

shaped structures, which can interfere with both the solvation of the anion and its departure.<sup>13,14</sup>

(13) This conclusion is reinforced by the observation that there appears to be a common pattern of reactivity for the bicyclo[3.3.0]octane, norbornane, and *endo*-5,6-trimethylenenorbornane systems which extends to the solvolytic results: H. C. Brown, W. J. Hammar, J. H. Kawakami, I. Rothberg, and D. L. Vander Jagt, *J. Am. Chem. Soc.*, **89**, 6381 (1967).

(14) J. P. Schaefer and C. A. Flegal, *ibid.*, **89**, 5729 (1967).

(15) Research assistant, 1964–1966, on a grant (G 19878) from the National Science Foundation; General Electric Company Fellow at Purdue University, 1966–1967.

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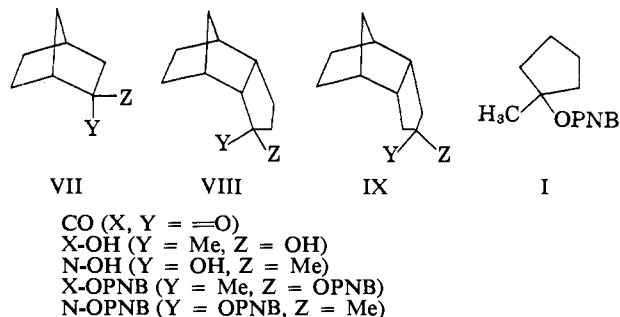
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### Rates of Solvolysis of the *p*-Nitrobenzoates of Tertiary 8- and 9-Methyl-*endo*-5,6-trimethylenenorbornanols. Evidence for Steric Hindrance to Ionization in the *endo* Derivatives

Sir:

An *exo:endo* rate ratio of 4300 is observed in the solvolysis of the epimeric *p*-nitrobenzoates of *endo*-5,6-trimethylene-8-methyl-8-norbornanol (VIII). For the more remote 9 derivatives (IX), an *exo:endo* rate ratio of 19 is observed. In both cases the *exo* isomer exhibits a rate that is very similar to that of the model compound, 1-methylcyclopentyl *p*-nitrobenzoate (I). Consequently, the high *exo:endo* rate ratios in these derivatives apparently arise primarily as a result of markedly decreased rates for the *endo* isomers.



requires that the effect should be considerably reduced at the more remote 9 position, and the epimeric IX-OPNB's were prepared to test this conclusion.

Hydrogenation of *endo*-dicyclopentadiene over P-2 nickel boride<sup>3</sup> afforded *endo*-5,6-trimethylene-8-norbornene, mp 48.5–50°. Hydroboration–oxidation (H<sub>2</sub>-CrO<sub>4</sub>) yielded VIII-CO, mp 98–99°, and IX-CO, mp 105–105.5°, in a 60:40 ratio, quantitatively separated with sodium bisulfite. Treatment with methylmagnesium iodide gave the *endo* tertiary alcohols, VIII-N-OH, mp 59–60°, and IX-N-OH, mp 78–79°. The *exo* alcohols were obtained by dehydration to the olefins and epoxidation, followed by reduction with lithium aluminum hydride: VIII-X-OH, mp 77–78°; IX-X-OH, mp 113–113.5°. The *p*-nitrobenzoates were prepared in the usual manner<sup>1</sup> and the rates of solvolysis were determined in 80% aqueous acetone (Table I).

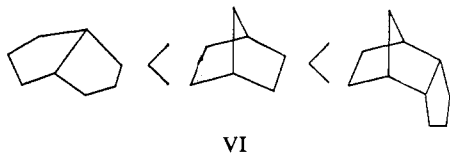
The products formed in the solvolysis of VIII-OPNB were determined in 60% acetone in the presence of 10%

Table I. Rates of Solvolysis of Tertiary Methyl *p*-Nitrobenzoates of the *endo*-5,6-Trimethylenenorbornane System

Compd <sup>a</sup>	Mp, °C	$k_1 \times 10^6 \text{ sec}^{-1}$					Rel rates, 25°	<i>exo:endo</i> rate ratios, 25°
		25° (calcd)	75°	100°	125°	150°		
I	82–83	$2.11 \times 10^{-3}$					1.00	
VIII-X-OPNB	120–122	$5.38 \times 10^{-3}$	5.79	93.4			2.55	4300
VIII-N-OPNB	80–82	$1.25 \times 10^{-6}$			1.10	12.1	0.0006	
IX-X-OPNB	137–138	$1.99 \times 10^{-3}$		16.9	162		0.94	
IX-N-OPNB	127–128	$1.06 \times 10^{-4}$			29.4	260	0.05	19

<sup>a</sup> All new compounds gave spectral and microanalytical data consistent with the proposed structure.

An examination of molecular models indicates that the U-shaped character of the bicyclic structures becomes enhanced in the series VI. We previously estab-



lished that the *exo:endo* rate ratio for the epimeric *p*-nitrobenzoates of *cis*-bicyclo[3.3.0]octan-2-ol is 17,<sup>1</sup> considerably less than the value of 885 observed for 2-norbornyl<sup>2</sup> (VII). Accordingly, we undertook to synthesize the epimeric VIII-OPNB's in order to test the deduction that the rate of VIII-N-OPNB should be very low, leading to a high *exo:endo* rate ratio. The theory

(1) H. C. Brown and W. J. Hammar, *J. Am. Chem. Soc.*, **89**, 6378 (1967).

(2) This value is for 80% acetone to provide comparable data for a common solvent.

excess sodium acetate. The results are summarized in Table II.

It should be noted that only the *exo* alcohol is formed in significant amounts in the solvolysis. (The 1% *endo* alcohol from VIII-N-OPNB probably arises from a small amount of competing acyl oxygen fission.)

In contrast to the bicyclo[3.3.0]octane system, where the rate effects were sufficiently small as to require great caution in their interpretation,<sup>1</sup> the present results reveal large effects, which permit relatively unambiguous conclusions.

It appears possible to conclude that  $\sigma$  participation cannot contribute significantly to the high *exo:endo* ratio observed<sup>5</sup> for VIII-X-OPNB. First, in VIII-X-

(3) H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, **85**, 1004 (1963).

(4) H. C. Brown and C. P. Garg, *ibid.*, **83**, 2951 (1961).

(5) It has been suggested that torsional effects may contribute to the observed *exo:endo* rate ratio in norbornyl derivatives: P. von R. Schleyer, *ibid.*, **89**, 701 (1967). However, such effects would not be expected to make a major contribution to the *exo:endo* rate ratio in the present system.

OPNB the 4-5 bond is in a very poor position geometrically to participate. Participation would involve resonance with a very highly strained tetracyclic cation. No rearrangements to this tetracyclic structure are observed in the solvolysis of the tertiary (Table II) or the secondary derivatives. The high *exo:endo* ratio arises not as a result of any very high rate for the *exo* isomer, compared to I, but because of a greatly reduced rate for the *endo*.

Table II. Products in the Solvolysis of VIII-OPNB

Compd	Temp, °C				
		HO-CH <sub>3</sub>	CH <sub>3</sub> -OH	CH <sub>3</sub>	CH <sub>2</sub>
VIII-X-OPNB	100	0% <sup>a</sup>	24%	22%	51%
VIII-N-OPNB	125	1%	19%	19%	44%

<sup>a</sup> <0.2%, the limit of detectability.

It follows that the *exo:endo* rate ratio of 4300 for the VIII and of 19 for the IX derivatives must be primarily steric in origin.

It should be noted that VIII-X-OPNB and IX-X-OPNB exhibit rates that are very similar to that of I. This may be fortuitous. It was pointed out earlier that decreased flexibility in the ring might be expected to result in a moderate decrease in rate.<sup>6</sup> Possibly relief of steric strain, engendered by the rotation of the methyl group out of the crowded *endo* environment, provides a driving force that compensates for the anticipated effect of reduced flexibility.

It follows from the similarity in the steric requirements of the methyl and acyloxy groups<sup>1</sup> that the same strains must be present in the *endo* isomers. The slow rate of the *endo* isomers can only mean that, in contrast to the *exo* isomers, such strains are not relieved in the transition state and do not contribute to an enhanced rate.<sup>7</sup>

In the past it has been customary to assume that steric strain in the ground state involving the leaving group (GS) becomes negligible in the transition state (TS ≈ 0).<sup>6</sup> Apparently this assumption works well for the usual aliphatic and alicyclic derivatives, whose flexibility can provide a relatively unhindered path for the departing group. However, the present results make it clear that this assumption can no longer be considered valid for rigid bicyclics. Here we shall have to estimate both GS and TS in order to estimate the effect of steric strains on the rate, and the possibility for both GS > TS (steric assistance to ionization) and GS < TS (steric hindrance to ionization) must be considered in individual instances.

(6) See discussion in H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U.S.A.*, **56**, 1653 (1966).

(7) See also J. P. Shaefer and C. A. Flegal, *J. Am. Chem. Soc.*, **89**, 5729 (1967).

(8) Postdoctorate Research Associate, 1963-1965.

(9) National Science Foundation Cooperative Fellow, 1965-1967.

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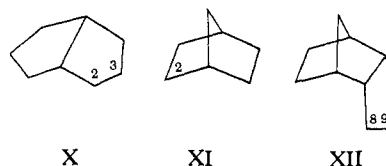
### *exo:endo* Relative Reactivities in Three Representative U-Shaped Systems. The *exo:endo* Rate Ratio in Solvolysis as a Steric Phenomenon

Sir:

We wish to report that in three representative U-shaped systems examined, *cis*-bicyclo[3.3.0]octane, norbornane, and *endo*-5,6-trimethylenenorbornane, non-carbonium ion reactions exhibit preferences for reaction at the *exo* face that are comparable in magnitude to the *exo:endo* rate ratios observed in the solvolyses of the tertiary methyl *p*-nitrobenzoates. This common pattern of reactivity suggests that steric factors must contribute to the greater reactivity from the *exo* direction exhibited by all reactions, carbonium ion as well as noncarbonium ion.

It is well known that *exo*-norbornyl derivatives undergo solvolysis at rates that are considerably greater than those of the corresponding *endo* isomers. Moreover, the resulting ion or ion pair undergoes substitution to give the *exo* isomer predominantly. This preference for *exo* reactivity and *exo* attack has been attributed to  $\sigma$  participation leading to the formation of a  $\sigma$ -bridged cation.<sup>1</sup>

It has become evident in recent years that this *exo* preference is not restricted to carbonium ion reactions. Many reactions not involving carbonium ions exhibit a similar preference for *exo* attack, although the magnitude of the effect may vary considerably from reaction to reaction.<sup>2,3</sup> With data now available for the solvolysis of the tertiary methyl *p*-nitrobenzoates of the *cis*-bicyclo[3.3.0]octane<sup>4</sup> (X), norbornane<sup>5</sup> (XI), and *endo*-5,6-trimethylenenorbornane<sup>5</sup> (XII) systems, we decided to examine a number of typical reactions of these systems in order to ascertain whether the parallelism previously noted for norbornane extends to these additional U-shaped structures.



The hydroboration-oxidation of the olefins corresponding to X, XI, and XII gave *exo:endo* product ratios of 96:4, 99.5:0.5, and >99.9:0.1, respectively. Similarly, epoxidation gave the *exo*-epoxides predominantly, in the *exo:endo* ratios of 87:13, 99.5:0.5, and >99.9:0.1, respectively. Similarly, oxymercuration-demercuration<sup>6</sup> gave *cis*-bicyclo[3.3.0]octan-2-ol in an *exo:endo* ratio of 90:10 and norbornanol in an *exo:endo* ratio of >99.8:0.2. The olefin corresponding to XII, *endo*-5,6-trimethylene-8-norbornene, did not react under the standard conditions.

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

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

(3) H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U.S.A.*, **56**, 1653 (1966).

(4) H. C. Brown and W. J. Hammar, *J. Am. Chem. Soc.*, **89**, 6378 (1967).

(5) H. C. Brown, I. Rothberg, and D. L. Vander Jagt, *ibid.*, **89**, 6380 (1967).