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

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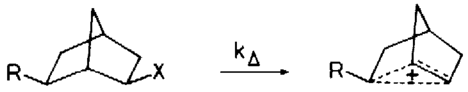
Summary. A comparison of polar substituent effects in the solvolysis of tertiary and secondary 2-exo-norbornyl derivatives indicates that a gradation of electron shifts provides a better mechanistic model that one involving the classical-non-classical ion dichotomy.

There is a widespread belief that secondary 2-exo-norbornyl derivatives 1, R = H, solvolyse with anchimeric assistance from the C(1)-C(6) σ-bond, whereas their tertiary analogues 3, R = H, react without such assistance. Furthermore, the former (k_Δ) process is thought to lead to a symmetrically bridged, i.e. non-classical cation 2, the latter (k_c) process, however, to an unbridged, i.e. classical cation 4 [1]. This rigorous mechanistic dichotomy cannot be upheld in the light of the following comparison of substituent effects in the solvolysis of tertiary and secondary 2-exo-norbornyl derivatives.



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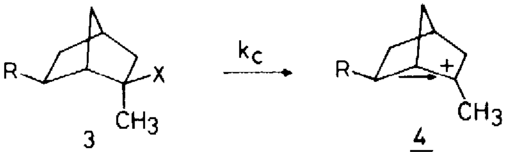

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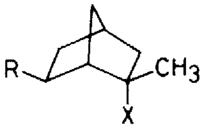

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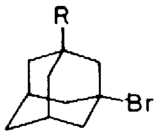

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First order rate constants for the reaction of tertiary exo-2,4-dinitrophenyl ethers 3a - 3h (X = 2,4-$(NO_2)_2C_6H_3O$) and for the corresponding endo ethers 5 [2] in 80 vol.% ethanol at 100° C are listed in the following TABLE.

TABLE

	R =	exo-ethers $\underline{3}$ $k(s^{-1})$	endo-ethers $\underline{5}$ $k(s^{-1})$	$\frac{k(exo)}{k(endo)}$
a)	CH_3	4.74×10^{-2}	1.74×10^{-4}	272
b)	H	2.70×10^{-2}	1.58×10^{-4}	171
c)	$(CH_3)_2CH$	6.34×10^{-2}	1.29×10^{-4}	491
d)	CH_2Br	2.23×10^{-3}	2.13×10^{-5}	105
e)	$COOCH_3$	3.97×10^{-4}	7.69×10^{-6}	52
f)	$OCOCH_3$	5.46×10^{-5}	4.18×10^{-6}	13
g)	COO^-	1.27×10^{-1}	2.89×10^{-4}	439
h)	CH_2OH	2.78×10^{-2}	1.08×10^{-4}	257

When log k for the ethers $\underline{3}$a - $\underline{3}$h are plotted against the inductive substituent constants σ_I^q for R [3] (Figure 1, plot 1) the points fit the regression line well if the electrofugal groups COO^- and CH_2OH are omitted. The latter are known to exert a special electron-donating effect in k_c processes [4] and lead to elevated rates by factors of 16 and 4, respectively. The reaction constant ρ of -1.30 for the exo ethers $\underline{3}$, as calculated from the slope of plot 1, is substancially larger than that for the endo ethers $\underline{5}$ (ρ = -0.75 [2]) (plot 2), but smaller than the ρ value of -2.0 for the recently reported secondary exo-tosylates $\underline{1}$, X = OTs [5]. Evidently, the ionization rates of $\underline{3}$ and $\underline{5}$ are mainly controlled by the polar effects of R, and these are more strongly transmitted in the W-like conformation $\underline{3}$ than in the sickle-like conformation $\underline{5}$. This is also reflected in the exo/endo rate ratios (TABLE) which decrease from 491 for R = $(CH_3)_2CH$ to 13 for R = $OCOCH_3$, i.e. as the electron attracting power of R increases. In addition the ρ-values for $\underline{3}$ and $\underline{1}$ show that ionization to tertiary cations $\underline{4}$ is less affected by substituents at C(6) than ionization to secondary cations $\underline{6}$.

log k for the tertiary exo ethers $\underline{3}$ also correlate well with log k for the tertiary endo ethers $\underline{5}$ (Figure 2, plot 1) and for the 1-substituted 3-bromoadamantanes $\underline{7}$ [4] (plot 2), as would be expected for like processes. However, the

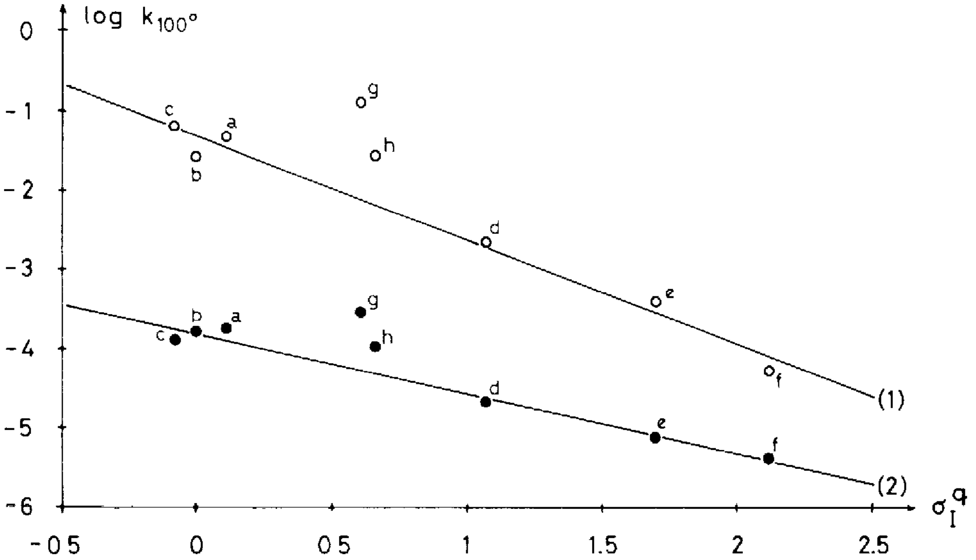

Figure 1 Plot (1) log k $\underline{3}$ vs σ_I^q Plot (2) log k $\underline{5}$ vs σ_I^q

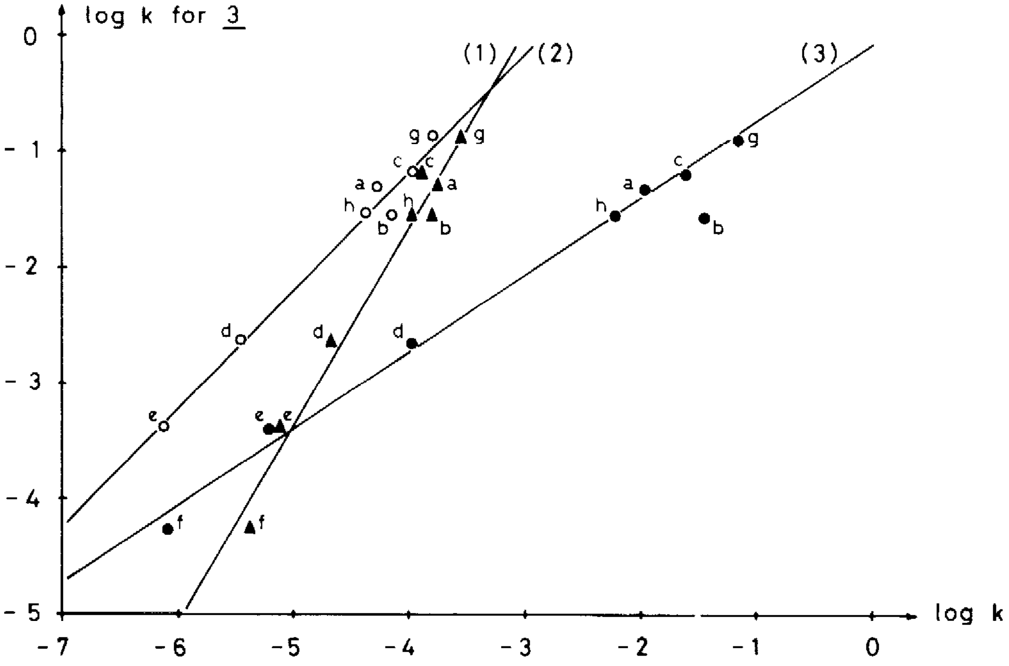

Figure 2 Plots of log k $\underline{3}$ vs (1) log k $\underline{5}$, (2) log k $\underline{7}$, (3) log k $\underline{1}$

ρ values are somewhat larger for the strained norbornyl ethers 3 (-1.20) than for the unstrained bromoadamantanes 7 (-1.14) [4].

The most important result is the excellent correlation between log k for the tertiary exo ethers 3 and the secondary exo tosylates 1 [5] (Figure 2, plot 3), showing that the two series are affected in the same way but in different degree (slope 0.66) by substituents at C(6). The only exception is the deviation of the point for R = H, which indicates that further factors are involved here [6].

The correlation in plot 3 suggests that the reactions of the secondary and tertiary derivatives, 1 and 3, respectively, differ only in the degree of displacement of the R-C(6)-C(1) electrons towards the incipient cationic centers at C(2). This induced polarization, symbolized by horizontal arrows in the cations 4 and 6, should be stronger in the secondary cation 6 and therefore lead to stronger bonding between C(6) and C(2). In the symbolism of conventional structural formulae this implies stronger bridging. On this basis bridging (σ-participation), as in 2, and longitudinal polarization, as in 4 and 6, are alternative descriptions of the transmission of polar effects in electron deficient molecules.

We thank Professor Paul von R. Schleyer, Erlangen, for stimulating criticism.

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6) e.g. the rates in the tertiary series 3 follow the inductive order i-Pr > CH_3 > H, whereas the order is H > i-Pr > CH_3 in the secondary series 1. This reversal is probably caused by the easier and stronger solvation of C(6) in the secondary cation 6, R = H.

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