0	25.5
{ <i>endo</i> -Cam	59.0	13.5	27.5

^a Infrared analysis; others by v.p.c.

Regarding 6,1- or 6,2-hydrogen shift in reactions of the apoiso or *exo*-cam esters, it is evident that hydrogen-shifted product is formed to the same extent from both esters and that the amount of such rearrangement is much smaller in the more nucleophilic aqueous solvents than in acetic acid. The results are interesting under conditions for still shorter carbonium ion lifetime. Thus, treatment of either apoiso- or *exo*-cam-OH with thionyl chloride in pentane at 0° yields chloride samples with typical melting ranges such as 47–49° and 49–50°, having an RCl content of *ca.* 97% as determined by infinity titers in solvolysis. The kinetic behavior of these chloride samples is essentially indistinguishable from that of pure apoiso-Cl, m.p. 53–54°, obtained by low-temperature recrystallization and sublimation. These samples are judged to contain no more than 2% of the less reactive *exo*-cam- or β -fenchol-Cl. Thus, it is possible to suppress 6,1-hydrogen shift to less

than 2% without noticeably suppressing the Wagner–Meerwein rearrangement. The evidence strongly suggests a sequential^{3b,c,4} relationship between 6,1- or 6,2-hydrogen shift and 1,2-carbon bridging rather than a competitive one. Regarding the mechanism of the 6,1- or 6,2-hydrogen shift we still^{3b,4} prefer an “edge-protonated” transition state or intermediate VI rather than the “face-protonated” nortricyclonium^{3c} type ion. In our opinion,^{3b} theoretical considerations favor edge-protonation rather than face-protonation of cyclopropanes.⁵

(6) This has also been suggested by H. C. Longuet-Higgins (ref. 4a) and C. A. Coulson (private communication). Extended Hückel calculations lead to the same conclusion (R. Hoffmann, private communication). See R. Baird and A. Aborodin [*Tetrahedron Letters*, No. 4, 235 (1963); *J. Am. Chem. Soc.*, **86**, 252, 2300 (1964)], for edge-protonated intermediates in closure and opening of the cyclopropane ring.^{3b}

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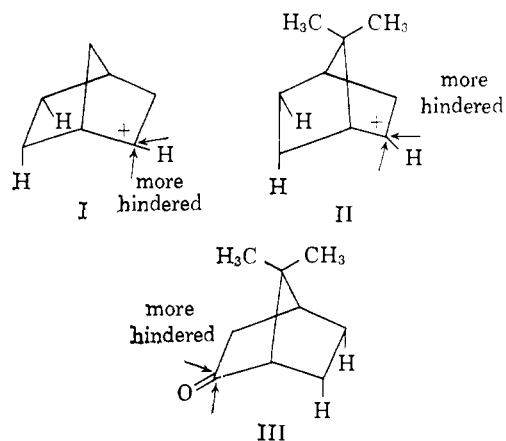
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The Apoisobornyl Bridged Ion. Borohydride Reduction of Apocamphor¹

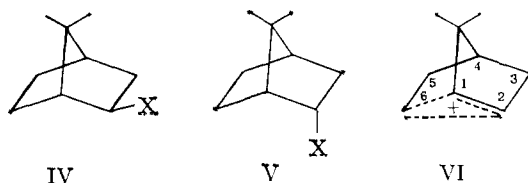
Sir:

In accounting for the very predominant *exo* nature of the solvolysis products in the norbornyl system^{2,3} on the basis of a classical cation I, Brown⁴ has employed a “steric hindrance to *endo* substitution” argument. With the apoisobornyl system,^{3,5} however, the same kind of “steric hindrance to substitution” argument would predict predominantly *endo* solvolysis product. The relative hindrance to *exo* approach to a presumed classical cation II may be judged from the results of reductions³ of the corresponding ketone III. Brown, himself, has suggested the use of ketones as models for classical carbonium ions.^{4a} In hydrolysis of apoiso-



- (1) Research sponsored by the U. S. Army Research Office (Durham).
- (2) S. Winstein, *et al.*, *J. Am. Chem. Soc.*: (a) **71**, 2953 (1949); **74**, 1147 (1952); (b) **74**, 1154 (1952); (c) **83**, 4485 (1961); **87**, 376 (1965); (d) S. Winstein, 15th National Organic Chemistry Symposium of the American Chemical Society, Rochester, N. Y., June 17–20, 1957, p. 29 of Abstracts.
- (3) J. A. Berson, in P. de Mayo, “Molecular Rearrangements,” Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.
- (4) (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.

bornyl bromobenzenesulfonate⁵ IV-OBs, the unrearranged alcohol IV-OH is very predominantly^{5c} *exo*, and we have now made a more rigorous search for the *endo* epimer V-OH.



Hydrolysis of IV-OBs was carried out in 70% acetone at 25° for 29 hr. The alcohol product,^{5c} consisting of 72.4% apoisoborneol, 10.2% *exo*-camphenilol, and 17.4% β -fenchoisocamphorol, which could be isolated in 88% yield, was examined directly by vapor phase chromatography under conditions which had been shown by suitable controls to permit reproducible detection of 0.05% V-OH in the IV-OH. No apo-borneol was detected in the solvolysis product from IV-OBs, so this sets the content of this material⁶ below 0.05%. To us, it would be completely inexplicable for a classical cation II to give rise to alcohol in which the *exo/endo* ratio is >2000. Instead, we take this as evidence that more than 99.9% of the alcohol arises from a bridged ion VI.

While we cannot here fully discuss Brown's alleged linear correlation^{4a} between rates of ROTs solvolysis ($k_{\text{ROT}s}$) and sodium borohydride ketone reduction (k_{CO}), as in eq. 1, and the proposed use^{4a} of this correlation in diagnosing for anchimeric effects in ROTs solvolysis, it is of interest to examine what happens when Brown's approach is employed on the norbornyl-norcamphor and apobornyl-apocamphor systems.

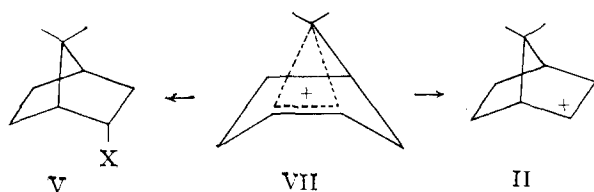
$$\Delta \log k_{\text{ROT}s} = \rho \Delta \log k_{\text{CO}} \quad (1)$$

$$\log (k_{\text{exo}}/k_{\text{endo}})_{\text{ROT}s} = \rho \log (k_{\text{exo}}/k_{\text{endo}})_{\text{CO}} \quad (2)$$

The compositions of the alcohol, which we have now determined, from reduction of norcamphor and apocamphor III with sodium borohydride, as well as lithium aluminum hydride, or from equilibration, are summarized in Table I. If the norbornyl and apoisobornyl cations were indeed classical, as claimed by Brown,⁴ and if a linear relation (1) really existed between rates of classical solvolysis of ROTs and ketone reduction, we might expect to apply eq. 1 to correlate *exo/endo* ROTs rate ratios with *exo/endo* ratios of ketone reduction products. This is shown in eq. 2.

(5) S. Winstein, *et al.*, *J. Am. Chem. Soc.*: (a) 77, 3054 (1955); (b) 86, 2721 (1964); (c) 87, 378 (1965).

(6) No ring-opened norterpineol⁵ is observed. Similarly, no apo-borneol or norterpineol are detected in hydrolysis of the *exo*- and *endo*-camphenilol brosylate.^{5c} On the other hand, in hydrolysis of the *endo*-apobornyl brosylate *ca.* 0.10 and 0.05% of materials having the correct retention times for apo-borneol V-OH and norterpineol, respectively, are detected. The 0.05% norterpineol shows that reversibility of the transformation^{5b} of the nopinyl-bridged ion VII to V or II is just detectable under these conditions. The 0.10% apo-borneol would appear to arise partly from the classical ion^{5b} II and partly from VII.^{5b}



Since the ROBs *exo/endo* rate ratio is a similar large number for both the norbornyl and apobornyl pairs,^{2,5} and yet reduction of norcamphor and apocamphor leads to different predominant epimers, we can see that the slopes (ρ) of eq. 2 would have similar magnitudes but opposite signs for the norbornyl correlation on the one hand and the apobornyl one on the other. It is obvious that the general approach fails miserably to fit the available data.

Table I. Per Cent *exo* Alcohol from Ketones

	LiAlH ₄ , ether	NaBH ₄ , <i>i</i> -PrOH, 50°	Equil. ^a <i>i</i> -PrOH, 100°
Norcamphor	9.9	20:1	80 ^b
Apocamphor (III)	90.0 ^c	78.4	37

^a Al(OPr-*i*), as catalyst. ^b C. F. Wilcox, *et al.*, *J. Org. Chem.*, 28, 1079 (1963). ^c S. Beckmann and R. Mezger, *Ber.*, 89, 2738 (1956), have previously reported a 91% yield of nearly pure apoisoborneol, but no v.p.c. analysis was performed.

All the evidence in solvolysis points to a preferred bridged or nonclassical structure for such ions as norbornyl or apoisobornyl.^{2,5} Therefore, the attempted direct observation of the norbornyl cation under inert nonsolvolyzing conditions by Olah and co-workers^{7a} is of great interest. While they have not yet been able to "freeze" out 6,2-hydrogen shifts and observe the n.m.r. spectrum of the "frozen" norbornyl cation, their general evidence, *e.g.*, slow 3,2- and fast 6,2-hydrogen shift, favors the bridged structure. While we regard direct observation of such intermediates in inert solvents as very desirable, we disagree with Deno,^{7b} who states that such direct observation should render "obsolete" the past solvolytic work. Solvation^{8a} and reaction possibilities are so different in the typical solvolyzing solvents than in the inert nonsolvolyzing ones that both types of investigation are essential.

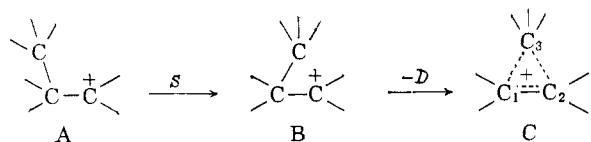
The present evidence points up again, as we have commented previously,^{2b} that strained bicyclo[2.2.1]-heptyl systems are more disposed toward nonclassical structures than are their open-chain analogs. There has been a tendency to ascribe the driving force for formation of the norbornyl type bridged ions partly or largely to relief of strain in going to the ion.⁹ However, this conclusion may be quite confusing without setting up a bookkeeping mechanism to disentangle strain (*S*) and electron delocalization (*D*) effects. Thus, in comparing a classical cation structure A with its nonclassical counterpart C we can consider the balance between strain energy *S* to deform the geometry of the localized classical cation to the final geometry B and the delocalization energy *D* then released due to nonclassical electron delocalization.^{8c} We believe the strain energy *S* which needs to be reckoned with is

(7) (a) G. A. Olah, *et al.*, *J. Am. Chem. Soc.*, 86, 5679, 5680, 5682 (1964); (b) N. C. Deno in "Progress in Physical Organic Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1964.

(8) (a) S. Winstein and B. K. Morse, *J. Am. Chem. Soc.*, 74, 1133 (1952); (b) S. Winstein and L. L. Ingraham, *ibid.*, 74, 1160 (1952); (c) R. J. Piccolini and S. Winstein, *Tetrahedron*, 19, 423 (1963).

(9) (a) H. M. Walborsky, *Experientia*, 9, 209 (1953); (b) A. Streitwieser, *Solvolytic Displacement Reactions*, McGraw-Hill Book Co., New York, N. Y., 1962, p. 134; (c) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, 87, 375 (1965).

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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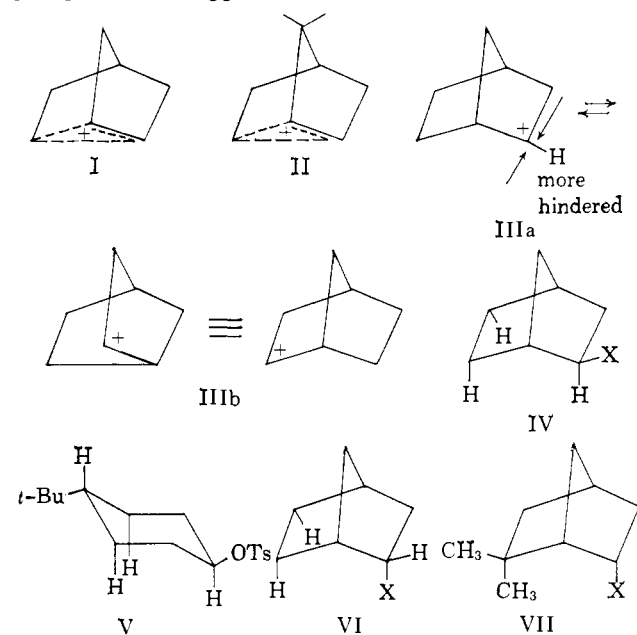
On Brown's Classical Norbornyl Cation

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.