74. Polar Effects

Part 12

Inductivity and Carbon Participation in the Solvolysis of 4-Substituted 2-Adamantyl Arenesulfonates

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The rate constants (log *k*) for the solvolysis of 4^e-substituted 2^e- and 2^a-adamantyl *p*-nitrobenzenesulfonates **14** and **15**, respectively, in 80% EtOH correlate linearly with the respective inductive substituent constants σ_I^q. Therefore, relative rates are controlled by the *I* effect of the substituents at C(4). The derived reaction constants, or inductivities, ρ_I of −0.80 and −0.64 for the series **14** and **15**, respectively, are far smaller than those previously determined for 6-substituted 2-norbornyl and 2-bicyclo[2.2.2]octyl sulfonates, in which the partial structure containing the substituent and the leaving group is the same. The ratio of the retained and inverted adamantanols obtained upon hydrolysis of the series **14** falls from 2.85 for R = CH_3 to *ca.* 1 for R = CN, *i.e.* as the substituent at C(4) becomes more electron-attracting. In the 2^a-series **15** this ratio is uniformly higher. These findings confirm that the 2-adamantyl cation is weakly bridged and that through-space induction in carbocations involves graded bridging of the cationic center by neighboring C-atoms.

Recent studies [1] have shown that the solvolysis rates of several series of bi- and tricyclic arenesulfonates correlate linearly with inductive substituent constants σ_I^q according to the equation $\log k = \rho_I \cdot \sigma_I^q + \log k_o$[1]. Since σ_I^q values were derived from the pK_a of 4-substituted quinuclidinium perchlorates **1** [3], in which steric, conjugative, and hyperconjugative effects are negligible or absent, these correlations indicate that relative ionization rates are controlled only by the inductive effect of the substituents. On the other hand, the reaction constants or inductivities ρ_I varied widely with structure, even when direct distances and the distances through the bonds between the substituents and the reaction center were practically the same. Thus, inductivity was highest ($\rho_I = -2.0$) in the 6-*exo*-R-2-*exo*-norbornyl series **2** [1c] and lowest ($\rho_I = -0.72$) in the 7-*anti*-2-*endo*-norbornyl series **3** [1g]. It was, therefore, concluded that inductivity is a directional property of molecules, and that these are anisotropic to the transmission of polar effects [2].

In rationalizing these results the stereochemical outcome of the reactions must also be taken into account. Thus, hydrolysis of 2-*exo*-norbornyl tosylate **2** (R = H) led to 2-*exo*-norbornanol **7** (R = H) with complete retention of configuration at C(2). In contrast, hydrolysis of 2-*endo*-norbornyl tosylate **3** (R = H) led to the same *exo*-alcohol **7** (R = H) but with complete inversion at C(2) [1c]. Furthermore, when the substituent R in

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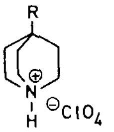
[1] For a recent review, see [2].



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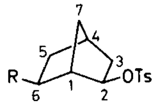

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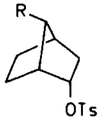

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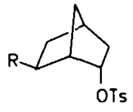

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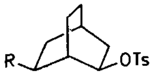

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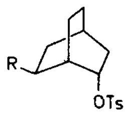

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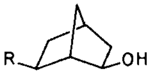

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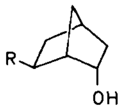

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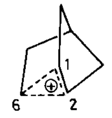

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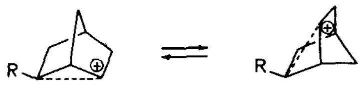
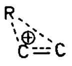


10a **10b**



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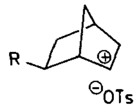

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2 was strongly electron-attracting, a mixture of 2-*exo*- and 2-*endo*-norbornanols **7** and **8**, respectively, was obtained [1c]. Consequently, substitution occurs with retention and/or inversion depending on the polar nature of the substituents and their position relative to the leaving group.

The pioneering work of *Winstein*²) revealed that the formation of solvolysis products with retention of configuration at the reaction center is usually caused by cyclization involving a neighboring nucleophilic group. Subsequent opening of the unstable cyclic intermediate by an external nucleophile leads to overall retention of configuration. To explain the observed retention in the solvolysis of 2-*exo*-norbornyl sulfonates **2** (R = H) *Winstein* proposed that ionization was assisted by the dorsal C(6) with formation of the symmetrically bridged ('nonclassical') cation **9**, in which the three centers C(1), C(2), and C(6) are bonded by the two electrons of the original C(1)–C(6) σ-bond³)⁴). Since the *endo*-side of the cation **9** is shielded by the partial C(2)–C(6) bond, attack by a nucleophile at C(2) takes place on the *exo* side and necessarily leads to retention.

As outlined in [1c] [2], there are reasons to describe this intermediate as an asymmetrically bridged cation **10a** (R = H) which interconverts extremely rapidly with its enantiomer **10b** (R = H) [1c]. This degenerate rearrangement is slowed down by strongly electron-attracting substituents at C(6), which reduce bridging and, hence, the rate of rearrangement [1d]. The dotted lines in **10a** and **10b** denote a longer and, therefore, weaker bond between C(2) and C(6) than between C(1) and C(6), a distinction that is not made in previous representations of asymmetrical bridging, such as **11** [6]. Briding of C(2) by the dorsal C(7) in the ion pair **12** from **3** ($\rho_I = -0.72$) would generate larger strain than bridging between C(2) and C(6) [1g]. On the other hand, bridging of C(2) by C(6) in the ionization of **4** ($\rho_I = -0.78$) to the ion pair **13** is stereoelectronically unfavorable and

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²) For a comprehensive review, see [4].

³) For a review, see [5].

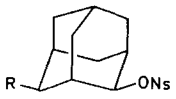
⁴) The symmetry of **9** no doubt contributed to its popularity. Meanwhile, it has been shown that symmetry does not confer special stability [1j] [2].

should be hindered by the departing anion [1c]. Similar arguments account for the ρ_I values and products of the 2-*exo*- and 2-*endo*-bicyclo[2.2.2]octyl tosylates **5** and **6**, respectively, which have ρ_I values of −1.5 and −1.0, respectively [1k].

These results can be readily rationalized if it is assumed that through-space induction involves graded bridging of the cationic center by neighboring C-atoms and that the strength of the resulting partial bonds depends on the generated bridging strain [2]. The following study of the solvolysis rates and products of 4^e-substituted 2^e- and 2^a-adamantyl *p*-nitrobenzenesulfonates (nisylates) **14** and **15**, respectively[5]), was undertaken to test this hypothesis.

The series **14** and **15** are particularly suited to this purpose because their partial structures **16** and **17**, respectively, are also present in the otherwise disparate norbornane and bicyclo[2.2.2]octane derivatives **2**, **4**, **5**, and **6**. Furthermore, in a series of papers [7][6]), *v. Schleyer* and coworkers have presented evidence that 2-adamantyl tosylate **14a** (TsO instead of NsO) is ionized without nucleophilic solvent participation to a highly unsymmetrical and weakly bridged 2-adamantylcation **18**. *Whiting* and coworkers [8] confirmed these findings and concluded that acetolysis occurs with little anchimeric assistance, although it leads to predominant retention of configuration at C(2) [8d]. They also reported that practically no 1→2 and 4→2 hydride shifts, nor elimination to 2,4-dehydroadamantane **19** take place [8c], and that less than 0.5% rearrangement to 4-protoadamantyl acetate (subsequently identified as the 4-*exo*-epimer **20** [7]) occurs.

As also pointed out by *v. Schleyer* and *Nicholas* [9], the adamantane structure should strongly resist changes which disrupt its rigid array of chair cyclohexane rings. The



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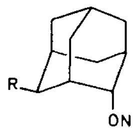

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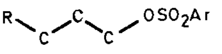

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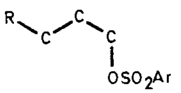

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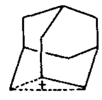

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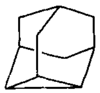

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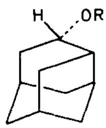

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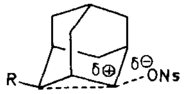

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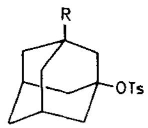

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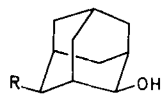

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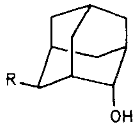

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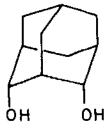

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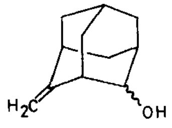

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R =
a H
b CH_3
c CH_2OAc
d CH_2Br
e COOH
f $COOCH_3$
g Cl
h Br
i CN
j COONa
k CO_2OH
l CH_2OCH_3
m $CONH_2$
o OH

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[5]) It is customary to indicate the orientation of the substituents in the same cyclohexane ring of adamantane as equatorial (e) or axial (a).

[6]) See also the list of references in footnote 19 of [7a].

introduction of two pentacoordinate C-atoms in a bridged transition state **21** for anchimerically assisted ionization clearly represents such a change. Therefore, if bridging and inductivity are related, as assumed [2], the ρ_I values for the solvolysis of 4^e-substituted 2^e-adamantyl arenesulfonates **14** should lie well below those observed in the solvolyses of the corresponding 2-*exo*-norbornyl and 2-*exo*-bicyclo[2.2.2]octyl derivatives **2** and **5**. Inductivity should be even further reduced in the transition state for the epimeric 2^a-adamantyl series **15** because bridging by C(4) is additionally hindered by the departing anion [1c]; *i.e.* if a C-atom is involved as a nucleophile, as in a S_N2 reaction, then preferably on the dorsal side of a C–ONs bond.

In this paper the rate constants[7]) for the nisylates **14a–m** and for several epimeric nisylates **15** in 80% EtOH are reported. Due to their low reactivity, only a small number of the corresponding tosylates were included in the study. The rates of some nisylates **14** were also measured in 97% trifluoroethanol (TFE) to determine the effect of higher solvent-ionizing power on inductivity. As recently reported [1h], ρ_I values are practically unchanged in this solvent when bridging strongly disperses positive charge, as in **10**. In contrast, ρ_I increases considerably in 97% TFE when bridging is weak, as in the series **3**. The syntheses of the series **14** and **15** as well as their hydrolysis products in 70% dioxane are described in [10].

Results and Discussion. – The rate constants for the 4^e-substituted 2^e- and 2^a-adamantyl nisylates **14** and **15**, respectively, in 80% (v/v) EtOH are listed in *Tables 1* and *2*; their hydrolysis products in 70% dioxane are summarized in *Table 3*. As shown in *Fig. 1*, the logarithms of the rate constants (log *k*) for the series **14** and **15** correlate linearly with the respective inductive substituent constants σ_I^q and lead to ρ_I values of −0.80 and −0.64,

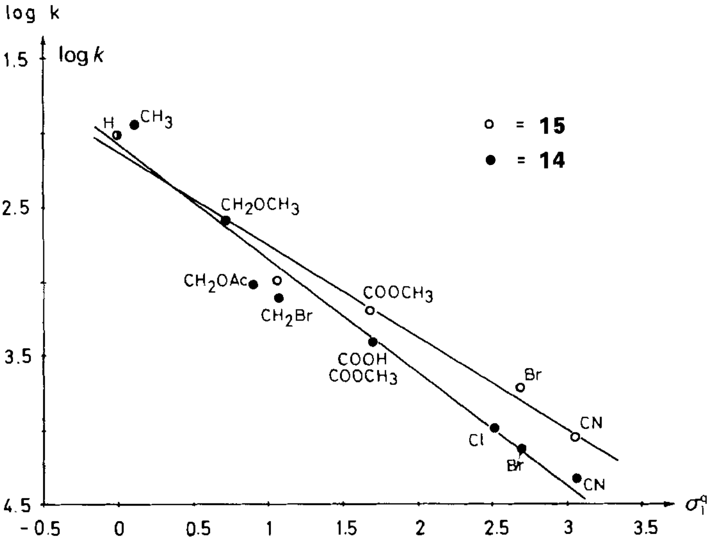

Fig. 1. *Plots of log* k *for* 10^{-3} M *solutions of* 4^e*-substituted* 2^e*-* (**14**) *and* 2^a*-adamantyl* p-*nitrobenzenesulfonates* **15** *in 80%* (v/v) *EtOH against inductive substituent constants* σ_I^q

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[7]) Determined by the conductometric method [13].

Table 1. *First-Order Rate Constants for* 10^{-3} M *Solutions of* 4^e*-R-*2^e*-Adamantyl* p-*Nitrobenzenesulfonates* **14** *in 80%* (v/v) *EtOH*

	R	T [°]	k [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol·degree]
14a	H	70.00	$4.68 \cdot 10^{-4}$	25.0	−1.1
		80.02	$1.38 \cdot 10^{-3}$		
		90.02	$3.75 \cdot 10^{-3}$		
		100.00[a])	$9.78 \cdot 10^{-3}$		
b	CH_3	70.00	$5.67 \cdot 10^{-4}$	24.8	−1.3
		80.00	$1.65 \cdot 10^{-3}$		
		90.00	$4.44 \cdot 10^{-3}$		
		100.00[a])	$1.15 \cdot 10^{-3}$		
c	CH_2OAc	70.00[a])	$4.17 \cdot 10^{-5}$	26.2	−2.5
		80.00	$1.26 \cdot 10^{-4}$		
		90.00	$3.75 \cdot 10^{-4}$		
		100.00	$9.84 \cdot 10^{-4}$		
d	CH_2Br	70.00[a])	$3.74 \cdot 10^{-5}$	26.0	−3.6
		90.00	$3.00 \cdot 10^{-4}$		
		100.00	$8.01 \cdot 10^{-4}$		
		110.00	$2.07 \cdot 10^{-3}$		
e	COOH	70.00[a])	$1.54 \cdot 10^{-5}$	26.8	−2.6
		100.00	$3.94 \cdot 10^{-4}$		
		110.01	$1.06 \cdot 10^{-3}$		
		119.92	$2.60 \cdot 10^{-3}$		
f	$COOCH_3$	70.00[a])	$1.19 \cdot 10^{-5}$	26.1	−5.2
		100.00	$3.94 \cdot 10^{-4}$		
		110.00	$7.28 \cdot 10^{-4}$		
		120.00	$1.77 \cdot 10^{-3}$		
g	Cl	70.00[a])	$3.85 \cdot 10^{-6}$	27.4	−3.9
		100.00[a])	$1.05 \cdot 10^{-4}$		
		110.05	$2.86 \cdot 10^{-4}$		
		120.16	$7.29 \cdot 10^{-4}$		
		129.40	$1.69 \cdot 10^{-3}$		
k	Br	70.00[a])	$2.93 \cdot 10^{-6}$	26.8	−6.0
		100.00[a])	$7.53 \cdot 10^{-5}$		
		100.30	$7.74 \cdot 10^{-5}$		
		110.74	$2.14 \cdot 10^{-4}$		
		120.60	$5.26 \cdot 10^{-4}$		
i	CN[b])	70.00[a])	$1.96 \cdot 10^{-6}$	26.4	−8.1
		100.00	$4.79 \cdot 10^{-5}$		
		110.00	$1.25 \cdot 10^{-4}$		
		120.00	$3.03 \cdot 10^{-4}$		
		130.00	$7.35 \cdot 10^{-4}$		
j	COONa	40.00	$3.09 \cdot 10^{-5}$	28.5	+11.9
		50.00	$1.33 \cdot 10^{-4}$		
		60.32	$5.41 \cdot 10^{-4}$		
		69.90	$1.85 \cdot 10^{-3}$		
		70.00[a])	$1.88 \cdot 10^{-3}$		
k	CH_2OH	70.00	$2.27 \cdot 10^{-4}$	25.5	−1.3
		80.00	$6.68 \cdot 10^{-4}$		
		90.00	$1.88 \cdot 10^{-3}$		
l	CH_2OCH_3	70.00[a])	$1.16 \cdot 10^{-4}$	25.8	−1.7
		80.00	$3.50 \cdot 10^{-4}$		
		90.00	$9.78 \cdot 10^{-4}$		
		100.00	$2.65 \cdot 10^{-3}$		
m	$CONH_2$	70.00[a])	$3.59 \cdot 10^{-5}$	26.1	−3.2
		90.00	$3.10 \cdot 10^{-4}$		
		100.03	$8.55 \cdot 10^{-4}$		
		109.40	$2.03 \cdot 10^{-3}$		

[a]) Extrapolated. [b]) Measured by Mr. *P. Herold.*

Table 2. *First-Order Rate Constants for* 10^{-3}M *Solutions of* 4^e*-R-*2^a*-Adamantyl* p-*Nitrobenzenesulfonates* **15** *in 80% (v/v) EtOH*

	R	*T* [°]	*k* [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol·degree]
15d	CH_2Br	70.00[a]	$4.37\cdot10^{-5}$	26.2	−2.4
		80.00	$1.34\cdot10^{-4}$		
		90.02	$3.84\cdot10^{-4}$		
		100.00	$1.05\cdot10^{-3}$		
f	$COOCH_3$	70.00[a]	$2.93\cdot10^{-5}$	25.6	−4.9
		90.00	$2.44\cdot10^{-4}$		
		100.00[a]	$6.54\cdot10^{-4}$		
		100.05	$6.67\cdot10^{-4}$		
		110.05	$1.65\cdot10^{-3}$		
h	Br	70.00[a]	$9.16\cdot10^{-6}$	25.3	−8.2
		99.61	$1.88\cdot10^{-4}$		
		100.00[a]	$1.97\cdot10^{-4}$		
		109.70	$4.86\cdot10^{-4}$		
		119.85	$1.15\cdot10^{-3}$		
i	CN	70.00[a]	$3.49\cdot10^{-6}$	26.9	−5.5
		100.00[a]	$9.03\cdot10^{-5}$		
		100.05	$9.20\cdot10^{-5}$		
		110.10	$2.34\cdot10^{-4}$		
		120.09	$6.15\cdot10^{-4}$		

[a] Extrapolated.

respectively, at 70°[8][9]. The ρ_I value of −0.82 derived from the rate constants for the corresponding tosylates **14a,c,f**, and **g** (Tso instead of NsO) *(Table 4)*, is equal to the ρ_I value for the nisylates **14** within the limits of accuracy imposed by the method. Evidently, inductivity is much lower in the adamantyl series **14** than in the corresponding norbornyl and bicyclo[2.2.2]octyl series **2** and **5**, respectively[10]. The decrease of ρ_I is striking, namely 60%, when the series **14** is compared with the series **2**, both of which possess the W-like partial structure **16**. The difference is smaller, namely 11%, between the series **4** and **15**, which contain the sickle-like partial structure **17**. The ρ_I value of −0.64 for the 2^a-adamantyl series **15** is the lowest yet encountered in a S_N1 process and appears characteristic of anchimerically unassisted ionization, where the inductive effect is largerly transmitted through σ bonds. It is also noteworthy that 2-adamantyl tosylate itself is *ca.* 2300 times less reactive than 2-*exo*-norbornyl tosylate and 322 times less reactive than 2-bicyclo[2.2.2]octyl tosylate (at 70°). While factors other than bridging could be involved, relative rates are consistent with the amount of bridging strain in the respective transition states [1k].

Furthermore, the ρ_I value of −1.12 derived from the rate constants for the series **14** in 97% TFE *(Table 5)* is 40% larger than in 80% EtOH, in keeping with a more localized

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[8] At 100° these values are −0.77 and −0.62, respectively.

[9] The points for the nisylates **14,j,k**, and **m**, with the electrofugal substituents COONa, CH_2OH and $CONH_2$, show the usual accelerations based on the regression line in *Fig. 1*. As in previous cases [1], they were, therefore, omitted in the regression.

[10] It is noteworthy that the point for **14i** (R = CN) in *Fig. 1* does not deviate significantly from the regression line, as in the case of the corresponding norbornyl and bicyclo[2.2.2]octyl derivatives **2** and **5** (R = CN), respectively [1c, 1k]. As recent experimental and theoretical work has shown (see [11] and further literature cited there), the CN group destabilizes cations less than anticipated on the basis of its inductive effect when it is directly attached to a center of positive charge. In contrast to **14i** strong bridging in **2** and **5** (R = CN) relays positive charge to C(6) in their cations.

Table 3. *Yields of the Hydrolysis Products* (in %) *of* 4^e*-R-*2^e*- and* (in brackets) *of* 4^e*-R-*2^a*-Adamantyl Nisylates* **14** *and* **15**, *Respectively, in 70%* (v/v) *Dioxane and Retention/Inversion* (Ret./Inv.) *Ratios*

	R	**23**	**24**	Ret./Inv.	Other products
a	H	100[a][b]		3.17[c]	
b	CH_3	74	24	2.85	
c	CH_2OAc	71	29	2.45	
d	CH_2Br	70 (20)	29 (78)	2.45 (3.9)	**26:** 1.5[d]
e	COOH	60	40	1.50	
f	$COOCH_3$	60 (22)	40 (74)	1.50 (3.4)	
g	Cl	58	40	1.44	**23o:** 0.9; **24o:** 1.1[e]
h	Br	38 (19)	36 (75)	1.27 (3.9)	**23o:** 11; **24o:** 13; **25:** 2[e]
i	CN	49 (30)	51 (70)	0.96 (2.2)	
j	COONa	68	29	2.33	**19:** 1.8[f]
k	CH_2OH	72	28	2.57	
l	CH_2OCH_3	70	30	2.33	
m	$CONH_2$	57	43	1.33	

[a] When R = H, **23** = **24**.

[b] In the presence of 1.1 equiv. of NEt_3 *ca.* 0.5% of a side product, probably 4-*exo*-protoadamantol **20** (R = H) is formed.

[c] Ratio reported by *Nordlander* and *Haky* [12] for 4^e-deutero-2^e-adamantyl tosylate in 60% dioxane.

[d] 2:1 mixture of 2^e- and 2^a-alcohols **26**.

[e] These products result from hydrolysis of **23** and **24g** and **h**.

[f] Beside 0.4% of an unidentified alcohol.

Table 4. *First-Order Rate Constants for* 10^{-3}M *Solutions of* 4^e*-R-*2^e*-Adamantyl* p*-Toluenesulfonates in 80%* (v/v) *EtOH*

	R	*T* [°]	*k* [s^{-1}]	$H^{\neq}$ [kcal/mol]	$S^{\neq}$ [cal/mol · degree]
14a	H	70.00[a]	$1.15 \cdot 10^{-5}$[b]	27.1	−2.5
		90.00	$1.08 \cdot 10^{-4}$		
		100.30	$3.15 \cdot 10^{-4}$		
		110.00	$8.09 \cdot 10^{-4}$		
c	CH_2OAc	70.00[a]	$9.28 \cdot 10^{-7}$	27.6	−6.0
		110.00	$7.06 \cdot 10^{-5}$		
		120.63	$1.96 \cdot 10^{-4}$		
		130.00	$4.48 \cdot 10^{-4}$		
		110.05	$1.65 \cdot 10^{-3}$		
f	$COOCH_3$	70.00[a]	$2.31 \cdot 10^{-7}$	29.1	−4.4
		110.00	$2.21 \cdot 10^{-5}$		
		120.00	$6.00 \cdot 10^{-5}$		
		129.00	$1.41 \cdot 10^{-4}$		
g	Cl	70.00[a]	$1.01 \cdot 10^{-7}$	28.2	−8.7
		114.82	$1.36 \cdot 10^{-5}$		
		122.20	$2.74 \cdot 10^{-5}$		
		129.03	$5.11 \cdot 10^{-5}$		

[a] Extrapolated. [b] *Bentley* and *Schleyer* reported a titrimetric value of $1.07 \cdot 10^{-5}$ at 70° [7c].

positive charge at C(2) in the transition state for these compounds [1h]. The fact that 2-adamantyl tosylate reacts almost ten times faster in 97% TFE than in the more nucleophilic solvent 80% EtOH supports *v. Schleyer*'s conclusion [7], that this compound ionizes with very little or no nucleophilic solvent participation. This is also borne out by the linear correlation between log *k* for the series **14** and log *k* for the 3-substituted

Table 5. *First-Order Rate Constants for* 10^{-3} M *Solutions of* 4^e*-R-*2^e*-Adamantyl* p-*nitrobenzenesulfonates in 97%* (w/w) *TFE*

R	T [°]	k [s^{-1}]	k(97 TFE)/k (80 EtOH)
H	70.00	$4.34 \cdot 10^{-3}$	9.3
CH_2OAc	70.00	$1.80 \cdot 10^{-4}$	4.3
$COOCH_3$	70.00	$3.09 \cdot 10^{-5}$	2.6
CN	70.00[a])	$1.40 \cdot 10^{-6}$	0.71
	109.52	$7.52 \cdot 10^{-5}$	
	119.18	$1.72 \cdot 10^{-4}$	
	129.17	$4.08 \cdot 10^{-4}$	

[a]) Extrapolated: $H^{\neq} = 25.55$ kcal/mol; $S^{\neq} = -11.15$ cal/mol·degree.

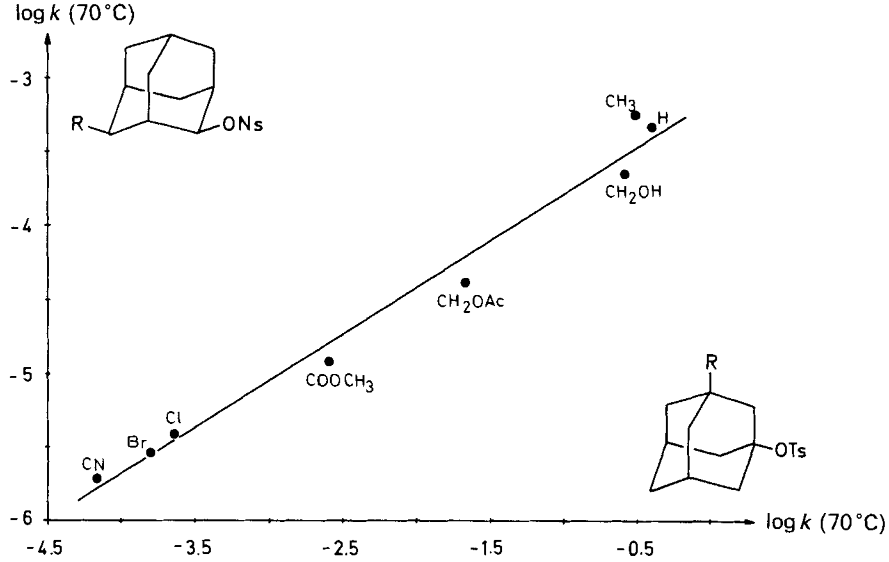

Fig. 2. *Plots of log* k *for* 4^e*-substituted* 2^e*-adamantyl* p-*nitrobenzenesulfonates* **14** *against log* k *for 3-substituted 1-adamantyl* p-*toluenesulfonates* **22**

adamantyl tosylates **22** [1e] *(Fig. 2)*, where nucleophilic solvent participation is excluded for structural reasons[11]). This finding also confirms that the series **14** react by the unimolecular S_N1 mechanism [7] [8], as does the fact that the entropies of activation are even less negative for the series **14** *(Table 1)* than they are for the series **22** [1e].

The hydrolysis products of the 4^e-substituted 2^e- and 2^a-adamantyl nisylates **14** and **15**, respectively, in 70% dioxane and the retention/inversion ratios obtained from the yields of the resulting epimeric adamantanols **23** and **24** are listed in *Table 3*. The yields of the mixtures of these alcohols were as a rule well over 97%, except in the case of the chloro- and bromo-substituted nisylates **14** and **15g**, and **h**, respectively, where the first formed halo alcohols **23** and **24** (R = Cl or Br) underwent further hydrolysis to the diols

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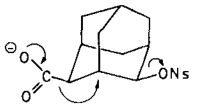
[11]) The ρ_I value for the 3-substituted 1-adamantyl tosylates **22** in 80% EtOH is -1.26 [1e] and, hence, *ca.* 58% higher than ρ_I for the secondary series **14**.

23o, **24o**, and **25**. The bromomethyl nisylate **14d** also led to small amounts of the unsaturated 2^e- and 2^a-adamantanols **26**. The sodium salt **14j** of the acid **14e** yielded *ca.* 1.8% of the 2,4-dehydroadamantane **19**, apparently by homofragmentation [1c], according to **27**.



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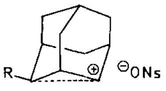

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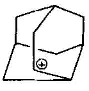

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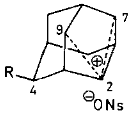

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A retention/inversion ratio of 3.17 for the 'unsubstituted' 4^e-deutero-2^e-adamantyl tosylate in 60% dioxane was recently reported by *Nordlander* and *Haky* [12]. This is somewhat larger than the value of 2.85 now determined for the 4^e-methyl-2^e-nisylate **14b** in 70% dioxane. The salient features of *Table 3,* however, are the decreasing retention/inversion ratios for the series **14**, which drop from 2.85 for R = CH_3 to 0.96 for R = CN, *i.e.* in the order of increasing electron attraction by the substituents. The ratio of *ca.* 1 for R = CN is in agreement with an essentially unbridged and symmetrically solvated 2-adamantylcation. The ratio is relatively high when R is an electrofugal group, such as COONa or CH_2OH, which are less electron-attracting in S_N1 reactions than expected on the basis of their σ_I^q values [1c]. It is also noteworthy that the transient cations show practically no tendency to rearrange to more strained protoadamantyl cations **28**.

The fact that the nisylates **14b–h** are hydrolyzed to adamantanols with predominant retention is further evidence for a weakly bridged highly unsymmetrical 2-adamantylcation, as claimed by *v. Schleyer* and coworkers [7]. However, formula **29** (R = H) is preferred to their formula **18**, because it illustrates that the partial C(2)–C(4) bond is longer and therefore weaker than the C(3)–C(4) σ-bond. The retention/inversion ratios for the 2^a-adamantyl nisylates **15** vary much less with the substituent at C(4), namely from 3.9 for R = CH_2Br to 2.2 for R = CN *(Table 3)*. This result points to very weak bridging of C(2) by C(4) in the formation of the ion pair **30**, as also indicated by the low ρ_I of −0.64. On the other hand, the fact that 70–79% of retained 2^a-adamantanols **24** are formed, indicates weak, but almost constant, bridging of C(2) by the dorsal C(7) and, for symmetry reasons, also by C(9), as illustrated in **30**.

In conjunction with the observed low inductivity of the series **14**, and especially of **15**, these findings also confirm that through-space induction in carbocations involves graded bridging by neighboring C-atoms according to the resultant bridging strain [2].

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