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INDUCTIVITY AND BRIDGING IN THE FORMATION OF 2-NORBORNYL CATIONS

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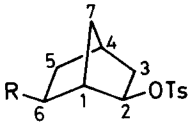
Abstract: The effects of substituents at C5, C6 and C7 on the solvolysis rates of 2-norbornyl p-toluene sulfonates confirm that through space induction is directional and depends on distance and bridging strain.

As recently reported[1] the relative rates of the 6-exo-substituted 2-exo-norbornyl p-toluenesulfonates 1 and their 7-anti-substituted 2-endo analogues 2 in 80% ethanol are controlled entirely by the inductive (I) effects of the dorsal substituents. Furthermore, the I effect is transmitted far more strongly between C6 and C2 than between C7 and C2 in the transition states leading to the respective ion pairs 3 and 4. This follows from the magnitude of the reaction constants ρ, i.e. their inductivity[2], derived from linear correlations between the logarithms of the rate constants and the inductive constants σ_I^q[4] of the substituents R in 1 and 2 (Figure, regression lines 1 and 2).



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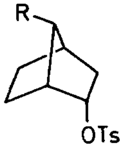

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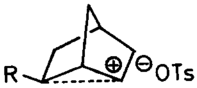

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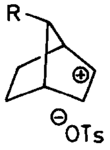

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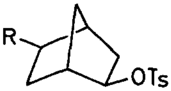
These results were not predictable by current theory and are surprising because the direct distances and the distance through the intervening bonds are practically the same in both series. It was therefore concluded that through space induction (the direct effect) is directional and involves graded bridging between the cationic center C2 and the respective dorsal C-atoms in the ion pairs 3 and 4 [1,3] and, furthermore, that bridging between C2 and C6 generates less strain than bridging between C2 and C7.



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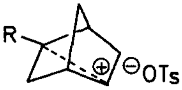

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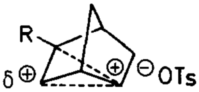

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TABLE. First order rate constants k for 5a-5j in 80% (v/v) ethanol at 70.0°C.

	R	k (s^{-1})
a	H	2.62×10^{-2} a)
b	CH_3	1.19×10^{-2} a)
c	CH_2OH	4.13×10^{-3}
d	CH_2OCH_3	2.79×10^{-3}
e	CH_2OAc	1.21×10^{-3}
f	CH_2Br	9.19×10^{-4}
g	CH_2OTs	4.50×10^{-4}
h	$COOCH_3$	3.58×10^{-4}
i	Cl	7.92×10^{-4} b)
j	CN	1.87×10^{-5} b)

a) extrapolated from lower, b) from higher temperatures.

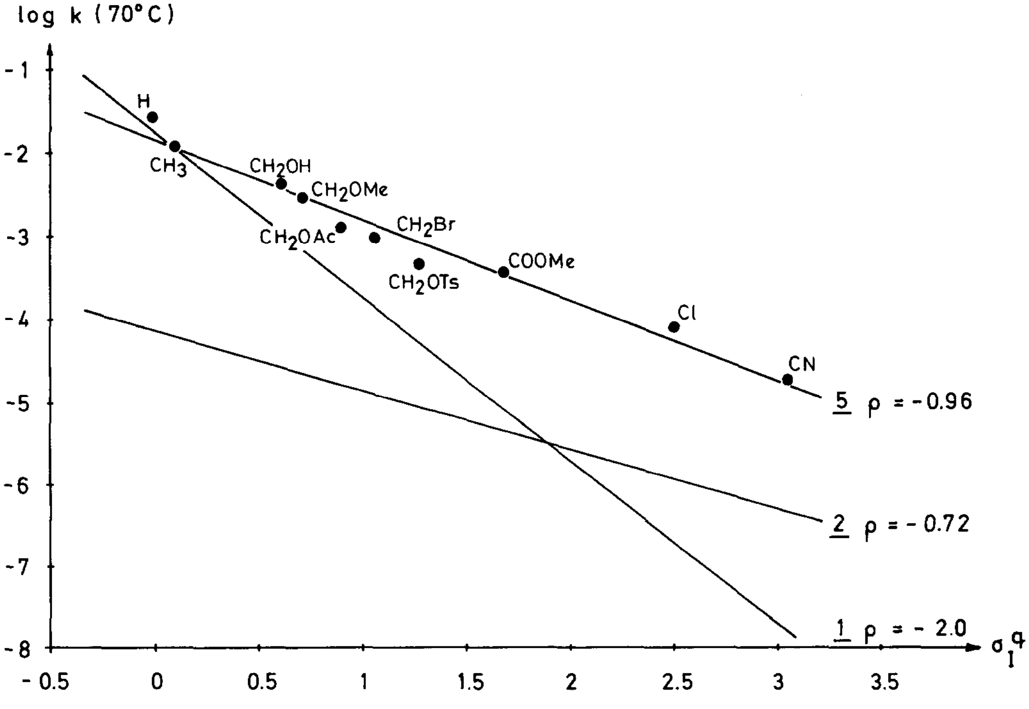

Figure. Plots of log k for 1, 2 and 5 vs. σ_I^q.

Further evidence for this hypothesis is now provided by the inductivity of 2-exo-norbornyl p-toluenesulfonates 5 which possess a variable exo-substituent at C5. In this series the C2-C5 distance is ca. 12% longer than the C2-C6 and C2-C7 distances. Were distance the decisive factor, the inductivity of 5 should be lower than of 1 and 2. On the other hand, bridging of C2 by C5, as in 6, generates less strain than bridging of C2 by C7, for a six-membered ring is subdivided into two quasi four-membered rings in the former case, whereas a five-membered ring is subdivided into quasi four- and three-membered rings in the latter. How these two factors, i.e. distance and bridging strain, balance could not be foreseen.

First order rate constants (k) for the tosylates 5a - 5j in 80% (v/v) ethanol at 70° are listed in the Table. In the Figure log k values for the series 1, 2 and 5 are plotted against σ_I^q. The linear correlation for 5 proves that ionization rates are again controlled by the I effect of the substituents and that nucleophilic solvent assistance is absent even when strong -I substituents, such as the cyano group are present. The inductivity of 5 (ρ = -0.96) is higher than that of 2 (ρ = -0.72), but much lower than that for 1 (ρ = -2.0). Hence, the reduced bridging strain in the transition states for the series 5 outweighs the shorter C2-C7 distance in the series 2. But bridging strain in 6 is still far greater than in 3.

The fact that the inductive interaction between C2 and C6 is much stronger than between C2 and the equidistant C7 refutes Brown's recent contention that the direct field effect should lead to comparable interactions in these cases[5,7]. It also supports the view that the 2-norbornyl cation is anisotropic to the transmission of polar effects.[3]

According to recent evidence[6] the solvolysis rates of 2-exo-norbornyl sulfonates, such as 5, are more sensitive to -I substituents at C5 than are the rates of the corresponding 2-endo epimers. In keeping with nonclassical ion theory[8], this finding was attributed to reduced participation of the electrons constituting the C1-C6 σ bond, as in 7. This rigorous allotment of two σ electrons to three carbon centers is not borne out by the observed graded effect of substituents, including hydrogen, on rates and products[3]. Moreover, the data suggest that all neighboring carbon atoms contribute to charge dispersal according to their distance from C2 and to the bridging strain involved. Evidently, bridging of C6 is especially favorable in the ionization of 2-exo-norbornyl tosylates[9]. Since C6 thereby acquires a considerable positive charge, as shown in 8, C6-participation will also be influenced by the I effect of substituents at C5. However, the extent to which the effect is relayed to C2 via C6 rather than directly, i.e. through space, is not ascertainable by the present measurements.

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