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Structural Effects in Solvolytic Reactions. 33. Exo–Endo Rate Ratios in Solvolysis of 2-Norbornyl Chlorides in Aqueous Acetone of Widely Variable Water Content

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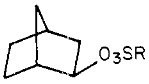
exo- and *endo*-norbornyl chlorides were prepared and solvolyzed in 80, 70, 60, 50, and 40% aqueous acetone to establish the effect of the water content of the solvent on the exo/endo rate ratio. The exo/endo rate ratios in these solvents are 221, 222, 227, 276, and 327, respectively. Extrapolation of these rate data to pure water gives an exo/endo rate ratio of 306. Over the entire range of solvents, log k_{exo} plots linearly against log k_{endo}, with a slope of 1.1. The solvolysis of *tert*-butyl chloride has been proposed as involving a model k_c process. The rate data for both *exo-* and *endo*-norbornyl chlorides correlate nicely with the rates of solvolysis of *tert*-butyl chloride over the wide range of solvent systems here examined, with slopes of 0.82 and 0.75, respectively. These results, together with other data recently published, make it necessary to reconsider the previous interpretation that the solvolysis of *exo*-norbornyl derivatives involves a k_Δ process and the solvolysis of *endo*-norbornyl derivatives involves a k_s process, with the exo/endo rate ratio arising from the operation of k_Δ/k_s processes. Instead, the facts are better accounted for in terms of essentially k_c processes for the solvolysis of both *exo-* and *endo*-norbornyl derivatives.

The precise nature of the solvolysis of 2-norbornyl derivatives has been a subject of reexamination for many years.[2] The reaction involves high exo/endo rate ratios: 350 for the acetolysis of the brosylates[3] and 280 for the acetolysis of the tosylates.[4]



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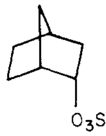

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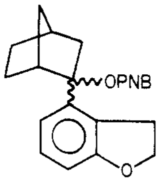
OBs	350	1.00
OTs	280	1.00

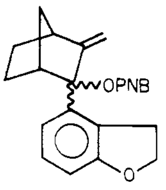
The high exo/endo rate ratios were originally interpreted in terms of participation by the 1,6-bonding pair in the transition state facilitating ionization of the *exo*-brosylate, leading to a σ-bridged nonclassical ion or ion pair (**3**), a k_Δ process.[3]

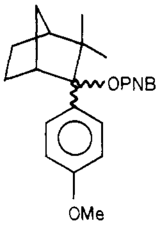
3

In the case of the endo isomer, such σ-participation was not considered to be stereoelectronically feasible. In contrast to the exo isomer which undergoes acetolysis with complete racemization, the endo isomer gives 7–8% of inverted acetate. Consequently, it was proposed that acetolysis of the *endo*-brosylate is facilitated by solvent assistance, a k_s process.[3]

Since then, solvolysis of 2-norbornyl derivatives and the high exo/endo ratios obtained have generally been discussed in terms of such k_Δ/k_s processes.[2] However, it has been observed recently that highly stabilized tertiary 2-aryl-2-norbornyl derivatives undergo solvolysis with equally high exo/endo rate ratios, **4–5**,[5] **6–7**,[6] and **8–9**.[7] Since such highly stabilized cations cannot involve σ-bridging, the high exo/endo rate ratios have been attributed to k_c/k_c processes, with the slow rate of the endo isomer arising from steric hindrance to ionization.[8]







	4,5	6,7	8,9
exo:endo	240	407	44 000

It was also observed that the Goering–Schewene diagrams for the solvolysis of such highly stabilized 2-norbornyl derivatives are extraordinarily similar to that for 2-norbornyl itself.[2] The question has been raised as to the desirability of interpreting phenomena that appear to be so similar in such different ways, as involving processes which are k_c/k_c in one case and k_Δ/k_s in the other.

Recently, the proposal that the solvolysis of 2-norbornyl derivatives proceeds through k_Δ/k_s processes was subjected to critical examination.[9,10] For example, the solvolysis of *exo-* and *endo*-norbornyl arenesulfonates in trifluoroethanol–water and ethanol–water mixtures correlated well with the rate data for the solvolysis of 2-adamantyl bromide in these solvents.[9] The authors concluded that their results were not consistent with the proposal that the solvolyses of the 2-norbornyl derivatives proceed by k_Δ/k_s processes. They tested this conclusion by applying other probes, such as the addition of azide ion.

Similarly, in another study, the solvolysis of 2-norbornyl derivatives in an exceptionally broad range of solvents was examined.[10] It was observed that the logarithms of the rates of *endo*-norbornyl derivatives were linearly related

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[1] Postdoctoral research associate on a grant provided by the Exxon Research and Engineering Co.

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[8] See ref 2, Chapter 8.

[9] Harris, J. M.; Mount, D. L.; Raber, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 3139.

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Table I. Rate Data for Solvolysis of *exo*- and *endo*-Norbornyl Chlorides in Aqueous Acetone

		$10^6 k_1$, s^{-1}					
isomer	% acetone	T_1, °C	T_2, °C	25 °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	exo:endo
X	80	250 (100)	21.5 (75)	4.63×10^{-2}	24.7	−9.0	221
N	80	69.8 (125)	5.5 (100)	2.09×10^{-4}	29.4	−4.2	
X	70	657 (100)	60 (75)	0.15	24.0	−9.0	222
N	70	126 (125)	11.2 (100)	6.75×10^{-4}	28.0	−6.9	
X	60	330 (75)	19.4 (50)	0.709	24.7	−3.7	227
N	60	296 (125)	30 (100)	3.12×10^{-3}	26.4	−8.7	
X	50	586 (75)	42.8 (50)	2.02	22.8	−8.1	276
N	50	69 (100)	5.06 (75)	7.3×10^{-3}	26.4	−7.3	
X	40	137 (50)		6.01	23.4	−4.1	
N	40	237 (100)	15.9 (75)	1.84×10^{-2}	27.3	−2.4	327
X	0			(72)[a]			(306)
N	0			(0.235)[a]			

[a] Estimated rate constants from extrapolation of the log *k*(*tert*-butyl)–log *k*(2-norbornyl chloride) plots (Figure 2).

to those for *exo*-norbornyl derivatives over the entire range of solvents. The authors argued that this is not compatible with the usual interpretation of the solvolysis of *exo*-norbornyl derivatives proceeding through a k_Δ process and that of *endo*-norbornyl derivatives through a k_s process. Comparison of the data with those for 2-adamantyl, a standard k_c substrate, revealed that the solvolysis of *exo*- and *endo*-norbornyl tosylates must involve a process that is essentially k_c. They therefore concluded that the exo/endo rate ratios in both the stabilized tertiary 2-norbornyl derivatives and secondary parent system must involve either a k_Δ/k_c or a k_c/k_c process.

Recently, questions have been raised as to whether the interpretation of such solvolytic data of esters, arenesulfonates, or *p*-nitrobenzoates may not be complicated by large steric effects. For example, we had attributed the large *t*-Bu/Me rate ratios for the solvolysis of tertiary *p*-nitrobenzoates of various structures to the rigidities of the parent structures which magnify steric effects.[11] However, Dubois and co-workers observed much lower *t*-Bu/Me rate ratios for the sulfuric acid catalyzed solvolysis of tertiary carbinols in anhydrous acetic acid.[12,13] They accounted for the difference in the two sets of data in terms of a large steric effect (F strain) influencing the solvolysis of the *p*-nitrobenzoates.

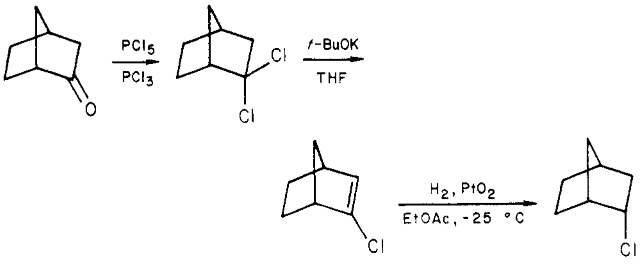
Indeed, in an earlier study, it was pointed out that "whenever possible, solvolytic reactivity studies should employ chloride or similar leaving groups, as opposed to esters, in order to minimize F strain effects."[14] Also, Schleyer and co-workers[15] have pointed out that the large increase in the tosylate/bromide ratios[16] in going from primary to tertiary substrates must owe a great deal to the relief of ground-state strain involving the departing ester group in sterically crowded systems.

In light of these developments, we decided it was desirable to explore the question as to whether such F strain might be affecting the results obtained in the solvolysis of *exo*- and *endo*-norbornyl tosylates and should be considered in analyzing the origin of the exo/endo rate ratios of these secondary derivatives.

To do so, we synthesized pure *exo*- and *endo*-norbornyl chlorides and solvolyzed them in acetone over a wide range of water content. The rates of solvolysis were determined and compared with those for *tert*-butyl chloride, a model k_c system.

Results

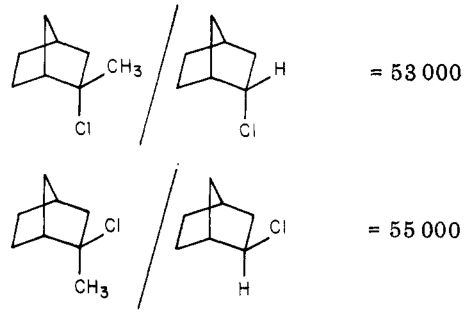
Synthesis. *exo*-Norbornyl chloride was prepared by the addition of hydrogen chloride to norbornene.[17] *endo*-Norbornyl chloride of high isomeric purity was prepared by a stereospecific route.[18]



Rate Studies. The rates of solvolysis of *endo*- and *exo*-norbornyl chlorides were measured in aqueous acetone of varying aqueous concentration—80, 70, 60, 50, and 40% (acetone–water). The rate data are summarized in Table I.

Discussion

In a recent study of the effect of 2-methyl substituents on the rates of solvolysis,[19] we utilized earlier data of Roberts and co-workers.[20,21] Roberts had reported rates of solvolysis for *endo*-norbornyl chloride[20] at 85 °C and for *exo*-norbornyl chloride[21] at 85 °C and 99.7 °C in 80% ethanol. These data gave an exo/endo rate ratio at 85 °C of 70. By assuming constant entropy of activation for the



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[16] Reference 6 as quoted in ref 14.

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solvolysis of both isomers, we estimated the exo/endo rate ratio to be 170 at 25 °C. A referee of that manuscript objected strongly to this extrapolation of the data as a means of arriving at the rate constants at 25 °C.

Consequently, it is important to note that the present study reveals an exo/endo rate ratio in 80% aqueous acetone at 25 °C of 221, in reasonable agreement with the extrapolated value.

Second, the present results reveal very similar exo/endo rate ratios for the tosylates and chlorides. Consequently, the large difference in the steric requirements of tosylates (or *p*-nitrobenzoates) and chlorides as leaving groups, found in other systems,[11-13] is not a significant factor in the parent 2-norbornyl system.

As the solvent is made more aqueous, there is a modest rise in the exo/endo rate ratio: 80%, 221; 70%, 222; 60%, 227; 50%, 276; and 40%, 327. As discussed later, an extrapolation of the data to 0% acetone (100% water) gives an exo/endo rate ratio of 306. There are two possible explanations for these modest increases. There could be a reduction in internal return as the solvent is made more aqueous. This would result in a relative increase in the rate constant for the exo isomer and an increase in the exo/endo rate ratio.

The value of k_α/k_t for *exo*-norbornyl brosylate in 75% aqueous acetone is 1.40.[3] Unfortunately, we do not have a comparable value for the *exo*-norbornyl chloride. The value for the bromide in the same solvent is 4.9.[22] Presumably, the chloride would have a value somewhere between these two numbers. Consequently, the internal-return factor can only be a relatively small number.

Of more significance is the solvent contribution to the solvolysis of *endo*-norbornyl chloride. Here we might expect much larger contributions if the solvolysis process were indeed k_s. However, the exo/endo rate data fail to reveal any significant variation. Clearly, the more aqueous solvents do not alter the exo/endo rate ratio in the manner one might anticipate for a k_Δ/k_s process.

A plot of log k_{exo} against log k_{endo} reveals an excellent linear correlation (Figure 1). The slope is 1.1. Consequently, there is little room for any significant solvent contribution to the rate of solvolysis of the endo isomer not present in that of the exo isomer.

The *tert*-butyl system has been proposed as a model system for a k_c process.[23] Consequently, it is of interest to compare the behavior of both *exo*- and *endo*-norbornyl chlorides with that of *tert*-butyl chloride (see Table II).

The data reveal an excellent plot of log k_{exo} vs. log $k_{t\text{-BuCl}}$, with a slope of 0.82 (Figure 2). Extrapolation of the line to 100% water gives the estimated value for the rate of solvolysis of *exo*-norbornyl chloride in 100% water.

The data for *endo*-norbornyl chloride also fit the *tert*-butyl chloride data (Figure 2). The slope in this case is modestly smaller, 0.75. The value for *endo*-norbornyl chloride in 100% water was obtained by extrapolation, as for the exo isomer.

The correlation of the data for *exo*-norbornyl chloride with the data for *tert*-butyl chloride is not surprising. Irrespective of whether *exo*-norbornyl chloride undergoes solvolysis by a k_Δ or a k_c process, such correlation with the data for *tert*-butyl chloride, a model k_c system, is anticipated.

A referee has argued that the present studies of the effect of variation in the water content of the acetone solvent is not as convincing as the earlier study of the solvolysis in ethanol–trifluoroethanol mixtures.[9] However, it is clear that none of the three available studies, variation in the ethanol–trifluoroethanol content,[9] variation in the nucleophilic properties of the solvent,[10] or variation in the water–acetone content (present study), yields any results

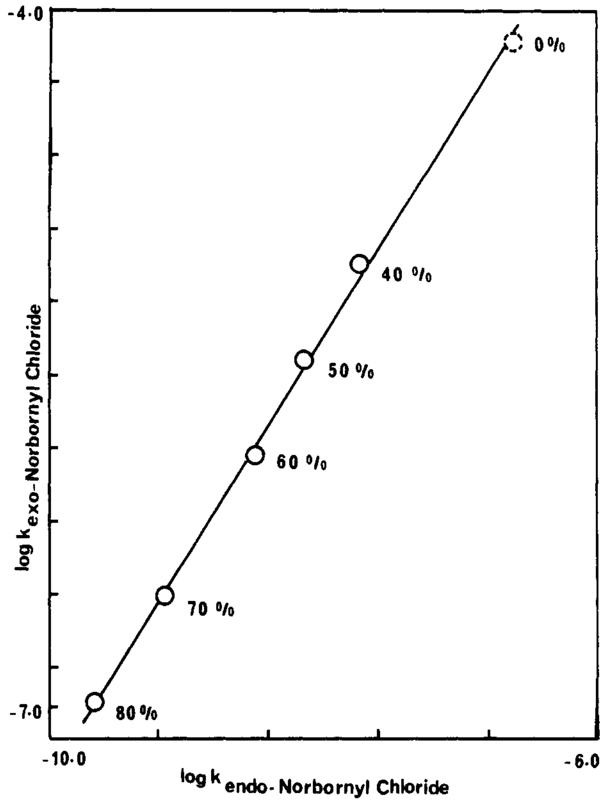

Figure 1. Linear free-energy relationship between the rates of solvolysis in aqueous acetone (acetone–water) of *exo*- and *endo*-norbornyl chlorides.

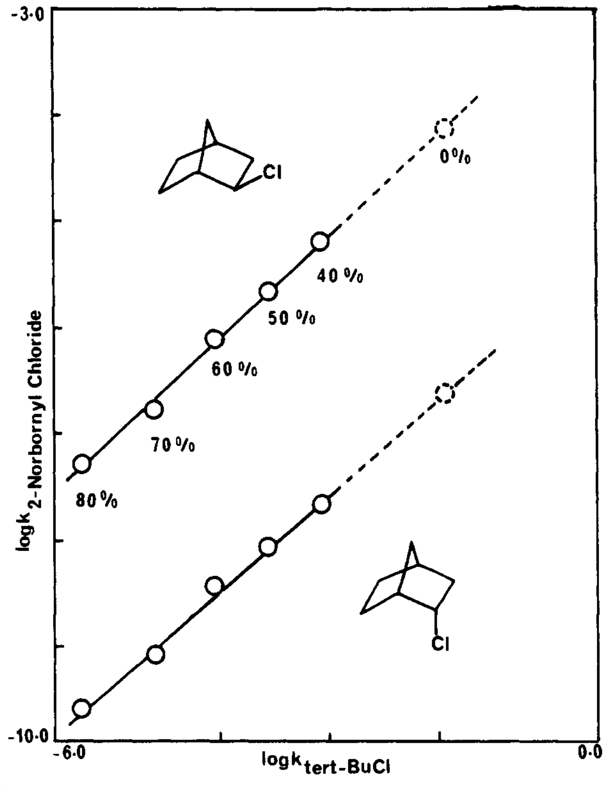

Figure 2. Linear free-energy relationship between the rates of solvolysis in aqueous acetone (acetone–water) of 2-norbornyl chlorides and *tert*-butyl chloride.

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[22] Winstein, S.; Gall, J. S.; Hojo, M.; Smith, S. *J. Am. Chem. Soc.* **1960**, *82*, 1010.

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Table II. Rate Data for Solvolysis of *tert*-Butyl Chloride and Norbornyl Chlorides in Aqueous Acetone at 25 °C

	10^6k_1, s^{-1}, 25 °C		
% acetone	*tert*-butyl chloride[a]	*exo*-norbornyl chloride	*endo*-norbornyl chloride
80	1.97	4.63×10^{-2}	2.09×10^{-4}
70	12.5	0.15	6.75×10^{-4}
60	58.0	0.709	3.12×10^{-3}
50	224	2.02	7.3×10^{-3}
40	887	6.01	1.84×10^{-2}
0	[22000][b]	[72][c]	[0.235][c]

[a] Data taken from Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* 1956, *78*, 2770. [b] Rate calculated from the Y–log k(*tert*-butyl chloride) plot; $Y_{H_2O} = 3.493$. [c] Calculated rates from log k(*tert*-butyl)–log k(norbornyl chloride) plots.

to support a proposal of any significant nucleophilic solvent contribution to the rates of solvolysis of *endo*-norbornyl derivatives.

Consequently, the present study of the effect of solvent on the exo/endo rate ratio in the 2-norbornyl chlorides confirms the conclusions reached earlier for the related study of the effect of solvents on the exo/endo rate ratio in the 2-norbornyl tosylates. Moreover, the results appear to be independent of the leaving group and are apparently not distorted significantly by F strain effects.

In conclusion, we now have three independent tests for the significance of nucleophilic solvent contribution to the exo/endo ratio in the solvolysis of the 2-norbornyl tosylates and chlorides. All three studies fail to reveal the solvent influence anticipated for true k_s processes. The results are in better agreement with the exo/endo rate ratio arising either from a k_Δ/k_c or a k_c/k_c solvolytic process.

Fortunately, it now appears possible to provide a reasonable means of deciding between these two possibilities. 2-Methyl-*endo*-norbornyl chloride undergoes solvolysis at a rate that is 53 000 times faster than the rate for *endo*-norbornyl chloride. The solvolyses of both compounds, tertiary and secondary, do not involve significant nucleophilic solvent contributions. That is, they are essentially k_c. Consequently, the factor of 53 000 measures primarily the activating effect of the tertiary methyl group in stabilizing the transition state, one which resembles closely the fully developed cation.[19] A factor of 53 000 is equivalent to 6.5 kcal mol^{-1} in energy.

If *exo*-norbornyl chloride solvolyzes with σ-bridging, the transition state will be stabilized by such σ-bridging. The Goering–Schewene diagram indicates that such nonclassical stabilization will be about 5.5 kcal mol^{-1}.[19] This will be lost in the solvolysis of 2-methyl-*exo*-norbornyl chloride, now accepted to solvolyze by a simple k_c process (see comments of P. v. R. Schleyer in ref 2). Consequently, the activating effect of the tertiary methyl substituent, 6.5 kcal mol^{-1}, will be largely negated by the loss of nonclassical resonance energy, 5.5 kcal mol^{-1}.

But the facts are not in accord with this prediction. The rate ratio for 2-methyl-*exo*-norbornyl chloride to *exo*-norbornyl chloride is 55 000 (≡6.5 kcal/mol^{-1}), essentially identical with that for the endo isomers.

On this basis, we conclude that the solvolysis of *exo*- and *endo*-norbornyl derivatives, both secondary and tertiary, must be the result of processes that are essentially k_c/k_c.

Experimental Section

exo- and *endo*-norbornyl chlorides were prepared according to literature procedures.[17,18]

Kinetic Measurements. *exo*- and *endo*-norbornyl chlorides were solvolyzed in 80, 70, 60, 50, and 40% aqueous acetone and their rates measured. Titrimetric procedure was employed. The rate data and the thermodynamic parameters are listed in Table I.

Registry No. *exo*-norbornyl chloride, 765-91-3; *endo*-norbornyl chloride, 2999-06-6.

9-(9-Borabicyclo[3.3.1]nonyl)-9-azabicyclo[3.3.1]nonane Radical Cation: A Failure of Bredt's Rule Kinetic Stabilization

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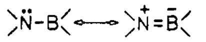
The PE spectrum of 9-(9-azabicyclo[3.3.1]nonyl)-9-borabicyclo[3.3.1]nonane (5) shows two low-energy ionizations which differ by only 0.53 eV (IP_v 8.31, 8.84 eV). Cyclic voltammetry shows an irreversible oxidation (CH_3CN, E_p^{ox} 1.75 V vs. SCE), demonstrating that the lifetime of $5^{+\cdot}$ is short in solution in contrast to other Bredt's rule protected π radical cations, including the isoelectronic olefin radical cation $4^{+\cdot}$. PE studies of the compounds with each of the bicycloalkyl groups replaced by a pair of methyl groups (9-Me_2N-9-BBN (7), 8.73, 9.18 eV; 9-Me_2B-9-ABN (8), 8.53, σ onset 9.8 eV) indicate that the HOMO of 5 is indeed the NB π orbital and that the high-lying σ orbital is associated with the 9-BBN group. The σ orbital is assigned to the antisymmetric σ_{CB}-dominated orbital on the basis of MO calculations.

Aminoboranes (I) are isoelectronic with olefins.[1] Tetramethylaminoborane (1) has a very low dipole moment,[2] implying that N ← B σ-bond polarization is just compensated by N → B π bonding, as emphasized in resonance structure IB. The double bond order is far lower than in an olefin, as indicated by the observed NB rotational barriers of 10–15 kcal/mol in compounds of proper symmetry for NMR studies.[1] The higher electronegativity of N than B makes the p-orbital coefficient at N much larger than at B in the π orbital. Bock and Fuss[3] emphasized



IA IB

Me_2NBMe_2

1

II

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