224. Carbon Participation in the Solvolysis of 6-*endo*-Substituted 2-*exo*-Norbornyl Toluenesulfonates. Norbornanes Part 6

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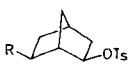
Summary

The solvolysis rate constants k for the 6-*endo*-substituted 2-*exo*-norbornyl toluenesulfonates **7** have been determined. Values of $\log k$ correlate well with the respective inductive constants of the substituents except when the latter are nucleophilic and therefore lead to *endo*-cyclization, or when they are *n*-electron donors and cause concerted fragmentation. In general 6-*endo*-substituted tosylates **7** react somewhat more slowly than their 6-*exo*-epimers.

Identical or different mixtures were obtained from the C(6)-epimers **7** and **1** depending on whether the substituent was an electron donor or acceptor. It is concluded that donor substituents at C(6) enhance 1,3-bridging in the intermediate epimeric cations and lead to their rapid and complete equilibration, and that electron acceptors reduce bridging and hence their equilibration rates.

Introduction. – As shown in the preceding article[2]) the solvolysis rates of 2-*exo*-**1**, and 2-*endo*-norbornyl toluenesulfonates **2** are controlled by the inductive effect of substituents at C(6), except for some well documented cases in which exalted substituent effects are observed. Invariably, the rates of the 2-*exo*-tosylates **1** were far more strongly affected by the substituent R than those of the 2-*endo*-tosylates **2**. Furthermore, donor substituents led to higher rates and suppressed the formation of 2-*endo*-substitution products, whereas acceptor substituents lowered the rates and led both to 2-*endo*- and 2-*exo*-substitution products.

The conclusion was that 6-*exo*-substituents determine reaction rates and products by controlling the participation of the neighboring C(6)-atom in the



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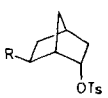

2

R = **a** H, **b** CH_3, **c** i-C_3H_7, **d** t-C_4H_9, **e** CH_2Br, **f** F, **g** Br, **h** CN, **i** CH_3COO, **j** $COOCH_3$, **k** NH_2CH_2, **l** $HOCH_2$, **m** COOH, **n** HO, **o** CH_3O, **p** NO_2

[1]) Corresponding author.

[2]) Norbornanes, Part 5: [1].

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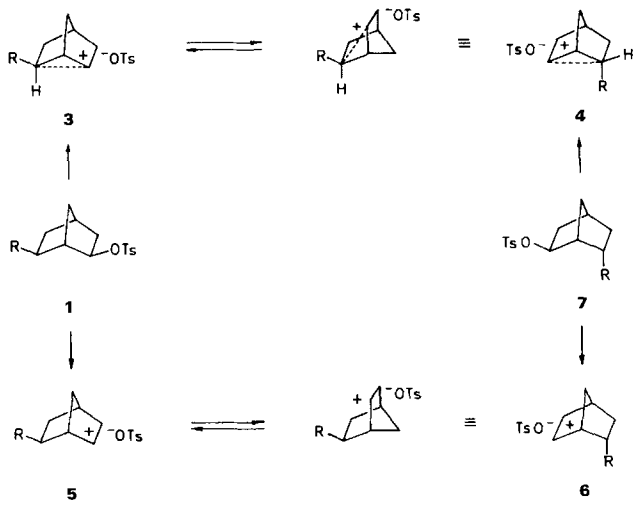
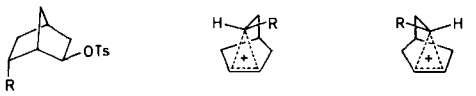
Scheme



ionization step and hence the degree of 1,3-bridging in the resultant cations **3** *(Scheme)*. Since the latter are attacked preferentially from the unbridged *exo*-side, donor substituents which favor bridging also favor the formation of 2-*exo*-substitution products. Conversely, acceptor substituents which reduce or prevent bridging in the resulting cations **5** undergo 2-*endo*-attack as well as 2-*exo*-attack. Bridging by C(6) appears to be strongly hindered in the 2-*endo*-series **2** because of repulsion of the electrons around C(6) by the incipient *endo*-tosylate anion.

1,3-Bridging as in **3** implies partial bonding between the cationic center at C(2) and the pentacoordinate C(6)-atom. The fact that the substituent R can occupy the 6-*exo*- and 6-*endo* positions, as in **1**, and **7**, respectively, raises the question whether its orientation affects the reactivity of these epimers. In the cation **3** from **1** the R,C(6)-bond is approximately colinear with the incipient bridge between C(6) and C(2), in the cation **4** from **7** it is approximately perpendicular *(Scheme)*. Hence, if induction were subject to a directional effect the reactivity of epimeric tosylates **1** and **7** should differ.

A further reason to compare the reactivity of the epimeric 6-substituted 2-*exo*-tosylates **1** and **7** becomes evident when considering the respective pairs of *Wagner-Meerwein* related norbornyl cations **3**⇄**4** or **5**⇄**6**. Regardless of whether they are bridged or unbridged, these pairs of epimeric cations should lead to the same or to different yields of products depending upon whether the rearrangement is faster or slower than capture by nucleophilic solvents.



This distinction between rapidly and slowly interconverting cations would not apply if they were symmetrically bridged, *i.e.* 'nonclassical', and therefore contained two partial bonds in the nortricyclene-like structures **8A** and **8B**; for these are enantiomers and necessarily lead to identical products. This viewpoint, first proposed by *Winstein* for the norbornyl cation (**8**, R = H) [2], was rejected in the preceding article [1] and will be discussed again below.

It is an important consequence of unsymmetrical 1,3-bridging, as depicted in **3** and **4**, that the stronger the partial bond, the easier rearrangement should become because this merely involves the simultaneous tightening and loosening of bonds and therefore resembles a skeletal vibration. On the other hand, unbridged or very loosely bridged cations, such as **5** and **6**, should be less disposed to rearrange[3]).

In this article the solvolysis rates and products of 6-*endo*-substituted 2-*exo*-norbornyl tosylates **7a–7o** are compared with earlier data for the 6-*exo*-epimers **1** [1]. As stressed in previous articles [3] [4] rearside attack by nucleophiles at C(2) in 2-*exo*-norbornyl derivatives is severely hindered, and will be even more so when 6-*endo*-substituents are present, as in **7b–7o**. Consequently, the positive charge generated at C(2) will tend to be dispersed internally and spread to the C(6)-atom and to the 6-*endo*-substituents, especially if the latter are nucleophilic, as in **7i–7m**[4]). Finally, concerted fragmentation [6] involving rupture of the C(1),C(6)-bond is anticipated in cases where the substituent is an *n*-electron donor, such as HO and CH_3O.

Results. – The first-order rate constants for **7a–7p** measured conductometrically in ethanol/water 80:20 (*v/v*) are listed in *Table 1* with the activation parameters. The reaction products were determined in dioxane/water 70:30 by weight and are listed in *Table 2* including (in brackets) the products of the epimeric tosylates **1**. Losses of volatile products were minimized by injection of the reaction solutions. The yields were determined by conventional or by capillary GC. employing automatic integration. The yields represent the average of several runs. Several previously unknown products listed in *Table 2* were prepared to enable comparison, as described in a subsequent paper.

The main solvolysis product (94%) obtained from the unsubstituted tosylate **7a** (= **1a**) was 2-*exo*-norbornanol (**9a** = **11a**) [7]. When the *p*-bromobenzenesulfonate of the optically active form of the alcohol **9a** ($[\alpha]_D^{22} = -2.49° \pm 0.05°$, $c = 1.18$, $CHCl_3$) was solvolyzed in abs. ethanol in ethanol/water 80:20, or in trifluoroacetic acid, the products were completely racemized[5]), thus confirming *Winstein*'s results [2]. Solvolysis is accompanied by degenerate *Wagner-Meerwein* rearrangements and hydride shifts which lead to racemization[6]). C(6) → C(2) hydride shifts also account for most of the products derived from the 6-*endo*-alkyl derivatives **7b**, **7c** and **7d**, namely tertiary alcohols **13** and the olefins **15** and **16** *(Table 2)*. The rest consisted mainly of the rearranged 6-*exo*-R alcohols **9** beside small amounts of unrearranged alcohols **11**.

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[3]) It should be emphasized that formulas **3** and **5** represent extremes and that bridging is graded according to the polar quality of the substituent.

[4]) This neighboring group participation [5] will lead to *endo*-cyclization.

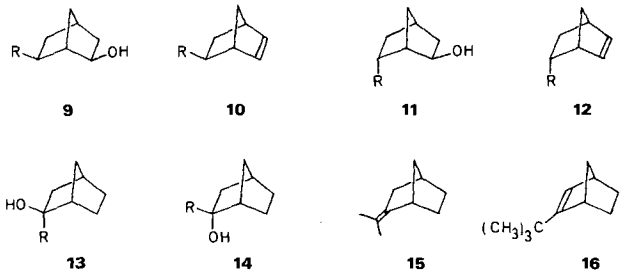
[5]) Unpublished work with *B. Schaub.*

[6]) See the comprehensive review by *Brown* [8].

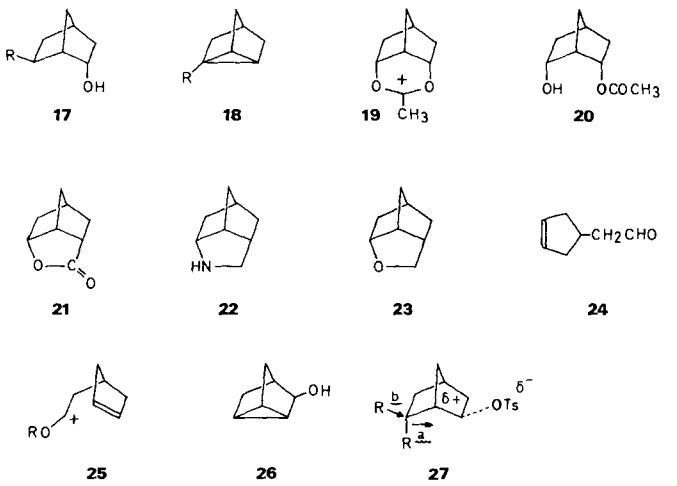
Table 1. *First-order solvolysis rate constants for 10^{-3} M 6-endo-substituted 2-exo- norbornyl p-toluenesulfonates* **7a–7p** *in 80 vol.% ethanol*

	R	T [°]	k [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol · degree]		R	T [°]	k [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol · degree]
a	H[a])	70.00	$3.58 \cdot 10^{-2}$[b])	22.04	−1.20	**h**	CN[c])	70.00	$4.33 \cdot 10^{-8}$[b])	28.73	−8.77
b	CH_3[c])	60.00	$2.05 \cdot 10^{-3}$	21.93	−5.21			120.00	$1.07 \cdot 10^{-5}$		
		69.76	$5.47 \cdot 10^{-3}$					130.00	$2.57 \cdot 10^{-5}$		
		70.00	$5.58 \cdot 10^{-3}$[b])					139.50	$6.65 \cdot 10^{-5}$		
		79.78	$1.39 \cdot 10^{-2}$			**i**	$OCOCH_3$[c])	70.00	$5.56 \cdot 10^{-5}$[b])	23.2	−10.7
c	i-C_3H_7[c])	39.40	$1.41 \cdot 10^{-4}$	23.23	−1.95			80.32	$1.54 \cdot 10^{-4}$		
		50.35	$5.06 \cdot 10^{-4}$					90.17	$3.94 \cdot 10^{-4}$		
		60.00	$1.52 \cdot 10^{-3}$					99.95	$9.23 \cdot 10^{-4}$		
		70.00	$4.32 \cdot 10^{-3}$[b])			**j**	$COOCH_3$[c])	60.20	$3.02 \cdot 10^{-4}$	22.7	−6.78
d	t-C_4H_9[c])	30.50	$5.56 \cdot 10^{-4}$	20.9	−4.63			69.80	$8.12 \cdot 10^{-4}$		
		39.00	$1.49 \cdot 10^{-3}$					70.00	$8.29 \cdot 10^{-4}$[b])		
		50.50	$5.04 \cdot 10^{-3}$					79.20	$2.03 \cdot 10^{-3}$		
		70.00	$3.40 \cdot 10^{-2}$[b])			**k**	CH_2NH_2[c])	−20.00	$6.02 \cdot 10^{-4}$	14.0	−17.8
e	CH_2Br[c])	70.00	$2.74 \cdot 10^{-4}$[b])	20.97	−14.0			−10.13	$1.73 \cdot 10^{-3}$		
		89.70	$1.53 \cdot 10^{-3}$					0.07	$4.99 \cdot 10^{-3}$		
		99.00	$3.30 \cdot 10^{-3}$					70.00	1.17[b])		
		109.40	$7.21 \cdot 10^{-3}$			**n**	OH	49.78	$2.38 \cdot 10^{-4}$	22.4	−5.8
f	F	70.00	$4.68 \cdot 10^{-7}$[b])	27.3	−8.1			59.59	$7.20 \cdot 10^{-4}$		
		110.22	$3.51 \cdot 10^{-5}$					70.15	$2.02 \cdot 10^{-3}$		
		119.31	$8.17 \cdot 10^{-5}$					70.00	$2.02 \cdot 10^{-3}$[b])		
		129.38	$2.03 \cdot 10^{-4}$			**o**	OCH_3	59.91	$8.93 \cdot 10^{-5}$	24.6	−3.6
g	Br	70.00	$1.95 \cdot 10^{-7}$[b])	27.0	−10.8			70.00	$2.75 \cdot 10^{-4}$		
		119.97	$3.45 \cdot 10^{-5}$					70.01	$2.76 \cdot 10^{-4}$		
		130.00	$8.32 \cdot 10^{-5}$					80.17	$7.95 \cdot 10^{-4}$		
		139.75	$1.90 \cdot 10^{-4}$			**p**	NO_2	70.00	$4.70 \cdot 10^{-6}$[b])	23.8	−13.9
								100.00	$8.40 \cdot 10^{-5}$		
								110.00	$2.01 \cdot 10^{-4}$		
								120.00	$4.52 \cdot 10^{-4}$		

[a]) See [1].
[b]) Extrapolated.
[c]) In the presence of 1.1 mol-equiv. of triethylamine.



6-*exo*-Bromo-2-*exo*-norbornanol (**9g**) and 2-*exo*-bromo-5-norbornene (**10g**) from the reaction of the tosylate **7g** were not isolated as such, since **9g** fragments in the presence of base [7] to the aldehyde **24**[7]) whereas **10g** undergoes homoallylic rearrangement to nortricyclenol (**26**) and to 5-norbornene-2-*exo*-ol (**10n**) [7]. The 2-*endo*-bromoolefin **12g** is the only stable primary product. These complications did not arise with the 6-*endo*-fluoride **7f**, since the derived fluoroalcohols **9f**, **11f** and **17f**, as well as the 2-*endo*-fluoroolefin **12f**, were stable in 70% dioxane below 130°.



The tosylates **7i**–**7m** underwent practically quantitative *endo*-cyclization to the compounds **20**–**23**. The *endo*-diol monoacetate **20** is formed by hydrolysis of the tricyclic cation **19**, whereas direct cyclization of **7j** or **7m** gives the lactone **21**, of **7k** gives the tricyclic amine **22**, and of **7l** gives the ether **23**. The tosylates **7l** and **7m** were too reactive to allow isolation and cyclized spontaneously. As anticipated, the 6-*endo*-hydroxy and methoxy tosylates **8n** and **8o** fragmented quantitatively to **25**, R = H or CH_3, the precursors of the aldehyde **24**.

[7]) Part of the isolated aldehyde **24** is undoubtably formed from the fragmentable 6-*exo*-bromo-2-*endo*-norbornanol (**17g**).

Discussion. – The rate constants k_7 for the tosylates **7a–7p** at 70° *(Table 3)* cover a range of more than 10^7, a sign that the 6-*endo*-substituents are strongly involved in

Table 2. *Yield of products* (in %) *from the reaction of* 6-endo-*substituted* **7** *and (in brackets)* 6-exo-*substituted* **1** *2-exo-norbornyl* p-*toluenesulfonates in 70 vol.% dioxane*

R =										
a H[a]	**9**	94	**10**	0.5	**12**	5.5				
b CH_3[b]	**9**	40 (40)	**11**	2 (2)	**13**	58 (58)				
c i-C_3H_7[b]	**9**	29 (32)	**11**	1 (1)	**13**	33 (33)	**15**	37 (36)		
d t-C_4H_9[b]	**9**	21 (18)	**13**	39 (39)	**14**	1 (1)	**16**	39 (42)		
e CH_2Br[b]	**9**	38 (70)	**10**	2 (10)	**11**	56 (20)	**12**	4 (–)		
f F[b][c]	**9**	5 (9)	**11**	5 (–)	**12**	81 (3)	**17**	4 (57)	**18**	1 (–)
g Br[c][d]	**9**	13 (44)	**10**	69 (54)	**12**	10 (2)				
h CN[b]	**9**	4 (11)	**10**	11 (43)	**12**	– (1)	**18**	78 (44)	**21**	7 (1)
i CH_3COO[b]	**9**	– (12)	**10**	– (42)	**12**	5 (–)	**20**	95 (41)		
j $COOCH_3$[b]	**9**	– (32)	**10**	– (24)	**11**	– (4)	**12**	– (1)	**18**	– (11)
k CH_2NH_2[b]	**9**	– (83)	**10**	– (14)	**11**	– (3)	**22**	100 (–)		
l CH_2OH[b]	**9**	– (85)	**10**	– (12)	**11**	– (3)	**23**	100 (–)		
m COOH	**9**	– (25)	**10**	– (12)	**12**	– (1)	**18**	– (36)	**21**	100 (26)
n OH	**24**	100 (100)								
o OCH_3[b]	**24**	100 (100)								
p NO_2[e]										

[a] **7a** and **1a** are identical, the rearrangements and C(6) → C(2) hydride shifts degenerate.
[b] In the presence of 1 to 2 equiv. of triethylamine.
[c] Beside unidentified products.
[d] With 2 equiv. of NaOH.
[e] Only tarry material obtained.

Table 3. *Solvolysis rate constants for* **7** *and* **1** *at 70° and* k_7/k_1 *rate ratios*

R	k_7	k_1[a]	k_7/k_1	Anchimeric and frangomeric accelerations[b]
a H	$3.58 \cdot 10^{-2}$	$3.58 \cdot 10^{-2}$	1	
b CH_3	$5.58 \cdot 10^{-3}$	$1.09 \cdot 10^{-2}$	0.51	
c i-C_3H_7	$4.32 \cdot 10^{-3}$	$2.46 \cdot 10^{-2}$	0.18	
d t-C_4H_9	$3.40 \cdot 10^{-2}$	$6.09 \cdot 10^{-2}$	0.56	
e CH_2Br	$2.74 \cdot 10^{-4}$	$1.06 \cdot 10^{-4}$	2.6	
f F	$4.68 \cdot 10^{-7}$	$7.21 \cdot 10^{-7}$	0.65	
g Br	$1.95 \cdot 10^{-7}$	$1.51 \cdot 10^{-7}$	1.3	
h CN	$4.33 \cdot 10^{-8}$	$1.23 \cdot 10^{-7}$	0.35	
i $OCOCH_3$	$5.56 \cdot 10^{-5}$	$8.14 \cdot 10^{-7}$	68	28
j $COOCH_3$	$8.29 \cdot 10^{-4}$	$6.33 \cdot 10^{-6}$	131	65
k CH_2NH_2	1.17	$8.84 \cdot 10^{-3}$	132	692
l CH_2OH	[c]	$5.97 \cdot 10^{-3}$		[c]
m COOH	[c]	$5.97 \cdot 10^{-6}$		[c]
n OH	$2.02 \cdot 10^{-3}$	$6.05 \cdot 10^{-4}$	3.3	204
o OCH_3	$2.75 \cdot 10^{-4}$	$2.88 \cdot 10^{-4}$	0.95	48
p NO_2	$4.70 \cdot 10^{-6}$	$1.13 \cdot 10^{-7}$	42	624

[a] See [1]
[b] Based on the deviations from the inductive regression line in *Figure 1.*
[c] Too fast to be measured.

the rate-determining ionization step of these compounds. Furthermore, the substituent effects fall into three groups. Thus, $\log k$ values for the first group of tosylates **7a**–**7h** correlate well with the respective inductive substituent constants σ_I^q [9] *(Fig. 1)*. This proves that rates are controlled by the inductive effects of the substituents, as in the 6-*exo*-series **1** [1]. But the reaction constant ρ of -1.75 for the 6-*endo*-series **7** is *ca.* 12% smaller than for the 6-*exo*-series **1** ($\rho = -2{,}0$ [1]), indicating a somewhat lower sensitivity of rates toward 6-*endo*-substituents. Possibly, transverse polarizability, as in **27** (arrow *a*) is less effective than longitudinal polarizability (arrow *b*) [10].

The small but not negligible directional effect of the R,C(6)-bond is reflected in the rate ratios k_7/k_1 *(Table 3)* which are less than one, except for the bromomethyl **7e**, **1e**, and for the bromo derivatives, **7g**, **1g**. In the latter cases the k_7/k_1 ratio is 2.6 and 1.3, respectively. This reversal is probably due to a small anchimeric effect[8]) of the bromine atom [5] leading to bridged intermediates of the type **28** and **29**. This view is supported by the unusually high yield (56%) of unrearranged 2-*exo*-alcohol **11e** from **7e** and of unrearranged olefin **12g** from **7g**.

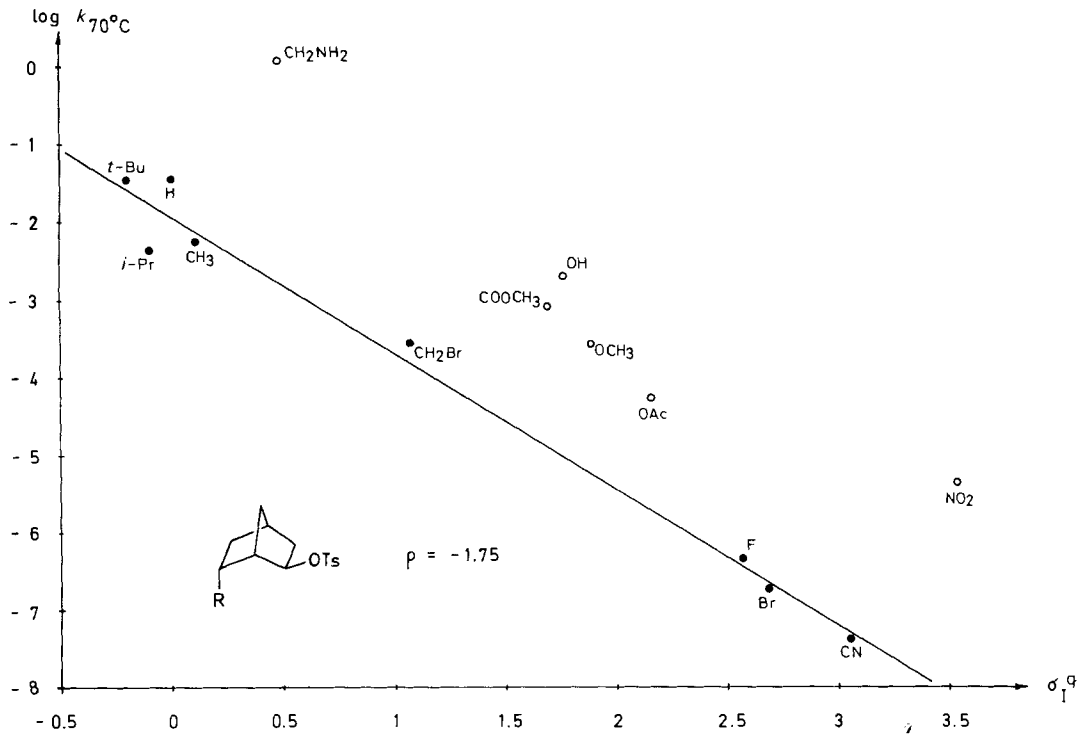
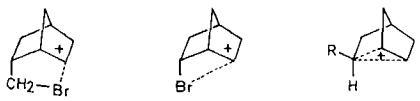


Figure 1. *Plot of* log*k for* 6-endo-*substituted* 2-exo-*norbornyl tosylates* **7** vs. *inductive substituent constants* σ_I^q (open circles not included in the regression)

[8]) The anchimeric effect is a measure of the rate increase due to the nucleophilic participation of a neighboring group [5].



28 **29** **30**

On the other hand the rates and products of the second group of tosylates **7i–7m** clearly indicate anchimeric participation of the 6-*endo*-substituents in the rate determining cyclization to **19**, **21**, **22** and **23**. The rate accelerations in *Table 3*, calculated from the deviations of the points for **7i**, **7j** and **7k** from the inductive regression line in the plot *(Fig. 1)*, are a measure of the anchimeric effects [5] of these groups. In the case of 6-*endo*-CH_2OH and COOH these are too large to be measured.

The substantial rate increases of 204 and 48 caused by the third kind of substituent, *i.e.* the *n*-electron donors HO and CH_3O, are due to their frangomeric effects [6] which cause concerted fragmentation to **25**. The large acceleration of 624 due to the 6-*endo*-nitro group *(Table 3)* could be ascribed either to the anchimeric effect of its O-atoms or to concerted 1,3-elimination leading to the nitronortricyclene (**18p**), an elimination already observed in the 6-*exo*-series **1**. However, this

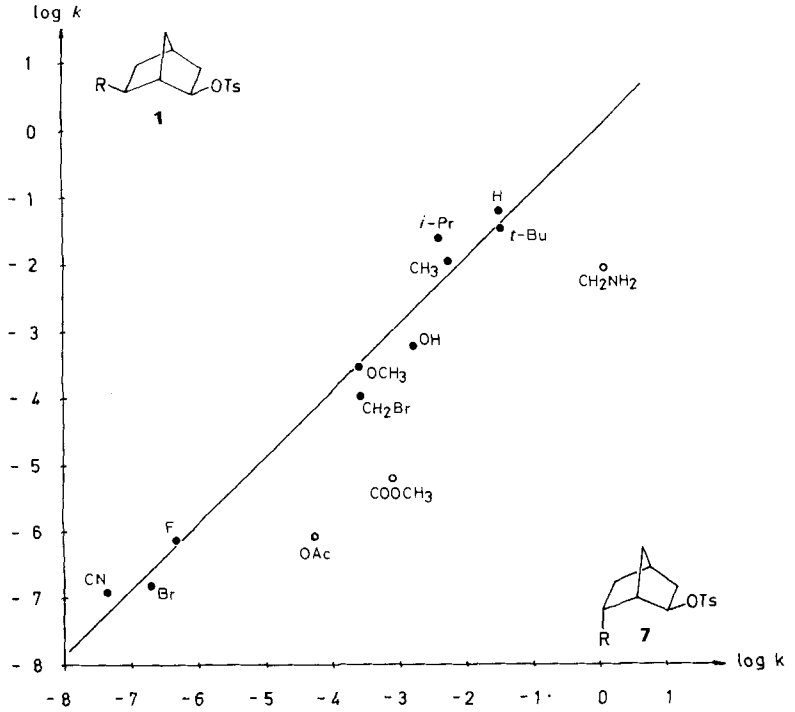


Figure 2. *Plot of* log*k for the series* **1** vs. log*k for the series* **7** (open circles not included in the regression)

question could not be resolved since only tarry material was obtained under the reaction conditions.

The above conclusions are supported by the plot of $\log k$ for the series **1** against $\log k$ for the series **7** *(Fig. 2)*. The points for the first group of substituents correlate well except when $R = CH_2Br$, a result of the small anchimeric acceleration of the 6-*endo*-epimer mentioned above. The points for the nucleophilic substituents CH_3COO, $COOCH_3$ and CH_2NH_2, which show a large anchimeric acceleration in the *endo*-series **7**, deviate strongly from the inductive regression line and are therefore not included in the regression.

The epimeric 6-alkyl-substituted tosylates **1** and **7**, **b**, **c** and **d**, furnish the *same products in identical amounts* within the limits of error ($\pm 2\%$) of the GC. technique *(Table 2)*. As mentioned in the introduction, this finding indicates either a very rapid equilibration of the bridged epimeric cations **3** ⇄ **4** or alternatively, the formation of enantiomeric 'nonclassical' intermediates **8A** and **8B**.

The latter explanation was rejected in the preceding article [1] for several reasons[9]). Thus, symmetrical bridging is very unlikely unless R is hydrogen. However, plots of $\log k$ for the series **7** *(Fig. 1)* and the series **1** [1] against σ_I^q fail to reveal any distinctive behavior of the unsubstituted 2-*exo*-tosylate **1a** (= **7a**), such as an unusually high rate which could be ascribed to the formation of an especially stable symmetrically bridged nonclassical cation [2] [8]. If, on the other hand, the existence of unsymmetrically bridged norbornyl cations is accepted[10]), a formula with one partial bond only, as in **3**, would seem more appropriate than a formula with two partial bonds, as in **30**, since it is established practice to indicate only abnormally long and therefore weak C,C-bonds by a dotted line.

In contrast, the tosylates **1** and **7**, **e**–**h**, with electron withdrawing substituents at C(6), *lead to different yields of products (Table 2)*. Rearrangement is therefore slowed to such a degree that capture of the epimeric cations by solvent competes success-

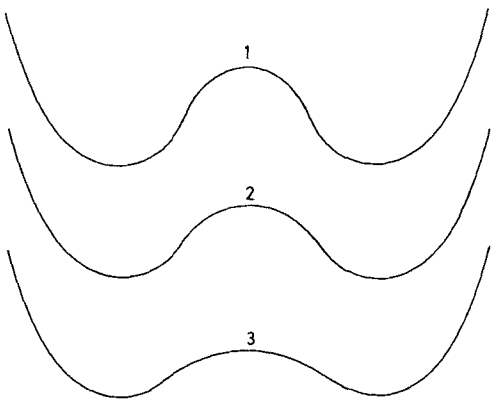


Figure 3. *Decreasing energy barrier for the interconversion of more strongly bridged and more stable C(6)-epimeric 2-norbornyl cations*

[9]) See also [4].

[10]) Unsymmetrically bridged carbocations have recently been proposed and discussed by *Olah* [11] and *Schleyer* [12].

fully. The fact that 2-*endo*-substitution accompanies 2-*exo*-substitution, especially in the series **1** [1], is evidence that the intermediate cations are either unbridged, as in **5** and **6**, or very loosely bridged.

These findings confirm the view [1] that donor substituents at C(6) assist 1,3-bridging and hence increase the rate of rearrangement **3** ⇄ **4**, whereas acceptor substituents have the opposite effect. This is illustrated by the energy diagrams in *Fig. 3*, in which the minima correspond to epimeric norbornyl cations, such as **3** and **4** or **5** and **6**, separated by a variable energy barrier, *viz.* the transition state for rearrangement.

Curve 1 corresponds to a high barrier due to the presence of electron acceptors at C(6) and hence to slow rearrangement of unbridged cations **5** and **6**. Curves 2 and 3 illustrate progressively lower barriers due to the presence of electron donors at C(6) which lead to faster interconversion of more strongly bridged cations **3** and **4**. A barrier of 2.5 kcal/mol corresponds to a skeletal vibration of the frequency 1000 cm^{-1}, beyond which a distinction between epimeric cations becomes meaningless[11]).

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Experimental Part

Rate measurements in ethanol/water 80:20 (*v/v*) were carried out as reported [14]. Preparative solvolyses in dioxane/water 70:30 by weight and product analyses have been described [1] [7]. The syntheses of the 6-*endo*-substituted 2-*exo*-norbornyl-*p*-toluenesulfonates **7** and their reaction products will be reported in subsequent papers.

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[11]) From his study of the deuterium isotope effect of the ^{13}C-NMR. spectrum of the 2-norbornyl cation under stable ion conditions *Saunders* has concluded that the energy barrier is less than 3 kcal/mol (private communication) and that a static symmetrical structure is consistent with the results [13].