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STEREOELECTRONIC CONTROL OF EXO/ENDO RATE RATIOS IN THE SOLVOLYSIS OF 2-NORBORNYL p-TOLUENESULFONATES

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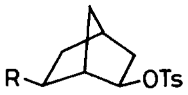
Summary. The variable exo/endo rate ratios observed in the solvolysis of 6-exo-substituted exo- and endo-2-norbornyl p-toluenesulfonates are due to differential transmission of polar effects in the transition state for ionization.

The hydrolysis of the exo- and endo-2-norbornyl p-toluenesulfonates 1a - ℓ and 2a - ℓ, respectively, in 70 % dioxane produced a similar series of unrearranged and rearranged substitution and elimination products, albeit in different yields [1,2]. Hence, stereoisomeric ion pairs [3] are implicated as intermediates. In contrast, 1 and 2, m - r, underwent quantitative fragmentation and hydrolysis to (cyclopent-3-en-1-yl)acetaldehyde 3 [1,2].



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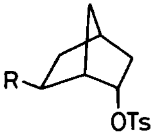

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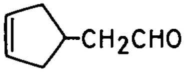

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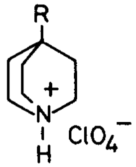

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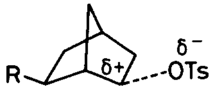

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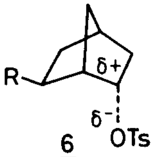

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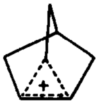

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The first order rate constants (k) for 1 and 2, a - r, vary over a range of ca. 10^6 and 10^3, respectively (Table). Thus, 6-exo-substituents control the ionization rates far more strongly in the exo- than in the endo-series. Furthermore, log k for 1 and 2, a - h, correlate well with the corresponding inductive substituent constants σ_I^q for R, as derived from pK_a values of 4-substituted quinuclidinium perchlorates 4 [4] (Figure 1). As evidenced by the reaction constants ρ of -2.0 and -0.86, respectively, the inductive effect of R is transmitted more

TABLE

	R =	$k(s^{-1})$, 70.0°		$\frac{k(\text{exo})}{k(\text{endo})}$	accelerations	
		exo-series 1	endo-series 2		exo	endo
a)	H	3.58×10^{-2}	8.42×10^{-5}	425		
b)	CH_3	1.09×10^{-2}	6.02×10^{-5}	181		
c)	CH_2Br	1.06×10^{-4}	6.75×10^{-6}	16		
d)	COOH	5.97×10^{-6}	2.88×10^{-6}	2		
e)	$COOCH_3$	6.33×10^{-6}	1.73×10^{-6}	3.7		
f)	$OCOCH_3$	8.14×10^{-7}	1.21×10^{-6}	0.67		
g)	Br	1.51×10^{-7}	4.06×10^{-7}	0.37		
h)	CN	1.23×10^{-7}	1.40×10^{-7}	0.88		
i)	CH_2NH_2	8.84×10^{-3}	3.73×10^{-5}	237	4	1.3
j)	CH_2OH	5.97×10^{-3}	4.39×10^{-5}	136	5	2
k)	$CONH_2$	7.56×10^{-5}	7.12×10^{-6}	11	16	3.6
l)	COO^-	7.04×10^{-2}	1.16×10^{-4}	607	95	6.7
m)	$NHCOCH_3$	2.21×10^{-4}	1.07×10^{-5}	21	22	4
n)	SCH_3	3.34×10^{-4}	2.09×10^{-5}	16	39	8.3
o)	OCH_3	2.88×10^{-4}	4.29×10^{-5}	7	84	25
p)	OH	6.05×10^{-4}	1.00×10^{-4}	6	97	46
q)	NH_2	2.25×10^{-2}	2.55×10^{-4}	88	160	30.5
r)	$N(CH_3)_2$	1.45×10^{-1}	6.25×10^{-5}	2320	1253	8

effectively in the "staggered" conformation 5 than in the "skew" conformation 6 of the transition state. This also applies to electrofugal substituents [5], i.e. potential σ-electron donors, such as CH_2NH_2, CH_2OH, $CONH_2$ and COO^-, or n-electron donors, such as $NHCOCH_3$, SCH_3, OCH_3, OH, NH_2 and $N(CH_3)_2$. In both cases the exo- and the endo-tosylates react faster than predicted from their σ_I^q values [6]. Again, the accelerations are larger in the exo series (Table).

Differential transmission of polar effects is reflected in variable exo/endo rate ratios (Table) which decrease from a maximum of 2320 for $(CH_3)_2N$ to 0.37 for Br, i.e. as the net electron attraction by R increases.

These results preclude an explanation for high exo/endo rate ratios based solely on sterically hindered and thus retarded ionization of the endo isomers 2 [7]. Nor is it necessary to postulate different mechanisms for 1a and 2a, i.e. one leading directly to a bridged or nonclassical ion 7 [8], the other to a conventional carbocation 8. In fact, a common mechanism is indicated for both series, since log k for 1a - 1ℓ and for 2a - 2ℓ correlate well with one another (Figure 2)

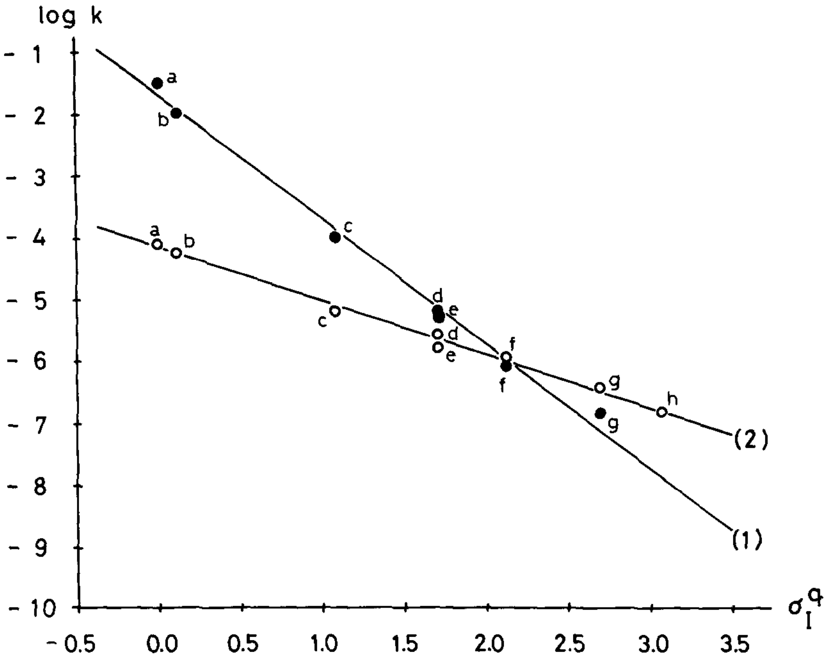


Figure 1. Plot of log k for $\underline{1}$ and $\underline{2}$ against σ_I^q.

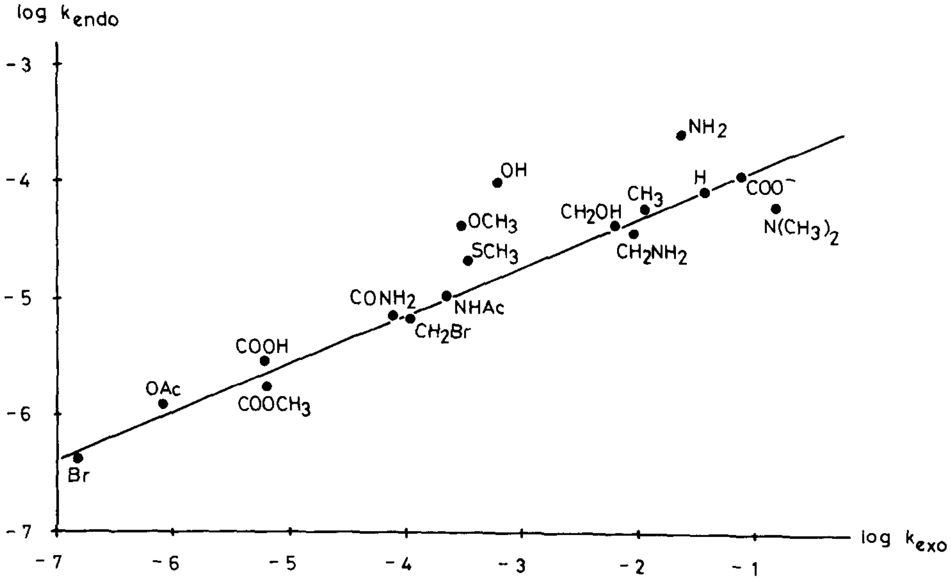
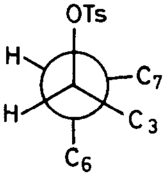
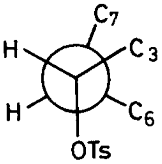


Figure 2. Plot of log k for endo-tosylates $\underline{2}$ against log k for exo-tosylates $\underline{1}$.

Significantly, the correlation fails when fragmentation occurs as with 1 and 2, n - r.



exo-9



endo-10

The results suggest that the exo/endo rate ratio of 425 for 1a and 2a is also stereoelectronically controlled. As illustrated in the Newman projections exo-9 and endo-10 the same ligands are attached to C(1) and C(2). However, they are differently aligned with respect to the C(2)-OTs bond. In exo-9 the C(1)-C(6) bond is antiperiplanar. It therefore exerts a stronger inductomeric or CC-hyperconjugative [6,9] effect than the deflected C(1)-C(7) bond in endo-10, which therefore provides less stabilization in the transition state. Conversely, an electron withdrawing substituent at C(6) will destabilize the transition state for exo-9 more than for endo-10 and thus reduce or even reverse the exo/endo rate ratio.

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