208. Polar *versus* Steric Effects in the Solvolysis of 6*endo*-substituted 2*endo*-Norbornyl *p*-Toluenesulfonates

Norbornanes[1]), Part 8

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Summary

The solvolysis rates and products of the 6*endo*-R-substituted 2*endo*-norbornyl toluenesulfonates **6a–6i** have been determined. The rates of **6a–6g** correlate with the inductive constants σ_I^q of the 6*endo*-substituents and are not related to the size of the latter. It is therefore concluded that polar rather than steric effects control the *exo*/*endo*-rate ratios of norbornyl sulfonates. Products are derived mainly from rearranged 6*exo*-R-norbornyl cations when the substituent is an electron donor and from unrearranged 6*endo*-R-substituted cations when the substituent is an electron acceptor.

In preceding articles [1–3] the solvolysis rates and products of 6-substituted 2*exo*- and 2*endo*-norbornyl toluenesulfonates **1–3** were reported. The polar effects of the substituents R were shown to be much more strongly transmitted in the 2*exo*-sulfonates **1** and **2** than in the 2*endo*-sulfonates **3**. In the case of **1** and **3** differential transmittance resulted in k_1/k_3 ratios which differed widely with the 6*exo*-substituent and decreased by a factor of more than 10^3 as the electron-attracting power of R increased [1]. It was therefore concluded that electron donating substituents – relative to the incipient cationic center C(2) – lead to bridging of C(2) by the pentacoordinate C(6)-atom with concomitant transfer of a substancial part of the positive charge in the incipient ion pair **4** to the substituent R. In contrast, electron-attracting substituents reduce or prevent bridging in the resulting ion pair **5**.

Graded 1,3-bridging in 2-norbornyl cations accounts not only for variable k_1/k_3 ratios but also for the formation of 2*exo*-norbornanols as the only substitution products when R is an electron donor. It also explains the formation of 2*exo*- and 2*endo*-norbornanols when R is an electron acceptor[2]). Evidently, the bridged

[1]) The IUPAC name of 'norbornane' is 8,9,10-trinorbornane.

[2]) The *p*-toluenesulfonates **1**, R = F and CN, yield 57 and 30%, respectively, of the corresponding 2*endo*-norbornanols ([1] and unpublished results).

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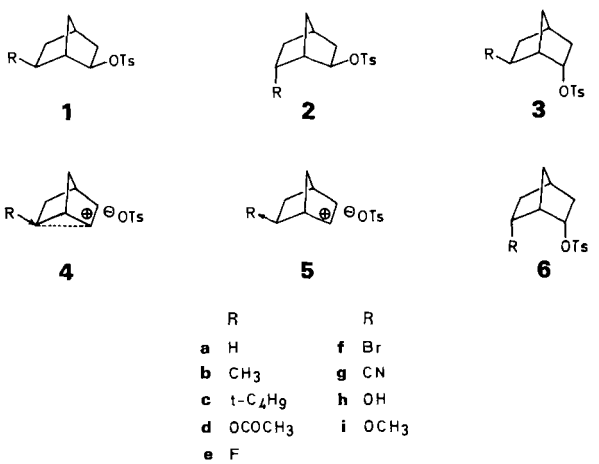

	R		R
a	H	**f**	Br
b	CH_3	**g**	CN
c	t-C_4H_9	**h**	OH
d	$OCOCH_3$	**i**	OCH_3
e	F		

2-norbornyl cation **4** is accessible to nucleophiles on the unshielded *exo*-side only, whereas the unbridged cation **5** is attacked on both the *exo*- and *endo*-side.

This conclusion is at variance with *Brown*'s steric explanation for the high *exo*/*endo*-rate ratio[3]) and the exclusive formation of 2*exo*-substitution products observed in the solvolysis of 6-unsubstituted 2*exo*- and 2*endo*-norbornyl *p*-toluenesulfonates **1** and **3** (R = H), respectively. According to *Brown*[4]) these findings reflect steric hindrance to ionization of the *endo*-epimer **3** and to favored *exo*-attack by nucleophiles at C(2) of the resultant unbridged, *i.e.* 'classical' 2-norbornyl cation.

Though rendered unlikely by the aforementioned investigation of the 6-substituted norbornyl *p*-toluenesulfonates **1**–**3**[5]) *Brown*'s hypothesis could be defended on the grounds that a strong polar effect is superposed on a steric effect. It was therefore desirable to test the concept of steric hindrance to ionization of *endo*-norbornyl sulfonates by investigating some 6*endo*-substituted 2*endo*-sulfonates **6**. If a steric effect were the primary cause of the k_1/k_3 ratio of 425 for R = H [1][6]), the latter should increase drastically as the 6*endo*-H-atom is replaced first by CH_3 and then by *t*-C_4H_9, because these groups should block the *endo*-ionization path more effectively than a H-atom. On the other hand, the rate constants for the series of 6*endo*-substituted 2*endo*-sulfonates **6a**–**6g** should correlate with the inductive constants of R [5] if polar rather than steric effects dominated.

Results. The preparation of the 6*endo*-R-2*endo*-norbornyl *p*-toluenesulfonates **6a**–**6i** and their hydrolysis in dioxane/water 7 : 3 are described in the accompanying contribution [6]. The products and their yields are summarized in *Table 1* and compared with those reported for the 6*exo*-R-2*endo*-sulfonates **3a**–**3i**. As a rule the same kind of products **7**–**20** were obtained from **3** and **6**, albeit in different yields (see *Discussion*).

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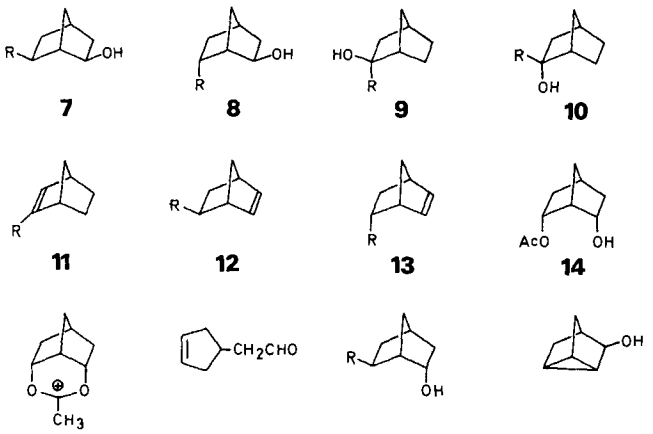
[3]) In 80 vol.-% ethanol k_1/k_3 for R = H is 425 at 70° [1].

[4]) For a comprehensive review of *Brown*'s hypothesis see [4].

[5]) For a review of this work see [3].

[6]) For R = H **1** and **3** equal **2** and **6**, respectively.



The rate constants for the reaction of **6a–6i** in ethanol/water 8:2 *(v/v)* were determined by the conductometric method [1] and are listed in *Table 2.*

Discussion. Introducing CH_3 and t-C_4H_9 in the 2*endo*-6*endo*-series **6** reduces the rate by factors of 7 and 4, respectively, in the 2*exo*-6*endo*-series **2** [1], where steric interference by R must be negligible, by factors of 1.4 and 3.3, respectively. Hence, there is no significant connection between the bulk of the substituent at C(6) and the rate. There is, however, a small configurational effect since 6*exo*-substituents lead to somewhat higher rates than 6*endo*-substituents, as the k_3/k_6 ratios in *Table 3* show[7]). A similar configurational effect of the substituent at C(6) was observed for the sulfonates **1** and **2**, where k_1/k_2 was also slightly larger than **1** [2]. It was there-

Table 1. *Yield of products (in %) from the reaction of* 6endo-*substituted* 2endo-*norbornyl* p-*toluenesulfonates* **6** *in 70 vol.-% dioxane* (in brackets the yields from the 6*exo*-substituted 2*endo*-norbornyl *p*-toluenesulfonates **3** [1])

6 (or **3**)	R	Products									
a	H	**7** 93	**20** 7								
b	CH_3	**7** 36(44)	**8** 19(2)	**9** 45(54)							
c	t-C_4H_9	**7** 23(27)	**8** 4(–)	**9** 20(23)	**10** 2(1)	**11** 51(49)					
d	$OCOCH_3$	**7** –(53)	**8** 64(–)	**12** –(37)	**13** 17(–)	**14** 15(10)[a])					
e	F	**7** 7(87)	**8** 63(–)	**12** –(4)	**13** 10(2)	**16**[b]) 10(–)	**17** –(7)[a])				
f	Br	**12**[c]) 13(9)	**13** 2(–)	**16**[b]) 75(81)[a])							
g	CN[d])	**7** 4(83)	**8** 76(1)	**12** 1(12)	**13**[e])	**17** 2(3)				**19** 4(–)	
h	OH	**16** 96[a]) (100)									
i	OCH_3	**8** 4(–)	**16**[a]) 92(100)								

[a]) Beside unidentified material. [b]) The precursors of **16** are probably 6*endo*-fluoro- or 6*endo*-bromo-2*exo*-norbornanol which fragment to **16**. [c]) Identified as the 'nortricyclanol' **18**. [d]) Unpublished results. [e]) Traces.

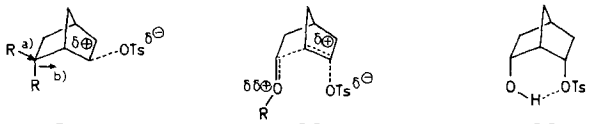
[7]) The relatively high k_3/k_6 ratio of 18 for the cyanonorbornyl *p*-toluenesulfonates will be discussed in a later paper.

Table 2. *First-order solvolysis rate constants* k *for* 10^{-3} M 6endo-*R*-2endo-*norbornyl* p-*toluenesulfonates* **6** *in 80 vol.-% ethanol*

R	*T* [°]	*k* [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol · degree]
6a H	70.00[a])	$8.42 \cdot 10^{-5}$	23.9	−7.9
	79.12	$2.41 \cdot 10^{-4}$		
	89.77	$5.96 \cdot 10^{-4}$		
	99.20	$1.42 \cdot 10^{-3}$		
	140.00[a])	$3.00 \cdot 10^{-2}$		
6b CH_3	70.00[a])	$1.18 \cdot 10^{-5}$	25.0	−8.5
	99.80	$2.39 \cdot 10^{-4}$		
	110.00	$6.00 \cdot 10^{-4}$		
	119.86	$1.39 \cdot 10^{-3}$		
	140.00[a])	$6.88 \cdot 10^{-3}$		
6c t-C_4H_9	70.00[a])	$2.04 \cdot 10^{-5}$	24.4	−9.2
	100.00	$3.99 \cdot 10^{-4}$		
	110.00	$9.39 \cdot 10^{-4}$		
	120.00	$2.23 \cdot 10^{-3}$		
	140.00[a])	$1.05 \cdot 10^{-2}$		
6d $OCOCH_3$	70.00[a])	$1.65 \cdot 10^{-7}$	27.3	−10.3
	119.99	$3.04 \cdot 10^{-5}$		
	126.72	$5.72 \cdot 10^{-5}$		
	134.71	$1.11 \cdot 10^{-4}$		
	140.00[a])	$1.74 \cdot 10^{-4}$		
6e F	70.00[a])	$3.35 \cdot 10^{-7}$	23.81	−19.07
	125.31	$4.96 \cdot 10^{-5}$		
	130.33	$7.28 \cdot 10^{-5}$		
	135.33	$1.06 \cdot 10^{-4}$		
	140.00[a])	$1.49 \cdot 10^{-4}$		
6f Br	70.00[a])	$3.10 \cdot 10^{-8}$	26.8	−15.2
	125.00	$8.31 \cdot 10^{-6}$		
	135.00	$1.79 \cdot 10^{-5}$		
	139.60	$2.92 \cdot 10^{-5}$		
	140.00[a])	$2.90 \cdot 10^{-5}$		
6g CN	140.00	$5.99 \cdot 10^{-6}$		
6h OH	54.81	$1.45 \cdot 10^{-4}$	23.5	−4.5
	64.77	$4.26 \cdot 10^{-4}$		
	70.00[a])	$7.46 \cdot 10^{-4}$		
	74.86	$1.23 \cdot 10^{-3}$		
	140.00[a])	$3.09 \cdot 10^{-1}$		
6i OCH_3	70.00[a])	$4.68 \cdot 10^{-6}$	25.2	−9.9
	99.91	$9.75 \cdot 10^{-5}$		
	109.97	$2.47 \cdot 10^{-4}$		
	120.05	$5.84 \cdot 10^{-4}$		
	140.00[a])	$2.92 \cdot 10^{-2}$		

[a]) Extrapolated.

19 **20**



21 **22** **23**

fore concluded that longitudinal polarizability of the R,C(6)-bond, as in **21** (arrow a)), is more effective than transverse polarizability (arrow b)).

However, a further factor appears to be involved because the k_3/k_6 ratio for t-C_4H_9, namely 1.3, is smaller than that for CH_3, *i.e.* 5.1 *(Table 3)*. This suggests that *endo*-crowding in **6c**, which is far less pronounced in **6b**, leads to a small steric acceleration. It is noteworthy that according to spacefilling models *endo*-crowding in **6c** does not prevent rotation around the C(6),(t-C_4H_9)-bond. This conclusion is supported by the ^{1}H-NMR. spectrum of **6c**, in which the nine methyl protons give rise to a single sharp signal at 0.98 ppm [6].

The k_2/k_6 ratios *(Table 3)* also indicate that polar rather than steric effects control *exo*/*endo*-rate ratios, for these show the same trend as the k_1/k_3 ratios reported earlier [1] in that they decrease from 1667 (for t-C_4H_9) to 469 (for CH_3) to 425 (for H) to 1.4 (for F), *i.e.* as the electron-attracting power of R increases. The large k_2/k_6 ratio for R=$OCOCH_3$ of 337 is due to the accelerative anchimeric effect of this nucleophilic substituent in the sulfonate **2d** which leads to cyclization to the cation **15** [2]. The enhanced k_2/k_6 ratio of 59 for R=OCH_3 is probably due to the accelerative hyperconjugative effect of this n-electron donor which, for stereoelectronic reasons, is more effective in **2i** than in **6i** (see below).

Since steric effects are small or negligible in the 2*endo*-6*endo*-series **6** it is not surprising that the substituents R control rates predominantly by their inductive

Table 3. *Relative rate constants for* **6** *at 70 and 140° and* k_2/k_6 *and* k_3/k_6 *rate ratios at 70°*

	R	$k_{rel}^{70°}$	$k_{rel}^{140°}$	k_3/k_6	k_2/k_6
6a	H	1	1	1	425
6b	CH_3	0.14	0.18	5.1	469
6c	t-C_4H_9	0.24	0.28	1.3	1667
6d	$OCOCH_3$	$2.0 \cdot 10^{-3}$	$4.6 \cdot 10^{-3}$	7.3	337
6e	F	$4.0 \cdot 10^{-3}$	$5.0 \cdot 10^{-3}$	4.5	1.4
6f	Br	$3.7 \cdot 10^{-3}$	$7.7 \cdot 10^{-4}$	13	6.3
6g	CN	–	$1.6 \cdot 10^{-4}$	18[a])	11[a])
6h	OH	8.9	8.3	0.134	2.7
6i	OCH_3	$5.6 \cdot 10^{-2}$	$7.7 \cdot 10^{-2}$	9.2	59

[a]) At 140°.

effects. This follows from the plot of log k for **6a–6g** (at 140°) against the respective inductive substituent constants σ_I^q [5] *(Fig.)*. Not included in the regression are the points for OH and OCH_3 which give rise to accelerations of 1100 and 14, respectively. It is now well-established that these n-electron donors exert enhanced polar effects in k_c processes [7][8]) even when the nucleofugal group has a *gauche* orientation with respect to the hyperconjugating C,C-bond [1][8], as shown for **6h** in **22**. This is confirmed by the practically quantitative fragmentation of **6h** and **6i** *(Table 1)*. The fact that the hydroxy sulfonate **6h** reacts more than 10^2 times faster than the methoxy sulfonate **6i** *(Table 3)* can be attributed to an intramolecular H-bond (see **23**)[9]) which should assist ionization in the manner of a protic solvent.

The correlation of the points for **6a–6g** in the plot *(Fig.)* is not as good as the ones for **1–3** [1][2]. This is not surprising since the rate constants for **6a–6f** were extrapolated to 140° in order to include the constant for the much less reactive cyano sulfonate **6g**. Furthermore, secondary steric effects, such as steric hindrance to solvation, are also bound to play a role. The reaction constant ρ for **6** is -0.94 and hence somewhat larger than for the 2*endo*-6*exo*-series **3** ($\rho = -0.78$), but considerably smaller than for the 2*exo*-6*exo*-series **1** ($\rho = -2.0$) [1] and the 2*exo*-6*endo*-series **2** ($\rho = -1.75$) [2].

The low ρ value for the series **3** [1] indicated a relatively small inductive interaction between C(6) and C(2) in the transition state for the ionization to the ion pair **24**. The slightly higher ρ value for **6** then indicates a somewhat larger inter-

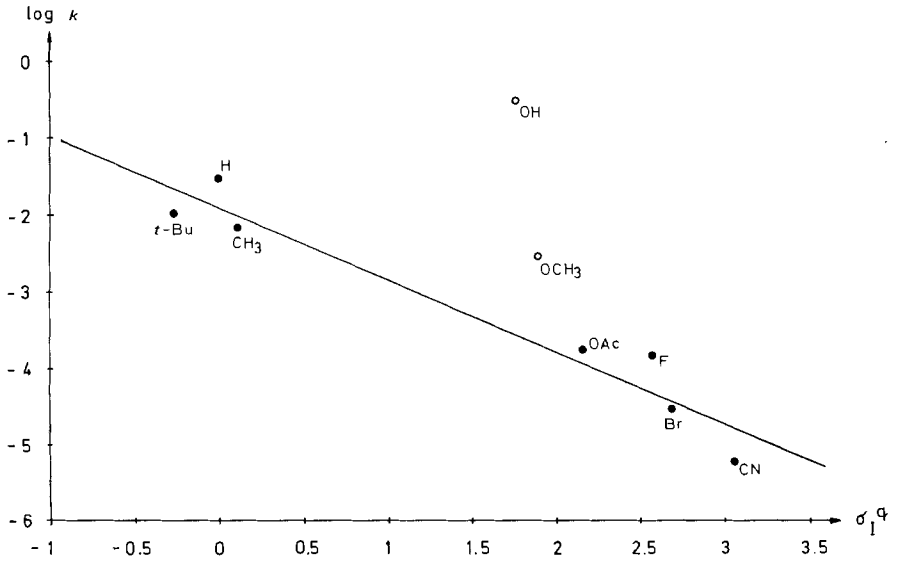


Figure. *Plot of log* k *for* **6a–6g** *in 80 vol.-% ethanol at 140°* vs. *inductive substituent constants for R* (OH and OCH_3 not included in the regression)

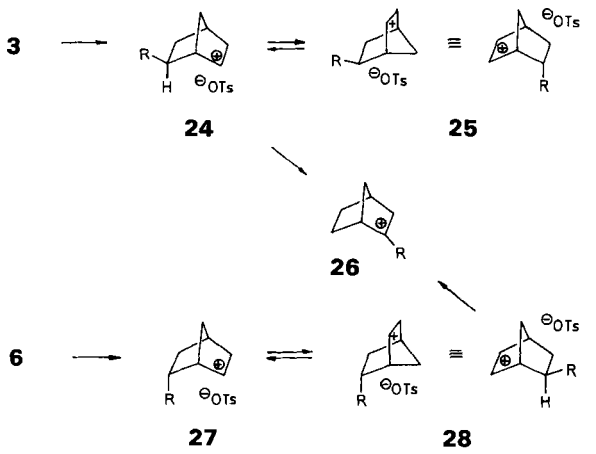
[8]) *I.e.* a carbocation is formed in the transition state without nucleophilic solvent assistance.

[9]) As evidenced by the dilution-independent broad band at 3350 cm^{-1}.

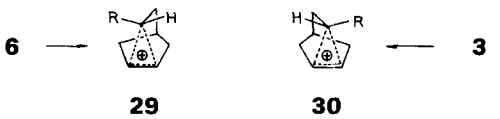
action in going to the ion pair **27**, due probably to the proximity of R and the reaction center and the concomitant exclusion of solvent. However, C-bridging should be weak in the *endo*-ion pairs **24** and **27** and hence justify the use of conventional formulae [3].

The products from **6b** and **6c** (R=CH_3 and *t*-C_4H_9, respectively) are derived mainly from the rearranged cations **26** and **28** (*Table 1* and *Scheme*). Thus, the precursors of the norbornanols **7b** and **7c** are the *exo*-R cations **28b** and **28c**, respectively, which arise from the cations **27** by a *Wagner-Meerwein* shift. A C(6)→C(2) *endo*-hydride shift converts **28** to the tertiary carbenium ions **26**, the precursors of **9**–**11**. In contrast, the products **8** and **13** from the sulfonates **6d**–**6g** are derived mainly from the unrearranged cations **27**, confirming that -I-substituents retard rearrangement [2].

Scheme



It is noteworthy that the same mixture of products should arise from the stereoisomeric *p*-toluenesulfonates **3** and **6** if the resultant cations were free and rearranged faster than they reacted with the solvent. As *Table 1* shows this is not the case, with the possible exception of the *t*-butyl-substituted sulfonates **3c** and **6c**. It is also worth mentioning that the same mixture of products should result from the sulfonates **3** and **6** if these ionized to the cations **24** and **27**, respectively, which were then converted to the respective 'nonclassical' cations of the type **29** and **30** proposed by *Winstein* [9]; for these are enantiomers and should therefore yield identical products. It is evident from *Table 1* that this is not so, except in the case of



3a and **6a** (R = H) where a symmetrical cation **29**, R = H, would be formed. This possibility was, however, rejected for other reasons [1][3].

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