

The Apoisobornyl-*exo*-Camphenyl Nonclassical Cation¹

Sir:

Because of recent discussions² of the norbornyl cation³ we are prompted to report the results of both former⁴ and very recent studies of the dimethyl-labeled norbornyl systems, the apoisobornyl (apois) and *exo*-camphenyl (*exo*-cam) *p*-bromobenzenesulfonates I and II-OBs, related by a Wagner-Meerwein rearrangement, and the isomeric β -fenchoisocamphoryl (β -fenchois) analog III-OBs, together with the corresponding *endo* epimers. These systems provide considerable insight into carbonium ion structure and 6,2-hydrogen shift.

Kinetics of acetolysis, summarized in Table I, are nicely first order for the various systems except in

derivatives, but even these are small and we still feel unable to make a really quantitative analysis of the various contributing effects.

The rates of acetolysis of the *exo* derivatives are substantially higher than those of their *endo* epimers, the *exo/endo* titrimetric rate ratios being quite substantial. Correcting for *exo* and *endo* ground-state free-energy differences would increase somewhat the *exo/endo* rate ratio in the case of the β -fenchocamphoryl (III) and camphenyl (II) systems and decrease it slightly for the apobornyl (I) pair. However, a more quantitative analysis of the *exo/endo* rate ratios as measures of anchimeric acceleration would require more information on ion-pair return than is at present available. The data do suggest, however, that anchimeric acceleration of ionization of the *exo* epimers to

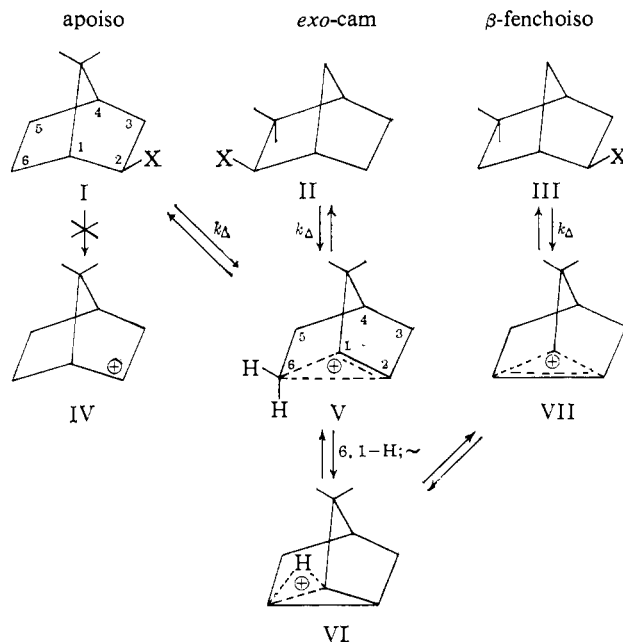
Table I. Acetolysis Rates of ROB^a at 25.0°

| System | M.p., °C. | | $10^8 k_t$, sec. ⁻¹ | <i>exo/endo</i> ratio |
|----------------------------------|-------------|-----------|------------------------------------|--------------------------|
| | ROH | ROBs | | |
| Apo ^{5a} | 131-132 | 98.5-99.5 | 0.188 | |
| β -Fencho | 65-66.5 | 72-73 | 0.180 | |
| <i>endo</i> -Cam ^{5b} | 73-73.5 | 98.0-98.4 | 0.0266 | |
| α -Fenchyl | <i>b</i> | 86.5-87.5 | 0.039 | |
| <i>exo</i> -Nor ^{3a, b} | 127.8-128.5 | 56-57 | 88.2 | 350 (1600) ^c |
| Apoiso ^{5b} | 141-142.5 | 61.6-62.5 | 770 | 4100 |
| <i>exo</i> -Cam ^{5b} | 106-106.5 | 79.0-79.8 | 32.9 | 1240 |
| β -Fenchois ^{5a} | 60-61 | 40-41 | 26.1 | 145 |

^a Satisfactory C, H analyses obtained on all new compounds. ^b Material, [α]_D²⁵ 1.20° (*c* 9.95, ether), kindly furnished by the Naval Stores Research Division of the Hercules Powder Co. through the courtesy of Dr. R. W. Ivett. ^c Polarimetric rate ratio.

the case of I-OBs. In this case, there is a disturbance from ion-pair return. Thus, in 50% AcOH-dioxane at 25.0°, the titrimetric rate constant is 5.52×10^{-5} sec.⁻¹, while the rate constant for isomerization to a slower ester with the reactivity corresponding to *exo*-cam-OBs is 2.57×10^{-5} sec.⁻¹. From such a solvolysis carried to *ca.* 75% reaction there was isolated some relatively pure *exo*-cam-OBs. In 80% dioxane, ion-pair return is much less important.

Examining the anchimerically unassisted *endo* derivatives, we see that the dimethyl- and two related trimethyl-substituted compounds have reactivities quite similar to that of *endo*-norbornyl OBs itself,^{3a} inductive and various steric effects due to the methyl groups tending to balance out. The biggest rate decreases, by factors of 7 or 8, are observed with the 3,3-dimethyl



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(2) (a) H. C. Brown, Special Publication No. 16, The Chemical Society, London, 1962, pp. 140-157, 176-178; H. C. Brown, *et al.*, *J. Am. Chem. Soc.*, **85**, 2322 (1963); **86**, 1246, 5008 (1964); (b) J. A. Berson in P. de Mayo, "Molecular Rearrangements," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

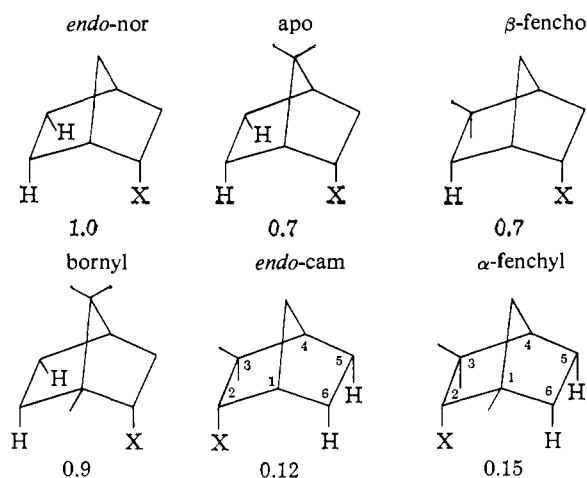
(3) (a) S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **71**, 2953 (1949); **74**, 1127, 1147 (1952); (b) S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952); (c) J. D. Roberts, *et al.*, *ibid.*, **73**, 5009 (1951); **76**, 4501 (1954).

(4) (a) S. Winstein, "1,2- and 1,3-Hydrogen Shifts," at Symposium on Molecular Rearrangements, Queen Mary College, London, April 6, 1954; see M. F. Ansell and M. J. S. Dewar, *Nature*, **173**, 898 (1954); (b) S. Winstein, *Experientia Suppl.*, **11**, 137 (1955); (c) S. Winstein, Abstracts of 15th National Organic Chemistry Symposium of the American Chemical Society, Rochester, N. Y., June 17-20, 1957, p. 29; (d) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 3054 (1955); (e) see E. C. Friedrich and S. Winstein, *ibid.*, **86**, 2721 (1964).

(5) (a) G. Komppa and S. Beckmann, *Ann.*, **522**, 137 (1936); **537**, 140 (1939); (b) S. Beckmann and R. Bamberger, *ibid.*, **574**, 65 (1951); (c) W. Huckel and H. Kindler, *Chem. Ber.*, **80**, 197 (1947).

bridged or nonclassical dimethyl-substituted norbornyl cations V and VII is substantial in all three systems and at least similar in magnitude to that for *exo*-norbornyl.

Product studies (Table II) also indicate strongly that the apoiso- and *exo*-cam-OBs isomers react by way of common bridged or nonclassical species, thus yielding identical mixtures of *exo* solvolysis products. The apoiso- and *exo*-cam-OH are presumed to arise from the apoiso cation V and the β -fenchois-OH from a β -fenchois ion VII after 6,1-hydrogen shift. No



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 -Fenchoiso | 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 -fencholiso-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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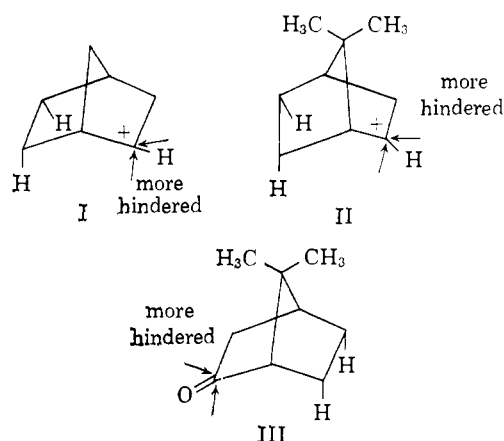
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The Apoisobornyl Bridged Ion. Borohydride Reduction of Apocamphor¹

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.