2-exo-norbornyl solvolysis transition states are essentially classical in nature, or (b) the transition states are nonclassical, but are not satisfactorily represented by III since structures such as Ic make no appreciable contribution to the resonance hybrid, or (c) structures such as Ic do make a contribution, but the effect this produces is being overwhelmed by some rate-retarding influence not considered by the simple theory.

The results do not appear to support possibility a. A 6-endo-methyl group (II, R = CH_3) would introduce a steric interaction with the endo-hydrogen at C-2. If the 2-exo-norbornyl transition state were classical, then the 2-endo-hydrogen should bend away from the 6-endo substituent during solvolysis. On this basis, the solvolysis of II (R = CH_3) should be accelerated roughly 10-fold over II (R = H) due to relief of steric strain. In fact, a 25-fold rate decrease is observed at 25° (Table I). Using the scheme for estimating anchimeric assistance which we have proposed,[4] an acceleration of less than 10^1 for II (R = CH_3) is calculated, compared to $10^{3.3}$ for II (R = H).[9] Solvolysis of II (R = CH_3), but not II (R = H), is largely unassisted and may be proceeding through a transition state very nearly classical.

Of the remaining possibilites, we favor (b) on the basis of greater simplicity. There appears to be no positive evidence from the literature[3] to support the idea of contributions from structures such as Ic. The acetolysis products from both II and IV (R = CH_3) support this contention. In both cases we have been able to detect by capillary gas chromatography only the acetate of 6,6-dimethyl-2-exo-norbornanol. Neither attack at C-6, fragmentation, nor 6,2-methyl shift[10] takes place under these conditions.

Perhaps the rate-depressing effect of the gem-dimethyl in II is due to unfavorable methyl group steric interactions with both C-1 and C-2 in a nonclassical transition state (III, R = CH_3). Models indicate that these interactions increase in going from II to III (R = CH_3). The rate enhancement in 2-exo-norbornyl solvolyses[4] is due, largely, to partial relief of strain in proceeding to the transition state, and not just to charge delocalization.[2,3] Hence, an unfavorable transition-state steric interaction (as III, R = CH_3) should remove much of the driving force for participation.

Acetolysis of 6,6-dimethyl-2-endo-norbornyl tosylate (III, R = CH_3) is also slower than that of the parent compound III (R = H). In the endo series there is no question of participation, so that a steric effect must be responsible. We believe the observed rate decrease, a factor of 19 at 25°, to be the first significant case of "steric deceleration" (transition state more crowded than the ground state)[4,11] in a unimolecular solvolysis reaction.[12]

The exo/endo rate ratio for the 6,6-dimethyl compounds (206 at 25°) is nearly as large as the ratio for the parent norbornyl derivatives (280 at 25°, Table I).

We regard this agreement to be fortuitous, and we agree with Brown, Chloupek, and Rei[11] that a large exo/endo rate ratio is not sufficient evidence upon which to base an assignment of nonclassical structure for a carbonium ion. In the present instance, we feel that steric factors contribute more to the rate difference between II and IV (R = CH_3) than does nonclassical electronic influence.

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The Nonclassical Norbornyl Cation[1]

Sir:

Some 15 years ago[2a] we extended our studies of neighboring group participation to neighboring saturated carbon and reported on the reactivity and stereochemistry in solvolysis of the exo- and endo-norbornyl p-bromobenzenesulfonates[2] (I-OBs and II-OBs). We considered equilibrating classical ion intermediates,[2d] but decided in favor of anchimerically assisted ionization of I-OBs leading to an internally compensated bridged or nonclassical three-center carbonium ion species A which gives rise to racemic exo product. On the other hand, endo-II-OBs was presumed to undergo anchimerically unassisted ionization to a classical carbonium ion species[2c] B. The latter was presumed to leak extensively into nonclassical A, while the remainder collapsed to inverted exo product.

Although he apparently subscribed to this interpretation at first,[3a] Brown has now for some years been questioning it and urging consideration of another interpretation of the facts involving only classical carbonium ions. Most recently he has referred to the norbornyl cation in his Transition State Symposium paper[3b] and in a series of communications in this journal.[3c,d] It seems appropriate to report further new evidence regarding solvolysis of norbornyl bromobenzenesulfonates and to consider all the evidence in the light of Brown's proposals.

Solvolysis of ROBs produces some hydrocarbon accompanying the substitution product. For example, from acetolysis of exo-I-OBs at 25°, 4% of elimination product is observed. Significantly, the hydrocarbon composition is 98% nortricyclene, 2%

(10) P. Yates and S. Danishefsky, J. Am. Chem. Soc., 84, 879 (1962).
(11) H. C. Brown in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p. 155; H. C. Brown, F. J. Chloupek, and M.-H. Rei, J. Am. Chem. Soc., 86, 1248 (1964).
(12) A similar 1,3-type $CH_3\cdots OTs$ axial-axial interaction in the cyclohexyl series does not produce steric deceleration, presumably because of greater flexibility. See H. P. Fischer, C. A. Grob, and W. Schwarz, Tetrahedron Letters, No. 1, 25 (1962); C. A. Grob, W. Schwarz, and H. P. Fischer, Helv. Chim. Acta, in press; S. Nishida, J. Am. Chem. Soc., 82, 4290 (1960).

(1) (a) Research supported by the National Science Foundation. (b) Research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.
(2) S. Winstein, et al., J. Am. Chem. Soc.: (a) 71, 2953 (1949); (b) 74, 1127 (1952); (c) 74, 1147 (1952); (d) 74, 1154 (1952); (e) 83. 4485 (1961); (f) 84. 4993 (1963).
(3) H. C. Brown, et al.: (a) J. Am. Chem. Soc., 74, 1894 (1952); (b) Special Publication No. 16, The Chemical Society, London, 1962, pp. 140–157, 176–178; (c) J. Am. Chem. Soc., 85. 2322 (1963); (d) ibid., 86. 1246, 5008 (1964)
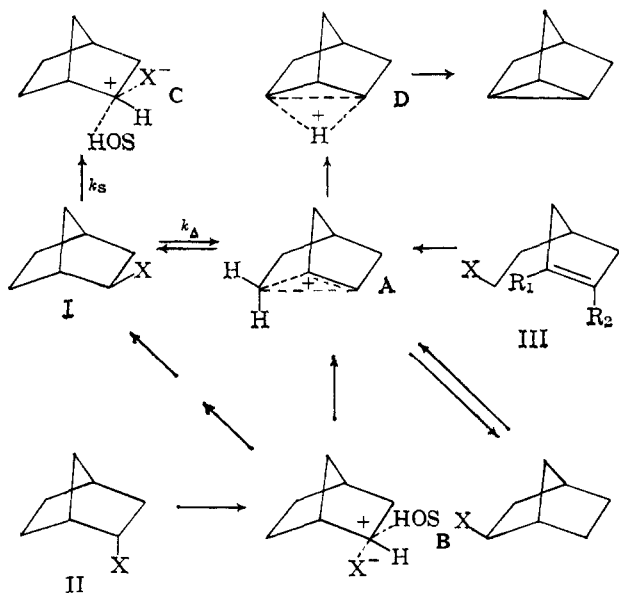
norbornene. Regarding the epimeric nature of the solvolysis products, previous evidence was that the acetolysis product was $>99.7\%$ exo^{2f} from acetolysis of both exo- and endo-ROBs or RHg+. Using more refined vapor phase chromatography we have now examined the norborneol from hydrolysis of endo-free exo-ROBs in the relatively nucleophilic solvent, 75% acetone. Controls on the work-up, isolation, and analytical procedures showed 0.02% endo epimer in exo-ROH to be reproducibly detectable. However, no endo-ROH was visible in the solvolysis product from 75% acetone, the endo content being definitely $<0.02\%$.

The stereochemical result of solvolysis of optically active I-OBs has been further examined by isolating the whole product and measuring its optical activity[2c,d,4a,b] in the form of the acetate, $n^{25}D$ 1.4565, in a 1-dm. tube under conditions where fully retained product would display a reading of ca. 10–12°. From solvolysis of exo-I-OBs, m.p. 55.8–56.6°, $[\alpha]^{25}D$ −2.05° (c 10, CHCl$_3$), in acetic acid, 80% dioxane and 75% acetone at 25°, and 90% dioxane at 50°, the exo-solvolysis product, measured as the acetate, uniformly displayed a measured rotation of 0.000 ± 0.005°. Thus, the survival of optical activity is less than 0.05% in all of these solvents, under conditions where active product would have retained its activity completely. The exo products from solvolysis of endo-ROBs, m.p. 60.5–61.2°, $[\alpha]^{25}D$ +12.7° (c 10, CHCl$_3$), do show appreciable activity. This corresponds to 13 ± 1% inversion in 80 and 75% aqueous acetone solvents at 75°, and 60% acetone at 60°, 7% inversion in acetic acid (0.12 M NaOAc) at 75°, and 3% inversion in formic acid (0.10 M NaOCHO) at 25°.

Solvolysis of exo-ROBs is strongly anchimerically accelerated, judging by the exo/endo solvolysis rate ratio. In taking the exo/endo rate ratio, angle and eclipsing strain effects tend to cancel,[2a–d] but the slightly higher ground-state free-energy of the endo derivative is not allowed for. The titrimetric rate ratio at 25° in acetic acid solvent[2a–b] is 350. However, the polarimetric rate ratio,[5] 1600, provides a better

(4) (a) J. A. Berson, et al., J. Am. Chem. Soc., 81, 4088, 4094 (1959); (b) ibid., 86, 1749 (1964); (c) E. J Corey, et al., ibid., 82, 2645 (1960); (d) ibid., 85, 169 (1963).

estimate of anchimeric acceleration. Thus the relative reactivities indicate a very high ratio (k_A/k_s) of anchimerically assisted to anchimerically unassisted rates. The direct formation of an internally compensated bridged ion also is indicated by the pure dl-exo nature of the solvolysis product, the stereochemical work having failed to detect chemical capture of an unsymmetrical norbornyl cation.[6] Similar failure has attended other tests of this kind where chemical capture of the norbornyl species is by the counterion in an ion pair. One such test involves a carboxylate anion group[4d] in an arenesulfonate counterion and another involves the sulfur atom in a thiobenzoate counterion[7a] in the thionbenzoate–thiolbenzoate isomerization.

In anchimerically unassisted solvolysis of endo-II-OBs chemical capture of an unsymmetrical norbornyl cationic species is quite evident, however. While most of the initially formed classical species B becomes nonclassical before giving rise to product an appreciable fraction does give optically active inverted product. In the more nucleophilic solvents this amounts to 13%.

There are other indications that a nonclassical structure is preferred by the norbornyl cation. One of them is the great tendency for the elimination product from solvolysis of I-ROBs to be nortricyclene instead of norbornene. This is structurally more easily rationalized with the bridged ion A than with a classical one.[8] Structure A is also supported by the substituent effects observed by Bartlett and Sargent[7b] in the π-route[2e] formation of norbornyl cations from Δ^3-cyclopentenylethyl derivatives (III). The first and second olefinic methyl substituents have nearly identical accelerating effects, indicating that the Δ^3-cyclopentenylethyl system (III, $R_1 = R_2 = H$) ionizes by way of a symmetrical transition state to a symmetrical cationic species.

The available evidence forces us to a bridged or nonclassical description for the norbornyl cation in solvolysis of exo-I-OBs. On the basis of classical cations we cannot account for reactivity, stereochemistry (e.g., an exo/endo ratio $>5 \times 10^3$ and a racemic-active ratio $>2 \times 10^3$ in the product), and the other evidence cited above.

(5) The pertinent k_α/k_t value for exo-ROBs to be employed is slightly in doubt because of experimental uncertainty and some dependence on acetate salt concentration. A value of ca. 4.6 leads to the figure of 1600 [E. Clippinger and A. Colter, Ph.D. Theses, U.C.L.A., 1955–1956.]

(6) See, also, ref. 4c. Judging by the behavior of endo-II-OBs, at least a small fraction of classical ion C resulting from anchimerically unassisted solvolysis (k_s) would be expected to yield inverted endo product. Ion-pair return[2d,5] and 6,2-hydrogen shift [ref. 2d; J D. Roberts, C. C. Lee, and W. H. Saunders, J. Am. Chem. Soc., 73, 5009 (1951); 76, 4501 (1954)] contribute substantially to the stereochemical result in acetolysis, but not very seriously in 75% acetone.

(7) (a) S. G. Smith and J. P. Petrovitch, Tetrahedron Letters, No. 45, 3363 (1964); (b) P. D. Bartlett and G. D. Sargent, J. Am. Chem. Soc., in press

(8) The loss of the proton may well involve an edge-protonated intermediate[2d] D. See R. L. Baird and A. A. Aborodin, Tetrahedron Letters, No. 4, 235 (1963); J. Am. Chem. Soc., 86, 252, 2300 (1964).

(9) (a) National Science Foundation Predoctoral Fellow, 1952–1953; U. S. Rubber Company Foundation Postgraduate Fellow in Physical and Engineering Science for 1953–1954; (b) National Science Foundation Predoctoral Fellow, 1961–1964.

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