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CHARGE DISPERSAL IN 1- AND 2-ADAMANTYL CATIONS

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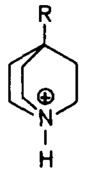
Abstract: Substituents at the remoter 5-position of 2-adamantyl arylsulfonates control solvolysis rates more strongly than substituents at the 4-position.

As recent studies have shown $^{1)2)}$, the transmission of inductive substituent effects in carbocations depends not only on direct and through bond distances to the reaction center, but also on a hitherto unrecognized factor, the so-called inductivity $^{1)}$. This factor corresponds to the reaction constant ρ_I in the Hammett-type equation $\log k/k_o = \rho_I \sigma_I^q$, where k and k_o are the solvolysis rate constants for substituted and unsubstituted reactants, respectively, and σ_I^q are the respective inductive substituent constants, as derived from the pK_a of 4-substituted quinuclidinium ions 1 $^{3)}$.



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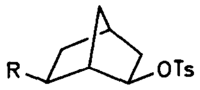

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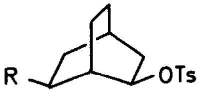

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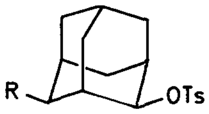

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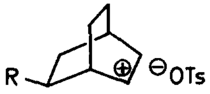

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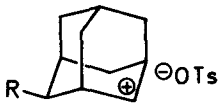

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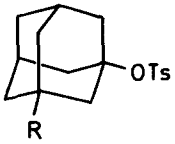

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The observed inductivities for solvolysis of the γ-substituted tosylates 2, 3 and 4 (TsO = p-$MeC_6H_4SO_2$) in 80% ethanol via the corresponding carbocations 5, 6 and 7 are -2.00, -1.50 and -0.80, respectively $^{1)}$. They differ markedly

Table. Yields in % of 2^e- and 2^a-alcohols 16 from 10 in 70% dioxane and retention / inversion (R/I) ratios. In brackets R/I ratios for alcohols 15 from 4.

R	σ_I^q	alcohols 16 2^e	2^a	R/I 16 2d)
H	0	100	$2^e = 2^a$	3.17 (3.17) 6)
CH_3	0.11	67	33	1.91 (2.85)
CH_2OH	0.62	48	52	0.92
CH_2OAc	0.90	52	48	1.1 (2.45)
CH_2Br	1.07	46	54	0.85 (2.45)
$COOCH_3$	1.69	45	55	0.82 (1.50)
OH	1.76	53	47	1.1
OAc	2.16	38	62	0.61
Cl	2.51	23	76	0.30 (1.44)
CN	3.06	20	80	0.25 (0.96)

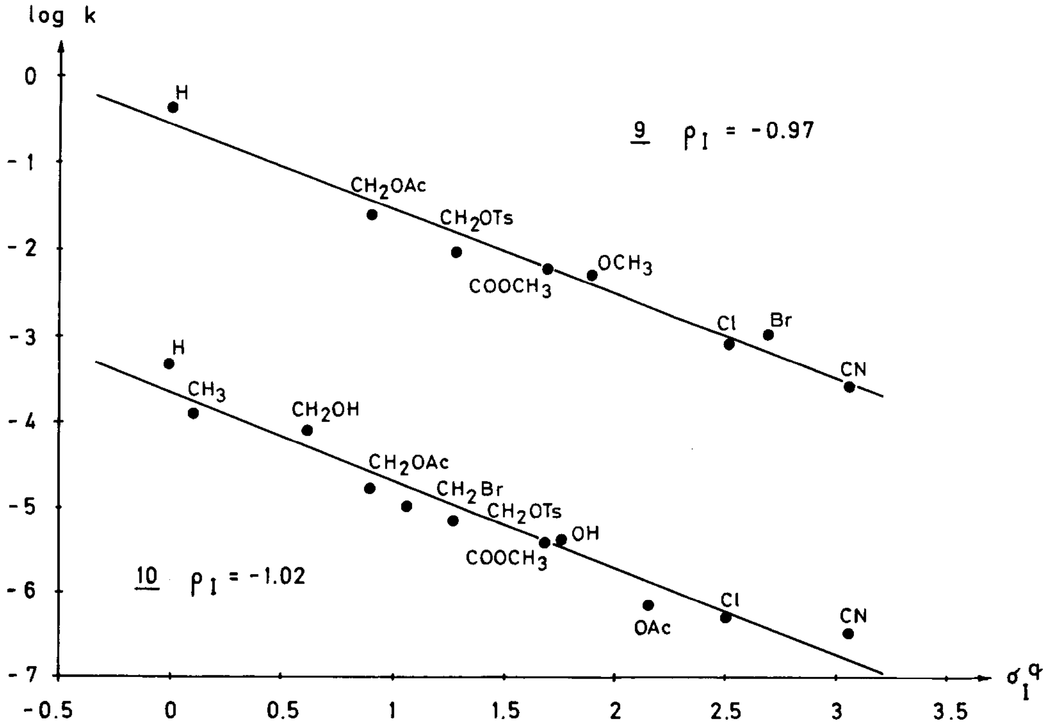
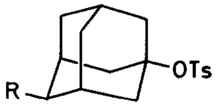


Figure. Plots of log k for 9 and 10 in 80% ethanol vs. inductive substituent constants σ_I^q at 70°.

although the direct and through bond distances are the same. It was, therefore, concluded, that local polarisability is determined by the structure of the whole molecule. The small inductivity of 4 (ρ_I = -0.80) compared to that of the γ-substituted 1-adamantyl tosylates 8 (ρ_I = -1.26)[2b] is particularly striking, since relevant distances are the same (Ca. 2.5 Å). It therefore became of interest to measure the ρ_I values of their δ-substituted counterparts 9 and 10, in which the direct distances (ca. 3.0 Å) are distinctly larger than in 4 and 8. Since the secondary tosylates 4 and 10 react too slowly to allow measurement of a wider range of substituents, the corresponding nisylates (NsO = p-$NO_2C_6H_4SO_2$) were employed, previous work having shown that their ρ_I values do not differ significantly[2d].



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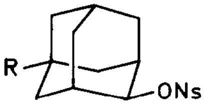

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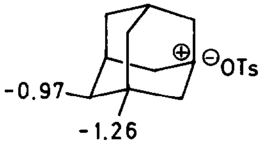

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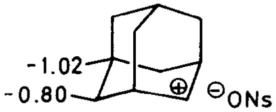

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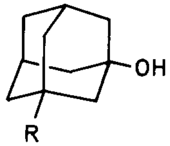
The plots in the Figure show that the logarithms of the rate constants (log k) in 80% ethanol correlate linearly with the respective σ_I^q values, thereby confirming the dominance of the I effect. The ρ_I values for 9 and 10 of -0.97 and -1.02, respectively, are equal within the error limit of the method. Formulas 11 and 12 summarize the ρ_I values for ionization of the γ- and δ-substituted adamantyl arylsulfonates. The shorter α,γ distance in 11 accounts for the higher inductivity of the γ-position. In 12, however, inductivity is higher for the more remote δ-position, which is contrary to current views on the transmission of polar effects in saturated molecules[4].



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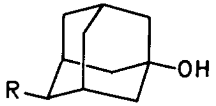

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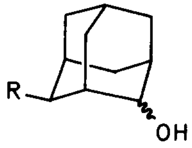

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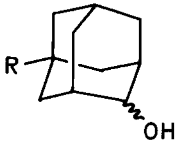

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Hydrolysis of the tertiary tosylates 8 and 9 in 70% dioxane yields the respective tertiary alcohols 13 and 14 only. On the other hand the secondary nisylates 4 and 10 hydrolyze to a mixture of epimeric 2^e- and 2^a-adamantanols[5] 15 and 16, respectively, i.e. with retention and inversion of configuration at C2 (Table). In agreement with the higher inductivity of the δ position in the cation 12, the retention to inversion (R/I) ratio decreases sharply from 3.17 for R = H to 0.25 for R = CN, i.e. by a factor of ca. 13, whereas the corresponding reduction for the γ position in 12 is only 3.3[2d].

These results support our conclusion that ρ_I values, as well as the configuration of solvolysis products, reflect the degree to which neighboring carbon atoms bridge the cationic center in cations such as 5, 6 and 7[1,2]. But the striking feature of the 2-adamantyl cation 12 is that the δ interaction is stronger than the γ interaction. The low ρ_I value of -0.80 in the latter case is possibly related to the fact that direct induction involves only the periphery of the molecule, i.e. a region of low electron density.

The above results also confirm le Noble's recent observation[9] that the stereochemical outcome of reactions via 2-adamantyl cations is controlled by the polarity of substituents at C5. But his conclusion that the latter affect the σ delocalization or hyperconjugation of dorsal $\beta\gamma$ bonds in the cation 12 conflicts with the observed lower inductivity of the γ carbon C4 compared to that of the δ carbon C5.

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7) In the present context the term bridging is used to describe a weaker than normal bonding interaction between the cationic center of a carbocation and neighboring carbon atoms. As in other cases of neighboring group participation[8] bridging affects the rate and the stereochemical outcome of substitution reactions.
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