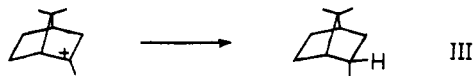


It is of major importance that both the 2-methylnorbornyl and the 2,7,7-trimethylnorbornyl cations undergo reaction with borohydride predominantly from the *exo* direction (III). Consequently, the tertiary



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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RECEIVED JULY 24, 1964

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

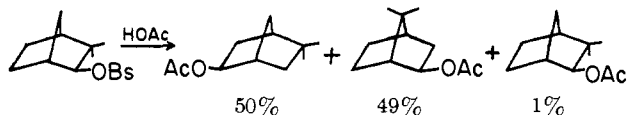
Sir:

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.¹ 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.^{2,3}

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

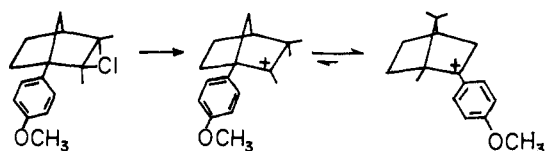
(2) J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 3.

(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* substitution⁴ 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 ions⁵ with no significant participation of the 1,6-bonding pair with the highly stabilized carbonium center.⁶

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)⁷ in the presence of borohydride.⁸



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-fenchosicamphoryl 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).

TABLE I

Products	Reaction 1	Reaction 2
<i>p</i> -Anisyltricyclene	0.3%	0.5%
2-(<i>p</i> -Anisyl)bornylene	1	1
1-(<i>p</i> -Anisyl)camphene	24	22
1-(<i>p</i> -Anisyl)isocamphene	0	0
<i>p</i> -Bornylanisole	66	64
<i>p</i> -Isobornylanisole	10	10

product with diborane to remove unsaturated materials, and isolating the saturated products by distillation. N.m.r. examination confirmed the presence of a mixture of *p*-bornyl- and *p*-isobornylanisole, with the former in large excess.

Consequently, the solvolysis of 1-(*p*-anisyl)camphene hydrochloride in the presence of borohydride produces 23% 1-(*p*-anisyl)camphene, presumably the result of the elimination of a proton from the highly hindered 1-(*p*-anisyl)hydrocamphenyl cation, 65% *p*-bornylanisole, arising from *exo* substitution of borohydride on the 2-(*p*-anisyl)bornyl cation, and 10% isobornylanisole, arising from *endo* substitution.

It follows that even this highly stabilized, presumably classical, norbornyl cation reacts to give predominantly *exo* substitution (*exo/endo* = 87:13), in spite of the steric influence of the *gem*-dimethyl substituents in the 7-position.

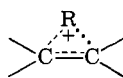
As was pointed out earlier⁷ the proposed nonclassical structure for the norbornyl cation has been justified on the basis of unusually high rates, high *exo/endo* rate ratios, and *exo* stereochemistry of substitution. On this basis a change in these characteristics would have been anticipated for tertiary norbornyl derivatives, containing substituents such as methyl, phenyl, and anisyl at the carbonium center which should form cations of increasing stability. However, no major changes in the relative rates,⁹ the *exo/endo* rate ratios,¹⁰ or the stereochemistry of substitution⁴ have been observed. It must be concluded either that these characteristics are not uniquely associated with the proposed nonclassical structure for the norbornyl cation and are characteristic of classical bicyclic cations, or that all norbornyl cations, highly stabilized or not, are nonclassical in spite of the evidence to the contrary.^{5,6}

If bicyclic cations are not resonance-stabilized species, how can we account for the marked preference for *exo* substitution? One possibility which should receive careful consideration is the proposal by Professor S. Winstein that the stereochemical behavior of a bridged ion may be simulated by an equilibrating pair of isomeric cations.¹¹ It is evident that this proposal

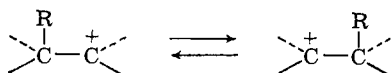
(9) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 1247 (1964).

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

(11) S. Winstein and B. K. Morse, *ibid.*, **74**, 1133 (1952), footnote 13: "Just as in the case of functional neighboring groups [S. Winstein, *Bull. soc. chim. France*, **18**, 55 (1951), and S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 828 (1948)], it must be kept in mind that the stereochemical results corresponding to formation and opening of



may, in some cases, be simulated by a dynamic pair of isomeric cations



would resolve the evident difficulty in reconciling the marked preference for *exo* substitution with the absence of any data supporting any unusual stability for norbornyl cations and the absence of any data (such as the effect of substituents) supporting the presence of electron deficiencies in the 1- and 6-positions, as required by the proposed nonclassical structure.

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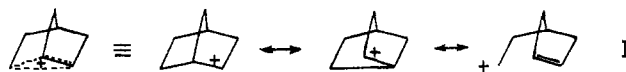
RECEIVED JULY 24, 1964

Comparison of the Effect of Substituents at the 2-Position of the Norbornyl System with Their Effect in Representative Secondary Aliphatic and Alicyclic Derivatives. Evidence for the Absence of Nonclassical Stabilization of the Norbornyl Cation

Sir:

Previous studies now appear to establish that tertiary norbornyl cations are essentially classical in nature.¹ We are left with the problem of the structure of secondary cations of the norbornyl type.²

The nonclassical formulation of the norbornyl cation requires that positive charge be delocalized to the 1- and 6-positions (I).



It has been previously demonstrated that methyl substituents in the 6-position fail to stabilize the electron-deficient transition state or intermediate.^{3,4} Similarly, in the symmetrical systems 1,2-di-*p*-anisylnorbornyl cation and 1,2-dimethyl-*exo*-norbornyl *p*-nitrobenzoate, the substituent in the 1-position fails to stabilize the electron-deficient intermediate or transition state.^{1a,i,5} In the present study we turn our attention to an experimental test of a major consequence of the nonclassical formulation—decreased electron deficiency at the 2-position of the norbornyl cation or transition state resulting from the proposed delocalization of the charge to the 1- and 6-positions.

Methyl and phenyl groups at a carbonium center stabilize the electron-deficient species because of their ability to supply electrons to the electron-deficient center. The greater the electron deficiency, the greater

(1) (a) P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 479 (1963); (b) P. Beltramé, C. A. Bunton, A. Dunlop, and D. Whittaker, *J. Chem. Soc.*, 658 (1964); (c) C. A. Bunton, "Nucleophilic Substitution at a Saturated Carbon Atom," Elsevier Publishing Co., New York, N. Y., 1963, p. 82; (d) H. C. Brown and F. J. Chloupek, *J. Am. Chem. Soc.*, **85**, 2322 (1963); (e) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *ibid.*, **86**, 1246 (1964); (f) *ibid.*, **86**, 1247 (1964); (g) *ibid.*, **86**, 1248 (1964); (h) H. C. Brown and H. M. Bell, *ibid.*, **86**, 5003 (1964); (i) H. C. Brown and M.-H. Rei, *ibid.*, **86**, 5004 (1964); (j) H. C. Brown and H. M. Bell, *ibid.*, **86**, 5006 (1964); (k) H. M. Bell and H. C. Brown, *ibid.*, **86**, 5007 (1964).

(2) S. Winstein and D. Trifan, *ibid.*, **74**, 1147, 1154 (1952).

(3) D. E. McGreer, *Can. J. Chem.*, **40**, 1554 (1962).

(4) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, in press.

(5) Modest rate enhancements, involving factors of 3.9 and 42, respectively, are observed in the ethanolysis at 25° of 1-phenyl- and 1-methyl-*exo*-norbornyl tosylate (research in progress with M.-H. Rei). However, in these cases the solvolyses proceed with rearrangement to the more stable tertiary cations, so that the results are not applicable to the question of whether carbon participation is significant in symmetrical norbornyl systems not involving rearrangement to more stable structures.