113. Norbornanes[1])

Part 21

Bridging Strain in Norbornyl and Oxanorbornyl Cations

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Further evidence is presented that the 2-norbornyl cation is stabilized primarily by C(2)–C(6) bridging, and that C(2)–C(7) bridging leads to prohibitive strain. Thus, a comparison of the heats of hydrogenation of nortricyclene **17** and bicyclo[3.2.0.0^{2,7}]heptane **18** indicates that the strain energy of the latter is *ca.* 21.5 kcal/mol higher than that of **17**. Furthermore, 6-*exo*-2-oxabicyclo[2.2.1]heptyl sulfonates **8** ionize with strong O(2) participation to the bridged oxonium ion **12**. In contrast, 2-*endo*-7-oxabicyclo[2.2.1]heptyl sulfonates **11** ionize without O(7) participation to form the unbridged carbenium ion **15**.

As pointed out in [1a], displacement (S_N2) reactions of bi- and tricyclic halides and sulfonates with nucleophilic solvents are sterically hindered, if the nucleofuge is adjacent to a bridgehead atom. In these cases, solvolysis reactions occur *via* carbenium ions (S_N1) and tend to be slow unless assisted by bridging of the cationic center by neighboring atoms.

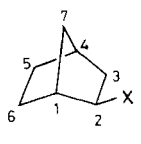
In carbocyclic compounds, bridging involves weak bonding between the electrophilic cationic center and neighboring C-atoms, thereby generating some of the strain associated with the subdivision of cyclic structures into smaller rings [2]. Differential bridging of neighboring C-atoms, therefore, accounts for the frequently different rates and products of epimeric bi- and tricyclic sulfonates [1b], such as the *exo*- and *endo*-2-norbornyl *p*-bromobenzenesulfonates (brosylates) and *p*-toluenesulfonates (tosylates) **1** (X = BsO) and **2** (X = TsO), respectively, which differ by factors of more than 300[2]).

In their original communications [3], *Winstein* and *Trifan* attributed the higher rate of **1**-OBs to anchimeric assistance of *exo*-ionization by the antiperiplanar C(1)–C(6) bonding electrons, *i.e.* by so-called σ participation[3]), which is absent in the *endo*-epimer **2**-OBs. According to a modified version of this rationale [6], the transition state for *exo*-ionization is stabilized by C,C hyperconjugation with the strained and antiperiplanar C(1)–C(6) σ bond. Thus, both interpretations stress the role of the C(1)–C(6) bonding electrons in controlling the relative rates of **1**-OBs and **2**-OBs. On the other hand, the role of the equally strained C(1)–C(7) bond, which is somewhat deflected from the plane

[1]) The IUPAC name for norbornane: *8,9,10-trinorbornane*.

[2]) The rate ratio at 25° is 350 in AcOH [3], 580 in 80% EtOH [1b], and *ca.* 2000 in H_2O [4].

[3]) For a definition of σ participation, see [5].



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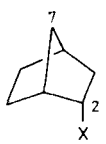

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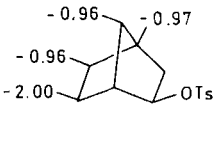

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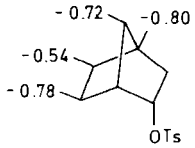

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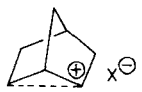

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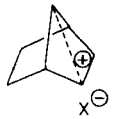

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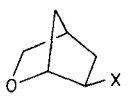

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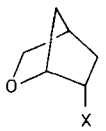

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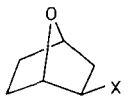

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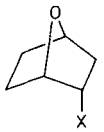

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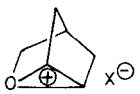

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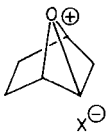

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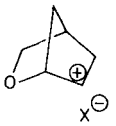

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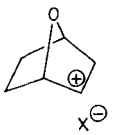

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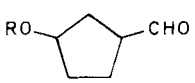

16a R = Ac
b R = H

17

18

defined by the C(1)–C(2) and the C(2)–(*endo*-OBs) bonds, is usually not considered in this context [7].

A somewhat different viewpoint resulted from the observation that the solvolysis rates of **1**-OTs and 2-OTs are controlled to a different degree by the inductive (*I*) effect of substituents at neighboring C-atoms [1c]. In particular, it was noted that the reaction constants or inductivities ρ_I [2][4]), which gauge the sensitivity of rates to the *I* effect of substituents, varied markedly for *exo*- and *endo*-ionization, as indicated by the numbers in the formulas **3** and **4** [1e]. The striking feature is the large ρ_I value of −2.00 for C(6) in **3** as compared to the low value of −0.78 for C(6) in **4**. As models show, C(6) is located at the rear of the C(2)–(*exo*-OTs) bond. It is, therefore, suitably positioned for dorsal nucleophilic participation in *exo*-ionization of **1**-OTs[5]), but not for *endo*-ionization of

[4]) As derived from the *Hammett* equation $\log k/k_o = \rho_I \sigma_I^q$ where k and k_o are rate constants for substituted and unsubstituted compounds, respectively, and σ_I^q are inductive substituent constants.

[5]) According to the principle of dorsal attack in S_N2 reactions.

2-OTs. It was, therefore, concluded that ρ_I values reflect graded bridging, and that **1**-OTs ionizes to the bridged ion pair **5**, whereas **2**-OTs ionizes to the unbridged ion pair **6.**

Differential bridging is strongly supported by the observation that both 2-*exo*- and 2-*endo*-norbornyl sulfonates hydrolyze to 2-*exo*-norbornanol [1c]. Consequently, *exo*-sulfonates react with complete retention of configuration at C(2), whereas *endo*-sulfonates react with complete inversion [3]. It is also well established that substitution occurs with retention, when neighboring nucleophilic atoms such as O, N, and S participate in the ionization step to form transient cyclic intermediates [8]. But in contrast to these atoms, sp^3-C does not possess nonbonding electrons and, therefore, becomes temporarily pentacoordinate when acting as a weak nucleophile toward an incipient carbenium-ion center.

C(7) is the only C-atom located at the rear of the C(2)–(*endo*-OTs) bond in **2**-OTs and might, therefore, be expected to participate more strongly than C(6) in *endo*-ionization. In fact, the ρ_I for 7-*anti*-substituted 2-*endo*-norbornyl tosylates **2**-OTs is only −0.72 [1d]. This finding led to the conclusion that bridging of C(2) by C(7), as shown in **7**, is very weak compared to bridging of C(2) by C(6), as in **5**, due to the much larger strain involved in dividing the five-membered ring in **7** into a four- and a three-membered ring as compared to the strain involved in dividing the six-membered ring in **5** into a five- and a three-membered ring [1d] [2].

Unfortunately, the relative strain energies of bridged carbenium ions cannot be determined. Therefore, less direct methods must be employed. One such method involves the substitution of CH_2 by O in **1** and **2** to form the oxanorbornane derivates **8** and **11**, respectively. In these cases, the rates and products should reflect the relative strain energies in the corresponding oxonium ions **12** and **13**.

In fact, some work along these lines has been reported. Thus, *Spurlock* and *Fayter* [9] have shown that 6-*exo*-2-oxabicyclo[2.2.1]heptyl brosylate (**8**-OBs) reacts *ca.* 10^8 times as fast as the *endo*-epimer **9**-OBs in AcOH at 25°, and that both compounds predominantly yield the same *exo*-acetate **8**-OAc. These findings, in conjunction with the outcome of deuterium labelling, strongly implicate the symmetric oxonium ion **12** as a common intermediate, which is formed with O participation from **8**-OBs, but *via* the unbridged cation **14** from **9**-OBs.

Furthermore, *Lambert* and *Larson* [10] have recently reported that 2-*exo*-7-oxabicyclo[2.2.1]heptyl brosylate (**10**-OBs) reacts *ca.* 450 times as fast as the corresponding *endo*-epimer **11**-OBs in AcOH at 100° [6]), a rate ratio that is similar to the one observed in solvolyses of the corresponding norbornyl brosylates **1**-OBs and **2**-OBs[2]). Acetolysis of **10**-OBs and **11**-OBs yielded both acetates **10**-OAc and **11**-OAc, respectively, and, in the case of the latter brosylate, also a small amount of rearranged 3-formylcyclopentyl acetate (**16a**)[7]). These results rule out O participation and implicate the unbridged intermediate **15** in both cases.

While these findings clearly indicate O participation in the ionization of **8**-OBs, and its virtual absence in **11**-OBs, they do not address the question of major concern here, namely the relative bridging strains present in the cations **12** and **13**. Consequently, a

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[6]) It was also shown that the rate ratio for **10**-OBs and **11**-OBs is reversed to 0.57, when a second OBs group is introduced at C(3), due to inductive enhancement of O participation in **11**-OBs [10].

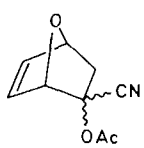
[7]) In 50% dioxane, the alcohol **16b** is obtained in quantitative yield from both chlorides **10**-Cl and **11**-Cl *[11]*.

direct comparison of the solvolysis rates and products of suitable sulfonates of the oxanorbornanols **8**-OH and **11**-OH was indicated[8]).

Another approach to an estimate of the relative strain energies generated by C(2)–C(6) and C(2)–C(7) bridging involves the determination of the heats of hydrogenation of the corresponding tricyclic dehydronorbornanes tricyclene **17** and tricyclo-[3.2.0.$0^{2,7}$]heptane **18** formally derived from the cations **5** and **7** by loss of a proton from C(6) and C(7), respectively. In fact, hydrolysis of both **1**-OTs and **2**-OTs in 70% dioxane led to **17** in yields of 5.5% and 7%, respectively, but no **18** was formed in keeping with its larger strain [1c].

The solvolysis rates and products of sulfonates of the type **8**, **9**, **10**, and **11** as well as the relative strain energies of the dehydronorbornanes **17** and **18** are reported in this communication.

Results. – *exo*- and *endo*-2-Oxabicyclo[2.2.1]heptan-6-ol (X = OH; **8**-OH and **9**-OH, respectively) were prepared as described in [9]. On the other hand, *exo*- and *endo*-7-oxabicyclo[2.2.1]heptan-2-ol (**10**-OH and **11**-OH, respectively) were obtained by a new route, namely by condensing 1-cyanovinyl acetate with furane by the method of *Black* and *Vogel* [12] to give **19** which was hydrolysed and hydrogenated to 7-oxabicyclo[2.2.1]-heptan-2-one (**20**) [13]. Reduction of **20** with $LiAlH_4$ gave the alcohols **10**-OH and **11**-OH in 7% and 93%, respectively, which were separated by chromatography on silica gel. In view of the reported low solvolytic reactivity [9] of the brosylates **9**-OBs and **11**-OBs at temperatures below 150°, the *p*-nitrobenzenesulfonates (nisylates; ONs) of the alcohols **8**-OH to **11**-OH were chosen for the rate measurements. However, **8**-ONs proved to be too unstable and was replaced by the tosylate **8**-OTs.



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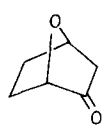

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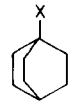

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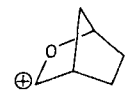

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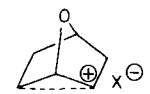

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24a ⇌ **24b**

25

The hydrolysis products of **8**-OTs, **9**-ONs, **10**-ONs, and **11**-ONs in 70% (*v*/*v*) dioxane were determined by capillary GC. The sulfonates **8**-OTs and **9**-ONs afforded 95% and 85%, respectively, of the *exo*-alcohol **8**-OH beside unidentified material. Therefore, the former had reacted with retention, the latter with inversion configuration, in agreement with the findings of *Spurlock* and *Fayter* [9][9]). Hydrolysis of the *exo*-nisylate **10**-ONs gave 3-hydroxycyclopentane aldehyde **16b** in quantitative yield, in agreement with the report

[8]) The combined data in [9] and [10] permit only a rough estimate of the rate ratio for **8**-OBs and **11**-OBs, since the measurements were carried out in different laboratories and involve extrapolations from 163° to 25°.

[9]) These authors also detected a small amount of the *endo*-acetate **9**-OAc in the acetolysis of **8**-OBs.

of *Martin* and *Bartlett* [11]. The *endo*-nisylate **11**-ONs, on the other hand, afforded a mixture of 25% **10**-OH, 45% **11**-OH, and 10% aldehyde **16b**.

The rate constants were measured conductometrically in 80% (*v*/*v*) EtOH at three temperatures (*Table 1*). Relative rates at 70° and *exo*/*endo* rate ratios are listed in *Table 2*. The rate constant for the hypothetical nisylate **8**-ONs was obtained by multiplying the rate constant for the tosylate **8**-OTs at 70° with 28.5. This is the factor by which bicyclo[2.2.2]octyl nisylate **21**-ONs [14] reacts faster than the tosylate **21**-OTs [15] in 80% (*v*/*v*) EtOH at 70°.

The heats of hydrogenation of **17** and **18** were measured in isooctane at 25°. The calorimeter, experimental method, and the accuracy of the measurements have already been reported [16]. Experimental data are given in *Table 3*. The heats of hydrogenation have not been corrected experimentally for differences in enthalpies of solution of educts and products, because for saturated hydrocarbons such differences are 0.1 kcal/mol in isooctane [17]. Differences in enthalpies of vaporization between educts and

Table 1. *First-Order Rate Constants for* 10^{-3} M *Solutions of* **8**-*OTs*, **9**-*ONs*, **10**-*ONs, and* **11**-*ONs in 80% (v/v) EtOH*[a])

	T[°C]	$k[s^{-1}]$		*T*[°C]	$k[s^{-1}]$
8-OTs	70.00[b])	$2.25 \cdot 10^{-2}$	**10**-ONs[b])	70.00[b])	$2.75 \cdot 10^{-4}$
	30.73	$4.03 \cdot 10^{-4}$		70.00	$2.75 \cdot 10^{-4}$
	40.25	$1.15 \cdot 10^{-3}$		79.78	$7.64 \cdot 10^{-4}$
	49.71	$3.19 \cdot 10^{-3}$		90.00	$2.00 \cdot 10^{-3}$
9-ONs	70.00[b])	$9.47 \cdot 10^{-8}$	**11**-ONs	70.00[b])	$1.17 \cdot 10^{-6}$
	119.86	$1.15 \cdot 10^{-5}$		109.98	$7.51 \cdot 10^{-5}$
	130.04	$2.62 \cdot 10^{-5}$		120.00	$1.85 \cdot 10^{-4}$
	135.07	$3.96 \cdot 10^{-5}$		130.00	$4.44 \cdot 10^{-4}$

[a]) Average of a least two independent measurements; mean deviation ● 1.15%. [b]) Extrapolated.

Table 2. *Rate Constants* k, *Relative Rates* k(*rel*), *and* exo/endo *Rate Ratios at 70°*

	$k[s^{-1}]$	*k*(rel)	*k*(rel)	k_{exo}/k_{endo}
8-OTs	$2.25 \cdot 10^{-2}$			
8-ONs	$6.41 \cdot 10^{-1}$[a])	$6.8 \cdot 10^{6}$	$5.5 \cdot 10^{5}$	$6.8 \cdot 10^{6}$
9-ONs	$9.47 \cdot 10^{-8}$	1.0		
10-ONs	$2.75 \cdot 10^{-4}$	$2.9 \cdot 10^{3}$		$2.4 \cdot 10^{2}$
11-ONs	$1.17 \cdot 10^{-6}$	12.4	1	

[a]) Calculated from *k* for **8**-OTs by multiplying by 28.5.

Table 3. *Heats of Hydrogenation of* **17** *and* **18**

Substrate	Titr. rate [mol/s · 10^7]	Catalyst [g]	H_2 Uptake [mol/s · 10^6]	Energy [mcal/s]	ΔH°_H [kcal/mol]
17	1.4280	0.41740[a])	0.16177	4.7666[b])	29.47
17	1.4280	0.47278[a])	0.16278	4.8012[b])	29.50
					29.48±0.02
18	1.0960	0.20243[c])	0.10843	5.7024[d])	52.60
18	1.0960	0.21141[c])	0.10868	5.7510[d])	51.92
18	1.0128	0.30500[c])	0.09981	5.2871[d])	52.97
18	1.2454	0.10489[c])	0.12572	6.6119[d])	52.60
					52.77±0.20

[a]) Rh/C (5%). [b]) Product: 86.4% norbornane, 13.6% ethylcyclopentane. [c]) Pd/C (10%). [d]) Product: 100% norbornane.

products were calculated on the basis of *Kováts* indices, which, in a series of structurally related substances, are linearly related to boiling points and, therefore, to heats of vaporization [17].

The product of hydrogenation of bicyclo[3.2.0.0^{2,7}]heptane (**18**) is exclusively norbornane, whereas in the case of nortricyclene (**17**) a mixture of norbornane and ethylcyclopentane (86.4:13.6) is obtained.

From the hydrogenation data in *Table 3*, the heats of formation for **17** and **18** are derived. They agree well with values calculated by force-field methods (*Table 4*).

Table 4. *Heats of Formation of* **17** *and* **18** *in kcal/mol*

Substrate	**17**	**18**
Exp. ΔH_H [a])	−33.43 ± 0.1	−52.77 ± 0.2
Corr. $\Delta\Delta H_{vap}$ [b])	+0.10	−0.20
Corr. for 13.48% ethylcyclopentane[c])	−2.40	
H°_H(g)[d])	−31.1±0.2	−52.6±0.2
H°_f(g) exp.	18.7	40.2
H°_f(g) cal[e])	19.5	41.3

[a]) Exper. heats of hydrogenation in isooctane.

[b]) Correction for heats of vaporization differences in isooctane on the basis of [10]): I^{60}(*OV101*): **17** = 744.0; **18** = 773.3; norbornane = 748.3.

[c]) Calculated with $\Delta\Delta H^\circ_f$: norbornane/ethylcyclopentane = 17.94 kcal/mol[11]).

[d]) Calculated for the reaction leading to norbornane and ΔH°_f(norbornane) = −12.4 kcal/mol[11]).

[e]) Calculated by MM2[19]).

Discussion. – The k(rel) values in *Table 2* show that **8**-ONs reacts *ca.* $5.5 \cdot 10^5$ times as fast as **11**-ONs. Furthermore, hydrolysis of **8**-OTs gave the retained *exo*-alcohol **8**-OH in almost quantitative yield, whereas **11**-ONs afforded a mixture of retained and inverted alcohols **11**-OH and **10**-OH, respectively, along with the hydroxyaldehyde **16b**. These results indicate that **8**-OTs ionizes with O(2) participation to the oxonium ion **12**, which then undergoes a ring opening by H_2O yielding **8**-OH, as previously reported [9], whereas **11**-ONs ionizes without O(7) participation to the cation **15**. Since the latter is unbridged, it undergoes *exo*- and *endo*-attack by H_2O besides rearranging to the oxacarbenium ion **22**, the precursor of **16b** [11].

The above rate ratio of $5.5 \cdot 10^5$ for **8**-ONs and **11**-ONs corresponds to a difference of activation free enthalpies $\Delta\Delta G^\neq$ of *ca.* 9 kcal/mol. This is more than twice the $\Delta\Delta G^\neq$ of *ca.* 4 kcal/mol for *exo*- and *endo*-2-norbornyl tosylate **1**-OTs and **2**-OTs, respectively, and is not unexpected in view of the high nucleophilicity of the ether O-atom compared to sp^3-carbon[12]). It is, therefore, surprising that **1**-OTs reacts 1.16 times faster than the oxa analog **8**-OTs at 70° [13]) and that **2**-OTs reacts $2.6 \cdot 10^4$ times faster than the oxa analog

[10]) If, as suggested by *Winstein* and *Trifan* [3], ionization of 2-*exo*-norbornyl tosylate **1** led directly to the symmetrically bridged cation **25**, C(1) would necessarily acquire a higher positive charge and, hence, would withdraw electrons from the adjacent C(7). However, as shown in **3** ρ_I for C(7), namely −0.96 [1d], is practically the same as for the more remote C(4) and C(5).

[11]) See the recent comprehensive literature review in [22].

[12]) In addition, the bridging distance in **12** is probably shorter than in **5**.

[13]) The rate constant for **1**-OTs at 70° is $2.62 \cdot 10^{-2}$ [1b].

9-OTs[14]). The relatively low rates of **8**-OTs and **9**-OTs are undoubtably due to the rate retarding *I* effect of the O-atoms, as already noted by *Spurlock* and *Fayter* [9]. Since **2**-OTs ionizes without O participation, the factor of $2.6 \cdot 10^4$ provides an approximate measure of the *I* effect of the β-O-atom.

The rate ratio for **8**-ONs and **9**-ONs of $6.8 \cdot 10^6$ *(Table 2)* confirms that the ionization of the former only is anchimerically assisted [9][15]). The relatively low rate ratio of 235 for **10**-ONs and **11**-ONs is close to the value of 311 for **1**-OTs and **2**-OTs in the same solvent [1b]. This indicates that **10**-ONs ionizes with C(6) participation to form the bridged cation **23** which subsequently rearranges to **22**.

The conclusion that the C(2)–C(7)-bridged norbornyl cation **7** is far more strained than the C(2)–C(6)-bridged cation **5** [2] is clearly borne out by the heats of hydrogenation of 52.6 and 31.1 kcal/mol *(Table 4)* for the dehydronorbornanes **18** and **17**, respectively. The strain-energy difference of *ca.* 21.5 kcal/mol[16]) readily explains why C(7) does not participate in the ionization of 2-*endo*-norbornyl sulfonates. According to *Kirmse* [20], however, a C(7)-bridged cation **7** may intervene in the decomposition of norbornane-*endo*-2-diazonium ion **2**-N_2 and in the proton-induced conversion of the dehydronorbornane **18** to *exo*- and *endo*-norbornan-2-ol.

These results confirm the earlier conclusion that the disparate reactivity of *exo*- and *endo*-2-norbornyl sulfonates is mainly due to the widely different strains involved in C(2)–C(6) and C(2)–C(7) bridging, respectively. The free 2-norbornyl cation is then adequately symbolized by an enantiomeric pair of asymmetrically bridged carbenium ions **24a** and **24b** which interconvert extremely rapidly by a process likened to a skeletal vibration [1c] [2] or a thermal motion [21]. *Winstein*'s symmetrically bridged cation **25** is then the time-averaged structure[10]).

This view differs somewhat from that of *Schleyer* and others[11]) who regard the 'nonclassical ion' **25** as a static structure held together by a three-center-two-electron bond. In contrast, the dotted lines in **24a** and **24b** symbolize a bonding interaction between C(2) and C(6) to which *all* the electrons in the bonds around C(6) contribute and not only the two electrons assigned to the C(1)–C(6) bond in a *Lewis* representation of norbornane[17]).

Experimental Part

exo-*2-Oxabicyclo[2.2.1]heptan-6-ol* (X=OH, **8**-OH) and the *endo*-epimer **9**-OH were prepared according to [9][18]). The alcohol **8**-OH was converted to the known *p*-toluenesulfonate **8**-OTs [9].

9-OH was converted to the *p*-nitrobenzenesulfonate (nisylate) **9**-ONs by the general method described in [23]. From $CHCl_3$/hexane, m.p. 135–136°. Anal. calc. for $C_{12}H_{13}NO_6S$: C 48.16, H 4.38, N 4.68; found: C 47.96, H 4.19, N 4.76.

7-Oxabicyclo[2.2.1]heptan-2-one (**20**)[19]). A mixture of 110 g of 1-cyanovinyl acetate *(Fluka)*, 270 g of freshly distilled furane, 160 g of ZnI_2 and 0.8 g of hydroquinone were stirred at 20° under Ar in the dark for 4 days. ZnI_2 was removed by filtration and the filtrate washed with H_2O and dried (Na_2SO_4). Excess starting material was removed at 20° and 0.1 Torr. leaving 176 g (99%) of *2*-exo- and *2*-endo-*cyano-7-oxabicyclo[2.2.1]hept-5-en-2-yl*

[14]) Calculated by dividing *k* (70°) for **9**-ONs *(Table 2)* by 28.5.

[15]) A far higher rate ratio of $7 \cdot 10^7$ in AcOH at 25° is reported in [9].

[16]) This value is in close agreement with force-field calculations (MM2), see *Table 4*.

[17]) *Schleyer* and coworkers [22] state that 'according to *Grob* the C(6) carbon participates through space ... without involving the C(1)–C(6) bonding electrons' and thereby misrepresent the position taken in [1] and [2].

[18]) IR- and ^{1}H-NMR spectra agreed well with published data.

[19]) Diplomarbeit *Michael Matthes*, 1985.

acetates (**19**) as a red oil which decomposes upon distillation. This material was converted to 7-oxabicyclo[2.2.1]-hept-5-en-2-one as described by *Vieira* and *Vogel* [24] to yield 53 g (50%) of 7-oxabicyclo[2.2.1]hept-5-ene-2-one, b.p. 66–67°/12 Torr ([25]: 79–80°/10 Torr). Hydrogenation of this material in 500 ml of AcOEt with 2.5 g Pd/C at normal pressure as described in [26] yielded 50 g (84%) of **20**, b.p. 65–66°/13 Torr ([13]: 68–72°/15 Torr).

exo- *and* endo-*7-Oxabicyclo[2.2.1]heptan-2-ol* (X=OH; **10**-OH and **11**-OH). A soln. of 44 g of **20** in 70 ml of dry Et_2O was added under stirring to 30 g of $LiAlH_4$ in 700 ml dry Et_2O during 1 h. After further stirring for 2.5 h at 20°, 120 ml of 1N NaOH were added dropwise under cooling to *ca.* 5°. The resulting mixture was filtered through *Celite* and the filtrate concentrated *in vacuo*. Destillation of the residue at 0.3 Torr yielded 35 g (78%) of a colorless wax, b.p. 57–58° ([13]: 40–50°/0.01 Torr). Cap. GC showed this material to contain 93% **11**-OH and 7% **10**-OH.

The above mixture was separated by chromatography on silica gel with Et_2O/acetone (8:1 *v/v*). **10**-OH: ^{1}H-NMR ($CDCl_3$): 4.65–4.25 (H–C(1), H–C(4)); 3.83 (H–C(2)); 2.10–1.17 (3 CH_2). **11**-OH: ^{1}H-NMR($CDCl_3$): 4.60–4.08 (H–C(1), H–C(2), H–C(4)); 2.24 (OH); 2.40–0.97 (3 CH_2).

endo-*7-Oxabicyclo[2.2.1]hept-2-yl* p-*Nitrobenzenesulfonate* (**11**-ONs) was prepared by the usual procedure [23]. From $CHCl_3$ hexane, m.p. 105–105.5°. Anal. calc. for $C_{12}H_{13}NO_6S$ (299.30): C 48.16, H 4.38, N 4.68; found: C 48.20, H 4.46, N 4.61.

exo-*7-Oxabicyclo[2.2.1]hept-2-yl* p-*Nitrobenzenesulfonate* (**10**-ONs). From hexane, m.p. 123–123.5°. Anal. calc. for $C_{12}H_{13}NO_6S$ (299.30): C 48.16, H 4.38, N 4.68; found: C 47.91, H 4.31, N 4.60.

Nortricyclene (**17**) [26] and *tricyclo[3.2.0.0^{2,7}]heptane* (= *pseudonortricyclene*) (**18**) [27] were prepared according to known procedures and purified by prep. GLC. The rate measurements were carried out as described in [28]; products were determined as described in [23].

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