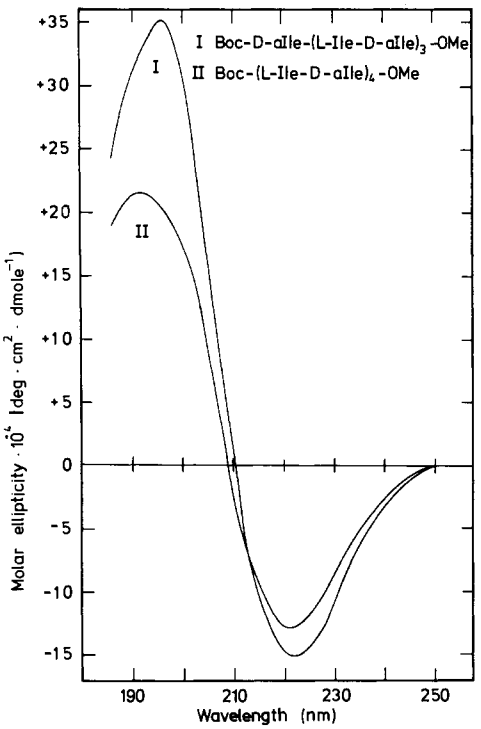

Figure 1. CD spectra of indicated cooligopeptides in cyclohexane solution: concn, 0.2 mg/ml; T, 25 °C. Values for the molar ellipticity of each oligomer are recorded.

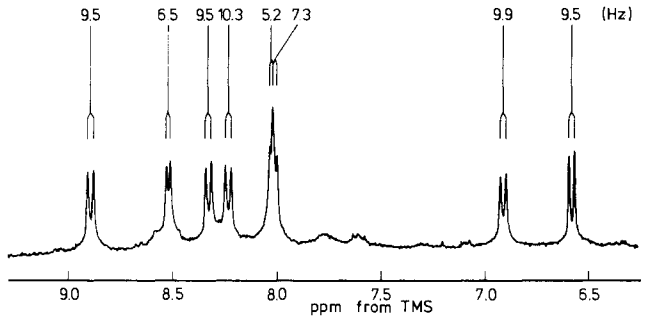

Figure 2. Peptide proton resonances in the 360-MHz FT ^{1}H NMR spectrum of II in cyclohexane-d_{12} (concn, 20 mg/ml; T, 25 °C). The assignment is based on the integrated spectrum and on NMR spectra of other oligopeptides.[5,11] The digital resolution is 0.488 Hz/point.

trations from 1 to 10 mg/10 ml and that vapor pressure osmometry measurements (at 37 °C) yield apparent molecular weights only 1.9 times the formula weights at concentrations as high as 200 mg/10 ml. In the case of I, for which measurements at different concentrations down to 50 mg/10 ml were carried out, the data extrapolate to the formula weight of the cooligopeptide at infinite dilution. Although the possibility of an association to dimer at high concentrations cannot be ruled out, these data suggest that I and II are monomeric in the conditions of our spectroscopic measurements. NMR spectra (360 MHz) of cyclohexane solutions of I and II show well-resolved peptide proton resonances with several vicinal coupling constants larger than 8.6 Hz. Figure 2 illustrates this for II. Using the refined relationship given by Bystrov et al.[7] such large coupling constants can be assigned with large confidence to dihedral angles θ between the H-N-C$^\alpha$ and the N-C$^\alpha$-H planes which are in the range of 150° to 180°. These correspond to conventional [8]dihedral angles ϕ about the N-C$^\alpha$ bond in the range of −90° to −150° for L-residues and of +90° to +150° for D-residues. Values of ϕ in these ranges characterize β-helices.[2,3] On these grounds we conclude that helical conformations of this type exist for I and II in cyclohexane. A regular β-helix, which would have a number of nonbonded NH protons at its two extremities, is not consistent with the results of IR-absorption measurements, which reveal only a very weak band at the frequencies expected (~3440 cm^{-1}) for nonbonded NH protons. The amide A region shows a band with a maximum (3310 cm^{-1}) in the range of frequencies typical[9] of the strong hydrogen bonds of L-oligopeptides in the β-sheet structure, implying there are hydrogen bonds of comparable strength in I and II in cyclohexane solution. This band has a shoulder on the high frequency side, suggesting that some of the hydrogen bonds may be weaker. It seems therefore that the NH protons, which are not involved in the strong interturn bonding, form less strong intramolecular bonds, possibly of the C_7 type.[10] These bonds and a distortion of the helix could account for the several coupling constants observed (Figure 2).

The similarity of the two curves of Figure 1 may evidence an identity of the sense of twist. For infinitely long chains of alternating diastereomeric L- and D-residues, the difference in energy of the two senses of twist of a β-helix is determined solely by the configuration of the side groups. For short chains such as those of I and II, the sequence number of the two different residues in the chain may play an important role in stabilizing or destabilizing one sense of twist with respect to the other. Further study is projected to establish the relative influence of the chiral side groups of identical configuration on the conformation of I and II.

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Solvolysis of Secondary Substrates by a Limiting Mechanism. The Cyclooctyl System

Sir:

The solvolysis reactions of secondary substrates have recently been described in terms of competitive neighboring-group (k_Δ) and nucleophilic solvent (k_s) assisted processes, eq 1,

$$k_t = k_\Delta + k_s \quad (1)$$

with these processes approaching a limiting or unassisted k_c process as assistance becomes weak.[1-4] There has been much debate concerning the importance of the k_c pathway for the

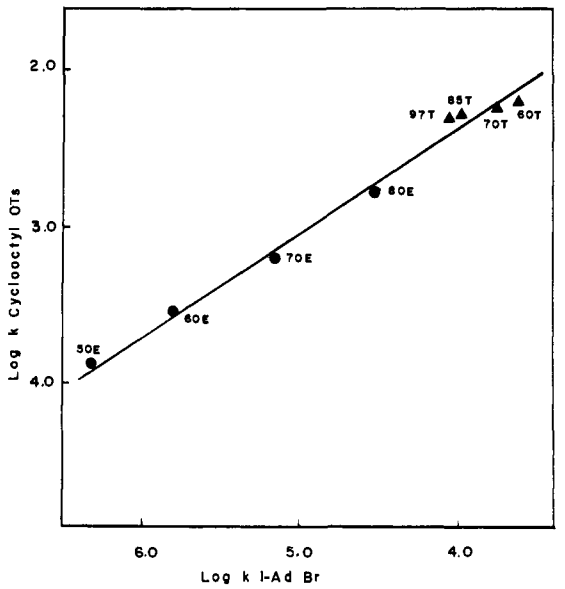
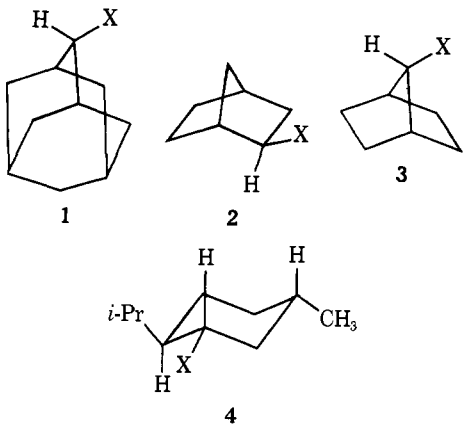


Figure 1. A plot of log of solvolysis rate of cyclooctyl tosylate and log solvolysis rate of 1-adamantyl bromide in aqueous ethanol (●) and in aqueous trifluoroethanol (▲) at 25 °C.

reactions of secondary derivatives.[5-9] Obviously, if the k_s and k_Δ pathways are unfavorable, reaction will occur by the limiting k_c mechanism. The k_s pathway is relatively unimportant for molecules in which there is steric hindrance to nucleophilic approach (e.g., in **1-4**)[3,8,10,11] or for solvolyses in solvents of very low nucleophilicity (e.g., in trifluoroacetic acid or hexafluoro-2-propanol).[4a,12] The occurrence of the k_Δ pathway with bridging by carbon σ electrons is often difficult to prove or disprove, and much controversy has centered on these systems.



The solvolyses of **1-3** have been shown to give rearranged substitution products with inversion of configuration and unrearranged substitution products with retention of configuration.[5,6,10] One group interprets these observations as indicating intervention of bridged ions and operation of the k_Δ mechanism.[5,6,8] These workers suggest that the k_Δ mechanism occurs in the solvolyses of most polycyclic hydrocarbon derivatives, and have proposed as examples of k_c substrates only the solvolyses in nonnucleophilic solvents (thus eliminating the k_s process) of acyclic and monocyclic substrates;[12a] these latter reactions are accompanied by hydride shifts, but studies of representative carbocations (e.g., 2-butyl and cyclopentyl) under stable-ion conditions have shown the rearrangements to involve equilibrating classical species, thus eliminating the k_Δ process.[13,14] However, it should be noted that the stereospecificity of hydride shifts in these molecules remains unexplained.[15] A second group of workers suggest that k_c processes are common, and interpret the majority[16] of stereochemical results such as those above in terms of steric control of nucleophilic approach.[9]

Table I. First-Order Rate Constants for the Solvolysis of Cyclooctyl Tosylate

Solvent[a]	T (°C)	10^4k (s^{-1})[b]	$\Delta H^\ddagger$ (kcal mol^{-1})	$\Delta S^\ddagger$ (eu)
80% EtOH	50.0	20.5 ± 0.2		
	30.2	2.38 ± 0.03		
	25.0[c]	1.30	20.5	−7.6
70% EtOH	50.0	43.1 ± 0.1		
	30.2	5.25 ± 0.03		
	25.0[c]	2.89	20.1	−7.5
60% EtOH	25.0	6.20 ± 0.18		
50% EtOH	25.0	17.1 ± 0.1		
97% TFE	25.0	51.6 ± 0.1		
85% TFE	25.0	52.8 ± 0.2		
70% TFE	25.0	58.0 ± 0.6		
60% TFE	25.0	65.0 ± 0.6		

[a] Ethanols are volume percent; trifluoroethanols are weight percent. [b] Determined conductometrically, and the result of at least two determinations; experimental uncertainties are average deviations. [c] Extrapolated.

The purpose of the present communication is to present evidence indicating that solvolysis of secondary substrates by a limiting mechanism may not be unusual, but rather may occur even in nucleophilic solvents for a molecule (cyclooctyl tosylate) which can readily adopt conformations permitting easy backside approach of the nucleophile to the reaction site.

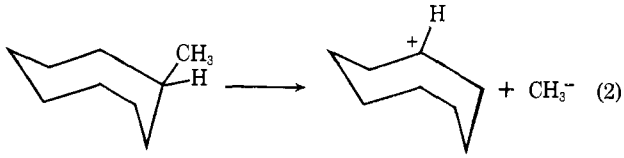
1-Adamantyl bromide has previously been suggested as a model k_c substrate, and plots of the logarithms of the solvolysis rate constants for k_Δ and k_c substrates against the logarithms of the solvolysis rate constants for 1-adamantyl bromide in aqueous ethanol (W-E) and aqueous trifluoroethanol (W-T) of varying percentages have been shown to be close to linear with the W-T points lying near the slope defined by the W-E points.[17] In contrast, this kind of plot for a k_s substrate gives separate lines for W-E and W-T because the k_s substrate shows a large response to the substantial changes in nucleophilicity accompanying changes in the water-trifluoroethanol ratio. For cyclooctyl tosylate the W-E/W-T plot is of the shape expected for k_c and k_Δ substrates, Table I and Figure 1. Thus the k_s mechanism is indicated to be inoperative despite cyclooctyl tosylate having available conformations equally as open to nucleophilic attack as cyclohexyl tosylate, for example, which has clearly been shown to be a k_s substrate.[1,3,17] Cyclooctyl tosylate has a $(k_E/k_{AcOH})_Y$ value (0.40) consistent with reaction by a k_c mechanism, but its m value (0.67) is intermediate between values expected for k_s and k_c substrates.[3a]

To verify that the k_s mechanism was inoperative, the effect of sodium azide on the products of aqueous ethanolysis at 25 °C of cyclooctyl tosylate was determined. A twofold excess of sodium azide (0.04 M) was added to cyclooctyl tosylate (0.02 M) in 70 (v/v) % aqueous ethanol containing lutidine (0.022 M). Product analysis by titration and gas chromatography revealed the absence of alkyl azide, and analysis by gas chromatography showed that the relative amounts of cyclooctene, cyclooctanol, and cyclooctyl ethyl ether were unchanged. These results are inconsistent with operation of the k_s mechanism.[18]

Before concluding that cyclooctyl tosylate reacts by a k_c mechanism, reaction by a k_Δ mechanism must be eliminated. Support for the possibility of a k_Δ mechanism comes from indication of rate acceleration (the σ_t^* method)[19] and from the observation of significant amounts of transannular hydride shift in the solvolysis.[20] However, a study of deuterium isotope

effects by Roberts[20] has shown that these shifts occur after the rate determining step. The solvolysis of cyclooctyl tosylate must be a limiting k_c process.

Some years ago Brown suggested that the solvolysis of medium ring derivatives was accelerated by relief of angle strain (I-strain).[21] Molecular mechanics calculations (Schleyer–Engler force field)[22] on the ionization of cyclooctane (with CH_3^- acting as a leaving group model, eq 2)[23] indicate that relief of strain may in fact facilitate ionization; other acyclic and monocyclic substrates show positive δ strain values.[25] Thus the rate acceleration of cyclooctyl tosylate predicted from the σ_t* correlation must result from relief of strain.



strain energy, (gas phase, 25 °C)

13.86 kcal/mol 10.80 kcal/mol

δ strain = −3.06 kcal/mol

In summary, strained secondary substrates can solvolyze without nucleophilic solvent assistance, even when there are no obvious barriers to nucleophilic approach, if the relief of ground-state strain upon reaction is sufficient to provide a competitive pathway.

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Preparation and Properties of Monolayer Films of Surfactant Ester Derivatives of Tris(2,2′-bipyridine)ruthenium(II)$^{2+}$

Sir:

There is intense interest in the photochemical properties of the tris(2,2′-bipyridine)ruthenium(II) cation, $(Ru^{II}(bpy)_3)^{2+}$.[1] It has recently been reported[2] that a substituted complex, $\{(bpy)_2Ru^{II}[bpy(COOC_{18}H_{37})_2]\}^{2+}(ClO_4^-)_2$ (where the substituents are in the 4,4′ positions of the bipyridine ligand), I, when incorporated in monolayer assemblies can efficiently catalyze the photodecomposition of water by visible light. We have found that during the preparation and handling of I, facile ester interchange and hydrolysis occurs under certain conditions. Further, the monolayer characteristics of I (vide infra) differ from those stated in ref 2. Accordingly, we believe that the reported photolysis observations involved a structure more complex than originally supposed, and careful characterization is required to obtain well-defined assemblies for further study.

The synthetic route to I[3] involves the esterification of 4,4′-dicarboxy-2,2′-bipyridine with *n*-octadecanol and subsequent reaction with $(bpy)_2Ru^{II}Cl_2$ in ethanol. Incomplete esterification, partial saponification during product workup, or ester interchange during the ligand insertion reaction can lead to alternate products. Most of a number of preparations we have examined have contained varying amounts of *n*-octadecanol, together with components of the type $\{[bpy]_2Ru^{II}[bpy(COOR_1)(COOR_2)]\}^{2+}$, where $R_1 = R_2 = H$ (II); $R_1 = C_{18}H_{37}$, $R_2 = H$ (III); or $R_1 = C_{18}H_{37}$, $R_2 = C_2H_5$ (IV). These separations have been accomplished by reverse phase (4 mm i.d. × 30 cm μBondapak/C_{18}) high pressure liquid chromatography employing a linear solvent gradient (50% aqueous THF/100% THF, both 0.015 M $MeSO_3H$, 0.5% HOAc). Under these conditions, I is chemically stable and is well separated from II, III, IV, and the dioctadecyl ester ligand (V), all of which are detected by their ultraviolet absorbancies at 254 and 280 nm. *n*-Octadecanol is detected by differential refractive index using 25% aqueous THF without $MeSO_3H$ and HOAc.

We have found that substantially pure I can be obtained by avoiding contact of either I or its precursor V with alkaline solution. The preparation of I used for this report contains:[4] <0.5 mol % (II + III + IV), <0.5 mol % V, <0.5 mol % *n*-octadecanol and 2.6 mol % $[bpy]_2Ru^{II}[bpy(COOC_{18}H_{37})$