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INDUCTIVE CHARGE DISPERSAL IN THE SOLVOLYSIS OF 2-EXO- AND 2-ENDO-NORBORNYL TOLUENESULFONATES.

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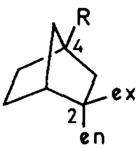
Abstract: The effect of substituents at C4, 5, 6 and 7 on solvolysis rates and products of 2-exo- and 2-endo-norbornyl tosylates confirms that differential carbon participation is responsible for varying exo/endo rate and product ratios.

The reason for differing ionization rates of epimeric bicyclic arenesulfonates, notably of 2-exo- and 2-endo-norbornane derivatives, continues to be a controversial issue [1]. A fresh aspect was introduced by the observation that relative rates are controlled by the inductive effect of neighbouring substituents including hydrogen [1a]. This followed from the linear correlation of the rate constants with the respective inductive substituent constants σ_I^q [2] according to the equation $\log k/k_o = \rho_I \sigma_I^q$. On the other hand the reaction constants ρ_I, which gauge the dispersal of positive charge to neighbouring C-atoms, varied widely with structure even when direct distances and the number of connecting σ-bonds were the same [1a].



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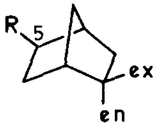

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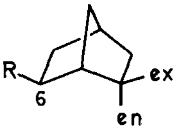

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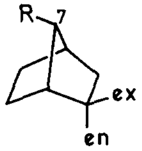

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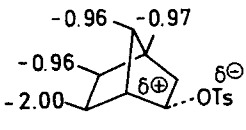
These observations called for a study of the factors which control the transmission of polar effects in the carbocations derived from the 4-, 5-, 6-

and 7-substituted 2-exo- and 2-endo-norbornyl tosylates 1 to 4 [3], where ex and en denote a secondary 2-exo or 2-endo tosyloxy group. The ρ_I values, or inductivities, for the 6- and 7-substituted 2-exo- and 2-endo-norbornyl tosylates 3 and 4, respectively, in 80% (v/v) ethanol were reported previously [4,5] (Table). In this communication the ρ_I values for the 4- and 5-substituted exo- and endo-tosylates, 1 and 2 respectively, derived from the observed linear correlation of their log k values with σ_I^q at 70.0°, are reported. They are listed in the Table together with the distances between C2 and the neighboring C-atoms [6]. The ρ_I values for the eight series of tosylates are also summarized in formulas 5 and 6, the numbers illustrating the distribution of charge among the C-atoms 4, 5, 6 and 7 in the transition states (t.s.) leading to the corresponding ion pairs.

Table. ρ_I values for solvolysis of 4-, 5-, 6- and 7-exo-substituted 2-exo- and 2-endo-norbornyl tosylates in 80% (v/v) ethanol at 70.0° [7].

	ρ_I	$\Delta\rho_I$	approximate distance in Å [6]
exo-1	-0.97	0.17	2.43
endo-1	-0.80		
exo-2	-0.96	0.42	2.95
endo-2	-0.54		
exo-3	-2.0	1.22	2.50
endo-3	-0.78		
exo-4	-0.96	0.24	2.40
endo-4	-0.72		



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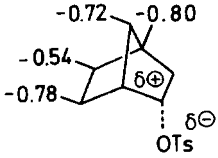

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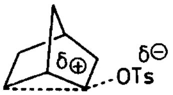

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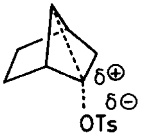

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In all cases interactions between C2 and neighbouring C-atoms in the t.s. are larger for the exo-tosylate than for the corresponding endo-tosylate. The difference $\Delta\rho_I$ (Table) is largest for 3 (1.22) and smallest for 1 (0.17); $\Delta\rho_I$ values for 2 (0.42) and 4 (0.24) are of intermediate size. Inductivity is exceptionally high (-2.0) for C6 in the exo-t.s. 5, but remarkably low for C7 (-0.72) in the endo-t.s. 6, even though the C2 - C7 distance is shorter than the C2 - C6 distance. It is also noteworthy that in the exo-t.s. 5 charge is dispersed equally to C4, C5 and C7, despite their different distances from C2.

Present models for the transmission of polar effects are unable to account for these results. They become intelligible, however, if it is assumed that in carbocations through space or direct induction involves graded electron shifts towards the cationic center and that the ρ_I values reflect directional electron mobility. On this basis electron shifts lead to graded bonding or bridging of C2 by neighbouring C-atoms, but especially when they are located at the rear of the C2-OTs bond and can therefore attack readily in the manner of a S_N2 reaction. As in ordinary covalent bonding the strength of these partial bonds should depend on the bond distances and angles imposed on the entire structure. The sum of these adjustments then determines the bridging strain in the resulting ion pair.

Models show that in the exo-t.s. 5 bridging strain is smallest for participation of C6, as illustrated in 7. This is confirmed by the high ρ_I as well as the sole formation of retained substitution products in the 2-exo-series (R = H)[4]. Participation of C4, C5 and C7 appears less favorable due to higher bridging strain and the nonlinear orientation of the C-atoms with respect to dorsal attack on the C2-OTs bond. In the endo-t.s. 6, however, none of the neighbouring C-atoms but C7 are positioned favorably for dorsal displacement of the OTs group. In the case of C7, however, bridging would lead to a more strained intermediate 8, in which a five-membered ring is subdivided into more strained quasi four- and three-membered rings. In fact, an unbridged endo-ion pair accounts for the low inductivity and the sole formation of inverted substitution products in the 2-endo-series (R = H)[5]. The ρ_I of -0.54 for C5 in endo-2 is the lowest inductivity observed in these series[8]. It is apparently due to the larger C2 - C5 distance of ca. 2.95 Å and the less favorable orientation of C5 relative to the leaving group.

The inductivity patterns for 5 and 6 thus confirm the hypothesis that differential C-participation is responsible for the high exo/endo rate ratios of 300 to 400 observed in the solvolyses of 2-norbornyl arenesulfonates.

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2. C.A. Grob, M.G. Schlageter, B. Schaub, Helv. Chim. Acta 1980, 63, 57.

3. The substituents were: H, CH_3, CH_2OCH_3, CH_2OAc, CH_2Br, CH_2OTs, $COOCH_3$, Cl or Br and CN.

4. W. Fischer, C.A. Grob, R. Hanreich, G. von Sprecher, A. Waldner, Helv. Chim. Acta 1981, 64, 2298.

5. P. Flury and C.A. Grob, ibid. 1983, 66, 1971.

6. Distances calculated from the data on norbornane in "Landolt-Börnstein", New series, Vol. 7, page 361.

7. The correlation coefficients for exo- and endo-1 were 1.00, for exo-2 0.985 and for endo-2 0.992.

8. Preliminary studies of 2-exo-norbornyl tosylates, in which the substituents are located at C1 and C3, i.e. adjacent to C2, surprisingly led to ρ_I values of less than -2.0.

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