Tetrahedron Letters, Vol.22, No.34, pp 3235 - 3238, 1981
Printed in Great Britain

0040-4039/81/343235-04$02.00/0

BRIDGING STRAIN IN THE SOLVOLYSIS OF EPIMERIC BICYCLIC TOLUENESULFONATES

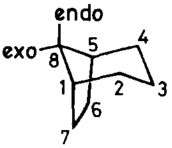
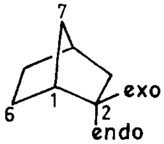
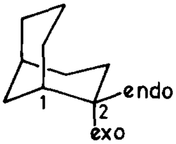
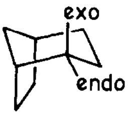
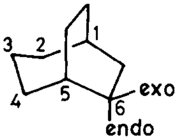
Cyril A. Grob* & Adrian Waldner
Institute of Organic Chemistry, University of Basel,
St. Johanns-Ring 19, CH-4056 Basel, Switzerland.

Summary. The large variations in the rate ratios for the epimeric bicyclic p-toluenesulfonates 1 to 5 are ascribed to differential bridging strain accompanying the formation of intermediate cations.

It is instructive to compare the solvolysis rates, exo/endo rate ratios (k_{exo}/k_{endo}) and products of the bicyclic secondary tosylates 1 - 5 (TABLE) [1] because the latter belong to a class of compounds which ionize with little or no nucleophilic assistance from the solvent; i.e. they react by a k_c process [2]. The positive charge generated in the transition state is therefore largely dispersed intramolecularly. This raises the question as to the cause of the decreasing k_{exo}/k_{endo} ratios listed in the TABLE. As shown in the sequel these variations can be explained by differential strain in a pair of epimers resulting from the bridging of the incipient cationic centers at Cα by the γ-carbon atoms at the rear of the Cα-OTs bond [3]. In effect 1,3-bridging amounts to electrophilic attack by an incipient cationic center on a saturated carbon atom.

The rate ratio of 1270 for 8-exo- and 8-endo-bicyclo[3.2.1]octyl tosylate 1 points to a large difference in the respective bridging strains. Thus, bonding of C(8) to C(2) or C(4), or to both, subdivides the 6-membered ring in the cation 6 into quasi 3- and 5-membered rings, as indicated by the dotted line. On the other hand bonding of C(8) to C(6) or C(7), or to both, subdivides the 5-membered ring in the cation 7 into quasi 3- and 4-membered rings which entails more strain. Consequently, the exo-tosylate 1 reacts much faster than the endo-epimer. This is also borne out by the reaction products formed in 70 % dioxane. Whereas most of the alcohols and olefins obtained from the exo-tosylate 1 are derived from the

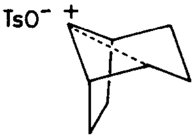
TABLE. First order rate constants in 80 vol.% ethanol at 40.0° (1 at 130°)

			$k\ (sec^{-1})$	$\frac{k_{exo}}{k_{endo}}$
	1	exo	$1.12 \cdot 10^{-6}$	1270
		endo	ca. $8.8 \cdot 10^{-10}$	
	2	exo	$1.48 \cdot 10^{-3}$	548
		endo	$2.70 \cdot 10^{-6}$	
	3	exo	$1.09 \cdot 10^{-4}$	57
		endo	$1.92 \cdot 10^{-6}$	
	4	exo	$8.71 \cdot 10^{-5}$	13
		endo	$6.68 \cdot 10^{-6}$	
	5	exo	$1.14 \cdot 10^{-4}$	1.45
		endo	$7.87 \cdot 10^{-5}$	

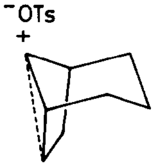
rearranged cation 8, none of the products from the endo-tosylate 1 stem from the rearranged and strained cation 9 [4].

Likewise, the high exo/endo rate ratio of 548 for the 2-norbornyl tosylates 2 (TABLE) reflects the large differential strain attending C(6)-C(2) bridging in the cation 10 from the exo-tosylate 2 and C(7)-C(2) bridging in the cation 11 from the endo-epimer. As has become increasingly clear [3] the exo-alcohol 2, which is obtained almost exclusively from both tosylates 2 [5], is derived from the bridged cation 10 [6].

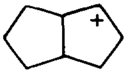
The rate ratio of 57 for the 2-exo- and 2-endo-bicyclo[3.3.1]nonyl tosylates 3 indicates an appreciable differential bridging strain accompanying the forma-



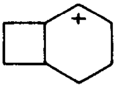
6



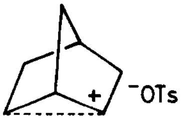
7



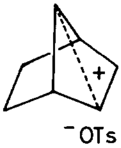
8



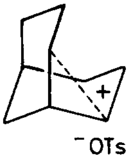
9



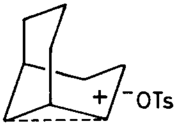
10



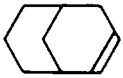
11



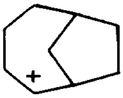
12



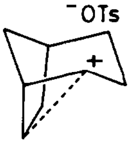
13



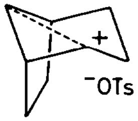
14



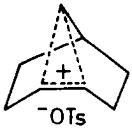
15



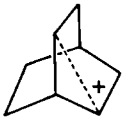
16



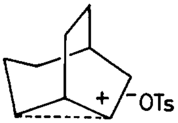
17



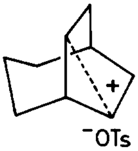
18



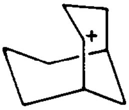
19



20



21



22

tion of the respective cations 12 and 13. It is noteworthy that the olefin 14 is practically the sole product from the exo-tosylate 3 and that no rearrangement to the more strained bicyclo[3.2.2]nonane system 5 [7] occurs. The endo-tosylate, however, yields mostly endo- and exo-alcohol 3 beside some epimeric alcohols derived from the bicyclo[4.2.1]nonyl-2-cation 15 [8].

The rate ratio of 13 for the 2-exo- and 2-endo-bicyclo[3.2.1]octyl tosylates 4 [9] implies an even smaller differential bridging strain in the cations 16 and 17 due to the conversion of a 7-ring to a quasi 6- and 3-ring and a 6-ring to a quasi 5- and 3-ring, respectively. The cation 17 is of special interest because it could assume the symmetrically bridged "non-classical" structure 18 which is often associated with unusual stability [10]. Nevertheless, the 2-endo-tosylate 4 is the less reactive epimer. Furthermore, the latter yields 92 % of endo-alcohol 4 with retention beside 8 % of exo-alcohol 4 with inversion, whereas about equal amounts of alcohols derived from 16 and the rearranged cation 19 are obtained from the exo-tosylate 4.

The rate ratio of 1.45 for 6-exo- and 6-endo-bicyclo[3.2.2]nonyl tosylate 5 indicates only a negligible differential bridging strain attending the formation of the cations 20 and 21. In both cases the products, i.e. alcohols and olefins, are derived exclusively from the rearranged cations 22 and 15 respectively.

Of the above pairs of epimeric tosylates 1 - 5 the exo-tosylates are the more reactive epimers, presumably because participation of the larger bridge generates the lesser strain.

REFERENCES

1) exo and endo denote exo- and endo-tosyloxy or hydroxy groups.
2) C.A. Grob & E. Lutz, Helv. chim. acta 64, 153 (1981) and references therein.
3) C.A. Grob, R. Hanreich & A. Waldner, Tetrahedron Letters 1981,
4) The acetolysis rates and products of the exo- and endo-tosylates 1 have been studied by C.S. Foote & R.B. Woodward, Tetrahedron 20, 687 (1964), who offer a similar explanation for the high k_{exo}/k_{endo} ratio.
5) W. Fischer, C.A. Grob, G. von Sprecher & A. Waldner, Helv. chim. acta 63, 928 (1980).
6) "The Nonclassical Ion Problem" by H.C. Brown, with comments by P. von R. Schleyer; Plenum Press, New York (1977). In this review of the norbornyl cation problem H.C. Brown espouses a steric explanation for the high exo/endo rate ratio and the formation of exo-alcohol 2.
7) E.E. Engler, J.D. Androse & P. von R. Schleyer, J. Amer. chem. Soc. 95, 8005 (1973).
8) M. Hanack, W. Kraus, W. Rothenwöhrer, W. Kaiser & G. Wentrup, Liebigs Annalen 703, 44 (1967).
9) The acetolysis of these compounds has been studied extensively by H.L. Goering & G.N. Fickes, J. Amer. chem. Soc. 90, 2848, 2856, 2862 (1968).
10) For reasons to be given elsewhere unsymmetrical bridging, as in 10 and 17, is preferred to S. Winstein's concept of symmetrically bridged nonclassical ions (see ref. 6).

(Received in Germany 21 May 1981)