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POLAR AND ANCHIMERIC EFFECTS IN THE SOLVOLYSIS OF 6-endo-SUBSTITUTED 2-NORBORNYL-p-TOLUENE-SULFONATES

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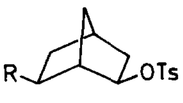
Summary. A study of the influence of 6-endo substituents on the reactivity of 2-exo- and 2-endo-norbornyl p-toluenesulfonates 3 and 4, respectively, confirms that polar rather than steric effects control relative rates.

Comparative studies of the rates and products of diastereomeric 6-substituted 2-norbornyl tosylates 1, 2 and 3 have provided valuable information regarding the solvolysis mechanism of the parent compounds, i.e. 2-exo and 2-endo-norbornyl tosylate, 1 and 2, R = H, respectively [1]. Now that additional 6-endo-R-2-exo-tosylates 3 and some 6-endo-R-2-endo-tosylates 4 have been prepared the importance of polar and steric effects in the reactions of norbornyl derivatives [2] can be discussed on a broader experimental basis.



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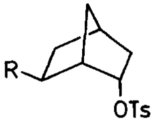

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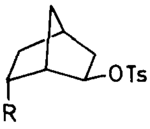

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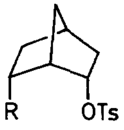

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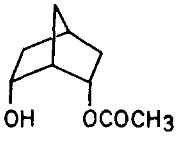
The reactions of the tosylates 3e - 3i (TABLE) in 70 % dioxane differ markedly from those of the recently reported tosylates 3a - 3d [1d]. Whereas the latter react via norbornyl cations, the tosylates 3e, 3f and 3g react with anchimeric assistance from the nucleophilic endo substituents $OCOCH_3$, $COOCH_3$ and CH_2NH_2, respectively, to form the known products 5, 6 and 7 (R = NH) [3]. This also follows from their rate constants k_3 in 80 % ethanol which are 68, 131 and 132 times as large as those for the corresponding 6-exo epimers 1e, 1f and 1g, as the rate

TABLE. First order rate constants k for 3 and 4 in 80 vol. % ethanol and rate ratios at 70.0° C (* denotes rates at 140° C).

	R =	k_3	k_4	k_3/k_1	k_3/k_4	$k_{2/4}$
a)	H	3.58×10^{-2}	8.42×10^{-5}	1	425	1
b)	CH_3	5.58×10^{-3}	1.19×10^{-5}	0.51	469	5.1
c)	Br	1.95×10^{-7}	3.10×10^{-8}	1.3	6.3	13
d)	CN	$6.65 \times 10^{-5*}$	$5.98 \times 10^{-6*}$	0.35	11^*	18^*
e)	$OCOCH_3$	5.56×10^{-5}	1.65×10^{-7}	68	337	7.3
f)	$COOCH_3$	8.29×10^{-4}		131		
g)	CH_2NH_2	1.17		132		
h)	OCH_3	2.75×10^{-4}	4.68×10^{-6}	0.95	59	9.2
i)	OH	2.02×10^{-3}	7.46×10^{-4}	3.3	2.7	0.134



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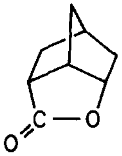

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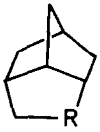

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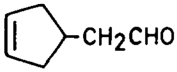

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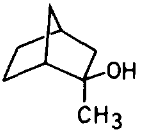

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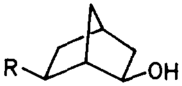

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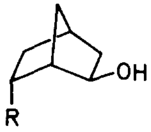

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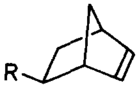

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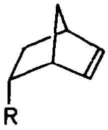

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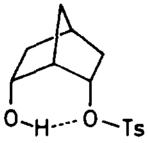

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ratios k_3/k_1 in the TABLE show. The tosylates of the endo-carboxylic acid 3, R = COOH, and the alcohol 3, R = CH_2OH, were not isolable and cyclized spontaneously to 6 and 7 (R = O), respectively. Like their 6-exo-epimers 1h and 1i [1a] the 6-endo-methoxy and 6-endo-hydroxy tosylates 3h and 3i, respectively, underwent concerted fragmentation to the aldehyde 8, and at similar rates (cf. k_3/k_1 in the TABLE).

The six 6-endo-substituted 2-endo-tosylates studied to date are 4b (R = CH_3), 4c (R = Br), 4d (R = CN), 4e (R = OAc), 4h (R = OCH_3) and 4i (R = OH) (TABLE). When reacted in 70 % dioxane the tosylate 4b yielded the tertiary alcohol 9 by a C(1) → C(2) carbon shift followed by a C(6) → C(2) hydride shift [1d] as well as the alcohols 10 and 11, R = CH_3. The tosylate 4c led to products derived mainly from the bromo alcohols 10 and 11, R = Br, and the bromo olefins 12 and 13, R = Br. The cyano tosylate 4d led to unidentifiable products due to the long reaction time (11 days) and the high temperature (140°) required. The acetate 4e yielded mainly 11 and 13, R = OAc, whereas 4h and 4i underwent fragmentation to the aldehyde 8.

The rate constants for the 6-endo-R-2-endo-tosylates 4 in 80 % ethanol are compared to those for the corresponding 2-exo-tosylates 3 in the TABLE. The ratios of the constants k_3/k_4 decrease as the electron-attracting power of the substituents a - d increase. Furthermore, log k values for 4a - 4e correlate well with the respective inductive substituents constants σ_I^q [4] (ρ = -1,13), a sign that rates are controlled by polar effects.

The high k_3/k_4 ratios of 337 and 59 when R = $OCOCH_3$ and OCH_3, respectively, are due to the anchimeric effect in the former compound 3e and to the frangomeric effect [5] in the latter compound 3h, both effects being excluded in the endo-endo series 4 for stereoelectronic reasons. Surprisingly, k_3/k_4 is only 2.7 when R = OH. This low ratio is due to the unusually high rate of 4i [6] and is evidently caused by hydrogen bonding of the 6-endo-OH to the endo-OTs group, as in 14 (broad band at 3350 cm^{-1}, unchanged on dilution), thus facilitating ionization of the latter in the manner of a protic solvent. Conversely, the 6-endo-OCH_3 group hinders solvation by a protic solvent and lowers the ionization rate. This conclusion is supported by the $k_{\underline{2}}/k_{\underline{4}}$ ratios which are larger than one except when R = OH (TABLE).

Steric hindrance to ionization [2] seems to be of minor importance in determining 2-exo/2-endo rate ratios, as the effect of an endo-methyl group at C(6) in 3 and 4 shows. Thus, the endo-methyl group in 3b lowers the rate of 2-exo-norbornyl tosylate 3a by a factor of 6.4 (TABLE), although it cannot hinder the ionization of the 2-exo-OTs group. In the 2-endo-tosylate 4b, where hindrance to the departure of the endo-OTs group might be expected [2] the endo-methyl group decreases rate by a similar factor, namely 7. This absence of a significant difference between the H/CH_3 ratios in 3 and 4 supports our view [1c] that 2-exo/2-endo rate ratios are determined mainly by polar and stereoelectronic effects. However, the rate decrease of approximately seven caused by the 6-endo-methyl group in 3b and 4b could well be the result of steric hindrance to solvation.

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   c. ibid. 1979, 1905; d. C.A. Grob, B. Günther & R. Hanreich, ibid., in press.

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6) 4i reacts 159 times faster than 4h, whereas 3i reacts only 7 times faster than 3h.

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