

COMMUNICATIONS TO THE EDITOR

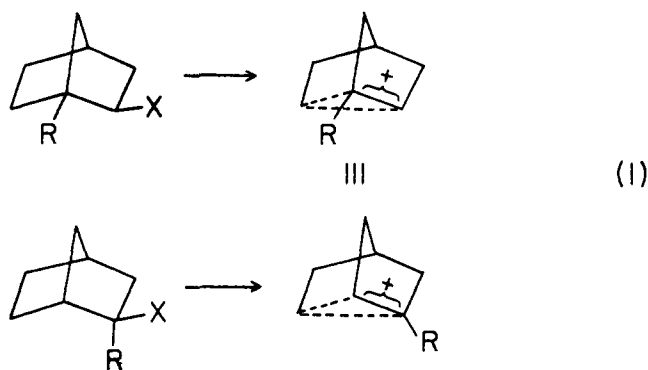
Synthesis and Rates of Ethanolysis of
2-Phenyl-*exo*-norbornyl Chloride. The
Question of a Nonclassical 1- and
2-Phenylnorbornyl Cation

Sir:

The rate of solvolysis of 2-phenyl-*exo*-norbornyl chloride at 25° is 10,000,000 times greater than that of the 1-phenyl-*exo*-norbornyl derivative. This vast difference in the effectiveness of a phenyl substituent in the 1- and 2-positions of the norbornyl system does not appear to be compatible with the formation of a highly stabilized nonclassical cation with its positive charge delocalized over the 1- and 2-positions.

Since the original proposal,¹⁻³ the nonclassical norbornyl cation has been widely utilized to interpret the reactions of bicyclic derivatives⁴ and the concept is intricately interwoven into the fabric of current theory.⁵ Nevertheless, the desirability of a critical re-examination of the concept has been urged.⁶

The nonclassical norbornyl cation distributes its positive charge equally over C-1 and C-2 of the norbornyl system. It would appear to be a consequence of the nonclassical proposal that a substituent in the 1- and 2-positions should have an identical effect on the stability of the nonclassical ion and very similar effects on the rates of solvolysis.⁷



A phenyl substituent in the 1-position increases the rate of solvolysis of *exo*-norbornyl tosylate by a factor of 3.9.⁸ Consequently, it would be predicted that a

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

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

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

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

(5) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(6) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, pp. 140-158, 174-178.

(7) The rates of reaction will depend primarily on the difference in energy between the initial and transition states. (Unless the substituent R is very bulky, large differences in the ground state energies would not be anticipated and will be ignored in this "first approximation" treatment.) In discussions of nonclassical ions it is commonly assumed that in an endothermic process, such as solvolysis, the transition state will resemble product (Hammond's postulate). Since the first product is presumed to be the nonclassical ion, it is customary to discuss the rates of solvolysis primarily in terms of the stabilities of the nonclassical ions which are presumed to be formed (ref. 5).

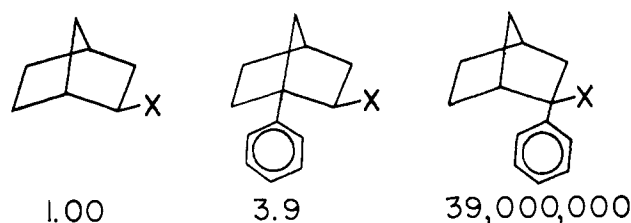
(8) P. Schleyer and D. C. Kleinfelter, Abstracts of Papers, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1960, p. 43P.

phenyl substituent in the 2-position should exert a similar effect (modified by the slightly higher ground state energy of the 2-phenyl derivative).

2-Phenyl-*endo*-norborneol,⁹ m.p. 44.2-44.6° (10 g.), from norcamphor and phenylmagnesium bromide, was treated for 1 hr. at 0° with 50 ml. of concentrated hydrochloric acid to form 8.5 g. of 2-phenyl-*exo*-norbornyl chloride, m.p. 44.5-46° (from pentane). *Anal.* Calcd. for C₁₃H₁₆Cl: C, 75.53; H, 7.27; Cl, 17.2. Found: C, 75.42; H, 7.27; Cl, 16.92. Hydrolysis in aqueous acetone containing sodium carbonate yielded an isomeric tertiary alcohol, m.p. 61-62° after vacuum sublimation, identified as 2-phenyl-*exo*-norborneol. *Anal.* Calcd. for C₁₃H₁₆O: C, 82.93; H, 8.57. Found: C, 82.73; H, 8.72.

The 2-phenyl-*exo*-norbornyl chloride was enormously reactive in solvolysis. Accordingly, the rates of ethanolysis were measured at -25°, $k_1 = 296 \times 10^{-6} \text{ sec.}^{-1}$, and at 0°, $k_1 = 9080 \times 10^{-6} \text{ sec.}^{-1}$. This leads to a calculated rate constant at 25° of $158,000 \times 10^{-6} \text{ sec.}^{-1}$, $\Delta H^* = 17.9 \text{ kcal./mole}$, and $\Delta S^* = -2.1$. For comparison, 1-phenyl-1-chlorocyclopentane, m.p. 16.5-18.5°, exhibits a rate of ethanolysis at 25° of $21,100 \times 10^{-6} \text{ sec.}^{-1}$, with $\Delta H^* = 18.9 \text{ kcal./mole}$ and $\Delta S^* = -9.1$.

It is evident that the phenyl substituent in the 2-position is enormously more effective in facilitating solvolysis than the phenyl group in the 1-position.



This result clearly requires that the solvolyses of 1- and 2-phenyl-*exo*-norbornyl derivatives do not proceed through transition states which closely resemble the postulated nonclassical intermediate (eq. 1).

To account for the minor effect of the phenyl group in the 1-position, in contrast to its enormous effect in the 2-, it appears necessary to assume that participation is not far along in the transition state for the acetolysis of the 1-phenyl derivative, although such participation must be well developed in the corresponding norbornyl derivative to be responsible for the observed high *exo-endo* rate ratio.³

It was previously noted that the 1,2-dianisylnorbornyl cation exists in sulfuric acid as a rapidly equilibrating pair of classical ions, and not as a single mesomeric species.¹⁰

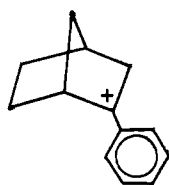
However, it has been argued that stabilized tertiary norbornyl cations, such as the 1,2-dianisylnorbornyl cation, should not require participation of the 1,6-bonding pair.¹¹ Indeed, it has been suggested that all relatively stable tertiary norbornyl cations possess essentially classical structures.¹²

(9) D. C. Kleinfelter and P. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961).

(10) P. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 479 (1963).

(11) S. Winstein, Reaction Mechanisms Conference at Brookhaven National Laboratory, Upton, N. Y., Sept. 5, 1962.

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



In view of this conclusion, the present results cannot be extrapolated to a consideration of the classical or nonclassical nature of the norbornyl cation itself.

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R. B. WETHERILL LABORATORY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

HERBERT C. BROWN
FRANK J. CHLOUPEK
MIN-HON REI

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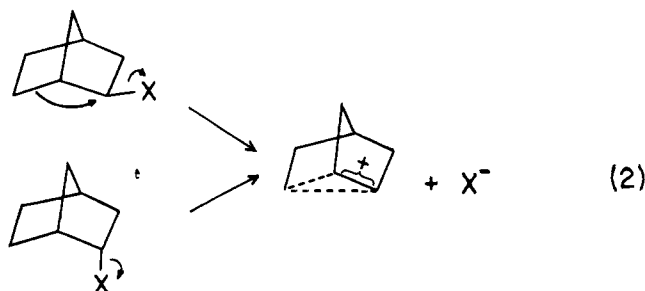
Comparison of the Rates of Solvolysis of Representative Norbornyl and Cyclopentyl Derivatives. A Critical Examination of Rates as a Basis for the Postulated Nonclassical Structure of Norbornyl Cations

Sir:

A critical examination of the huge mass of experimental data relating to the behavior of norbornyl derivatives reveals three major foundations for the



tives have been interpreted in terms of participation in the *exo*, but not in the *endo* (eq. 2).²



C. Stereochemistry of Substitution.—Exclusive *exo* substitution, even in norbornyl derivatives containing *gem*-dimethyl groups in the 7-position, has been interpreted as requiring shielding of the *endo* direction by partial bonding (eq. 3).^{2,3}

In the case of the 1,2-dianisylnorbornyl cation, direct nuclear magnetic resonance observation of the cation in sulfuric acid solution indicated that the ion exists as a rapidly equilibrating pair of classical ions, and not as a single mesomeric species.⁴ It has been proposed

TABLE I

RATES OF SOLVOLYSIS OF NORBORNYL AND CYCLOPENTYL DERIVATIVES

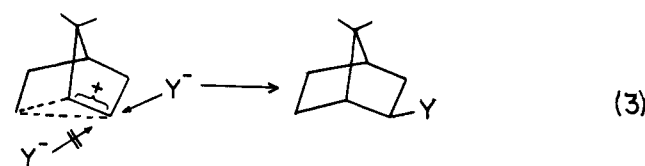
Y	X	Temp., °C.	Solvent	Rate constant, $k_1 \times 10^6 \text{ sec.}^{-1}$		Rate ratio norbornyl/cyclopentyl
				Norbornyl	Cyclopentyl	
H	OBs ^b	25	Methanol	166 ^f	42.5 ^f	3.9
H	OBs ^b	25	Ethanol	26.6 ^h	7.34 ^{i,k}	3.6
H	OBs ^b	25	Acetic acid	88.2 ⁱ	6.28 ⁱ	12.4
OBs	H	25	Methanol	0.374 ^f		(444) ^a
OBs	H	25	Acetic acid	0.252 ⁱ		(350) ^a
CH ₃	Cl	25	Ethanol	30.0 ^d	5.62 ^d	5.3
CH ₃	OPNB ^c	50	60% aq. dioxane	1.96 ^g	0.497 ^g	4.0
C ₆ H ₅	Cl	25	Ethanol	158,000 ^e	21,000 ^e	7.5
C ₆ H ₅	OPNB ^c	50	60% aq. dioxane	946 ^g	370 ^g	2.6

^a *exo-endo* ratio. ^b *p*-Bromobenzenesulfonate. ^c *p*-Nitrobenzoate. ^d H. C. Brown and F. J. Chloupek, *J. Am. Chem. Soc.*, **85**, 2322 (1963). ^e Ref. 8. ^f Present study. ^g Ref. 9. ^h Ref. 2. ⁱ S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1127 (1952). ^j H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956). ^k Estimate from the tosylate.

postulated existence of norbornyl cations as stabilized, nonclassical structures.

A. High Solvolysis Rates.—The rates of solvolysis of *exo*-norbornyl derivatives have been considered to be unusually fast and interpreted as requiring the formation of a stabilized mesomeric intermediate to provide the necessary driving force (eq. 1).¹

B. High *exo-endo* Rate Ratios.—The high *exo-endo* rate ratios for the solvolysis of norbornyl deriva-



(2) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1147, 1154 (1952).
(3) J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 3.
(4) P. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 479 (1963).

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