

## 34. Norbornanes

Part 20

### Inductivity and Bridging in 2-Norbornyl Cations

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The solvolysis rates and products of several 1-substituted 2-*exo*- and 2-*endo*-norbornyl *p*-toluenesulfonates **7** and **8**, respectively, have been determined. Hydrolyses of these epimeric tosylates yielded rearranged products in varying amounts, except when the substituent was COOCH<sub>3</sub> or CN. The logarithms of the rate constants (log *k*) for the *endo*-series **8** correlated linearly with the corresponding inductive constants  $\sigma_I^\ddagger$  with a reaction constant  $\rho_I$  of  $-1.24$ . On the other hand, log *k* values for the *exo*-series **7** appear to fit two regression lines, the first line ( $\rho_I = -1.90$ ) defined by the tosylates that ionize, with rearrangement, to the tertiary cations **11**, the second ( $\rho_I = -1.86$ ) by the tosylates **7** (R = H, COOCH<sub>3</sub>, and CN) that ionize to an asymmetrically bridged secondary cation **19**. These results confirm the unique participation of C(6) with a  $\rho_I$  of  $-2.00$  in the ionization of 2-*exo*-norbornyl tosylate.

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It was shown in previous communications [1] that the solvolysis rates and products of 2-*exo*- and 2-*endo*-norbornyl tosylates **1** and **2**, respectively, are controlled by the inductive (*I*) effect of substituents at C(4), C(5), C(6), and C(7). Furthermore, the sensitivity  $\rho_I$  of rates to the *I* effect of substituents at these C-atoms<sup>1)</sup>, their so-called inductivity [3], varied markedly, as indicated by the numbers in *Formulae 3* and *4*<sup>2)</sup>.

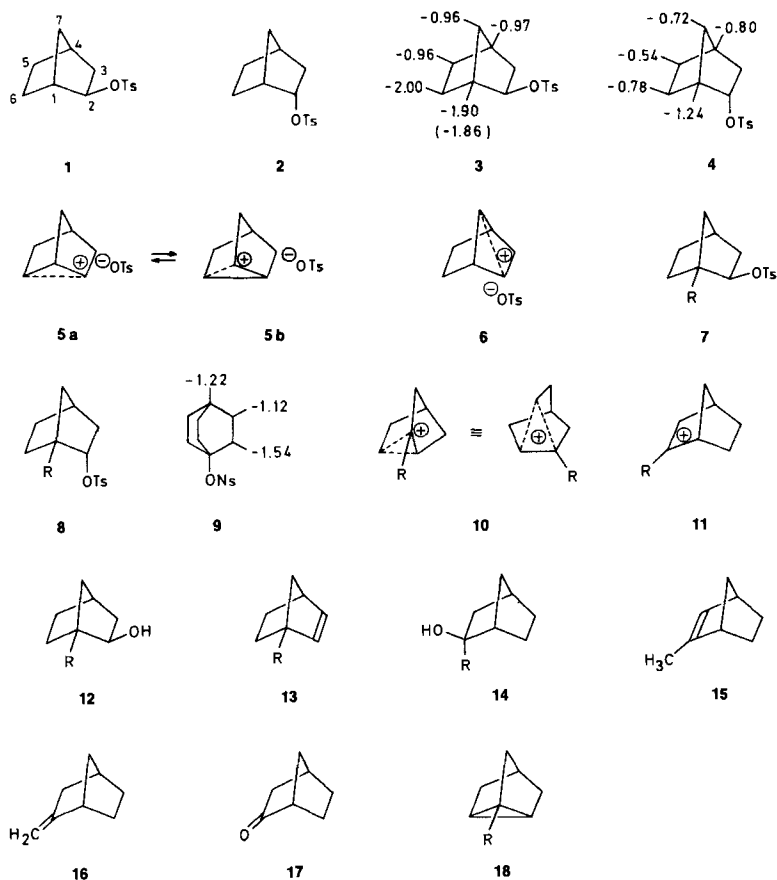
These numbers show that inductivity at a given C-atom is uniformly higher for *exo*- than for *endo*-ionization, a result ascribed to differential participation of neighboring C-atoms in the ionization process. *exo*-Ionization is influenced most strongly by substituents, as well as by H–C(6), as evidenced by the relatively large  $\rho_I$  of  $-2.00$  in **3** [1a]. This finding, in conjunction with the stereochemical outcome of the reactions, led to the conclusion that the parent *exo*-tosylate **1** ionizes to the asymmetrically bridged ion pair **5a** which subsequently undergoes an extremely rapid and reversible rearrangement to its enantiomer **5b**.

The term bridging implies a bonding interaction<sup>3)</sup> between the electrophilic center of a carbenium ion and a temporarily pentacoordinate C-atom. Bridging, thus, contributes to the transmission of the *I* effect of attached substituents. Strong bridging as in **5** leads to substitution with predominant retention of configuration due to shielding of the *endo*-side of the cation towards nucleophilic attack. C(6) participates far less effectively in

<sup>1)</sup> As derived from the Hammett equation  $\log k/k_0 = \rho_I \cdot \sigma_I^\ddagger$  where *k* and *k*<sub>0</sub> are rate constants for substituted and unsubstituted tosylates, respectively, and  $\sigma_I^\ddagger$  are inductive substituent constants [2].

<sup>2)</sup> The  $\rho_I$  values for C(1) in **3** and **4** are presented and discussed in this communication.

<sup>3)</sup> The dotted lines in **5** symbolize a weak bonding interaction.



*endo*-ionization, as evidenced by the much smaller  $\rho_1$  of  $-0.78$  [1a]. This is, apparently, because dorsal assistance to ionization of the *endo*-OTs group by C(6) is precluded.

The even lower  $\rho_1$  value of  $-0.72$  at C(7) for *endo*-ionization in **4** [1d] suggested that a further factor, namely bridging strain, determines inductivity in carbenium ions. As shown in a following communication [4], bridging of C(2) by C(7), as in **6**, generates far more angle strain than bridging of C(2) by C(6), as in **5**. For structural reasons, bridging of C(2) by C(4) or C(5) would also generate large strains, a conclusion supported by the low  $\rho_1$  values for these C-atoms in **3** and **4** [1e].

In contrast to C(4), C(5), and C(7), C(1) is directly bonded to the incipient cationic center C(2) in **1** and **2**. Therefore, attached substituents, as in **7** and **8**, should affect ionization rates far more strongly. In fact, a recent study [5] has shown that the solvolysis rates of 2-, 3-, and 4-monosubstituted bicyclo[2.2.2]octyl *p*-nitrobenzenesulfonates **9** led to  $\rho_1$  values of  $-1.54$ ,  $-1.12$ , and  $-1.22$ , respectively, as listed in **9**. Thus, inductivity is clearly largest at the adjacent C(2). Moreover, the surprisingly good linear correlation of  $\log k$  vs.  $\sigma_1^\dagger$  for substituents at C(2) indicated that steric bulk effects are negligible.

This finding encouraged the present study which is concerned with the solvolysis rates and products of 1-substituted 2-*exo*- and 2-*endo*-norbornyl tosylates **7** and **8**, respectively, where spatial relationships between adjacent substituents are practically the same as in **9**.

There are several references to solvolyses of tosylates and bromides of the type **7** and **8** in the literature. *Schleyer* and *Kleinfelder*<sup>4)</sup> observed that, in AcOH, 1-methyl-2-*exo*-norbornyl tosylate **7** (R = CH<sub>3</sub>) reacted 51 times as fast as the parent tosylate **7** (R = H), whereas the *endo* tosylate **8** (R = CH<sub>3</sub>) reacted less than 20% faster than **8** (R = H). According to *Sargent* [6], these results constitute evidence for participation of the C(1)–C(6) bond in the transition state for *exo*-ionization, but fail to establish whether the transition state leads to the bridged intermediate **10** (R = CH<sub>3</sub>) or directly to the rearranged tertiary cation **11** (R = CH<sub>3</sub>). On the other hand, the finding of *Schleyer et al.* [7] that the *exo/endo*-rate ratio of *ca.* 300 for the parent tosylates **7** and **8** (R = H) (in AcOH at 25°) is increased by a 1-methyl or a 1-methoxy group to 14000 and 6200, respectively, indicates that in these cases ionization and rearrangement of the *exo*-tosylates are concerted.

In their study of the rates and products of several 1-substituted 2-*exo*-norbornyl bromides **7** (Br instead of OTs), *Wilt* and *Wagner* [8] found that rearrangement to tertiary carbenium ions **11** took place when R = OAc, NHCOC<sub>6</sub>H<sub>5</sub>, NH<sub>2</sub>, and COO<sup>-</sup>, but not when R = COOCH<sub>3</sub>. This fact established that substituents also control the course of the reaction. More recently, *Lenoir* [9] has determined the solvolysis rates and products of several tosylates and bromides of type **7** and **8**. However, his results and conclusions differ in some respects from those of the present study, as will be discussed below.

The preparation of the 1-substituted 2-*exo*- and 2-*endo*-norbornyl tosylates **7** and **8**, respectively, listed in *Tables 1* and *2*, respectively, and their hydrolysis products are

Table 1. First-Order Rate Constants for 10<sup>-3</sup>M Solutions of 1-R-2-*exo*-Norbornyl Tosylates **7** in 80% (v/v) EtOH<sup>a)</sup>

R	T[°C]	k[s <sup>-1</sup> ]	R	T[°C]	k[s <sup>-1</sup> ]	R	T[°C]	k[s <sup>-1</sup> ]
H <sup>b)</sup>	70.00 <sup>c)</sup>	2.62 · 10 <sup>-2</sup>	CH <sub>2</sub> Cl	70.00 <sup>c)</sup>	7.38 · 10 <sup>-2</sup>	OAc <sup>d)</sup>	70.00 <sup>c)</sup>	7.45 · 10 <sup>-5</sup>
CH <sub>3</sub>	70.00 <sup>c)</sup>	4.13 · 10 <sup>-1</sup>		40.25	3.11 · 10 <sup>-4</sup>		69.81	7.32 · 10 <sup>-5</sup>
	0.36	1.61 · 10 <sup>-4</sup>		50.10	9.37 · 10 <sup>-3</sup>		70.02	7.45 · 10 <sup>-5</sup>
	10.03	6.15 · 10 <sup>-4</sup>		60.05	2.73 · 10 <sup>-3</sup>		109.98	3.28 · 10 <sup>-3</sup>
	20.15	2.17 · 10 <sup>-3</sup>	CH <sub>2</sub> OTs	70.00 <sup>c)</sup>	1.83 · 10 <sup>-3</sup>	Br	70.00 <sup>c)</sup>	3.80 · 10 <sup>-6</sup>
CH <sub>2</sub> OH	70.00 <sup>c)</sup>	4.32 · 10 <sup>-1</sup>		49.99	1.96 · 10 <sup>-4</sup>		120.08	4.67 · 10 <sup>-4</sup>
	-0.51	1.19 · 10 <sup>-4</sup>		60.00	5.93 · 10 <sup>-4</sup>		130.08	1.08 · 10 <sup>-3</sup>
	9.16	4.70 · 10 <sup>-4</sup>		69.99	1.86 · 10 <sup>-3</sup>		140.10	2.32 · 10 <sup>-3</sup>
	20.57	2.07 · 10 <sup>-3</sup>	COOCH <sub>3</sub>	70.00 <sup>c)</sup>	4.39 · 10 <sup>-5</sup>			
CH <sub>2</sub> OAc	70.00 <sup>c)</sup>	1.15 · 10 <sup>-2</sup>		80.39	1.30 · 10 <sup>-4</sup>	CN	70.00 <sup>c)</sup>	5.84 · 10 <sup>-8</sup>
	30.08	1.36 · 10 <sup>-4</sup>		90.10	3.41 · 10 <sup>-4</sup>		119.75	1.27 · 10 <sup>-5</sup>
	40.04	4.67 · 10 <sup>-4</sup>		100.00	8.59 · 10 <sup>-4</sup>		129.84	3.16 · 10 <sup>-5</sup>
	50.06	1.43 · 10 <sup>-3</sup>	COCH <sub>3</sub>	60.00	1.60 · 10 <sup>-4</sup>		139.96	7.83 · 10 <sup>-5</sup>
			70.00	4.60 · 10 <sup>-4</sup>				
			80.33	1.28 · 10 <sup>-3</sup>				

<sup>a)</sup> The *k* values are the average of at least two measurements; mean deviation ± 1.15%.

<sup>b)</sup> [lg].

<sup>c)</sup> Extrapolated.

<sup>d)</sup> Only one measurement.

<sup>4)</sup> Cited by *Sargent* in [6].

Table 2. First-Order Rate Constants for  $10^{-3}$  M Solutions of 1-R-2-exo-Norbornyl Tosylates **8** in 80% EtOH (v/v) EtOH<sup>a)</sup>

R	T[°C]	k[s <sup>-1</sup> ]	R	T[°C]	k[s <sup>-1</sup> ]	R	T[°C]	k[s <sup>-1</sup> ]
H <sup>b)</sup>	70.00 <sup>c)</sup>	$8.42 \cdot 10^{-5}$	CH <sub>2</sub> Cl	70.00 <sup>c)</sup>	$3.91 \cdot 10^{-6}$	COOCH <sub>3</sub>	70.00 <sup>c)</sup>	$8.91 \cdot 10^{-7}$
CH <sub>3</sub>	70.00 <sup>c)</sup>	$1.01 \cdot 10^{-4}$		99.86	$8.42 \cdot 10^{-5}$		110.08	$4.89 \cdot 10^{-5}$
	79.88	$2.77 \cdot 10^{-4}$		109.94	$2.12 \cdot 10^{-4}$		118.63	$1.02 \cdot 10^{-4}$
	89.94	$7.28 \cdot 10^{-4}$		119.90	$5.10 \cdot 10^{-4}$		129.89	$2.64 \cdot 10^{-4}$
	100.00	$1.83 \cdot 10^{-3}$	CH <sub>2</sub> OTs	70.00 <sup>c)</sup>	$1.68 \cdot 10^{-6}$	Br	70.00 <sup>c)</sup>	$4.84 \cdot 10^{-8}$
CH <sub>2</sub> OAc	70.00 <sup>c)</sup>	$6.04 \cdot 10^{-6}$		109.91	$9.90 \cdot 10^{-5}$		124.97	$1.21 \cdot 10^{-5}$
	99.98	$1.36 \cdot 10^{-4}$		119.97	$2.41 \cdot 10^{-4}$		129.81	$1.85 \cdot 10^{-5}$
	109.78	$3.39 \cdot 10^{-4}$		130.04	$5.71 \cdot 10^{-4}$		135.04	$2.84 \cdot 10^{-5}$
	119.89	$8.30 \cdot 10^{-4}$						

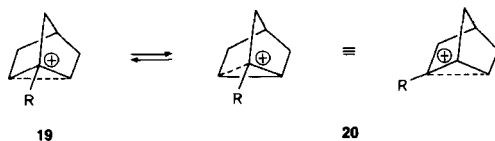
a) Average of at least two independent measurements; mean deviation  $\pm 1.15\%$ .

b) [gl].

c) Extrapolated.

reported in [10]. First-order rate constants were measured conductometrically in 80% EtOH at three temperatures (Tables 1 and 2). Rate constants at 70° and *exo/endo*-rate ratios are summarized in Table 3. Table 4 lists the yields of the main hydrolysis products obtained from **7** and **8** after reaction for ten half lives in 70% dioxane. Yields were determined by capillary gas chromatography and by comparison with authentic samples.

**Results and Discussion.** - Hydrolysis of **7** and **8** (Table 4) yielded more rearranged tertiary alcohols **14** than unrearranged secondary alcohols **12**, except when R = COCH<sub>3</sub>, COOCH<sub>3</sub>, and CN. In these cases, unrearranged alcohols **12** and olefins **13** were obtained almost exclusively. When R = CH<sub>3</sub> and OAc, rearrangement was practically quantitative and surprisingly high even for R = Br. On the other hand, it is well known that the substituents RO and Br stabilize an adjacent cationic center, such as C(2) in the cation **11** by their +M effect. As expected, the tertiary alcohols **14** (R = OAc and Br) were unstable and were converted to norbornan-2-one **17**. Strong -I substituents, namely Br, COCH<sub>3</sub>, COOCH<sub>3</sub>, CN and, to a lesser degree H, led to considerable amounts of the corresponding nortricyclanes **18** by elimination. While both the secondary and tertiary cations **19** and **20** are potential precursors of **18**, the secondary cations **19** appear more likely, because the yields of **18** are highest from **7** and **8** (R = COCH<sub>3</sub> and COOCH<sub>3</sub>) which afford very little or no rearranged products (Table 4).



The formation of secondary and tertiary alcohols **12** and **14** from **7** and **8**, respectively, implicates either the bridged secondary and tertiary cations **19** and **20**<sup>5)</sup>, respectively, or the nonclassical cations **10** as intermediates. However, since the yield of products obtained from pairs of epimeric tosylates **7** and **8** are widely different, a single intermediate **10** is unlikely. In addition, 1-substituted cations **10** would not be symmetri-

<sup>5)</sup> The  $\rho_1$  values for the formation of the tertiary 2-methyl-2-norbornyl cations **11** (R = CH<sub>3</sub>) indicate bridging of C(2) by C(6) [11].

Table 3. Rate Constants for **7** (*exo*) and **8** (*endo*) and *exo/endo* Rate Ratios at 70°

R	$k_{exo}$	$k_{endo}$	$k_{exo}/k_{endo}$	R	$k_{exo}$	$k_{endo}$	$k_{exo}/k_{endo}$
H	$2.62 \cdot 10^{-2}$	$8.42 \cdot 10^{-5}$	311	CH <sub>2</sub> OTs	$1.83 \cdot 10^{-3}$	$1.68 \cdot 10^{-6}$	1089
CH <sub>3</sub>	$4.13 \cdot 10^{-1}$	$1.01 \cdot 10^{-4}$	4089	Br	$3.80 \cdot 10^{-6}$	$4.84 \cdot 10^{-8}$	79
CH <sub>2</sub> OAc	$1.15 \cdot 10^{-2}$	$6.04 \cdot 10^{-6}$	1904	COOCH <sub>3</sub>	$4.39 \cdot 10^{-5}$	$8.91 \cdot 10^{-7}$	49 <sup>a)</sup>
CH <sub>2</sub> Cl	$7.38 \cdot 10^{-3}$	$3.91 \cdot 10^{-6}$	1887	CN	$5.84 \cdot 10^{-8}$	$1.44 \cdot 10^{-8b)}$	4 <sup>c)</sup>

<sup>a)</sup> Lenoir [9] observed a ratio of 25 in 60% EtOH at 24°.

<sup>b)</sup> Calculated from the plot in Fig. 2.

<sup>c)</sup> Lenoir [9] obtained a ratio of 3 in 60% EtOH at 100°.

cally bridged due to their overall asymmetry. The intermediates are, therefore, better described as pairs of rapidly interconverting asymmetrically bridged cations **19** and **20**. Formula **10**, then, better represents the transition state for their interconversion.

The plots of  $\log k$  vs.  $\sigma_1^+$  for the tosylates **7** and **8** (Figs. 1 and 2) provide further mechanistic information. The satisfactory linear regression ( $r = 0.995$ ) for the *endo*-tosylates **8** (Fig. 1) reveals that ionization is again controlled only by the *I* effect of the substituents at C(1), as in the case of the 4-, 5-, 6-, and 7-substituted 2-*endo*-norbornyl tosylates [1a–e]. The  $\rho_1$  of  $-1.24$  is considerably larger than the other  $\rho_1$  values given in the Formula 4, presumably because in **8** the substituents are nearer to the reaction center. On the other hand,  $\rho_1$  for the series **8** is significantly smaller than the  $\rho_1$  value of  $-1.54$  for the 2-substituted bicyclo[2.2.2]octane series **9** [5]. A possible reason for this difference is that dorsal solvation of the cationic center in the transition state for **8**, which is not possible in the t.s. for **9**, disperses some of the charge and thereby lowers  $\rho_1$ . Also, the geometry of the *endo*-tosylates **8** precludes concerted ionization and migration of C(6) in the transition state. Therefore, interconversion of the first-formed secondary cation **19** and the tertiary cation **20** must occur in a subsequent step.

In contrast to the *endo*-tosylates **8**, the *exo*-tosylates **7** do not fit a common regression line (Fig. 2). It is striking, however, that the points for the tosylates that yield rearranged products, including **7** (R = COCH<sub>3</sub>)<sup>6)</sup>, correlate linearly with a  $\rho_1$  of  $-1.90$  ( $r = 0.998$ ). On the other hand, the tosylates that do not yield rearranged products, namely **7** (R = COOCH<sub>3</sub> and CN), react 9 and 17 times, respectively, more slowly than expected on the basis of the regression line in Fig. 2.

Table 4. Yields of Products (in %,  $\pm 2\%$ ) from the Reactions of 1-*R*-2-*exo*- (**7**) and (in brackets) 1-*R*-2-*endo*-Norbornyl Tosylates **8** in 70% (v/v) Dioxane (t = traces)

R	<b>12</b>	<b>13</b>	<b>14</b>	<b>18</b>	R	<b>12</b>	<b>13</b>	<b>14</b>	<b>18</b>
H <sup>a)</sup>	94 (93) <sup>b)</sup>		<sup>b)</sup>	7 (7)	OAc	– (–)		96 <sup>d)</sup>	
CH <sub>3</sub>	– (7)		96 (86) <sup>c)</sup>		COCH <sub>3</sub>	53 (–)	3	2 (–)	42
CH <sub>2</sub> OAc	t (19)		80 (64)	t (5)	COOCH <sub>3</sub> <sup>e)</sup>	52 (53)	9 (3)		40 (54)
CH <sub>2</sub> Cl	15 (29)		65 (34)		CN	26	51		23
Br	4 (41)		74 (49) <sup>d)</sup>	20 (3)					

<sup>a)</sup> See [1a].

<sup>b)</sup> In this case, **12** and **14** are identical.

<sup>c)</sup> Beside 2% of **15** and 2% of **16**.

<sup>d)</sup> Isolated as norbornan-1-one.

<sup>e)</sup> Lenoir [9] reported a higher yield of **12** but no **14** in 60% acetone.

<sup>6)</sup> Carbenium ions are stabilized by  $\alpha$ -carbonyl groups of ketones, see [14].

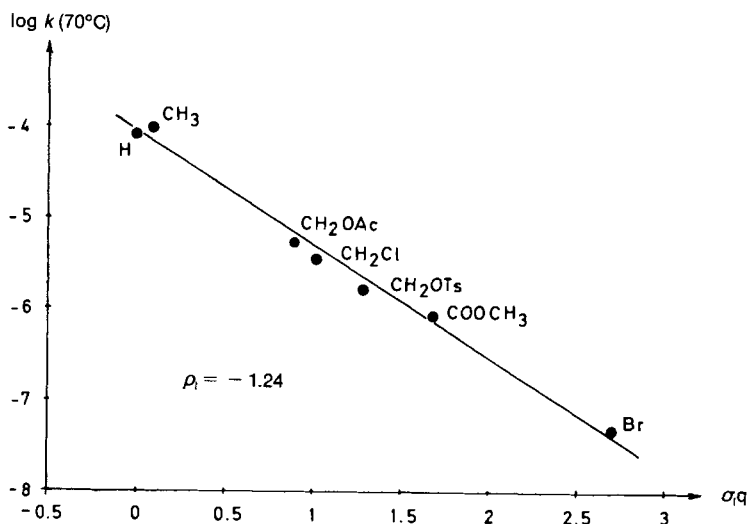


Fig. 1. Plot of  $\log k$  for  $10^{-3}$  M solutions of 1-substituted 2-endo-norbornyl tosylates **8** in 80% (v/v) EtOH vs. inductive substituent constants  $\sigma_I^q$

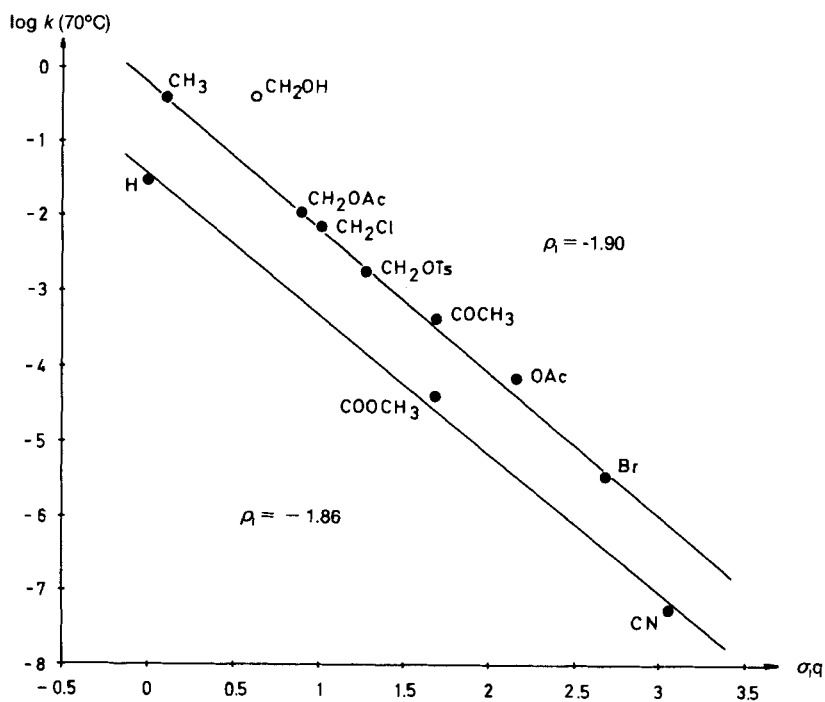
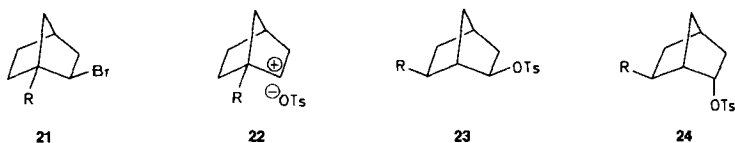


Fig. 2. Plots of  $\log k$  for  $10^{-3}$  M solutions of 1-substituted 2-exo-norbornyl tosylates **7** in 80% (v/v) EtOH vs. inductive substituent constants  $\sigma_I^q$

It is of special interest that the parent tosylate **7** ( $R = H$ ) also reacts more slowly, namely by a factor of 21. Furthermore, the points for  $R = H$ ,  $\text{COOCH}_3$ , and  $\text{CN}$  define the second lower line in *Fig. 2* ( $r = 0.998$ ) with a  $\rho_1$  of  $-1.86$  (see number in brackets in **3**). Assuming that these correlations are not fortuitous, it can be concluded that the transition state for the *exo*-tosylates **7** vary with the substituents and more closely resemble either one or other of the intermediates **19** or **20** according to the extent to which the C(1)–C(6) bond is loosened. The first group of seven tosylates (*Fig. 2*) then ionizes with rearrangement to tertiary cations **20**, as previously suggested in some cases [6] [8] [9], whereas the second group of three tosylates ionizes to secondary cations **19**. The fact that the first group also yields variable amounts of unrearranged products (*Table 4*) indicates that the cations **19** and **20** interconvert rapidly prior to nucleophilic solvent attack.

The above findings contrast with *Lenoir's* claim that  $\log k$  for 1-substituted 2-*exo*-norbornyl bromides **21** ( $R = H$ ,  $\text{COOCH}_3$ , and  $\text{CN}$ )<sup>7)</sup> do not correlate linearly with *Taft's*  $\sigma^*$  values and that the rate of the parent tosylate is accelerated by a factor of *ca.*  $10^2$  [9]. Actually, it is the inclusion of the point for  $\text{CH}_2\text{OH}$  which causes this discrepancy. Like other electrofugal substituents (*e.g.*  $\text{COO}^-$ ,  $\text{CONH}_2$ )  $\text{CH}_2\text{OH}$  exerts an exalted *I* effect in reactions *via* carbocations [12]. As shown in *Fig. 2*, the point for  $\text{CH}_2\text{OH}$  corresponds to an acceleration by a factor of *ca.* 10.



The  $\rho_1$  values of  $-1.90$  and  $-1.86$  for the two groups of tosylates **7** in *Fig. 2* are almost the same, considering the accuracy of the method. They indicate that the positive charge generated in the cations **19** and **20** is similarly dispersed to C(1) and C(6). The slightly higher  $\rho_1$  of  $-2.00$  for 6-substituted 2-*exo*-norbornyl tosylates **23** confirms the dominant role of C(6) in dispersing positive charge, a conclusion previously questioned by *Brown* [13]. It also supports the conclusion that in carbenium ions, induction involves graded bridging of neighboring C-atoms [1] [3]. On the other hand, the low  $\rho_1$  of  $-1.24$  for the *endo*-series **8** confirms the absence of significant C(2)–C(6) bridging in the transition state for *endo*-ionization to the ion pairs **22**.

Rate ratios for epimeric tosylates, *i.e.*  $k_{\text{exo}}/k_{\text{endo}}$ , are often useful guides to bridging [1g]. Thus, for the parent tosylates **1** and **2** the ratio is 311, and for the 6-*exo*-methyl derivatives **23** and **24** ( $R = \text{CH}_3$ ), it is 181 [1a]. In contrast,  $k_{\text{exo}}/k_{\text{endo}}$  for the 1-methyl derivatives **7** and **8** ( $R = \text{CH}_3$ ) is 4098 (*Table 3*). However, the relatively small rate increase by a factor of 16 caused by the introduction of a Me group at C(1) of the parent tosylate **7** ( $R = H$ , *Table 3*) shows that rearrangement to the tertiary cation **20** is not far advanced in the transition state, as noted by *Wilt* and *Wagner* [8]. As the substituents at C(1) become more electron attracting, and the tendency to rearrange is reduced,  $k_{\text{exo}}/k_{\text{endo}}$  drops to 49 for  $R = \text{COOCH}_3$  and to 4 for  $R = \text{CN}$  (*Table 3*).

These results again raise the question, whether the solvolytically generated norbornyl cation is better represented by the asymmetrically bridged structure **19** ( $R = H$ ) or by the 'nonclassical' symmetrically bridged structure **10** proposed by *Winstein* and *Trifan* [15]

<sup>7)</sup> In 20% EtOH at 25°.

and endorsed by Lenoir [9] and many other authors<sup>8)</sup>. The main argument presented for the former view was that  $\log k$  for substituted norbornyl tosylates, including the parent tosylates **1** and **2**, fit one and the same regression line when plotted vs. the corresponding inductive constants [1] [3]. Since the substituted cations are necessarily asymmetric<sup>9)</sup> and presumably less strained than **10**, there is no apparent reason why the parent 2-norbornyl cation should be an exception. However, only in this case is the ensuing rearrangement **5a**  $\rightleftharpoons$  **5b** degenerate and hence extremely rapid<sup>10)</sup>, in contrast to norbornyl cations with strongly electron-attracting substituents [1b].

The 1-substituted 2-*exo*-norbornyl tosylates **7** are the first series which fail to fit a common linear regression, and where two mechanistic types are discernible. Moreover, the fact that the tosylates **7** (R = H, COOCH<sub>3</sub>, and CN) apparently belong to the same type lends further support to the view that the parent norbornyl cation is asymmetrically bridged. It should be stressed, however, that this does not necessarily apply to the long-lived cation at low temperature and in non-nucleophilic media, as studied by Olah *et al.* [18], notwithstanding the recent crystal-structure analysis of Laube [19] according to which the asymmetric tertiary 1,2,4,7-*anti*-tetramethyl-2-norbornyl cation is asymmetrically bridged.

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<sup>8)</sup> For recent reviews, see [16].

<sup>9)</sup> With the exception of 4-substituted norbornyl cations [1e].

<sup>10)</sup> The automerization **5a**  $\rightleftharpoons$  **5b** has been likened to a skeletal vibration [1a] [3] or, more recently, to a thermal motion [17].