195. Carbon Participation in the Solvolysis of 6- and 7-Substituted 2-Norbornyl *p*-Toluenesulfonates

Norbornanes, Part 11

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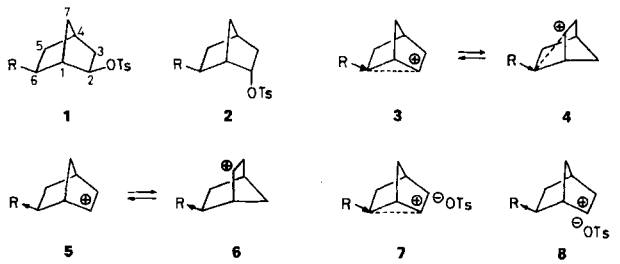
Summary

The solvolysis rates and products of several 7-*anti*-substituted 2-*endo*-norbornyl *p*-toluenesulfonates **11** have been determined and compared with those of the previously reported 6-*exo*-substituted 2-*exo*-norbornyl *p*-toluenesulfonates **1**. Although the number of bonds between the substituent and the reaction site is the same in the two series, the inductive effect of the substituents is transmitted far more strongly in the 6-*exo*-2-*exo*-series **1** than in the 7-*anti*-2-*endo*-series **11**; *i.e.* their inductivities differ widely. It is concluded that through space induction involves graded bridging of the substituent-bearing C-atom to the incipient cationic center at C(2) and that this involves differential bridging strain. The different reactivities of unsubstituted 2-*exo*- and 2-*endo*-norbornyl derivatives can then be ascribed to a stereoelectronic effect.

1. Introduction. – Recent studies of the solvolysis rates and products of 6-*exo*-substituted 2-*exo*- and 2-*endo*-norbornyl *p*-toluenesulfonates[1]) **1** and **2**, respectively, [1] have shown that the intermediate cations are bridged, as in **3**, when the substituent is an electron donor – relative to the cationic center at C(2) – and unbridged, as in **5**, when it is an electron acceptor[2]).

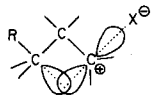


[1]) Referred to as tosylates.

[2]) For a review of this work see [2].

This follows from the observed changes of the rate constants as well as the 2-*exo*/2-*endo* rate ratios and the products with the substituent R. In conjunction with other evidence [3] these results eliminated steric hindrance to *endo*-ionization as an explanation for high 2-*exo*/2-*endo* rate ratios [4]. Furthermore, hydrolysis of **1** and **2** yielded 2-*exo*-norbornanols only when R was a donor substituent, a sign that nucleophilic solvents attack the cation **3** from the unbridged *exo*-side only. On the other hand 2-*exo*- and 2-*endo*-norbornanols were obtained when R was an acceptor, indicating that unbridged cations **5** are attacked from both sides of C(2) [1] [5]. Finally, reversible *Wagner-Meerwein* rearrangements of the cations **3** and **4** were fast relative to their capture by solvent when R was a donor, but slow when R was an acceptor, as in **5** and **6** [6], a sign that bridging and rearrangement are related.

It was proposed recently[3]) that the reaction constant ρ_I in the *Hammett-Taft* equation $\log k/k_0 = \rho_I \sigma_I^q$ is a measure of C-bridging in the transition state leading to the formation of carbocations. The ρ_I-values for **1** and **2** were -2.0 and -0.78, respectively, revealing a much higher inductivity (*i.e.* sensitivity of rate to the *I* effect of the substituents[4])) in the 6-*exo*-2-*exo*-series **1** compared to the 6-*exo*-2-*endo*-series **2** [1]. Assuming that induction can be roughly separated into a through-bond and a through-space component and that the latter involves graded bridging [2], these ρ_I-values confirm that bridging is strong in the transition state leading to the *exo*-ion pair **7** and weak or negligible in the transition state leading to the *endo*-ion pair **8**. It was, therefore, concluded that in the latter case bridging of C(2) by C(6) is hindered by the departing *endo*-tosylate ion.



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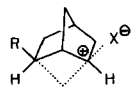

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It was also pointed out recently that bridging resembles ordinary bonding in that it is subject to stereoelectronic constraints, notably steric strain [2] [9]. For bridging to be effective, the back lobe of an orbital of the bridging C-atom should overlap with the p-orbital of the incipient cationic center, as illustrated in **9**; this in turn implies that the respective orbital axes (represented in **9** by dotted lines) should intersect at an angle of at least 90°. This is the case in the ion pair **10** derived from the 2-*exo*-tosylate **1**, but not in other bicyclic cations which, therefore, exhibit larger bridging strains [2] [9].

Support for this hypothesis comes from the following study of the rates and products of the 7-*anti*-substituted 2-*endo*- and 2-*exo*-norbornyl tosylates **11** and **12** (**a**–**h**), respectively. While the number of intervening bonds and the direct distances between R and C(2) are the same in all four compounds **1**, **2**, **11** and **12** the strains which accompany bridging of C(2) with C(6) and C(7), respectively,

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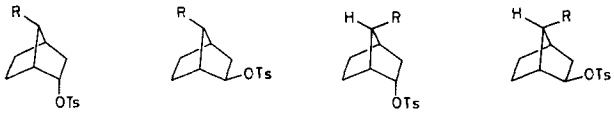
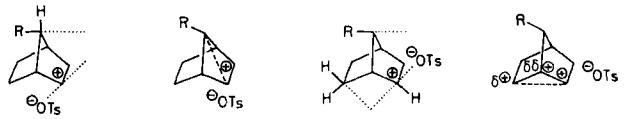
[3]) *Cf.* [7] and earlier papers in the series 'Polar Effects'.

[4]) This term was introduced recently [8] to designate the intensity with which the *I*-effect is transmitted to a reaction center.



11 **12** **13** **14**

a R = H **b** R = CH_3 **c** R = CH_2OAc **d** R = CH_2Br **e** R = $COOCH_3$ **f** R = Cl **g** R = Br **h** R = CN



15 **16** **17** **18**

are clearly different[5]). Thus, in the ion pairs **15** derived from the *endo*-tosylates **11** the orbital axes of C(2) and C(7) do not intersect. Hence, overlap will be poor. Expressed in other terms: bridging, as illustrated in **16**, subdivides a five-membered ring into three- and four-membered rings and, therefore, generates considerable strain. Furthermore, conversion of the tetrahedral configuration at C(7) to the trigonal bipyramidal arrangement preferred by pentacoordinate atoms [10] will tend to increase bridging strain because the rigid C(1)–C(7)–C(4) angle in norbornanes of 94° [11] resists widening to 120°.

In the ion pairs **17** derived from the *exo*-tosylates **12** overlap of the relevant orbitals at C(7) and C(2) is hindered by the departing anion, but also for the reasons stated above. On the other hand strong bridging is expected to occur between C(2) and the unsubstituted C(6), as shown in **18**. It was, therefore, of interest to test these hypotheses by determining the rates and products of the solvolysis of **11** and **12** and, especially, the reaction constants ρ_I for these series of compounds.

2. Results. – The syntheses of the tosylates **11** and **12** (**b**–**h**) and the solvolysis products obtained in 70:30 (*w/w*) dioxane/water (summarized in *Table 4*) have been reported [12]. The rate constants were measured in ethanol/water 80:20 (*v/v*) by the conductometric method and are listed in *Tables 1* and *2*. Included are the rate constants for the 7-*syn*-chloro-2-*endo* and 2-*exo*-norbornyl tosylates **13f** and **14f** and the corresponding bromides **13g** and **14g**, respectively *(Table 3)*. The former compounds had already been studied by *Gassman & Hornback* [13]; they were included in the present investigation to determine the directional effect of substituents at C(7) on inductivity.

3. Discussion. – The same types of product were obtained from the *endo*- and *exo*-tosylates **11** and **12**, respectively, albeit in different yields *(Table 4)*. The main products were the 7-*anti*-substituted-2-*exo*-norbornanols **19** which are formed from **11** with inversion and from **12** with retention of configuration[6]). This result

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[5]) This can be shown with plastic framework models *(Prentice Hall)* using trigonal bipyramidal metal clusters to indicate the orientation of the orbitals at C(2), C(6) and C(7).

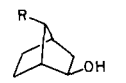
[6]) It was shown in [14] that solvolysis of 2-norbornane derivatives does not involve appreciable nucleophilic solvent participation.

Table 1. *First-Order Rate Constants for 10^{-3} M 7-anti-Substituted 2-endo-Norbornyl p-Toluenesulfonates* **11** *in 80 Vol.-% Ethanol with 1.1 Equiv. of Triethylamine*

11	R	T [°]	k [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol degree]
a	H	70.00	$8.42 \cdot 10^{-5}$ a)	23.84	−7.98
b	CH_3	70.00	$1.04 \cdot 10^{-4}$ b)	23.66	−8.10
		79.87	$2.84 \cdot 10^{-4}$		
		90.01	$7.40 \cdot 10^{-4}$		
		99.29	$1.73 \cdot 10^{-3}$		
c	CH_2OCOCH_3	70.00	$1.20 \cdot 10^{-5}$ b)	24.20	−10.82
		89.69	$8.66 \cdot 10^{-5}$		
		98.89	$2.08 \cdot 10^{-4}$		
		109.05	$4.99 \cdot 10^{-4}$		
d	CH_2Br	70.00	$8.07 \cdot 10^{-6}$ b)	24.79	−9.86
		99.44	$1.55 \cdot 10^{-4}$		
		109.62	$3.87 \cdot 10^{-4}$		
		119.73	$9.22 \cdot 10^{-4}$		
e	$COOCH_3$	70.00	$2.77 \cdot 10^{-6}$ b)	25.62	−9.58
		99.47	$5.87 \cdot 10^{-5}$		
		109.58	$1.50 \cdot 10^{-4}$		
		119.57	$3.63 \cdot 10^{-4}$		
f	Cl	70.00	$1.64 \cdot 10^{-6}$ b)	24.03	−15.27
		109.61	$7.01 \cdot 10^{-5}$		
		119.68	$1.62 \cdot 10^{-4}$		
		130.13	$3.69 \cdot 10^{-4}$		
g	Br	70.00	$1.45 \cdot 10^{-6}$ b)	25.06	−12.50
		109.52	$7.20 \cdot 10^{-5}$		
		119.65	$1.73 \cdot 10^{-4}$		
		129.70	$3.94 \cdot 10^{-4}$		
h	CN	70.00	$3.65 \cdot 10^{-7}$ b)	25.15	−14.99
		109.52	$1.84 \cdot 10^{-5}$		
		119.57	$4.38 \cdot 10^{-5}$		
		129.88	$1.03 \cdot 10^{-4}$		

a) *Cf.* [1]. b) Extrapolated.

alone indicates that C(7)–C(2)-bridging must be negligible in the ion pair **15** from **11** and that C(6)–C(2)-bridging is strong in the ion pair **18** from **12**. Small amounts of 7-*syn*-substituted 2-*exo*-norbornanols **20** were also obtained. These alcohols are derived from the cations **25** which are in turn formed by C(6)–C(2) hydride shifts from the original ion pairs **15** and **17**.



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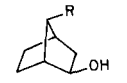

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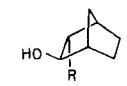

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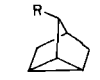

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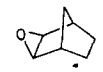

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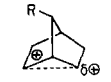

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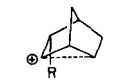

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Table 2. *First-Order Rate Constants for 10^{-3} M 7-anti-Substituted 2-exo-Norbornyl p-Toluenesulfonates* **12** *in 80 Vol.-% Ethanol with 1.1 Equiv. of Triethylamine*

12	R	T [°]	k [s^{-1}]	$H^{\neq}$ (kcal/mol]	$S^{\neq}$ [cal/mol degree]
a	H	70.00	$3.58 \cdot 10^{-2}$ a)	22.04	−1.20
b	CH_3	70.00	$3.68 \cdot 10^{-2}$ b)	21.08	−3.94
		30.05	$5.51 \cdot 10^{-4}$		
		40.04	$1.84 \cdot 10^{-3}$		
		50.06	$5.12 \cdot 10^{-3}$		
c	CH_2OCOCH_3	70.00	$3.34 \cdot 10^{-3}$ b)	21.92	−6.28
		49.55	$4.08 \cdot 10^{-4}$		
		59.72	$1.21 \cdot 10^{-3}$		
		69.95	$3.31 \cdot 10^{-3}$		
d	CH_2Br	70.00	$2.01 \cdot 10^{-3}$ b)	20.65	−10.98
		64.93	$1.26 \cdot 10^{-3}$		
		75.08	$3.19 \cdot 10^{-3}$		
		85.15	$7.54 \cdot 10^{-3}$		
e	$COOCH_3$	70.00	$9.52 \cdot 10^{-4}$ b)	21.94	−8.71
		49.55	$1.16 \cdot 10^{-4}$		
		59.76	$3.46 \cdot 10^{-4}$		
		69.94	$9.44 \cdot 10^{-4}$		
f	Cl	70.00	$1.57 \cdot 10^{-4}$ b)	22.83	−9.70
		90.17	$1.06 \cdot 10^{-3}$		
		99.75	$2.49 \cdot 10^{-3}$		
		109.80	$5.65 \cdot 10^{-3}$		
g	Br	70.00	$1.43 \cdot 10^{-4}$	21.37	−14.15
		89.86	$8.34 \cdot 10^{-4}$		
		99.40	$1.86 \cdot 10^{-3}$		
		109.48	$4.01 \cdot 10^{-3}$		
h	CN	70.00	$2.42 \cdot 10^{-5}$	23.02	−12.84
		99.40	$3.78 \cdot 10^{-4}$		
		109.48	$8.72 \cdot 10^{-4}$		
		119.84	$2.01 \cdot 10^{-3}$		

a) *Cf.* [1]. b) Extrapolated.

Considerable amounts of the rearranged 3-*endo*-substituted 2-*exo*-norbornanols **21** were detected when R was an electron donor such as alkyl or a weak acceptor (CH_2OAc, CH_2Br, $COOCH_3$), not, however, when R was a stronger acceptor (Cl, Br, CN). The alcohols **21** are probably formed from the cations **26** which are related to the cations **18** and **25** by way of *Wagner-Meerwein* rearrangements. The formation of nortricyclanes **22** by 1,3-elimination and of small amounts of the lactone **23** by cyclization when R = $COOCH_3$ and CN is not unusual for reactions *via* 2-norbornyl cations [1] [2]. The precursors of small amounts of the epoxide **24** from **11** and **12** (**f** and **g**) are probably the *trans*-halohydrins **21**, R = Cl and Br.

Although the number of intervening bonds and the direct distances between R and C(2) are the same in the series **11** and **1**, the rates change far less with the *I* effect of R in the former case. This is strikingly demonstrated by the corresponding reaction constants of −0.72 and −2.0 [1], which were derived from the plots of

Table 3. *First-Order Rate Constants for* 10^{-3}M 7-syn-*Chloro- and* 7-syn-*Bromo-2*-endo- *and* -2-exo-*norbornyl* p-*Toluenesulfonates* **13** *and* **14** *in 80 Vol.-% Ethanol*[a])[b])

Tosylate	T [°]	k [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol degree]
13f	70.00	$6.88 \cdot 10^{-7}$[c])	24.34	−16.07
	110.18	$3.22 \cdot 10^{-5}$		
	120.29	$7.76 \cdot 10^{-5}$		
	130.32	$1.67 \cdot 10^{-4}$		
14f	70.00	$1.63 \cdot 10^{-4}$[c])	22.80	−9.70
	70.11	$1.64 \cdot 10^{-4}$		
	80.18	$4.47 \cdot 10^{-4}$		
	90.36	$1.12 \cdot 10^{-3}$		
13g	70.00	$6.61 \cdot 10^{-7}$[c])	24.48	−15.75
	110.18	$3.19 \cdot 10^{-5}$		
	120.29	$7.41 \cdot 10^{-5}$		
	130.32	$1.67 \cdot 10^{-4}$		
14g	70.00	$2.09 \cdot 10^{-4}$[c])	22.70	−9.49
	70.07	$2.09 \cdot 10^{-4}$		
	80.18	$5.72 \cdot 10^{-4}$		
	90.36	$1.42 \cdot 10^{-3}$		

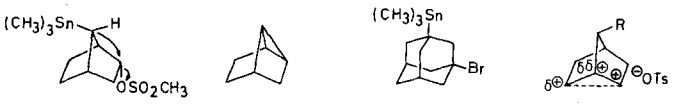
[a]) In the presence of 1.1 equiv. of triethylamine. [b]) Prepared as described by *Gassman & Hornback* [13]. [c]) Extrapolated.

Table 4. *Yield of Products* (%) *from the Reaction of* 7-anti-*Substituted* 2-endo-(**11**) *and* (in brackets) *of* 2-exo-*Norbornyl* p-*Toluenesulfonates* (**12**) *in 70 Vol.-% Dioxane*[a])

11 (**12**)	R	**19**	**20**	**21**	**22**	**23**	**24**
a	H	93 (94)	[b])	[b])	7 (5.5)		
b	CH_3	51 (31)	2 (2)	42 (35)	2 (20)		
c	CH_2OAc	48 (67)	5 (6)	14 (18)	28 (9)		
d	CH_2Br	69 (56)	6 (8)	9 (14)	15 (18)		
e	$COOCH_3$	65 (60)	5 (8)	5 (10)	20 (14)	1 (1)	
f	Cl	80 (64)	8 (9)	-	1 (20)	-	7 (2)
g	Br	82 (64)	9 (9)	-	1 (3)	-	3 (14)
h	CN	71 (58)	2 (1)		23 (25)	3 (7)	

[a]) Containing 1.1 equiv. of triethylamine. [b]) When R = H the norbornanols **19**, **20** and **21** are identical and are formed *via* hydride shifts and *Wagner-Meerwein* rearrangements [1] [2].

$\log k$ *vs.*$p\bar{f}$ [15] in the *Figure*. Inductivity in the transition state is, therefore, much smaller in the series **11** than in the series **1**. Assuming that transmission of the I effect through space involves graded bridging by a β-C-atom at the rear of the C(2)–OTs-bond, it follows that electron mobility is much smaller between C(7) and C(2) than between C(6) and C(2). A plausible explanation for this difference is that C(7)–C(2)-bridging, as in **16**, generates far more strain than does C(6)–C(2)-bridging, as in **7**. In fact, the exclusive formation of the inverted 2-*exo*-alcohols **19** from **11** indicates that the product-forming intermediates are unbridged. The residual low inductivity must then be ascribed to through-bond induction.



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Nevertheless, bridging between C(7) and C(2) can become prominent if the 7-*anti*-substituent is a highly electrofugal group and therefore a powerful electron donor, such as trimethyltin. In fact *Davis & Johnson* have reported that the methylsulfonate **27** of 7-*anti*-(2-*endo*-hydroxynorbornyl)trimethyltin undergoes accelerated acetolysis to tricyclo[3.2.0.0^{2,7}]heptane **28** and trimethyltin acetate [16]. These results show that ionization is assisted by bridging of C(7), as illustrated in **27**, but they do not show whether this fragmentation[7]) is a concerted or a two-step process *via* a bridged cation[8]). An exalted *I* effect of a β-trimethyltin group was observed recently in the solvolysis of the 1-bromoadamantane **29** which reacted 26 times faster (in 80% ethanol at 70°) than anticipated on the basis of the inductive constant σ_I^q (−0.26) for this substituent [17]. But in this case the presumably 1,3-bridged cation failed to cyclize due to the excessive strain involved.

Table 5. *Relative Rates of 6- and 7-Substituted 2-Norbornyl* p-*Toluenesulfonates in 80 Vol.-% Ethanol at 70.0°*

R	k_{13}/k_{11}[a])	k_{14}/k_{12}[b])	k_{12}/k_{11}[c])	k_{14}/k_{13}[d])	k_1/k_{11}[e])	k_1/k_2[f])	k_{11}/k_2[g])
H			425		425	425	1
CH_3			354		105	181	1.73
CH_2OAc			278		16	24	1.48
CH_2Br			249		13	16	1.2
$COOCH_3$			344		2.3	2	1.6
Cl	2.4	1.04	96	237	–	–	–
Br	2.2	1.46	99	316	0.10	0.37	3.6
CN			66		0.34	0.88	2.6

a) *Tables 1* and *3*.
b) *Tables 2* and *3*.
c) *Tables 1* and *2*.
d) *Table 3*.
e) *Table 2* and [1].
f) [1]. The rate constants for **1** and **2** (R = CH_2OAc) at 70.0° are $1.96 \cdot 10^{-4}$ and $8.09 \cdot 10^{-6}$ (s^{-1}), respectively.
g) *Table 1*, [1] and f).

The conclusion that through-bond induction *via* C(1) dominates in the 7-*anti*-series **11** is supported by a comparison of the rates of the 7-*anti*-chloro and bromo derivatives **11f** and **11g** with the corresponding 7-*syn*-halogen derivatives **13f** and **13g**, respectively. As shown by the small k_{13}/k_{11} ratios of 2.4 and 2.2 *(Table 5)*, the rates are indeed almost the same.

The reaction constant ρ_I of −0.97 for the 7-*anti*-2-*exo*-norbornyl tosylates **12** is considerably larger than that for the *endo*-tosylates **11** (−0.72) but much smaller

7) This type of fragmentation which generates a cyclopropane ring was termed homofragmentation [1].
8) Extremely facile homofragmentation to nortricyclane **22**, R = H, accounts for the failure to isolate the 6-*exo*-trimethyltin derivative of 2-*exo*-norbornyl tosylate **1**, R = $(CH_3)_3Sn$, in this laboratory.

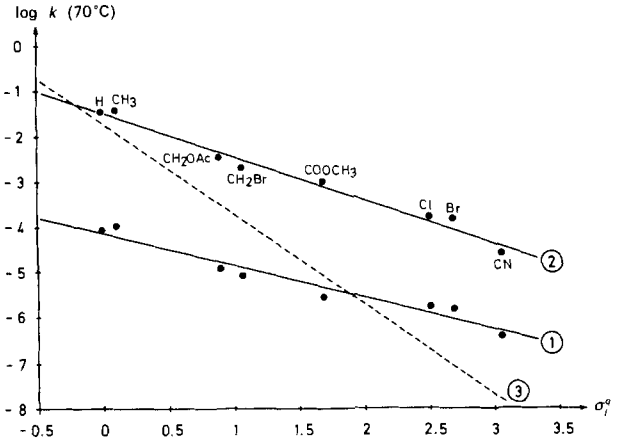

Figure. *Plot of* log k *for* 7-anti-*substituted* 2-endo- *and* 2-exo-*norbornyl* p-*toluenesulfonates* **11** (line 1) *and* **12** (line 2), *respectively, against* σ_I°-*values* (Broken line 3: 6-*exo*-2-*exo*-norbornyl series **1** [1])

than that for the 6-*exo*-2-*exo*-isomers **1** (−2.0) *(Figure)*. This indicates that C(6)–C(2)-bridging occurs in the incipient ion pair **18** from **12**. But not being directly attached to C(6), the 7-*anti*-substituents have less effect on rates, as the lower ρ_I-value shows. Bridging in the intermediate cations **18** is confirmed by the exclusive formation of the 2-*exo*-norbornanols **19** with retention of configuration. Bridging transfers part of the positive charge to C(6) which, like C(2), withdraws electron density from C(1). This deshielding of C(1) should increase its through-bond interaction with the substituents at C(7), thereby raising the ρ_I-value for the series **12** relative to that of **11**.

This assumption is confirmed by a comparison of the 7-*syn*- and 7-*anti*-chloro- and bromo derivatives **12** (**f** and **g**) and **14** (**f** and **g**), respectively. The small rate ratios k_{14}/k_{12} of 1.04 and 1.46 for **f** and **g**, respectively, *(Table 5)* again point to substituent effects that are transmitted entirely *via* the equidistant C(1) and would not be expected if C(7)–C(2)-bridging were important[9]). Furthermore, the 2-*exo*/2-*endo* rate ratios k_{12}/k_{11} and k_{14}/k_{13} are high in spite of the strong *I* effects of the halogen atoms at C(7) *(Table 5)*. This supports the conclusion that the 2-*exo*-tosylates **12** and **14** (**f** and **g**) benefit from bridging of C(6), whereas the 2-*endo*-epimers **11** and **13** (**f** and **g**) receive no such assistance.

It is also noteworthy that the *exo*/*endo* rate ratios, *i.e.* k_1/k_2 and k_1/k_{11}, decrease from 425 for R=H to well below unity as the electron-withdrawing power of the substituent at C(6) and C(7), respectively, increases *(Table 5)*. This constitutes further proof that *exo*/*endo* rate ratios are determined by the polar effect of substituents (including hydrogen) rather than by steric *endo*-hindrance of the norbornane structure, as argued by *Brown* [4]. On the other hand k_{11}/k_2-ratios

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[9]) In their careful study of the acetolysis rates and products of the four epimeric 7-chloro-2-norbornyl tosylates **11f**–**14f** *Gassman & Hornback* [13] come to a somewhat different conclusion, namely that C(1)–C(6) σ-bond participation is not important.

differ little from unity which confirms that substituents at C(7) and C(6) exert almost equal through-bond *I* effects in the ionization of 2-*endo*-tosylates.

In conclusion[10]), a comparison of the influence of substituents at C(6) and C(7) on the rates and products of 2-*exo*- and 2-*endo*-norbornyl tosylates indicates that the reactivity of 2-*exo*-tosylates is dominated by through-space induction, whereas the reactivity of corresponding 2-*endo*-tosylates is controlled by a much weaker through bond interaction. Assuming that through-space induction involves bridging, *exo/endo* rate ratios are determined by differential bridging strain, which is essentially a stereoelectronic effect and, hence, includes polar and steric factors. Confirmation of this hypothesis should help to reconcile the opposing views [4] [18], that either polar or steric effects are responsible for the different behavior of *exo*- and *endo*-norbornyl derivatives.

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Experimental Part[11])

*7-syn-Bromo-2-*endo*-norbornyl p-toluenesulfonate* (**13g**). A solution of 397 mg (2.1 mmol) of 7-*syn*-bromo-2-*endo*-norbornanol (m.p. 56–57°) [19] and 789 mg (4.1 mmol) of *p*-toluenesulfonyl chloride in 7 ml of abs. pyridine was kept at 20° for one week. Ice and 4N HCl were added to the reaction mixture which was then extracted three times with 30 ml of CH_2Cl_2. The extracts were washed with 2N $NaHCO_3$ and then H_2O, dried over Na_2SO_4 and evaporated *i.v.* The oily residue was chromatographed on silica gel with $CHCl_3$ to yield 405 mg (56%) of a colorless oil. ^{1}H-NMR ($CDCl_3$): 1.1–2.65 (*m*, 8 H); 2.45 (*s*, 3 H, CH_3–Ar); 3.9 (*m*, 1 H, H–C(7)).

$C_{14}H_{17}BrO_3S$ (345.26) Calc. C 48.70 H 4.96% Found C 48.83 H 4.89%

*7-syn-Bromo-2-*exo*-norbornyl p-toluenesulfonate* (**14g**). 7-*syn*-Bromo-2-*exo*-norbornanol (**20**, R = Br) [19] [20] (564 mg, 2.9 mmol) was treated with 1.13 g (5.7 mmol) of *p*-toluenesulfonyl chloride in 10 ml of abs. pyridine for 3 days at 20° and worked up as for **13g**. After chromatography on silica gel with CH_2Cl_2 and crystallization from Et_2O/pentane 571 mg (57%) of **14g** was obtained; m.p. 70–73°. ^{1}H-NMR ($CDCl_3$): 0.95–2.70 (*m*, 11 H); 3.70 (*s*, 1 H, H–C(7)).

$C_{14}H_{17}BrO_3S$ (345.26) Calc. C 48.70 H 4.96% Found C 48.63 H 5.16%

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[10]) For a summary of these results see also [12b].
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