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DIFFERENTIAL BRIDGING IN THE SOLVOLYSIS OF 6- AND 7-SUBSTITUTED 2-EXO- AND 2-ENDO-NORBORNYL p-TOLUENESULFONATES

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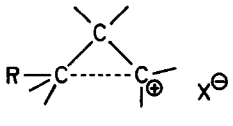
SUMMARY. The large difference between the reaction constants ρ_I for the solvolysis of the 6-exo- and 7-anti-substituted norbornyl tosylates 3 and 7, respectively, is further proof for the hypothesis that 2-norbornyl cations are anisotropic with regard to the transmission of polar effects and that through space induction involves graded bridging.

Evidence was recently presented that the ionization rates of bicyclic sulfonates in protic solvents are strongly affected by the bridging of the cationic center to a pentacoordinate β-carbon atom, as in 1 [1]. It was also suggested that the differences between the rates of epimeric sulfonates are due mainly to differential bridging strain in the respective transition states [2] and that effective 1,3-bridging requires that the back lobe of the $R\text{-}C_\beta$ orbital overlap strongly with the incipient p-orbital of the cationic center, as illustrated in 2 [3].



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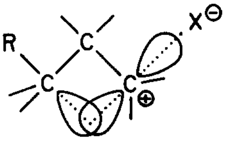

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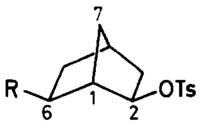
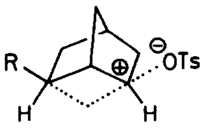


3 ($\rho_I = -2.0$)



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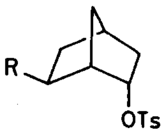
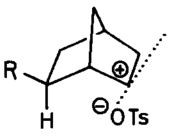


5 ($\rho_I = -0.78$)



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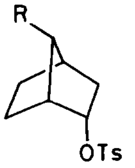
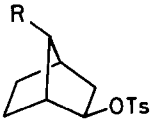
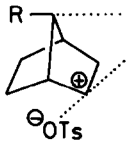
This condition is satisfied in the 2-norbornyl cation 4, derived from 2-exo-norbornyl tosylate 3, R = H, where the orbital axes (indicated by dotted lines) converge and intersect. On the other hand the corresponding orbitals of the cation in the ion pair 6, R = H, derived from the 2-endo epimer 5, R = H, cannot overlap as long as the endo side is blocked by the departing anion. Hence, bridging should be weak or negligible in the transition state. Differential bridging was, therefore, considered to be the major cause of the high exo/endo rate ratio of 425 for 3 and 5 (R = H) in 80 % ethanol at 70.0° [1].

Among other data, this conclusion was based upon the magnitude of the reaction constants ρ_I of -2.0 and -0.78, respectively, for solvolysis of the 6-exo-substituted tosylates 3 and 5 in 80 % ethanol. As shown before [4] ρ_I values measure the sensitivity of the rates to the inductive substituent constants σ_I^q of the β-substituents [5]. Assuming that induction can be roughly partitioned into a through bond and a through space component and that the latter involves graded bridging, these ρ_I values confirm that bridging is strong in the exo ion pair 4 and weak or negligible in the endo ion pair 6.


7 (ρ_I=-0.72)

R = a) H
b) CH_3
c) CH_2OAc
d) CH_2Br
e) $COOCH_3$
f) Cl
g) Br
h) CN


8 (ρ_I=-0.97)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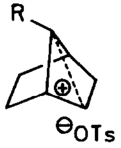
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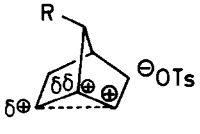
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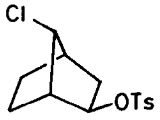
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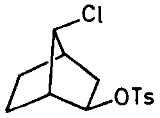
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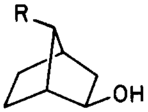
Further support for this hypothesis is supplied by the present study of the rates (in 80 % ethanol) and the products of the 7-anti-substituted 2-endo and 2-exo-norbornyl tosylates 7 (b-h) and 8 (b-h), respectively. While the number of transmitting bonds in these compounds is the same as in 3 and 5 the strains which accompany the bridging of C2 with C6 and C7 are clearly different. Thus, the orbital axes at C2 and C7 in the ion pair 9 from 7 converge at first but do not intersect, indicating that overlap is weak and that bridging, as illustrated in 10, generates a large strain. This is supported by the unusually low ρ_I value of -0.72 for the series 7 (a-h) ^{6}. The residual inductive effect of the substituents at C7 must then be due mainly to through bond induction.

The ρ_I value of -0.97 for the 7-anti-substituted 2-exo-tosylates 8 (a-h) is much smaller than that for the 6-exo-substituted stereoisomers 3, but considerably larger than that for the epimeric tosylates 7. In the ion pair 11 derived from 8 overlap of the rear lobes of the orbitals at C2 and C7 is hindered due to the presence of the anion and also for geometrical reasons. However, C2 in 11 should be strongly bridged and thereby transmit part of its positive charge to C6 which, like C2, withdraws electron densitiy from C 1. Deshielding of C 1 increases its through bond interaction with the substituents at C7 and hence raises the ρ_I value. This conclusion is supported by the practically identical rates of the 7-anti- and 7-syn-chlorides 12 and 13, respectively ^{7}. This would not be the case if bridging were important.



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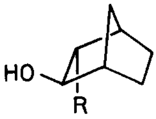

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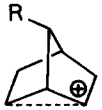

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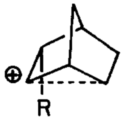

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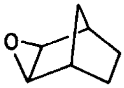

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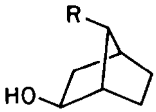

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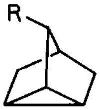

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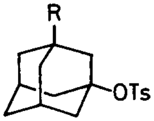

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In dioxane/water 7:3 containing 1.1 equiv. of triethylamine the tosylates 7 and 8 (b-h) afforded different yields of the same products, which consisted mainly of the 7-anti- and the 3-endo-substituted 2-exo-norbornanols 14 and 15, respectively. The alcohols 14 from 7 are formed with inversion, those from 8 with retention of configuration at C2, thus confirming preferential C2, C6 bridging in the cation 16. Rearrangement of the latter leads to 17, the precursor of 15. When R in 15 was chlorine or bromine small amounts of the epoxide 18 were formed by O-3 participation. The cation 16 also yielded considerable amounts of the 7-syn substituted 2-exo-alcohols 19 by a C6, C2 hydride shift, beside nortricyclenes 20 by 1,3-elimination.

In conjunction with our earlier work [1,2,3] these results show clearly that the transmission of inductive substituent effects in norbornyl cations is strongly dependent on hitherto unrecognized stereoelectronic factors.

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2) for a review of this work see C.A. Grob, Angew. Chemie 94, 87 (1982); Int. Ed. Engl. 21, 87 (1982).

3) C.A. Grob & U. Zutter, Tetrahedron Lett. 23, 2849 (1982).

4) C.A. Grob & B. Schaub, Helv. Chim. Acta 65, 1720 (1982) and earlier papers cited therein.

5) derived from the pK of 4-substituted quinuclidines; see C.A. Grob, B. Schaub & M.G. Schlageter, ibid. 63, 57 (1980).

6) It is noteworthy that the ρ_I values for the tosylates 3, 5 and 7 are somewhat larger in trifluoroethanol than in 80 % ethanol. However, this also applies to 3-substituted 1-adamantyl tosylates 21, which cannot undergo rearside nucleophilic attack. It can, therefore, be concluded that 2-exo- and 2-endo-norbornyl tosylates react essentially by a k_c process.

7) In 80 vol.% ethanol at 70.0° these are 1.57×10^{-4} and 1.63×10^{-4}, respectively. In a careful study of the acetolysis of all four 7-chloro-2-norbornyl tosylates a rate ratio 12/13 of 1.54 was found by P.G. Gassman & J.M. Hornback, J. Amer. Chem. Soc. 94, 7010 (1972). These authors concluded that participation of the C 1, C6 bond is not important.

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