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POLAR SUBSTITUENT EFFECTS IN THE SOLVOLYSIS OF 2-METHYL-2-ENDO-NORBORNYL 2,4-DINITROPHENYL ETHERS

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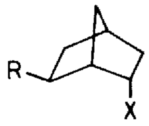
Summary. The solvolysis rates of tertiary 2-endo-norbornyl derivates 2 are less strongly controlled by the polar effects of substituents at C(6) than the rates of the secondary analogues 1.

There is now general agreement that both secondary and tertiary 2-endo-norbornyl derivatives, 1 and 2, respectively, solvolyse by socalled k_c processes, i.e. they ionize to the respective cations 3 and 4 without appreciable nucleophilic involvement of the solvent [1].



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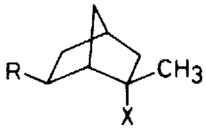

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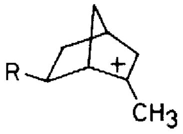

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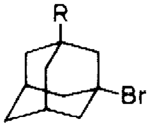
It was also established recently that neutral and electron-withdrawing 6-exo-substituents R control ionization rates of secondary 2-endo-tosylates 1 (X = $p\text{-}CH_3C_6H_4SO_3$) by their inductive effects, whereas electrofugal substituents, such as COO^- and CH_2OH, lead to enhanced rates [2], since these groups act as net electron donors in k_c processes [3]. It was therefore of interest to study the effect of polar substituents in the ionization of corresponding tertiary 2-endo derivatives 2. 2,4-Dinitrophenyl ethers (X = $2,4\text{-}(NO_2)_2C_6H_3O$) were chosen because of their conveniently measureable rates. The TABLE lists first order rate constants for the ethers 2a - 2h in 80 vol.% ethanol at 100° C and the corresponding inductive substituent constants σ_I^q of R [4].

TABLE

$\underline{2}$	R =	$k(s^{-1})$	σ_I^q
a	CH_3	1.74×10^{-4}	0.11
b	H	1.58×10^{-4}	0
c	$(CH_3)_2CH$	1.29×10^{-4}	-0.08
d	CH_2Br	2.13×10^{-5}	1.07
e	$COOCH_3$	7.69×10^{-6}	1.70
f	$OCOCH_3$	4.18×10^{-6}	2.12
g	COO^-	2.89×10^{-4}	0.61
h	CH_2OH	1.08×10^{-4}	0.66

In Figure 1 log k for the tertiary endo ethers $\underline{2}$a - $\underline{2}$h (plot 1) and, for comparison, log k for the secondary endo tosylates $\underline{1}$a - $\underline{1}$h [2] (plot 2) are plotted against σ_I^q. It is evident that both series correlate equally well if the points for the electrofugal substituents COO^- and CH_2OH are omitted. However, the two series differ in their sensitivity to changes of σ_I^q, as evidenced by the reaction constants ρ of -0.75 for $\underline{2}$ and -0.86 for $\underline{1}$ [2]. Thus, formation of the tertiary cations $\underline{4}$ is somewhat less affected by the polar effect of R than the formation of the less stable secondary cations $\underline{3}$. As observed with the tertiary halides $\underline{5}$ and $\underline{6}$ the electrofugal groups COO^- and CH_2OH act as net electron donors [3, 5] and therefore lead to elevated rates by factors of 5.5 and 2.2, respectively.



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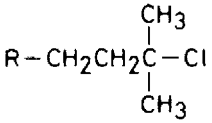

$$R-CH_2CH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-Cl$$

$\underline{6}$

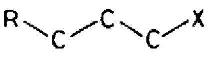

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Figure 2 includes plots of log k for the tertiary endo ethers $\underline{2}$a - $\underline{2}$h vs. log k for the secondary tosylates $\underline{1}$a - $\underline{1}$h (plot 1) and vs. log k for 1-substituted 3-bromoadamantanes $\underline{5}$ [3] (plot 2). The excellent correlations point to a common k_c mechanism for these series of compounds. They show further that relative rates are controlled by polar rather than by steric effects, as is often claimed [6].

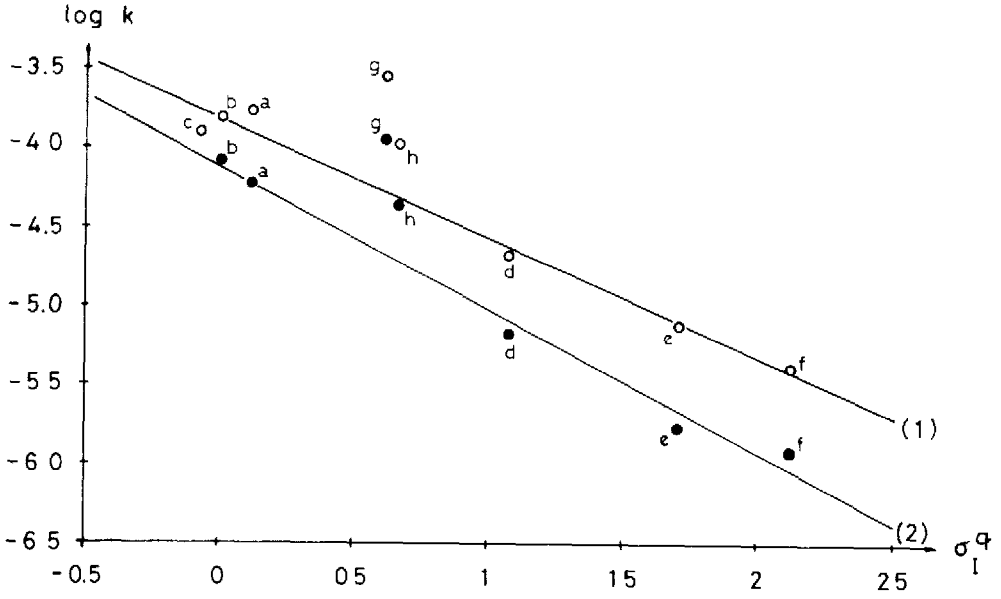

Figure 1 (1) Plot of log k for 2 vs σ_I^q (2) Plot of log k for 1 vs σ_I^q

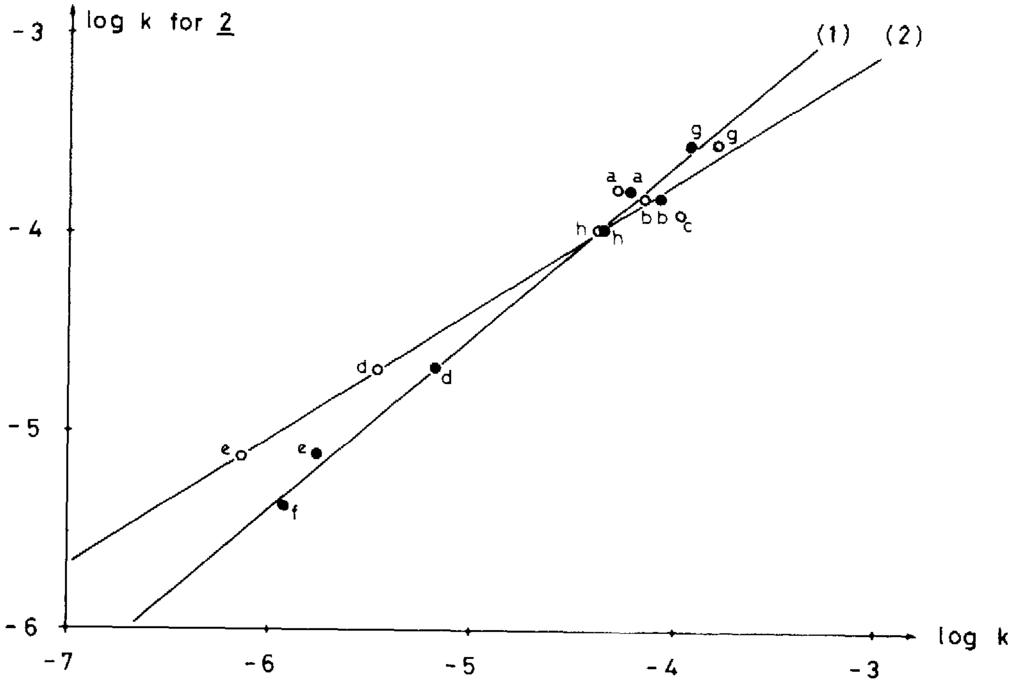

Figure 2 (1) Plot of log k for 2 vs log k for 1
(2) Plot of log k for 2 vs log k for 5

It is also instructive to compare the reaction constants ρ for 1 (-0.86), 2 (-0.75), 5 (-1.14) and 6 (-0.71). Of these models only 5, which has the highest ρ value, possesses the planar W-like conformation 7 shown to be most favorable for the transmission of polar effects [2].

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