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THE GENERATION OF SUBSTITUTED CLASSICAL SECONDARY 2-NORBORNYL CATIONS

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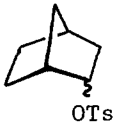
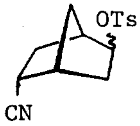
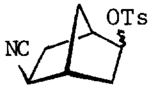
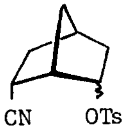
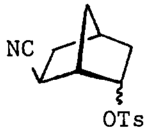
Abstract: All possible stereoisomers of 5-cyano- and 6-cyano-2-norbornyl tosylate have been synthesized (except the endo, endo isomer) and solvolyzed in 97% hexafluoroisopropanol. The rates and products are most easily interpreted in terms of classical ions. An approximate model of substituent effects allows an estimate of anchimeric assistance in the parent norbornyl ion to be a factor of about 540 at 25° and 18 at 125°.

The electronic structure of the 2-norbornyl cation has remained controversial for over 30 years as has the related question of whether the high exo/endo rate ratios observed for the solvolysis rates of various 2-norbornyl derivatives provides sufficient evidence of the importance of σ-participation in the solvolytic transition states for the exo-isomers.[1] Gassman and Marshall studied the solvolysis of the 7-oxo derivatives, compounds designed to show minimal σ-participation.[2] A number of subsequent studies have also utilized this approach[3] with results suggesting that suppression of σ-participation is correlated with a diminution of the exo/endo rate ratio. Unfortunately, the interpretation is complicated by the possibility that introduction of strongly electron withdrawing substituents to favor solvolysis through classical transition states might also induce a greater degree of nucleophilic solvent participation with the sterically more accessible endo-tosylates.[1b] With the development of non-nucleophilic solvents, particularly the fluorinated alcohols, the potential for solvent participation is greatly reduced. In particular, 97 wt-% aqueous hexafluoroisopropanol (HFIP) represents the medium of choice as a limiting solvent.[4]

The work reported here is a kinetic and product study of the solvolysis in 97% HFIP of 2-norbornyl systems containing the strongly rate retarding 5- or 6-cyano substituent. The importance of σ-participation in the unsubstituted parent system is estimated from the kinetic data.

The conductomeric rate constants for the solvolysis of seven of the eight possible 2,5- and 2,6-norbornane cyanotosylates are summarized in Table I. Large rate retardations are observed for all of the substituted compounds. In addition the exo/endo rate ratios are reduced by factors of between 10 and 1000 relative to the unsubstituted exo/endo-norbornyl tosylate ratio.

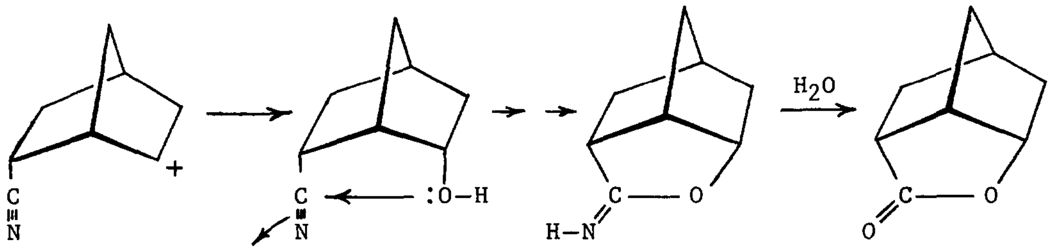
TABLE I
Kinetic Data for Solvolysis of Norbornyl Tosylates in 97% HFIP

	exo-tosylate			endo-tosylates			
System	k(sec-1)[a]	T,oC	%4	k(sec-1)	T,oc	%4	R(exo/endo)
	1.06x10-2[b]	0.1		7.85x10-6[c]	25.0		1400 (25°)
	1.1 x10-1[c]	25.0		8.91x10-4[b]	50.1		340 (125°)
	1.1 x10-1[c]	25.0	--	[2.1x10-1]	125.0		
	[7.2 x10±1]	125.0					
	[2.4 x10^{-7}]	25.0		[1.8x10^{-7}]	25.0		1.3 (25°)
	(2.03±0.15)x10^{-5}	74.4		(6.64±0.28)x10^{-6}	99.7		36 (125°)
	(1.25±0.15)x10^{-4}	99.7	57	(1.72±0.08)x10^{-5}	125.2	74	
	[6. 2x10^{-4}]	125.0					
	[1.4x10^{-7}]	25.0		[2.8x10^{-8}]	25.0		5.0 (25°)
	(1.95±0.27)x10^{-5}	74.4		(1.72±0.08)x10^{-5}	99.7		11 (125°)
	(1.47±0.15)x10^{-4}	99.9		(8.7±1.4)x10^{-5}	125.3	94	
	[8.81x10^{-4}]	125.0	49				
	(1.01±0.03)x10^{-5}	126.4	87	not studied			
	(1.17±0.09)x10^{-5}	125.6	62	(1.58±0.22)x10^{-6}	126.3	81	8

(a) Values in square brackets are calculated from data at other temperatures.
(b) D. Lenior cited in H.C. Brown, et al., J.Am.Chem.Soc., 100, 3143 (1978).
(c) Calculated from brosylate rate data.
(d) This work.

Although 10-12 component product mixtures were observed, the dominant solvolysis product[6] in all cases was the endo-2,6-lactone,4, shown below. Lactone 4 presumably arises from the classical endo-6-cyano-2-norbornyl cation, 1 (or its ion-pair). Apparently cation 1 preferentially captures solvent from the endo face to give nitrile 2 that then, as demonstrated independently, spontaneously cyclizes to 4.

It is interesting that no other endo-OH products were observed and that the endo-cyano ion, 1, shows a preference for endo capture. This could arise from a strong interaction between the nitrile and the known 1:1 HFIP-H$_2$O complex[5] which if disrupted would give rise to a "free" H$_2$O on the endo-face of the ion leading



1 2 3 4

preferentially to 2 (and ultimately to 4).

The combination of marked rate retardation and dimished exo/endo rate ratios suggests the involvement of essentially classical transition states and intermediates in the solvolysis of the cyano tosylates.

The dominance of 4 among the products indicates extensive ion-pair rearrangements in this solvent with a facile reaction channel leading from 1 or the corresponding ion-pair.

In order to estimate the magnitude of the rate acceleration attributable to σ-participation in the unsubstituted exo-tosylate, a semi-empirical model for the cyano substituent effects was applied. The nitrile dipole was treated as a pair of point charges centered on the carbon and nitrogen atoms separated by 1.15 A; a C-CN bond length of 1.48 A was used. It was assumed that the structure of the solvolysis transition state could be represented as a free carbocation and that this was adequately represented by the idealized norbornane geometry.[8]

The observed substituent effects were fitted using equation (1).

$$\log(k/k_h)_{obs} = \frac{1}{D_E}\left(\frac{e^2}{2.3RT}\right)\left(\frac{1}{r_{+-}} - \frac{1}{r_{++}}\right) - b \qquad (1)$$

where r_{++} is the distance between the carbocation center and the electron-deficient nitrile carbon, r_{+-} is the distance between the carbocation center and the nitrogen, D_E is the effective dielectric constant, and b is a parameter included only for the solvolysis data for the cyano-substituted exo-tosylates (i.e., b = o for the endo-tosylates). Least squares analysis of the combined 125° data gave $D_E = 2.28$ and $b = 1.26$ with $\sigma = 0.50$.

Given the crudity of the model and the uncertainties of the temperature extrapolations , the correlation is remarkable. The 2500-fold variation in the cyano-substituted rates is fit with a standard deviation corresponding to a rate factor of three; if the parent norbornyl tosylate is included, the rate ratio variation is $10^{6.8}$. Of particular interest is the calculated value of $10^b = 10^{1.26} = 18$, which represents the lower limit for the rate retardation at 125° resulting from the loss of σ-participation upon introduction of a nitrile substituent. An F-test indicates that inclusion of b is statistically significant at the 90% confidence level. Addition of a third parameter to assign separate D_E's to the $1/r_{++}$ and $1/r_{+-}$ terms of equation (1) results in a slight but statistically insignificant improvement of the fit.

The data at 25° is less complete and less certain, but the same treatment yields an estimate of the rate factor from anchimeric assistance of 540. Combination of the data at the two temperatures gives a ΔH for non-classical stabilization of about 8 kcal/mole and a ΔS of about -14 eu.

A referee has kindly drawn attention to the work of Lajunen and co-workers[9] on the hydration of exo- and endo-5-cyano-2-norbornenes. Although carried out in an aqueous medium (different D_E, and solvation properties) their results appear to be consistent with the substituent effect model described here.

References and Notes

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6. All of the products (including the exo-alcohols) proved to be stable under the reaction conditions except for exo- and endo-2-cyano-5-norbornene which slowly hydrolyzed to the corresponding 2,5-exo-alcohol in the presence of excess tosic acid. The product mixture composition did not appear to be significantly affected by this.
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