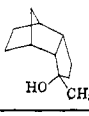
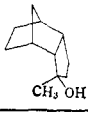
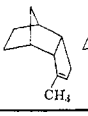
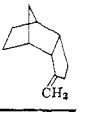
OPNB the 4–5 bond is in a very poor position geometrically to participate. Participation would involve resonance with a very highly strained tetracyclic cation. No rearrangements to this tetracyclic structure are observed in the solvolysis of the tertiary (Table II) or the secondary derivatives. The 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				
VIII-X-OPNB	100	0%[a]	24%	22%	51%
VIII-N-OPNB	125	1%	19%	19%	44%

[a] <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.[6] 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[1] 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.*[7]

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).[6] 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.*, **56**, 1653 (1966).

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

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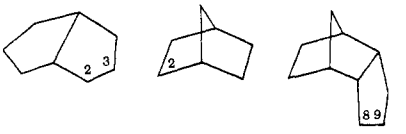
exo:*endo* Relative Reactivities in Three Representative U-Shaped Systems. The *exo*:*endo* Rate Ratio in Solvolysis as a Steric Phenomenon

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, noncarbonium 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 σ participation leading to the formation of a σ-bridged cation.[1]

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.[2,3] With data now available for the solvolysis of the tertiary methyl *p*-nitrobenzoates of the *cis*-bicyclo[3.3.0]octane[4] (X), norbornane[5] (XI), and *endo*-5,6-trimethylenenorbornane[5] (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.



X XI XII

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[6] 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.*, **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).

Reduction of the corresponding ketones (carbonyl group at the 2, 2, and 8 positions, respectively) exhibited lower stereoselectivity, but the same pattern: an *exo*:*endo* ratio of attack of 75:25 for X, 89:11 for XI, and >99.9:0.1 for XII. On the other hand, the addition of methylmagnesium iodide to the ketones exhibited a very high degree of steric control: 98:2, 99.5:0.5, and >99.9:0.1 preferential *exo* attack, respectively, producing predominantly the corresponding tertiary methyl *endo* alcohols. Similarly, oxymercuration–demercuration of the 2-, 2-, and 8-methylene derivatives of X, XI, and XII, respectively, resulted in the preferential formation of the corresponding tertiary methyl *exo* alcohols: 89:11, 99.5:0.5, and >99.9:0.1, respectively.[6b]

These results are summarized in Table I.

Table I. Comparison of the Relative Stereoselectivities Exhibited by Three Representative U-Shaped Systems (X, XI, and XII)

Reaction	*exo*:*endo* ratios X	XI	XII
Hydroboration–oxidation of olefin	24	200	>1000
Epoxidation of olefin	6.7	200	>1000
Oxymercuration–demercuration of olefin	8	>500	
Lithium aluminum hydride reduction of ketone	3	8.1	>1000
Addition of CH_3MgX to ketone	50	200	>1000
Oxymercuration–demercuration of methylene derivatives	8.1	200	>1000
Solvolysis of the tertiary methyl *p*-nitrobenzoate	17	885	4300

Although individual reactions evidently differ considerably in the stereoselectivities they exhibit, the results reveal a consistent pattern. In all cases, the *cis*-bicyclo[3.3.0]octane system (X) exhibits the least preference for *exo* attack, presumably because of its higher flexibility, and the *endo*-5,6-trimethylenenorbornane system (XII) exhibits the highest stereoselectivity for *exo* attack. Indeed, an examination of a model reveals that the *endo* position in this structure is highly hindered. Finally, the norbornane system (XI) is intermediate.

The exo:endo rate ratios exhibited by the corresponding tertiary methyl p-nitrobenzoates exhibit the same pattern of behavior: 17 for X, 885 for XI, and 4300 for XII (Table I)!

It appears to us that this common pattern of reactivity for carbonium ion and noncarbonium ion reactions makes it necessary to reopen the question as to whether both types of reactions may not have a common physical basis for the unique stereospecificity.[7] Such a common physical basis could well be the greater steric accessibility of the *exo* face of these bicyclic structures and the steric difficulties involved in approaching or leaving the *endo* face. This does not mean that other effects, such as torsional interactions[8] and σ participation, may not contribute to the observed *exo*:*endo* rate ratios. It appears to us that the failure of numerous studies to find significant charge delocalization from the 2 to the 1 and 6 positions in the solvolysis of norbornyl derivatives[9] clearly establishes that σ participation cannot be a major factor in the observed *exo*:*endo* rate ratios. However, the tools available to test for charge delocalization, such as the introduction of substituents in appropriate positions, may not provide a truly satisfactory probe for minor contributions.

In the past, steric effects do not appear to have received serious consideration as a factor in the observed *exo*:*endo* rate ratios in norbornyl and related bicyclic derivatives. It is our opinion that the present results make it necessary to recognize steric effects as a factor in such *exo*:*endo* rate ratios.

(6) (a) H. C. Brown and P. Geoghegan, Jr., *J. Am. Chem. Soc.*, **89**, 1522 (1967); (b) H. C. Brown and W. J. Hammar, *ibid.*, **89**, 1524 (1967); (c) H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967).

(7) It is, of course, possible that this similarity is merely the result of a fortuitous coincidence. We are extending these studies to other systems to test this possibility. In particular, the 7,7-dimethylnorbornane system offers a critical test for the steric interpretation, and the reactions of this system are under intensive study: research in progress with J. H. Kawakami.

(8) P. von R. Schleyer, *J. Am. Chem. Soc.*, **89**, 701 (1967).

(9) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966).

(10) Research assistant on grants (G 19878 and GP 6492 X) supported by the National Science Foundation.

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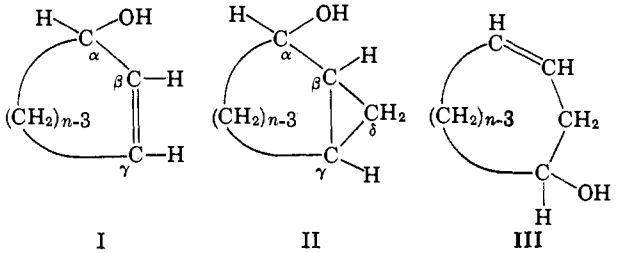
Nonclassical Homoallylic Cations and Homoallylic Ring Expansions[1]

Sir:

Conversion of a cyclic allylic alcohol I to the cyclopropane derivative II, together with acid-catalyzed isomerization of the latter to the homoallylic isomer III, can constitute a useful ring-expansion method.[2a,b] In this communication we describe such homoallylic ring expansions of some medium-size unsaturated ring systems which illustrate a very useful synthetic method and provide important new information about homoallylic rearrangements and nonclassical homoallylic ions.[2d]



I II III

(1) (a) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research; (b) research supported in part by the National Science Foundation.

(2) (a) E. Friedrich, unpublished work; (b) A. C. Cope, S. Moon, and P. E. Peterson, *J. Am. Chem. Soc.*, **84**, 1935 (1962); (c) H. L. Goering and K. E. Rubinstein, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 28–31, 1966, p 5K; (d) L. Birladeanu, T. Hanafusa, B. Johnson, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 2316 (1966), and references there quoted.