213. Solvent Dependence of Inductivity in the Solvolyses of Substituted Norbornyl *p*-Toluenesulfonates

Norbornanes, Part 14

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Summary

A comparison of the solvolysis rates of the substituted 2-*exo*- and 2-*endo*-norbornyl *p*-toluenesulfonates **1**, **2**, **3** and **4** and the substituted 1- and 2-adamantyl sulfonates **9** and **10**, respectively, in 80% ethanol and 97% trifluoroethanol has shown that the sensitivity of rates to the *I*-effect of substituents, *i.e.* the inductivity of these compounds, varies strongly with structure, configuration and solvent. In 97% trifluoroethanol, a solvent of low nucleophilicity and high ionizing power, the inductivities of the 2-*endo*-norbornyl *p*-toluenesulfonates **2** and **4** as well as the inductivities of the adamantyl derivatives **9** and **10** were larger than in 80% ethanol. In contrast, the inductivity of the 2-*exo*-norbornyl *p*-toluenesulfonates **1** was practically unchanged. It was, therefore, concluded that the transition states for the former compounds are not, or only weakly, bridged, whereas the transition states for the 2-*exo*-norbornyl *p*-toluenesulfonates **1** involve graded bridging by C(6). These results confirm that, due to differential bridging strain, 2-norbornyl cations are anisotropic to polar effects.

Introduction. – Recent studies [1] [2] [3] have shown that the solvolysis rates of the 6- and 7-substituted 2-*exo*- and 2-*endo*-norbornyl *p*-toluenesulfonates (tosylates) **1**, **2**, **3** and **4** in 80% EtOH are strongly dependent on the position and orientation of the substituents relative to the nucleofugal tosyloxy group. In fact, the response of rates to the *I*-effect of the substituents, the so-called inductivity of the system[1]), varied from −2.0 for the series **1** to −0.72 for the series **4**, although the number of bonds between the substituent and the reaction site is the same in all cases. It was, therefore, concluded that through-space induction, rather than through-bond induction, is responsible for these large differences and that the former involves graded bridging of C(6) and, to a far smaller extent, of C(7), to the incipient cationic center at C(2).

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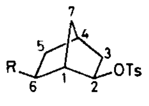
[1]) Inductivity corresponds to the reaction constant ρ_I derived from the equation $\log k/k_0 = \rho_I \sigma_I^q$, where σ_I^q denotes the inductive constant of the substituent R and k and k_0 are the first-order rate constants for the substituted and unsubstituted tosylates, respectively [4].



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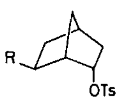

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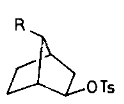

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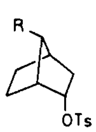

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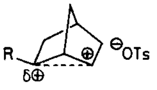

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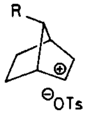

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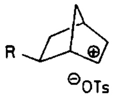

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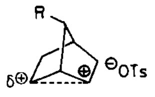

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It was also pointed out that 1,3-bridging is subject to steric and electrostatic constraints[2]). Thus, bridging of the reaction site by the substituent-bearing, dorsal C(6) in the transition state for the ionization of **1** to the ion pair **5** involves less strain than bridging by the dorsal C(7) in the ionization of **4** to the ion pair **6**. Furthermore, through-space induction of C(6) in the ionization of **2** to the ion pair **7** should be reduced due to repulsion of the electrons around C(6) by the proximate negatively charged tosylate ion. This would account for the lower inductivity of **2**, namely −0.86, as compared to **1** (−2.0) [1]. The inductivity of **3**, namely −0.97, is again somewhat increased due to the charge dispersal which accompanies the bridging of C(2) by the dorsal C(6) in the ionization to **8** [3].

Inductivity, however, depends also on the magnitude of the positive charge at C(2) in the transition state. It should, therefore, also be influenced by the solvent which, like bridging, can disperse charge. Of the relevant solvent properties, namely nucleophilicity (N) and ionizing power (Y), the former (N) has been shown to disperse the charge on the cation and therefore to reduce inductivity [4] [6]. However, recent papers have stressed the absence or insignificance of nucleophilic solvent participation in the ionization of 2-*exo*- and 2-*endo*-norbornyl derivatives [7]. But the question remains how ionizing power of the solvent affects C-participation, *i.e.* bridging.

It was, therefore, of interest to compare the inductivities of the series **1**, **2**, **3** and **4** in 80% EtOH [4], a solvent of medium Y- and N-values, with their inductivities in a solvent of higher Y-, but lower N-value, such as 97% trifluoroethanol (TFE). On their more recent Y- and N-scales *Schadt et al.* [8] have assigned values of 1.83 and −2.79 for Y and N, respectively, to this solvent, whereas both Y and N are zero by definition for 80% EtOH.

This article reports the inductivities derived from the rate constants for the substituted norbornyl tosylates **1**, **2**, **3** and **4** in 97% TFE. Also presented are the rate constants and inductivities for 3-substituted 1-adamantyl tosylates **9** and for the 4-substituted 2-adamantyl *p*-nitrobenzenesulfonates **10** [9], a series of secondary arylsulfonates which also reacts by a S_N1 mechanism[3]). Inclusion of the latter two series is

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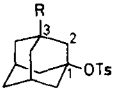
[2]) For a review see also [5].

[3]) It was shown that ρ_I-values for tosylates and *p*-nitrobenzenesulfonates are practically identical [9]. However, in this case the ρ-values are less accurate because they are based on four substituents only.

essential to a discussion of solvent effects on inductivity because nucleophilic solvent participation is excluded in **9** and, at most, weak in **10** [10][4]). Any change of inductivity in the series **9** and **10** resulting from the change from 80% EtOH to 97% TFE must then be due mainly to the larger Y-value of the latter solvent. Conversely, reduced or unchanged inductivity should indicate nucleophilic C-participation, *i.e.* 1,3-bridging.



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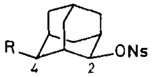

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Results. – The compounds included in this study have been reported with the exception of **1** and **2**, R = CH_2OCOCH_3 and CH_2OTs. The preparation of the latter is described in the *Exper. Part.* Rates were measured by the conductometric method. First-order rate constants in 97% (*w*/*w*) TFE are listed in *Tables 1–5*, those previously not determined in 80% (*v*/*v*) EtOH are listed in *Table 6*. With few exceptions the derived inductivities are based on the same substituents. In *Fig. 1–5* the logarithms of the rate constants (log*k*) are plotted *vs.* the corresponding inductive substituent constants σ_I^q [11]. In most cases satisfactory linear correlations were obtained. They show

Table 1. *First-Order Rate Constants for 10^{-3}* M *Solutions of 6-*exo*-Substituted 2-*exo*-Norbornyl* p*-Toluenesulfonates* **1** *[15] in 97%* (w/w) *TFE*

R	*T* [°C]	*k* [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol degree]
H	5.00	$5.42 \cdot 10^{-4}$	17.6	−10.1
	15.00	$1.72 \cdot 10^{-3}$		
	25.00	$4.92 \cdot 10^{-3}$		
	70.00	$2.80 \cdot 10^{-1}$[a])		
CH_2OCOCH_3	59.92	$4.45 \cdot 10^{-4}$	21.3	−10.2
	70.00	$1.18 \cdot 10^{-3}$[a])		
	70.05	$1.19 \cdot 10^{-3}$		
	80.20	$2.98 \cdot 10^{-3}$		
CH_2Br	70.00	$7.14 \cdot 10^{-4}$		
CH_2OTs	70.00	$1.33 \cdot 10^{-4}$		
$COOCH_3$	70.00	$3.42 \cdot 10^{-5}$[a])	23.0	−12.2
	99.90	$5.54 \cdot 10^{-4}$		
	109.90	$1.30 \cdot 10^{-3}$		
	120.00	$2.85 \cdot 10^{-3}$		
Br	70.00	$7.62 \cdot 10^{-7}$[a])	25.4	−12.9
	110.00	$4.14 \cdot 10^{-5}$		
	115.07	$6.46 \cdot 10^{-5}$		
	120.10	$1.00 \cdot 10^{-4}$		

[a]) Extrapolated.

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[4]) Weak nucleophilic solvent participation is indicated in 80% EtOH when R is a strong electron-withdrawing substituent [9].

that reaction rates are controlled mainly, if not exclusively, by the *I*-effect of the substituents. The reaction constants ρ_I in 80% EtOH, taken from previous articles, and in 97% TFE, are listed in *Table 7* together with the respective $\Delta\rho_I$ values which measure the effect of solvent on inductivity.

It is noteworthy that in 80% EtOH the 2-*endo*-tosylates **2**, R = CH_2OH and $CONH_2$, reacted 2.4 and 2.1 times faster than calculated on the basis of their σ_I^q values

Table 2. *First-Order Rate Constants for* 10^{-3} M *Solutions of 6-*exo*-Substituted 2-*endo*-Norbornyl* p-*Toluenesulfonates* **2** *[16] in 97%* (w/w) *TFE*

R	*T* [°C]	*k* [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol degree]
H	68.86	$5.71 \cdot 10^{-4}$	19.93	−15.37
	70.00	$6.34 \cdot 10^{-4}$a)		
	79.86	$1.49 \cdot 10^{-3}$		
	90.00	$3.34 \cdot 10^{-3}$		
CH_3	59.82	$2.15 \cdot 10^{-4}$	21.88	−9.83
	70.00	$5.93 \cdot 10^{-4}$		
	79.92	$1.50 \cdot 10^{-3}$		
CH_2OH	70.00	$1.72 \cdot 10^{-4}$a)	19.12	−20.31
	100.01	$1.72 \cdot 10^{-3}$		
	110.02	$3.88 \cdot 10^{-3}$		
	120.07	$6.74 \cdot 10^{-3}$		
CH_2OCOCH_3	70.00	$2.77 \cdot 10^{-5}$a)	23.36	−11.58
	100.14	$4.77 \cdot 10^{-4}$		
	110.17	$1.13 \cdot 10^{-3}$		
	120.21	$2.51 \cdot 10^{-3}$		
CH_2Br	70.00	$1.65 \cdot 10^{-5}$a)	23.08	−13.44
	100.17	$2.75 \cdot 10^{-4}$		
	110.10	$6.46 \cdot 10^{-4}$		
	120.13	$1.41 \cdot 10^{-3}$		
CH_2OTs	70.00	$8.50 \cdot 10^{-6}$a)	24.04	−11.97
	100.13	$1.59 \cdot 10^{-4}$		
	110.19	$3.81 \cdot 10^{-4}$		
	120.21	$8.78 \cdot 10^{-4}$		
$COOCH_3$	70.00	$2.89 \cdot 10^{-6}$a)	25.22	−10.67
	100.14	$6.24 \cdot 10^{-5}$		
	110.15	$1.54 \cdot 10^{-4}$		
	120.18	$3.72 \cdot 10^{-4}$		
$CONH_2$	70.00	$8.40 \cdot 10^{-6}$a)	24.06	−11.93
	99.97	$1.56 \cdot 10^{-4}$		
	110.00	$3.71 \cdot 10^{-4}$		
	120.05	$8.61 \cdot 10^{-4}$		
$OCOCH_3$	70.00	$1.08 \cdot 10^{-6}$a)	23.41	−17.91
	110.00	$4.32 \cdot 10^{-5}$		
	115.10	$6.63 \cdot 10^{-5}$		
	120.11	$9.77 \cdot 10^{-5}$		
Br	70.00	$3.73 \cdot 10^{-7}$a)	23.61	−19.43
	110.15	$1.57 \cdot 10^{-5}$		
	115.20	$2.38 \cdot 10^{-5}$		
	120.13	$3.53 \cdot 10^{-5}$		

a) Extrapolated.

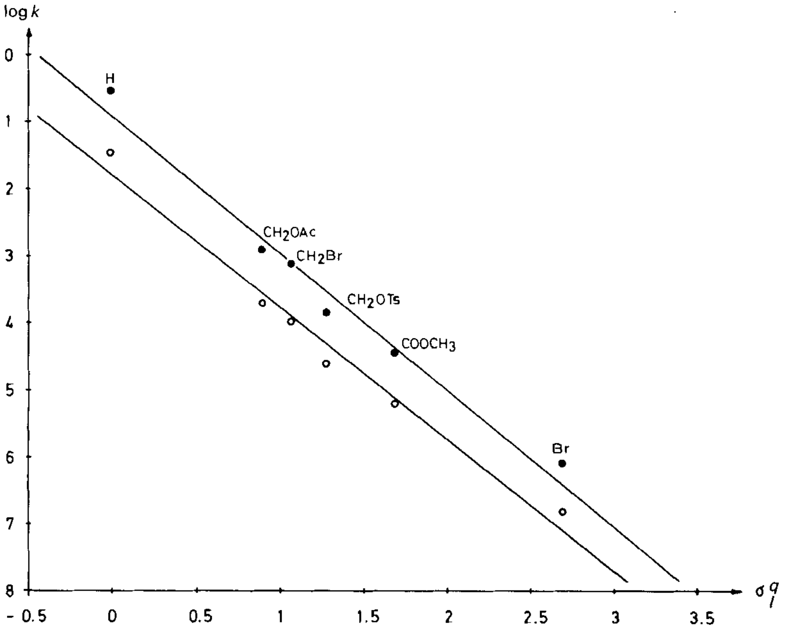

Fig. 1. *Plots of log* k *for 6-*exo*-substituted 2-*exo*-norbornyl* p*-toluenesulfonates* **1** *in 97% TFE* (filled circles) *and 80% EtOH* (open circles) vs. σ_I^q

Table 3. *First-Order Rate Constants for* 10^{-3} M *Solutions of 7-*anti*-Substituted 2-*exo*-Norbornyl* p*-Toluenesulfonates* **3** *[17] in 97%* (w/w) *TFE*

R	*T* [°C]	*k* [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol degree]
H	70.00	$2.80 \cdot 10^{-1}$[a])		
CH_3	0.00	$5.71 \cdot 10^{-4}$	16.74	−11.90
	25.55	$9.04 \cdot 10^{-3}$		
	34.95	$2.10 \cdot 10^{-2}$		
	70.00	$3.90 \cdot 10^{-1}$[b])		
CH_2OCOCH_3	70.00	$1.24 \cdot 10^{-2}$		
CH_2Br	70.00	$8.00 \cdot 10^{-3}$		
$COOCH_3$	70.00	$3.07 \cdot 10^{-3}$		
Cl	70.00	$6.11 \cdot 10^{-4}$		
Br	70.00	$5.14 \cdot 10^{-4}$		
CN	70.00	$1.69 \cdot 10^{-5}$[b])	21.72	−17.35
	99.98	$2.38 \cdot 10^{-4}$		
	115.08	$7.70 \cdot 10^{-4}$		
	120.04	$1.12 \cdot 10^{-3}$		

[a]) See *Table 1.*

[b]) Extrapolated.

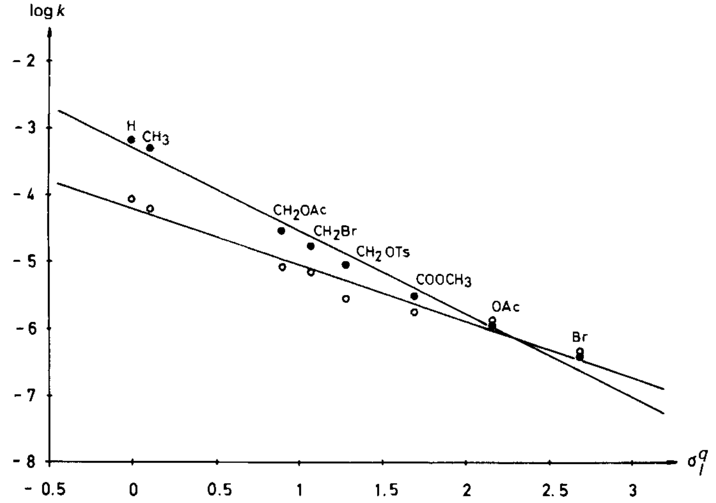

Fig. 2. *Plots of log* k *for 6-*exo-*substituted 2-*endo-*norbornyl* p-*toluenesulfonates* **2** *in 97% TFE* (filled circles) *and 80% EtOH* (open circles) vs. σ_I^q

Table 4. *First-Order Rate Constants for* 10^{-3} M *Solutions of 7-*anti-*Substituted 2-*endo-*Norbornyl* p-*Toluenesulfonates* **4** *[17] in 97%* (w/w) *TFE*

R	T [°C]	k [s^{-1}]	$H^{\ddagger}$ [kcal/mol]	$S^{\ddagger}$ [cal/mol degree]
H	70.00	$6.34 \cdot 10^{-4}$[a]		
CH_3	70.00	$1.09 \cdot 10^{-3}$		
CH_2OCOCH_3	70.00	$3.81 \cdot 10^{-5}$		
CH_2Br	70.00	$3.10 \cdot 10^{-5}$[b]	22.08	−15.11
	94.98	$2.98 \cdot 10^{-4}$		
	105.07	$6.93 \cdot 10^{-4}$		
	115.09	$1.50 \cdot 10^{-3}$		
$COOCH_3$	70.00	$5.34 \cdot 10^{-6}$[b]	25.46	−8.73
	100.03	$1.19 \cdot 10^{-4}$		
	110.20	$2.91 \cdot 10^{-4}$		
	115.08	$4.58 \cdot 10^{-4}$		
	120.10	$7.27 \cdot 10^{-4}$		
Cl	70.00	$3.72 \cdot 10^{-6}$[b]	24.95	−10.96
	100.00	$7.74 \cdot 10^{-5}$		
	110.02	$1.84 \cdot 10^{-4}$		
	120.06	$4.54 \cdot 10^{-4}$		
Br	70.00	$3.23 \cdot 10^{-6}$[b]	24.31	−13.11
	100.03	$6.17 \cdot 10^{-5}$		
	115.09	$2.33 \cdot 10^{-4}$		
	120.04	$3.42 \cdot 10^{-4}$		
CN	70.00	$6.19 \cdot 10^{-7}$[b]	20.12	−28.60
	115.08	$2.20 \cdot 10^{-5}$		
	120.23	$2.96 \cdot 10^{-5}$		
	130.12	$5.98 \cdot 10^{-5}$		

[a] See *Table 2*.

[b] Extrapolated.

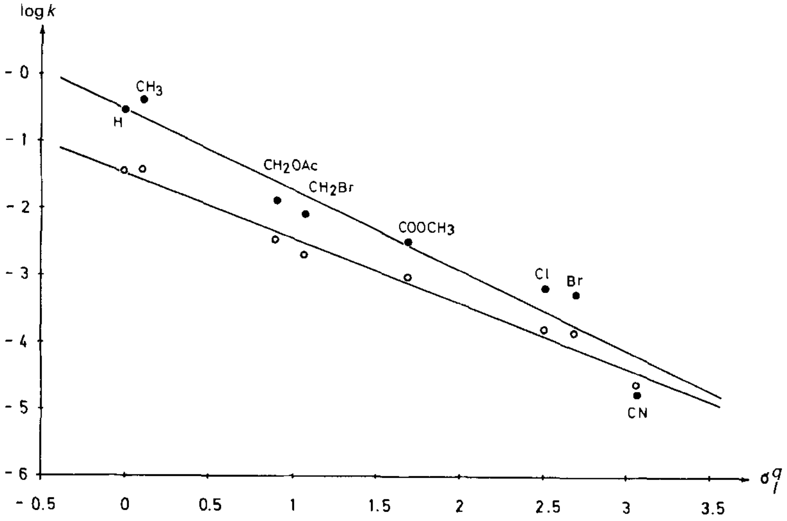

Fig. 3. *Plots of log* k *for 7-*anti*-substituted 2-*exo*-norbornyl* p*-toluenesulfonates* **3** *in 97% TFE* (filled circles) *and 80% EtOH* (open circles) vs. σ_I^q

Table 5. *First-Order Rate Constants for* 10^{-3} M *Solutions of 3-Substituted 1-Adamantyl* p*-Toluolsulfonates* **9** *[18] in 97%* (w/w) *TFE*

R	*T* [°C]	*k* [s^{-1}]	$H^{\ddagger}$ [kcal/mol]	$S^{\ddagger}$ [cal/mol degree]
H	−20.02	$3.95 \cdot 10^{-3}$	17.63	0.43
	−15.02	$7.79 \cdot 10^{-3}$		
	−10.00	$1.56 \cdot 10^{-2}$		
	70.00	$5.24 \cdot 10^{-1}$ a)		
CH_3	−25.03	$2.02 \cdot 10^{-3}$	17.18	−1.25
	−15.00	$8.28 \cdot 10^{-3}$		
	−10.00	$1.56 \cdot 10^{-2}$		
	70.00	$4.35 \cdot 10^{-1}$ a)		
CH_2OTs	15.00	$4.55 \cdot 10^{-4}$	19.15	−7.30
	25.00	$1.48 \cdot 10^{-3}$		
	35.00	$4.26 \cdot 10^{-3}$		
	70.00	$1.16 \cdot 10^{-1}$ a)		
CH_2OCOCH_3	−10.02	$1.12 \cdot 10^{-4}$	18.70	−5.31
	0.00	$4.32 \cdot 10^{-4}$		
	10.00	$1.51 \cdot 10^{-3}$		
	70.00	$6.11 \cdot 10^{-1}$ a)		
$COOCH_3$	20.00	$2.93 \cdot 10^{-4}$	19.36	−7.71
	30.00	$9.38 \cdot 10^{-4}$		
	40.21	$2.75 \cdot 10^{-3}$		
	70.00	$4.67 \cdot 10^{-2}$ a)		
Cl	70.00	$4.27 \cdot 10^{-3}$		
CN	70.00	$2.38 \cdot 10^{-4}$		
NO_2	70.00	$5.65 \cdot 10^{-5}$		

a) Extrapolated.

and the plot in *Fig. 2*. In 97% TFE the rates were even higher, namely 4.3 and 3.2 times the calculated values, respectively. Enhanced rates are usually observed when the substituents are electrofugal and, hence, less electron-attracting [13]. These points were omitted in the regression.

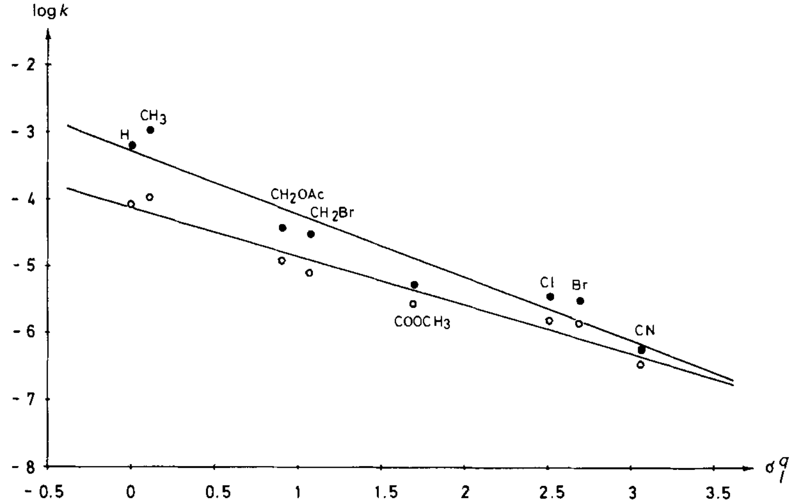

Fig. 4. *Plots of log* k *for 7-*anti*-substituted 2-*endo*-norbornyl* p*-toluenesulfonates* **4** *in 97% TFE* (filled circles) *and 80% EtOH* (open circles) vs. σ_I^q

Table 6. *First-Order Rate Constants for* 10^{-3} M *Solutions of 6-*exo*-Substituted 2-*exo*-* (**1**) *and 2-*endo*-norbornyl* p*-Toluenesulfonates* **2** *in 80%* (v/v) *EtOH*

Compound	T [°C]	k [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol degree]
1 R = CH_2OCOCH_3	70.00	$1.96 \cdot 10^{-4}$		
1 R = CH_2OTs	70.00	$2.44 \cdot 10^{-5}$		
2 R = CH_2OCOCH_3	70.00	$8.09 \cdot 10^{-6}$[a]	24.56	−10.55
	100.12	$1.61 \cdot 10^{-4}$		
	110.18	$3.91 \cdot 10^{-4}$		
	120.22	$9.23 \cdot 10^{-4}$		
2 R = CH_2OTs	70.00	$2.68 \cdot 10^{-6}$[a]	24.87	−11.83
	110.15	$1.34 \cdot 10^{-4}$		
	120.16	$3.31 \cdot 10^{-4}$		
	130.24	$7.19 \cdot 10^{-4}$		

[a]) Extrapolated.

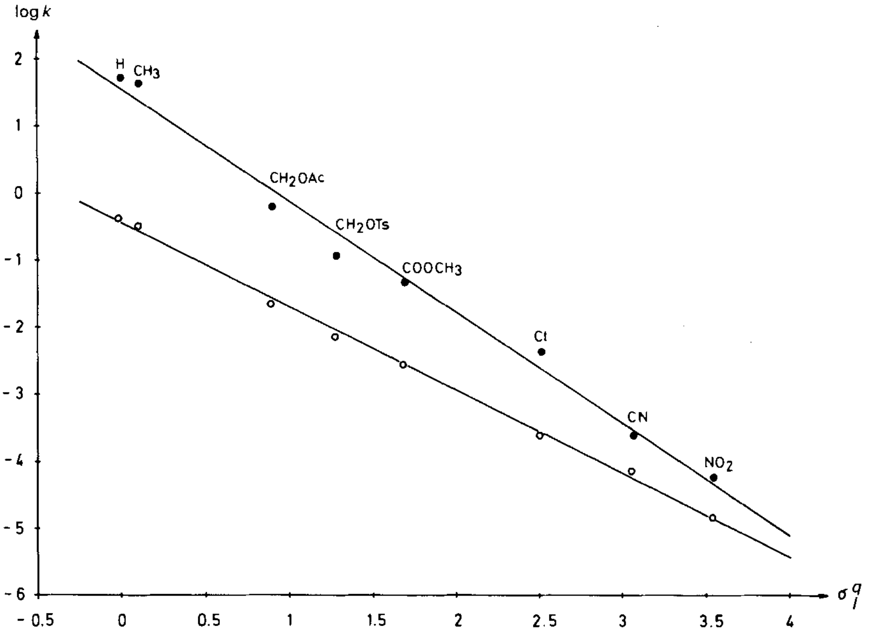

Fig. 5. *Plots of log* k *for 3-substituted 1-adamantyl* p-*toluenesulfonates* **9** *in 97% TFE* (filled circles) *and 80% EtOH* (open circles) vs. σ_I^q

Table 7. *Reaction Constants ρ_I for Solvolysis of* p-*Toluenesulfonates in 80% EtOH and 97% TFE at 70.0°*

Series	ρ_I 80% EtOH	ρ_I 97% TFE	$\Delta\rho_I$	%-Increase in 97% TFE
1	−2.0[a])	−2.05	0.05	2.5
2	−0.86[a])	−1.25	0.39	45
3	−0.97[b])	−1.20	0.23	24
4	−0.72[b])	−0.94	0.22	31
9	−1.26[c])	−1.67	0.41	33
10	−0.82[d])	−1.12	0.30	37

[a]) [1]. [b]) [3]. [c]) [13]. [d]) [9].

Discussion. – The 1- and 2-adamantyl series **9** and **10**, respectively, provide a basis for the discussion of solvent effects on inductivity, for they both react by the limiting S_N1 mechanism, *i.e.* without nucleophilic solvent participation. Furthermore, their respective ρ_I-values in 80% EtOH of −1.26 and −0.82 [4] [9] were ascribed to medium bridging in the former case [13] and to very weak or negligible bridging in the latter[4])[5]).

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[5]) As mentioned in [4] bridging between C(2) and C(4) in **10** would be accompanied by large deformations and, hence, strain.

In 97% TFE their ρ_I-values increase by 33% and 37%, respectively. These enhanced inductivities must be due to the greater ionizing power of TFE which leads to more charge separation in the transition state and, hence, to a greater interaction between the cationic center and the substituents. The unequal response of the rates of the series **9** to the substituents in the two solvents is apparent from the different slopes of the regression lines in *Fig. 5* which converge as the $-I$-effects of the substituents increase.

In contrast, the ρ_I-values for the 6-*exo*-substituted 2-*exo*-norbornyl tosylates **1** are practically the same in the two solvents (*Table 7* and *Fig. 1*). The slight increase of 2.5% is hardly significant in view of the limited accuracy of the method[6]). The strikingly high inductivity of the series **1** ($\rho_I = -2.0$) was attributed to graded 1,3-bridging in the transition state leading to the ion pairs **5** [1]. The insensitivity of ρ_I to solvent ionizing power confirms this view, for bridging disperses positive charge in the cation, thereby reducing its interaction with the counter ion. This phenomenon is well-known in solvolyses involving neighboring group or nucleophilic solvent participation [12].

The increase of the ρ_I-value for the 6-*exo*-substituted 2-*endo*-norbornyl tosylates **2** of 45% in 97% TFE is markedly higher than those for **9** (33%) and **10** (37%) (*Table 7* and *Fig. 2*). This finding confirms that bridging of C(6) or C(7) is insignificant in the transition state for the 2-*endo*-series **2** [1] [3], so that the more localized charge at C(2) tends to increase the importance of solvent ionizing power. Apparently, solvent nucleophility does not play an appreciable role.

The respective ρ_I-values for the 7-*anti*-substituted 2-*exo*- and 2-*endo*-norbornyl tosylates **3** and **4**, respectively, are again larger in 97% TFE than in 80% EtOH (*Table 7* and *Fig. 3* and *4*). The $\Delta\rho_I$-value for the series **4** (30%) resembles that for the series **9** (33%) which react by the limiting S_N1 mechanism. The smaller $\Delta\rho_I$-value displayed by the 2-*exo*-series **3** (24%) indicates that some bridging of C(2) by the dorsal C(6) disperses positive charge in the incipient ion pair **8**.

Conclusion. – The comparison of inductivity in norbornyl and adamantyl derivatives in solvents of different ionizing power confirms graded C-participation in 2-*exo*-norbornyl derivatives and its insignificance in the 2-*endo*-epimers.

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Experimental Part

General Remarks. The melting points (m.p.) were determined on a *Kofler* block; they are corrected. IR spectra are recorded in cm^{-1}, ^1H-NMR spectra in ppm.

*6-*exo*-(Acetoxymethyl)-2-*exo*-norbornyl* p*-toluenesulfonate* (**1**, R = CH_2OCOCH_3). To a solution of 1.7 g (5.74 mmol) of 6-*exo*-(hydroxymethyl)-2-*exo*-norbornyl *p*-toluenesulfonate (**1**, R = CH_2OH) [14] in 15 ml of abs. pyridine 2.5 ml (35.2 mmol) of acetyl chloride were added dropwise with stirring and cooling to 0°. After 30 min at 20° CH_2Cl_2 and ice were added. The org. layer was washed with 2N HCl and then H_2O, dried over Na_2SO_4 and evaporated to dryness. The crude acetate (2.45 g) was chromatographed on silica gel with Et_2O to

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[6]) As in other *Hammett*-type relationships rate constants are correlated here with equilibrium constants, *i.e.* with the pK_a values of 4-substituted quinuclidines [11].

yield 1.33 g (69%) pure product. M.p. (from Et_2O) 85–86°. ^{1}H-NMR ($CDCl_3$): 2.03 (*s*, 3 H, CH_3COO); 3.8 (*d*, $J = 8$, 2 H, OCH_2).

$C_{17}H_{22}SO_5$ (338.422) Calc. C 60.34 H 6.55% Found C 60.19 H 6.69%

*6-*exo*-(Tosyloxymethyl)-2-*exo*-norbornyl* p*-toluenesulfonate* (**1**, R = CH_2OTs). To a solution of **1** (R = CH_2OH) [14] in 4 ml of dry pyridine were added 966 mg (5.07 mmol) TsCl. After 15 h at 20° ice water and then conc. HCl were added until the mixture had pH 1. The mixture was extracted with CH_2Cl_2 and the latter washed with H_2O and dried over Na_2SO_4. After evaporation the residue, 1.44 g, was crystallized from Et_2O. Yield 1.24 g (82%), m.p. 101–102°. ^{1}H-NMR ($CDCl_3$): 2.45 (*s*, 6 H, 2 CH_3Ar); 3.8 (*d*, $J = 8$, 2 H, CH_2OTs).

$C_{22}H_{26}S_2O_6$ (450.572) Calc. C 58.65 H 5.82% Found C 58.50 H 5.92%

*6-*exo*-(Acetoxymethyl)-2-*endo*-norbornyl* p*-toluenesulfonate* (**2**, R = CH_2OCOCH_3). Following the above procedure for the 2-*exo*-tosylate **1** (R = CH_2OCOCH_3) **2** was obtained in 62% yield; m.p. (from Et_2O/pentane) 62–63°. ^{1}H-NMR ($CDCl_3$): 2.0 (*s*, 3 H, CH_3O); 3.75 (*d*, 2 H, CH_2O).

$C_{17}H_{22}SO_5$ (388.422) Calc. C 60.34 H 6.55% Found C 60.44 H 6.44%

*6-*exo*-(Tosyloxymethyl)-2-*endo*-norbornyl* p*-toluenesulfonate* (**2**, R = CH_2OTs). This compound was prepared following the above procedure for **1** (R = CH_2OTs). M.p. (from Et_2O/hexane) 66–67°. ^{1}H-NMR ($CDCl_3$): 2.4 (*s*, 6 H, 2 CH_3Ar); 3.6 (*d*, 2 H, CH_2O).

$C_{22}H_{26}S_2O_6$ (450.572) Calc. C 58.66 H 5.82% Found C 58.46 H 5.75%

Rate Measurements. These were carried out according to [1] and [14]. 97% (*w/w*) TFE was prepared from commercial *TFE (Fluka)*. After storing over molecular sieve (3 Å) the solvent was distilled under exclusion of moisture, b.p. 72.5–73°. Titration with *Karl Fischer* reagent revealed 0.013% residual H_2O. To 3136.5 g of this TFE were added 96.59 g of bidistilled H_2O.

REFERENCES

[1] *W. Fischer, C.A. Grob, R. Hanreich, G. von Sprecher & A. Waldner,* Helv. Chim. Acta *64*, 2298 (1981).
[2] *C.A. Grob, B. Günther & R. Hanreich,* Helv. Chim. Acta *64*, 2312 (1981).
[3] *P. Flury & C.A. Grob,* Helv. Chim. Acta *66*, 1971 (1983).
[4] *C.A. Grob,* Acc. Chem. Res. in press.
[5] *C.A. Grob,* Angew. Chem. *94*, 87 (1982); Angew. Chem. Int. Ed. *21*, 87 (1982).
[6] *C.A. Grob & A. Waldner,* Helv. Chim. Acta *63*, 2152 (1980).
[7] *J.M. Harris, D.L. Mount & D.J. Raber,* J. Am. Chem. Soc. *100*, 3139 (1978); *D.J. Raber, W.C. Neal, M.D. Dukes, J.M. Harris & D.L. Mount,* ibid. *100*, 8137 (1978); *H.C. Brown, M. Ravindranathan, F.J. Chloupek & I. Rothberg,* ibid. *100*, 3143 (1978); *C.A. Grob & E. Lutz,* Helv. Chim. Acta *64*, 153 (1981).
[8] *F.L. Schadt, T.W. Bentley & P. v. R. Schleyer,* J. Am. Chem. Soc. *98*, 7667 (1976).
[9] *Gerhard Wittwer,* Ph.D. thesis, Basel, 1982.
[10] *T.W. Bentley & P. v. R. Schleyer,* J. Am. Chem. Soc. *98*, 7658 (1976).
[11] *C.A. Grob, B. Schaub & M.G. Schlageter,* Helv. Chim. Acta *63*, 57 (1980).
[12] *S.G. Smith, A.H. Fainberg & S. Winstein,* J. Am. Chem. Soc. *83*, 618 (1961).
[13] *C.A. Grob & B. Schaub,* Helv. Chim. Acta *65*, 1720 (1982).
[14] *C.A. Grob, F.M. Unger, E.D. Weiler & A. Weiss,* Helv. Chim. Acta *55*, 501 (1972).
[15] *W. Fischer, C.A. Grob & G. von Sprecher,* Helv. Chim. Acta *63*, 806 (1980).
[16] *W. Fischer, C.A. Grob, G. von Sprecher & A. Waldner,* Helv. Chim. Acta *63*, 816 (1980).
[17] *P. Flury & C.A. Grob,* Helv. Chim. Acta *66*, 1991 (1983).
[18] *R. Bielmann, C.A. Grob & B. Schaub,* Helv. Chim. Acta *65*, 1728 (1982).