80. Differential Bridging in the Solvolysis of Epimeric Bicyclic Sulfonates

Norbornanes, Part 17

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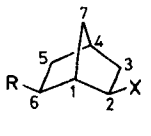
Summary

The solvolysis rates and products of the 2-*exo*- and 2-*endo*-norbornyl, bicyclo[3.2.1]oct-8-yl, bicyclo[3.3.1]non-2-yl, bicyclo[3.2.1]oct-6-yl, bicyclo[3.2.1]oct-2-yl and bicyclo[3.2.2]non-6-yl *p*-toluenesulfonates **10**–**15**, respectively, are reported. The *exo*/*endo* rate ratios for these epimeric secondary tosylates in 80% EtOH varied from 1125 for **11** to 1.6 for **15**. The relative rates varied between 2278 for *exo*-**10** and $4 \cdot 10^{-3}$ for *endo*-**11**. The hydrolysis products were mainly rearranged alcohols and olefins. The unrearranged alcohols from the *exo*-tosylates were formed with complete or predominant retention of configuration, whereas those derived from the *endo*-tosylates were mostly inverted. These results confirm the hypothesis that relative rates, as well as products, are largely determined by the degree of bridging between the cationic center and a dorsal C-atom in the transition state and in the resulting ion pairs. Since bridging is a directed bonding interaction, it is subject to the same angle and conformational strains as ordinary covalent bonds. But bridging requires less geometrical change than the formation of normal bonds and of nonclassical ions.

Introduction. – The frequently disparate solvolytic reactivity of epimeric bicyclic halides and sulfonates has attracted attention ever since *Winstein & Trifan* reported the rates and products of the 2-*exo*- and 2-*endo*-norbornyl *p*-bromobenzenesulfonates (brosylates) **1a** and **2a**, respectively, in AcOH [1]. They observed that the *exo*-epimer **1a** reacted *ca.* 350 times as fast as the *endo*-epimer **2a** and that both compounds yielded the 2-*exo*-acetate **1b** as the sole substitution product[1]). Therefore, **1a** had reacted with retention of configuration at C(2), **2a** with inversion. The authors attributed these results to participation of the C(1)–C(6) bond (so-called σ-participation) in the ionization of **1a** with formation of the symmetrical nonclassical ion **5**, R = H[2]), and to the absence of such participation in the ionization of the *endo*-epimer **2a**. As is well

[1]) The fact that the 2-*exo*-acetate **1b** from optically active **1a** was completely racemized, and **1b** from optically active **2a** was predominantly racemized shows that degenerate rearrangements had occurred [1].

[2]) In this article the term 'nonclassical' is restricted to carbocations which are assumed to undergo three-center-two-electron bonding as in **5**; 'classical' refers to unbridged cations.



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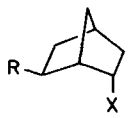

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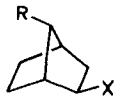

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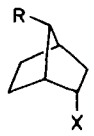

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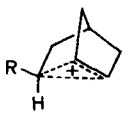
a R = H, X = *p*-$BrC_6H_4SO_3$
b R = H, X = CH_3COO
c R = variable substituent, X = *p*-$CH_3C_6H_4SO_3$



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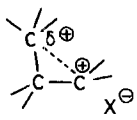

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known, this hypothesis was the cause of a protracted controversy over the fine-structure of the norbornyl cation [2] [3][3]).

Meanwhile, studies of the effect of substituents at C(6) and C(7) on the rates and products of the 2-*exo*- and 2-*endo*-norbornyl *p*-toluenesulfonates (tosylates) **1c**–**4c** (R = variable substituent) have led to a different view of the factors that determine the formation and subsequent reactions of carbocations in solution. Most important was the finding that substituents, including hydrogen, control solvolysis rates by their inductive (*I*) effects and that these effects are transmitted far more strongly from C(6) to C(2) than from C(7) to C(2) [5]. Inductivity[4]) is, therefore, a directional property that differs widely in norbornyl derivatives even when the number of intervening bonds and the direct distances are the same. It was also found that inductivity controls the configuration of the substitution products, *i.e.* whether these are formed with retention or inversion at the reaction center.

It was, therefore, concluded that through-space induction (the direct effect) involves graded bridging between the cationic center and a β-C-atom[5]), as in **6** [3] [4], and that this partial or secondary bonding is already effective in the transition state. Thus, in the transition state for the *exo*-series **1** bridging between C(6) and C(2), as in **7**, is strong when R is an electron donor relative to the cationic center, and weak or negligible when R is an electron acceptor. In the transition state for the *endo*-series **4**, however, bridging between C(7) and C(2) is weak regardless of the *I* effect of R, as illustrated by the unbridged formula **8**. On this basis a 2-norbornyl cation can be formulated as an unsymmetrically 1,3-bridged ion **9**.

The widely different tendency of C(6) and C(7) to undergo bridging was attributed to the strain involved in partial bonding of these atoms to C(2) [3] [4a]. Thus, bridging

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[3]) See the recent reviews on the nonclassical ion problem: [4a–d].

[4]) Inductivity was defined as the sensitivity of reaction rates to the *I* effect of substituents σ_I^q. It is expressed quantitatively by the magnitude of the reaction constant ρ in the equation $\log k/k_0 = \rho\sigma_I^q$ [4] [5].

[5]) Bridging can also involve more remote C-atoms, as in 1,4-bridging [4a].

7 **8** **9a** **9b**

between C(6) and C(2), generates less strain than bridging between C(7) and C(2), because a six-membered ring is subdivided into *quasi* five- and three-membered rings in the former case, whereas a five-membered ring would be subdivided into more strained *quasi* four- and three-membered rings in the latter. On this basis bridging is subject to the same stereochemical constraints as ordinary bonding[6]). It was also suggested that optimal bridging of a cationic C-atom by a neighboring C-atom requires that both centers adopt the trigonal bipyramidal configuration of pentacoordinate atoms. Deviations from this preferred geometry should then lead to an increase in bridging strain [3] [4a] [6].

The transient cations in the solvolysis of unsubstituted 2-*exo*- and 2-*endo*-norbornyl sulfonates **1** and **2**, R = H, were represented as a pair of rapidly interconverting unsymmetrically bridged carbocations **9a** and **9b**[7])[8]) rather than as a static symmetrically bridged nonclassical ion **5**, R = H. While formula **9** implies that *all* the electrons around C(6) are involved in bridging, formula **5** stresses that only the electron pair constituting the C(6)–C(1) bond are engaged in three-center-two-electron bonding[9]). This rigorous allotment of σ-electrons is not borne out by the graded effect of substituents, including hydrogen, on rates and products. Moreover, 6-*exo*-substituted norbornyl tosylates **1c** and **2c**, some of which exhibit higher *exo*/*endo* rate ratios than the parent tosylates, cannot form symmetrical cations like **5** due to their overall asymmetry. Nevertheless, their rates correlate equally well with the respective inductive substitutent constants as that of **1c**, R = H [5a]. As will be shown below, even the ability to form a symmetrical nonclassical ion does not confer special stability as was assumed for the nonclassical norbornyl ion **5**, R = H.

The concept of differential bridging strain as a major factor contributing to the high rate ratios of the norbornyl tosylates *exo*- and *endo*-**10** *(cf. Table 2)* should apply to other bicyclic secondary sulfonates, such as the *exo*- and *endo*-tosylates **11**–**15**. These compounds resemble the norbornyl tosylates **10** in that the nucleofugal groups are located next to one or two bridgehead C-atoms where dorsal nucleophilic attack is severely hindered [7]. They should, therefore, also ionize without nucleophilic solvent assistance and lead to transient carbocations, a precondition for bridging by the nearest dorsal methylene groups. In these cases the 'substituents' are H-atoms. Since steric hindrance to ionization is absent or negligible in the norbornyl series **10** [5c], it can also

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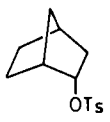
[6]) For a more detailed account see [4a].

[7]) The dashed line denotes a longer and hence weaker bond.

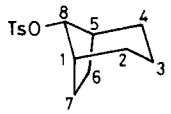
[8]) In previous articles this facile degenerate rearrangement was likened to a skeletal vibration with an energy barrier of less than 3 kcal/mol [3] [4] [5a].

[9]) See the reviews [2] [4c].

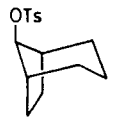
exo-**10**



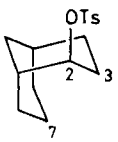
endo-**10**



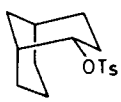
exo-**11**



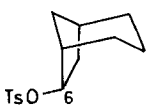
endo-**11**



exo-**12**

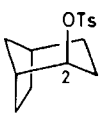


endo-**12**

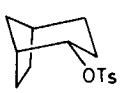


exo-**13**

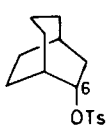
endo-**13**



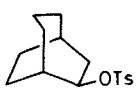
exo-**14**



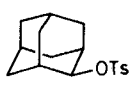
endo-**14**



exo-**15**



endo-**15**



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be disregarded in the epimeric bicyclic systems **11**–**15**. In this article the rates and products of these compounds are reported and discussed with reference to structure[10]).

Results. – The alcohols from which the *exo*- and *endo*-tosylates **11**–**15** are derived were known (see *Exper. Part*). In a few cases the rates and products of their tosylates or brosylates in AcOH had been measured. In the present case rates were determined in 80% (v/v) EtOH, products in 70% (v/v) dioxane.

Table 1 lists the first-order rate constants for *exo*- and *endo*-**10**–**15** including revised values for *exo*-**10**. Rate constants were steady for seven to eight half lives except in the case of *exo*-**14** where they increased slightly with time due to isomerization to bicyclo[2.2.2]oct-2-yl tosylate (**44**)[11]) (see *Discussion*). Rate constants were therefore calculated from measurements during the first half live. The tosylate *endo*-**11** was too unreactive for convenient conductometric rate measurements below 130°, and at higher temperature measurements were less accurate. The *exo*/*endo* rate ratios for the tosylates **10** to **15** are listed in *Table 2* together with their rates relative to 2-adamantyl tosylate **16**. This compound was chosen for comparison because it resists bridging between C(2) and C(4) and undergoes less than 0.5% rearrangement [9], presumably because bridging would entail severe distortion of the practically strain-free chair conformation. Products were determined quantitatively using GLC and by comparison of retention times with those for authentic samples.

Discussion. – The unsubstituted 2-norbornyl tosylates *exo*- and *endo*-**10** are typical of compounds that ionize with very strong and very weak bridging, respectively [5a]. This is reflected in the large *exo*/*endo* rate ratio of 311 (at 70°) and the high relative rate of *exo*-**10** based on 2-adamantyl tosylate (**16**) *(Table 2)*. It is further supported by

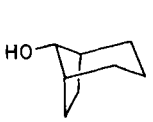
[10]) For preliminary communications see [3] [4] [6].

[11]) This isomerization has been thoroughly studied by *Goering et al.* [8].

Table 1. *Conductometric First-Order Rate Constants for 10^{-3} M Solutions of the* exo- *and* endo-p-*Toluenesulfonates* **10–15** *in 80% (v/v) EtOH*

		T [°C]	k [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol °C]
2-Norbornyl	*exo*-**10**[a])	25.07	$2.48 \cdot 10^{-4}$	20.22	− 7.12
		35.02	$8.00 \cdot 10^{-4}$		
		45.00	$2.35 \cdot 10^{-3}$		
		54.95	$6.39 \cdot 10^{-3}$		
		70.00	$2.62 \cdot 10^{-2}$ [b])		
	endo-**10** [5a]	70.00	$8.42 \cdot 10^{-5}$ [b])		
Bicyclo[3.2.1]oct-8-yl	*exo*-**11**	70.00	$4.61 \cdot 10^{-5}$ [b])	25.9	− 3.3
		80.00	$1.39 \cdot 10^{-4}$		
		90.00	$3.94 \cdot 10^{-4}$		
		130.00	$1.53 \cdot 10^{-2}$		
	endo-**11**	130.00	$1.36 \cdot 10^{-5}$		
Bicyclo[3.3.1]non-2-yl	*exo*-**12**	52.00	$4.56 \cdot 10^{-4}$	23.4	− 2.0
		59.50	$1.05 \cdot 10^{-3}$		
		65.00	$1.91 \cdot 10^{-3}$		
		70.00	$3.21 \cdot 10^{-3}$ [b])		
	endo-**12**	50.00	$7.38 \cdot 10^{-6}$	22.9	−11.2
		65.00	$3.79 \cdot 10^{-5}$		
		69.92	$6.22 \cdot 10^{-5}$		
		70.00	$6.29 \cdot 10^{-5}$ [b])		
Bicyclo[3.2.1]oct-6-yl	*exo*-**13**	70.00	$9.68 \cdot 10^{-5}$ [b])	24.9	− 4.50
		80.00	$2.79 \cdot 10^{-4}$		
		90.00	$7.77 \cdot 10^{-4}$		
		100.00	$1.98 \cdot 10^{-3}$		
	endo-**13**	70.00	$7.50 \cdot 10^{-6}$ [b])	24.8	−10.1
		100.00	$1.51 \cdot 10^{-4}$		
		110.00	$3.73 \cdot 10^{-4}$		
		120.00	$8.70 \cdot 10^{-4}$		
Bicyclo[3.2.1]oct-2-yl[c])	*exo*-**14**	50.12	$3.36 \cdot 10^{-4}$	22.76	− 4.18
		59.80	$9.66 \cdot 10^{-4}$		
		69.43	$2.62 \cdot 10^{-3}$		
		70.00	$2.77 \cdot 10^{-3}$ [b])		
	endo-**14**	44.81	$1.18 \cdot 10^{-5}$	24.6	− 3.7
		54.81	$3.98 \cdot 10^{-5}$		
		64.81	$1.26 \cdot 10^{-4}$		
		70.00	$2.23 \cdot 10^{-4}$ [b])		
Bicyclo[3.2.2]non-6-yl	*exo*-**15**	40.00	$1.14 \cdot 10^{-4}$	23.20	− 1.64
		50.00	$3.79 \cdot 10^{-4}$		
		60.00	$1.17 \cdot 10^{-3}$		
		70.00	$3.39 \cdot 10^{-3}$ [b])		
	endo-**15**	50.00	$2.55 \cdot 10^{-4}$	22.9	− 4.19
		60.00	$7.62 \cdot 10^{-4}$		
		70.00	$2.17 \cdot 10^{-3}$		
2-Adamantyl **16**[d])		70.00	$1.15 \cdot 10^{-5}$	27.1	− 2.5

[a]) The revised rate constants for *exo*-**10** were measured by Dr. *P. Sawlewicz* and checked by *Yao Guo-Wei*.
[b]) Extrapolated.
[c]) *R. Hanreich* (unpublished).
[d]) Ph. D. thesis *Gerhard Wittwer*, Basel 1982.



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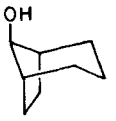

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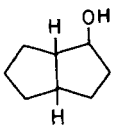

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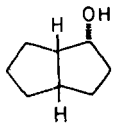

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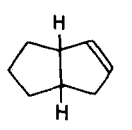

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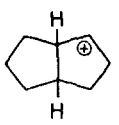

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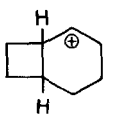

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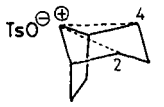

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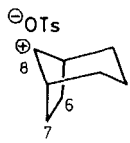

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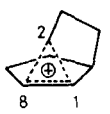

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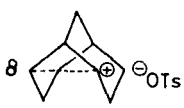

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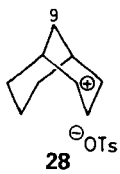

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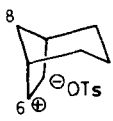

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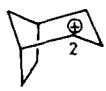

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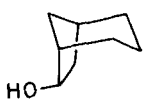

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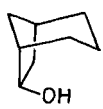

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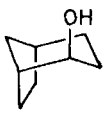

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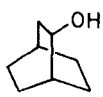

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the formation of *exo*-norbornan-2-ol in both cases, *i.e.* with retention from *exo*-**10** and with inversion from *endo*-**10** [5a].

The *exo*/*endo* rate ratio of 1125 (at 130°) for the epimeric bicyclo[3.2.1]oct-8-yl tosylates **11** is even larger than that for the norbornyl tosylates **10** *(Table 2)*, although the former are less reactive by a factor of *ca.* 10^3. Whereas *exo*-**11** hydrolyzes to the *exo*-alcohol **17** with retention, *endo*-**11** yields the latter with inversion at C(8) and only

Table 2. *Relative Rate Constants and* exo/endo *Rate Ratios for the* p-*Toluenesulfonates* **10–15** *in 80%* (v/v) *EtOH at 70°*

		k (rel)	k_{exo}	k_{endo}
2-Norbornyl	*exo*-**10**	2278	311[a])	
	endo-**10**	7.3		
Bicyclo[3.2.1]oct-8-yl	*exo*-**11**	4.5		
	endo-**11**	$4 \cdot 10^{-3}$	1125	(130°)
Bicyclo[3.3.1]non-2-yl	*exo*-**12**	279		
	endo-**12**	5.5	51	
Bicyclo[3.2.1]oct-6-yl	*exo*-**13**	8.4		
	endo-**13**	0.65	13	
Bicyclo[3.2.1]oct-2-yl	*exo*-**14**	247		
	endo-**14**	18.7	12	
Bicyclo[3.2.2]non-6-yl	*exo*-**15**	338		
	endo-**15**	189	1.6	
2-Adamantyl (**16**)		1		

[a]) Revised value (see *Table 1*).

Table 3. *Yields of Products* (in %) *from the Reaction of Epimeric* p-*Toluenesulfonates in 70% Dioxane*

	17 [10]	**18** [10]	**19** [10]	**20** [27]	**21** [10]
exo-**11**	14	–	28	14	44
endo-**11**	36	2	18	5	39
	34 [17]	**35** [17]	**36** [17]	**37** [23]	**38** [26]
exo-**13**	13	1	50	17	19
endo-**13**	60	–	11	12	17
	38 [26]	**40** [23]	**41** [23]		
exo-**14**	54	45	–		
endo-**14**	–	8	92		
	29 [28]	**52** [28]	**55** [28]		
exo-**15**	94	6	–		
endo-**15**	–	–	100		

small amounts of the retained alcohol **18** *(Table 3)*. In both cases the main products are the rearranged *exo*- and *endo-cis*-bicyclo[3.3.0]octan-2-ols **19** and **20**, respectively, beside the rearranged olefin **21**. They are derived from the bicyclo[3.3.0]oct-2-yl cation **22** and not from the isomeric and more strained bicyclo[4.2.0]oct-2-yl cation **23**.

These results, in conjunction with a consideration of relative bridging strain in the transition state for ionization of *exo*- and *endo*-**11**, indicate that partial bonding of C(8) to C(2) and the equivalent C(4), as shown in **24**, is much stronger than of C(8) to C(6) and C(7) in **25**. But a further factor must be responsible for the exceptionally low rates of *exo*- and *endo*-**11**.

Foote & Woodward [10], who made a thorough study of the acetolysis rates and products of these tosylates, attributed their low reactivity to the angle strain (i-strain) generated at C(8) during ionization[12]). In addition, hyperconjugation of the C–H

[12]) In the cation, the C(1)–C(8)–C(5) angle is constrained to be smaller than the preferred angle of 120°. The same factor accounts for the extremely low reactivity of 7-norbornyl tosylate, as pointed out by *Schleyer & Nicholas* [11].

bonds at C(1) and C(5) is excluded because they are orthogonal to the incipient p-orbital at C(8). Their data [10] leads to an *exo/endo* rate ratio of *ca.* 1553 in AcOH at 70°[13]) which is in reasonable agreement with the value of 1125 in 80% EtOH. Their acetolysis products also correspond well with those listed in *Table 3*. These authors assumed, however, that ionization of *exo*-**11** was assisted by participation of the C(1)–C(2) σ-bond and led directly to the nonclassical ion **26** which was subsequently converted to the acetates of the alcohols **17** and **19** by solvent attack at C(8) and C(1), respectively. Since the acetate of the *endo*-alcohol **20** was also formed, they were required to postulate an additional intermediate, namely the classical, *i.e.* unbridged *cis*-bicyclo[3.3.0]oct-2-yl cation **22**. It seems unlikely, however, that an overall unsymmetrical structure like **26** would have equivalent C(2)–C(1) and C(2)–C(8) partial bonds. The doubly 1,3-bridged cation **24**, in which the two equivalent dorsal C-atoms C(2) and C(4) are partially bonded to C(8) is, therefore, preferred. The structure **26** then represents the transition state for the rearrangement of the cation **24** to the cation **22**. On this basis, ionization and rearrangement are discrete processes. There is agreement, however, that *endo*-**11** ionizes without participation of the dorsal C(6) and C(7) because of the excessive bridging strain involved.

According to several structure determinations [12] the epimeric bicyclo[3.3.1]non-2-yl tosylates **12** prefer twin-chair conformations that are somewhat deformed due to the repulsive interaction between the *endo*-H-atoms at C(3) and C(7). The *exo/endo* rate ratio of 51 *(Table 2)* cannot be ascribed to differential solvent participation, for models show that nucleophilic attack is equally hindered in these epimers. *Schaefer & Flegal* [13], who observed an *exo/endo* rate ratio of 75 for the brosylates in AcOH, ascribed the lower rate of the *endo*-epimer to steric hindrance of ionization on the grounds that the environment of the nucleofuge in *endo*-**12** is similar to that in the corresponding 2-*endo*-norbornyl tosylate **10**. Now that steric bulk effects have been excluded in the latter case [5c], other factors such as differential bridging strain and C–H hyperconjugation should be considered.

It is not immediately clear, why bridging of C(2) by C(8) in the ionization to **27** should generate less strain than bridging of C(2) by C(9) in the incipient ion pair **28**. Models show, however, that incorporating two pentacoordinate C-atoms symmetrically in the eight-membered ring of **27** distributes the resultant angle-strain better than when they are incorporated in the six-membered ring of **28**. Also, the H-atoms at C(3) and C(7) are separated more in **27** due to the flattening of both six-membered rings. On this basis, *exo*-**12** derives more driving force from C-participation than does *endo*-**12**, a conclusion that is supported by the fact that the former reacts *ca.* 280 times as fast as 2-adamantyl tosylate **16**, while *endo*-**12** reacts only six times as fast *(Table 2)*.

Unfortunately, this conclusion is only partially verifiable by an analysis of the products, for *Schaefer & Flegal* [13] have reported that the only identifiable product (> 90%) from *exo*-**12** in AcOH is bicyclo[3.3.1]non-2-ene **29**. On the other hand *Felkin et al.* [14] have reported that roughly equal amounts of the acetates of *exo*- and *endo*-bicyclo[3.3.1]nonan-2-ol are formed from *endo*-**12** which confirms the absence of significant bridging in the *endo* ion pair **28**. Nevertheless, it is difficult to exclude C–H hyperconjugation as a factor contributing to the higher rate of *exo*-**12**. In fact, the

[13]) Their rate constants for *exo*-**11** increased somewhat with time due to isomerization.

axial tosyloxy group is favorably oriented for participation of the antiperiplanar C(3)–H bond in the ionization step[14]) and for the subsequent elimination to the olefin **29**. On the other hand, the *exo/endo* rate ratio of 51 for the tosylates **12** far exceeds the usual epimer rate ratio for cyclohexyl and *trans*-2-decalyl tosylates in 80% EtOH of *ca.* 5 [16]. There is, therefore, still a strong case for 1,3-bridging in the ionization of *exo*-**12**.

Since the *exo*- and *endo*-bicyclo[3.2.1]oct-6-yl tosylates **13** resemble the 2-*exo*- and 2-*endo*-norbornyl tosylates **10**, they would be expected to show similar reactivity. But this is not the case, for *exo*-**13** is 370 times *less* reactive than *exo*-**10** and reacts only eight times faster than 2-adamantyl tosylate **16**. The *endo*-epimer **13** is eleven times less reactive than *endo*-**10** and is even slower than **16**. The larger rate reduction for the *exo*-epimer **13** causes the *exo/endo* rate ratio to decrease to 13 *(Table 2)*. In their careful study of the acetolysis of these tosylates *Parker et al.* [17] also observed a rate ratio of 13.

As briefly noted [6b] differential bridging strain provides an explanation for these results. Thus, effective bridging between the cationic center C(6) and C(4) in the ionization of *exo*-**13** to **30** would force C(4) to adopt a trigonal bipyramidal configuration, thereby distorting the chair conformation of the six-membered ring[15]). Bridging of C(6) by C(8) in the ionization of *endo*-**13** to **31** would generate even more strain because the five-membered ring is thereby subdivided into *quasi* four- and three-membered rings. In addition, bridging would generate angle-strain at C(8)[12]). The conclusion is, therefore, that bridging is weak in the transition state leading to **30** and negligible in **31**[16]).

The hydrolysis products *(Table 3)*, which correspond to the acetolysis products [17], support these conclusions. Thus, *exo*-**13** yielded the 6-*exo*- and 6-*endo*-alcohols **34** and **35**, respectively, in the ratio 13:1, *i.e.* with predominant retention of configuration, whereas the *endo*-epimer afforded only the *exo*-alcohol **34** with inversion. In both cases substantial amounts of the olefin **36** and the rearranged alcohols **37** and **38** were obtained. The olefin is formed *via* loss of a proton from the cations **30** and **31**; the alcohols **37** and **38** result from a C(4)–C(6) hydride shift in the cations leading to the bicyclo[3.2.1]oct-2-yl cation **32**, the precursor of **37**. A *Wagner-Meerwein* shift in the cation **32** furnishes the bicyclo[2.2.2]oct-2-yl cation **33**, the precursor of **38**.

Parker et al. [17] have pointed out that participation of the C(4)–C(5) σ-bond in the ionization of *exo*-**13** would lead directly to the symmetrically bridged nonclassical ion **39**, but he did not rule out the possibility of equilibrating classical bicyclo[3.2.1]oct-6-yl cations. While there is evidence for weak bridging in the transition state for *exo*-**13**, there is no reason to postulate a transient nonclassical ion **39** except as a transition state for the interconversion of the enantiomeric 1,3-bridged cations **30a** and **30b**.

The bicyclo[3.2.1]oct-2-yl tosylates *exo*- and *endo*-**14** are isomers of the afore mentioned tosylates *exo*- and *endo*-**13**, in which the nucleofugal groups are located in the

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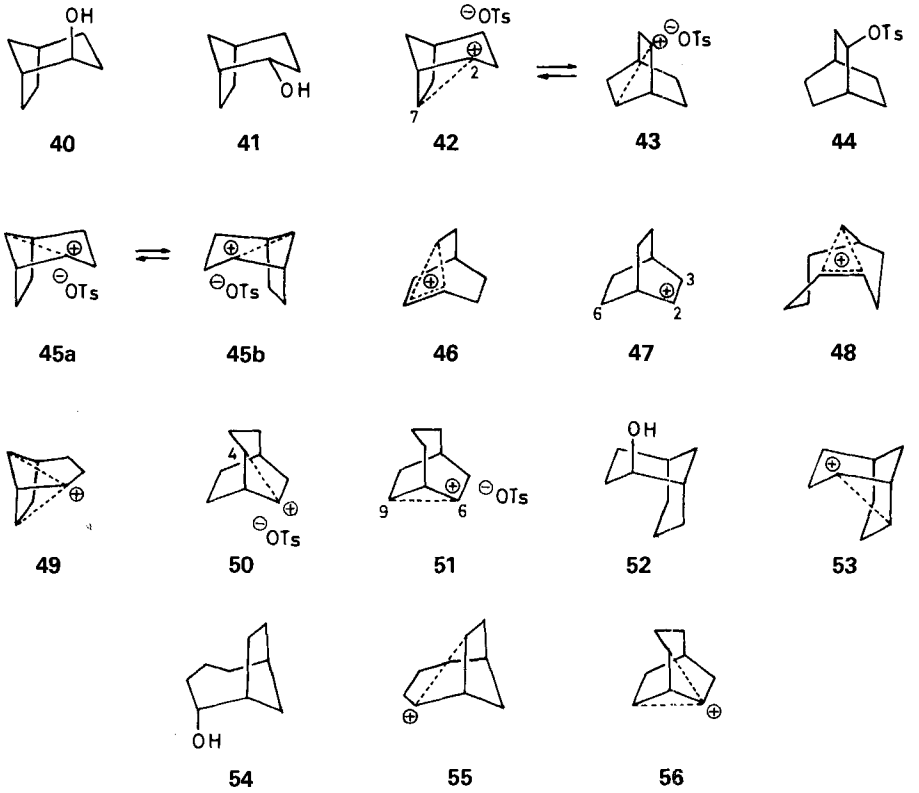
[14]) *Whiting et al.* [15] attribute the higher solvolysis rates of axial cyclohexyl derivatives, as compared to their equatorial epimers, to stereoelectronically favored antiperiplanar orientation of the nucleofuge and a β-C–H bond.

[15]) Distortion of the cyclohexane ring by incorporation of a pentacoordinate C-atom is thought to contribute to the low reactivity of cyclohexyl halides in S_N2 reactions [18].

[16]) According to a current study in this laboratory inductivity between C(4) and C(6) in bicyclo[3.2.1]octanes is greatly reduced in comparison to the observed inductivity between C(2) and C(6) in norbornanes.



more flexible trimethylene bridge. This difference strongly affects their reactivity, for both epimers react *ca.* 30 times faster than the corresponding tosylates of the series **13** *(Table 2)*. Nevertheless, the *exo*/*endo*-ratio is practically the same, namely 12. Hydrolysis of *exo*-**14** yields the *exo*-alcohol **40** with complete retention beside a comparable amount of the rearranged bicyclo[2.2.2]octan-2-ol (**38**). On the other hand, hydrolysis of *endo*-**14** yields the retained *endo*-alcohol **41** beside 8% of the inverted *exo*-alcohol **40**. Rates and products therefore indicate that bridging occurs in the transition state of both epimers and that it is more pronounced in the transition state of *exo*-**14**[17]).

In the latter case bridging between C(2) and the dorsal C(7) leads to the ion pair **42**, the precursor of the *exo*-alcohol **40**. Rearrangement of **42** affords the bridged bicyclo[2.2.2]oct-2-yl-cation **43**, the precursor of the alcohol **38**. This facile and reversible rearrangement occurs by ion pair return in **42** and **43** to form the tosylates *exo*-**14** and **44**, respectively. It is noticeable in the drifting rate constant for *exo*-**14** which increases with time and approaches the rate constant for **44**. Conversely, the rate constant for **44** decreases gradually during solvolysis in 80% EtOH[18]).

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[17]) Bridging in the transition state of *exo*-**14** is confirmed by the size of deuterium isotope effects [19].

[18]) The initial constant for **44** is $3.70 \cdot 10^{-3}$ [s^{-1}] at 70°; unpublished results.

Bridging of C(2) by the dorsal C(8) in the ion pair **45** from *endo*-**14** is apparently weaker since 8% of the inverted *exo*-alcohol **40** is obtained beside the *endo*-isomer **41**. According to models the reason is that incorporation of two pentacoordinate C-atoms in the six-membered ring generates more i-strain than placing them both in the more flexible seven-membered ring. Also, subdivision of the cyclohexane ring in **45** involves more strain than subdivision of the cycloheptane ring in **42**. Obviously, the differences are not large.

In the course of their thorough study of the acetolysis of *exo*- and *endo*-**14**, *Goering* and co-workers [8] obtained similar results but proposed somewhat different mechanisms. Thus, *exo*-**14** and the isomeric bicyclo[2.2.2]oct-2-yl tosylate (**44**) were considered to ionize to the same nonclassical ion **46**, the common precursor of the alcohols **40** and **38** (isolated as acetates). Since optically active *exo*-**14** and **44** afforded partially racemized products, 'leakage' to an additional, but symmetrical, intermediate, namely the classical bicyclo[2.2.2]oct-2-yl cation **47** was invoked[19]). However, *Goering*'s results are plausibly explained by rapid interconversion of the bridged cations in **42** and **43**, for the latter yields the symmetrically bridged cation **33** when it becomes symmetrically solvated. *Goering*'s nonclassical structure **46** then represents the transition state for the interconversion of **42** and **43**.

Goering and co-workers obtained the completely racemized acetate of the *endo*-alcohol **41** as the main product in the acetolysis of optically active *endo*-**14** and, consequently, postulated an intermediate nonclassical ion **48**, which possesses a plane of symmetry [8d]. However, since smaller amounts of the acetates of the inverted *exo*-alcohol **40** and of bicyclo[2.2.2]octan-2-ol (**38**) were also isolated, 'leakage' of **48** to the classical bicyclo[3.2.1]oct-2-yl cation and the bicyclo[2.2.2]oct-2-yl cation was considered to compete with its capture by solvent. But again, racemization is equally well explained by rapid interconversion of the 1,3-bridged ion pairs **45a** and **45b** for which **48** represents the transition state. In the free bicyclo[3.2.1]oct-2-yl cation **49**, however, C(2) is bridged to C(7) and, somewhat less strongly, also to C(8), thus, accounting for the formation of the acetates of all three alcohols **40**, **41** and **38**. It is particularly relevant that of the epimeric tosylates **14**, only *endo*-**14** could ionize directly to the symmetrical nonclassical ion **48**. Nevertheless, it is *less* reactive than *exo*-**14** *(Table 2)*.

The *exo/endo* rate ratio of 1.6 for the epimeric bicyclo[3.2.2]non-6-yl tosylates **15** and their high relative rates *(Table 2)* indicate that bridging by the dorsal C(4) and C(9), respectively, is strong in the transition state and leads to the ion pairs **50** and **51**. Also, both epimers yield rearranged products only. Thus, *exo*-**15** affords bicyclo[3.3.1]non-2-ene (**29**) beside small amounts of *exo*-bicyclo[3.3.1]nonan-2-ol (**52**). These products are formed by a shift of C(4) in the ion pair **50** which leads to the bridged bicyclo[3.3.1]non-2-yl cation **27**. On the other hand *endo*-**15** yields only *exo*-bicyclo[4.2.1]nonan-2-ol (**54**), namely by way of the shift of C(9) in the ion pair **51** which leads to the bridged bicyclo[4.2.1]non-2-yl cation **55**. In the *free* bicyclo[3.2.2]non-6-yl cation, C(6) should be almost equally bridged by C(4) and by C(9), as in **56**, and

[19]) According to these authors, 3,2- and 6,2-hydride shifts in the bicyclo[2.2.2]oct-2-yl cation could also contribute to racemization [8d].

therefore lead to both alcohols **52** and **54**. But this is not the case. Nor are nonclassical ions needed to explain the stereospecificity of these rearrangements[20]).

Conclusion. – Differential 1,3-bridging explains the observed *exo/endo* rate ratios of 1125 to 1.6 in the solvolysis of the epimeric bicyclic tosylates **10–15** without resort to steric effects or nonclassical ions. Unlike the latter, 1,3-bridged cations are formed with little geometrical change. Nevertheless, they can undergo *Wagner-Meerwein* rearrangements that are largely predetermined by 1,3-bridging in the transient ion pairs. Unbridged, *i.e.* classical carbocations are formed only when bridging is hindered by excessive strain or by strongly electron-withdrawing substituents.

Experimental Part

General. The melting points (m.p.) were determined on a *Kofler* block; they are corrected.

The *exo*- and *endo*-bicyclo[3.2.1]oct-8-yl *p*-toluene-sulfonates **11** were prepared from the corresponding alcohols by the procedure of *Foote & Woodward* [10]. The *exo*- and *endo*-bicyclo[3.3.1]nonan-2-ols were known [21], also the p-toluenesulfonate *endo*-**12** [22].

exo-*bicyclo[3.3.1]non-2-yl* p-*toluenesulfonate* (exo-**12**) was prepared from the alcohol with TsCl in pyridine following the procedure for *endo*-**12** [22]. Crystallization from hexane/pentane yielded 64% *exo*-**12**, m.p. 38–39°. Anal. calc. for $C_{16}H_{22}O_3S$ (294.30): C 65.29, H 7.55; found: C 65.49, H 7,63.

The preparation of the exo- and endo-*bicyclo[3.2.1]oct-6-yl* p-*toluenesulfonates* **13** has been described [17], also the preparation of the exo- and endo-*bicyclo[3.2.1]oct-2-yl* p-*toluenesulfonates* **14** [23]. exo- and endo-*Bicyclo[3.2.2]nonan-6-ol* were known [24]. They were converted to the corresponding *p*-toluenesulfonates by reaction with a 10% excess of TsCl in six parts of pyridine during 18 h at 0°. After addition of a small amount of H_2O the mixture was evaporated to dryness. The residue was taken up in Et_2O. The Et_2O-extract was washed with 2N HCl, 2N Na_2CO_3 and H_2O and evaporated to dryness.

exo-**15**. From Et_2O/pentane m.p. 65–66°. The compound decomposes when dried in a high vacuum. ^{1}H-NMR ($CDCl_3$): 1.20–2.30 (*m*, 14H, $6CH_2$, 2CH); 2.44 (*s*, 3H, CH_3-Ar); 4.70–5.00 (*m*, 1H, CH–OTs); 7.55 (A_2B_2-splitting, 4H, Ar). Anal. calc. for $C_{16}H_{22}O_3S$ (294.11): C 65.29, H 7.53; found: C 65.09, H 7.54.

endo-**15**. From Et_2O/pentane m.p. 61–64°. ^{1}H-NMR ($CDCl_3$): 1.20–2.30 (*m*, 14H, $6CH_2$, 2CH); 2.43 (*s*, 3H, CH_3-Ar); 4.50–4.85 (*m*, 1H, CH–OTs); 7.52 (A_2B_2-splitting, 4H, Ar). Anal. calc. for $C_{16}H_{22}O_3S$ (294.41): C 65.29, H 7.53; found: C 65.35, H 7.72.

Rate measurements were carried out in 80% (v/v) EtOH by the conductometric method described in [25]. The solvolysis products were determined by GLC (10% *Carbowax* on 20M *Chromosorb WAW*) of *ca.* $2 \cdot 10^{-2}$M solutions after ten half lives. The products were identified by comparison of their retention times with those of authentic samples *(Table 3)*.

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[20]) Stereospecificity in the rearrangements of some bicyclic carbocations has been referred to by *Berson* as a 'memory effect' [20].

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