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BRIDGING STRAIN IN BICYCLIC CARBOCATIONS

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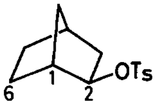
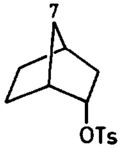
Summary. The solvolysis rates and products of 6-exo- and 6-endo-bicyclo[3.2.1]-octyl toluenesulfonate confirm that differential bridging strain is a major factor in determining the reactivity of epimeric bicyclic sulfonates.

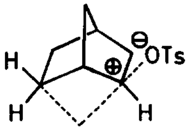
Evidence was presented recently [1,2] that bicyclic cations, to which nucleophiles have limited access [3], can be stabilized by bridging of the cationic center by a pentacoordinate carbon atom in the 3-position; and it was concluded that differential bridging strain is a major cause of different ionization rates of epimeric bicyclic sulfonates in 80 % ethanol [2,4]. Thus bridging by C(6) during the ionization of 2-exo-norbornyl tosylate (exo-1) to the ion pair 2 involves far less strain than bridging by C(7) in the ionization of endo-1 to the ion pair 3, the strain difference leading to an exo/endo rate ratio of 425 [1] (Table 1).



exo-1



endo-1



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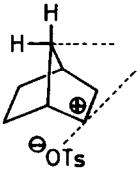

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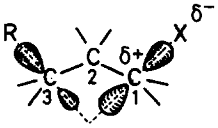
Effective 1,3-bridging implies that the back lobe of the C(3)-R orbital in 4 overlap strongly with the p-orbital of the incipient cationic center C(1) [5]. This condition is satisfied in the cation 2, since the orbital axes (dotted lines) converge and intersect, but not in the cation 3 where the orbital axes are well separated.

It is instructive to compare exo-1 and endo-1 with the homologous 6-exo- and 6-endo-bicyclo[3.2.1]octyl tosylates [6], exo-5 and endo-5, respectively, because their rates differ markedly despite the structural similarities. Thus, exo-5 reacts 371 times slower than exo-1 while endo-5 reacts only 11 times slower than endo-1 (Table 1). The much larger rate reduction for exo-5 causes the exo-5/endo-5 rate ratio to drop to 13 (Table 1) [7].



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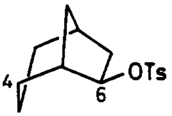
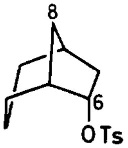
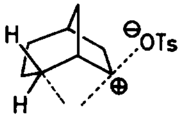


exo-5



endo-5



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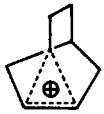

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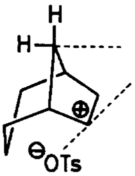

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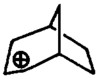

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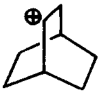

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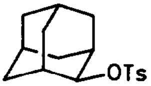
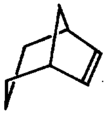
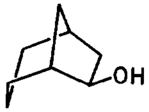
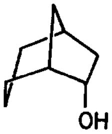
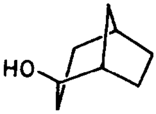
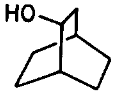
Table 1. First order rate constants for exo-1, endo-1, exo-5 and endo-5 in 80 vol.% ethanol at 70.0° C.

	k (sec^{-1})	k_{rel}	k_{exo}/k_{endo}
exo-1	$3.58 \cdot 10^{-2}$	4786	425
endo-1	$8.42 \cdot 10^{-5}$	11	
exo-5	$9.66 \cdot 10^{-5}$	13	13
endo-5	$7.48 \cdot 10^{-6}$	1	
	$1.15 \cdot 10^{-5}$	0,65	

For C(4) to bridge effectively in the cation 6 derived from exo-5 it should adopt a trigonal bipyramidal configuration, thereby distorting the chair conformation of the cyclohexane ring [8]. However, the orbital axes of C(4) and

C(6) do not intersect in this case and overlap is therefore strongly reduced. It is noteworthy that participation of the C(4)-C(5) sigma bond in exo-5, as suggested by Parker [6], would lead to the symmetrically bridged "nonclassical" cation 7, an intermediate that is, however, not required by the present data. In the cation 8 the orbital axes of C(6) and C(8) converge even less than in 3, which explains the further rate reduction of endo-5. In fact, it reacts almost as slowly as 2-adamantyl tosylate (Table 1) which also resists bridging for stereoelectronic reasons [2].

Table 2. Reaction products (in %) from 0.01 M exo-5 and endo-5 in 70 % dioxane (with 1 equiv. of NEt_3) at 100° C.

	 11	 12	 13	 14	 15
exo-5	50	13	1	17	19
endo-5	11	60	–	12	17

A study of the hydrolysis products of exo-5 and endo-5 in 70 % dioxane (Table 2) confirms Parker's results for acetolysis [6], i.e. exo-5 reacts via the cation 6 to yield 50 % of bicyclo[3.2.1]oct-6-ene (11) beside 13 % of 6-exo-bicyclo[3.2.1]octan-6-ol 12 with retention and ca. 1 % of the 6-endo-alcohol 13 with inversion. But the rearranged alcohols 14 (17 %) and 15 (19 %) are also formed, the former by a C(4) ⟶ C(6) hydride shift to the cation 9, the latter by a Wagner-Meerwein rearrangement of 9 to 10. Hydrolysis of endo-5 took a similar course, except that the inverted 6-exo-alcohol 12 was the main product (Table 2). These results support the conclusion that bridging is weak in the cation 6 and negligible in the cation 8.

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2) C.A. Grob, Angew. Chemie 94, 87 (1982); Int. Ed. Engl. 21, 87 (1982).

3) C.A. Grob & E. Lutz, Helv. Chim. Acta 64, 153 (1981).

4) C.A. Grob & A. Waldner, Tetrahedron Letters 1981, 3235.

5) This idea was introduced by Olah to explain the 2.2 ppm deshielding of the 6-exo-H resonance vs. the 6-endo-H resonance in the ^{1}H-NMR-spectrum of the 2-methyl-2-norbornyl cation: G.A. Olah, A.M. White, J.R. DeMember, A. Commeyras & C.Y. Lui, J. Amer. Chem. Soc. 92, 4627 (1970).

6) R.A. Appleton, J.C. Fairlie, R. McCrindle & W. Parker, J. Chem. Soc.(C) 1968, 1716.

7) In acetic acid the rate ratio was also 13 (see ref. 6).

8) Distortion of the cyclohexane ring by pentacoordinate carbon is also thought to contribute to the inertness of cyclohexyl halides in S_N2 reactions; cf. H.C. Brown, R.S. Fletcher & R.B. Johannesen, J. Amer. Chem. Soc. 73, 212 (1951).

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