

Concerning rule 3, the positive charge of the molecular ion is not concentrated at a point near one end of the molecule, as in normal paraffins,⁴ which are ordered parallel to the electrical field lines,⁵ but is distributed over the points of the branches. This reduces the fragmentation probability per branch as compared with a singly branched or a normal paraffin.

Concerning rule 4, the same argument holds as mentioned under (3), but the bonds of quaternary carbon atoms are so weak that field dissociation is possible to a large extent.

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(4) H. D. Beckey, *Z. Naturforsch.*, **19a**, 71 (1964).

(5) H. D. Beckey, *ibid.*, **17a**, 1103 (1962).

H. D. Beckey

Institut fuer Physikalische Chemie der Universität Bonn
Bonn, West Germany

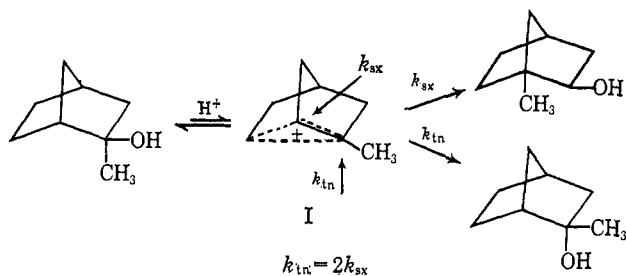
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Equilibration of 2-Methylnorbornanols. A Fast Acid-Catalyzed Conversion of 2-Methyl-*exo*-norbornanol into 2-Methyl-*endo*-norbornanol

Sir:

It is our pleasure to report that the acid-catalyzed equilibration of 2-methyl-, 1,2-dimethyl-, and 2-phenyl-*exo*-norbornanols reveals approximately equal stabilities for the *exo* and *endo* tertiary isomers. These results render untenable the argument that the similarity in the *exo/endo* rate ratios observed in the solvolysis of norbornyl, 2-methylnorbornyl, and 2-phenylnorbornyl derivatives¹ results from a fortuitous cancellation of increasing steric assistance in this series with decreasing σ participation by the 1,6-electron pair.²

We further wish to report that under the influence of aqueous acids 2-methyl-*exo*-norbornanol is converted into the *endo* isomer, 2-methyl-*endo*-norbornanol, at a rate twice that at which it forms the *exo* derivative, 1-methyl-*exo*-norbornanol. This result does not appear to be compatible with the formulation of the carbonium ion intermediate as a bridged, nonclassical species (I).



The equilibration was initially carried out by stirring each of the alcohols dissolved in cyclohexane with an equal volume of aqueous sulfuric acid (2, 4, and 6 *M*) at room temperature. Aliquots were removed at

(1) H. C. Brown, F. J. Chloupek, and M. -H. Rei, *J. Am. Chem. Soc.*, **86**, 1248 (1964).

(2) P. von R. Schleyer, Symposium on Linear Free Energy Correlations, U. S. Army Research Office, Durham, N. C., Oct 19-21, 1964. See discussion in the review by M. J. S. Dewar and A. P. Marchand, *Ann. Rev. Phys. Chem.*, **16**, 321 (1965).

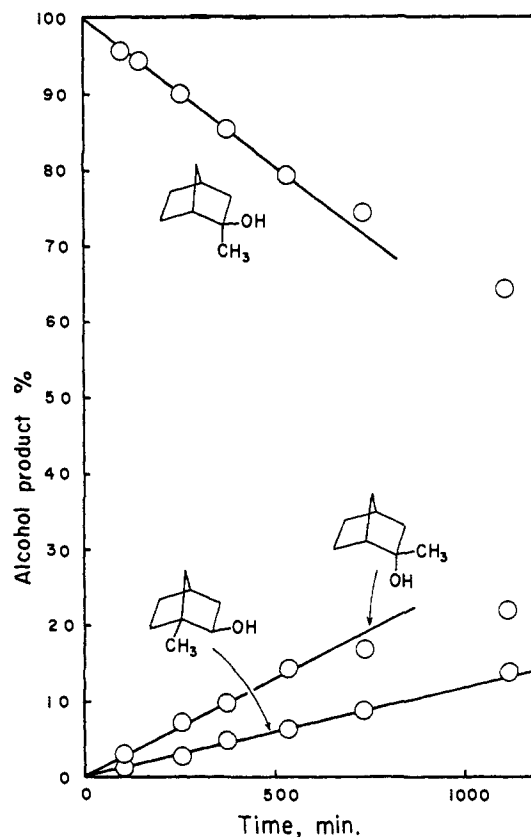


Figure 1. Acid-catalyzed solvolysis at 25° of 2-methyl-*exo*-norbornanol in 60% aqueous dioxane, 1.75 *M* in perchloric acid.

appropriate intervals of time and analyzed by capillary gas chromatography. We were surprised by the observation that 2-methyl-*endo*-norbornanol was being formed at twice the rate of 1-methyl-*exo*-norbornanol in the initial phases of the equilibration of 2-methyl-*exo*-norbornanol.³ In order to eliminate the possibility that this was an artifact of the heterogeneous conditions, we repeated a number of the experiments utilizing the homogeneous conditions adopted by Bunton for his oxygen-18 exchanges, namely 1.75 *M* perchloric acid in 60% aqueous dioxane.⁴ As shown by the data in Figure 1, the results fully confirm the conclusion that the cation from 2-methyl-*exo*-norbornanol undergoes substitution by the solvent at the *endo* tertiary position at a rate twice that at which it undergoes substitution at the *exo* secondary position.

At equilibrium⁵ we observed that the ratio of 1-methyl-*exo*-, 2-methyl-*exo*-, and 2-methyl-*endo*-norbornanol is 3.6:1.3:1.00. In the case of 1,2-dimethyl-*exo*-norbornanol, the *exo/endo* product ratio is 2.6. In the 2-phenyl system, the *exo/endo* product ratio for the tertiary alcohols³ is 2.1. In all cases the equilibrium value was approached starting with two or more isomeric alcohols.

The *exo/endo* equilibrium ratio of 1.3 obtained for 2-methyl-*exo*- and -*endo*-norbornanols is actually in good

(3) Perhaps even more remarkable, either isomer of 2-phenyl-2-norbornanol could be converted into the equilibrium mixture of tertiary isomers before any significant amount of the secondary isomer appeared.

(4) C. A. Bunton, K. Khaleeluddin, and D. Whittaker, *Tetrahedron Letters*, 1825 (1963).

(5) The rate of formation of 1-methyl-*endo*-norbornanol was very slow. Consequently, we were content to establish essential equilibrium among the more reactive isomers.

agreement with the *exo/endo* distribution of 4 at 100° for 2-norbornanol⁶ (8 at 25°, extrapolated from data at 100 and 116°), and 5 at 50°⁷ (estimated as 5.6 at 25°) for 2-methylnorbornane.

Let us consider possible explanations for the high *exo/endo* rate ratios in tertiary norbornyl derivatives in the light of the present results.

(1) The high tertiary *exo/endo* ratios are due to differences in ground-state energies.^{2,8} Since the present data reveal that the *exo* and *endo* tertiary isomers start at the same ground-state energy,⁹ this possibility is no longer tenable.

(2) The *exo* and *endo* tertiary ground states are comparable in energy, but both are quite strained. This strain is relieved more effectively by departure of an *exo* leaving group, rather than an *endo*. This possibility is refuted by the present observation that the secondary derivative, 1-methyl-2-norbornanol, which should be an essentially strain-free material as far as the substituent groups are concerned, is only slightly more stable than either of the tertiary isomers.

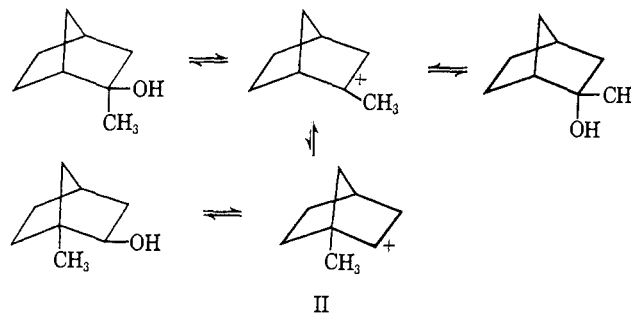
(3) The high *exo/endo* rate ratios in the tertiary norbornyl derivatives are due to participation in the *exo* isomer. This seems unlikely even to nonclassical supporters,⁸ and is rendered highly questionable both by the earlier failure to observe any significant effect of a 1-methyl substituent in the tertiary derivatives¹¹ and by the excellent correlation of the substituted 2-arylnorbornyl derivatives with the σ^+ constants.¹²

(4) The high *exo/endo* rate ratios in these tertiary derivatives are due to steric hindrance to *endo* ionization. Unless we wish to have recourse to some new explanation or some new effect not yet available, this would appear to be the sole remaining possibility.

In the acid-catalyzed treatment of 2-methyl-*exo*-norbornanol, the carbonium ion intermediate must be formed and reconverted back to the *exo* tertiary alcohol many times before the ion is finally captured by the solvent molecules to form the less reactive *endo* tertiary or *exo* secondary alcohols.⁴ Nonclassical σ bridging was postulated in the norbornyl cation primarily to account for its remarkable retention of *exo* stereochemistry.^{13,14} Consequently, it appears difficult to rationalize the more rapid substitution of the solvent at the *endo* tertiary position in terms of a σ -bridged structure for the intermediate (I).¹⁵

On the other hand, the transformations are readily rationalized in terms of a classical 2-methylnorbornyl

cation in mobile equilibrium with a small concentration of the less stable secondary 1-methylnorbornyl cation (II).



Secondary and tertiary norbornyl derivatives exhibit a remarkable similarity in their behavior, including their rates relative to an external standard, their *exo/endo* rate ratios, and their preference for *exo* substitution.¹⁶ The present results establish that the ground-state energies for the *exo* and *endo* tertiary isomers examined are quite similar and render untenable explanations based on an assumed or estimated higher ground-state energy for the tertiary *exo*-norbornyl derivatives.^{2,8}

(16) For a summary of the data, with references, see H. C. Brown, *Chem. Brit.*, 199 (1966).

(17) Research assistant on a grant (G 19878) supported by the National Science Foundation.

Min-Hon Rei,¹⁷ Herbert C. Brown
R. B. Wetherill Research Laboratory
Purdue University, Lafayette, Indiana 47907
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Solvolysis of Substituted 2-Aryl-*exo*-norbornyl Chlorides. Application of the Hammett Correlation as a Test for σ Participation in the Norbornyl System

Sir:

We wish to report that the rates of solvolysis of substituted 1-arylcyclopentyl and 2-aryl-*exo*-norbornyl chlorides both yield excellent linear plots *vs.* the σ^+ constants. Consequently, there is no evidence for significant participation by the 1,6-electron pair of the norbornyl system over a range of reactivity of the carbonium ion center of 10⁷.

The Goering-Schewene diagram¹ makes it clear that the factor responsible for the difference in energy between the *exo* and *endo* transition states must likewise be responsible for the stereoselectivity resulting in the almost exclusive formation of *exo* product. This factor might be (1) stabilization of the *exo* transition state by bridging, (2) destabilization of the *endo* transition state by steric strain, (3) a combination of (1) and (2), or (4) some new phenomenon not yet recognized in theory.^{2,3}

The heart of the norbornyl problem appears to involve either the demonstration of nonclassical resonance stabilization of the *exo* transition state or the demon-

(1) H. L. Goering and C. B. Schewene, *J. Am. Chem. Soc.*, **87**, 3516 (1965).

(2) For an excellent discussion of the implications of the Goering-Schewene diagram, see B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms," 1965, Interscience Publishers, Inc., New York, N. Y., 1966, Chapter I.

(3) H. C. Brown, *Chem. Brit.*, 199 (1966).

(6) F. Wilcox, Jr., M. Sexton, and M. F. Wilcox, *J. Org. Chem.*, **28**, 1079 (1963).

(7) N. A. Belikova, A. F. Platé, and K. E. Sterin, *Zh. Obshch. Khim.*, **34**, 126 (1964).

(8) G. D. Sargent, *Quart. Rev.* (London), **20**, 301 (1966).

(9) We are assuming that the steric requirements of the acyloxy and hydroxy groups are very similar in this system. This is supported by the similarity in the results for the equilibration of 2-norbornyl acetate¹⁰ with those for 2-norbornanol.⁶

(10) H. L. Goering and C. B. Schewene, *J. Am. Chem. Soc.*, **87**, 3516 (1965).

(11) H. C. Brown and M.-H. Rei, *ibid.*, **86**, 5004 (1964).

(12) H. C. Brown and K. Takeuchi, *ibid.*, **88**, 5337 (1966).

(13) T. P. Nevell, E. de Salas, and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939).

(14) J. A. Berson in "Molecular Rearrangements," Part I, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 130.

(15) The present phenomena are remarkably similar to the transformations observed by Cristol and his co-workers [*J. Am. Chem. Soc.*, **87**, 2870, 2879 (1965)] in the dibenzobicyclic [2.2.2]- and [3.2.1]octadienyl cations which led them to conclude that they were dealing with classical intermediates. See also J. Paasivirta, *Ann.*, **686**, 1 (1965).