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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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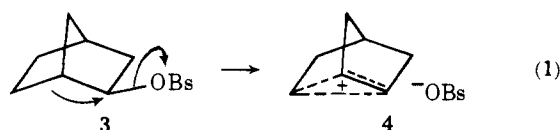
Contribution from the Richard B. Wetherill Laboratory, Purdue University,
West Lafayette, Indiana 47907. Received August 21, 1977

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).

	1	2
rel rate (25 °C)	OBs 350	1.00
	OTs 280	1.00

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).



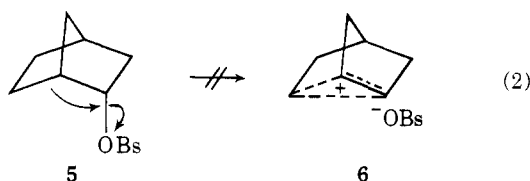
It was argued that a different process was involved in the acetolysis of the *endo* isomer. First, such σ participation was

Table I. Rates of Solvolysis of Mesylates in Pure Water

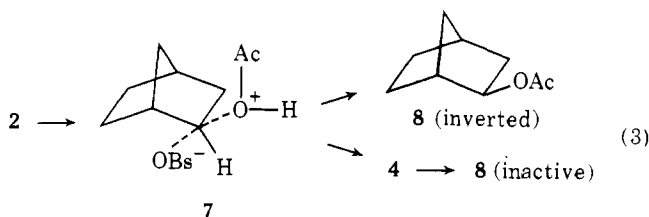
Mesylate	$10^6 k_1, s^{-1}$		$\Delta H^\ddagger,$ kcal mol ⁻¹	$\Delta S^\ddagger,$ eu
	0 °C	25 °C		
Isopropyl	7.38	201	20.8	5.7
Cyclopentyl	333	6930 ^a		
Cyclohexyl	14.5	392 ^a		
<i>endo</i> -Norbornyl	4.45	133	21.4	6.9
<i>exo</i> -Norbornyl	14 000	213 000 ^b		
2-Adamantyl		150 ^c		

^a Calculated by comparing with the rate of isopropyl tosylate at 0 °C assuming constant entropy. ^b Estimated by extrapolating the *exo*:*endo* rate ratio from 0 °C to 25 °C assuming constant entropy. ^c Private communication from T. W. Bentley.

not considered to be stereoelectronically feasible, since it would require attack by the 1,6-bonding pair on the same side as the leaving group (5) to give a nonclassical ion or ion pair with the anion in the *endo* position (6) (eq 2).



In contrast to the *exo* isomer, which undergoes acetolysis with complete racemization, the *endo* isomer gives 7–8% of inverted acetate.⁵ The authors therefore proposed that the acetolysis of *endo*-norbornyl brosylate (eq 3) is facilitated by



solvent assistance to give an intermediate (7) which can collapse either into the inverted solvolysis product (8) or undergo leakage into the bridged cation (4). The latter possesses a plane of symmetry and the acetate from it would be inactive.

Ever since this original proposal, solvolysis of 2-norbornyl derivatives and the high *exo*:*endo* rate ratios obtained have frequently been discussed in terms of k_Δ/k_s processes.^{7–11} Indeed, Nordlander and his co-workers proposed a value of 30 for k_s/k_c for the acetolysis of *endo*-norbornyl tosylate, implying much higher *exo*:*endo* rate ratios in solvents of lower nucleophilicities where $k_s \rightarrow k_c$.⁸

Recently it has been observed that highly stabilized tertiary 2-aryl-2-norbornyl derivatives undergo solvolysis with equally high *exo*:*endo* rate ratios,¹² 9:10 and 11:12.

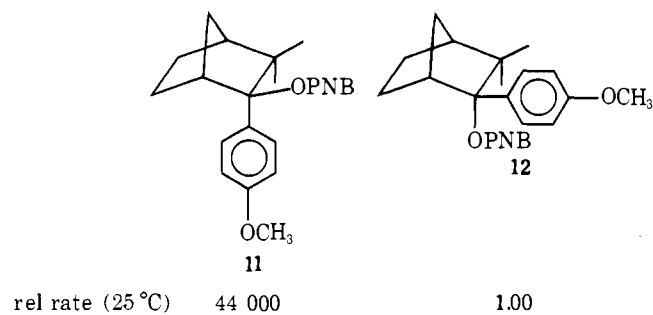
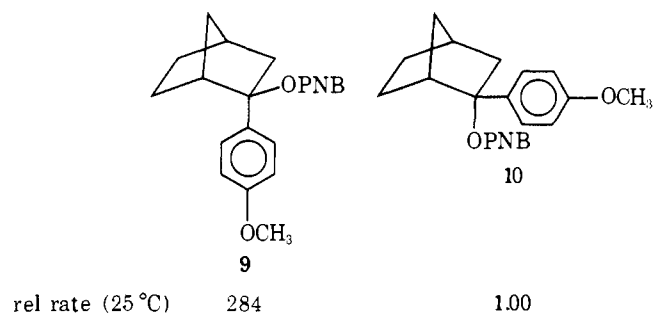
Yet such highly stabilized 2-aryl-2-norbornyl cations cannot involve σ bridging. This position was accepted by Winstein himself⁷ and has been supported by NMR studies of Farnum and Mehta.^{13,14}

The solvolyses of such highly stabilized tertiary derivatives are believed to proceed through carbonium ions which do not require additional stabilization either by solvent or by the neighboring carbon structure. That is, such solvolyses are essentially k_c processes. (One of the referees has argued that k_c should be used only for an idealized process with absolutely zero solvent contribution. However, we prefer to use k_c to represent real solvolytic processes with insignificant, but not necessarily zero, solvent contributions to the ionization stage.) Consequently, the high *exo*:*endo* rate ratios observed for 9:10

Table II. Rates of Solvolysis of Mesylates in 60% Aqueous Acetone

Mesylate	$10^6 k_1, s^{-1}$		$\Delta H^\ddagger,$ kcal mol ⁻¹	$\Delta S^\ddagger,$ eu
	0 °C	25 °C		
Isopropyl		2.78		
Cyclopentyl	1.40	34.9	20.3	0.3
Cyclohexyl		1.23		
<i>endo</i> -Norbornyl		0.56		
<i>exo</i> -Norbornyl	35.0	595 ^a		
2-Adamantyl		0.055 ^b		

^a Calculated by extrapolating the relative rates of cyclopentyl and *exo*-norbornyl from 0 °C to 25 °C assuming constant entropy. ^b Reference 20b.



and 11:12 are attributed to k_c/k_s processes with the slow rate of the *endo* isomer arising from steric hindrance to ionization.^{15–17}

The Goering–Schewene diagrams for the solvolysis of such highly stabilized 2-norbornyl derivatives, 9 and 10, 11 and 12, are extraordinarily similar to that for 2-norbornyl itself.¹⁸ Is it reasonable that phenomena that are so similar in their characteristics involve such different processes, k_c/k_s in one case and k_Δ/k_s in the other? We believe not.¹⁹ Accordingly, we decided to subject to critical examination the proposal that the solvolysis of 2-norbornyl derivatives involves k_Δ/k_s processes.

A number of valuable new procedures have recently become available for such determinations.^{20–22} However, we decided to adopt a simple approach which does not depend upon specialized techniques, underlying assumptions, or involved manipulation of data.

The experimental approach adopted was to determine the rates of solvolysis for appropriate *exo*- and *endo*-norbornyl derivatives in a wide variety of solvents. This included the mesylates in pure water and 60% aqueous acetone and tosylates in methanol and in formic acid. Isopropyl, cyclopentyl, and cyclohexyl derivatives were included for comparison. In the meantime, data had become available for the “limiting” solvents,²³ trifluoroacetic acid⁸ and hexafluoroisopropyl alcohol.^{23,24} Consequently, it now became possible to examine solvolytic data over an exceptionally wide range of solvents to test directly for the sensitivity of the *exo*:*endo* rate ratio to solvent nucleophilicity.

Table III. Rates of Solvolysis of Mesylates and Tosylates in Methanol

Alkyl group, R	$10^6 k_1, s^{-1}, 25^\circ C$	
	Mesylate	Tosylate
Isopropyl		1.18
Cyclopentyl		9.85
Cyclohexyl		0.159
<i>endo</i> -Norbornyl	0.050	0.102
<i>exo</i> -Norbornyl	20.5 ^a	34.8
2-Adamantyl		0.0029 ^b

^a Rate constant for racemization of the mesylate in methanol at 25 °C: $10^6 k_a 25^\circ C = 25.0 s^{-1}$. ^b Reference 20b.

Results

Mesylates in Pure Water. The tosylates or brosylates of the organic groups of interest are essentially insoluble in water. Fortunately, the methanesulfonates proved to have solubilities adequate to permit determination of their rates of solvolysis by the standard titrimetric procedure. The data are summarized in Table I.

Mesylates in Aqueous Acetone. We explored the rates of solvolysis in aqueous acetone of widely varying aqueous content. However, the broad range of data is of interest in connection with other theoretical questions.²⁵ For the present study, we report data only for 60% aqueous acetone, summarized in Table II.

Tosylates in Methanol. The rates of solvolysis in methanol offered no problem. The results are summarized in Table III.

Tosylates in Formic Acid. The chief difficulty we encountered is the exceptionally fast rate of solvolysis of *exo*-norbornyl tosylate in formic acid. The titrimetric rate constant for the *exo* derivative is $5.125 \times 10^{-2} s^{-1}$ at 25 °C, which corresponds to a half-life of 13.5 s at that temperature. An inverse mixing procedure was followed to measure the rate (see Experimental Section). The average deviation for the formolysis of the tosylate was found to be 10% due to the difficulty inherent in determining very rapid solvolysis rates. The *exo*:*endo* rate ratio for the formolysis of the tosylate is 1700 at 25 °C (Tables IV and V).

Internal Return. A possible difficulty in discussing *exo*:*endo* rate ratios for the solvolysis of 2-norbornyl derivatives in the various solvents is the ambiguity introduced by internal return.⁵ Should we use the observed titrimetric rate data, or the polarimetric rate data? Unfortunately, only very few polarimetric rate constants have been determined. Moreover, there is even some question as to whether it is appropriate to assume that the polarimetric rate constants measure the rate of ionization to be compared to the titrimetric rate constants in systems which are not subject to such racemization.²⁶

Therefore, both for practical reasons, the paucity of such data, and for theoretical reasons, as pointed out by Wilcox, we decided to restrict ourselves to the titrimetric rate constants. Fortunately, the uncertainty introduced is not serious. The largest ratio of k_a/k_t for organosulfonate esters appears to be a factor of approximately 4 reported for solvolysis in acetic acid. In ethanol the factor is only 2.94; in aqueous acetone, it is even lower, 1.40,⁵ and in methanol, lower still, 1.22. We believe that in the more ionizing solvents, such as water, trifluoroacetic acid, and hexafluoroisopropyl alcohol, the value of k_a/k_t will be close to unity.

The available data are summarized in Table IV.

Discussion

For convenience, all of the available rate constants for isopropyl, cyclopentyl, cyclohexyl, *endo*-norbornyl, *exo*-norbornyl, and 2-adamantyl tosylates are summarized in Table

Table IV. Titrimetric and Polarimetric Rate Ratios of 2-Norbornyl Derivatives in Various Solvents

Solvent	X	Rel rates, 25 °C	
		$k_{t,exo}/k_{t,endo}$	$k_{a,exo}/k_{t,exo}$
EtOH ^a	OBs		2.94
AcOH ^a	OBs	350	3.46 ^b
	Br ^c		24.0
MeOH	OMs ^d	410	1.22
	OTs ^d	340	
80% EtOH ^e	OTs	580	
60% Me ₂ CO ^d	OMs	1060	
75% Me ₂ CO ^a	OBs		1.40
	Br ^c		4.9
97% TFE ^f	OTs	1030	
HCOOH ^d	OTs	1700	
97% HFIP ^f	OTs	1400	
	OBs	1750	
H ₂ O ^d	OMs	1600	
TFA ^g	OTs	1120	

^a Reference 5. ^b A higher k_a/k_t ratio of 4.6 was reported later, but without data: S. Winstein, E. Clippinger, R. Howe, and E. Vogel-fanger, *J. Am. Chem. Soc.*, **87**, 376 (1965). ^c S. Winstein, J. S. Gall, M. Hojo, and S. Smith, *J. Am. Chem. Soc.*, **82**, 1010 (1960). ^d This study. ^e D. Lenoir, *Chem. Ber.*, **108**, 2055 (1975). ^f Reference 24. ^g Reference 8.

V. The values for the mesylates or brosylates were converted to the values for the tosylates by utilizing appropriate conversion factors (Table V).

In Table V we have summarized data for solvents over the broadest available range of nucleophilicities and ionizing powers. If *endo*-norbornyl solvolyzes by a k_s process, whereas *exo*-norbornyl solvolyzes by a k_Δ process, these two solvolyses should be affected differently by the markedly different characteristics of these solvents. Strongly nucleophilic solvents, such as methanol and ethanol, should cause *endo*-norbornyl to exhibit enhanced rates relative to the behavior of *exo*-norbornyl. Solvents of high ionizing power with negligible nucleophilicity should bring about a decreased rate of *endo*-norbornyl relative to *exo*-norbornyl.

However, a plot of $\log k_{exo}$ against $\log k_{endo}$ reveals no such effects of the various solvents. The data yield a remarkably good linear plot (Figure 1).

It should be pointed out that Olah has reported an exceptionally high *exo*:*endo* value of 5200 for solvolysis of 2-norbornyl derivatives in CF₃CO₂H-SO₂ClF. Unfortunately, the temperature was not explicitly defined. Moreover, neither the individual rate constants nor the experimental details have yet been reported. Consequently, we were unable to include this unusually high *exo*:*endo* rate ratio in our analysis.

The 2-adamantyl system has been proposed as a model system for a k_c process.^{20,28} Moreover, nucleophilic properties of trifluoroacetic acid (TFA) and hexafluoroisopropyl alcohol (HFIP) are so low that it has been argued that in these solvents the solvolyses of secondary arenesulfonates are limiting.²³ Considerable evidence to support this position has now appeared. Consequently, it was of interest to plot the data for isopropyl, cyclopentyl, *exo*-norbornyl and *endo*-norbornyl against the data for 2-adamantyl tosylate. The line passing through the points for TFA and HFIP defines the value to be anticipated for a k_c (or k_Δ) process with negligible solvent participation.

Indeed, we observe that for isopropyl (Figure 2), the experimental points for all other solvents come well above the limiting line. Presumably, the magnitude of the vertical displacement of each point from the line measures the nucleophilic contribution of each solvent to the solvolysis.

The behavior of cyclopentyl (Figure 3) and cyclohexyl (Figure 4) is similar. Here the magnitudes of the deviations

Table V. Solvolytic Rate Constants for Secondary Tosylates at 25 °C

Solvent (N ^x)	Isopropyl	Cyclopentyl	10 ⁶ k ₁ , s ⁻¹ , 25 °C			2-Adamantyl
			Cyclohexyl	endo-Norbornyl	exo-Norbornyl	
EtOH (0.00) ^y	0.286 ^b	2.68 ^k	0.0456 ⁿ	0.0156 ^p	4.39 ^s	0.000 43 ^v
AcOH (-2.35)	0.0774 ^c	1.65 ^k	0.0488 ^m	0.0828 ^q	23.3 ^q	0.005 9 ^v
MeOH (-0.04) ^y	1.18 ^d	9.85 ^d	0.159 ^d	0.102 ^d	34.8 ^d	0.002 9 ^v
80% EtOH (0.00)	2.94 ^{b,c}	29.1 ^k	0.750 ^k	0.397 ^r	231 ^r	0.024 1 ^v
60% Me ₂ CO (-0.41) ^y	5.56 ^{d,e}	69.8 ^{d,e}	2.46 ^{d,e}	1.13 ^{d,e}	1 190 ^{d,e}	0.111 ^v
97% TFE ^a (-2.79)	0.69 ^{f,g}	100.0 ⁱ	1.49 ^{f,g}	4.60 ^g	4 750 ^g	1.64 ^v
HCOOH (-2.35)	23.8 ^h	747 ^m	38.7 ⁿ	30.1 ^d	51 000 ^d	26.5 ^v
97% HFIP ^a (-4.27) ^y	1.55 ⁱ	303 ^g	18.1 ⁱ	78.5 ^g	110 000 ^{t,u}	97.5 ⁱ
H ₂ O (-0.44) ^z	402 ^{d,e}	13 860 ^{d,e}	784 ^{d,e}	266 ^{d,e}	426 000 ^{d,e}	310 ^{e,w}
TFA (-5.56)	21.4 ^j	2 730 ^j	270 ^o	417 ^j	468 000 ^j	900 ^v

^a 3% water by weight. ^b R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953). ^c P. v. R. Schleyer, J. L. Fry, L. K. M. Lam, and C. J. Lancelot, *J. Am. Chem. Soc.*, **92**, 2542 (1970). ^d This study. ^e Calculated from the rate of mesylate using the ratio $k_{OTs} = k_{OMs} \times 2$. ^f Calculated from the rate of brosylate using the ratio $k_{OBs} = k_{OTs} \times 3$. ^g J. M. Harris, private communication. ^h P. E. Peterson, R. E. Kelly, Jr., R. Belloli, and K. A. Sipp, *J. Am. Chem. Soc.*, **87**, 5169 (1965). ⁱ Reference 23. ^j Reference 8. ^k D. D. Roberts, *J. Org. Chem.*, **33**, 118 (1968). ^l R. E. Hall, Ph.D. Thesis, Princeton University, 1970. ^m S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1127 (1952). ⁿ S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955). ^o D. D. Roberts and W. Hendrickson, *J. Org. Chem.*, **34**, 2415 (1969). ^p Calculated using $\text{exo}:\text{endo} = 280$. ^q Reference 6. ^r Table IV. ^s M.-H. Rei, Ph.D. Thesis, Purdue University, 1967. ^t Reference 24. ^u The $\log k_{\text{exo}} - \log k_{\text{endo}}$ plot (Figure 1) gives a value of $10^6 k_1$ of 126 000 s⁻¹ at 25 °C. ^v Reference 20b. ^w T. W. Bentley, private communication. ^x Nucleophilicities, from ref 23, except where otherwise indicated. ^y Reference 20. ^z Footnote c, Table I.

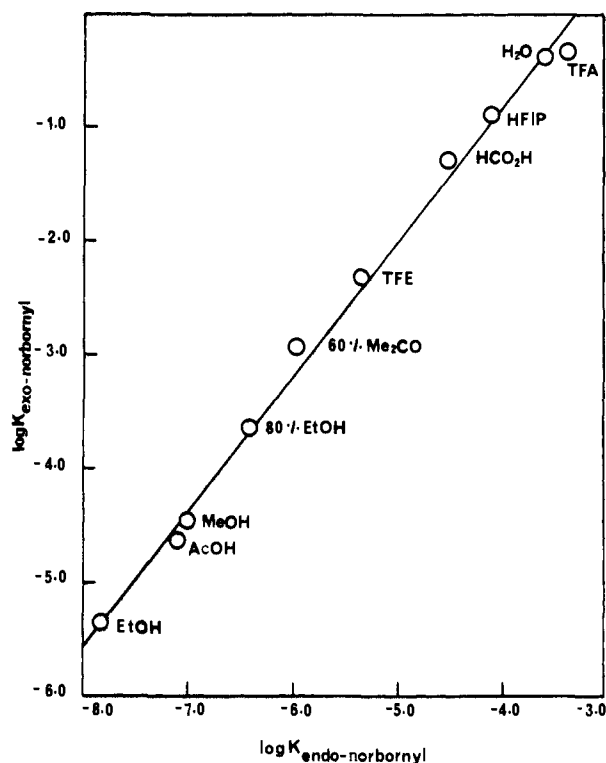


Figure 1. Linear free energy relationship between the rates of solvolysis in various solvents of *exo*- and *endo*-norbornyl derivatives.

from the limiting line are somewhat smaller than those observed for isopropyl. Presumably, nucleophilic solvent participation, although considerable, is somewhat smaller in these alicyclic systems than in the isopropyl system.

exo-Norbornyl behaves differently. Here, unfortunately, the limiting line cannot be drawn because of the considerable uncertainty in the experimental value for *exo*-norbornyl in HFIP (the values for TFA and water are also exceptionally fast and may involve significant uncertainty). However, it is quite clear that the data are linearly correlated with reasonable precision. Of course this is to be anticipated irrespective of whether *exo*-norbornyl solvolyzes by a k_{Δ} process, as originally suggested,⁵ or by a k_c process similar to that of 2-adamantyl.

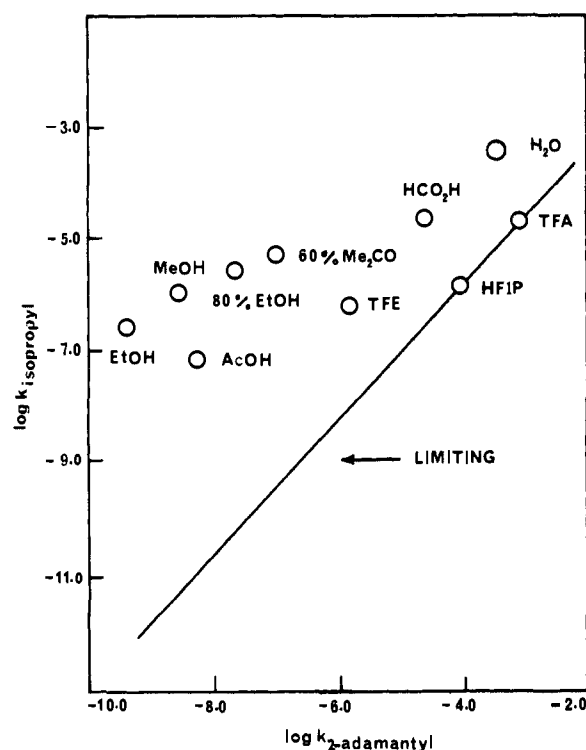


Figure 2. Nonlinear free energy relationship between the rates of solvolysis in various solvents of isopropyl and 2-adamantyl derivatives.

It is now appropriate to examine the data for *endo*-norbornyl. Will they reveal a solvent contribution similar to that shown by isopropyl (Figure 2), or cyclopentyl (Figure 3), and cyclohexyl (Figure 4), all of which solvolyze by k_s processes in solvents other than HFIP and TFA? Or will they reveal no significant solvent contributions, corresponding to a k_c process similar to that proposed for 2-adamantyl itself?^{20,28}

The results (Figure 6) and conclusions appear crystal clear.

It has been suggested to the authors by Paul von R. Schleyer that the data in Figure 6 might still allow for a small k_s contribution to the ionization process. The limiting line drawn through the TFA and HFIP points, as in Figures 2-4, comes slightly below the least-squares line of Figure 6. The dis-

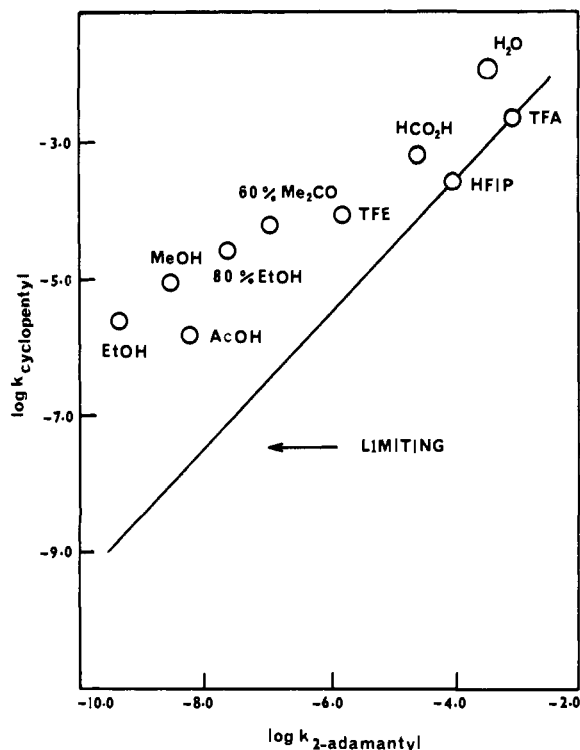


Figure 3. Nonlinear free energy relationship between the rate of solvolysis in various solvents of cyclopentyl and 2-adamantyl derivatives.

placement is such as to permit a solvent contribution of somewhat less than a factor of 2 for the acetolysis of *endo*-norbornyl tosylate.

This treatment requires both great reliance on the accuracy of the two experimental points and a long extrapolation to indicate quite small solvent contributions. In our opinion, even if this treatment can be relied upon, such small solvent contributions cannot be considered a significant factor in arriving at an understanding of *exo*:*endo* rate ratios in the range of 300–1600. Consequently, as discussed earlier, we prefer to define a k_c process, not as one with absolutely no solvent contributions, but as one with insignificant solvent contributions.

Attention is called to the fact that Nordlander and his co-workers, using the treatment advocated by Schleyer and his co-workers,²⁰ calculated the solvent contribution to the acetolysis of *endo*-norbornyl tosylate to be a factor of 30,⁸ slightly larger than the factor of 28 for acetolysis of cyclohexyl tosylate.^{20b} If we utilize that factor of 30 to calculate the k_c point for AcOH, that point would lie 1.5 log units below the experimental point of Figure 6. This calculated k_c point would lie far below the “limiting” line, defined by the TFA and HFIP points, as advocated by Schleyer. A major discrepancy is thus evident between these two theoretical approaches.

The slopes of the two lines in Figures 5 and 6 are 0.81 and 0.69, respectively. Schleyer has argued that the fact that the slope for the *exo*-norbornyl plot (Figure 5) is less than unity indicates that there is a greater degree of charge dispersion in the transition state, attributed to carbon bridging in 2-norbornyl, than is enjoyed by 2-adamantyl. On the other hand, he attributes to solvent assistance the fact that the slope for the *endo*-norbornyl plot (Figure 6) is also less than unity.²⁹ However, even if we adopt this proposed limiting line, the possible solvent contribution appears to be far too small to be responsible for the decreased slope.

As was pointed out earlier, we had decided to test the importance of solvent participation in this study by utilizing a simple basic approach which would not depend upon special-

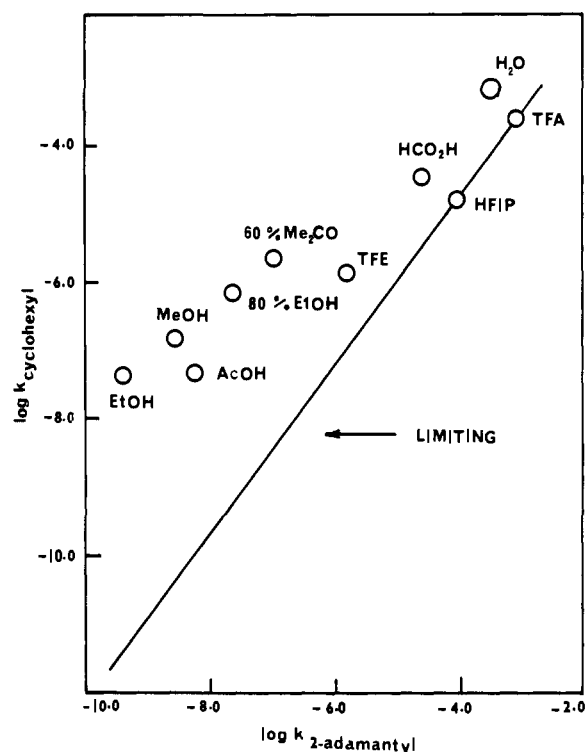
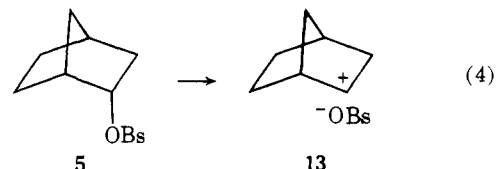


Figure 4. Nonlinear free energy relationship between the rates of solvolysis in various solvents of cyclohexyl and 2-adamantyl derivatives.

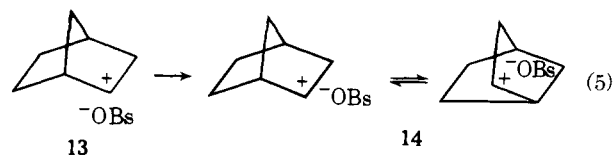
ized techniques, uncertain underlying assumptions, or involved manipulation of data. We are relying only on the prior conclusion of Schleyer and his co-workers that the solvolysis of 2-adamantyl tosylate is essentially a k_c process.^{20,28} We have subjected *endo*-norbornyl tosylate to the full range of solvolytic media available for 2-adamantyl. Over this full range there is no evidence for any significantly larger solvent contributions to *endo*-norbornyl than to 2-adamantyl (Figure 6) itself. We believe that it is reasonable to conclude that the solvolysis of *endo*-norbornyl over this range of solvents is essentially a k_c process.

Recently, using a different approach, Harris, Mount, and Raber have come to the same conclusion, the solvolysis of *endo*-norbornyl must involve a k_c process.³⁰

If the solvolysis of *endo*-norbornyl must proceed through a k_c process, how can we explain the original observation of Winstein and Trifan that the acetolysis of optically active *endo*-norbornyl brosylate gives *exo*-norbornyl acetate with 7–8% retention of optical activity (eq 3)?⁵ This could be accounted for by a simple conversion of the reactant (5) into the corresponding tight ion pair³¹ (13) (eq 4). This tight ion pair



can now react with solvent with inversion to give the optically active *exo* acetate (7–8%), or collapse either to the proposed nonclassical ion pair (4) or to the related classical ion pair (14) which undergoes rapid equilibration with its optical isomer (eq 5).



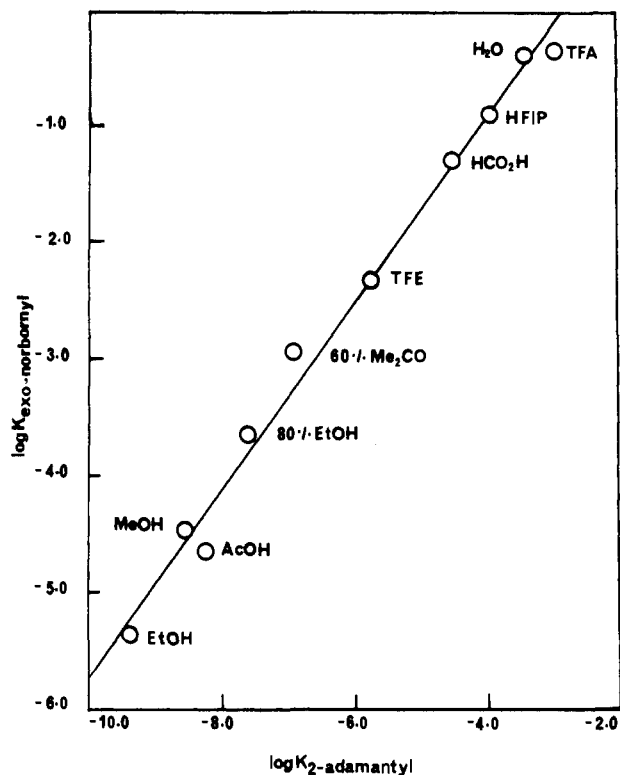


Figure 5. Linear free energy relationship between the rates of solvolysis in various solvents of *exo*-norbornyl and 2-adamantyl derivatives.

To what extent is the *exo:endo* rate ratio, long proposed to be a k_{Δ}/k_s process, a function of solvent nucleophilicity? Let us compare the rates of *exo*-norbornyl in solvents of greatly varying nucleophilicities with the rates in these solvents of isopropyl (k_s), 2-adamantyl (k_c), and *endo*-norbornyl (k_{Δ}). Values of $k_{exo-norbornyl}/k_{isopropyl}$ vary from 15 to 81 000, over a range of nearly 6000, attributable to greatly varying nucleophilic contributions of the solvent to the rate of solvolysis of the isopropyl derivatives. On the other hand, $k_{exo-norbornyl}/k_{2-adamantyl}$ varies over a much smaller range, only 20, from 520 to 12 000. This corresponds to the much lower influence of solvent nucleophilicity on the rates of solvolysis of both components. But note that $k_{exo-norbornyl}/k_{endo-norbornyl}$ varies over an even more limited range, from 280 to 1750, a factor of only 6! Clearly, this argues that *endo*-norbornyl possesses characteristics, very similar to those of 2-adamantyl, considered to be a model representative of a true k_c process.²⁸

σ -Bridging should cause the charge to be significantly delocalized from the 2 position to the 1 position.³² It is difficult to believe that such delocalization should not result in significant effects of solvent on the rates of ionization. Yet solvolysis of *endo*-norbornyl (now clearly a k_c process) and of *exo*-norbornyl are affected by solvent in a manner very similar to the way 2-adamantyl (proposed as a model k_c process^{20,28}) is affected.

We previously argued that the similarities in the Goering-Schewene diagrams for the solvolysis of 2-norbornyl and for the solvolysis of 2-anisyl-2-norbornyl and 2-anisyl-2-camphenyl argue for a common origin of the factors responsible for the high *exo:endo* rate ratios.³³ We now argue that the similarities in the effects of a wide variety of solvents on the rates of solvolysis of 2-adamantyl (proposed as a k_c process) and those of *endo*-norbornyl (now shown to be a k_c process) with those of *exo*-norbornyl strongly support a k_c process for the solvolysis of *exo*-norbornyl derivatives.

Conclusion

In the present study we have examined the solvolysis of 2-

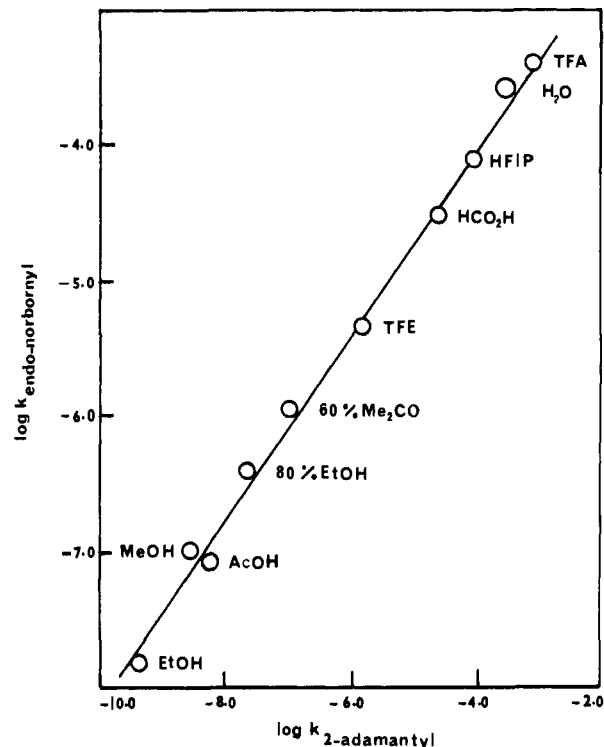


Figure 6. Linear free energy relationship between the rates of solvolysis in various solvents of *endo*-norbornyl and 2-adamantyl derivatives.

norbornyl derivatives in an exceptionally broad range of solvents. Yet the logarithms of the rates for *endo*-norbornyl are linearly related to those for *exo*-norbornyl over the broad range of solvents. This result is not compatible with the usual interpretation of the solvolysis of *exo*-norbornyl as a k_{Δ} process and *endo*-norbornyl as a k_s process.

Comparison of the data with those for 2-adamantyl, a standard k_c substrate, again reveals regularities that require that the solvolysis of *endo*-norbornyl must involve a process that is essentially k_c .

Finally, the similarities in the Goering-Schewene diagrams for the solvolysis of 2-norbornyl and for the solvolysis of 2-anisyl-2-norbornyl and 2-anisyl-2-camphenyl argue for a common origin of the phenomena. Likewise, the similarity in the effects of solvent on the rates of solvolysis of 2-adamantyl (a k_c process) with those of *endo*-norbornyl (now shown in this study to be a k_c process) with those of *exo*-norbornyl argues strongly for the conclusion that the latter must also undergo solvolysis by a k_c process. We, therefore, conclude that the *exo:endo* rate ratios in both the stabilized tertiary 2-norbornyl derivatives and secondary parent system must involve k_c/k_c processes.

Experimental Section

Preparation of Tosylates. All tosylates were prepared by reacting the alcohols with *p*-toluenesulfonyl chloride in pyridine at 0 °C³⁴ and purified by crystallization. The physical properties were in good agreement with literature values.³⁵⁻³⁷

Preparation of Mesylates. These derivatives were prepared by treating the alcohol with methanesulfonyl chloride in pyridine at 0 °C. They were obtained as a colorless oil and their purity was checked by thin layer chromatography. Refractive indexes were in agreement with literature values.^{38,39}

Kinetic Measurements. The general procedure utilized to follow the rates of acetolysis, formolysis, and methanolysis of alkylsulfonates was essentially the same as reported in the literature.^{40,41} The exceptionally fast rates exhibited in the formolysis of the norbornyl tosylates and in the solvolysis of mesylates in pure water necessitated a modified procedure.⁴² The fast rates were measured by thermostating the solvent and the standard base (made up in the same solvent)

and adding the ester, followed by indicator and a measured amount of base. Enough base was added to put the indicator on the basic side and then the time at which the solution became acidic was noted. At this point, another portion of base was added to make the solution basic and the color change again noted with time. Mean deviation of five runs using this method varied from 5 to 10%.

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On the Role of Newman Projections in Conformational Analysis. Evidence for Nonalternating Ground States in Highly Strained Molecules

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Abstract: Newman projections of substituted ethanes are commonly assumed to display a regular alternation of front and back substituents. However, symmetry arguments lead to the conclusion that the torsional itineraries of even the most simply substituted ethanes must involve conformations which do not exhibit this alternation. Empirical force field calculations show that the ground state conformations of two highly strained molecules, racemic 1,2-bis(2,6-dimethylphenyl)-1,2-di-*tert*-butylethane (**1f**) and 1,1,2,2-tetra-*tert*-butylethane (**2**), have nonalternating Newman projections. An enumeration and description of the topologically distinct Newman projections perpendicular to a bond with any number of ligands is derived group theoretically.

In discussions dealing with the ground state conformations of acyclic substituted ethanes,¹ it seems to be taken for granted that the Newman projections display a regular alternation of front (F) and back (B) ligands in the sense that each F in the projection is flanked by two B's, and vice versa. To our knowledge, this tacit assumption has never been challenged. However, although F/B alternation in molecular ground states is the general rule, we intend to show that in certain cases involving sterically strained molecules this assumption breaks down, and may consequently lead to misinterpretation of experimental results and incorrect conclusions concerning the preferred conformations of such molecules. Beyond this, we shall demonstrate that on the basis of symmetry arguments alone, nonalternation is expected to be a routine occurrence

for many substituted ethanes in conformations other than those of the ground state.

Nomenclature. To facilitate our discussion, we introduce an ad hoc nomenclatural scheme which is illustrated for the nine possible ethane skeletons in Figure 1. Projections are onto a plane perpendicular to the ethane C-C bond, ligands are labeled F and B as described above, and E designates a pair of eclipsed ligands. Descriptors are obtained by reading ligand labels in a sequential order around the periphery of the projection, and that descriptor is chosen which gives the largest numeral when priority rankings 2, 1, and 0 are substituted for F, B, and E, respectively. For example, FEFE is correct, whereas EBEF, BEFE, or EFEB are not. For all but one skeleton, the equivalence of the two ethane ends assures the