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THE EFFECT OF POLAR SUBSTITUENTS ON THE SOLVOLYSIS OF SECONDARY AND TERTIARY 2-NORBORNYL DERIVATIVES[1].

D.Lenoir*, W.Röll, E.Weiss, and G.Wenke

Organisch-Chemisches Institut der Technischen Universität
D 8000 München 2.

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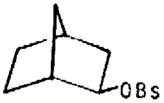
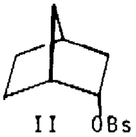
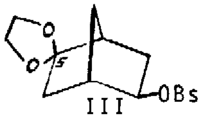
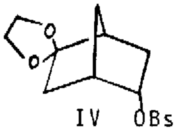
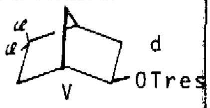
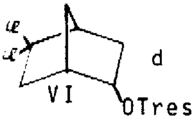
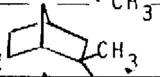
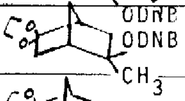
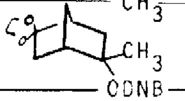
The origin of the large exo-endo (I/II) rate ratios in solvolysis of epimeric 2-norbornyl brosylates[2] is still under debate[3]. To probe this problem, we studied previously the influence of polar substituents[4] at C-1 on solvolysis of exo- and endo-2-norbornyl sulfonates[5]. Electron-withdrawing groups decelerate the rate of 2-exo-norbornyl tosylate much more than the 2-endo isomer and, as a result, a strong reduction of k_{exo}/k_{endo} is observed[5].

Since groups at C-1 may exert not only electronic but also steric influences, we have now studied the effects of two remotely attached groups (at C-5) with different polarities: ethylene ketal (compounds III and IV) and geminal dichloro (compounds V and VI). These groups should not manifest the steric influence on the reaction demonstrated previously for mono 5- and 6-exo substituents[6].

Solvolysis of tertiary 2-methyl-2-norbornyl benzoates (compounds VII and VIII) are supposed to proceed via classical carbocations[7]. Since the influence of polar substituents on the solvolysis of tertiary 2-norbornyl derivatives has not been studied, we investigated the effect of the ethylene ketal group on the isomeric 2-methyl-2-norbornyl 3,5-dinitrobenzoates (compounds IX and X).

Compounds III-X (see table I) were prepared from 5-exo-acetoxy-2-norbornanone[8] by appropriate functionalization of the keto group and subsequent derivatization of the acetoxy group[9]. The solvolysis rates of the sulfonates I-VI were determined in 60% aq. ethanol. Since deactivated 2-norbornyl sulfonates as well as 2-endo-norbornyl brosylate (II) are likely to react by nucleophilic solvent participation in normal solvents,[5] the rates of the brosylates I-IV were also determined in 97%

Table I. Summary of Solvolysis Rates of Norbornyl Derivatives I-X

Compound	Solvent	Temp [°C]	k^a [sec^{-1}]	ΔH‡ [kcal/°mole]	ΔS‡ [e.u.]	k_{exo}/k_{endo}
 I	60%Ethanol	25.0	8.3×10^{-3}			858
	97% HFIP[b]	-4.7	1.74×10^{-2}			
		0.1	3.77×10^{-2}			
		5.25	5.45×10^{-2}	15.6	-8.0	
		9.20	8.20×10^{-2}			
		25.0[c]	3.91×10^{-1}			1746
 II	60%Ethanol	74.9	2.28×10^{-3}			
		49.6	1.76×10^{-4}	21.9	-7.9	
		25.0[c]	9.67×10^{-6}			
	97% HFIP	50.1	2.54×10^{-3}			
		25.0[c]	2.24×10^{-4}	18.0	-15.0	
 III	60%Ethanol	75.3	1.71×10^{-3}			
		50.1	4.84×10^{-5}	25.0	0.3	
		25.0[c]	3.30×10^{-6}			57.1
	97% HFIP	52.9	1.34×10^{-3}			
		24.4	6.73×10^{-5}	19.6	-11.7	
		25.0[c]	7.21×10^{-5}			26.6
 IV	60%Ethanol	99.4	3.75×10^{-4}			
		75.0	3.13×10^{-5}	25.4	-6.5	
		25.0[c]	5.78×10^{-8}			
	97% HFIP	75.0	4.32×10^{-4}			
		49.9	4.11×10^{-5}	20.3	-16.0	
		25.0[c]	2.71×10^{-6}			
 V [d]	60%Ethanol	80.6	9.20×10^{-4}			
		55.8	4.76×10^{-5}	21.6	-12.8	
		25.0[c]	1.42×10^{-6}			9.4
 VI [d]	60%Ethanol	99.5	2.10×10^{-4}			
		80.7	2.64×10^{-5}	20.1	-22.0	
		55.8	4.65×10^{-6}			
		25.0[c]	1.51×10^{-7}			
VII 	60%Acetone	100.0	4.20×10^{-3}			150.0
VIII 	60%Acetone	100.0	2.80×10^{-5}			
IX 	60%Acetone	100.0	1.04×10^{-4}			24.2
X 	60%Acetone	100.0	4.30×10^{-6}			

[a] Determined conductometrically, average of two runs, deviation not more than ±3%
[b] Det. conductometrically, using a high speed recording technique [c] Calculated from rates at other temperatures [d] Tres = $SO_2CH_2CF_3$; no ionic chlorine could be detected after solvolysis of two half-lives

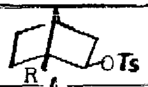
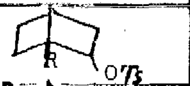
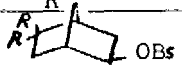
hexafluoroisopropanol (HFIP).This solvent has been shown to have very low nucleophilicity[10].Hence,solvolysis should occur without nucleophilic solvent participation;consequently the k_{exo}/k_{endo} value should reflect the difference of the true carbonium ion reactivity of 2-norbornyl isomers. Unsubstituted (VII and VIII) as well as 5-substituted 3,5-dinitrobenzoates (IX and X) were solvolysed in 60% aq. acetone at 100°.The kinetic results are summarized in Table I.

The following conclusions can be drawn from these results:

1. The magnitude of the value k_{exo}/k_{endo} of unsubstituted,epimeric 2-norbornyl brosylates depends on the solvent.[5] In less nucleophilic solvents like TFA[11],TFE[5] and HFIP the value is increased in comparison with 350,found in acetic acid[2]. The ratio, 1746 ,calculated for solvolysis in HFIP at 25.0° ,is of the same magnitude found for the ratio of HOAc polarimetric rates.[2] Therefore,the absence of internal return for the *exo*-brosylate I and of nucleophilic solvent assistance of the *endo*-brosylate II is a likely explanation of this behavior.

2. Polar substituents decelerate the rate of either epimeric brosylate; The rates of *exo* brosylates are reduced more than the *endo* isomers,depending on the polarity of the group.Thus,for the gem-dichloro group,the k_{exo}/k_{endo} value is strongly reduced from 858 to 9.4.The rate constants of either series can be correlated by a Hammett-Taft treatment.[12] Table II summarizes these results together with those of some 1-substituted 2-norbornyl tosylates.[5]

Table II.Hammett-Taft plot[12] of epimeric 1-and 5-substituted 2-norbornyl sulfonates

Series of *exo*-compounds	Substituent R[13]	ρ^* (Corr.c.)	Series of *endo*-compounds	Substituent R[13]	ρ^* (Corr.c)
	CN,CO_2CH_3,H, CH_3,C_2H_5	-5.00 (0.989)		CN,OCH_3,CO_2CH_3 C_6H_5,H,CH_3,C_2H_5	-2.34 (0.976)
	Cl_2,OCH_2CH_2O OCH_3,H	-2.62 (0.996)		Cl_2,OCH_2CH_2O, OCH_3,H	-1.65 (0.994)

It is apparent that the response of the transition state of solvolysis of secondary *exo*- and *endo*-norbornyl sulfonates is quite different towards substituents,[14] esp. when more polar substituents are employed.This is to be expected when the transition state of the *exo* sulfonate I is stabilized by σ-delocalization or another electronic effect.

The reduction of the value k_{exo}/k_{endo} for the ethylene ketal brosylates II and III is still observed in HFIP;therefore this reduction is an effect of true carbonium reactivity of deactivated 2-norbornyl isomers without solvent assistance; solvolysis of epimeric, deactivated norbornyl sulfonates does not show a common intermediate in normal solvents.

3. The polar ethylene ketal group reduces the *exo*/*endo* ratio in the series of tertiary 2-norbornyl benzoates VII and VIII from 150 to 24.This reduction is much less pronounced than in the secondary series.

Investigation of additional electronegative 5-*exo*-substituents on the solvolysis of 2-norbornyl brosylates and detailed product studies is in progress.[15]

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