

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.

Acknowledgment.—This investigation was assisted by Project No. AT(11-1)-70, supported by the Atomic Energy Commission, and by Grant 19878, provided by the National Science Foundation.

R. B. WETHERILL LABORATORY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

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

RECEIVED JANUARY 6, 1964

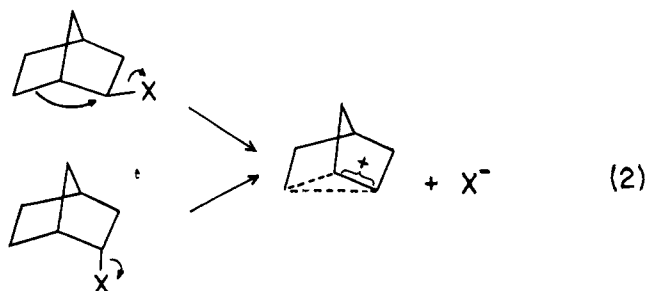
Comparison of the Rates of Solvolysis of Representative Norbornyl and Cyclopentyl Derivatives. A Critical Examination of Rates as a Basis for the Postulated Nonclassical Structure of Norbornyl Cations

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

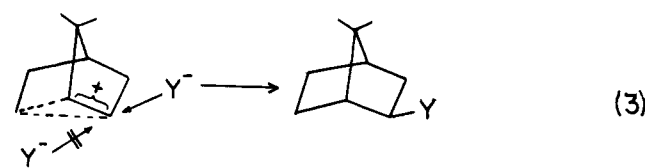
Y	X	Temp., °C.	Solvent	Rate constant, $k_1 \times 10^6 \text{ sec.}^{-1}$		Rate ratio norbornyl cyclopentyl
				Norbornyl	Cyclopentyl	
H	OBs ^b	25	Methanol	166 ^f	42.5 ^f	3.9
H	OBs ^b	25	Ethanol	26.6 ^h	7.34 ^{i,k}	3.6
H	OBs ^b	25	Acetic acid	88.2 ⁱ	6.28 ⁱ	12.4
OBs	H	25	Methanol	0.374 ^f		(444) ^a
OBs	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).

that the anisyl group at the 2-position stabilizes the carbonium ion so strongly that participation of the 1,6-bonding pair is not required.⁵ Indeed, Bunton has suggested that even a simple 2-methyl substituent converts the nonclassical norbornyl cation into an essentially classical 2-methylnorbornyl cation.⁶

In view of the difficulties which appear to prevent the direct physical observation of the parent norbornyl cation, we have undertaken an alternative approach to the problem. We are examining the rates, the *exo-endo* rate ratios, and the stereochemistry of substitution of stabilized tertiary norbornyl cations. It is evident that if the above characteristics are uniquely associated with the nonclassical structure of the norbornyl cation, then essentially classical tertiary norbornyl cations should not exhibit these characteristics.⁷

Alternatively, if these essentially classical tertiary ions exhibit these unique characteristics, then these properties cannot be used as the primary justification for the proposed existence of the norbornyl cation as a nonclassical structure.

The present communication reports our observations on the relative rates of reaction of norbornyl⁸ and cyclopentyl derivatives. The following communication reports our results on the *exo-endo* ratio.⁹ A subsequent communication will report our studies of the stereochemistry of substitution.¹⁰

The reactivities of norbornyl derivatives are frequently compared with those of the corresponding cyclohexane compounds.³ However, the norbornane system, with its opposed bonds, would appear to resemble cyclopentane more closely than the strain-free cyclohexane system.¹¹ Accordingly, data comparing the norbornyl compounds with the corresponding cyclopentyl derivatives are summarized in Table I.

2-Phenyl-*exo*-norbornyl chloride undergoes ethanolysis at a rate that is 7.5 times that of 1-phenylcyclopentyl chloride. Similarly, 2-methyl-*exo*-norbornyl chloride undergoes ethanolysis at a rate 5.3 times that of the cyclopentyl derivative. The corresponding factors for the solvolysis of the corresponding *p*-nitrobenzoates are slightly smaller.

exo-Norbornyl brosylate undergoes solvolysis at a rate approximately 350-444 times that of the *endo* isomer (Table I). If this factor is the result of participation, which should be essentially absent in the 2-phenyl and 2-methyl tertiary derivatives, we should expect to find an increase in the *exo*-norbornyl to cyclopentyl brosylate rate ratio to a value in the neighborhood of 2000 ($\sim 5 \times 400$). However, the observed factor, *exo*-norbornyl to cyclopentyl derivative, is of the

(5) S. Winstein, Reaction Mechanisms Conference at Brookhaven, Sept. 5, 1962.

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

(7) In this discussion we are adopting Bunton's conclusion (ref. 6) that the tertiary norbornyl cations are essentially classical. However, this position is not essential to our study. It is adequate to postulate that with increasing stability of the cationic center, such as is encountered in the series 2-norbornyl, 2-methylnorbornyl, 2-phenylnorbornyl, and 2-anisylnorbornyl, there will be decreasing participation of the 1,6-bonding pair with a resulting decrease in the magnitude of the nonclassical contribution to the structure of the cation. Under this condition, the characteristics now associated with the nonclassical structure of the norbornyl cation should reveal a marked decrease with the increasing classical nature of the cation, vanishing in a truly classical norbornyl cation derivative.

(8) See also H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 1246 (1964).

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

(10) Research in progress with H. M. Bell.

(11) For a discussion of the relative merits of cyclohexyl and cyclopentyl derivatives as models for the norbornyl system, see S. Winstein, *et al.*, *J. Am. Chem. Soc.*, **74**, 1127 (1952). However, the similarities in the observed magnitude of the carbonyl group stretching vibration (cyclopentanone, 1750 cm^{-1} ; cyclohexanone, 1717; norcamphor, 1751) support a preference for the cyclopentyl system as an appropriate model.

same order of magnitude as observed with the tertiary derivatives: 3.9 for methanolysis, 3.6 for ethanolysis, and 1.4 for acetolysis.¹²

All in all, the remarkable similarity in the rates of reaction of a given norbornyl derivative with its related cyclopentyl derivative, a similarity which is independent of major differences in the stabilities of the ions examined, argues strongly for the position that there is no major factor influencing the solvolysis of the secondary norbornyl derivative that is not present in the highly stabilized tertiary norbornyl cations. The data appear difficult to reconcile with the postulated formation of a highly stabilized nonclassical structure for the norbornyl cation, with classical or essentially classical structures for the tertiary norbornyl cations.

Acknowledgment.—This investigation was assisted by Project No. AT(11-1)-70, supported by the Atomic Energy Commission, and by Grant 19878, provided by the National Science Foundation.

(12) A possible difficulty with this argument should be pointed out. The observed rate of solvolysis of cyclopentyl brosylate may be enhanced by solvent participation, which is absent or negligible in the tertiary derivatives. However, it has been concluded that the rates of solvolysis of secondary sulfonates are only slightly dependent upon the nucleophilicity of the solvent [S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951)].

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PURDUE UNIVERSITY
LAFAYETTE, INDIANA

HERBERT C. BROWN
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Rates of Solvolysis of the *p*-Nitrobenzoates of *exo-endo* Tertiary Norborneols. A Critical Examination of the *exo-endo* Rate Ratio as a Basis for the Postulated Nonclassical Structure of the Norbornyl Cation

Sir:

We wish to report that the rates of solvolysis of the *p*-nitrobenzoates of several isomeric tertiary norborneols exhibit high *exo-endo* ratios of the same order of magnitude as those observed in the solvolysis of representative secondary norbornyl derivatives. Since it is now believed that these tertiary norbornyl derivatives undergo ionization to classical tertiary cations,^{1,2} it would appear that a high *exo-endo* ratio does not provide a unique basis for concluding that a given system undergoes ionization to a nonclassical norbornyl cation.

exo-Norbornyl brosylate undergoes acetolysis at a rate some 350 times greater than that of the *endo* isomer.³ This is a phenomenon of some generality, with the observed *exo-endo* ratio varying from a low of 13 for the *exo*-trimethylene-2-norbornyltosylates⁴ to a high of 1230 for the 3,3-dimethyl-2-norbornyl brosylates.⁵⁻⁷

The greater rate of the *exo* isomer has been attributed to its more favorable geometry for participation of the 1,6-bonding pair in the ionization stage (eq. 1).

In the *endo* isomer the 1,6-electron pair is not in position to participate (eq. 2).

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

(2) See discussion in preceding communication: H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 1247 (1964).

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

(4) P. Schleyer, Ph.D. Thesis, Harvard University, 1956.

(5) A. Colter, Ph.D. Thesis, University of California at Los Angeles, 1956.

(6) For a summary of the data, see J. A. Berson, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 3.

(7) This discussion is necessarily restricted to the titrimetric rate ratios, since polarimetric rate data (ref. 3) are not generally available.