222. Inductivity and Bridging in 2-Bicyclo[2.2.2]octyl Cations

Polar Effects, Part 11

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Summary

The solvolysis rates and products of several 6-substituted 2-*exo*- and 2-*endo*-bicyclo[2.2.2]octyl *p*-toluenesulfonates, **12** and **13**, respectively, are reported. Inductivity, as measured by the reaction constants ρ_I, is considerably less in the *exo*-series **12** ($\rho_I = -1.50$) than in the corresponding 2-*exo*-norbornyl *p*-toluenesulfonates **1** ($\rho_I = -2.0$). It is proposed that, for geometrical reasons, bridging of the cationic center C(2) by C(6) is not as strong in the bicyclooctane series **12** as it is in the norbornane series **1**. On the other hand, inductivity is higher in the 2-*endo*-bicyclooctane series **13** ($\rho_I = -1.0$) than in the corresponding 2-*endo*-norbornane series **3** ($\rho_I = 0.78$), probably, because in the former case bridging of C(6) is less hindered by the departing anion. The relative yields of *exo*- and *endo*-substitution products from the series **12** and **13**, are in accord with graded bridging of C(6) in the incipient bicyclooctyl cations. But almost constant bridging of C(2) by C(7) is indicated in the ionization of the 2-*endo*-bicyclooctane series **13**. Consequently, in the free unsubstituted bicyclooctane cation C(2) is bridged symmetrically by C(6) and C(7), in contrast to the current concept of 'non-classical' two-electron-three-center bonding.

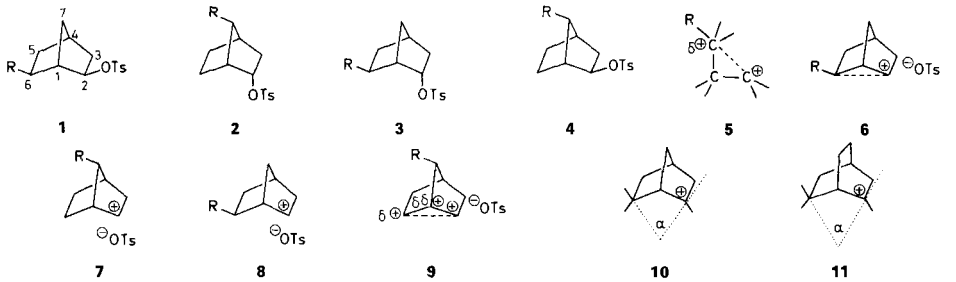
According to studies of substituent effects in the solvolysis of the 2-*exo*- and 2-*endo*-norbornyl *p*-toluenesulfonates (tosylates) **1**–**4**, the norbornane structure is anisotropic to the inductive (*I*) effect of substituents [1] [2a]. In fact, an evaluation of the sensitivity of the reaction rates of these tosylates to substituents at C(6) and C(7), *i.e.* their inductivity ρ_I[1]), has led to an alternative explanation for the disparate reactivity of 2-*exo*- and 2-*endo*-norbornyl (NB) derivatives[2]).

Inductivity was much larger in the 6-*exo*-R-2-*exo*-NB series **1** ($\rho_I = -2.0$ [1a]) than in the 7-*anti*-R-2-*endo* series **2** ($\rho_I = -0.72$ [1e]) although the conformations and direct distances are practically the same[3]). It was, therefore, concluded that through-space

[1]) Inductivity was defined as the reaction constant ρ_I in the equation $\log (k/k_o) = \rho_I \sigma_I^q$, where k and k_o are first-order rate constants for the substituted and unsubstituted tosylates, respectively, in 80% EtOH and σ_I^q is the corresponding inductive substituent constant [3].

[2]) For recent reviews, see [2].

[3]) X-ray data [4a] show that the C(2)–C(7) distance (2.40 Å) in **2** is actually shorter than the C(2)–C(6) distance (2.50 Å) in **1**.



induction (the direct effect) involves graded bridging of a β- or more remote C-atom to the cationic center, as in **5**, and that this bonding interaction is subject to so-called bridging strain [2a]. On this basis, bridging of C(2) by the dorsal C(6) in the ionization of **1** to the ion pair **6** is much stronger than bridging of C(2) by the dorsal C(7) in the ionization of **2** to the ion pair **7**, a conclusion that is warranted on stereoelectronic grounds, because in **6** partial bonding between C(2) and C(6) subdivides a six-membered ring into *quasi* five- and three-membered rings, whereas in **7** bonding between C(2) and C(7) would subdivide a five-membered ring into *quasi* four- and three-membered rings.

Bridging controls rates and products. Thus, in 80% EtOH at 70°, the unsubstituted *exo*-tosylate **1** (R = H) reacts 311 times faster than the *endo*-epimer **2** and affords only *exo*-substitution products with retention. But with electron-attracting substituents at C(6), which strongly reduce bridging in the *exo*-series **1**, *exo*/*endo* rate ratios fall well below one and *exo*- and *endo*-substitution products are formed [1a,d][4]). In contrast, the *endo*-tosylates **2** yield only inverted products regardless of the substituent at C(7) and in keeping with an unbridged transient ion pair **7** [1e].

Inductivity in the 6-*exo*-R-2-*endo*NB series **3** ($\rho_I = -0.78$), is also much lower than in the series **1** ($\rho_I = -2.0$). In this case, however, the departing anion hinders bridging between C(2) and C(6) in the transition state leading to the ion pair **8**. Bridging of C(2) by C(7) is likewise hindered in the series **4**. But here, inductivity is somewhat higher ($\rho_I = -0.97$), probably because bridging of the dorsal C(6) is not restricted by the departing anion in **9**, so that more positive charge is transferred to C(1). This enhances the influence of substituents at C(7) on rates [1e].

To bridge effectively, both participating C-atoms should adopt the trigonal-bipyramidal configuration preferred by pentacoordinate atoms. In the 2-norbornyl cation **10** the axis of the axial orbital at C(6), around which electron density is concentrated, intersects with the axis of the p-orbital at C(2) at an angle α of *ca.* 70°. This follows from a rough calculation[5]) and from plastic framework models[6]). Modifying the NB structure in such a way as to reduce the angle α should then weaken bridging.

Models and calculation show that in the 2-bicyclo[2.2.2]octyl (BO) cation **11** the angle α is reduced to *ca.* 60°, while maintaining the same conformation and C(6)–C(2) distance as in the NB cation **10**. The inductivity of the 6-*exo*-substituted 2-*exo*-BO

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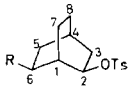
[4]) Bridging also controls the rates of subsequent *Wagner-Meerwein* rearrangements [1b].

[5]) Based on X-ray data for norbornane [4a] and bicyclo[2.2.2]octane [4b]. We thank Dr. *Eva Honegger* for this information.

[6]) *Prentise-Hall, Inc.*, Englewood Cliffs, N.J., USA.

tosylates **12** should, therefore, be lower than that of the corresponding 2-*exo*-NB tosylates **1**. On the other hand, the inductivity of the 6-*exo*-substituted 2-*endo*-BO tosylates **13** should be higher than that of the norbornyl series **3** because the trajectory of the ionizing tosyloxy group is further away from C(6). Also bridging of C(7) in the resulting ion pair **14** disperses positive charge to C(1) and thereby increases the influence of the substituent.



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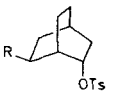
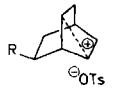


13

R =

a H **f** $COOCH_3$
b CH_3 **g** CN
c CH_2OCH_3 **h** COONa
d CH_2OAc **i** CH_2OH
e CH_2OTs



14

15

16

As pointed out in [1h], the free 2-NB and 2-BO cations differ in their symmetry properties; for the latter **15** (R = H) has a plane of symmetry through C(1), C(2), C(3) and C(4). Therefore, C(6) and C(7) should be equally bridged to C(2), unless the substituent at C(6) destroys the symmetry because it has a different *I* effect than the H-atom. It also follows that the degree to which C(6) and C(7) become bridged to C(2) during ionization depends on the *exo*- or *endo*-location of the anion.

In this article, the rates of the 6-*exo*-substituted 2-*exo*- and 2-*endo*-BO tosylates, **12a–i** and **13a–i**, respectively, in 80% (v/v) EtOH and in 97% (w/w) trifluoroethanol are reported together with the derived inductivities ρ_I. 80% EtOH is a solvent of medium nucleophilicity and ionizing power, 97% TFE a solvent of much lower nucleophilicity and much higher ionizing power [5]. It was recently shown [1f] that the inductivity of the 2-*exo*-NB series **1** is practically the same in these two solvents, whereas the inductivities of the series **2**, **3**, and **4** are considerably higher in 97% TFE than in 80% EtOH. The insensitivity of inductivity to solvent in the series **1** was attributed to the extensive charge dispersal which accompanies strong bridging. Since bridging is expected to be reduced in the BO series **12** and **13**, their ρ_I values should be more sensitive to solvent change.

First-order rate constants for **12** and **13** in 80% EtOH and 97% TFE, determined conductometrically [1b], are listed in *Tables 1–4*. For the hydrolysis products and their yields, determined in 70% dioxane, *cf. Table 6* [6]. It was already known from the work of *Goering & Sloan* [7] that acetolysis and ethanolysis of BO tosylate **12a** is accompanied by isomerization to 2-*exo*-bicyclo[3.2.1]octyl tosylate **16**. This facile rearrange-

Table 1. *First-Order Rate Constants for* 10^{-3} M *Solutions of* 6-exo-*R*-2-exo-*bicyclo[2.2.2]octyl* p-*Toluenesulfonates* **12** *in 80%* (v/v) *EtOH*

	R	*T* [°]	*k* [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol·degree]
a	H	70.00[a])[b])	$3.70 \cdot 10^{-3}$	18.61	− 15.71
		40.45	$2.56 \cdot 10^{-4}$		
		50.31	$6.75 \cdot 10^{-4}$		
		59.80	$1.54 \cdot 10^{-3}$		
b	CH_3	70.00[a])	$2.23 \cdot 10^{-3}$	23.06	− 3.76
		48.62	$2.19 \cdot 10^{-4}$		
		58.27	$6.60 \cdot 10^{-4}$		
		68.02	$1.81 \cdot 10^{-3}$		

Table 1 (cont.)

	R	*T* [°]	*k* [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol·degree]
c	CH_2OCH_3	70.00[a])	$3.58 \cdot 10^{-4}$	23.63	− 5.73
		70.30	$3.65 \cdot 10^{-4}$		
		80.38	$1.05 \cdot 10^{-3}$		
		90.69	$2.69 \cdot 10^{-3}$		
d	CH_2OAc	70.00[a])	$7.91 \cdot 10^{-5}$	24.24	− 6.95
		80.28	$2.28 \cdot 10^{-4}$		
		90.52	$6.27 \cdot 10^{-4}$		
		99.88	$1.48 \cdot 10^{-3}$		
e	CH_2OTs	70.00[a])	$2.31 \cdot 10^{-5}$	23.61	− 11.23
		90.51	$1.71 \cdot 10^{-4}$		
		99.85	$4.05 \cdot 10^{-4}$		
		109.78	$9.32 \cdot 10^{-4}$		
f	$COOCH_3$	70.00[a])	$1.58 \cdot 10^{-5}$	24.25	− 10.12
		99.80	$2.95 \cdot 10^{-4}$		
		110.02	$7.18 \cdot 10^{-4}$		
		120.15	$1.69 \cdot 10^{-3}$		
g	CN	70.00[a])	$1.44 \cdot 10^{-6}$	24.32	−14.66
		120.43	$1.58 \cdot 10^{-4}$		
		130.64	$3.69 \cdot 10^{-4}$		
		138.91	$6.64 \cdot 10^{-4}$		
h	COONa	70.00[a])	$1.91 \cdot 10^{-2}$	26.45	10.41
		39.94	$4.20 \cdot 10^{-4}$		
		49.60	$1.55 \cdot 10^{-3}$		
		58.01	$4.51 \cdot 10^{-3}$		
i	CH_2OH	70.00[a])	$8.52 \cdot 10^{-4}$	26.50	− 4.37
		58.80	$2.23 \cdot 10^{-4}$		
		71.10	$9.62 \cdot 10^{-4}$		
		80.28	$2.73 \cdot 10^{-3}$		

[a]) Extrapolated. [b]) All rates for **12a** calculated from measurements during the first half life.

Table 2. *First-Order Rate Constants for* 10^{-3} M *Solutions of* 6-exo-*R*-2-endo-*bicyclo[2.2.2]octyl* p-*Toluenesulfonates* **13** *in 80%* (v/v) *EtOH*

	R	*T* [°]	*k* [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol·degree]
b	CH_3	70.00[a])	$4.18 \cdot 10^{-3}$	22.03	− 5.52
		49.17	$4.82 \cdot 10^{-4}$		
		58.19	$1.31 \cdot 10^{-3}$		
		66.84	$3.03 \cdot 10^{-3}$		
c	CH_2OCH_3	70.00[a])	$1.53 \cdot 10^{-3}$	23.00	− 4.68
		59.66	$5.12 \cdot 10^{-4}$		
		69.78	$1.56 \cdot 10^{-3}$		
		79.87	$3.97 \cdot 10^{-3}$		
d	CH_2OAc	70.00[a])	$4.32 \cdot 10^{-4}$	24.00	− 4.27
		65.29	$2.59 \cdot 10^{-4}$		
		75.47	$7.76 \cdot 10^{-4}$		
		85.64	$2.08 \cdot 10^{-3}$		
e	CH_2OTs	70.00[a])	$1.40 \cdot 10^{-4}$	24.52	− 5.00
		72.19	$1.76 \cdot 10^{-4}$		
		80.33	$4.15 \cdot 10^{-4}$		
		92.56	$1.37 \cdot 10^{-3}$		

Table 2 (cont.)

	R	*T* [°]	*k* [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol·degree]
f	$COOCH_3$	70.00[a])	$8.46 \cdot 10^{-5}$	24.74	− 5.35
		80.33	$2.53 \cdot 10^{-4}$		
		90.53	$6.90 \cdot 10^{-4}$		
		99.84	$1.68 \cdot 10^{-3}$		
g	CN	70.00[a])	$4.00 \cdot 10^{-6}$	24.95	− 10.80
		110.20	$2.08 \cdot 10^{-4}$		
		120.40	$4.93 \cdot 10^{-4}$		
		130.58	$1.15 \cdot 10^{-3}$		
h	COONa	70.00[a])	$3.27 \cdot 10^{-2}$	26.48	11.55
		32.30	$2.39 \cdot 10^{-4}$		
		40.62	$8.06 \cdot 10^{-4}$		
		50.08	$2.78 \cdot 10^{-3}$		
i	CH_2OH	70.00[a])	$2.93 \cdot 10^{-3}$		
		53.07	$4.74 \cdot 10^{-4}$		
		59.96	$1.02 \cdot 10^{-3}$		
		66.52	$2.04 \cdot 10^{-3}$		

[a]) Extrapolated.

Table 3. *First-Order Rate Constants for* 10^{-3} M *6-exo-R-2-exo-bicyclo[2.2.2]octyl* p-*Toluenesulfonates* **12** *in 97%* (w/w) *TFE*

	R	*T* [°]	*k* [s^{-1}]		R	*T* [°]	*k* [s^{-1}]
a	H	70.00[a])	$6.10 \cdot 10^{-2}$	**c**	CH_2OCH_3	70.00	$2.48 \cdot 10^{-3}$
		11.74	$2.51 \cdot 10^{-4}$	**d**	CH_2OAc	70.00	$4.38 \cdot 10^{-4}$
		19.94	$6.49 \cdot 10^{-4}$	**e**	CH_2OTs	70.00	$7.83 \cdot 10^{-5}$
		30.62	$1.86 \cdot 10^{-3}$	**f**	$COOCH_3$	70.00	$4.65 \cdot 10^{-5}$
b	CH_3	70.00[a])	$5.15 \cdot 10^{-2}$	**g**	CN	70.00[a])	$1.68 \cdot 10^{-6}$
		20.04	$3.95 \cdot 10^{-4}$			99.76	$2.50 \cdot 10^{-5}$
		30.62	$1.23 \cdot 10^{-3}$			109.87	$5.69 \cdot 10^{-5}$
		40.54	$3.53 \cdot 10^{-3}$			119.88	$1.23 \cdot 10^{-4}$

[a]) Extrapolated.

Table 4. *First-Order Rate Constants for* 10^{-3} M *6-exo-R-2-endo-bicyclo[2.2.2]octyl* p-*Toluenesulfonates* **13** *in 97%* (w/w) *TFE*

	R	*T* [°]	*k* [s^{-1}]		R	*T* [°]	*k* [s^{-1}]
b	CH_3	70.00[a])	$9.23 \cdot 10^{-2}$	**d**	CH_2OAc	70.00	$2.61 \cdot 10^{-3}$
		11.74	$2.34 \cdot 10^{-4}$	**e**	CH_2OTs	70.00	$7.47 \cdot 10^{-4}$
		19.94	$6.22 \cdot 10^{-4}$	**f**	$COOCH_3$	70.00	$4.45 \cdot 10^{-4}$
		30.62	$2.08 \cdot 10^{-3}$	**g**	CN	70.00[a])	$4.77 \cdot 10^{-6}$
c	CH_2OCH_3	70.00[a])	$1.27 \cdot 10^{-2}$			99.77	$8.07 \cdot 10^{-5}$
		19.94	$3.83 \cdot 10^{-3}$			109.87	$1.92 \cdot 10^{-4}$
		30.62	$1.54 \cdot 10^{-4}$			119.89	$4.30 \cdot 10^{-3}$
		40.54	$5.20 \cdot 10^{-4}$				

[a]) Extrapolated.

ment, which causes the rate constant to decrease slightly with time, was not observed in the C(6)-substituted BO series **12** and **13**, whereas the rate decreased by a factor of 1.8 in the case of **12a**.

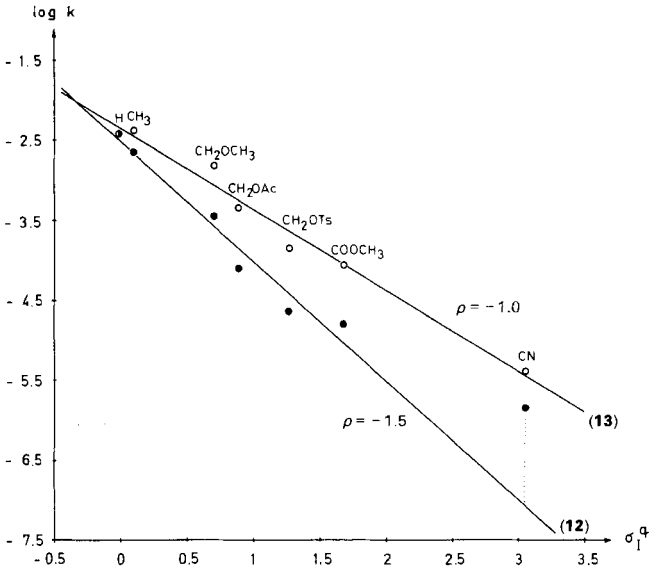


Fig. 1. *Plots of log* k *for 6-*exo*-substituted 2-*exo- (**12**) *and 2-*endo-(**13**) *bicyclo[2.2.2]octyl* p*-toluenesulfonates, in 80%* (v/v) *EtOH, against inductive substituent constants* σ_I^q. Point for **12g** (acceleration = 18) not included in regression.

Results and Discussion. – *Fig. 1* shows that the logarithms of the rate constants (log k) for the series **12** and **13**, **a**–**g**, in 80% EtOH correlate well with the respective inductive substituent constants ρ_I^q, except the points for **12g**, **h**, and **i**, which were omitted from the plots for the reasons given below. The correlations confirm the dominating role of the I effect of substituents (including the H-atom) in controlling the rates of both series. The regression lines correspond to ρ_I values of −1.5 and −1.0 for **12** and **13**, respectively; *i.e.* the rates of the *exo*-BO series **12** are less sensitive to substituents at

Table 5. *First-Order Rate Constants for* **12** *and* **13**, **a**–**i**, *and* k_1/k_{12}[a]), k_{13}/k_{12} *and* k_{13}/k_3[a]) *Rate Ratios at 70°*

	R	k_{12}	k_{13}	k_1/k_{12}	k_{13}/k_{12}	k_{13}/k_3
a	H	$3.70 \cdot 10^{-3}$	$3.70 \cdot 10^{-3}$	7.1	1	44
b	CH_3	$2.23 \cdot 10^{-3}$	$4.18 \cdot 10^{-3}$	4.9	1.9	70
c	CH_2OCH_3	$3.58 \cdot 10^{-4}$	$1.53 \cdot 10^{-3}$		4.3	
d	CH_2OAc	$7.91 \cdot 10^{-5}$	$4.32 \cdot 10^{-4}$		5.5	
e	CH_2OTs	$2.31 \cdot 10^{-5}$	$1.40 \cdot 10^{-4}$		6.1	
f	$COOCH_3$	$1.58 \cdot 10^{-5}$	$8.46 \cdot 10^{-5}$	0.4	5.4	49
g	CN	$1.44 \cdot 10^{-6}$[b])	$4.00 \cdot 10^{-6}$	0.08	2.8	29
h	COONa	$1.91 \cdot 10^{-2}$[b])	$3.72 \cdot 10^{-2}$[b])	3.7	1.7	282
i	CH_2OH	$8.52 \cdot 10^{-4}$[b])	$2.93 \cdot 10^{-3}$[b])	7.0	1.7	67

[a]) k_1 and k_3 values taken from [1a].

[b]) Accelerations calculated from the regression line in *Fig. 1*: **12g**, 18; **12h**, 73; **12i**, 2.3; **13h**, 39; **13i**, 2.8.

C(6) than the rates of the *exo*-NB series **1** ($\rho = -2.0$). This is also borne out by the k_1/k_{12} ratios *(Table 5)* which are larger than one when R is an electron donor, such as H and CH_3, but much smaller when R is an electron acceptor, such as $COOCH_3$ and CN. Since the distances through space and through the bonds are practically the same in **1** and **12**, the unequal ρ_I values must be due mainly to different bridging strains in the BO and NB structures.

On the other hand, the rates of the 2-*endo*-BO series **13** ($\rho_I = -1.0$) are more sensitive to substituents at C(6) than the rates of the 2-*endo*-NB series **3** ($\rho_I = -0.78$); *i.e.* inductivity is higher in the BO series **13** than in the NB series **3**. This observation supports the view that bridging of C(6) is less hindered by the departing anion because its trajectory is further away from C(6).

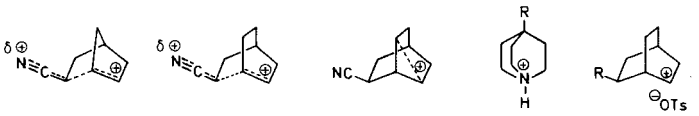
It could be argued that nucleophilic solvent assistance to the ionization of the cyano tosylate **12g** should also cause its point in the plot *(Fig. 1)* to deviate upwards. In fact, hydrolysis yielded the inverted 2-*endo*-alcohol **23** only *(Table 6)*, as if dorsal solvent attack had occurred. If this were the case, however, the acceleration should be smaller in the far less nucleophilic solvent 97% TFE. In fact, a larger acceleration, namely by a factor of 46 is observed, because the higher ionizing power of this solvent favors a more ionic transition state. It is also noteworthy that the unsubstituted BO tosylate **12a** reacts 16 times faster in 97% TFE than in the far more nucleophilic 80% EtOH. As in the case of the 2-*exo*- and 2-*endo*-NB tosylates **1a** and **2a**, respectively [1f], this result confirms that these bicyclic compounds solvolyze without nucleophilic solvent participation and, hence, by a limiting S_N1 mechanism [2a].

Table 6. *Yields of the Hydrolysis Products* (in %)[a] *of the* 2-exo-*BO Tosylates* **12** *and of the* 2-endo-*BO Tosylates* **13** (in brackets) *in 70%* (v/v) *Dioxane*[b]

	R	22	23	24	25	26	27	28	29
a	H	61			39				
b	CH_3	48(10)	20(50)	5(2.5)	–	20(3.5)	3(30)		
c	CH_2OCH_3	35(13)	45(55)	12(5)					
d	CH_2OAc	14(9)	55(65)	21(17)					
e	CH_2OTs	6(9)	55(62)	38(25)					
f	$COOCH_3$	2(5)	65(66)	22(13)			1(3)	6(7)	4(6)
g	CN	– (11)	55(41)	39(42)					

[a] Beside unidentified rearrangement products.
[b] Taken from [6].

A striking feature of the substituted 2-*endo*-BO tosylates **13** is that they all react somewhat faster than the corresponding 2-*exo*-BO tosylates **12** (k_{13}/k_{12} in *Table 5*). Furthermore, the 2-*endo*-BO tosylates **13** are all more reactive than the corresponding 2-*endo* NB tosylates **3** (k_{13}/k_3 in *Table 5*) due to the fact that bridging between C(7) and C(2) is constant in the series **13**, where the 'substituents' at C(7) are the H-atoms. In contrast, the 2-*endo*-NB tosylates **3** react much more slowly than their *exo*-epimers **1**, except when they possess strong *-I* substituents, such as CH_3COO, Br or CN at C(6) [1a]. In these cases the rates of the *exo*-epimers are greatly reduced so that k_1/k_3 ratios fall below one.



17 18 19 20 21

As mentioned above, **12g** reacts *ca.* 18 times faster than calculated from its σ_I^q value on the regression line in *Fig. 1 (Footnote b* in *Table 5)*. A similar acceleration was observed in the solvolysis of 6-*exo*-cyano-2-*exo*-norbornyl tosylate **1** (R = CN) [1a] and ascribed to C,C-hyperconjugation involving the electrons of the CN-group and the electrons of the C(1)–C(6) σ-bond as shown in **17** [1d]. This conclusion appears justified in view of the finding of *Gassman et al.* [8] that the usually latent conjugative effect of the CN-group more than balances its strong -*I* effect when attached to a cationic center. A comparable situation arises in the NB cation **17** as well as the BO cation **18** when positive charge is transferred to C(6) by hyperconjugation of the C(1)–C(6) σ-bond.

It is significant that the accelerating effect of the CN-group at C(6) is not observed in the solvolysis of the 2-*endo*-NB and 2-*endo*-BO tosylates **3** (R = CN) and **13g**, respectively[7]), where C,C-hyperconjugation is expected to be weak for stereoelectronic reasons. The fact that **13g** yields almost four times more retained 2-*endo*-alcohol **23** than inverted 2-*exo*-alcohol **22** points to a weakly C(7) bridged transient cation **19**.

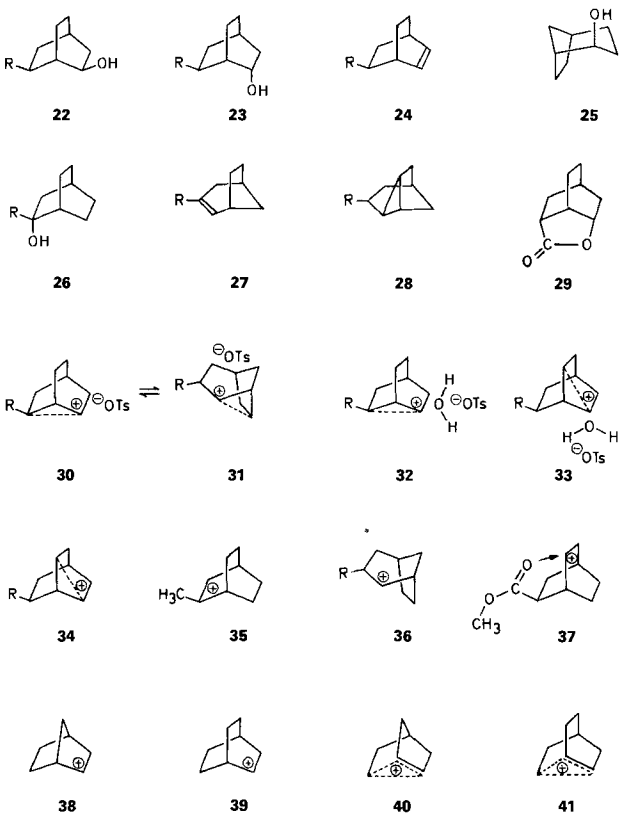
Substantial accelerations also resulted when the substituent at C(6) was $COO^{\ominus}$ and CH_2OH as in **12** and **13**, **h** and **i**, *(Footnote 6* in *Table 5)*. These accelerations are comparable to those observed in the norbornane series **1** and **3** and are normal for groups that are electrofugal in solvolytic fragmentation [9] [10]. These rate increases were ascribed to enhanced through-space induction caused by the stronger electron attraction of $C^{\oplus}$ as compared to $N^{\oplus}$ in quinuclidinium salts **20**, the models used to derive inductive substituent constants σ_I^q [3].

The log *k* values for the series **12** and **13** in 97% TFE also correlated satisfactorily with the respective σ_I^q values *(Fig. 2)*. The respective ρ_I values of -2.0 and -1.4 are 33% and 40% higher than those obtained in 80% EtOH, a finding that indicates less bridging and, hence, less charge dispersal in the transition state for **12** and **13** than for the norbornane series **1** [1f].

The nature and yields of the products *(Table 6)* complement the above kinetic results. Hydrolysis of the unsubstituted BO tosylate **12a** (or **13a**) yielded 61% of the corresponding alcohol **22a** beside 39% of rearranged *exo*-bicyclo[3.2.1]octan-2-ol **25.** Since the starting material **12a** was racemic, it could not be determined whether **22a** was formed with retention or inversion at C(2) or both. It had, however, already been established by *Walborsky* and his coworkers [11] [12] and by *Goering & Fickes* [13] that the solvolyses of optically active tosylate **12a** in AcOH and in 80% acetone lead to partially racemized bicyclo[2.2.2]octan-2-ol **22a** and to *exo*-bicyclo[3.2.1]octan-2-ol **25**, *i.e.* with predominant retention[8]). This result indicates rapid equilibration of weakly

[7]) No accelerating effect of a β-CN-group in tertiary halides and sulfonates was observed sofar even when the geometry was favorable for C,C-hyperconjugation.

[8]) In both [12] [13a] the authors advocate a transient asymmetric 'nonclassical' ion with 'leakage' to an unbridged 'classical' 2-bicyclo[2.2.2]octyl cation, as discussed later.



bridged bicyclo[2.2.2]oct-2-yl and bicyclo[3.2.1]oct-2-yl cations **30** and **31** (R = H) the respective precursors of the partially racemized alcohols **22a** and **25**. This facile rearrangement merely requires the tightening of a partial bond and the loosening of a full bond in the cations **30** and **31**, respectively. It is noteworthy that hydrolysis of *exo*-bicyclo[3.2.1]oct-2-yl tosylate **16** under the same conditions as for **12a** yielded the same two alcohols **22a** and **25**, but in distinctly different ratios of 54% and 46%[9]) [1h]. This result indicates that solvent attack occurs before equilibrium has been reached.

The steric course of hydrolysis is more easily followed when the H-atom at C(6) of **12a** is replaced by a CH_3-group, which has a slightly more positive σ_I^q value (0.11) than H (0.00) and, therefore, lowers the rate slightly *(Table 5)*. Hydrolysis of **12b** yielded 48% of the *exo*-alcohol **22b** with retention beside 20% of the 2-*endo*-alcohol **23b** with inversion *(Table 6)*. In addition, 20% of 2-methylbicyclo[2.2.2]octan-2-ol (**26**) and 3% of 3-methylbicyclo[3.2.1]-2-ene (**27**) were formed beside unidentified material. A different ratio of the same products was obtained from the 2-endo-tosylate **13b** *(Table 1)*, namely 50% of the 2-endo-alcohol **23b** with retention and 10% of the 2-exo-alcohol **22b** with inversion. In addition, 2.5% of the olefin **24**, 30% of the rearranged olefin **27b**, and 3.5% of the tertiary alcohol **26** were found.

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[9]) According to *Goering & Fickes* [13b], the same ratio of alcohols **22a** and **25** is obtained upon hydrolysis in 80% acetone.

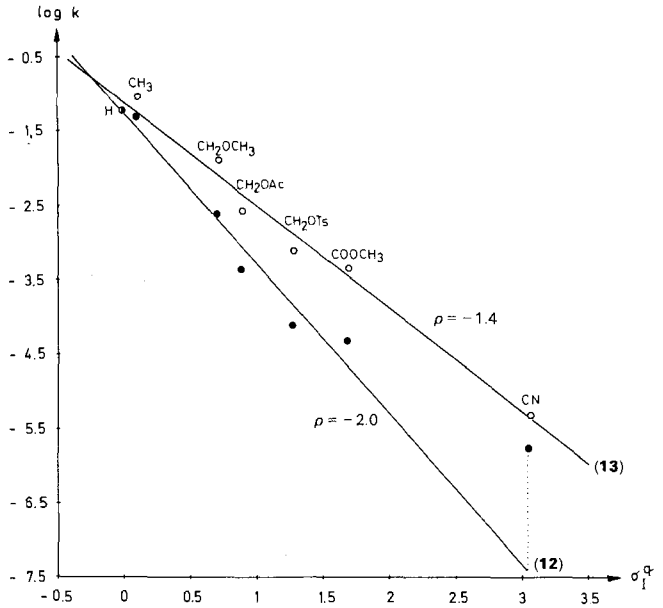

Fig. 2. *Plots of log* k *for* 6-exo-*substituted* 2-exo- (**12**) *and* 2-endo- (**13**) *bicyclo[2.2.2]octyl* p-*toluenesulfonates, in* 97% (w/w) TFE, *against inductive substituent constants* σ_I^q. Point for **12g** (acceleration = 48) not included in regression.

It is remarkable that both tosylates **12b** and **13b** yield alcohols with practically the same amount (*ca.* 49%) of retention at C(2) (accuracy of the gaschromatographic analysis ± 1.5%), a finding that suggests that these products are derived from stereoisomeric solvent-separated ion pairs, namely **32** and **33**, respectively. Due to shielding by solvent and anion, these cations are asymmetrically bridged and attacked by solvent mainly on the unbridged side. If the cations were symmetrically bridged as in **15a**, the same ratio of inverted and retained alcohols **22b** and **23b** should be obtained from either **12b** or **13b**. Since inverted alcohol is also obtained in both cases, namely 20% from **12b** and 10% from **13b**, bridging is not strong enough to prevent entirely solvent attack on the unbridged side of the cations **32** and **33**. This finding is in marked contrast to the behavior of 2-norbornyl cations [1a,e].

As bridging of C(6) is reduced by electron-attracting substituents in **12c–f**, less retained **22** and more inverted alcohols **23** are obtained. In the case of **12f**, the yields of **22f** and **23f** were 2% and 65%, respectively. This result points to an intermediate **34f** which is more strongly bridged by C(7) than by C(6) and hence undergoes more solvent attack on the *endo*-side. In the *endo*-series **13c–f**, however, the ratio of *endo*- to *exo*-attack is even increased, a result that indicates predominant bridging of C(2) by C(7) in the solvent-separated ion pairs **33**.

The small amounts of the tertiary alcohol **26** obtained from **12b** and **13b** are readily explained by a C(6)→C(2) H-shift in the cations **32b** and **33b** to yield the tertiary cation **35**. The rearranged olefins **27b** and **27f** and the tricyclic compound **28** are derived from the rearranged bicyclo[3.2.1]oct-2-yl cation **36**, which must have been

formed by migration of C(7) in the corresponding bicyclo[2.2.2]octyl cations. The low yields of the lactone **29** obtained from the esters **12f** and **13f**, 4% and 6%, respectively, can only be explained by a C(7)→C(2) H-shift in the cation **34f** to yield **37**. Hydrolysis of the cyano *exo*-tosylate **12g** led to the 2-*endo*-alcohol **23g** with complete inversion at C(2), confirming the absence of significant bridging by C(6). The cyano *endo*-tosylate **13g**, however, reacted with predominant retention at C(2) to give **23g** in 41% yield beside 11% of the inverted alcohol **22f**. In both cases considerable amounts of 2-cyanobicyclo[2.2.2]oct-5-ene (**24g**) were also formed.

Conclusions. – These results confirm that the ionization of the 2-*exo*-BO series **12** is accompanied by graded bridging of C(6). Although weaker than in the 2-*exo*-NB series **1**, bridging is sufficiently strong to cause predominant retention at C(2). With *-I* substituents at C(6), however, inversion prevails. In the 2-*endo*-BO series **13**, bridging of C(6) is reduced due to anion repulsion. Nevertheless, substitution occurs with predominant retention at C(2) because of almost constant bridging by the C(7) CH_2-group.

It follows that the free and unsubstituted BO cation **15a** is symmetrically bridged and that symmetry is lost when substituents are attached to C(6), especially when their *I* effects differ from that of the H-atom. Ion pairs, such as **14** and **30** are necessarily unsymmetrically bridged due to the presence of the counter ion $TsO^{\ominus}$.

These conclusions are at variance with current views which regard carbocations as being either unbridged (classical) or bridged (nonclassical), the paradigm of the latter species being the 2-norbornyl cation. This dichotomy, which originated in the pioneering work of *Winstein* [14], is particularly stressed in the most recent review of the subject by *Barkhash* [15]. It also forms the basis of past [12] [13] and current [16] discussions of the bicyclo[2.2.2]octyl-2-cation. The nonclassical ion concept is based on the assumption that the two electrons which constitute the C(1)–C(6) σ-bond in the *Lewis* structures of the NB and BO cations **38** and **39** are released to form the two-electron-three-center bonds, involving C(1), C(2), and C(6), in the nonclassical cations **40** and **41**, respectively [2c]. Apart from inherent stereochemical difficulties [1h], this rigorous allotment of electrons is not borne out by the graded effect of substituents, including the H-atom, on the rates and products of the substituted BO tosylates **12** and **13** as well other bi- and tricyclic structures [2a].

As pointed out in [2a], electron density is high not only between adjacent but also between alternate C-atoms, so that a 1,3-bonding interaction results when ionization generates an electron deficient center, as shown in **5**. The strength of this interaction, however, is variable and depends on distance and bridging strain as well as the *I* effect of substituents. Also, the remarkable effect of substituents on rates and products renders the view, that only the C(2)–C(3) bonding electron pair in **5** is involved in bridging, untenable. In fact, recent results suggest that all neighboring C-atoms contribute to charge dispersal according to their distance from the reaction center and to bridging strain [17].

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