222. Norbornanes

Part 18

Inductive Charge Dispersal in the Solvolyses of 4- and 5-Substituted 2-Norbornyl *p*-Toluenesulfonates

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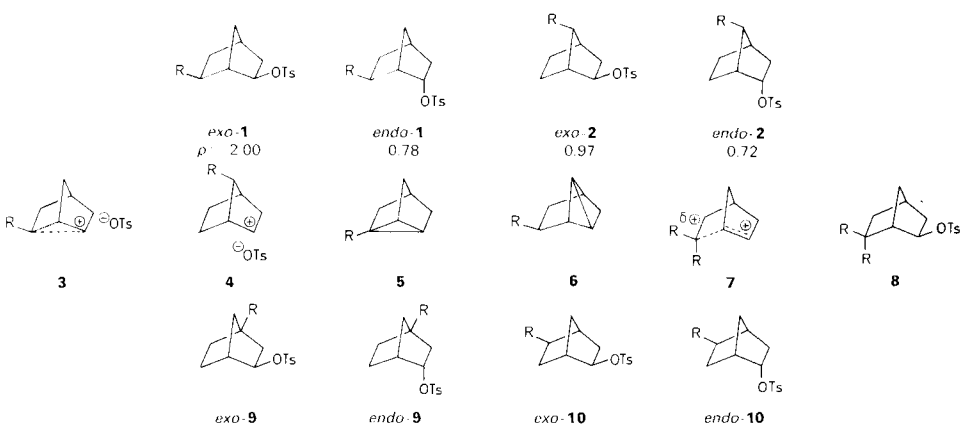
The solvolysis rates and products of 4- and 5-*exo*-substituted 2-*exo*- and 2-*endo*-norbornyl tosylates **9** and **10**, respectively, are reported. The logarithms of the rate constants (log k) correlate linearly with the inductive constants σ_I^q for the substituents. A comparison of the reaction constants ρ_I for the 4-, 5-, 6-, and 7-substituted 2-*exo*- and 2-*endo*-tosylates **9**, **10**, **1**, and **2** respectively, indicates that inductivity is higher for 2-*exo*-ionization than for 2-*endo*-ionization in all series. This observation is attributed to the more favorable alignment of neighboring C-atoms for dorsal participation in *exo*-ionization, especially, in the case of C(6).

It was shown in previous communications [1] that the solvolysis rates and products of 2-*exo*- and 2-*endo*-norbornyl *p*-toluenesulfonates (tosylates) **1** and **2**, respectively, are controlled by the inductive (*I*) effect[1]) of 6-*exo*- and 7-*anti*-substituents[2]). Furthermore, the sensitivity of rate to the *I* effect of substituents[3]), ρ_I, the so called inductivity [4a], was much higher for *exo*-**1** than for the other three series.



[1]) As measured by the pK_a of 4-substituted quinuclidines [3].

[2]) For the influence of 6-*endo*-substituents, see [2].

[3]) Derived from the equation $\log k = \rho_I \sigma_I^q + \log k_o$.

The large difference between the ρ_I values for *exo*-**1** and *endo*-**2** ($\Delta\rho_I = 1.28$) is especially pertinent to the frequently discussed high *exo*/*endo* rate ratios of more than 300 observed in the solvolyses of the parent tosylates *exo*-**1** and *endo*-**1** (R = H)[4]). The rate ratio of 311 observed in 80% EtOH was discussed earlier [5] in terms of differential C,C hyperconjugation of the C(1)–C(6) and C(1)–C(7) σ bonds, respectively, in the strained norbornane structure. However, this view was modified in the light of further results [1]. Thus, hydrolysis of *exo*-**1** led to 2-*exo*-norbornanols with complete retention of configuration at C(2), except when R was a strong electron acceptor, such as $COOCH_3$, F, and CN. In these cases, retention *and* inversion were observed while *exo*/*endo* rate ratios dropped to less than one [1]. In contrast, hydrolysis of *endo*-**1** and *endo*-**2** yielded only 2-*exo*-norbornanols with complete inversion, regardless of the *I* effect of R.

These results indicated graded bridging of the cationic center C(2) by C(6) in the ion **3** from the *exo*-**1**-series and the absence of such bridging in the ion **4** from the *endo*-**2**-series. The dotted bond in **3** implies a weak bonding interaction between C(6) and C(2) that hinders *endo*-attack by nucleophiles, as in all cases of neighboring-group participation [6]. It was also noted that considerable amounts of nortricyclanes **5** were formed from both series **1** and **2**; however, the more strained tricyclo[2.2.1.$0^{2,7}$]heptanes **6** were not observed. It was, therefore, concluded that bridging, as revealed by ρ_I and the stereochemical outcome, is subject to bridging strain and that direct or 'through-space' induction involves graded electron shifts from neighboring atoms[5]).

The large difference between the inductivities of *exo*-**1** and *endo*-**2** ($\Delta\rho_I = 1.28$) indicates high electron mobility between C(6) and C(2) and low mobility between C(7) and C(2), although the distance is somewhat shorter in the latter case *(cf. Table 9)*. This is not accounted for in current models for the transmission of polar effects [8]. Nor does differential C,C hyperconjugation of the C(6)–C(1) and C(7)–C(1) bonds provide a satisfactory explanation. The latter model implies the involvement of two electrons from the C(6)–C(1) bond only, as illustrated in **7** (R = H). While such σ participation was not detectable in the solvolyses of several unstrained alicyclic compounds [9], it could well be a stabilizing factor in norbornyl cations, especially in the 6,6-dimethyl derivative **7** ($R = CH_3$). But in fact, the opposite is observed, for 6,6-dimethyl-2-*exo*-norbornyl tosylate **8** ($R = CH_3$) reacts 25 times slower than the parent tosylate **8** (R = H)[6]).

In view of the strong directional dependence of inductivity in 2-norbornyl cations, it was of interest to investigate the rates, ρ_I values and hydrolysis products of the 4- and 5-substituted 2-*exo*- and 2-*endo*-norbornyl tosylates **9** and **10**, respectively, listed in *Tables 1–4*[7]). *Lenoir et al.* [12] studied the effect of substituents at C(5) on solvolysis rates and products of some 2-*exo*-norbornyl arylsulfonates. Subsequently, *Apeloig et al.* [13] and *Wilcox* and *Tuszynski* [14] reported kinetic studies on 5-*exo*- and 5-*endo*-CN-substituted norbornyl sulfonates. Their conclusions are discussed below.

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[4]) For a recent discussion, see [4].

[5]) Charge dispersal in carbocations is also revealed by NMR spectroscopy as shown by the fundamental work of *Olah* [7].

[6]) In AcOH [10]; in 80% EtOH the deceleration is a factor of 28 (unpublished results).

[7]) A short communication has been published [11].

Table 1. *First-Order Rate Constants for 10^{-3} M Solutions of 1-R-3-*exo*-Norbornyl Tosylates (exo-***9***)* (in 80% (*v*/*v*) EtOH)[a]

R	T [°]	k [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol·degree]
H[b])	70.00	$2.62 \cdot 10^{-2}$	20.2	− 7.1
CH_2OH	40.01	$5.62 \cdot 10^{-4}$	21.7	− 4.3
	50.02	$1.75 \cdot 10^{-4}$		
	60.03	$4.84 \cdot 10^{-3}$		
	70.00[c])	$1.30 \cdot 10^{-2}$		
CH_2OAc	50.11	$5.01 \cdot 10^{-4}$	21.9	− 6.2
	59.97	$1.42 \cdot 10^{-3}$		
	69.99	$3.82 \cdot 10^{-3}$		
	70.00[c])	$3.83 \cdot 10^{-3}$		
CH_2Cl	50.01	$4.08 \cdot 10^{-4}$	21.7	− 7.2
	59.97	$1.16 \cdot 10^{-3}$		
	69.63	$2.98 \cdot 10^{-3}$		
	70.00[c])	$3.09 \cdot 10^{-3}$		
CH_2OTs	50.69	$1.99 \cdot 10^{-4}$	22.5	− 6.3
	60.31	$5.70 \cdot 10^{-4}$		
	69.98	$1.50 \cdot 10^{-3}$		
	70.00[c])	$1.51 \cdot 10^{-3}$		
$COOCH_3$	61.04	$2.15 \cdot 10^{-4}$	23.0	− 6.8
	69.95	$5.56 \cdot 10^{-4}$		
	79.95	$1.45 \cdot 10^{-3}$		
	70.00[c])	$5.50 \cdot 10^{-4}$		
OAc	70.13	$2.36 \cdot 10^{-4}$	23.6	− 6.7
	80.08	$6.53 \cdot 10^{-4}$		
	90.04	$1.66 \cdot 10^{-3}$		
	70.00[c])	$2.34 \cdot 10^{-4}$		
Cl	79.99	$2.64 \cdot 10^{-4}$	23.1	− 9.8
	90.06	$6.84 \cdot 10^{-4}$		
	99.92	$1.62 \cdot 10^{-3}$		
	70.00[c])	$9.88 \cdot 10^{-5}$		
CN	90.03	$2.10 \cdot 10^{-4}$	23.6	− 10.9
	100.17	$5.32 \cdot 10^{-4}$		
	110.17	$1.23 \cdot 10^{-3}$		
	70.00[c])	$2.97 \cdot 10^{-5}$		

[a]) Mean deviation in all cases ±1.5%. [b]) [18]. [c]) Extrapolated.

Table 2. *First-Order Rate Constants for 10^{-3} M Solutions of 1-R-3-*endo*-Norbornyl Tosylates (endo-***9***)* (in 80% (*v*/*v*) EtOH)

R	T [°]	k [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol·degree]
H[a])	70.00	$8.42 \cdot 10^{-5}$		
CH_2OH	79.98	$1.32 \cdot 10^{-4}$	24.5	− 7.3
	90.05	$3.56 \cdot 10^{-4}$		
	99.94	$9.02 \cdot 10^{-4}$		
	70.00[b])	$4.64 \cdot 10^{-5}$		
CH_2OAc	80.20	$4.50 \cdot 10^{-5}$	24.9	− 8.3
	90.04	$1.19 \cdot 10^{-4}$		
	100.06	$3.14 \cdot 10^{-4}$		
	70.00[b])	$1.51 \cdot 10^{-5}$		

Table 2 (cont.)

R	T [°]	k [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol·degree]
CH_2Cl	90.11	$9.09 \cdot 10^{-5}$	24.3	− 10.5
	100.06	$2.29 \cdot 10^{-4}$		
	110.13	$5.57 \cdot 10^{-4}$		
	70.00[b])	$1.19 \cdot 10^{-5}$		
CH_2OTs	99.98	$1.23 \cdot 10^{-4}$	25.0	− 9.8
	109.97	$3.03 \cdot 10^{-4}$		
	120.02	$7.24 \cdot 10^{-4}$		
	70.00[b])	$5.92 \cdot 10^{-6}$		
$COOCH_3$	109.95	$1.91 \cdot 10^{-4}$	25.5	− 9.5
	120.05	$4.60 \cdot 10^{-4}$		
	130.07	$1.07 \cdot 10^{-3}$		
	70.00[b])	$3.45 \cdot 10^{-6}$		
OAc	110.03	$8.97 \cdot 10^{-5}$	25.7	− 10.4
	120.05	$2.17 \cdot 10^{-4}$		
	130.01	$5.04 \cdot 10^{-4}$		
	70.00[b])	$1.56 \cdot 10^{-6}$		
Cl	109.97	$3.91 \cdot 10^{-5}$	25.1	− 13.7
	120.03	$9.27 \cdot 10^{-5}$		
	130.01	$2.12 \cdot 10^{-4}$		
	70.00[b])	$7.50 \cdot 10^{-7}$		
CN	119.92	$4.30 \cdot 10^{-5}$	26	− 13.0
	125.03	$6.71 \cdot 10^{-5}$		
	129.97	$1.01 \cdot 10^{-4}$		
	70.00[b])	$2.99 \cdot 10^{-7}$		

[a]) [18]. [b]) Extrapolated.

Table 3. *First-Order Rate Constants for* 10^{-3} M *Solutions of 2-R-5-*exo*-Norbornyl Tosylates (endo-***10***)* (in 80% (*v*/*v*) EtOH)

R	T [°]	k [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol·degree]
CH_3	40.22	$6.31 \cdot 10^{-4}$	20.5	− 8.1
	51.10	$1.77 \cdot 10^{-3}$		
	60.09	$4.75 \cdot 10^{-3}$		
	70.00[a])	$1.19 \cdot 10^{-2}$		
CH_2OH	49.81	$4.99 \cdot 10^{-4}$	22.4	− 4.5
	59.44	$1.46 \cdot 10^{-3}$		
	70.00	$4.13 \cdot 10^{-3}$		
CH_2OCH_3	59.44	$9.79 \cdot 10^{-4}$	22.1	− 6.1
	70.00	$2.80 \cdot 10^{-3}$		
	79.92	$7.22 \cdot 10^{-3}$		
CH_2OAc	51.38	$1.65 \cdot 10^{-4}$	23.1	− 5.0
	59.44	$3.89 \cdot 10^{-4}$		
	70.00	$1.21 \cdot 10^{-3}$		
CH_2Br	70.00	$9.19 \cdot 10^{-4}$	21.8	− 9.1
	79.93	$2.40 \cdot 10^{-3}$		
	90.12	$5.72 \cdot 10^{-3}$		
CH_2OTs	70.00	$4.50 \cdot 10^{-4}$	23.3	− 6.1
	79.93	$1.25 \cdot 10^{-3}$		
	90.12	$3.17 \cdot 10^{-3}$		

Table 3 (cont.)

R	T [°]	k [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol·degree]
$COOCH_3$	70.00	$3.58 \cdot 10^{-4}$	23.7	− 5.6
	79.93	$1.01 \cdot 10^{-3}$		
	90.12	$2.59 \cdot 10^{-3}$		
Cl	70.00[a])	$7.92 \cdot 10^{-5}$	22.7	− 11.5
	90.09	$5.25 \cdot 10^{-4}$		
	99.68	$1.23 \cdot 10^{-3}$		
	109.97	$2.83 \cdot 10^{-3}$		
CN	70.00[a])	$1.87 \cdot 10^{-5}$	23.4	− 12.4
	100.02	$3.18 \cdot 10^{-4}$		
	110.02	$7.56 \cdot 10^{-4}$		
	120.01	$1.66 \cdot 10^{-3}$		

[a]) Extrapolated.

Table 4. *First-Order Rate Constants for* 10^{-3} M *Solutions of 2-R-5-*endo*-Norbornyl Tosylates* (*endo*-**10**) (in 80% (*v*/*v*) EtOH)

R	T [°]	k [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol·degree]
CH_3	70.00[a])	$6.36 \cdot 10^{-5}$	23.8	− 8.7
	80.28	$1.77 \cdot 10^{-4}$		
	90.38	$4.91 \cdot 10^{-4}$		
	99.93	$1.11 \cdot 10^{-3}$		
CH_2OCH_3	70.00[a])	$3.98 \cdot 10^{-5}$	23.4	− 10.9
	90.02	$2.77 \cdot 10^{-4}$		
	99.32	$6.39 \cdot 10^{-4}$		
	109.52	$1.52 \cdot 10^{-3}$		
CH_2OH	70.00[a])	$5.22 \cdot 10^{-5}$	23.8	− 9.2
	89.86	$3.54 \cdot 10^{-4}$		
	99.92	$8.89 \cdot 10^{-4}$		
	109.97	$2.02 \cdot 10^{-3}$		
CH_2OAc	70.00[a])	$2.15 \cdot 10^{-5}$	24.5	− 8.4
	89.89	$1.62 \cdot 10^{-4}$		
	99.28	$3.97 \cdot 10^{-4}$		
	109.41	$9.64 \cdot 10^{-4}$		
CH_2OTs	70.00[a])	$1.30 \cdot 10^{-5}$	21.8	− 17.7
	89.90	$7.95 \cdot 10^{-5}$		
	99.29	$1.73 \cdot 10^{-4}$		
	110.46	$4.23 \cdot 10^{-4}$		
CH_2Br	70.00[a])	$1.63 \cdot 10^{-5}$	23.4	− 12.6
	100.55	$2.89 \cdot 10^{-4}$		
	109.96	$6.55 \cdot 10^{-4}$		
	120.05	$1.45 \cdot 10^{-3}$		
$COOCH_3$	70.00[a])	$1.01 \cdot 10^{-5}$	24.5	− 10.3
	99.30	$1.84 \cdot 10^{-4}$		
	109.55	$4.54 \cdot 10^{-4}$		
	119.67	$1.08 \cdot 10^{-3}$		
Cl	70.00[a])	$3.04 \cdot 10^{-6}$	22.7	− 18.0
	109.92	$1.07 \cdot 10^{-4}$		
	119.87	$2.41 \cdot 10^{-4}$		
	129.00	$4.92 \cdot 10^{-4}$		

Table 4 (cont.)

R	T [°]	k [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol·degree]
CN	70.00[a])	$1.72 \cdot 10^{-6}$	24.7	– 13.4
	109.33	$7.89 \cdot 10^{-5}$		
	119.54	$1.87 \cdot 10^{-4}$		
	129.75	$4.30 \cdot 10^{-4}$		

[a]) Extrapolated.

Results. – The preparation of the tosylates **9** and **10**, as well as their hydrolysis products, are reported elsewhere[9]). First-order rate constants for all four series were measured conductometrically in 80% (v/v) EtOH at three temperatures *(Tables 1–4)*. Rate constants at 70° and *exo/endo* rate ratios are shown in *Tables 5* and *6*. *Tables 7* and *8* summarize the hydrolysis products obtained after ten half lives in 70% (v/v) dioxane at the medium temperatures listed in *Tables 1–4*. Yields in % were determined by capillary GC.

Table 5. *Rate Constants for* exo-**9** *and* endo-**9**, *and* exo/endo *Rate Ratios at 70°*

R	k (*exo*-**9**)	k (*endo*-**9**)	k_{exo}/k_{endo}
H	$2.62 \cdot 10^{-2}$	$8.42 \cdot 10^{-5}$	311
CH_2OH	$1.30 \cdot 10^{-2}$	$4.64 \cdot 10^{-5}$	280
CH_2OAc	$3.83 \cdot 10^{-3}$	$1.51 \cdot 10^{-5}$	254
CH_2Cl	$3.09 \cdot 10^{-3}$	$1.19 \cdot 10^{-5}$	260
CH_2OTs	$1.51 \cdot 10^{-3}$	$5.92 \cdot 10^{-6}$	255
$COOCH_3$	$5.50 \cdot 10^{-4}$	$3.45 \cdot 10^{-6}$	159
OAc	$2.34 \cdot 10^{-4}$	$1.56 \cdot 10^{-6}$	150
Cl	$9.88 \cdot 10^{-5}$	$7.50 \cdot 10^{-7}$	132
CN	$2.97 \cdot 10^{-5}$	$2.99 \cdot 10^{-7}$	99

Table 6. *Rate Constants for* exo-**10** *and* endo-**10**, *and* exo/endo *Rate Ratios at 70°*

R	k (*exo*-**10**)	k (*endo*-**10**)	k_{exo}/k_{endo}
H	$2.62 \cdot 10^{-2}$	$8.42 \cdot 10^{-5}$	311
CH_3	$1.19 \cdot 10^{-2}$	$6.36 \cdot 10^{-5}$	187
CH_2OH	$4.13 \cdot 10^{-3}$	$5.22 \cdot 10^{-5}$	79
CH_2OCH_3	$2.80 \cdot 10^{-3}$	$3.98 \cdot 10^{-5}$	70
CH_2OAc	$1.21 \cdot 10^{-3}$	$2.15 \cdot 10^{-5}$	56
CH_2Br	$9.19 \cdot 10^{-4}$	$1.63 \cdot 10^{-5}$	56
CH_2OTs	$4.50 \cdot 10^{-4}$	$1.30 \cdot 10^{-5}$	35
$COOCH_3$	$3.58 \cdot 10^{-4}$	$1.01 \cdot 10^{-5}$	35
Cl	$7.92 \cdot 10^{-5}$	$3.04 \cdot 10^{-6}$	9
CN	$1.87 \cdot 10^{-5}$	$1.72 \cdot 10^{-6}$	11

Table 7. *Yields of Products* ([%], ± 2%) *from the Reaction of 1-R-3-*exo (exo-**9**) *and* (in brackets) *3-*endo-*Norbornyl Tosylates* (endo-**9**) *in 70% Dioxane*

R	H [1]	CH_2OH	CH_2OAc	CH_2Cl	CH_2OTs[a])	$COOCH_3$	OAc	Cl	CN
13	94 (93)	94 (82)	96 (94)	92 (88)	88 (85)	91 (88)	96 (95)	93 (89)	89 (88)
14	6 (7)	6 (8)	4 (6)	8 (12)	12 (15)	9 (12)	4 (5)	7 (11)	11 (12)

[a]) Products determined by ^{1}H-NMR spectroscopy.

[9]) See a following communication as well as the doctoral dissertation of *Francesco Fuso*, Basel, University Library, to appear 1987.

Table 8. *Yields of Products* ([%], ± 2%) *from the Reaction of 2-R-5-*exo- (*exo-***10**) *and* (in brackets) 5-endo-*Norbornyl Tosylates* (*endo-***10**) *in 70% Dioxane*

R	19	20	21	22
CH_3	41 (51)	43 (27)		9 (10)
CH_2OH	43 (53)	47 (31)		
CH_2OCH_3	44 (62)	47 (32)		
CH_2OAc	45 (53)	49 (23)		
CH_2Br	43 (59)	50 (29)		
CH_2OTs[a])	51 (72)	45 (21)		
$COOCH_3$	43 (70)	52 (28)		
Cl[b])	38 (58)	57 (36)	3 (–)	
CN	42 (72)	47 (20)	1 (–)	

[a]) After 3.5 half-lives. [b]) After one half-live, the ionization of **19** (R=Cl) becomes noticeable.

Discussion. – In *Figs. 1* and *2*, the log *k* values for **9** and **10** are plotted against the respective inductive substituent constants σ_I^q [3]. The linear correlations[10]) show that

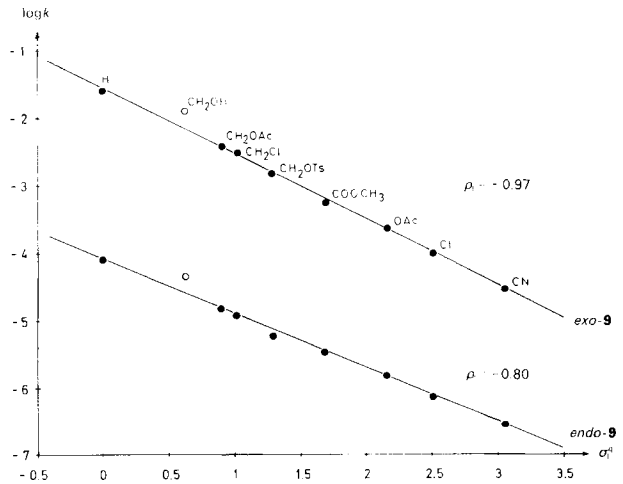


Fig. 1. *Plots of log* k *for* 10^{-3} M *solutions of 4-substituted 2-*exo- *and 2-*endo-*norbornyl tosylates* **9** *in 80% (v/v) EtOH* vs. *inductive substituent constants* σ_I^q

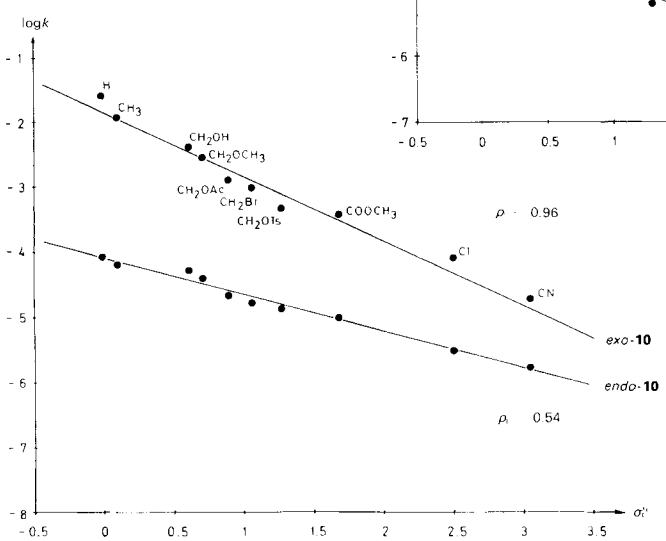
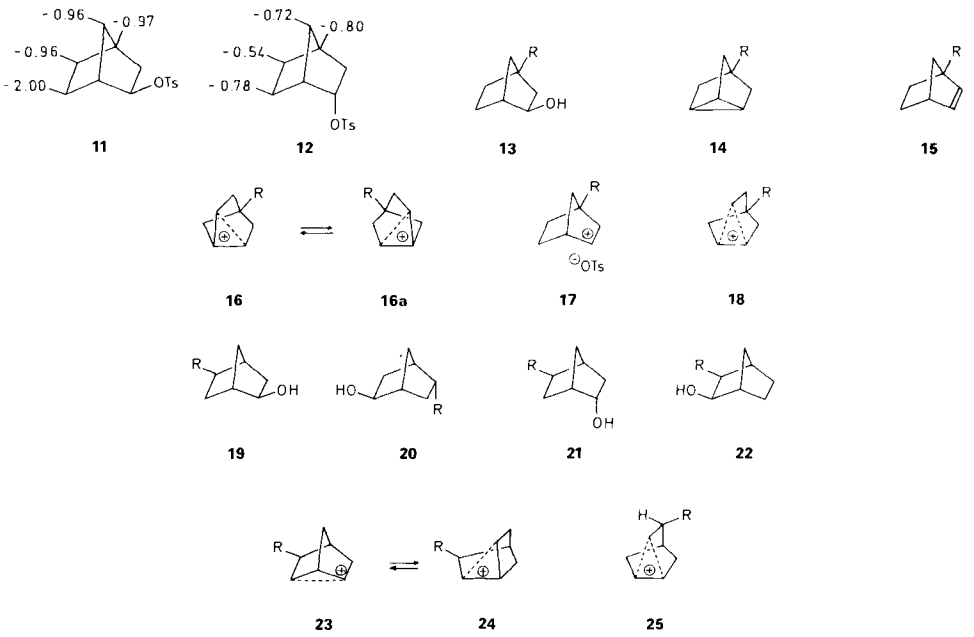


Fig. 2. *Plots of log* k *for* 10^{-3} M *solutions of 5-*exo-*substituted 2-*exo- *and 2-*endo-*norbornyl tosylates* **10** *in 80% (v/v) EtOH* vs. *inductive substituent constants* σ_I^q

[10]) Except for the points for *exo-***9** and *endo-***9** (R = CH_2OH). Electrofugal groups in the γ-position give rise to exalted rates [15] and are, therefore, omitted.

substituents at C(4) and at C(5) control ionization rates by their *I* effects, as they do at C(6) and C(7) [1]. This fact excludes other possible controlling factors, such as steric bulk effects [4b] or changes of mechanism from S_N1 to solvent S_N2[11]).

The ρ_I values for C(4), C(5), C(6), and C(7) *(Figs. 1* and *2)* are presented in formulas **11** and **12**. They show that, in the *exo*-series **11**, ρ_I is practically the same for C(4), C(5), and C(7) (−0.96), but much larger for C(6) (−2.00). This emphasizes the special role of C(6) in dispersing positive charge from C(2). In the *endo*-series **12**, the ρ_I values are smaller and decrease in the order C(4) > C(6) > C(7) > C(5). A possible explanation for the reduced inductivity of these C-atoms is that they are unfavorably aligned for dorsal participation in the ionization of the C(2)–(*endo*-OTs) bond.



This is supported by the differences $\Delta\rho_I$ between the ρ_I for the 2-*exo*- and 2-*endo*-epimers of the 4-, 5-, 6-, and 7-substituted norbornyl tosylates in *Table 9*. A comparison between the largest $\Delta\rho_I$ value of 1.22 for C(6) and the lowest $\Delta\rho_I$ of 0.17 for C(4) is instructive. As models show, C(6) is favorably placed to assist the ionization of the C(2)–(*exo*-OTs) bond, not, however, of the C(2)–(*endo*-OTs) bond. On the other hand, C(4) and its substituents are only slightly better orientated to assist *exo*-ionization than *endo*-ionization. C(5) again is somewhat better positioned for *exo*-ionization than for *endo*-ionization. Although C(7) is dorsal to the C(2)–(*endo*-OTs) bond, it does not participate effectively due to bridging strain [1b]. Different degrees of participation could, therefore, be the cause of directional inductivity and, hence, also for varying *exo*/*endo* rate ratios.

[11]) Nucleophilic solvent participation reduces the charge at the reaction site with concomitant lowering of the ρ_I value [16].

Table 9. *$\Delta\rho_I$ Values (= ρ_I (exo) − ρ_I (endo)) for 4-, 5-, 6-, and 7-Substituted 2-*exo- and *2-*endo*-Norbornyl Tosylates* (70°), k_{exo}/k_{endo} *for R=CN and Approx. Distances from C(2)*[a])

R at	$\Delta\rho_I$	$k_{exo}^{CN}/k_{endo}^{CN}$	Distance [Å]
C(6)	1.22	0.88	2.50
C(5)	0.42	11	2.95
C(7)	0.24	66	2.40
C(4)	0.17	99	2.43

[a]) Calculated from X-ray data in *'Landolt-Börnstein*, New Series', Vol. 7, p. 361.

It has been known for some time that electron-attracting substituents at C(5) decelerate the ionization of a 2-*exo*-nucleofuge more strongly than the ionization of the 2-*endo*-epimer, thereby reducing the k_{exo}/k_{endo} ratio relative to the parent compounds. Thus, *Lenoir et al.* reported that substituting 5-*exo*-Cl for H in 2-norbornyl brosylates reduces k_{exo}/k_{endo} in 60% EtOH from 858 to 94 [12]. According to *Apeloig et al.* [13], k_{exo}/k_{endo} for the 5-*exo*-CN-substituted brosylates is 25 compared to 561 for the parent compounds. In the more ionizing solvent hexafluoroisopropanol, *Wilcox* and *Tuszynski* [14] observed a reduction of k_{exo}/k_{endo} from 1400 to 5 for the corresponding tosylates. These authors attributed the decelerating effect of $-I$ substituents at C(5) to reduced σ participation of the C(1)–C(6) bond.

The present study shows that a CN group at C(4), C(7), C(5), and C(6) reduces k_{exo}/k_{endo} from 311 for the parent tosylates to 99, 66, 11, and 0.88, respectively, *i.e.* in the order of increasing $\Delta\rho_I$ values *(Table 9)*. This striking correspondence between rate ratios and $\Delta\rho_I$ suggests a more general rationale for charge dispersal in the norbornyl cation, namely differential participation of neighboring C-atoms, of which C(6) plays the dominant role in 2-*exo*-ionization.

The hydrolyses of the 4-substituted tosylates *exo*-**9** and *endo*-**9** yield practically the same amounts of two products, namely the 2-*exo*-norbornanols **13** and smaller amounts of the nortricyclanes **14** *(Table 7)*[12]). The alcohols **13** are formed from *exo*-**9** by substitution with complete retention, and from *endo*-**9** with complete inversion of configuration at C(2). The formation of the same amounts of the same products strongly suggests a common intermediate for both *exo*- and *endo*-**9**, namely the bridged 2-norbornyl cation **16**. This can be directly formed from *exo*-**9** or *via* the ion pair **17** from *endo*-**9**.

Strong bridging as in **16** is a prerequisite for substitution with retention, but it also favors the formation of nortricyclanes **14** and rearrangement to **16a**, the enantiomer of **16**. This degenerate rearrangement, which is not detectable with unlabelled material[13]), must be extremely fast, as in the case of the parent ion **16** (R = H) [1]. The isomerisation **16** ⇄ **16a** (R = H) resembles a skeletal vibration [1] [4a] and, as suggested more recently by *Bader* [17], a thermal motion, the symmetrical ion **18** then representing the vibrationally averaged structure.

In contrast, the hydrolyses of the 5-*exo*-substituted tosylates *exo*-**10** and *endo*-**10** yield different amounts of the two main products **19** and **20** *(Table 8)*. The norbornanols **19** result from substitution with retention, the alcohols **20** from substitution with rearrangement. This result again points to a common intermediate, namely the bridged ion

[12]) Only traces of 4-substituted norbornenes **15** were detected by GLC.

[13]) For instance, C(2)-deuterated *exo*-**7** and *endo*-**7** would lead to 1- and 2-deuterated 2-norbornanols **13**.

23, which equilibrates rapidly with the epimeric ion **24**. In this case, the rearrangement is not degenerate and the transition state **25**, therefore, unsymmetrical. Bridging in **23** is weakened by the $-I$ substituents Cl and CN, since significant amounts of the 2-*endo*-alcohols **21** are formed in these cases. Finally, *exo*-**10** (R = CH_3) yields 9% of 3-*exo*-methyl-2-*exo*-norbornanol **22** by way of a 1,3-hydride shift in **23**. This reaction probably also occurs in the **9** series, but is not detectable due to symmetry.

In conclusion, the inductivities ρ_I in **11** and **12** reveal the degree of charge dispersal to C(4), C(5), C(6), and C(7) in the transition states for the ionization of 2-*exo*- and 2-*endo*-norbornyl tosylates. Inductivity is highest for C(6) in the *exo*-series **11** and lowest for C(5) in the *endo*-series **12**.

ρ_I Values reflect directional electron mobility, which in all cases is higher for 2-*exo*-ionization than for 2-*endo*-ionization. This can be ascribed to the fact that the C(2)-(*exo*-OTs) bond is better aligned than the C(2)-(*endo*-OTs) bond for the participation of dorsal C-atoms. In addition, participation of C(7) in C(2)-(*endo*-OTs) bond cleavage generates more bridging strain. It would be interesting to determine charge dispersal in the free 2-norbornyl cation. This is precluded, however, because of the extremely fast rearrangements and hydride shifts which take place under stable-ion conditions [4c].

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