Structural Effects in Solvolytic Reactions. 50. Steric Retardation in the Solvolysis of Tertiary Endo Bicyclic Derivatives. Evidence That the Exo:Endo Rate/Product Ratios for Typical Reactions in Rigid U-Shaped Bicyclics Is a General Steric Phenomenon[1]

Herbert C. Brown,* David L. Vander Jagt,[2] Irvin Rothberg,[3] W. James Hammar,[4] and James H. Kawakami[5]

Richard B. Wetherill Laboratory, Purdue University, West Lafayette, Indiana 47907

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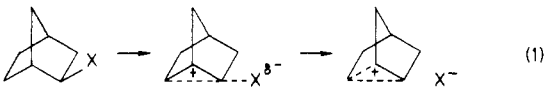
The exo:endo rate ratios for the solvolysis in 80% acetone at 25 °C of the *p*-nitrobenzoates of tertiary bicyclic alcohols of widely varying U-shape character, such as 2-methyl- and 3-methyl-*cis*-bicyclo[3.3.0]octanols, 2-methyl-2-norbornanol, and 2-, 8-, and 9-methyl-*endo*-5,6-trimethylene-2-, -8-, and -9-norbornanols increase with increasing U-shape character of the bicyclic skeleton. This supports the proposal that steric retardation of ionization of the endo isomer is a major factor in governing the exo:endo rate ratios in these tertiary systems. A comparison of the solvolysis data with those of representative nonsolvolytic reactions in these U-shaped systems indicates that the exo/endo relative reactivities reveal a similar pattern for all of the reactions. The exo:endo ratios (product or rate) increase with increasing U-shape character of the bicyclic skeleton. Thus the large exo:endo rate ratio in the solvolysis of tertiary 2-norbornyl derivatives may as well be due to steric rather than to the long proposed electronic factor.

A high exo:endo rate ratio is generally observed in the solvolysis of 2-norbornyl derivatives.[6] It is of major interest to understand the precise factor responsible for these high exo:endo rate ratios.

Originally, Winstein and his co-worker attributed the high exo:endo rate ratio to σ-participation in the exo and its absence in the endo isomer (eq 1).[7] At the time we



(1)

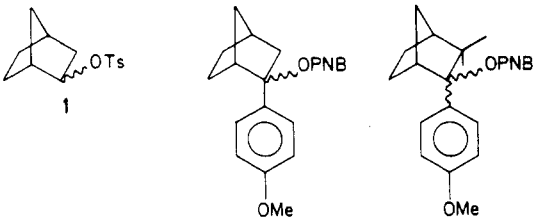
began to question this interpretation, an analysis of the available publications appeared to provide three independent foundations for the concept: (1) Unusually fast rates of solvolysis for the exo derivatives; (2) High exo:endo rate ratios in the solvolysis of 2-norbornyl substrates; (3) High exo substitution products in the solvolysis of both exo and endo derivatives.

The first of these foundations is illustrated in the Ingold proposal that the very fast rate for the ethanolysis of camphene hydrochloride, 13 600 times that of *tert*-butyl chloride, must require a new factor, σ-participation, in place of steric assistance.[8] However, we have suggested that *tert*-butyl chloride may not be a suitable model.[9] Compared with 1-methylcyclopentyl chloride and its α-methyl derivative as better models, the huge rate factor essentially vanishes.[9] Consequently, the first of these three independent foundations is no longer valid.

Goering and Schewene[10] expressed the thermochemistry of the solvolysis in terms of an energy diagram[11] (Figure 1). Analysis of the implication of this diagram revealed that foundations 2 and 3 are essentially the same. Whatever the factor is that is responsible for the difference in free energy of the two transition states is responsible for the distribution of the intermediate, classical or nonclassical, between the two products, *exo*-norbornyl and *endo*-norbornyl.[12]

Consequently, the precise origin of the high exo:endo rate ratio in the solvolysis of 2-norbornyl is the heart of the nonclassical ion problem. What is the physical factor that is responsible for this high exo:endo rate ratio?

Investigation revealed that the tertiary 2-norbornyl derivatives, even those having highly stabilizing groups, showed comparable high exo:endo rate ratios[13] (1–3).



1 2 3

exo/endo	280	288	44 000

It had been originally argued that such tertiary derivatives must also be nonclassical: "the older evidence for typical tertiary 2-norbornyl cations is in line with preferred

(1) For pertinent preliminary communications, see: (a) Brown, H. C.; Hammar, W. J. *J. Am. Chem. Soc.* **1967**, *89*, 6378. (b) Brown, H. C.; Rothberg, I.; Vander Jagt, D. L. *Ibid.* **1967**, *89*, 6380. (c) Brown, H. C.; Hammar, W. J.; Kawakami, J. H.; Rothberg, I.; Vander Jagt, D. L. *Ibid.* **1967**, *89*, 6381. (d) Brown, H. C.; Vander Jagt, D. L. *Ibid.* **1969**, *91*, 6848.

(2) National Science Foundation Cooperative Fellow, 1965–1967, Ph.D. Thesis, Purdue University, 1967.

(3) Postdoctoral research associate, 1963–1965.

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

(5) Research assistant on grants (G 19878 and GP 6492X) from the National Science Foundation.

(6) For a compilation, see: Brown, H. C. (with comments by P. v. R. Schleyer) "The Nonclassical Ion Problem"; Plenum Press: New York, 1977; pp 202, 208.

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

(8) Brown, F.; Hughes, E. D.; Ingold, C. K.; Smith, J. F. *Nature (London)* **1951**, *168*, 65.

(9) Brown, H. C.; Chloupek, F. J.; Takeuchi, K. *J. Org. Chem.* **1985**, *50*, 826.

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

(11) Goering and Schewene (ref 10) expressed the energy relationships in terms of enthalpy. However, we have been using free energies as they are more precise.

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

(13) Brown, H. C.; Takeuchi, K. *J. Am. Chem. Soc.* **1968**, *90*, 2691, 5268, 5270.

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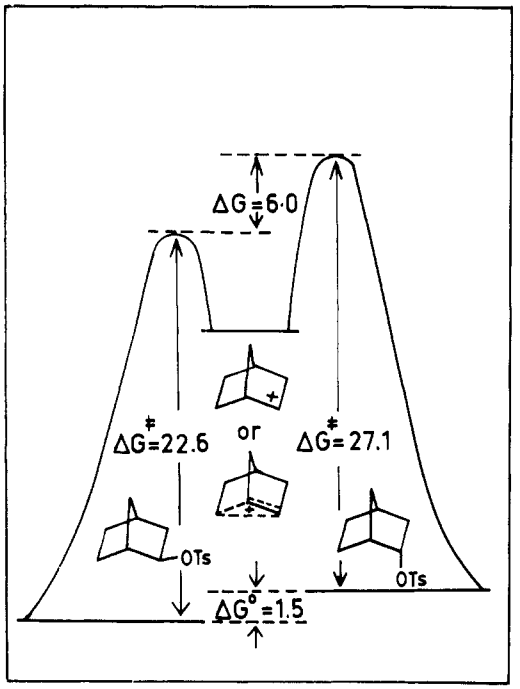


Figure 1. Goering–Schewene diagram for the acetolysis of *exo*- and *endo*-norbornyl tosylates at 25 °C (all numbers in kcal mol^{-1}).

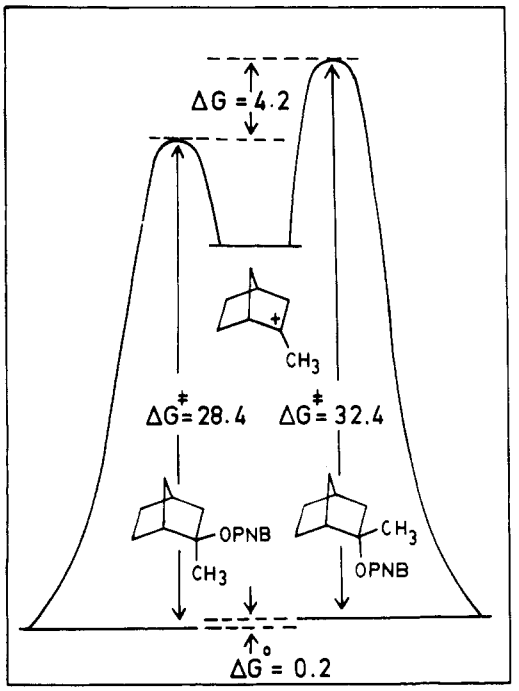


Figure 2. Goering–Schewene diagram for the solvolysis of 2-methyl-*exo*- and 2-methyl-*endo*-2-norbornyl *p*-nitrobenzoates in 80% aqueous acetone at 25 °C (all numbers in kcal mol^{-1}).

bridged structures."[14] However, a mass of evidence soon convinced the staunchest nonclassical supporters that the more stable tertiary cationic center in tertiary 2-norbornyl derivatives cannot be involved in significant σ-bridging with C6.[15]

Consequently, we are faced with a problem. The high exo:endo rate ratio in the solvolysis of 2-norbornyl tosylate (Figure 1) is attributed to σ-participation. The very similar high exo:endo rate ratios in the solvolysis of tertiary 2-norbornyl derivatives (Figure 2) cannot be attributed to this factor.

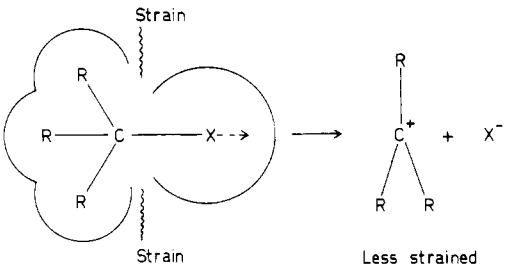


Figure 3. Solvolysis of a strained tertiary substrate.

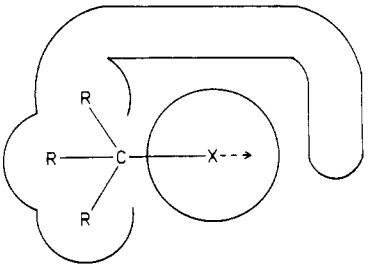


Figure 4. Steric retardation of ionization in U-shaped systems.

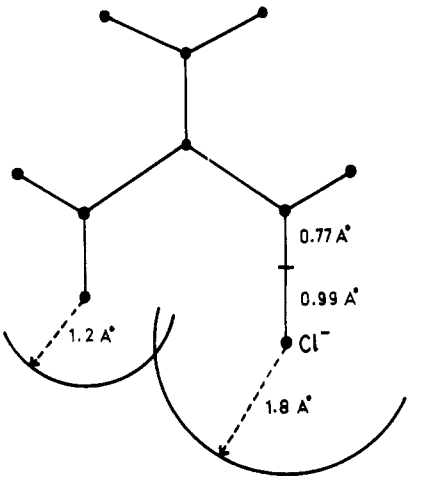


Figure 5. End-on view of *endo*-2-norbornyl chloride.

We suggested that the high exo:endo rate ratios in both secondary and tertiary 2-norbornyl derivatives might arise from a normal exo rate and an unusually slow endo rate caused by steric retardation to ionization in the endo isomer.[16]

In simple, highly branched substrates, the strain of the crowded system is readily relieved during ionization of the leaving group X (Figure 3). In such a system, X will depart along a line perpendicular to the face of the developing carbonium ion and the steric interactions between X and the developing carbonium ion, as well as the interactions between the three R groups, will decrease monotonically as the C---X distance increases.

Consider the situation that arises when the movement of X away from the developing ion encounters a portion of a relatively rigid organic structure (Figure 4). Now the strain will not decrease monotonically with increase in the C---X distance. The strain may well increase with crowding of X against the obstructing structure before X can finally depart and relieve the strain.

(14) Winstein, S. *J. Am. Chem. Soc.* **1965**, *87*, 381.
(15) For a summary, see: Brown, H. C. *Acc. Chem. Res.* **1983**, *16*, 432 and pertinent references cited therein.
(16) Brown, H. C.; Chloupek, F. J.; Rei, M.-H. *J. Am. Chem. Soc.* **1964**, *86*, 1248.

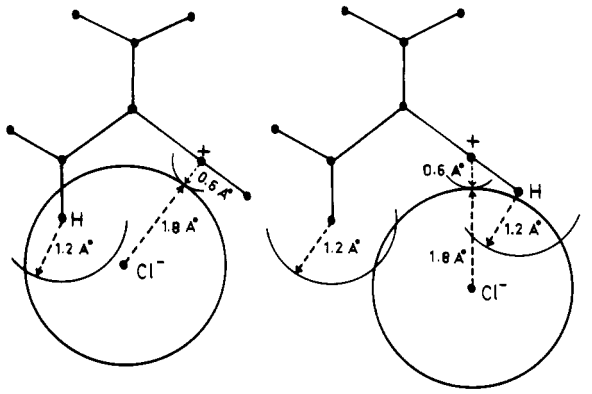


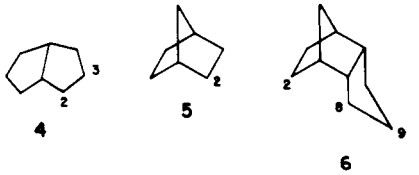
Figure 6. End-on view of the two extreme transition states for the solvolysis of *endo*-2-norbornyl chloride.

Indeed, *endo*-norbornyl derivatives would appear to incorporate this particular structural feature. Consider the structure of *endo*-norbornyl chloride (Figure 5). In the ionization process, the chlorine substituent would be expected to move along a curved path away from the carbon atom at the 2-position, maintaining the chlorine substituent perpendicular to the face of the developing carbonium ion so as to retain maximum overlap of the orbitals undergoing separation. In this way, the system should pass through the transition state to the first intermediate, the idealized ion pair shown in Figure 6. Clearly, there would be a major steric overlap of the chlorine substituent with the endo 6-hydrogen. Moreover, the group undergoing ionization should be strongly, and probably symmetrically, solvated by the medium; yet the U-shaped structure obviously makes difficult such solvation of the developing anion. Only the exposed section should be so solvated.

An alternative model for ionization has been suggested.[17] In this model, the departing group would move initially along the direction of the C–X bond leading to the first intermediate, the idealized ion pair shown in Figure 6. This path does not avoid the steric difficulty, although in this model, it is transferred largely to the hydrogen atom or other group at the 2-position. This model appears less probable mechanistically than the previous one discussed.

The large steric interactions of both models will presumably cause some other path, providing decreased steric interactions at the cost of poorer overlap, to be selected as a compromise. Such a compromise would still result in an increase in the energy of the transition state relative to that for a derivative without this particular structural feature.

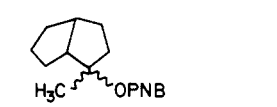
However, there has been considerable reluctance to accept this concept.[18] Consequently, we undertook to test it by examining the behavior of three different systems (**4**–**6**) of variable U-shape character (the numbers in the



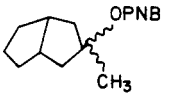
structures represent the reaction centers) in solvolysis and a number of typical reactions which do not necessarily involve a cationic intermediate.[1] A consideration of the models predicts that exo/endo relative reactivity/selectivity should increase in the order **4** to **6**, as is borne out by the present study.

Results

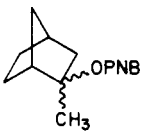
Solvolysis of the Tertiary *p*-Nitrobenzoates. For the solvolysis study, the following *p*-nitrobenzoates were included: 2-methyl-*cis*-bicyclo[3.3.0]oct-2-yl (**7**), the corresponding 3-substituted derivative 8, 2-methyl-2-norbornyl (**9**), 8-methyl-*endo*-5,6-trimethylene-8-norbornyl (**10**), 9-methyl-*endo*-5,6-trimethylene-9-norbornyl (**11**), 2-methyl-*endo*-5,6-trimethylene-2-norbornyl (**12**), and some analogous phenyl-substituted derivatives (**13**–**15**). The *p*-nitrobenzoates were prepared from the respective alcohols by using known procedures.[19] The alcohols were prepared as follows.



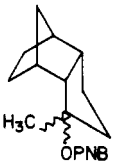
7a; *endo*-CH_3; *exo*-OPNB
7b; *endo*-OPNB; *exo*-CH_3



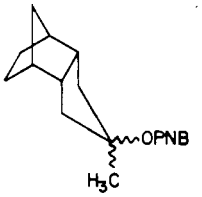
8a; *endo*-CH_3; *exo*-OPNB
8b; *endo*-OPNB; *exo*-CH_3



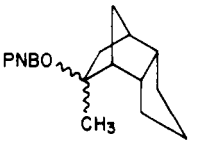
9a; *endo*-CH_3; *exo*-OPNB
9b; *endo*-OPNB; *exo*-CH_3



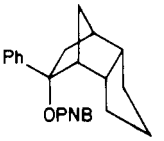
10a; *endo*-CH_3; *exo*-OPNB
10b; *endo*-OPNB; *exo*-CH_3



11a, *endo*-CH_3; *exo*-OPNB
11b, *endo*-OPNB; *exo*-CH_3



12a; *endo*-CH_3; *exo*-OPNB
12b; *endo*-OPNB; *exo*-CH_3



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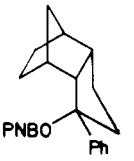
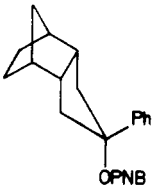


14a; *endo*-Ph; *exo*-OPNB
14b; *endo*-OPNB; *exo*-Ph

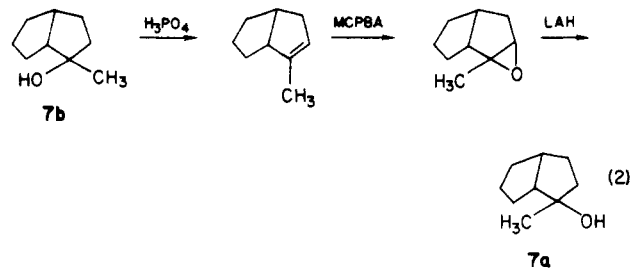


15

Preparation of *exo*-2-, *endo*-2-, *exo*-3-, and *endo*-3-Methyl-*cis*-bicyclo[3.3.0]octan-2- and -3-ols (7a,b, 8a,b). 2-Methyl-*cis*-bicyclo[3.3.0]octan-*endo*-3-ol (**7b**) was prepared by the addition of MeMgI to *cis*-bicyclo[3.3.0]-octan-2-one (**16**) in 98% isomeric purity. The corresponding 3-substituted derivative **8b** was prepared from *cis*-bicyclo[3.3.0]octan-3-one (**17**) in 99% isomeric purity (GC). 2-Methylbicyclo[3.3.0]octan-*exo*-2-ol (**7a**) was prepared from the endo alcohol by dehydration followed by epoxidation and LAH reduction (eq 2). The corresponding 3-substituted derivative **8a** was prepared from **8b** by a similar route.

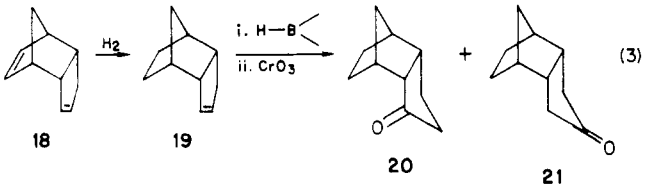
Preparation of 8-Methyl-, 9-Methyl-, 8-Phenyl-, and 9-Phenyl-5,6-*endo*-trimethylenenorbornan-8- and -9-ols. Dicyclopentadiene (**18**) was selectively hydrogenated to yield *endo*-5,6-trimethylenenorborn-8-ene (**19**), which,

(17) Schleyer, P. v. R.; Donaldson, M. M.; Watts, W. E. *J. Am. Chem. Soc.* **1965**, *87*, 375.
(18) le Noble, W. J. "Highlights of Organic Chemistry"; Marcel Dekker: New York, 1974.
(19) Brown, H. C.; Peters, E. N. *J. Am. Chem. Soc.* **1975**, *97*, 1927.



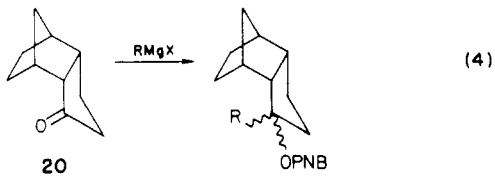
7b 7a (2)

on hydroboration–CrO_3 oxidation, gave a mixture of 5,6-*endo*-trimethylenenorbornan-8- and -9-ones (**18** and **19**) (eq 3). These were readily separated by formation of the



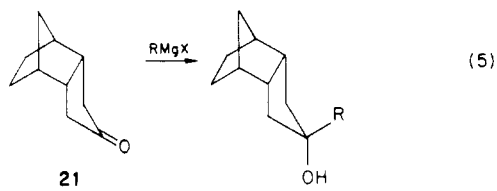
18 19 20 21 (3)

$NaHSO_3$ addition compounds. The endo isomers of 8- and 9-phenyl-5,6-*endo*-trimethylenenorbornan-8- and -9-ol were prepared by the addition of the appropriate RMgX to 5,6-*endo*-trimethylenenorbornan-8- and -9-ones, respectively (eq 4 and 5). The corresponding exo alcohols were



20 (4)

10b, R = Me
14b, R = Ph

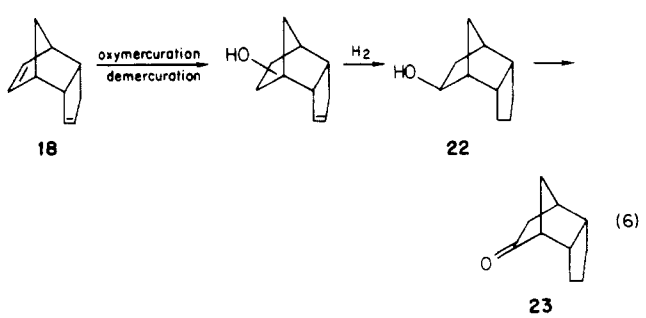


21 (5)

11b, R = CH_3
15, R = Ph

prepared by the same method described for the *cis*-bicyclo[3.3.0]octanols, namely, dehydration followed by epoxidation and LAH reduction (eq 2).

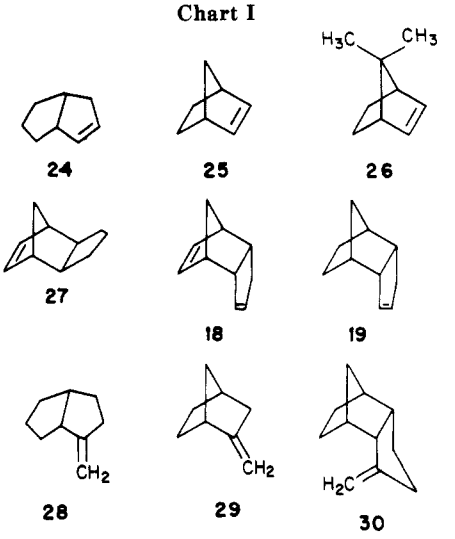
Preparation of Exo and Endo Isomers of 2-Methyl- and 2-Phenyl-5,6-*endo*-trimethylenenorbornan-2-ols. Dicyclopentadiene (**18**), on oxymercuration–demercuration followed by hydrogenation gave 5,6-*endo*-trimethylene-2-*exo*-norbornanol (**22**), which, on CrO_3 oxidation, gave 5,6-*endo*-trimethylene-2-norbornanone (**23**) (eq 6). **23**, on



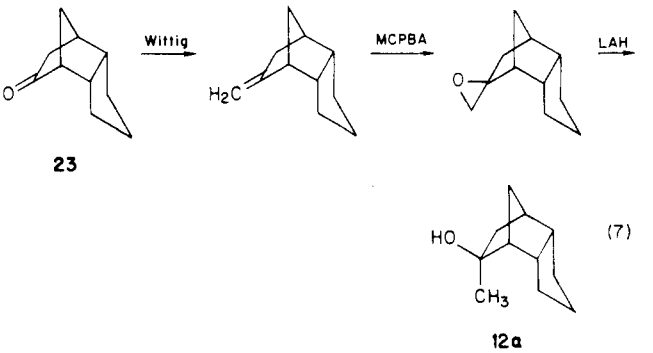
18 22 23 (6)

treatment with MeMgI and PhMgBr, gave 2-methyl- and 2-phenyl-5,6-*endo*-trimethylene-2-*endo*-norbornanols (**12b** and **13**). **23**, on Wittig methylenation, followed by epoxidation and subsequent reduction (LAH) gave 2-methyl-5,6-*endo*-trimethylene-2-*exo*-norbornanol (**12a**) (eq 7).

Chart I



24 25 26 27 18 19 28 29 30



23 (7) 12a

The rates of solvolysis of the *p*-nitrobenzoates were measured in 80% aqueous acetone[19] and are provided in Table I.

Products in the Solvolysis of Model U-Shaped Tertiary *p*-Nitrobenzoates. For product studies, the solvolysis was conducted in a sealed tube at a convenient high temperature. The reaction mixture was worked up after 10 half-lives and analyzed by GC. The data for the methyl-*cis*-bicyclo[3.3.0]octyl *p*-nitrobenzoates are given in Table II. Tables III, IV, and V provide the product analysis for the 8-, 9-, and 2-methyl-5,6-*endo*-trimethylene-8-, -9-, and -2-norbornyl *p*-nitrobenzoates. The data are self-explanatory. Alkenes were formed predominantly in all cases. No rearrangements could be observed in the *cis*-bicyclo[3.3.0]octyl and 8-methyl- and 9-methyl-5,6-*endo*-trimethylene-8- and -9-norbornyl systems. The only alcohols obtained are the exo and endo alcohols corresponding to the starting ester. In these two cases, the product alcohols were found to be stable at the temperature used. However, the tertiary alcohols from 2-methyl-5,6-*endo*-trimethylenenorbornyl ester isomerized to the secondary 1-methyl-5,6-*exo*-trimethylene-2-norbornanol on polar GC columns. Hence, the analysis was made on several different columns. The data in Table III indicate that the rearranged product is formed significantly. However, both the exo and endo esters behave similarly.

Exo:Endo Relative Reactivities in Representative U-Shaped Systems. One of the major interests of this study was to compare the exo/endo rate ratios in the solvolysis of U-shaped *p*-nitrobenzoates with the exo/endo relative selectivities realized in a number of other representative reactions, such as hydroboration–oxidation, ox-

Table I. Rates of Solvolysis of Representative U-Shaped Tertiary *p*-Nitrobenzoates in 80% Aqueous Acetone

no.	*p*-nitrobenzoate	mp, °C	$10^{-6}k_1$, s^{-1} 25 °C (calcd)	50 °C	75 °C	100 °C	125 °C	150 °C	rel rate at 25 °C	exo:endo rate ratios at 25 °C
	1-methylcyclopentyl[a]	82–83	2.11×10^{-3}			23.0	236		1.00	
7a	2-methyl-*cis*-bicyclo[3.3.0]oct-2-yl[b] (exo)	102	2.00×10^{-3}			29.7	347		0.95	17
7b	2-methyl-*cis*-bicyclo[3.3.0]oct-2-yl[c] (endo)	84	0.118×10^{-3}			2.95	37		0.056	
8a	3-methyl-*cis*-bicyclo[3.3.0]oct-3-yl[d] (exo)	80	0.438×10^{-3}			10.6	132		0.21	1.7
8b	3-methyl-*cis*-bicyclo[3.3.0]oct-3-yl[e] (endo)	106	0.251×10^{-3}			5.91	73		0.12	
9a	2-methyl-2-*exo*-norbornyl[f]	114–115	1.00×10^{-2}		6.94	94.6			4.74	855
9b	2-methyl-2-*endo*-norbornyl[f]	100–100.5	1.13×10^{-5}			0.395	5.41		0.005 36	
10a	8-methyl-5,6-*endo*-trimethylene-8-exo-norbornyl[g]	120–122	5.38×10^{-3}		5.79	93.4			2.55	4300
10b	8-methyl-5,6-*endo*-trimethylene-8-*endo*-norbornyl[h]	80–82	1.25×10^{-6}				1.10	12.1	0.0006	
11a	9-methyl-5,6-*endo*-trimethylene-9-*exo*-norbornyl[i]	137–138	1.99×10^{-3}			16.9	162			19
11b	9-methyl-5,6-*endo*-trimethylene-9-*endo*-norbornyl[j]	127–128	1.06×10^{-4}				29.4	268	0.05	
12a	2-methyl-5,6-*endo*-trimethylene-2-*exo*-norbornyl[k]	104 dec	10.9[l]	265					5167	5 266 000
12b	2-methyl-5,6-*endo*-trimethylene-2-*endo*-norbornyl[m]	150–150.8	2.07×10^{-6}				1.64	18.0	0.000 98	
	1-phenylcyclopentyl[n]		2.37	55	904				(1.00)	
14a	8-phenyl-5,6-*endo*-trimethylene-8-*exo*-norbornyl[o]	175 dec	14.5[l]	393					(6.1)	11 600
14b	8-phenyl-5,6-*endo*-trimethylene-8-*endo*-norbornyl[p]	124–125	1.25×10^{-3}			27.2	330		(0.000 53)	
15	9-phenyl-5,6-*endo*-trimethylene-9-*endo*-norbornyl[q]	153 dec	8.7×10^{-2}		44.7	540			(0.037)	
13	2-phenyl-5,6-*endo*-trimethylene-2-*endo*-norbornyl[r]	151.5–152	2.3×10^{-3}			31.3	338		(0.000 97)	
	2-phenyl-*endo*-norbornyl[s]		5.3×10^{-2}[l]						(0.0222)	

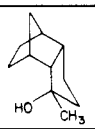
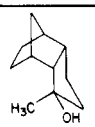
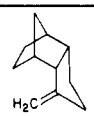
[a] $\Delta H^{\ddagger}$ = 26.8 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −8.5 eu. [b] $\Delta H^{\ddagger}$ = 28.3 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −4.4 eu. [c] $\Delta H^{\ddagger}$ = 29.1 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −6.3 eu. [d] $\Delta H^{\ddagger}$ = 29.1 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −4.0 eu. [e] $\Delta H^{\ddagger}$ = 29.0 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −5.4 eu. [f] Taken from ref 31. [g] $\Delta H^{\ddagger}$ = 28.1 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −2.3 eu. [h] $\Delta H^{\ddagger}$ = 31.5 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −7.2 eu. [i] $\Delta H^{\ddagger}$ = 26.0 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −11.3 eu. [j] $\Delta H^{\ddagger}$ = 28.8 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −7.5 eu. [k] $\Delta H^{\ddagger}$ = 23.8 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −1.7 eu. [l] Determined at 25 °C. [m] $\Delta H^{\ddagger}$ = 31.3 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −7.0 eu. [n] $\Delta H^{\ddagger}$ = 24.4 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −2.8 eu. [o] $\Delta H^{\ddagger}$ = 24.6 kcal mol^{-1}; $\Delta S^{\ddagger}$ = 2.0 eu. [p] $\Delta H^{\ddagger}$ = 28.8 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −2.9 eu. [q] $\Delta H^{\ddagger}$ = 25.1 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −6.9 eu. [r] $\Delta H^{\ddagger}$ = 27.4 kcal mol^{-1}; $\Delta S^{\ddagger}$ = −6.3 eu. [s] From ref 32.

Table II. Alcohol Products from the Solvolysis of Tertiary Methyl-*cis*-bicyclo[3.3.0]octyl *p*-Nitrobenzoates[a,b]

cis-bicyclo[3.3.0]octyl *p*-nitrobenzoates	total alcohol,[c] %	alcohol ratio exo:endo
2-methyl-2-*exo*-	5	80:20
2-methyl-2-*endo*-	8	75:25
3-methyl-3-*exo*-	3	73:27
3-methyl-3-*endo*-	6	71:29

[a] At 125 °C in 80% acetone. [b] The alcohol products are stable at analysis conditions. [c] The predominant products are alkenes.

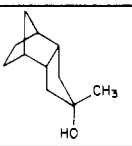
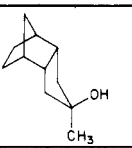
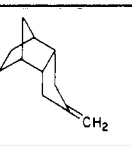
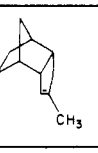
Table III. Products in the Solvolysis of 8-Methyl-5,6-*endo*-trimethylene-8-norbornyl *p*-Nitrobenzoates[a,b] 9a and 9b

isomer	temp, °C				
exo	100	<0.2%	24%	51%	22%
endo	125	1%	19%	44%	19%

[a] In 60% acetone containing 10% excess sodium acetate. [b] The alcohol products were stable at analysis condition.

ymercuration–demercuration, and epoxidation of the appropriate alkenes, as well as reduction and Grignard reaction of the ketones. The alkenes chosen for the first study are *cis*-bicyclo[3.3.0]octene (**24**), norbornene (**25**), 7,7-dimethylnorbornene (**26**), 5,6-*exo*-trimethylene-2-norbornene (**27**), dicyclopentadiene (**18**), 8,9-didehydro-5,6-*endo*-trimethylenenorbornane (**19**), and the exocyclic alkenes **28–30**. (Chart I).

Table IV. Products in the Solvolysis of 9-Methyl-5,6-*endo*-trimethylene-9-norbornyl *p*-Nitrobenzoates[a,b]

isomer				
exo	<0.2%	2%	9%	89%
endo	~0.2%	23%	28%	49%

[a] In 60% acetone containing 10% excess sodium acetate at 125 °C. [b] Alcohol products are stable at analysis conditions.

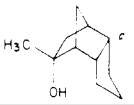
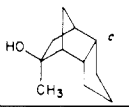
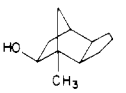
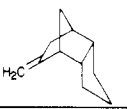
The ketones chosen for the second study are *cis*-bicyclo[3.3.0]octan-2- and -3-ones (**16** and **17**), 2-norbornanone (**31**), 7,7-dimethyl-2-norbornanone (**32**), 5,6-*exo*- and 5,6-*endo*-trimethylene-2-norbornanones (**33** and **23**), and 5,6-*endo*-trimethylenenorbornan-8- and -9-ones (**20** and **21**) (Chart II).

All of these compounds were prepared by standard procedures from available starting materials. The exo:endo relative selectivities were determined by GC analysis of the products after the reactions.

Discussion

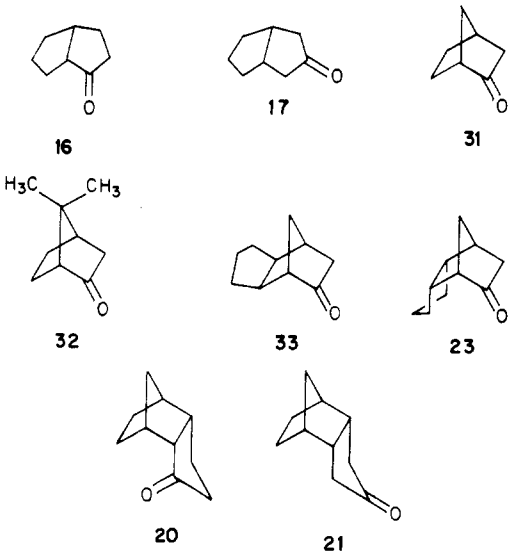
Solvolysis of Model U-Shaped Tertiary *p*-Nitrobenzoates. (a) *cis*-Bicyclo[3.3.0]octyl Nitrobenzoates.

Table V. Products in the Solvolysis of 2-Methyl-5,6-*endo*-trimethylene-2-norbornyl *p*-Nitrobenzoates[a,b]

isomer	temp, °C				
exo	75	<0.2%	13.1%	9.3%	33.9%
endo	125	0.5%	16.0%	9.2%	62.9%

[a] In 60% acetone. [b] Percentages not normalized. [c] The alcohol products undergo rearrangement to the 1-methyl 2-exo alcohol in polar columns and elimination to the alkene in nonpolar columns (see Discussion section).

Chart II

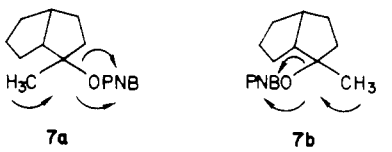


The rates of solvolysis of 2- and 3-methyl-*cis*-bicyclo[3.3.0]octyl *p*-nitrobenzoates are given in Table I. 1-Methylcyclopentyl *p*-nitrobenzoate is also included for comparison. The exo isomer of 2-methyl-*cis*-bicyclo[3.3.0]oct-2-yl *p*-nitrobenzoate (**7a**) undergoes solvolysis at a rate (×0.95) only slightly slower than that of 1-methylcyclopentyl *p*-nitrobenzoate while the endo isomer solvolyzes much slower (0.056). Consequently, if 1-methylcyclopentyl is a suitable model for the *cis*-bicyclo[3.3.0]octyl system, it is possible to consider that it is the endo isomer that behaves abnormally. However, consideration of the relative rates of 3-methyl-*cis*-bicyclo[3.3.0]oct-3-yl *p*-nitrobenzoates indicates that both the exo and endo isomers solvolyze significantly slower than does 1-methylcyclopentyl *p*-nitrobenzoate. Obviously the reduction in the flexibility of the cyclopentane ring accompanying the cis fusion must modify its reactivity.

Consequently, it appears preferable to work with the exo:endo rate ratios rather than with the individual rates. At the 2-position (**7**), the exo:endo rate ratio is 17 and this decreases to 1.7 in the more remote 3-position (**8**). We are again faced with the question whether the exo:endo ratio of 17 for **7** is due to σ-participation or has its origin in other structural effects.

We believe that σ-participation in **7** to form a nonclassical intermediate cannot be important in this system. Such an intermediate would involve resonance between canonical structures corresponding to the relatively stable **7** cation and the strained high-energy secondary bicyclo[3.2.1]oct-8-yl cation. Resonance involving structures which differ so greatly in energy cannot be significant. Even in the more favorable norbornyl system, as discussed earlier, there is growing acceptance for the position that σ-participation is not important in tertiary derivatives.[15]

If the effect is steric in origin, we are faced with the problem that both the exo and endo derivatives **7** have very similar ground-stage energies, with very similar steric requirements for the groups CH_3 and OPNB.[20] For example, it might be argued that the rate of solvolysis of the exo isomer **7a** is facilitated by the relief of steric strain



accompanying the outward movement of the methyl group from the crowded endo environment **31**. However, in the endo isomer **7b** the interactions of the leaving group with the endo environment are just as large (**32**). If the usual assumption that steric strain vanishes in the transition state[21] holds for these bicyclic derivatives, then the solvolysis of the endo isomer should likewise be enhanced and the exo:endo rate ratio should remain close to unity.

The observation of an appreciable exo:endo rate ratio can only mean that the rate of the endo isomer is not facilitated by relief of steric strain. The relief of strain, which is readily afforded in flexible aliphatic and alicyclic derivatives, may not occur in rigid U-shaped structures, which can interfere with both solvation of the anion and its departure.[21]

(b) Solvolysis of 8-Methyl-, 9-Methyl-, 8-Phenyl-, and 9-Phenyl-5,6-*endo*-trimethylene-8- and 9-norbornyl *p*-Nitrobenzoates. Our observation that the exo:endo rate ratio is much larger for the 2-methyl-*cis*-bicyclo[3.3.0]oct-2-yl system than for the less crowded 3-substituted derivative **8b** clearly indicated that exo:endo rate ratio increases with increasing U-shape character. Consequently, we decided to study the rates of solvolysis of 8- and 9-methyl-5,6-*endo*-trimethylene-8- and -9-norbornyl *p*-nitrobenzoates (**10**, **11**) and the corresponding phenyl-substituted derivatives (**14**, **15**). The rate data are given in Table I. The exo:endo rate ratio is 4300 for the 8-methyl-5,6-*endo*-trimethylene-8-norbornyl (**10**) and 19 for the 9-methyl-5,6-*endo*-trimethylene-9-norbornyl system. The high exo:endo rate ratio for the former system (**10**) seems to arise not as a result of any large rate for the exo isomer **10a** (relative rate 2.55 compared to that of 1-methylcyclopentyl *p*-nitrobenzoate) but because of a greatly reduced rate for the endo isomer (relative rate 0.0006). σ-Participation in **10a** cannot be an important factor since the 4,5-bond is geometrically in a very poor position to participate. Moreover, such participation would involve resonance with a very highly strained tetracyclic cation, which is prohibitive. Moreover, the product studies indicate the absence of rearranged products (Table III). Consequently, only steric factors appear to play a significant role in the solvolysis of **10a** and **10b**. **10a** exhibits a rate which is close to that of the model, 1-methylcyclopentyl *p*-nitrobenzoate. 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.

(20) Rei, M-H.; Brown, H. C. *J. Am. Chem. Soc.* **1966**, *88*, 5335.
(21) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 701.

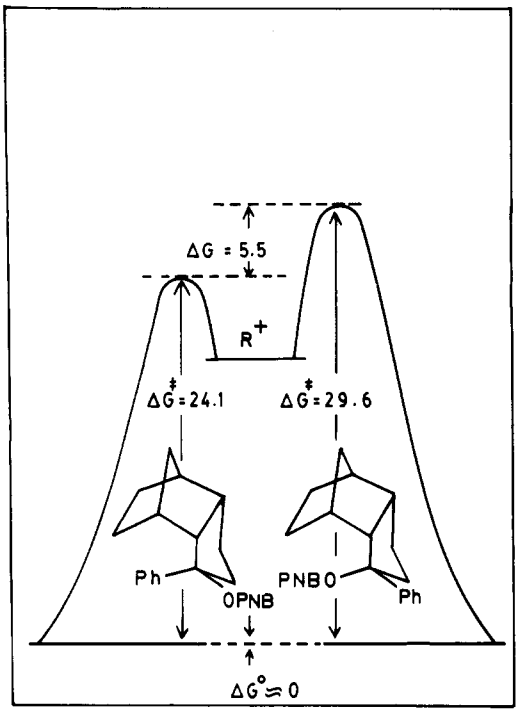


Figure 7. Goering–Schewene diagram for the solvolysis of 8-phenyl-5,6-*endo*-trimethylene-8-norbornyl *p*-nitrobenzoates.

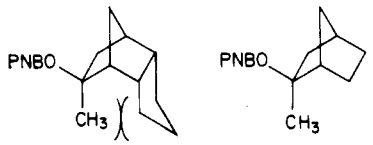
Possibly relief of steric strain, engendered by the rotation of the methyl group out of the crowded endo environment, provides a driving force that compensates for the anticipated effect of reduced flexibility.

It follows from the similarity in the steric requirements of the methyl and acyloxy groups[20] that the same strains must be present in the endo isomer. The slow rate of the endo isomer can only mean that, in contrast to the exo isomer, such strains are not relieved in the transition state and do not contribute to an enhanced rate. Rather, the strain increases when going from the ground state to the transition state[12] due to steric retardation of the ionization of the leaving group as it moves into the endo cavity.

The exo:endo rate ratio for the analogous phenyl derivatives (**14a, 14b**) is even larger (11 600) than that for the methyl derivative. Again, when compared with 1-phenylcyclopentyl *p*-nitrobenzoate, the exo isomer reacts only 6.1 times faster while the endo isomer reacts 1900 times slower. On the basis of our explanation for the methyl system, the large exo:endo rate ratio must be due to steric retardation of ionization in the endo isomer since chances of σ-participation are even more remote for the phenyl derivative due to the enormous stabilization of the positive charge at the cationic center by the phenyl group. Interestingly, the Goering–Schewene diagram (Figure 7) shows that the free energies of the exo and endo transition states differ by 5.5 kcal mol^{-1}, which is comparable to that observed in norbornyl (Figure 1). Consequently, steric factors must play a major role in reactions of these U-shaped systems.

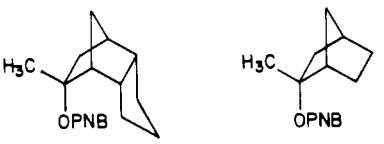
In conformity with our explanation based on steric retardation of ionization in the endo isomer, the exo:endo rate ratio is significantly lower in 9-methyl-5,6-*endo*-trimethylene-9-norbornyl *p*-nitrobenzoates (**11a, 11b**) since the 9-position is more open and especially its endo face is much less crowded than for the 8-position. However, the exo:endo rate ratio is larger for the 9-methyl-5,6-*endo*-trimethylene-9-norbornyl system than that for the 3-methylbicyclo[3.3.0]oct-3-yl system, probably because of the greater U-shape character for the former system. 9-Phenyl-5,6-*endo*-trimethylene-9-*endo*-norbornyl *p*-nitrobenzoate (**15**) undergoes solvolysis 27 times slower than the 1-phenylcyclopentyl ester. The slow rate is probably due to steric retardation of ionization. However, we could not measure the exo:endo rate ratio for this system since the exo isomer could not be made cleanly.

(c) Solvolysis of 2-Methyl-5,6-*endo*-trimethylene-2-norbornyl *p*-Nitrobenzoates. On the basis of molecular models, the U-shape character must be as pronounced in the 2-methyl-5,6-*endo*-trimethylene-2-norbornyl system as in the 8-methyl analogue. Consequently, we studied their rates of solvolysis in 80% acetone (Table I) at 25 °C. The exo:endo rate ratio increases to a phenomenal 5 266 000. It is better to compare the rates of exo and endo isomers with a suitable model before attributing it to any specific factor. *exo*- and *endo*-2-Methyl-2-norbornyl *p*-nitrobenzoates (**9a, 9b**) appear to be suitable models. The exo isomer **12a** undergoes solvolysis 1090 times faster than 2-methyl-*exo*-2-norbornyl *p*-nitrobenzoate (**9a**). Doubtless



12a 1090 **9a** 1.0

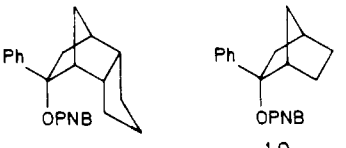
this rate enhancement arises from the relief of steric strain present in **12a**. At the same time, there is steric retardation in the ionization of the endo isomer **12b**. **12b** reacts 6 times slower than 2-methyl-*endo*-2-norbornyl *p*-nitrobenzoate (**9b**), which is attributed to greater steric retardation caused by the trimethylene bridge. It is very important to consider the rate decrease of **12b** over **9b** in light of the enormous rate acceleration exhibited by the exo isomer. Since the methyl and OPNB groups are of similar size,[20] the same driving force to relieve strain should be present in the endo isomer as well. Thus, the fact that **12b** reacts



12b 0.18 **9b** 1.00

significantly slower than **9b** in spite of the anticipated driving force provided by the relief of the large strain involved is a clear indication for a large steric retardation in the ionization of **12b**.

The phenyl derivative **13** solvolyzes 1030 times slower than 2-phenyl-2-*endo*-norbornyl *p*-nitrobenzoate, again showing the importance of steric factors in the behavior of U-shaped systems. Unfortunately, the exo ester could not be made.



13 1/1030 1.0

Steric Behavior of the Model U-Shaped Systems toward Representative Reactions. Our study on the solvolysis of the tertiary *p*-nitrobenzoates indicates that the exo:endo rate ratio increases directly with increased U-shape character. Thus it is possible to arrange the three systems, *cis*-bicyclo[3.3.0]octyl, 2-norbornyl, and 5,6-

Table VI. Exo:Endo Selectivities in U-Shaped Alkenes toward Representative Reactions

olefin	hydroboration	epoxidation	oxymercuration–demercuration
24	96	87	90, 2-ol
25	99.5[a]	99.5[b]	99.8[c]
26	27[a]	6[b]	>99.8[c]
27	91.4		>99.8
18	>99.8[2,3]		>99.8[2,3]
19	>99.8	>99.8	
28			89[d]
29			99.5[d]
30			100[d]

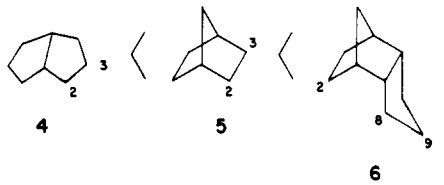
[a] Taken from ref 33. [b] Taken from ref 34. [c] Taken from ref 35. [d] Taken from ref 36.

Table VII. Exo:Endo Selectivities in U-Shaped Ketones toward Representative Reactions

ketone	LAH reduction in THF	MeMgI addition
16	75	98
17	94	99
31	89[a]	>99[b]
32	10[c]	
33	95	
23	99.2	
20	>99.8	>99.8
21	>99	>99

[a] Taken from ref 37. [b] Taken from ref 38. [c] Taken from ref 39.

endo-trimethylenenorbornyl, in the order of increasing U-shaped character:



4 **5** **6**

If this were true, this order must hold in many other reactions as well. We tested this by examining the exo:endo selectivity for a number of typical reactions involving these three U-shaped systems. The reactions chosen do not proceed through cationic intermediates and consequently do not suffer from the controversies which plague the solvolysis reaction. The data are given in Tables VI and VII and the results are summarized in Table VIII.

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 (**4**) exhibits the least preference for exo attack, presumably because of its higher flexibility, and the *endo*-5,6-trimethylenenorbornane system (**6**) 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 (**5**) is intermediate.

*The exo:endo rate ratios exhibited in the solvolysis of the corresponding tertiary methyl p-nitrobenzoates exhibit the same pattern of behavior: 17 for **4**, 885 for **5**, and 4300 for **6** (Table VIII).*

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. 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. All of the difficulties involved in approaching or leaving the endo face in the case of solvolysis reaction, such as

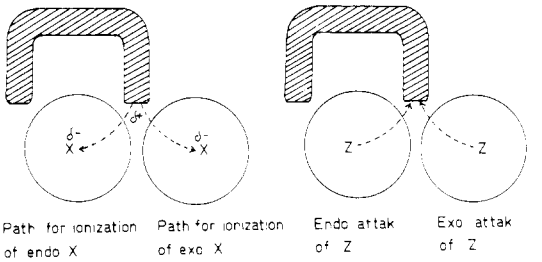


Figure 8. Common steric factors in the departure of endo leaving group in solvolysis and attack on endo face in other reactions of U-shaped bicyclic systems.

Table VIII. Comparison of the Relative Stereoselectivities Exhibited by Three Representative U-Shaped Systems

reaction	exo:endo ratios 4	5	6
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 (8 position)

approach of solvent molecules or departure of the solvated leaving group, are embodied in our term "steric retardation of ionization". The concept is better illustrated in Figure 8.

Conclusion

It is clear that the solvolysis of tertiary derivatives of the three model U-shaped systems reveals changes in the exo:endo rate ratios that parallel closely the increasing U-shaped character.

Indeed, all of the representative reactions examined reveal comparable effects of the U-shaped system. Consequently, the solvolytic behavior is not unique but fits the common pattern of chemical behavior shown by these three systems in all of their reactions.

There is still a question as to whether we can extend steric retardation of ionization to the secondary U-shaped derivatives, including 2-norbornyl. We plan to discuss that question in a forthcoming paper.

Experimental Section

All melting points are uncorrected. Analytical data within accepted precision were obtained for all new compounds. ^1H NMR spectra were recorded on a Varian A60A or T-60 spectrophotometer. All compounds showed satisfactory NMR and IR behavior. GC analyses were used extensively for identification and estimation of products.

Preparation and Separation of *cis*-Bicyclo[3.3.0]octan-2-one (16) and *cis*-Bicyclo[3.3.0]octan-3-one (17). To an ice-cold solution of sodium borohydride (17 g, 0.45 mol) and *cis*-bicyclo[3.3.0]oct-2-ene[22] in anhydrous tetrahydrofuran (THF) (500 mL) was added a solution of freshly distilled boron trifluoride etherate (85.2 g, 0.60 mol) in THF (100 mL) over a period of 1 h.[23] After stirring at room temperature for 2 h, water was carefully added to destroy the excess hydride followed by a careful addition of chromic acid[24] (1 L), prepared by dissolving sodium dichromate dihydrate (200 g, 0.74 mol) in 96% sulfuric acid (165 mL, 2.95

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mmol) and diluting with water to 1 L, maintaining the temperature between 15 °C and 20 °C. After the addition, the mixture was stirred at room temperature (2 h). The layers were separated and the aqueous phase was washed twice with 100-mL portions of ethyl ether (EE). The combined organic layers were washed with saturated sodium carbonate (100 mL), diluted with EE to 1 L, and stirred vigorously with aqueous sodium bisulfite (48 g in 75 mL of H_2O; 0.46 mol) for 15 h. The bisulfite adduct was filtered and washed 4 times with EE (150 mL). *cis*-Bicyclo[3.3.0]octan-3-one (17) was regenerated from the adduct by stirring with saturated aqueous sodium carbonate (400 mL) and EE (200 mL). The layers were separated and the aqueous layer was washed 3 times with EE (50 mL). After drying over anhydrous magnesium sulfate, the ether was removed. Distillation afforded **17** in 31% yield (bp 90 °C (13.5 mm), n^{20}_D 1.4801; lit.[25] bp 78 °C (10 mm), n^{18}_D 1.4811).

The ether phase containing mostly *cis*-bicyclo[3.3.0]octan-2-one was retreated with aqueous sodium bisulfite (10 g in 15 mL of H_2O) for 15 h. After filtering off the adduct, the ether layer was dried over anhydrous magnesium sulfate. EE was removed and the product (43.1 g, 33% yield) was distilled (bp 84 °C (14 mm), n^{20}_D 1.4762; lit.[26] bp 50 °C (2.3 mm), n^{25}_D 1.4766).

2-Methyl-*cis*-bicyclo[3.3.0]octan-*endo*-2-ol (7b). To a solution of methyl magnesium iodide, MeMgI, prepared from methyl iodide (227 g, 1.6 mol) and magnesium (38.9 g, 1.6 mol) in EE (300 mL) was added dropwise *cis*-bicyclo[3.3.0]octan-2-one (99.2 g, 0.8 mol) in EE (200 mL) at 0 °C. After the addition, the mixture was refluxed for 15 min, cooled, and poured slowly into aqueous ammonium chloride (86 g in 200 mL of H_2O). The aqueous layer was extracted with EE and combined with the ether layer. The combined ether extracts were washed twice with cold 5% sulfuric acid solution, saturated sodium carbonate solution, and finally with water. After drying over anhydrous magnesium sulfate, ether was stripped off. A GC analysis showed that it is a 98:2 mixture of two alcohols (endo and exo). Distillation provided the pure product (bp 90 °C 14 mm), n^{21}_D 1.4848) in 84% yield.

3-Methyl-*cis*-bicyclo[3.3.0]octan-*endo*-3-ol (8b). A procedure analogous to that employed above afforded this alcohol (99% GC pure before distillation) in 73% yield (bp 88 °C (9 mm), mp 37.5–38 °C).

2-Methyl-*cis*-bicyclo[3.3.0]oct-2-ene. A mixture of 2-methyl-*cis*-bicyclo[3.3.0]octan-*endo*-2-ol (42 g, 0.30 mol) and 85% phosphoric acid (1 mL) was heated in an oil bath and the olefin co-distilled with H_2O. The olefin was extracted with pentane. After drying and removing the pentane, the product was distilled to afford 29.4 g of the product (80% yield) (bp 153 °C (748 mm), n^{17}_D 1.4772; lit.[27] n^{20}_D 1.4802).

3-Methyl-*cis*-bicyclo[3.3.0]oct-2-ene. When the same procedure was followed, this compound was prepared from 3-methyl-*cis*-biyclo[3.3.0]octan-*endo*-2-ol in 75% yield (bp 150 °C (752 mm), n^{22}_D 1.4723; lit.[28] bp 153 °C, n^{20}_D 1.4712).

2-Methyl-*cis*-bicyclo[3.3.0]octan-*exo*-2-ol (7a). A solution of *m*-chloroperbenzoic acid (53 g of 80% pure material, 0.238 mol) in chloroform (500 mL) was added dropwise to a solution of 2-methyl-*cis*-bicyclo[3.3.0]oct-2-ene (29 g, 0.238 mol) in chloroform (350 mL) at 0 °C. After being stirred for 30 min at 0 °C, the mixture was treated with dilute sodium bisulfite solution until the reaction mixture no longer gave a positive test with starch iodide paper. The mixture was filtered at 0 °C, and the clear chloroform layer was washed with cold saturated sodium bicarbonate solution and saturated sodium chloride solution and dried. A GC analysis showed a mixture of two epoxides (17:83). The solvent was removed and the epoxide mixture was reduced as follows.

The residual epoxide mixture was dissolved in THF (100 mL) and added dropwise to lithium aluminum hydride (LAH) (9.03 g) in THF (250 mL) at 0 °C. After stirring for 1 h at room temperature, the excess hydride was destroyed carefully with H_2O, and the contents were washed with saturated sodium potassium tartrate solution and dried over magnesium sulfate. After removal of the solvent, GC analysis showed the product (21.4 g, 64%) to be a mixture of exo and endo alcohols (83:17). Recrystallization from pentane afforded a GC pure sample of **7a** (mp 79.0–79.5 °C).

3-Methyl-*cis*-bicyclo[3.3.0]octan-*exo*-3-ol (8a). When the above procedure was followed, 3-methyl-*cis*-bicyclo[3.3.0]oct-2-ene was epoxidized and reduced to give a mixture of exo and endo alcohols (88:12) as shown by GC analysis. Recrystallization from pentane gave GC pure **8a** (mp 78–78.5 °C) in 30% yield.

8-Methyl-5,6-*endo*-trimethylene-8-*endo*-norbornanol (10b). This compound was prepared by the reaction of 5,6-*endo*-trimethylene-8-norbornanone[28] (**20**) with MeMgI by a procedure similar to that described for **7b**. The crude product after workup was an oil which on crystallization gave the tertiary alcohol in 72% yield (mp 52–56 °C). GC analysis showed it to be contaminated with 2.2% starting ketone and 0.9% of an unidentified material. Recrystallization from pentane gave pure **10b**, mp 59–60 °C.

9-Methyl-5,6-*endo*-trimethylene-*endo*-9-norbornanol (11b). The reaction of 5,6-*endo*-trimethylene-9-norbornanone[28] (**21**) with MeMgI using the above procedure gave 81% **11b** and 19% starting ketone. The reaction was repeated on the crude product in THF. The reaction mixture was refluxed for 2 h and stirred at room temperature for 12 h. After workup, GC analysis showed 90.8% **11b** and 9.2% ketone. Distillation (bp 108 °C (3 mm)) followed by recrystallization from EE–pentane mixture gave pure **11b**, mp 74–75 °C, in 36% yield.

8-Phenyl-5,6-*endo*-trimethylene-8-*endo*-norbornanol (14b). This compound was prepared by the reaction of phenylmagnesium bromide (100% excess) with 5,6-*endo*-trimethylene-8-norbornanone, as described above, in 85% crude yield. Recrystallization from hexane afforded a pure sample, mp 91.5–92.3 °C.

9-Phenyl-5,6-*endo*-trimethylene-9-*endo*-norbornanol (15b). Using the above procedure, this compound was prepared from **21** in 55% yield. Recrystallization from pentane gave a pure sample (mp 93.5–94.5 °C).

8-Methyl-5,6-*endo*-trimethylene-8-*exo*-norbornanol (10a). This compound was prepared from the corresponding endo alcohol (**10b**) as described for **7a** by dehydration with phosphoric acid followed by epoxidation with *m*-chloroperbenzoic acid and reduction with LAH in 80% yield (mp 77–78 °C after recrystallization).

9-Methyl-5,6-*endo*-trimethylene-9-*exo*-norbornanol (11a). The same above procedure was employed to prepare this compound from its endo epimer **11b**. The reduction of the epoxide took 12 days in refluxing THF. The crude product was a 9:1 mixture of the desired exo alcohol and an unidentified material (*not* the endo isomer). Selective recrystallization afforded the pure sample, mp 113–113.5 °C.

8-Phenyl-5,6-*endo*-trimethylene-8-norbornene. A solution of 8-phenyl-5,6-*endo*-trimethylene-8-*endo*-norbornanol (2.96 g, 0.013 mol) in methylene chloride (13 mL) was reacted with hydrogen chloride at 0 °C in a Brown® Automatic Gasimeter.[29] The mixture was stirred for 8 h at room temperature. The solvent was removed after drying over magnesium sulfate to get an oil (2.64 g, 97%) which showed no OH absorption in IR analysis or active chloride (titration). Purification by preparative GC on an SE-30 column gave 8-phenyl-5,6-*endo*-trimethylene-8-norbornene.

Epoxidation of 8-Phenyl-5,6-*endo*-trimethylene-8-norbornene. The epoxidation was carried out by the method of Payne[30] since *m*-chloroperbenzoic acid or monoperphthalic acid

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oxidations were not clean. A 30% hydrogen peroxide solution (~0.03 mol) was added slowly to a mixture of 8-phenyl-5,6-*endo*-trimethylene-8-norbornene (4.2 g, 0.02 mol), methanol (20 mL), potassium bicarbonate (0.4 g), and benzonitrile (2.66 g, 0.025 mol). The reaction mixture was kept at 40 °C for 36 h and then cooled, added to water, and extracted with hexane (2 × 50 mL). The hexane layer was washed with aqueous potassium carbonate (1 M) and dried over magnesium sulfate. It was then passed through a column of alumina, and the epoxide was eluted with hexane–EE. Removal of the solvent gave the epoxide in 75% yield.

8-Phenyl-5,6-*endo*-trimethylene-8-*exo*-norbornanol (14a). The above epoxide was reduced with LAH in refluxing THF (overnight). After workup as described for the preparation of **7a**, the crude exo alcohol was obtained in 94% yield. Recrystallization from hexane gave the pure sample, mp 118.2–118.8 °C.

2-Methyl-5,6-*endo*-trimethylene-2-*endo*-norbornanol (12b). The reaction of 5,6-*endo*-trimethylene-2-norbornanone[28] (**23**) with MeMgI in refluxing EE (100% excess) over a period of 18 h followed by workup as described for **7b** afforded the tertiary alcohol **12b** in 70% yield, mp 106.5–107.3 °C.

5,6-*endo*-Trimethylene-2-methylenenorbornane. To a solution of methyltriphenylphosphonium iodide (20.5 g, 0.051 mol) in THF (50 mL) was added *n*-butyllithium (33.8 mL of 15% solution in hexane, 0.051 mol) under nitrogen. After stirring for 1.5 h, 5,6-*endo*-trimethylene-2-norbornanone (6.0 g, 0.04 mol) in THF (50 mL) was added slowly. The resulting solution was refluxed for 72 h. The reaction was then complete, as checked by IR. Water (1 mL) was added and the solvents were removed after drying over magnesium sulfate. Distillation afforded the desired olefin in 73% yield, bp 102–104 °C (60 mm), mp 34–34.2 °C.

2-Methyl-5,6-*endo*-trimethylene-2-*exo*-norbornanol (12a). The above alkene was epoxidized with *m*-chloroperbenzoic acid at room temperature (15 min) in methylene chloride. Removal of the solid by filtration and the solvent by rotary evaporation led to a semisolid material which was reduced as such with LAH in THF at room temperature (36 h). The mixture was worked up as reported in the case of **7a**. The crude product was recrystallized from hexane to a constant melting point (116.5–117.0 °C). GC analysis was difficult in this case. Use of polar columns caused rearrangement to 5,6-*exo*-trimethylene-1-methyl-2-*exo*-norbornanol while nonpolar columns caused elimination to olefins, mainly 5,6-*endo*-trimethylene-2-methylenenorbornane.

2-Phenyl-5,6-*endo*-trimethylene-2-*endo*-norbornanol (13). Using the described procedure, 5,6-*endo*-trimethylene-2-norbornanone (**23**) was reacted with phenylmagnesium bromide (excess) to obtain **13** in 66% yield, mp 94.7–95 °C.

Preparation of *p*-Nitrobenzoates of the Tertiary Alcohols 7–15. All of the alcohols were esterified with *p*-nitrobenzoyl chloride by a known procedure.[19] The melting points are given in Table I.

Kinetics of Solvolysis of the *p*-Nitrobenzoates. The kinetics were measured in 80% acetone.[19] Except for fast solvolyses, the rate constants were determined at higher temperatures in a sealed tube by a titrimeteric procedure. The data are given in Table I.

Products in the Solvolysis of Tertiary *p*-Nitrobenzoates. Products of solvolysis were determined in 60% acetone in the presence of an internal standard in a sealed tube and heated for approximately 10 half-lives at suitable temperatures. The sealed tubes were opened and the organic layer was washed with saturated sodium bicarbonate and saturated sodium chloride and then dried over magnesium sulfate. The solution was then analyzed by GC. The data are given in Tables IV and V.

Exo:Endo Selectivity of U-Shaped Alkenes toward Representative Reactions. (a) Hydroboration. Hydroboration of *cis*-bicyclo[3.3.0]oct-2-ene (**24**) is representative. To a solution of **24** (5.4 g, 0.05 mol) in dry THF (50 mL) was added BH_3·THF (0.03 mol). The solution was stirred at room temperature for 2 h. The excess hydride was destroyed by a careful addition of water. The organoborane was oxidized with alkaline H_2O_2 by using sodium hydroxide (0.6 g) and 30% H_2O_2 (6.0 mL) at 30–40 °C (1 h). The reaction mixture was saturated with potassium carbonate and the solvent was removed to get 3.97 g of a product. GC analysis on a Quadrol column showed it to be a mixture of endo-2, exo-2, exo-3, endo-3 alcohols in the ratio 2:53:43:2. Consequently, the percent of exo attack is 96 and that of endo attack is 4. The data for this and other alkenes are given in Table VI.

(b) Epoxidation. The alkenes were oxidized with *m*-chloroperbenzoic acid and the epoxides were analyzed as such or after reducing to alcohols with LAH or Li/ethylenediamine. The epoxidation of *cis*-bicyclo[3.3.0]oct-2-ene is representative. *m*-Chloroperbenzoic acid (10.0 g of 80% pure sample, 0.05 mol) in chloroform (120 mL) was added dropwise to a solution of *cis*-bicyclo[3.3.0]oct-2-ene (5.4 g, 0.05 mol) in chloroform (50 mL) at 0 °C. The mixture was stirred at 0 °C and then filtered while cold. The filtrate was washed with cold saturated sodium carbonate solution and dried over magnesium sulfate. The solvent was removed and the product was distilled (bp 64 °C (20 mm)) to give 4.9 g (79%) of material. GC analysis on a diethylene glycol succinate capillary column showed two peaks (exo and endo) in a ratio of 87:13.

Hydride reduction of the epoxide mixture with LAH in THF at room temperature (3 h) followed by GC analysis gave a mixture of four *cis*-bicyclo[3.3.0]octanols, endo-2, exo-2, endo-3, exo-3, in a ratio of 10:73:4:13. This means a ratio of 86:14 for the epoxides. The data for this and other alkenes are provided in Table VI.

(c) Oxymercuration–Demercuration. The reaction of *cis*-bicyclo[3.3.0]oct-2-ene is typical. The olefin (10 mmol) in THF (5 mL) was added rapidly to a mixture of mercuric acetate (3.1 g, 10 mmol) in water (10 mL) and THF (5 mL). The mixture was stirred for 5 min and then treated with sodium hydroxide (3 M, 10 mL) and sodium borohydride in 3 M sodium hydroxide (0.5 M, 10 mL). The reaction mixture was saturated with sodium chloride and the organic layer was dried over magnesium sulfate. This solution was then analyzed by GC to determine the distribution of alcohols. The data for this and other alkenes are presented in Table VI.

Exo:Endo Selectivity in U-Shaped Ketones toward Typical Reactions. The LAH reduction of the ketones and the Grignard reaction with MeMgI were done by established procedures and the product ratios were determined by GC analyses. The data are given in Table VII.

Acknowledgment. We thank the National Science Foundation for financial support.

Registry No. **7a**, 70598-81-1; **7a** (PNB), 19037-39-9; **7b**, 63641-24-7; **7b** (PNB), 19037-40-2; **8a**, 70598-82-2; **8a** (PNB), 19037-41-3; **8b**, 70598-78-6; **8b** (PNB), 19037-42-4; **9a** (PNB), 22467-58-9; **9b** (PNB), 13351-30-9; **10a**, 19138-61-5; **10a** (PNB), 19138-55-7; **10b**, 10271-47-3; **10b** (PNB), 19262-48-7; **11a**, 19138-64-8; **11a** (PNB), 96346-19-9; **11b**, 19138-63-7; **11b** (PNB), 19262-49-8; **12a**, 96259-52-8; **12a** (PNB), 96259-53-9; **12b**, 96259-51-7; **12b** (PNB), 96259-54-0; **13**, 27296-90-8; **13** (PNB), 27296-89-5; **14a**, 27409-22-9; **14a** (PNB), 27296-94-2; **14b**, 72796-92-0; **14b** (PNB), 27296-91-9; **15b**, 27409-21-8; **15b** (PNB), 27362-80-7; **16**, 32405-37-1; **17**, 19915-11-8; **19**, 2825-86-7; **20**, 17364-68-0; **21**, 19138-60-4; **23**, 31351-12-9; **27**, 10466-50-9; **33**, 34748-64-6; 2-methyl-*cis*-bicyclo[3.3.3]oct-2-ene, 63641-23-6; 3-methylbicyclo[3.3.3]octan-2-ol, 96259-48-2; 3-methyl-*cis*-bicylco-[3.3.3]oct-2-ene, 26472-31-1; 8-phenyl-5,6-*endo*-trimethylene-8-norbornene, 96259-49-3; 8-phenyl-5,6-*endo*-trimethylene-8-norbornene epoxide, 96259-50-6; 5,6-*endo*-trimethylene-2-methylnorbornane, 59691-24-6; *cis*-bicyclo[3.3.3]oct-2-ene, 930-99-4; methyltriphenylphosphonium iodide, 2065-66-9.

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