

ternation and the dependence of the nitrogen hfs constant on NaBPh_4 concentration. The kinetic parameters for the formation ($k_f = 122.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at 20°C in THF, $E_a = 4.9$ kcal/mol) and the ionization ($k_i = 7.7 \times 10^7 \text{ s}^{-1}$ at 20°C in THF, $E_a = 7.6$ kcal/mol) of the triple ion have been determined. The thermodynamic equilibrium constant controlling the formation of the triple ion in THF is 156 M^{-1} at 20°C ($\Delta H = -2.6$ kcal/mol, $\Delta S \approx 0$ eu). If $\text{DNP}^- \cdot \text{Na}^+$ forms a contact triple ion, one fully solvated Na^+ ion changes into a nonsolvated one, according to eq 4. Desolvation of ions increases the entropy of the system and makes the association endothermic.³⁷ As the heats of formation of the triple ion both in THF and in DME are low (-2.6 to 0 kcal/mol), it can be inferred that the triple ions as well as the ion pairs³⁸ are solvent separated.

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Nucleophilic Solvent Assistance in the Solvolysis of *endo*-2-Norbornyl Derivatives

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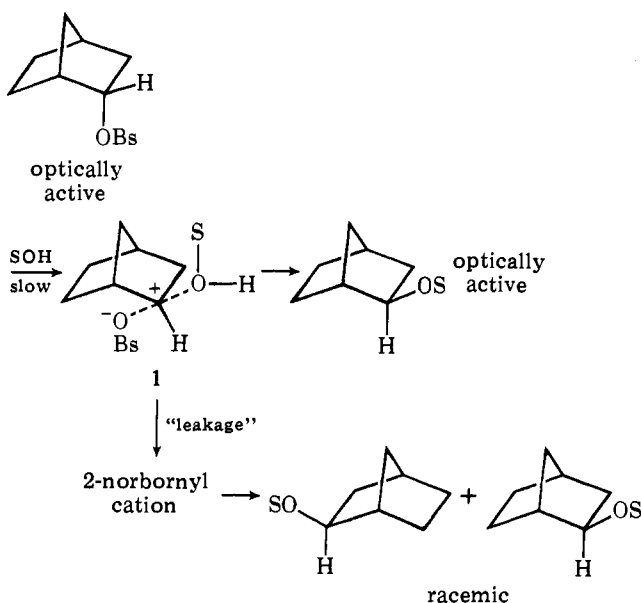
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Abstract: *endo*-2-Norbornyl derivatives have in many instances served as models with which to compare the solvolysis of *exo*-2-norbornyl derivatives. Consequently, it is important that the solvolysis of the *endo* epimer be well characterized if the nature of *exo*-norbornyl solvolysis is to be determined. In the present paper nine probes of nucleophilic solvent assistance are applied to *endo*-norbornyl solvolysis, and it is determined that the amount of solvent assistance is small. The implications of this conclusion are considered.

That *endo*-2-norbornyl derivatives solvolyze with nucleophilic solvent assistance has become an important argument^{2,3} in the controversy⁴ over the nature of the 2-norbornyl cation. Winstein originally proposed⁶ that *endo*-2-norbornyl brosylate ionization is aided by weak nucleophilic solvent assistance to yield what is best described as a nucleophilically solvated ion pair, **1**, which then reacts further by collapsing (without rearrangement) to inverted solvolysis product, or undergoes leakage to the 2-norbornyl cation (Scheme I). Important supporting evidence for this conclusion was the observation of

8% excess inverted (unrearranged) acetate upon acetyloysis.^{6,7}

The work of Schleyer's group in the late 1960s established the importance of nucleophilic solvent assistance in the solvolysis of secondary derivatives,⁵ and this raised the possibility that such assistance might be important in the solvolysis of *endo*-2-norbornyl derivatives. While Schleyer himself has argued^{4a} that *endo*-2-norbornyl derivatives solvolyze with only weak solvent assistance, much greater importance has at times been suggested for the role of solvent in these reactions.^{2,3} The

Scheme I. Winstein's Proposed Mechanism for the Solvolysis of *endo*-2-Norbornyl Brosylate

conflicting interpretations of the significance of nucleophilic solvent assistance in this system requires that the original proposal be tested and the magnitude of solvent assistance, if present, be more precisely defined.

For example, it has been noted that the rate ratios for *exo*- and *endo*-2-norbornyl derivatives are essentially constant for the secondary norbornyls and for a large variety of 2-substituted norbornyls.^{4c} The tertiary derivatives presumably⁸ react by a k_c mechanism (i.e., without nucleophilic solvent (k_s) or neighboring group (k_A) assisted processes),^{5c} so it might be assumed that the secondary derivatives also solvolyze by a k_c mechanism and that the constancy of the *exo*/*endo* rate ratio is of steric origin.^{4c} Alternatively, it could be argued that the constancy of the *exo*/*endo* rate ratios results from both the *exo* and *endo* secondary systems being assisted (by neighboring carbon and by solvent, respectively).^{2,3} A third view of these data is that the *exo*/*endo* rate ratio for the secondary derivatives is large because of neighboring carbon assistance and that this enhanced ratio is maintained in the tertiary cases by steric hindrance to ionization of the tertiary *endo* derivatives;^{9,10} conversely, Sargent has argued for steric assistance of the tertiary *exo* derivatives.^{4b}

Interpretation of the α -methyl-hydrogen rate ratio (α -Me-H ratio) for norbornyl solvolyses therefore requires knowledge of the extent of nucleophilic solvent assistance in *endo*-2-norbornyl solvolysis. The α -Me-H ratios for solvolysis of both *exo*- and *endo*-2-norbornyl derivatives^{11a} are approximately 10^5 , and are thus significantly lower than the limiting value of 10^8 expected^{5b,11b} for k_c substrates. This discrepancy can be explained by assuming that both compounds solvolyze with assistance of 10^3 , this assistance being neighboring carbon assistance for *exo* and nucleophilic solvent assistance for *endo*.^{2,3} Alternatively, it has been suggested that there may be significant variation in the limiting value of the α -Me-H rate ratio.^{2b,5b,12} A choice between these two possibilities can be made if the mechanism of *endo*-2-norbornyl solvolysis is characterized. Similarly, the σ_c^* method is based on the α -Me-H rate ratio, and this method has also been used to provide evidence that *exo*-norbornyl is anchimerically assisted and that *endo*-norbornyl is nucleophilically assisted.^{2c}

We now review the existing evidence and present new evidence showing that the amount of nucleophilic solvent assistance in the solvolysis of *endo*-2-norbornyl arenesulfonates is small, and we consider the implications of this conclusion.

Table I. Solvolysis Rates for Alkyl Arenesulfonates in Aqueous Ethanols and Trifluoroethanols

Compd	Solvent ^a	Temp, °C	$k, s^{-1} \times 10^4$	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
<i>endo</i> -2-Norb -OBs	70% EtOH	75.7	16.1 ± 0.1		
		50.2	0.925 ± 0.016		
		25 ^b	0.0343	24.4	-1.6
	60% EtOH	75.7	29.2 ± 0.9		
		50.2	1.76 ± 0.03		
	50% EtOH	25 ^b	0.0695	24.0	-1.7
		65.0	15.5 ± 0.5		
	85% TFE	45.1	1.96 ± 0.06		
		25 ^b	0.184	21.6	-8.2
	70% TFE	75.7	32.3 ± 0.01		
		50.2	2.74 ± 0.01		
	60% TFE	25 ^b	0.159	21.0	-9.9
75.7		46.7 ± 0.3			
60% TFE	50.2	3.59 ± 0.10			
	25 ^b	0.186	21.9	-5.6	
60% TFE	75.7	50.8 ± 1.4			
	50.2	4.45 ± 0.05			
60% TFE	25 ^b	0.268	20.7	-9.9	
	<i>exo</i> -2-Norb -OTs	80% EtOH	50.3	35.4 ± 1.6	
25.1			2.34 ± 0.01		
25 ^b			2.31	20.0	-7.9
70% EtOH		25.0	6.04 ± 0.25		
		60% EtOH	25.0	16.0 ± 1.0	
97% TFE		25.2	46.8 ± 1.6		
		0.0	2.87 ± 0.02		
85% TFE		25 ^b	47.5	17.6	-10.1
		10.0	11.5 ± 0.7		
70% TFE		0.0	2.63 ± 0.2		
		25 ^b	87.5	22.1	6.2
70% TFE		10.0	13.8 ± 0.6		
	0.0	3.15 ± 0.2			
85% TFE	25 ^b	105	22.1	6.7	
	74.95	6.60 ± 0.05			
2-Adam OTs	49.9	0.450 ± 0.013			
	25 ^b	0.0200	23.3	-6.5	
70% TFE	75.05	11.4 ± 0.5			
	49.9	0.640 ± 0.010			
50% TFE	25 ^b	0.0230	25.0	-0.7	
	74.95	19.2 ± 0.1			
50% TFE	49.9	1.01 ± 0.01			
	25 ^b	0.0335	25.6	2.2	

^a EtOH = aqueous ethanol; TFE = aqueous trifluoroethanol. Ethanols are volume percent, trifluoroethanols are weight percent.

^b Calculated from rates at other temperatures.

Results and Discussion

We have previously shown that nucleophilic solvent assistance can be detected by comparison of solvolysis rates in aqueous ethanol and aqueous trifluoroethanol.^{13,14} These solvent families differ in that variation of the water content has little effect on the nucleophilicity of aqueous ethanol but has a dramatic effect on the nucleophilicity of aqueous trifluoroethanol; in both systems an increase in ionizing power accompanies an increase in water content.¹⁵ Therefore, logarithmic plots of rate constants for substrates solvolyzing without nucleophilic solvent assistance against those of a limiting model (e.g., 1-adamantyl bromide)^{13,14} are linear. In contrast the corresponding data for a solvent-assisted substrate relative to a limiting model cannot be adequately described by a single straight line. This deviation is caused by the obvious inability of a limiting model to predict the response of a non-limiting substrate to variations in solvent nucleophilicity which are not proportional to variations in solvent ionizing power.^{15b}

Table II. Solvolysis Rates ($-\log k$) for Alkyl Derivatives in Various Solvents at 25 °C^a

Substrate	100E	90E	80E	70E	60E	50E	97T	85T	70T	60T	50T	HCOOH	AcOH
2-Propyl brosylate	5.71 ^{b,c}	5.20 ^d	4.84 ^c			4.40 ^d	5.68 ^d		4.94 ^d		4.55 ^d	4.33 ^{b,c}	6.59 ^{e,c}
<i>exo</i> -2-Norbornyl tosylate	5.35 ^f		3.64	3.22	2.80		2.32	2.06	2.03			1.29 ^g	4.63 ^h
<i>endo</i> -2-Norbornyl brosylate	7.23 ^{c,f}		5.70 ^c	5.46	5.16	4.74	4.86 ^c	4.80	4.73	4.57		4.04 ^{c,g}	6.60 ^{c,e}
2-Adamantyl tosylate	9.37 ^b	8.19 ^b	7.62 ^b		6.70 ^b	6.33 ^b	5.71 ⁱ	5.70	5.64		5.47	4.59 ⁱ	8.23 ⁱ
1-Adamantyl bromide ^k	9.06 ^j	7.61	6.29	5.81	5.14	4.54	4.02	3.97	3.75	3.64	3.46	4.08	8.62

^a E = aqueous ethanol; T = aqueous trifluoroethanol. Ethanols are volume percent, trifluoroethanols are weight percent. ^b Reference 15a. ^c Assuming OBs/OTs = 5 in aqueous ethanol and 3 in acetic and formic acids and trifluoroethanol: D. D. Roberts, *J. Org. Chem.*, **37**, 1510 (1972). ^d V. J. Shiner, Jr., R. D. Fisher, and W. Dowd, *J. Am. Chem. Soc.*, **91**, 7748 (1969). ^e Reference 2. ^f W. Huckel and O. Vogt, *Justus Liebig's Ann. Chem.*, **695**, 16 (1966). ^g H. C. Brown and I. Rothberg, unpublished results. ^h P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, **87**, 375 (1965). ⁱ Reference 15b. ^j Reference 10. ^k D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 5977 (1970).

Table III. Mechanistic Criteria for Solvolysis of Alkyl Arenesulfonates^a

Method	2-Propyl -OBs	<i>exo</i> -2- Norbornyl -OTs	<i>endo</i> -2- Norbornyl -OBs	2-Adamantyl -OTs
EtOH-TFE ^b Correlation coefficient (standard deviation)	0.55 (0.52)	1.00 (0.11)	0.98 (0.17)	1.00 (0.14)
Azide rate enhancement ^c	58 ^{d,e}	2 ^f	3 ^{d,f}	4 ^e
k_N/k_W	740 ^{d,g}	11 ^f	39 ^{d,f}	2 ^g
m_{EW}	0.41	0.81	0.66	0.82
m_{AF}	0.61	0.90	0.69	1.0
$[k_{EW}/k_{AcOH}]_Y$	12	0.5	0.66	0.2
$[k_{EW}/k_{HCOOH}]_Y$	2.1	0.2	0.5	0.05
$\alpha-k_H/k_D$	1.08 ^h	1.12 ⁱ	1.19 ⁱ	1.23 ^h
k_s/k_c	547	8	30	1

^a Unless otherwise noted data are calculated from the rate constants given in Table II. ^b Figures 1 and 2. ^c The value of k/k^0 in eq 1 extrapolated to unit azide concentration; 80% ethanol. ^d Tosylate. ^e Reference 17a. ^f D. J. Raber, J. M. Harris, and P. v. R. Schleyer, unpublished results. ^g Reference 17b. ^h In 80% ethanol: J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **93**, 2551 (1971). ⁱ In 80% ethanol: B. L. Murr and J. A. Conkling, *ibid.*, **92**, 3462 (1970).

In Tables I and II we have presented the requisite rate data for construction of ethanol-trifluoroethanol plots for 2-adamantyl and *exo*-2-norbornyl tosylates and for *endo*-2-norbornyl and 2-propyl brosylates. Figure 1 illustrates typical plots for 2-propyl brosylate and 2-adamantyl tosylate. The data for 2-adamantyl tosylate are well correlated by a single straight line, but this is clearly not the case for 2-propyl tosylate; the correlation coefficients and standard deviations reported in Table III reinforce this conclusion. The corresponding plots for the epimeric norbornyl compounds are shown in Figure 2; the data in each case can be accommodated by single lines (Table III), although the trifluoroethanol points lie slightly below a line defined by the ethanol points.¹⁶ The similarity in response of the norbornyl compounds to changes in solvent nucleophilicity is even more clearly demonstrated by a plot of *exo* rate constants against those for the *endo* isomer (Figure 3). Clearly, substantial nucleophilic solvent assistance in the solvolysis reactions of *endo*-2-norbornyl arenesulfonates is not indicated.

A second technique which has been shown to detect nucleophilic assistance is the use of added azide ion,¹⁷ and information is available from both rate and product data. The reaction rates of both k_s and k_c (or k_{Δ}) substrates show a linear dependence on the concentration of azide ion according to

$$k_{\text{obsd}}/k^0 = 1 + \beta[\text{N}_3^-] \quad (1)$$

where k_{obsd}/k^0 represents the rate enhancement relative to the rate in the absence of azide ion, i.e., k^0 . For carbonium ion reactions the rate increases result from ionic strength effects and only small rate enhancements are observed.¹⁷ In contrast k_s substrates show large rate enhancements as a consequence of direct displacement by azide ion.¹⁷ Inspection of Table III shows that both of the norbornyl isomers exhibit azide rate

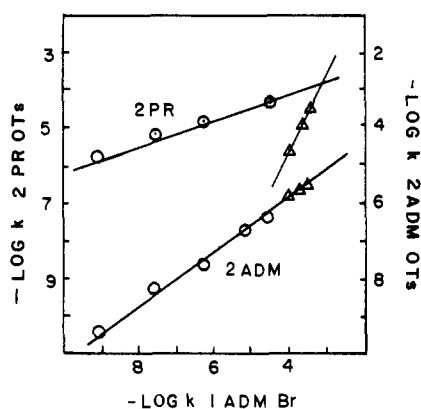


Figure 1. A plot of log of solvolysis rate of 2-propyl brosylate and 2-adamantyl tosylate against log of solvolysis rate of 1-adamantyl bromide in aqueous ethanol (O) and in aqueous trifluoroethanol (Δ) at 25 °C. Data from Table II.

enhancements comparable to that found for 2-adamantyl tosylate, values which are not consistent with strong nucleophilic assistance by solvent.

For either nucleophilically assisted or carbonium ion processes involving irreversible competitive attack by azide ion and water the product distribution^{17,18} is given by

$$\frac{k_N[\text{N}_3^-]}{k_W[\text{H}_2\text{O}]} = \frac{\% \text{RN}_3}{\% \text{ROH}} \quad (2)$$

where k_N and k_W are the second-order rate constants for formation of alkyl azide and alcohol, respectively. While high azide selectivity is observed for k_s substrates, for carbonium ion processes the selectivity is dependent on cation stability and

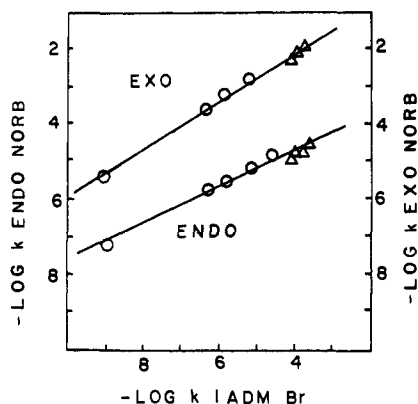


Figure 2. A plot of log of solvolysis rate of *endo*-2-norbornyl brosylate and *exo*-2-norbornyl tosylate against log of solvolysis rate of 1-adamantyl bromide in aqueous ethanol (O) and in aqueous trifluoroethanol (Δ) at 25 °C. Data from Table II.

rather low values of k_N/k_W are expected for secondary cations.^{17c} As shown by Table III the selectivity of the *endo*-2-norbornyl system (39) is far less than the value of 740 observed for 2-propyl brosylate, again providing solid evidence against strong nucleophilic assistance in the solvolysis of *endo*-2-norbornyl derivatives. The considerably smaller selectivity of 2-adamantyl tosylate should not be taken to indicate substantial differences in solvent assistance for it and for *endo*-2-norbornyl brosylate; the difference in selectivities presumably reflects the greater stability of the 2-norbornyl cation.^{17c} Indeed, the two epimeric norbornyl derivatives exhibit selectivities which differ by about a factor of 4, a factor which again indicates a small (although real) degree of nucleophilic assistance in reactions of the *endo* isomer.

A third approach to the detection of nucleophilic assistance by the use of azide ion involves the question of a rate-product correlation. For a strongly assisted process in which the rate-determining and product-determining steps are identical there exists a mathematical relationship between the reaction rate and the product ratio.^{17,18} On the other hand, carbonium ion processes, for which the rate-determining step is different from the product-determining step, are not required to exhibit such a correlation (although they may fortuitously do so). *endo*-2-Norbornyl solvolysis is known^{6,7} to involve a significant amount of free norbornyl cation, so a simple test for a k_s process by examination for a rate-product correlation is not possible. Also the azide rate enhancements and selectivities are not large enough relative to experimental errors for any significance to be assigned to a comparison of rate and product data.

The last six entries in Table III are measures of nucleophilic solvent assistance developed by others, primarily Schleyer.^{5,15a} In general these measures indicate, in agreement with those above, the absence of substantial solvent assistance in *endo*-norbornyl solvolysis. Regarding the k_s/k_c ratios, it should be noted that this ratio should not be applied to k_Δ processes since there is by definition no solvent assistance in such cases. Nevertheless, their m values are lowered by charge dispersal, thus resulting in k_s/k_c values of greater than unity. Of course, it is usually difficult to determine the operation of a k_Δ process, and thus it is difficult to know when the k_s/k_c probe is applicable. Similarly, the k_s/k_c value is increased by ion pair return and by the solvent acting as a base to promote elimination. Significant elimination (13%)⁷ occurs during acetolysis of *endo*-norbornyl brosylate, although it is not known whether this occurs in the rate-limiting step. These considerations indicate that the k_s/k_c value of 30 for *endo*-norbornyl acetolysis (which exceeds that for the *exo* isomer by only a factor of 4) is best interpreted as an upper limit of the extent of nucleophilic solvent assistance in this reaction.

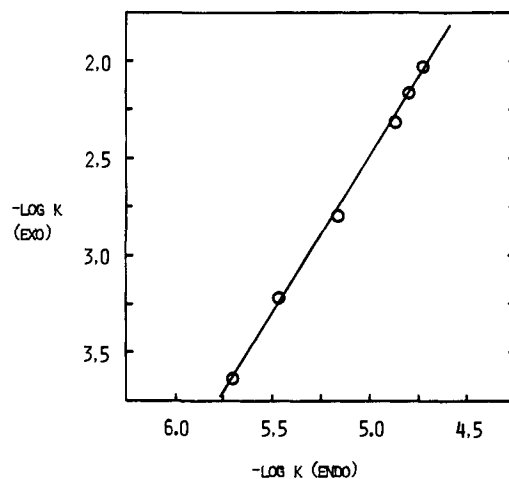


Figure 3. A plot of solvolysis rate of *exo*-2-norbornyl tosylate against solvolysis rate of *endo*-2-norbornyl brosylate in aqueous ethanol and trifluoroethanols.

Conclusions

The available evidence substantiates Winstein's earlier proposal⁶ that nucleophilic solvent assistance is weak in the solvolysis of *endo*-2-norbornyl arenesulfonates. Consequently, there must be significant variation in the limiting value of the α -Me-H rate ratio since we can calculate¹⁹ that the limiting value for *endo*-norbornyl is less than 3×10^6 rather than the previously proposed^{5b,11b,12} limiting value of 10^8 . Prior conclusions for *exo*-norbornyl solvolysis based on the α -Me-H ratio^{2,3} are therefore questionable. Weak nucleophilic solvent assistance in the solvolysis of secondary *endo*-2-norbornyl arenesulfonates also requires (see introduction) that the observed (nearly constant) *exo/endo* rate ratios^{4e} must be interpreted in terms of the secondary *exo* derivative reacting by a k_c (i.e., unassisted) mechanism, in terms of the tertiary *endo* derivative reacting slowly because of steric hindrance to ionization,^{9,10} or in terms of the tertiary *exo* derivative reacting at a greater rate as a consequence of steric acceleration.^{4b}

Many of the earlier arguments adduced as evidence for the nonclassical nature of the norbornyl cation have now been vitiated, and the present results allow the idea of substantial nucleophilic solvent assistance in *endo*-2-norbornyl solvolysis to be added to this chemical graveyard. In spite of the numerous investigations which have been carried out,⁴ the question of the mechanism of 2-norbornyl solvolyses has not yet been adequately resolved.

Experimental Section

The arenesulfonates were prepared as usual by allowing the appropriate alcohol and arenesulfonyl chloride to react in pyridine solution. Melting points were in agreement with literature values.^{6,7,15a} Solvents were prepared and rate constants were determined (conductometrically) as described previously.²⁰

Acknowledgment is made to the National Aeronautics and Space Administration for partial support of this research, and to S. P. McManus and P. v. R. Schleyer for critical comments.

References and Notes

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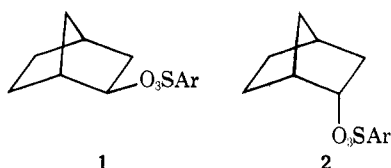
Structural Effects in Solvolytic Reactions. 26. A Critical Study of the Effect of Solvent on the Exo:Endo Rate Ratio in the Solvolysis of 2-Norbornyl Derivatives. Evidence That the Exo:Endo Rate Ratio Is Not the Result of K_{Δ}/K_s Processes

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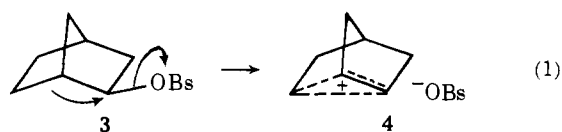
Contribution from the Richard B. Wetherill Laboratory, Purdue University,
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Abstract: The generally accepted position that the exo:endo rate ratio in the solvolysis of 2-norbornyl derivatives is the result of a k_{Δ} process for exo and a k_s process for endo was subjected to critical examination by investigating the exo:endo rate ratio as a function of solvent. These mesylates were synthesized, along with several representative derivatives (isopropyl, cyclopentyl, and cyclohexyl), and solvolyzed in pure water and in 60% aqueous acetone. The tosylates were solvolyzed in methanol and in formic acid. These data, as well as other data, including those for solvolysis in trifluoroacetic acid and hexafluoroisopropyl alcohol, were then subjected to critical examination. Over the entire range of solvents, $\log k_{\text{exo}}$ plots linearly against $\log k_{\text{endo}}$. This is not consistent with the usual interpretation that the solvolysis of the exo isomer involves a k_{Δ} process, insensitive to the nucleophilicity of the solvent, whereas the solvolysis of the endo isomer involves a k_s process, sensitive to the nucleophilicity of the solvent. The solvolysis of 2-adamantyl tosylate has been proposed as a representative k_c process. Both *exo*- and *endo*-norbornyl tosylates are nicely correlated with the rates of solvolysis of 2-adamantyl tosylates over the exceptionally wide range of solvents here examined. On the other hand, isopropyl, cyclopentyl, and cyclohexyl derivatives, postulated to involve k_s processes, are not so correlated. Clearly it is necessary to reconsider the previous interpretation of the solvolysis of *endo*-norbornyl derivatives as involving a k_s process and the exo:endo rate ratio as arising from the operation of k_{Δ}/k_s processes. The data are in better agreement with the solvolyses of both *exo*- and *endo*-norbornyl proceeding through processes that are essentially k_c .

Few reactions have aroused more interest than the precise nature of the solvolysis of 2-norbornyl derivatives.⁴ The reaction involves a high exo:endo rate ratio: 350 for the acetolysis of the brosylates⁵ and 280 for the acetolysis of the tosylates⁶ (1:2).



Winstein and Trifan⁵ proposed that the high exo:endo rate ratio was the result of a k_{Δ} process for the exo isomer and a k_s process for the endo. Participation by the 1,6-bonding pair in the transition state (3) facilitated the ionization of the brosylate group leading to a σ -bridged nonclassical ion or ion pair (4) (eq 1).



It was argued that a different process was involved in the acetolysis of the endo isomer. First, such σ participation was