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INDUCTIVE, CC-HYPERCONJUGATIVE AND FRANGOMERIC EFFECTS IN THE SOLVOLYSIS OF 6-EXO-SUBSTITUTED 2-EXO-NORBORNYL P-TOLUENESULFONATES

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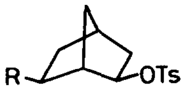
As recently reported [1] the inductive effect alone fails to account for polar substituent interactions in the solvolysis of saturated tri- and bicyclic halides. This applies particularly to the strained 6-exo-substituted 2-exo-norbornyl tosylates 1a - 1q (Table), as the following study shows.



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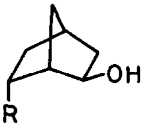

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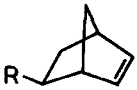

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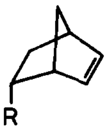

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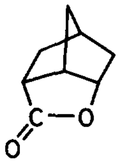

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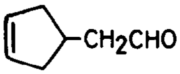

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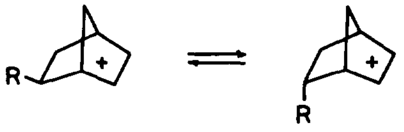
Hydrolysis of the tosylates 1a - 1k in 70 % aqueous dioxane yielded predominantly unrearranged 2-exo-R-2-exo-norbornanols 2a and exo-R-norbornenes 3a beside their rearranged epimers 2b and 3b. When R was $COOCH_3$, COOH, COO^- and $CONH_2$, the lactone 4 was also formed. Furthermore, 1d, 1e and 1k yielded substancial amounts of the corresponding nortricyclenes 5. In the case of 1a (R = H), where the rearrangement is degenerate, 94 % of 2-exo-norbornanol were obtained in addition to 5.5 % nortricyclene and 0.5 % norbornene. In contrast, the tosylates 1ℓ - 1q underwent quantitative fragmentation to (cyclopent-3-en-1-yl)-acetaldehyde 6.

Relative rate constants for the tosylates 1a - 1q, measured in 80 vol. % ethanol, and the corresponding inductive substituent constants σ_I^q [2] for R are listed in the following Table.

TABLE

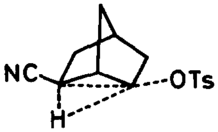
1	R =	k_{rel} (70° C)	σ_I^q	acceleration
a)	H	1	0	
b)	CH_3	0.304	0.11	
c)	CH_2Br	3×10^{-3}	1.07	
d)	$COOCH_3$	1.8×10^{-4}	1.69	
e)	COOH	1.7×10^{-4}	1.69	
f)	Br	4.2×10^{-6}	2.69	
g)	CN	3.5×10^{-6}	3.06	8
h)	CH_2NH_2	0.247	0.48	4
i)	CH_2OH	0.167	0.62	5
j)	$CONH_2$	2.1×10^{-3}	1.82	16
k)	COO^-	1.97	0.72	95
l)	$NHCOCH_3$	6.2×10^{-3}	1.66	22
m)	SCH_3	9.3×10^{-3}	1.69	39
n)	OCH_3	8.0×10^{-3}	1.89	84
o)	OH	1.69×10^{-2}	1.76	97
p)	NH_2	0.628	1.08	160
q)	$N(CH_3)_2$	4.03	1.12	1200

The logarithms of the rate constants for 1a - 1f correlate well with the corresponding σ_I^q values (Figure). Ionization is therefore controlled by the inductive effect of R and leads to normal and rearranged cations 7a $\rightleftarrows$ 7b, the precursors of the substitution, 1,2- and 1,3-elimination products [3]. It is noteworthy that log k for 2-exo-norbornyl tosylate 1a also fits the inductive correlation line defined by the tosylates 1b - 1f, some of which possess strongly electron attracting substituents. It is therefore doubtful whether the derived cationic intermediates should be formulated as bridged species **8** [4], i.e. as non-classical ions [5].



7a **7b**

8



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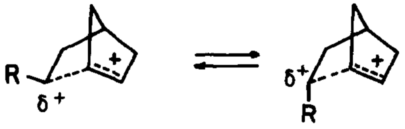

10a **10b**

11

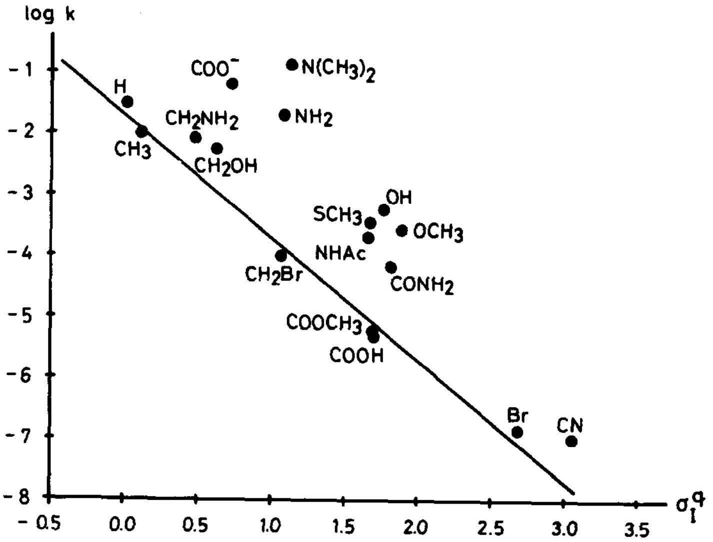

Figure. Plot of log k for 6-exo-substituted 2-exo-norbornyl tosylates against σ_I^q.

The eightfold rate increase shown by the nitrile 1g, as calculated from the deviation of the point from the regression line (Figure), can be ascribed to participation of the "loosened" C(6)- endo-H bond in the transition state 9, a view that is supported by the formation of 44 % nortricyclene 5, R = CN.

When the potentially electrofugal groups [6] CH_2NH_2, CH_2OH, $CONH_2$ and COO^- (1h - 1k) are attached to C(6) ionization occurs 4 to 95 times faster than expected on the basis of their σ_I^q values (Figure, Table). It follows that the positive charge generated at C(2) is increasingly transferred to C(6) by CC-hyperconjugation, as expressed in 10a and its rearranged epimer 10b. Finally, with strongly conjugating donor (+M) substituents at C(6), as in 1ℓ - 1q, accelerations of 22 - 1200 (Table) and concomitant fragmentation are observed. The concerted fragmentation mechanism [7] is indicated for the amines 1p and 1q leading to frangomeric accelerations of 120 and 1200, respectively, although a double bond is generated at an unfavorable bridgehead position in the transition state 11. However, a two-step pathway via hyperconjugated cations 8 is probably favored for the less reactive tosylates 1ℓ - 1 o.

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5) For an extensive discussion see H.C. Brown, "The Nonclassical Ion Problem", Plenum Press, New York, 1977.

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