223. Carbon Participation in the Solvolysis of 6-*exo*-substituted 2-*exo*- and 2-*endo*-Norbornyl *p*-Toluenesulfonates. Norbornanes Part 5

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Summary

The solvolysis rates and products of the 6-*exo*-substituted 2-*exo*- **1a**–**1u**, and 2-*endo*-norbornyl *p*-toluenesulfonates **2a**–**2u**, have been determined. In general, the rate constants for **1** and **2** ($\log k$) correlate well with the inductive constants σ_I^q of the substituents at C(6); however, their sensitivity to σ_I^q is much larger in the 2-*exo*-series **1** than in the 2-*endo*-series **2**. This differential transmission of polar effects is the cause of decreasing 2-*exo*/2-*endo* rate ratios from 2388 for R = *t*-C_4H_9 to 0.37 for R = Br, *i.e.* with increasing electron attraction by the substituent. The high sensitivity of the rate constants for the 2-*exo*-*p*-toluenesulfonates **1** to σ_I^q indicates an unusually strong inductive interaction between C(6) and the incipient cationic center at C(2). This interaction is ascribed to the participation of the pentacoordinate C(6)-atom, *i.e.* to 1,3-bridging, a consequence of steric hindrance of nucleophilic solvent participation in norbornanes. Donor substituents enhance 1,3-bridging, lead to faster reactions and to the formation of 2-*exo* substitution products. Conversely, acceptor substituents reduce 1,3-bridging, decrease rates and facilitate the formation of 2-*endo* substitution products. Graded 1,3-bridging is discussed in the light of *Winstein*'s nonclassical ion concept.

1. Introduction. – The 6-*exo*-substituted 2-*exo*- and 2-*endo*-norbornyl *p*-toluenesulfonates **1** and **2** belong to a class of sterically hindered compounds which undergo solvolysis with little or no nucleophilic participation by the solvent or by added nucleophiles [1][2], *i.e.* they react by a so-called k_c process [2]. Consequently, the positive charge generated at C(2) in the transition state is largely dispersed intramolecularly. Also, due to the tightly bridged boat conformation and the reduced bond angle of 94° at C(7) [3] the norbornanes **1** and **2** are considerably more strained [4] than the previously studied 1-substituted 3-bromoadamantanes **3** [5][3]) which possess the same W-like arrangement of the R–C–C–C–X sequence as the 2-*exo*-6-*exo*-substituted norbornanes **1**. A comparison of the effect of γ-

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[2]) See [1] for further references.

[3]) The calculated strain difference is *ca.* 10 kcal/mol [4].

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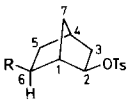
substituents on the reaction rates of **1** and **3** should therefore reveal the influence of strain on the transmission of polar effects in saturated compounds. Furthermore, a comparison of the rates for the 2-*exo*-*p*-toluenesulfonates **1** with those for the corresponding 2-*endo*-*p*-toluenesulfonates **2**, in which the R–C–C–C–X chain possesses a sickle-like conformation, should provide information regarding the directional effect of substituents on reaction rates.



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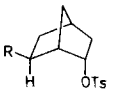

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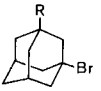


3

R = **a**	t-C_4H_9	R = **g**	$OCOCH_3$	R = **m**	CH_2NH_2	R = **s**	OCH_3
b	i-C_3H_7	**h**	F	**n**	CH_2OH	**t**	SCH_3
c	CH_3	**i**	Br	**o**	$CONH_2$	**u**	$NHCOCH_3$
d	CH_2Br	**j**	CN	**p**	$N(CH_3)_2$	**v**	NO_2
e	$COOCH_3$	**k**	H	**q**	NH_2		
f	COOH	**l**	COONa	**r**	OH		

An investigation of this kind, in conjunction with a study of C(6)-epimers of **1**[4]), should also provide information concerning the nature of 2-norbornyl cations, a topic which for decades has been at the center of the 'nonclassical ion' controversy[5]). The question is, briefly, whether the large rate ratios observed for unsubstituted 2-*exo*- and 2-*endo*-norbornyl sulfonates[6]) and the exclusive formation of 2-*exo* substitution products is due to the ionization of the *exo*-epimer **1** to a bridged nonclassical cation **33**, as proposed by *Winstein* [9], or whether rates and products reflect sterically hindered ionization of 2-*endo*-sulfonates **2** and sterically hindered *endo*-attack of nucleophiles at C(2) of the resulting unbridged classical 2-norbornyl cation **20** (R = H) as contended by *Brown*[5]).

In order to answer these questions the solvolysis rates and products of twenty 6-*exo*-substituted 2-*exo*- **1a**–**1u**, and twenty 2-*endo*-*p*-toluenesulfonates, **2a**–**2u**, were studied. The results are reported and discussed in this paper[7]).

2. Results. – The syntheses of the above sulfonates have already been reported [11] with the exception of **1** and **2**, **a**, **b** and **h**, which are described in a subsequent paper. The rate constants in ethanol/water 80:20 (*v*/*v*), which were determined by the conductometric method, are listed in *Tables 1* and *2*. The reaction products in dioxane/water 70:30 have also been reported [12]. They are listed in *Table 3* with the products from the new tosylates **1** and **2**, **a**, **b** and **h**. Also included are the corrected yields of the products from **1** and **2**, **c** and **l**, which have been reexamined using an improved GC. technique.

The 6-*exo*-alkyl *p*-toluenesulfonates **1** and **2**, **a**, **b** and **c** yielded mainly the tertiary alcohols **8** and the rearranged olefins **10** and **11** (by C(6) → C(2) hydride shifts) in addition to the unrearranged 2-*exo*-alcohols **4**. As already noted [12], it was not

[4]) See the following paper [6].

[5]) For a detailed discussion see [7].

[6]) The rate ratio for **1k** and **2k** in ethanol/water 80:20 at 25° is reported to be 582 [8].

[7]) Most of the results have been reported in preliminary communications [10a–g].

Table 1. *First-order solvolysis rate constants for 10^{-3} M 6-(exo-R-2-exo-norbornyl p-toluenesulfonates* **1** *in 80 vol. –% ethanol, and activation parameters*

	R	T [°]	k [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol · degree]
a	t-C_4H_9	30.29	$1.00 \cdot 10^{-3}$	20.78	−3.83
		39.96	$2.95 \cdot 10^{-3}$		
		49.81	$8.58 \cdot 10^{-3}$		
		70.00	$6.09 \cdot 10^{-2}$ a)		
b	i-C_3H_7	30.00	$3.09 \cdot 10^{-4}$	21.95	−2.20
		40.00	$1.04 \cdot 10^{-3}$		
		50.00	$3.14 \cdot 10^{-3}$		
		70.00	$2.46 \cdot 10^{-2}$ a)		
c	CH_3	40.25	$4.31 \cdot 10^{-4}$	22.51	−2.22
		50.18	$1.37 \cdot 10^{-3}$		
		59.80	$3.81 \cdot 10^{-3}$		
		70.00	$1.09 \cdot 10^{-2}$ a)		
d	CH_2Br	70.00	$1.06 \cdot 10^{-4}$ a)	23.28	−9.18
		79.00	$2.84 \cdot 10^{-4}$		
		90.00	$7.27 \cdot 10^{-4}$		
		101.50	$2.04 \cdot 10^{-3}$		
e	$COOCH_3$	70.00	$6.33 \cdot 10^{-6}$ a)	26.15	−6.39
		99.60	$1.44 \cdot 10^{-4}$		
		109.85	$3.84 \cdot 10^{-4}$		
		120.08	$9.57 \cdot 10^{-4}$		
f	COOH	70.00	$5.97 \cdot 10^{-6}$ a)	26.98	−4.08
		110.35	$4.31 \cdot 10^{-4}$		
		120.48	$1.08 \cdot 10^{-3}$		
		130.70	$2.70 \cdot 10^{-3}$		
g	$OCOCH_3$	70.00	$8.14 \cdot 10^{-7}$ a)	25.29	−12.99
		109.80	$4.29 \cdot 10^{-5}$		
		119.70	$1.01 \cdot 10^{-4}$		
		129.85	$2.36 \cdot 10^{-4}$		
h	F	70.00	$7.21 \cdot 10^{-7}$ a)	24.3	−16.2
		110.51	$3.45 \cdot 10^{-5}$		
		120.20	$7.76 \cdot 10^{-5}$		
		129.52	$1.62 \cdot 10^{-4}$		
i	Br	70.00	$1.51 \cdot 10^{-7}$ a)	30.9	0.1
		110.00	$1.91 \cdot 10^{-5}$		
		120.00	$5.64 \cdot 10^{-5}$		
		130.00	$1.51 \cdot 10^{-4}$		
j	CN	70.00	$1.23 \cdot 10^{-7}$ a)	26.58	−12.95
		120.48	$2.11 \cdot 10^{-5}$		
		130.70	$5.10 \cdot 10^{-5}$		
		140.70	$1.16 \cdot 10^{-4}$		
k	H	25.00	$2.37 \cdot 10^{-4}$ b)	22.04	−1.20
		30.25	$4.62 \cdot 10^{-4}$		
		40.20	$1.49 \cdot 10^{-3}$		
		49.90	$4.55 \cdot 10^{-3}$		
		70.00	$3.58 \cdot 10^{-2}$ a)		
l	COONa	40.25	$1.72 \cdot 10^{-3}$	26.03	11.75
		50.00	$6.19 \cdot 10^{-3}$		
		60.15	$2.22 \cdot 10^{-2}$		
		70.00	$7.04 \cdot 10^{-2}$ a)		
m	CH_2NH_2	40.00	$3.28 \cdot 10^{-4}$	22.51	−2.62
		50.00	$1.16 \cdot 10^{-3}$		
		60.00	$3.08 \cdot 10^{-3}$		
		70.00	$8.84 \cdot 10^{-3}$ a)		
n	CH_2OH	40.20	$2.34 \cdot 10^{-4}$	22.60	−3.15
		50.00	$7.16 \cdot 10^{-4}$		
		59.90	$2.13 \cdot 10^{-3}$		
		70.00	$5.97 \cdot 10^{-3}$ a)		
o	$CONH_2$	70.00	$7.56 \cdot 10^{-5}$ a)	23.85	−8.18
		90.40	$5.65 \cdot 10^{-4}$		
		100.00	$1.38 \cdot 10^{-3}$		
		110.25	$3.29 \cdot 10^{-3}$		
p	$N(CH_3)_2$	15.00	$2.39 \cdot 10^{-4}$	22.3	2.24
		25.00	$9.02 \cdot 10^{-4}$		
		35.00	$3.19 \cdot 10^{-3}$		
		70.00	$1.45 \cdot 10^{-1}$ a)		
q	NH_2	25.00	$2.21 \cdot 10^{-4}$	20.2	−7.2
		35.00	$7.15 \cdot 10^{-4}$		
		45.00	$2.01 \cdot 10^{-3}$		
		70.00	$2.25 \cdot 10^{-2}$ a)		
rc)	OHc)	50.00	$1.01 \cdot 10^{-4}$	19.0	−18.2
		60.00	$2.57 \cdot 10^{-4}$		
		70.00	$6.04 \cdot 10^{-4}$		
s	OCH_3	60.00	$9.77 \cdot 10^{-5}$	23.7	−6.0
		70.00	$2.88 \cdot 10^{-4}$		
		80.00	$7.86 \cdot 10^{-4}$		
t	SCH_3	70.00	$3.33 \cdot 10^{-4}$	24.0	−4.9
		80.03	$9.37 \cdot 10^{-4}$		
		90.00	$2.44 \cdot 10^{-3}$		
u	$NHCOCH_3$	70.00	$2.21 \cdot 10^{-4}$	24.7	−3.7
		80.00	$6.32 \cdot 10^{-4}$		
		90.00	$1.72 \cdot 10^{-3}$		
v	NO_2	100.00	$2.80 \cdot 10^{-6}$	26.5	−13.4
		110.05	$7.34 \cdot 10^{-6}$		
		120.03	$1.82 \cdot 10^{-5}$		
		70.00	$1.13 \cdot 10^{-7}$		

a) Extrapolated.

b) A value of $2.31 \cdot 10^{-4}$ has been reported [7].

c) In the presence of 0.10 M NaOH at 15.0° $k = 5.28 \cdot 10^{-3}$ which corresponds to an acceleration of 2110 due to the presence of the conjugate base of **1r**.

Table 2. *First-order solvolysis rate constans for 10^{-3} M 6-exo-R-2-endo-norbornyl p-toluenesulfonates* **2** *in 80 vol.-% ethanol, and activation parameters*

	R	T [°]	k [s^{-1}]	H^+ [kcal/mol]	S^+ [cal/mol · degree]		R	T [°]	k [s^{-1}]	H^+ [kcal/mol]	S^+ [cal/mol · degree]
a	*t*-C_4H_9	90.00	$1.98 \cdot 10^{-4}$	24.76	−7.69	**k**	H	70.00	$8.42 \cdot 10^{-5}$ a)	23.88	−7.87
		100.00	$5.17 \cdot 10^{-4}$					79.12	$2.15 \cdot 10^{-4}$		
		110.00	$1.25 \cdot 10^{-3}$					89.77	$5.97 \cdot 10^{-4}$		
		70.00	$2.55 \cdot 10^{-5}$ a)					99.20	$1.43 \cdot 10^{-3}$		
b	*i*-C_3H_7	70.00	$5.30 \cdot 10^{-5}$ a)	24.29	−7.61	**l**	COONa	60.00	$3.66 \cdot 10^{-5}$	25.78	−1.69
		80.01	$1.47 \cdot 10^{-4}$					70.00	$1.16 \cdot 10^{-4}$		
		90.02	$4.01 \cdot 10^{-4}$					80.00	$3.52 \cdot 10^{-4}$		
		100.05	$1.01 \cdot 10^{-3}$			**m**	CH_2NH_2	70.00	$3.73 \cdot 10^{-5}$ a)	22.96	−12.18
c	CH_3	64.60	$3.37 \cdot 10^{-5}$	24.25	−7.46			99.10	$5.60 \cdot 10^{-4}$		
		70.00	$6.02 \cdot 10^{-5}$ a)					109.75	$1.39 \cdot 10^{-3}$		
		90.00	$4.40 \cdot 10^{-4}$					119.85	$3.04 \cdot 10^{-3}$		
		99.60	$1.12 \cdot 10^{-3}$			**n**	CH_2OH	70.00	$4.39 \cdot 10^{-5}$ a)	23.76	−9.51
d	CH_2Br	70.00	$6.75 \cdot 10^{-6}$ a)	23.18	−14.94			99.50	$7.55 \cdot 10^{-4}$		
		110.05	$2.64 \cdot 10^{-4}$					109.70	$1.81 \cdot 10^{-3}$		
		120.30	$5.91 \cdot 10^{-4}$					119.80	$4.18 \cdot 10^{-3}$		
		130.50	$1.30 \cdot 10^{-3}$			**o**	$CONH_2$	70.00	$7.12 \cdot 10^{-6}$ a)	24.78	−10.17
e	$COOCH_3$	70.00	$1.73 \cdot 10^{-6}$ a)	25.16	−11.86			109.90	$3.50 \cdot 10^{-4}$		
		110.00	$9.15 \cdot 10^{-5}$					119.75	$8.08 \cdot 10^{-4}$		
		120.00	$2.15 \cdot 10^{-4}$					130.00	$1.87 \cdot 10^{-3}$		
		130.00	$4.96 \cdot 10^{-4}$			**p**	$N(CH_3)_2$	70.00	$6.24 \cdot 10^{-5}$ a)	27.0	0.69
f	COOH	70.00	$2.88 \cdot 10^{-6}$ a)	24.80	−11.90			80.00	$1.98 \cdot 10^{-4}$		
		110.00	$1.43 \cdot 10^{-4}$					90.04	$5.82 \cdot 10^{-4}$		
		120.00	$3.34 \cdot 10^{-4}$					99.64	$1.59 \cdot 10^{-3}$		
		129.60	$7.33 \cdot 10^{-4}$			**q**	NH_2	70.00	$2.55 \cdot 10^{-4}$	24.64	−3.46
g	$OCOCH_3$	70.00	$1.21 \cdot 10^{-6}$ a)	22.99	−18.91			79.65	$7.19 \cdot 10^{-4}$		
		110.15	$4.63 \cdot 10^{-5}$					90.15	$2.00 \cdot 10^{-3}$		
		119.70	$9.85 \cdot 10^{-5}$			**r**	OH	70.00	$1.00 \cdot 10^{-4}$	24.0	−7.2
		129.80	$2.12 \cdot 10^{-4}$					89.89	$7.26 \cdot 10^{-4}$		
h	F	70.00	$1.50 \cdot 10^{-6}$ a)	22.92	−18.66			100.25	$1.89 \cdot 10^{-3}$		
		115.42	$8.65 \cdot 10^{-5}$			**s**	OCH_3	70.00	$4.29 \cdot 10^{-5}$ a)	24.1	−8.6
		124.65	$1.77 \cdot 10^{-4}$					90.00	$3.19 \cdot 10^{-4}$		
		134.36	$3.60 \cdot 10^{-4}$					100.00	$7.91 \cdot 10^{-4}$		
i	Br	70.00	$4.06 \cdot 10^{-7}$ a)	26.42	−11.07			110.05	$1.93 \cdot 10^{-3}$		
		119.99	$6.42 \cdot 10^{-5}$			**t**	SCH_3	70.00	$2.09 \cdot 10^{-5}$ a)	24.1	−9.99
		130.02	$1.53 \cdot 10^{-4}$					99.93	$3.86 \cdot 10^{-4}$		
		139.72	$3.39 \cdot 10^{-4}$					109.99	$9.36 \cdot 10^{-4}$		
j	CN	70.00	$1.40 \cdot 10^{-7}$ a)	24.91	−17.06			119.95	$2.13 \cdot 10^{-3}$		
		120.18	$2.21 \cdot 10^{-5}$			**u**	$NHCOCH_3$	70.00	$1.07 \cdot 10^{-5}$ a)	24.14	−11.22
		129.80	$4.78 \cdot 10^{-5}$					100.04	$2.01 \cdot 10^{-4}$		
		139.84	$1.06 \cdot 10^{-4}$					110.02	$4.85 \cdot 10^{-4}$		
								120.05	$1.11 \cdot 10^{-3}$		

a) Extrapolated.

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

	R											
a	t-C_4H_9	**4**	18 (27)	**8**	39 (23)	**9**	1 (1)	**10**	42 (49)			
b	i-C_3H_7	**4**	32 (36)	**6**	0.5 (0.4)	**8**	32 (15)	**11**	36 (49)			
c	CH_3	**4**	40 (44)	**6**	2 (2)	**8**	58 (54)					
d	CH_2Br	**4**	70 (82)	**5**	10 (11)	**6**	20 (7)					
e	$COOCH_3$	**4**	32 (79)	**5**	24 (4)	**6**	4 (1)	**7**	1 (–)	**12**	11 (11)	**13** 28 (5)
f	COOH	**4**	25 (61)	**5**	12 (22)	**7**	1 (–)	**12**	36 (9)	**13**	26 (8)	
g	$OCOCH_3$	**4**	12 (53)	**5**	42 (37)	**6**	5 (–)	**14**	41 (10)			
h[a])	F	**4**	9 (87)	**5**	24 (4)	**7**	3 (2)	**15**	57 (7)			
i[b])	Br	**4**	44 (81)[c])	**5**	54 (9)[d])	**7**	2 (–)					
j	CN	**4**	11 (71)	**5**	43 (14)	**7**	1 (–)	**12**	44 (14)	**13**	1 (–)	
k	H	**4**	94 (93)	**5**	0.5 (–)	**12**	5.5 (7)					
l[e])	COONa	**4f**	40 (50)	**8f**	20 (21)	**12f**	13 (20)	**12k**	12 (3)	**13**	8 (3)	
m	CH_2NH_2	**4**	83 (64)	**5**	14 (24)	**6**	3 (9)	**16**	– (3)			
n	CH_2OH	**4**	85 (70)	**5**	12 (4)	**6**	3 (–)	**17**	– (26)			
o	$CONH_2$	**4**	50 (73)	**5**	15 (5)	**12**	– (6)	**13**	35 (16)			
p–u		**18**	100 (100)									

[a]) **1h** yielded *ca.* 7% of unidentified products.
[b]) **2i** yielded *ca.* 9% of unidentified products.
[c]) Isolated as the fragmentation product **18**.
[d]) Isolated as nortricyclanol (**19** and 5-norbornen-2-*exo*-ol (**5**, R = OH).
[e]) **1l** yielded 7% unidentified products, **21** *ca.* 3%.

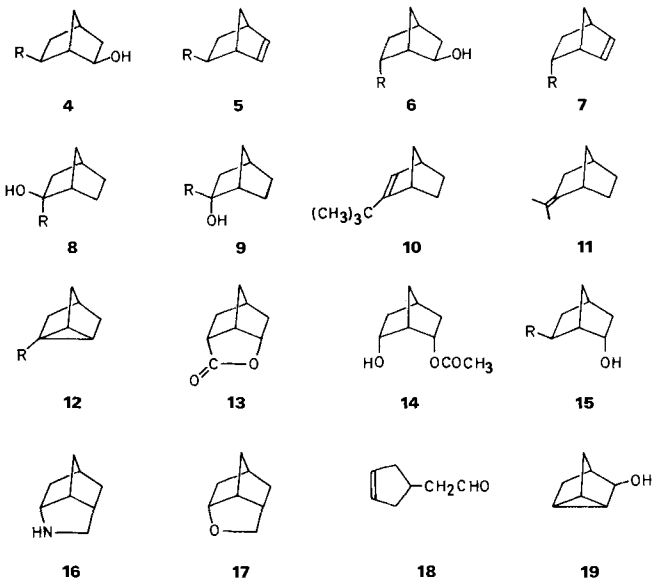
possible to determine accurately the products derived from the bromides **1i** and **2i** because the originally formed products, presumably the bromoalcohols **4i** and **15i**, and the bromoolefin **5i** underwent secondary reactions, *viz.* fragmentation of **4i** and **15i** to the aldehyde **18** and homoallylic rearrangement of **5i** to nortricyclanol **19**. Only the *endo*-bromoolefin **7i** was stable and determined as such. These complications did not arise in the case of the fluoro-*p*-toluenesulfonates **1h** and **2h** *(Table 3).*

A reexamination of the solvolyses of the 6-*exo*- (**1l**) and 6-*endo*-tosyloxynorbornane-2-carboxylic acids (**2l**), showed the reaction to be more complicated than previously assumed [12]. The main product, the 6-*exo*-hydroxy acid **41**, was accompanied by sizable amounts of the 2-*exo*-hydroxy acid **81** formed by a 1,3-hydride shift[8]). In addition, both tosylates **1l** and **2l** yielded tricyclene carboxylic acid (**12l**) by 1,3-elimination of HOTs as well as nortricyclene (**12k**) by decarboxylation (homofragmentation), only minor amounts of the lactone **13**, *viz.* 8 and 3% respectively, being formed by *endo*-cyclization.

As previously reported [12] all twelve sulfonates **1** and **2**, **p**–**u**, fragmented quantitatively to (3-cyclopentenyl)acetaldehyde **18**. The unreactive nitro-*p*-toluenesulfonate **1v** yielded tarry material only because of the high temperature and long reaction time required.

3. Discussion. – 3.1. *Products (Table 3).* The 2-*exo*- **1a**–**o** and 2-*endo*-*p*-toluenesulfonates **2a**–**o**, in general lead to different amounts of the same products, as is

[8]) The acids **4**, **8** and **12**, R = COOH, were converted to their methyl esters before GC. analysis.



often observed in reactions of stereoisomers [13][9]). This indicates that products are formed *via* the stereoisomeric ion pairs **20** and **22**. The unsubstituted sulfonates **1k** and **2k** are notable exceptions since they yield equal amounts of the same products within the error limit of GC. analysis. Furthermore, larger amounts of unrearranged norbornanols **4** and norbornenes **5** than of rearranged epimers **6** and **7** are obtained[10]) except when the substituent at C(6) is a nucleophile, such as $COOCH_3$, COOH, COONa, $CONH_2$, CH_3COO, CH_2NH_2 and CH_2OH. In these cases the rearranged cations **21** and **23** are removed from the equilibria with the more stable 6-*exo*-substituted cations **20** and **22** by *endo*-cyclization to **13**, **14**, **16** and **17**.

The most remarkable result, however, is the formation of 6-*exo*-fluoro-2-*endo*-norbornanol (**15h**) from **1h** (57%) and from **2h** (7%). This proves that *endo* attack on 2-norbornyl cations is not sterically prohibited as commonly assumed [7], or restricted to entropy-favored *endo*-cyclization. The fact that *endo* attack is only observed when the substituent is an electron-attracting group, such as fluorine, $COOCH_3$ or a strong nucleophile, such as COO^-, suggests that the intermediate cations are unbridged, as in **20**, **21**, **22** and **23**, or only loosely bridged, as in **24** and **25**.

Another noteworthy result is the high incidence of 1,3-hydride shifts when the substituent is alkyl, COONa or hydrogen [14]. In these cases the rearrangement produces the more stable tertiary cation **26** (R = alkyl), or the same secondary cation **26** (R = H) to which the solvent has freer access after the dislocation of the positive charge.

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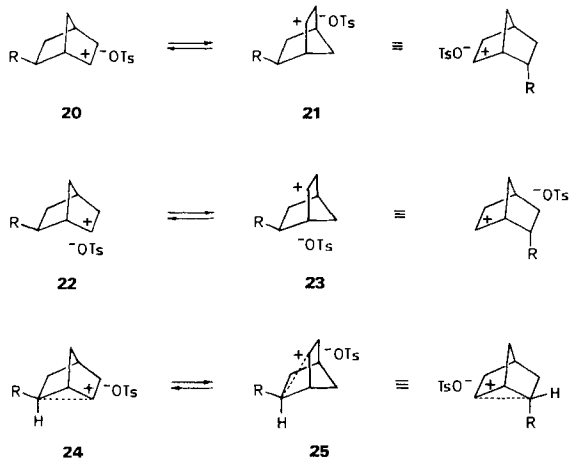
[9]) See also references in [13].

[10]) 2-*exo*-Norbornyl *p*-toluenesulfonate (**1k**) is a notable exception since the optically active enantiomers yield racemic norbornanol (**4k**) [9], *i.e.* the enantiomeric alcohols are formed in equal amounts.



20 **21**

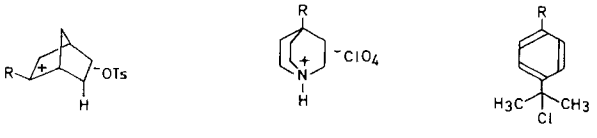
22 **23**

24 **25**

The fact that 1,3-elimination to nortricyclenes **12** occurs when R = COOH, $COOCH_3$, but especially when R = CN, *(Table 3)* suggests that these rate-retarding *-I* substituents facilitate deprotonation. However, some nortricyclene (**12k**) is also formed from the unsubstituted tosylates **1k** and **2k** and from the sodium salts **1l** and **2l** which do not contain *-I* substituents and belong to the most reactive *p*-toluenesulfonates (see 3.2).

3.2. *Reaction rates (Table 4).* The solvolysis rate constants for the *exo-p*-toluenesulfonates **1** reveal an unusually large effect of substituents at C(6). Thus, the *t*-butyl derivative **1a** reacts $5 \cdot 10^5$ times as fast as the cyano derivative **1j**, the dimethylamino derivative **1p**, which undergoes concerted fragmentation, *ca.* 10^6 as fast. The influence of substituents is much smaller in the *endo*-series **2**, as the rate difference of $1.8 \cdot 10^2$ between **2a** and **2j** shows[11]).

The different response of the *p*-toluenesulfonates **1** and **2**, **a**–**j**, to substituents at C(6) is illustrated by the plots of $\log k$ against the respective inductive substituent constants σ_I^q (*Fig. 1* and *2*). Since the latter were derived from the p*K* values of 4-substituted quinuclidinium perchlorates **27** [16], in which conjugative or hyperconjugative effects are absent or negligible, the linear correlations indicate that the rates are controlled by the *I* effects of the substituents only and that the *Hammett-Taft* equation $\log k/k_0 = \rho\sigma_I^q$ is obeyed. The slopes of the regression lines for **1** and **2**,



26 **27** **28**

[11]) Substituents at C(1) [8] and at C(5) [15] also affect the reaction rates of 2-*exo*-norbornyl sulfonates more strongly than those of the 2-*endo* epimers.

Table 4. *Solvolysis rate constants for* **1** *and* **2** *at 70.0° and* k_1/k_2 *rate ratios*

R		k_1	k_2	k_1/k_2	Accelerations[a])	
					1	**2**
a	t-C_4H_9	$6.09 \cdot 10^{-2}$	$2.55 \cdot 10^{-5}$	2388		
b	i-C_3H_7	$2.46 \cdot 10^{-2}$	$5.30 \cdot 10^{-5}$	464		
c	CH_3	$1.09 \cdot 10^{-2}$	$6.02 \cdot 10^{-5}$	181		
d	CH_2Br	$1.06 \cdot 10^{-4}$	$6.75 \cdot 10^{-6}$	16		
e	$COOCH_3$	$6.33 \cdot 10^{-6}$	$1.73 \cdot 10^{-6}$	3.7		
f	COOH	$5.97 \cdot 10^{-6}$	$2.88 \cdot 10^{-6}$	2		
g	CH_3COO	$8.14 \cdot 10^{-7}$	$1.21 \cdot 10^{-6}$	0.67		
h	F	$7.21 \cdot 10^{-7}$	$1.50 \cdot 10^{-6}$	0.48	5	3.3
i	Br	$1.51 \cdot 10^{-7}$	$4.06 \cdot 10^{-7}$	0.37		
j	CN	$1.23 \cdot 10^{-7}$	$1.40 \cdot 10^{-7}$	0.88	8.0	
k	H	$3.58 \cdot 10^{-2}$	$8.42 \cdot 10^{-5}$	425	1.8	
l	COONa	$7.04 \cdot 10^{-2}$	$1.16 \cdot 10^{-4}$	607	97	8.9
m	NH_2CH_2	$8.84 \cdot 10^{-3}$	$3.73 \cdot 10^{-5}$	237	4.0	1.9
n	$HOCH_2$	$5.97 \cdot 10^{-3}$	$4.39 \cdot 10^{-5}$	136	5.2	2.8
o	$CONH_2$	$7.56 \cdot 10^{-5}$	$7.12 \cdot 10^{-6}$	11	16.5	4.0
p	$N(CH_3)_2$	$1.45 \cdot 10^{-1}$	$6.25 \cdot 10^{-5}$	2320	1261	10
q	NH_2	$2.25 \cdot 10^{-2}$	$2.55 \cdot 10^{-4}$	88	163	38
r	OH	$6.05 \cdot 10^{-4}$	$1.00 \cdot 10^{-4}$	6	100	50
s	OCH_3	$2.88 \cdot 10^{-4}$	$4.29 \cdot 10^{-5}$	7	87	27
t	SCH_3	$3.34 \cdot 10^{-4}$	$2.09 \cdot 10^{-5}$	16	40	9.3
u	$NHCOCH_3$	$2.21 \cdot 10^{-4}$	$1.07 \cdot 10^{-5}$	21	23	4.5
v	NO_2	$1.13 \cdot 10^{-7}$	–		68	

[a]) Calculated from the inductive regression lines in *Fig. 1* and *2*.

which intersect at a $\sigma^q{}_I$ value of *ca.* 2.2, correspond to reaction constants ρ of -2.0 and -0.78, respectively. These values illustrate numerically that the *I* effect is transmitted far more strongly in the W-like conformation of **1** than in the sickle-like conformation of **2**. Furthermore, induction is much more effective in the strained norbornanes **1** than in the bromoadamantanes **3**, which have a ρ value of -1.14 [5][12]).

The points for the *p*-toluenesulfonates **1** and **2**, **l**–**o**, have been omitted from the plots in *Figure 1* and *2*, because they deviate from the inductive regression line by factors of 4 to 97 in the series **1** and by *ca.* 2 to 9 in the series **2** *(Table 4)*. Rate enhancements have been observed in other k_c processes [5] [17] [18] and are typical for electrofugal substituents, such as COO^-, $CONH_2$ and CH_2OH, which act as σ-electron donors a – b in fragmentation of the type $a-b-c-d-X \rightarrow a-b+c=d+:X$. Evidently such processes elicit a stronger response from σ-donors than the reversible protonation of quinuclidines **27** which serve as a gauge for the *I* effect[13]). The unsubstituted 2-*exo*-*p*-toluenesulfonate **1k** is a borderline case in that its rate is slightly elevated, *i.e.* by a factor of 1.8 *(Table 4)*, which is in keeping with the weakly electrofugal nature of the hydrogen atom. In *Figure 3* $\log k$ values for the 2-*endo*-

[12]) Reaction constants ρ are not only a function of the interacting charges. They also depend on a transmission factor which reflects the polarisability of the intervening dielectric.

[13]) The exalted effects of σ- and certain π-electron donors in k_c processes [5] resemble the exalted effects of *para*-donor substituents in the ionization of cumyl chlorides **28**, where the need for electrophilic substituent constants σ^+ first arose [19].

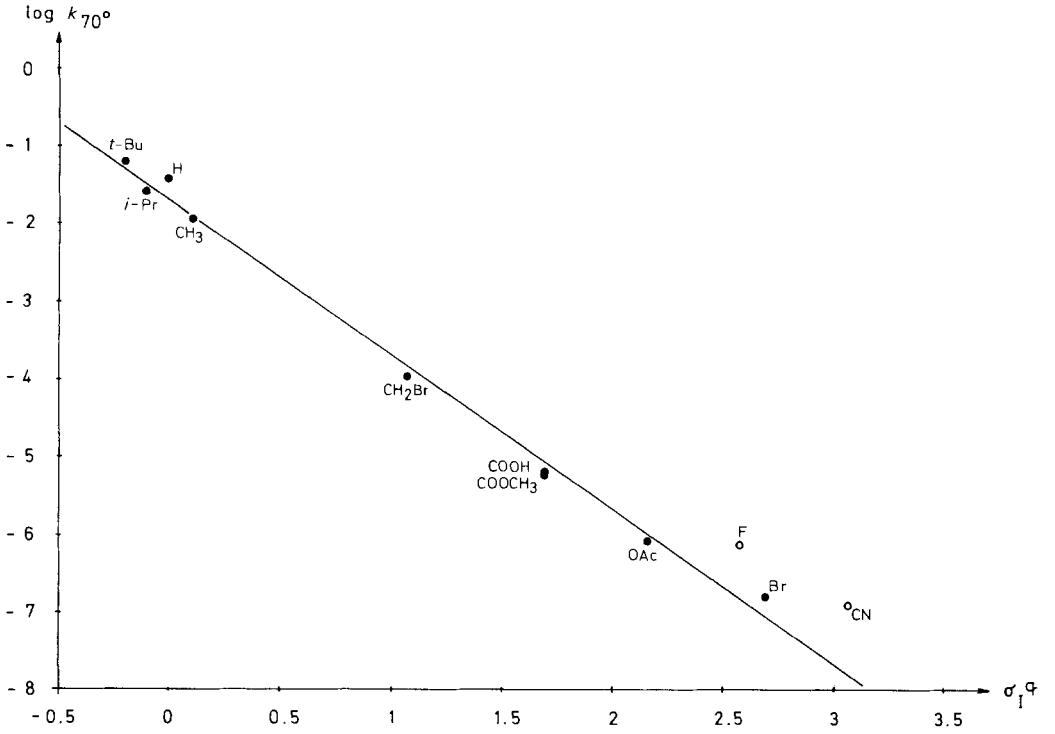


Fig. 1. *Plot of log* k *for* **1a**–**k** *in 80%* (v/v) *ethanol* vs. *inductive substituent constants for R* (F and CN not included in regression)

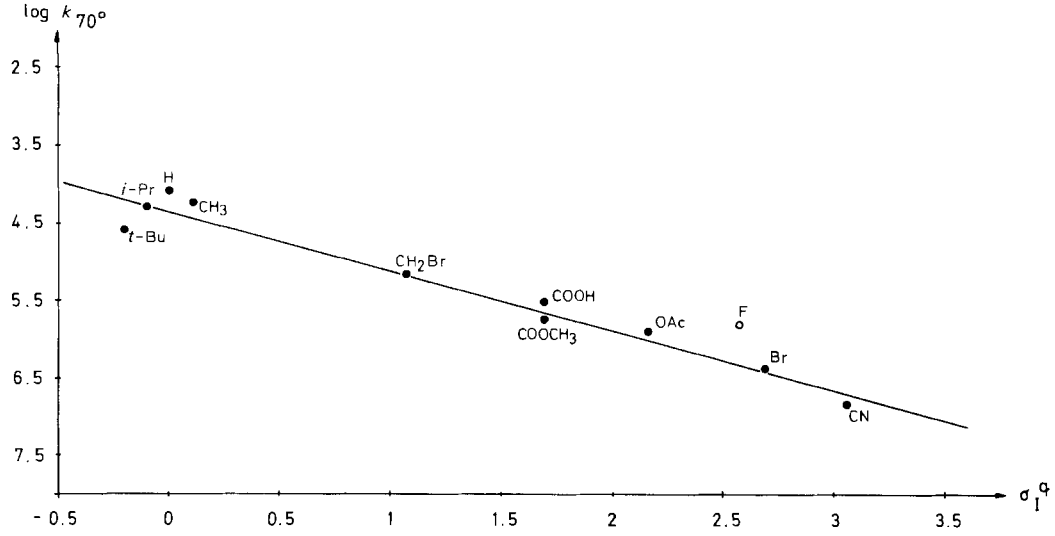


Fig. 2. *Plot of log* k *for* **2a**–**k** *in 80%* (v/v) *ethanol* vs. *inductive substituent constants for R* (F not included in regression)

p-toluenesulfonates **2a–2o** are plotted against the corresponding values for the 2-*exo*-*p*-toluenesulfonates **1a–1o**. The linear correlation proves that, except for the cyano derivatives **1j** and **2j** (see below), the rates are controlled by polar effects in the same way.

The *exo*-*p*-toluenesulfonates **1**, **p–u**, which possess n-electron donor substituents, show the frangomeric accelerations associated with concerted fragmentation [20]. For stereoelectronic reasons these are again much larger in the 2-*exo* series **1**, **p–u** *(Table 4)*.

The fluoro-*p*-toluenesulfonate **1h** and **2h** also show small accelerations of *ca.* 5 and 3.3, respectively, not however the bromo-*p*-toluenesulfonate **1i** and **2i**. A possible reason for the exceptional behaviour of fluorine is its net electron-donating conjugative effect, as evidenced by its negative electrophilic substituent constant σ^+ of -0.073 [19]. A 6-*exo*-F-atom should therefore assist the delocalization of the C(1), C(6)-bonding electrons in the incipient cation **29** and thereby facilitate ionization.

The *exo*-cyano-*p*-toluenesulfonate **1j** reacts eight times faster than anticipated on the basis of the σ_I^q value for the cyano group (*Fig. 1* and *Table 4*). Since the *endo*-cyano-*p*-toluenesulfonate **2j** and the 6-*endo*-cyano-2-*exo*-*p*-toluenesulfonate **30j**[14]), react normally, this acceleration was tentatively ascribed to participation of the 'loosened' C(6)-*endo*-H bond in the incipient cation **31** [10a], a conclusion supported by the formation of 44% of the nortricyclene **12j** *(Table 3)* and by the large deviation of the point for R = CN in the plot of log *k (endo) vs.* log *k (exo) (Fig. 3)*.

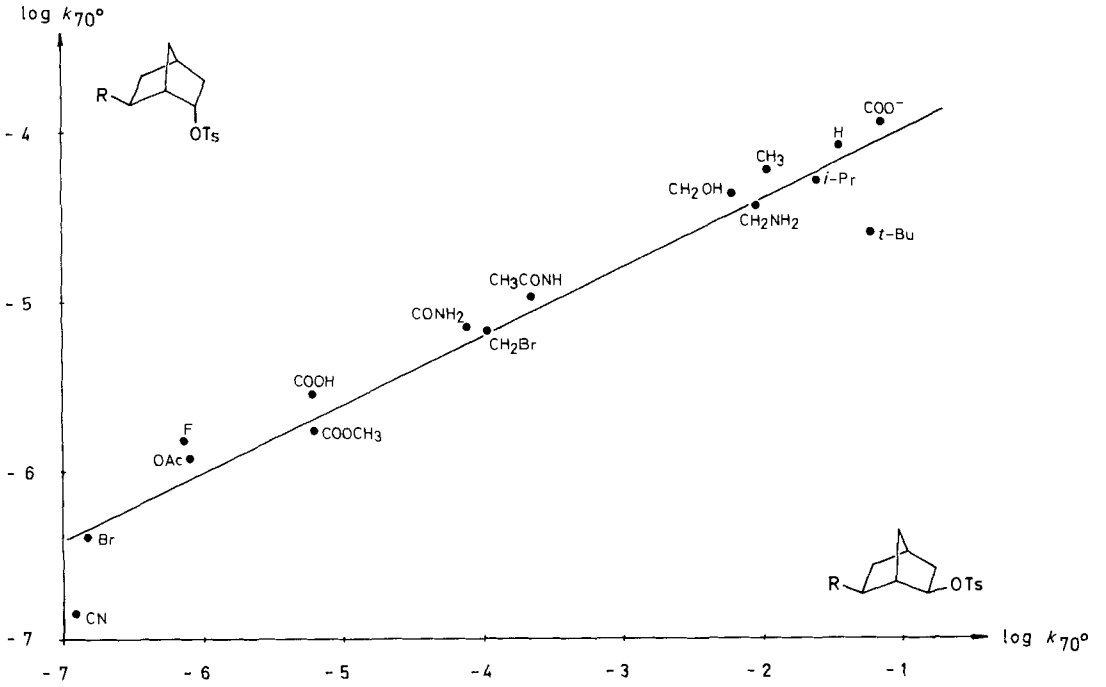
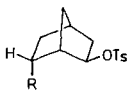


Fig. 3. *Plot of* log k *for the series* **1** vs. **2**

[14]) See part 6 [6].

29



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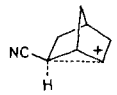

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3.3. exo/endo *Rate ratios (Table 4).* Differential transmission of the *I* effect of substituents at C(6) in the series **1** and **2** results in variable *exo/endo* solvolysis rate ratios k_1/k_2. They decrease steadily from 2388 for *t*-butyl to 0.37 for bromine, *i.e.* as the electron-attracting power of the substituent increases. The large ratios for hydrogen (425) and COONa (607) imply that these substituents are electron donors k_c processes. The main conclusion, however, is that steric hindrance to ionization of 2-*endo*-sulfonates **2** cannot be the cause of high *exo/endo* rate ratios, as proposed by *Brown* [7][15]. As *Figure 1* shows, variable rate ratios are determined by polar effects.

Steric effects are, however, not entirely absent, as the k_1 and k_2 values in *Table 4* show. Thus, in the *exo* series **1** the rates for the 6-alkyl derivatives increase in the inductive order $CH_3 < i\text{-}C_3H_7 < t\text{-}C_4H_9$ but decrease slightly in the same order in the *endo* series **2**. This reversal could be due to the buttressing effect of bulky 6-*exo*-substituents causing the 6-*endo* H-atom to bend towards the 2-*endo*-OTs group and thus hinders its exit. It is also the reason for the deviation of the point for *t*-butyl in the plot of *Figure 3*.

3.4. *The intermediates.* The large response of the solvolysis rates of 2-*exo*-*p*-toluenesulfonates **1** to substituents at C(6) points to an unusually strong inductive interaction between the latter C-atom and the incipient cationic center at C(2). This raises the question of whether induction involves C-participation *i.e.* bridging of C(2) by the pentacoordinate C(6)-atom, as illustrated in **24** and **32**.

As space-filling models show[16]), the electrons which link a chain of C-atoms are not confined to the region between consecutive atoms; they also occupy the space between alternate atoms, such as C(2) and C(6) in norbornanes. However, a bonding 1,3-interaction will only result in the latter case if C(2) is a cationic (sp^2) center and thus able to attract the electrons surrounding C(6), as in **32**. Donor substituents at C(6) will favor such bonding, whereas acceptor substituents will have the opposite effect. In k_c processes, induction therefore involves graded electron donation from a neighboring C-atom, *i.e.* C-participation or bridging. Conversely, the latter may be regarded as resulting from an electrophilic attack of a cationic center on a sp^3 C-atom. This view is supported by the rates and products discussed in 3.1 and 3.2.

Thus, donor substituents at C(6) lead to high rates and to 2-*exo* substitution products because nucleophiles tend to attack the unbridged *exo* side of the cation **24**. On the other hand acceptor substituents at C(6) lower the rate and also permit *endo* attack at C(2). Bridging should also be greatly reduced in the ionization of 2-*endo* *p*-toluenesulfonates **2** owing to the repulsion of the electrons around C(6) by the anion of the incipient ion pair **22**.

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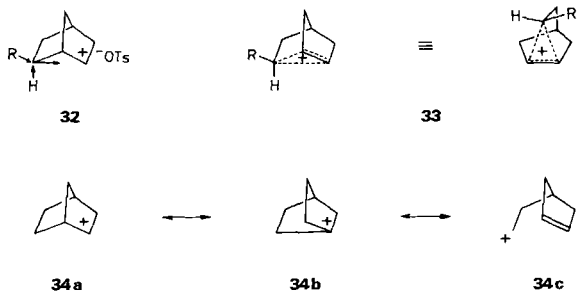
[15]) The reason for the high *exo/endo* ratio of 425 for **1k** and **2k** will be discussed in a subsequent article; see also [10g].

[16]) *E.g. CPK* Precision molecular models *(Ealing)*.

The formation of *endo*-cyclization products and of 6-*endo* substituted norbornanols **6** and norbornenes **7** from both **1** and **2** shows that the initially formed cations **20**, **22** and **24** undergo *Wagner-Meerwein* rearrangements to the epimeric cations **21**, **23** and **25**, respectively. As shown in the following article [6] the rate of rearrangment is also affected strongly by substituents at C(6), a further indication that the latter control the extent of 1,3-bridging.

1,3-Bridging, as illustrated by **24**, differs from *Winstein*'s concept of symmetrical bridging, as illustrated by the 'nonclassical ion' norbornyl cation **33** [9]. In this case C(1), C(2) and C(6) are held together by a two electron-three center bond in a nortricyclene-like structure. The charge of the cation is therefore shared by all three C-atoms, as expressed by the canonical structures **34a**, **b** and **c**, of the 'resonance hybrid' **33** [9][17]). In contrast, 1,3-bridging, as symbolized by **24** and **32**, implies a loose and therefore weak C(2), C(6)-bond to which the electrons surrounding C(6) make the largest contribution. The cation **24** thus retains a norbornane-like geometry[18]) and its capacity for facile rearrangement, which involves only a tightening of the C(2), C(6)-bond accompanied by a loosening of the C(1), C(6)-bond; rearrangement thus resembles a skeletal vibration.



There are further reasons to prefer 1,3-bridging as in **24**. Thus, symmetrical bridging as in **33** is unlikely unless the substituent is hydrogen as in **1k**. However, the plot of log k *vs.* σ_1^9 *(Fig. 1)* for the tosylates **1a**–**1k** does not reveal such exceptional behavior of **1k** as would justify the assumption of a special type of bonding. Furthermore, high *exo/endo* rate ratios *(Table 4)*, which are often associated with the formation of nonclassical ions, are also observed in the solvolysis of homologs of **1k** and **2k** where symmetrical bridging is ruled out for structural reasons [10g].

If the use of the term 'nonclassical' is to be extended to include unsymmetrically bridged carbocations like **35**, as recently proposed by *Olah* [23] and *Schleyer* [24], it would seem desirable to maintain the distinction between shorter and therefore stronger bonds and longer, weaker bonds by indicating the latter only by a dotted line. This, however, is tantamount to 1,3-bridging as formulated in **24**. However,

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[17]) Recent work by *Brown* [21] has shown that there is no significant charge delocalization from C(2) to C(1), as implied by **33** and **34b**.

[18]) The strain energy of nortricyclene (**12k**) is estimated to be more than twice that of norbornane [22].

35 is a suitable expression for fragmentation of a carbocation **36** to R^+ and an olefin and for the reverse reaction, the condensation of the latter to **36**.

35

36

This work was carried out with financial support from the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung.*

Experimental Part

For syntheses see p. 5.

Preparative solvolyses were carried out in dioxane/water 70:30 by weight [12]. Solutions were injected directly into the GC. apparatus equipped with normal columns [12] or capillary columns coated with silicone OV-17, OV-101 or OV-225 *(Applied Science Laboratories, Inc.)*.

The solvolyses of the sodium salts **1l** and **2l** were effected by allowing 0.01 M solutions to react in the presence of 3.3 mol-equiv. NaOH for 10 half-lives at 40° and 70°, respectively. Nortricyclene (**12k**) and the lactone **13** were determined by direct injection of the reaction solution. The latter was then evaporated to dryness, acidified with 2N HCl and extracted with ether. To the ether solution containing the carboxylic acids, was added diazomethane in ether. Evaporation of the ether yielded the lactone **13** and a mixture of the methyl esters of the acids **4f**, **8f** and **12f**, as listed in *Table 3*, beside small amounts of unidentified material. The known compounds were identified by comparison with authentic samples. The methyl ester of the hydroxyacid **8f** was prepared as follows.

*Methyl 2-hydroxy-2-*exo- *and 2-*endo*-norbornane carboxylates* **9e** *and* **8e**. To a mixture of 5.1 g (50 mmol) of 2-norbornanone, 2.61 g (53.1 mmol) NaCN and 7 g ice was added a solution of 6.34 g (33.3 mmol) of sodium pyrosulfite ($Na_2S_2O_5$) in 9 ml water. The temperature of the well-stirred two-phase mixture rose to 37°, when 50 ml ether and 10 ml water were added and, after shaking, the top layer was separated, dried (Na_2SO_4) and evaporated to dryness. The yellowish oil was taken up in 10 ml of dry methanol saturated with dry HCl at 0° and kept at 0° for 2 days. After addition of 100 g ice the mixture was extracted twice with ether. The combined extracts were washed with 2N $KHCO_3$, dried (Na_2SO_4) and evaporated to dryness. Distillation yielded 4.34 g (51%), b.p. 49–50°/0.02 Torr, of a mixture containing *ca.* 80% of the *exo*-ester **9e** and 20% of the *endo*-ester **8e**. – ^{1}H-NMR. ($CDCl_3$): 1.0–2.5 (*m*, 10 H, CH_2 and CH); 3.0 (*s*, 1 H, *exo*-OH (20%)); 3.2 (*s*, 1 H, *endo*-OH (80%)); 3.75 (*s*, 3 H, CH_3O). The latter was identical with the methyl ester obtained by solvolysis of **1l** and **21**.

$C_9H_{14}O_3$ (170.21) Calc. C 63.51 H 8.29% Found C 63.41 H 8.38%

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