

**Solvolysis of Some Representative Norbornyl Derivatives in the Presence of Borohydride. *exo* Substitution as a Basis for the Postulated Nonclassical Structure of the Norbornyl Cation**

Sir:

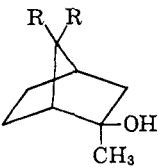
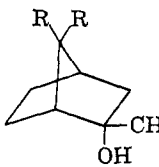
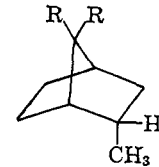
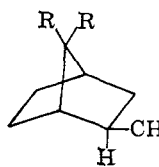
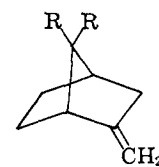
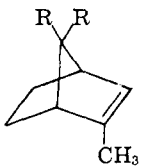
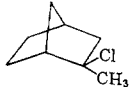
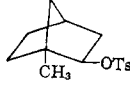
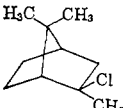
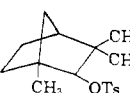
Three major categories of evidence have been used to justify nonclassical structures for the norbornyl and related cations: (1) unusually fast rates, attributed to the formation of a highly stabilized cation<sup>1</sup>; (2) high *exo/endo* solvolytic rate ratios, attributed to carbon participation in the *exo*, but not in the *endo* derivative<sup>2</sup>; and (3) *exo* substitution, even in norbornyl

high *exo/endo* rate ratio, *exo* stereochemistry of substitution) are uniquely associated with the nonclassical structure of the norbornyl cation, such characteristics should not be exhibited by the essentially classical tertiary norbornyl cations.

It was previously reported that both the reactivities<sup>6</sup> and the *exo/endo* rate ratios<sup>7</sup> exhibit no significant difference in behavior in the secondary and tertiary norbornyl derivatives examined. The present communication examines the stereochemical behavior of several norbornyl derivatives in their solvolysis in 65% aqueous diglyme, in the absence and presence of

TABLE I

PRODUCTS OF SOLVOLYSIS OF SEVERAL NORBORNYL DERIVATIVES IN 65% AQUEOUS DIGLYME IN THE PRESENCE OF 1.8 M SODIUM BOROHYDRIDE

Compound <sup>a</sup>	NaBH <sub>4</sub> , M	R	Products, <sup>b</sup> %					
								
	0	H	80	0 <sup>d</sup>			6	6
	1.8	H	57	0 <sup>d</sup>	35	0.5	3	3
	0	H	95	0 <sup>d</sup>			2.5	2.5
	1.8	H	56	0 <sup>d</sup>	42	0.6	0.8	0.8
	0	CH <sub>3</sub>	22 <sup>c</sup>				68	7
	1.8	CH <sub>3</sub>	5 <sup>c</sup>		56	0 <sup>d</sup>	34	4
	0	CH <sub>3</sub>	40 <sup>c</sup>				54	4
	1.8	CH <sub>3</sub>	7 <sup>c</sup>		65	0 <sup>d</sup>	19	2

<sup>a</sup> The solutions were 0.01–0.02 M in the compound and 0.04 M in sodium hydroxide or 1.8 M in sodium borohydride. <sup>b</sup> The yields reported are actual yields (not normalized) relative to internal standards. A Perkin-Elmer No. 226 temperature-programmed capillary gas chromatograph was used. The essential absence of products resulting from attack on the isomeric secondary ions was established.

<sup>c</sup> This alcohol has been assigned the *exo*-hydroxyl structure by J. A. Berson (ref. 3) and the *endo*-hydroxyl structure by W. Hückel and D. Volkmann, *Ann.*, **664**, 31 (1963). <sup>d</sup> It was established that the presence of this component in analytically significant quantities (0.5% or greater) could be detected by the procedures utilized.

derivatives containing *gem*-dimethyl groups in the 7-position, attributed to shielding of the *endo* direction by the nonclassical bond.<sup>2,3</sup>

The presence of a methyl, phenyl, and anisyl group at the 2-position should greatly stabilize the norbornyl cation and give a family of carbonium ions of increasing stability. It has been suggested that such tertiary cations should be sufficiently stable as to require little or no participation by the 1,6-bonding pair.<sup>4,5</sup> It follows that if the above characteristics (high rates,

1.8 M sodium borohydride. The latter has previously been shown to be a good trap for carbonium ions.<sup>8</sup> The results are summarized in Table I.

It is of considerable interest that the Wagner-Meerwein related pair of derivatives (1-methyl-*exo*-norbornyl tosylate and 2-methyl-*exo*-norbornyl chloride; *exo*-fenchyl tosylate and  $\alpha$ -fenchene hydrochloride) solvolyzes in each pair to give essentially the same products, derived from the same tertiary carbonium ion.<sup>9</sup> No products corresponding to the secondary ion could be identified. It therefore appears that the secondary derivatives ionize directly to the same tertiary ion produced in the ionization of the tertiary derivative (I, II).

(6) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *ibid.*, **86**, 1247 (1964).

(7) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *ibid.*, **86**, 1248 (1964).

(8) H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962).

(9) The same result has been observed for the isobornyl chloride–camphene hydrochloride pair: P. Beltramé, C. A. Bunton, A. Dunlop, and D. Whittaker, *J. Chem. Soc.*, 658 (1964).

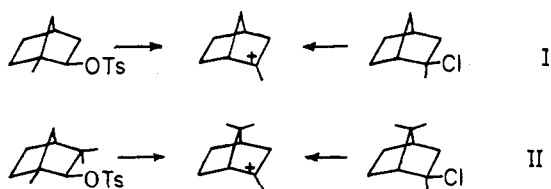
(1) F. Brown, E. D. Hughes, C. K. Ingold, and J. F. Smith, *Nature*, **168**, 65 (1951).

(2) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147, 1154 (1952).

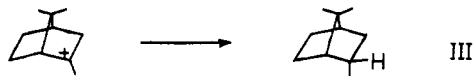
(3) For an excellent summary of the data and detailed interpretation in terms of the nonclassical concept, see J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 3.

(4) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, p. 62.

(5) H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, **86**, 5003 (1964); H. C. Brown and M.-H. Rei, *ibid.*, **86**, 5004 (1964).



It is of major importance that both the 2-methylnorbornyl and the 2,7,7-trimethylnorbornyl cations undergo reaction with borohydride predominantly from the *exo* direction (III). Consequently, the tertiary



2-methylnorbornyl derivatives exhibit all of the characteristics (fast rates, high *exo/endo* rate ratios, and *exo* substitution) previously considered to be diagnostic of the nonclassical structure for the secondary norbornyl cation. Clearly it is necessary to give careful consideration to the question whether all norbornyl cations, secondary and tertiary, are classical, with the above properties being characteristic of bicyclic cations, or whether all norbornyl cations, secondary and tertiary, possess nonclassical structures.

(10) Ethyl Corporation Fellow, 1963-1964.

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### Solvolysis of 1-(*p*-Anisyl)camphene Hydrochloride in the Presence of Sodium Borohydride. Predominant *exo* Substitution in the Highly Stabilized 2-(*p*-Anisyl)bornyl Cation

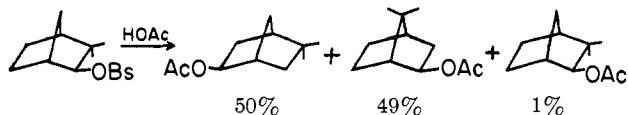
Sir:

It has been argued by Professor P. von R. Schleyer that the nonclassical structure for the norbornyl cation is required by his observation that the rates of solvolysis of *exo*-norbornyl derivatives are faster than those calculated with the aid of his proposed semiempirical correlation.<sup>1</sup> On the other hand, Professor J. A. Berson has concluded that kinetics cannot resolve the question, but that the nonclassical structure is required by exclusive *exo* substitution in norbornyl systems containing *gem*-dimethyl substituents.<sup>2,3</sup>

(1) C. S. Foote, *J. Am. Chem. Soc.*, **86**, 1853 (1964); P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

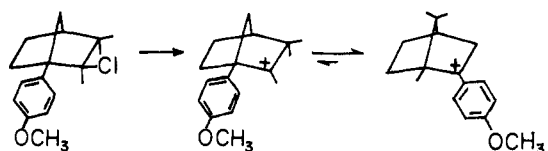
(2) J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 3.

(3) Although it is probably true that such cations substitute predominantly *exo*, a search of the literature reveals very little solvolytic data obtained under truly kinetically controlled conditions on which to base this conclusion. There is no evidence that the thoroughly studied rearrangement of camphene hydrochloride to isobornyl chloride involves dissociated, independent ions. The solvolysis of isobornyl and bornyl chlorides under kinetically controlled conditions yields derivatives of camphene hydrate—*exo* substitution in a simple norbornyl system [P. Beltramé, C. A. Bunton, A. Dunlop, and D. Whitaker, *J. Chem. Soc.*, 658 (1964)]. Only the study of the solvolysis of *exo*-camphenyl and apoisobornyl brosylates [A. Colter, Ph.D. Thesis, University of California at Los Angeles, 1956] provides evidence for kinetically controlled *exo* substitution in a norbornyl derivative containing *gem*-dimethyl substituents in the 7-position. The 50% yield of



The observation reported in the previous communication that borohydride reacts with the tertiary 2,7,7-trimethylnorbornyl cation to give essentially exclusive *exo* substitution<sup>4</sup> made it desirable to examine the stereochemical behavior of a related ion highly stabilized by the anisyl group. It has been concluded that the 1,2-dianisylnorbornyl cation exists as an equilibrating pair of classical ions<sup>5</sup> with no significant participation of the 1,6-bonding pair with the highly stabilized carbonium center.<sup>6</sup>

Since solvolysis of a Wagner-Meerwein related pair proceeds to give products derived from the more stable of the two possible ions, we undertook a study of the solvolysis of 1-(*p*-anisyl)camphene hydrochloride (I)<sup>7</sup> in the presence of borohydride.<sup>8</sup>



The 1-(*p*-anisyl)camphene hydrochloride was dissolved in dry diglyme and a solution of sodium borohydride in water was added to give a reaction mixture 70% (by volume) aqueous diglyme, 1.8 *M* sodium borohydride, 0.1 *M* chloride. After 1 hr. at 25°, sodium hydroxide was added to separate the diglyme layer, pentane was added, and the diglyme was removed by washing with ice-water. The internal standard, 1,2-diphenylethane, was added, and the solution was analyzed on the Perkin-Elmer No. 226 temperature-programmed capillary gas chromatograph using both a 150-ft. polyphenyl ether and a 150-ft. Apiezon L column. All peaks were compared with authentic samples on each of the two columns. The results of duplicate reactions are summarized in Table I.

The identity of the *p*-bornylanisole and isobornylanisole was confirmed by isolating material from a large-scale solvolysis, treating the crude reaction

*β*-fenchoisocamphoryl acetate must arise from a 6,2-hydride shift so rapid that it can compete with the reaction of the carbonium ion with solvent. The rapidity of this hydride shift is all the more remarkable if we recognize that it is believed to occur in the same direction as the bond in the presumed nonclassical intermediate. Normally it is considered that the nonclassical



structure protects the ion from such attack in the *endo* direction.

The situation is rendered more complex by recent observations on the acetolysis of *β*-nopinyl brosylate [E. C. Friedrich and S. Winstein, *J. Am. Chem. Soc.*, **86**, 2721 (1964)]. Here acetolysis is postulated to proceed through the nonclassical *β*-nopinyl cation. Although the nonclassical ion



should direct substitution only to the *endo* direction, and protect the ion from *exo* substitution, the kinetics indicate the formation of some 25% of *exo* brosylates. We are faced with the highly interesting problem of how the weakly nucleophilic brosylate anion moves from the *endo* position to return to form *exo* brosylate.

(4) H. C. Brown and H. M. Bell, *ibid.*, **86**, 5006 (1964).

(5) P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *ibid.*, **85**, 479 (1963).

(6) S. Winstein, Reaction Mechanisms Conference, Brookhaven, N. Y., Sept. 5, 1962.

(7) H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, **86**, 5003 (1964).

(8) H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962).