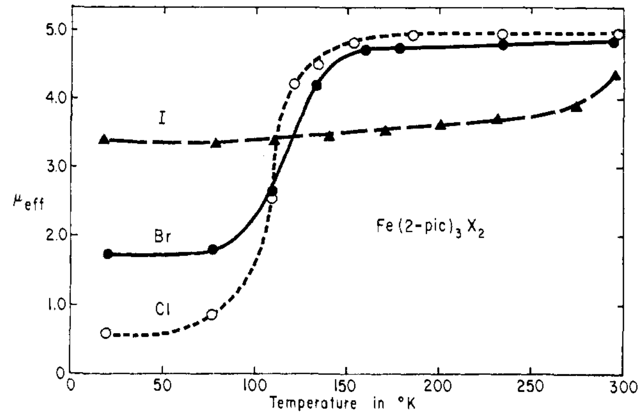

Figure 1. Plot of the magnetic moment (Bohr magnetons) *vs.* temperature.

these data to a model which involves a $^1A_{1g}$ ground state in thermal equilibrium with a $^5T_{2g}$ excited state, which is split into three levels by spin–orbit coupling, were futile. As was observed for some Co(II) systems,[6,8] the data seem to suggest that the separation between states varies with temperature.

Table I. Analytical Data for the Tris(2-aminomethylpyridine)iron(II) Salts

	Calcd, %			Found, %		
Compound	C	H	Fe	C	H	Fe
[Fe(2-pic)$_3$]Cl$_2$	47.91	5.36	...	47.65	5.63	...
[Fe(2-pic)$_3$]Br$_2$	40.02	4.48	10.34	39.98	4.99	10.16
[Fe(2-pic)$_3$]I$_2$	34.09	3.81	...	34.16	3.64	...

In spite of the lack of quantitative agreement, the postulate of the simultaneous existence of two spin states is adequately supported by Mössbauer data. Such data have been obtained for the chloride and iodide salts. Because of absorption by bromine of the 13-Kev γ rays used in ^{57}Fe resonance studies, the bromide salt gave very poor spectra. For the chloride salt, the room temperature spectrum shows a pair of lines which are obviously a result of quadrupole splitting with an isomer shift of 0.98 and a splitting of 2.04 mm/sec.[12] These parameters are typical of high-spin iron(II).[13] At 77°K, the spectrum shows two pairs of lines, an inner doublet with an isomer shift of 0.52 and a splitting of 0.55 mm/sec, and an outer doublet corresponding to the one seen at room temperature. The intensity of the inner doublet is about seven times that of the outer doublet, however. Further, the parameters of the inner doublet are about what are usually observed for low-spin iron(II).[14] At 4.2°K, only the inner doublet is observed. For the iodide, the spectrum is not as well resolved as for the chloride, but it is clear that both the high-spin and low-spin components are observable at room temperature as well as at 77°K. Further, at liquid nitrogen temperature the relative intensities of the two components are about the same with the parameters being, within experimental error, the same as for the chloride. Thus the Mössbauer data agree almost perfectly with what would be predicted from the magnetic data.

Finally, we would like to mention that we have diluted the chloride salt with the corresponding zinc complex which from X-ray powder data is seen to be isomorphous with the iron complex. Magnetic and Mössbauer data for mixtures containing as little as 15% iron complex are identical, thus ruling out the possibility that the magnetic data could be explained by an antiferromagnetic interaction.

Acknowledgments. This work was supported by the National Science Foundation. We also thank Professor R. L. Collins of the University of Texas for obtaining the Mössbauer data at liquid helium temperature as well as confirming the data at other temperatures.

Gordon A. Renovitch, W. A. Baker, Jr.
Department of Chemistry, Syracuse University
Syracuse, New York 13210
Received September 1, 1967

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[12] Relative to natural iron foil.

[13] R. L. Collins, R. Pettit, and W. A. Baker, Jr., *J. Inorg. Nucl. Chem.*, **28**, 1010 (1966).

[14] The isomer shift is actually more positive than any we have seen in the literature for low-spin iron(II). This is perhaps to be expected since in this case the ligand field is as weak as it can be and still cause spin pairing, and, in general, the isomer shift decreases as the field increases.

Rates of Solvolysis of the *p*-Nitrobenzoates of the Tertiary 2-Methyl- and 3-Methyl-*cis*-bicyclo[3.3.0]octanols. Evidence for Steric Hindrance to Ionization in the *endo* Derivatives

Sir:

In 1946 it was proposed that relief of steric strain accompanying the ionization of sterically crowded tertiary derivatives could provide a potent driving force to enhance the rate of solvolysis.[1] Today steric assistance to ionization is an accepted factor in calculating rates of solvolysis.[2]

In 1961 it was suggested that the *endo* derivatives of rigid bicyclics with U-shaped structures[3] might undergo solvolysis with an increase in steric strain in the transition state, resulting in a decreased rate of solvolysis.[4,5] However, this proposal for steric hindrance to ionization has not yet received serious consideration.[6,7] Accordingly, we undertook to prepare and solvolyze suitable derivatives with representative U-shaped structures: bicyclo[3.3.0]octane, which the model suggests should provide smaller steric hindrance to ionization than norbornane, and *endo*-5,6-trimethylenenorbornane, which should exhibit larger.[8]

As was pointed out earlier, the use of secondary derivatives suffers from the disadvantage that the

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[1] H. C. Brown, *Science*, **103**, 385 (1946).

[2] P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1854 (1964).

[3] It is convenient to extend the *exo,endo* terminology of norbornyl derivatives to the corresponding "outer" and "inner" derivatives of other U-shaped structures.

[4] H. C. Brown and S. Nishida, paper presented to the Division of Organic Chemistry at the 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961.

[5] H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, pp 140–157, 176–178.

[6] S. Winstein, *J. Am. Chem. Soc.*, **87**, 381 (1965).

[7] However, see 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); P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, **87**, 375 (1965).

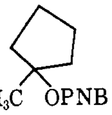
[8] The results with the latter system are reported in the following communication: H. C. Brown, I. Rothberg, and D. L. Vander Jagt, *J. Am. Chem. Soc.*, **89**, 6380 (1967).

Table I. Rates of Solvolysis of the Tertiary Methyl *p*-Nitrobenzoates of the Bicyclo[3.3.0]octane System

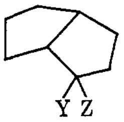
Compd[a]	Mp, °C	$k_1 \times 10^6$ sec^{-1} 25° (calcd)	100°	125°	Rel rates, 25°	*exo*:*endo* rate ratios, 25°
I	82–83	2.11×10^{-3}	23.0	236	1.00	
II-X-OPNB	102	2.00×10^{-3}	29.7	347	0.95	17
II-N-OPNB	84	0.118×10^{-3}	2.95	37.0	0.056	
III-X-OPNB	80	0.438×10^{-3}	10.6	132	0.21	1.7
III-N-OPNB	106	0.251×10^{-3}	5.91	73	0.12	

[a] All new compounds exhibited spectral and microanalytical data consistent with the proposed structures.

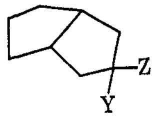
ground-state energies of the *exo* and *endo* isomers differ considerably, so that the data must be corrected for this factor to obtain a realistic estimate of the true *exo*:*endo* rate ratio.[7] On the other hand, the evidence is that methyl and acyloxy groups do not differ significantly in their steric requirements.[9] Consequently, the *exo* and *endo* tertiary isomers, such as II and III, possess almost identical ground-state energies, so that the observed rate ratios do not need to be subjected to an uncertain correction for major differences in the ground-state energies.[7]



I



II



III

CO (X, Y = =O)
X-OH (Y = Me, Z = OH)
N-OH (Y = OH, Z = Me)
X-OPNB (Y = Me, Z = OPNB)
N-OPNB (Y = OPNB, Z = Me)

Hydroboration–oxidation (H_2CrO_4) of *cis*-bicyclo-[3.3.0]octene-2 produced 32% II-CO and 31% III-CO after separation with sodium bisulfite. Treatment of the ketones with methylmagnesium iodide produced II-N-OH, bp 90° (14 mm), n^{21}D 1.4848, and III-N-OH, mp 37.5–38°. The *exo* alcohols were prepared by dehydration to the olefin, epoxidation, and reduction of the epoxides with lithium aluminum hydride: II-X-OH, mp 79.0–79.5°; III-X-OH, mp 78.0–78.5°.[10]

The *p*-nitrobenzoate esters (OPNB) were prepared by the standard procedure[11] and the rates of solvolysis were determined in 80% aqueous acetone (Table I).

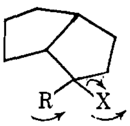
Experiments established that solvolysis proceeds without significant acyl oxygen cleavage or rearrangement, producing only olefins and alcohols corresponding in structure to the starting materials. Consequently, it appears that solvolysis proceeds to the corresponding carbonium ion, without rearrangement of the carbon structure.

If I were a suitable standard (rel rate 1.00) for the bicyclooctyl derivatives, it would be easy to conclude that II-X-OPNB (0.95) was normal and II-N-OPNB (0.056) was retarded. However, the observation that the rates for the III derivatives are appreciably slower than the proposed standard negates this approach. Possibly the reduction in the flexibility of the cyclopentane ring accompanying the *cis* fusion modifies its reactivity.

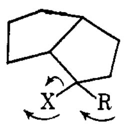
Consequently, it appears preferable to work with the *exo*:*endo* rate ratios rather than with the individual rates. At the 2 position (II), the *exo*:*endo* rate ratio is 17, and this decreases to 1.7 in the more remote 3 position (III). We are again faced with the question whether the *exo*:*endo*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

We believe that σ participation in II 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 II cation and the strained high-energy secondary bicyclo[3.2.1]octyl-8 cation. Resonance involving structures which differ so greatly in energy cannot be significant. Even in the more favorable norbornyl system, there is growing acceptance for the position that σ participation is not important in tertiary derivatives.[12]

If the effect is steric in origin, we are faced with the problem that both the *exo* and *endo* derivatives (II) have very similar ground-stage energies, with very similar steric requirements for the groups Y and Z. For example, it might be argued that the rate of solvolysis of the *exo* isomer, II-X-OPNB, is facilitated by the relief of steric strain accompanying the outward movement of the methyl group from the crowded *endo* environment (IV). However, in the *endo* isomer, V, the interactions of the leaving group with the *endo* environment are just as large. If the usual assumption that steric strain vanishes in the transition state[12] 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.



IV



V

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 (V). The relief of strain, which is readily afforded in flexible aliphatic and alicyclic derivatives, may not occur in rigid U-

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(9) M.-H. Rei and H. C. Brown, *J. Am. Chem. Soc.*, **88**, 5335 (1966).

(10) Oxymercuration–demercuration now provides a more convenient route: H. C. Brown and W. J. Hammar, *ibid.*, **89**, 1524 (1967).

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

(12) P. von R. Schleyer, *ibid.*, **89**, 701 (1967).

shaped structures, which can interfere with both the solvation of the anion and its departure.[13,14]

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[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.

Herbert C. Brown, W. James Hammar[15]
Richard B. Wetherill Laboratory
Purdue University, Lafayette, Indiana 47907

Received August 23, 1967

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:

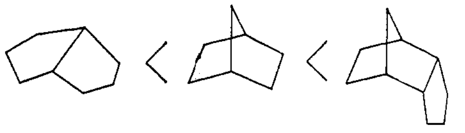
An *exo*:*endo* rate ratio of 4300 is observed in the solvolysis of the epimeric *p*-nitrobenzoates of *endo*-5,6-trimethylene-8-methyl-8-norbornanol (VIII). For the more remote 9 derivatives (IX), an *exo*:*endo* rate ratio of 19 is observed. In both cases the *exo* isomer exhibits a rate that is very 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.

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

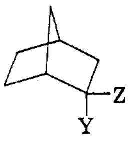
		$k_1 \times 10^6$ sec^{-1}						*exo*:*endo*
Compd[a]	Mp, °C	25° (calcd)	75°	100°	125°	150°	Rel rates, 25°	rate ratios, 25°
I	82–83	2.11×10^{-3}					1.00	
VIII-X-OPNB	120–122	5.38×10^{-3}	5.79	93.4			2.55	4300
VIII-N-OPNB	80–82	1.25×10^{-6}			1.10	12.1	0.0006	
IX-X-OPNB	137–138	1.99×10^{-3}		16.9	162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

[a] All new compounds gave spectral and microanalytical data consistent with the proposed structure.

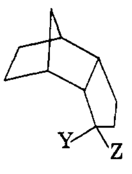
An examination of molecular models indicates that the U-shaped character of the bicyclic structures becomes enhanced in the series VI. We previously established that the *exo*:*endo* rate ratio for the epimeric *p*-nitrobenzoates of *cis*-bycyclo[3.3.0]octan-2-ol is 17,[1] considerably less than the value of 885 observed for 2-norbornyl[2] (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 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.



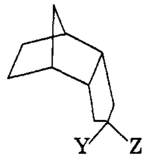
VI



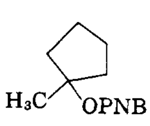
VII



VIII



IX



I

CO (X, Y = =O)
X-OH (Y = Me, Z = OH)
N-OH (Y = OH, Z = Me)
X-OPNB (Y = Me, Z = OPNB)
N-OPNB (Y = OPNB, Z = Me)

Hydrogenation of *endo*-dicyclopentadiene over P-2 nickel boride[3] afforded *endo*-5,6-trimethylene-8-norbornene, mp 48.5–50°. Hydroboration–oxidation (H_2CrO_4[4]) 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[1] 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% 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,[1] the present results reveal large effects, which permit relatively unambiguous conclusions.

It appears possible to conclude that σ participation cannot contribute significantly to the high *exo*:*endo* ratio observed[5] for VIII-X-OPNB. First, in VIII-X-

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[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.

[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.