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The Mechanism of Solvolysis of 2,2-Dimethyl-3-pentyl and 1-(1-Adamantyl)propyl Sulfonates*

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Solvolysis rates, alpha and beta deuterium isotope rate effects and product yields have been determined for some 1-(1-adamantyl) propyl sulfonate esters, **4**, in some ethanol-water, trifluoroethanol-water and hexafluoroisopropyl alcohol-water mixtures. For comparison, similar measurements have been made for solvolysis of 2,2-dimethyl-3-pentyl sulfonates, **5**. For the esters **5**, the alpha-*d* and beta-d_2 effects vary little with solvent in the ranges of 1.164–1.165 and 1.215–1.241, respectively, and only small yields of unrearranged products are formed; it is concluded that the mechanism involves rate determining formation of the secondary cation-ion pair followed by rapid rearrangement. For the adamantyl analogs, **4**, the alpha-*d* effects vary in the different solvents from 1.162 to 1.213 and the beta-d_2 effects vary from 1.339 to 1.649; significant yields of unrearranged and Wagner-Meerwein rearranged (ring expansion) products are formed. The steady state treatment, which had been used previously to fit the results for 1-(1-adamantyl)ethyl esters, was applied to the results for **4**; a mechanism which involves partially reversible ionization to the intimate ion-pair followed by competing elimination and solvent separation, to give the substitution products, fits the results reasonably well.

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* Dedicated to the memory of Professor Stanko Borčić.

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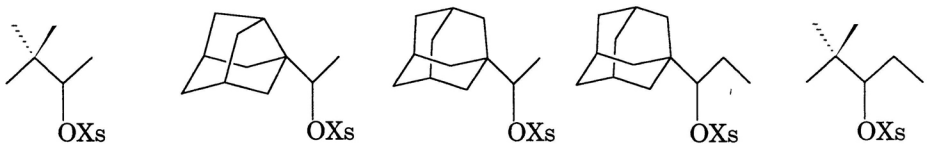
INTRODUCTION

It was suggested some years ago that 3,3-dimethyl-2-butyl (»pinacolyl«) esters, **1**, would be useful reference reactants for the estimation of unassisted ionization rates of secondary sulfonate esters in the absence of internal return.[1,2] Pinacolyl esters react in solvents, ranging in nucleophilicity from trifluoroacetic acid to ethanol, by rate-determining, unassisted ionization to the intimate secondary cation-ion pair, followed by rapid, irreversible Wagner-Meerwein rearrangement to the tertiary ion from which the products are derived. Internal return from the first-formed intimate ion pair does not take place because it is much slower than rearrangement. Nucleophilic attack by solvent on the ester or on the ion pair is not significant because it is sterically inhibited by the alpha *t*-butyl group. This interpretation is supported by the facts that 1) >98% of the products have the rearranged structure, 2) the alpha and beta deuterium isotope rate effects do not vary appreciably with solvent and 3) no ^{18}O scrambling can be detected in the recovered unreacted ester.[3,4]



1 2 3 4 **5**

OXs = a sulfonate ester

To further test this interpretation we have more recently examined the solvolysis of analogs of pinacolyl sulfonate esters having structures **2**[5,6] and **3**[7]. In structure **2**, one of the beta carbon atoms is incorporated into the strained noradamantyl ring; consequently the Wagner-Meerwein rearrangement, which would involve the release of strain to form the adamantyl ring structure, is energetically more favorable than it is for the pinacolyl analogs. It was shown that the solvolyses of **2** were more than one-thousand times faster than the solvolyses of pinacolyl analogs and that only rearranged products were formed. The β-d_3 effects on the rates of solvolyses of **2** were in the range of 1.14–1.15, significantly smaller than the 1.20–1.21 for the pinacolyl esters; surprisingly the α-*d* effects were about the same as those for the pinacolyl esters. It was concluded that the mechanism for the solvolyses of **2**, 1-(3-noradamantyl)ethyl sulfonates, involved rate determining ionization with neighboring carbon participation to form directly the tertiary cation-ion pair, a »k_Δ« process.

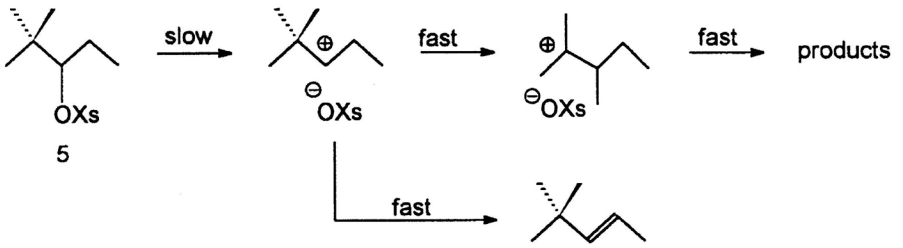
In contrast, the sulfonate esters of structure **3** have one of the beta carbon atoms incorporated into the relatively strain-free adamantyl ring; the Wagner-Meerwein rearrangement that would accompany solvolyses of these esters involves an increase in strain energy to form the homoadamantyl ring structure. The solvolyses of these sulfonate esters were shown 1) to produce significant yields of both rearranged and unrearranged products, 2) to involve extensive internal return as signaled by ^{18}O scrambling in the recovered unreacted ester and 3) to show α-d rate effects which varied in different solvents from 1.116 to 1.147 and β-d_3 effects which varied from 1.12 to 1.256. A steady state treatment, based on the reversible formation of intimate ion pair intermediates having unrearranged and rearranged structures, gave a good correlation between the isotope rate effects and product yields with the expected single step isotope rate effects. Thus the three analogous esters solvolyze by three different mechanisms: rate determining ionization with σ-carbon participation, $»k_{\Delta}«$, **2**; simple rate determining ionization without concurrent rearrangement or return, $»k_c«$, **1**; and ionization with internal return, **3**. In the present paper we extend the results to the study of the next higher homolog of **3**, 1-(1-adamantyl)propyl sulfonate esters, **4**. For closer comparison of structural analogs we have also determined the isotope effects in the solvolyses of the next higher homolog of the pinacolyl sulfonates, 2,2-dimethyl-3-pentyl *p*-bromobenzenesulfonate, **5**.

RESULTS AND DISCUSSION

Solvolysis of 2,2-Dimethyl-3-propyl Brosylate, 5

The ^2H-MR spectra of the products of solvolysis of 2,2-dimethyl-3-pentyl-3-*d* brosylate in buffered ethanol-water (φ = 60%), and in buffered hexafluoroisopropyl alcohol-water (w = 80%), showed only 13% and 6% respectively of the deuterium in the vinyl position, and none in the alpha position; all of the other deuterium resonances were in positions characteristic of solvent deuterium, allyl deuterium or deuterium beta to an alcohol or ether function. Thus, except for 13% and 6% respectively of unrearranged elimination, all of the other products were formed after Wagner-Meerwein rearrangement; this provides support for the conclusion that ionization proceeds first to the unrearranged secondary carbenium ion, which can undergo an E1 elimination, and that the rearranged tertiary ion is formed subsequent to formation of the intimate secondary cation-ion pair, as outlined in Scheme 1.

Rate constants and isotope rate effects for the solvolysis of alpha and beta deuterated isotopomers of 2,2-dimethyl-3-pentyl brosylate are given in Table I.



Scheme 1.

TABLE I

Solvolysis rate constants[a] and isotope effects for 2,2-dimethyl-3-pentyl sulfonate esters at 25°C

Solvent[b]	Lvg gp[c]	k_H[d]	$k_H/k_{\alpha\text{-}d}$	k_H/k_{td}[e]	k_H/k_{ed}[f]	$k_H/k_{\beta\text{-}d2}$	k/k_{pin}[g]
80H	OTs	79.39	1.164	–	–	1.235	8.0
97T	OBs	57.71	1.166	1.176	1.052	1.215	7.0
60E	OBs	16.81	1.164	1.157	1.083	1.241	4.0

[a]Determined spectrophotometrically. [b]80H is hexafluoroisopropyl alcohol (w = 80%) – water (w = 20%) mixture, *etc*; 97T is trifluoroethanol (w = 97%) – water (w = 3%) mixture, *etc*; 60E is ethanol (φ = 60%) – water (φ = 40%) mixture, *etc*. [c]OTs is *p*-toluenesulfonate, OBs is *p*-bromobenzenesulfonate and OPms is pentamethylbenzene sulfonate. [d]Units are 10^{-5} sec^{-1}. [e]Deuterium at C-4 in the threo position. [f]Deuterium at C-4 in the erythro position. [g]Rate relative to pinacolyl (3,3-dimethyl-2-butyl) sulfonate in the same solvent.

The alpha deuterium effects on the rates of solvolysis are in the narrow range of 1.164–1.165, only slightly higher than the values of 1.152–1.159 reported for pinacolyl brosylate; this difference may be due to the slightly enhanced steric congestion of the alpha CH bond in the initial state. The β-d_2 isotope effects are in the range of 1.215–1.241, also slightly higher than the values in the range of 1.188–1.205 found for the β-d_3 effects on the solvolysis rate of pinacolyl brosylate; this may be due to a slightly greater hyperconjugative ability of methylene hydrogens over methyl hydrogens.

In the original application of the EtOH-TFE method,[8] the authors presented a plot of the logs of the solvolytic rate constants of pinacolyl brosylate (incorrectly referred to as pinacolyl tosylate in the text) *vs.* the logs of the solvolysis rate constants of 1-adamantyl bromide, the standard used at that time. The plot showed only a small break and it was concluded that the method did not detect any nucleophilic assistance. In order to eliminate the effects of different leaving groups and of possible errors in using extrapolated rate constants, Stoelting[6,9] determined the solvolysis rates of pinacolyl tosylate and 2,2-dimethyl-3-pentyl tosylate in several different EtOH-water

and TFE-water solvents and examined the EtOH-TFE plots against the logs of the observed solvolysis rate constants for the current standard, 2-adamantyl tosylate. The plots were characterized by a slope (m_e) and correlation coefficient (r) for the ethanol-water line and the distance from this line for the 97% TFE-water point referred to as Δ97T, given positive values when below the line (relatively slower rates) and negative values when above the line (relatively faster rates). The EtOH-TFE plot for pinacolyl tosylate (*vs.* 2-adamantyl tosylate) showed an ethanol-water slope (m_e) of 0.936 (r = 0.9998) and a Δ97T value of 0.35, 2.2 times slower in solvolysis rate than it would be if it were on the correlation line. The plot for 2,2-dimethyl-3-pentyl tosylate showed an m_e of 0.88 (r = 0.9995) and a Δ97T of only 0.009; the 97T point is essentially on the line. Thus, by the EtOH-TFE criterion, 2,2-dimethyl-3-pentyl sulfonate esters solvolyze without solvent nucleophilic assistance. It seems clear that the EtOH-TFE criterion is not adequate to argue that there is solvent nucleophilic assistance for the solvolysis of pinacolyl esters even though the 97T point is clearly not on the line.

The β-d effects for the stereospecifically deuterated 2,2,-dimethyl-3-pentyl brosylates, Table I, can be used to determine certain aspects of the conformation of the solvolytic transition state. The Servis, Sunko, Hehre equation expresses the variation of the β-d effects on solvolysis rates with the dihedral angle that the CH/CD bond makes with the developing vacant p-orbital on the α-C atom:[10]

$$\log (k_H/k_D)_\theta = \cos^2 \theta \, [\log (k_H/k_D)_{0°}] - 0.00656$$

where θ is the dihedral angle between the CH/CD bond and the developing vacant p-orbital and log $(k_H/k_D)_{0°}$ is the isotope effect that would apply if the value of θ is zero. The –0.00656 is the log of the isotope effect that would apply if θ is equal to 90°, where the hyperconjugative effect would be nil and only the inductive effect would be operative. This effect would vary, depending on electron demand at the reaction center, but variations in this small number would hardly be significant. In addition we have measured the γ-d_3 effect on this solvolysis rate and found it to be 0.985 in 60E at 25°; given that the inductive effect falls off by a factor of about three for every additional C-atom between the reaction center and the substituent, the inductive isotope rate effect (per d-atom) for the β-deuteriums would be very close to the number given in the formula. For the erythro and threo β-d effects in each solvent, there would be two equations with three unknowns, the two dihedral angles and the log $(k_H/k_D)_{0°}$; if we assume that the dihedral angle separating the threo and erythro CH/CD bonds is 120°, we have a third equation that $\theta_e + \theta_t + 120 = 180$, or $\theta_e = 60 - \theta_t$. Trial and error solutions give the angle between the erythro CH/CD bond and the p-orbital, θ_e, as

about 42° for the 60E and 53° for the 97T results; the angle θ_t is about 18° (60E) and 7° (97T); the $(k_H/k_D)_{0°}$ value in both cases is 1.197. This suggests that the transition state conformations are as shown in Figure 1, assuming that the position of the methyl group approximately *trans* to the *t*-butyl group is more favorable than it is when approximately *cis*; the threo position, which shows the larger H/D isotope effect, is *cis* to the leaving group; the arrangement of the substituents about the α-C atom is not established but is arbitrarily indicated as planar.

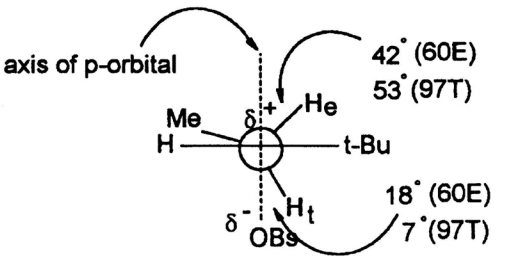


Figure 1.

In summary, the evidence shows that 2,2-dimethyl-3-pentyl sulfonates, **5**, like their pinacolyl analogs, **1**, solvolyze by the mechanism shown in Scheme 1; the secondary cation ion pair is an intermediate, there is no solvent nucleophilic assistance and no significant internal return. The alpha-*d* and beta-*d* isotope effects for the higher homologs, **5**, are slightly larger than those for the pinacolyl analogs and provide more accurate values for the isotope effects on the ionization step, to use in the simplex fitting procedure for the results from the solvolyses of 1-(1-adamantyl)propyl sulfonate esters (see below).

Solvolysis of 1-(1-Adamantyl)propyl Sulfonate Esters, 4

The products of solvolysis of the α-*d* and β-d_2 esters determined by recording the ^{2}H-NMR spectra of spent reaction mixtures are recorded in Tables II and III.

Solvolysis rates for the sulfonate esters, **4**, and the α-*d* and β-d_2 effects on the solvolysis rates, which were determined in several ethanol-water, trifluoroethanol-water and hexafluoroisopropyl alcohol-water mixtures by the spectrophotometric method, are shown in Table IV.

As in the case of the lower homologs, 1-(1-adamantyl)ethyl sulfonates, solvolyses of **4** give significant proportions of both rearranged and unrearranged substitution, Table II. However, in contrast, the higher homologs show much greater proportions of elimination, as might be expected from

TABLE II

Products of solvolysis[a] of 1-(1-adamantyl)propyl-1-*d* sulfonate esters at 25 °C from ^{2}H-NMR analysis

Solvent[b]	Lvg Grp[c]	% Sub[d]	% Rearr Sub[e]	% Elim[f]
98H	OPms	15.0	36.5	49.5
90H	OPms	18.5	43.9	37.6
97T	OTs	10.5	20.6	69.8
80T	OTs	19.8	34.1	46.1
90E	OBs	13.5	7.6	79.0
80E	OBs	18.5	7.5	73.9
70E	OBs	34.0	5.0	60.9

[a]Buffered with lutidine. [b,c]See footnotes to Table I. [d]Yield of 1-(1-adamantyl)-1-*d*-propanol. [e]Yield of 4-methyl-4-deuterio-3-homoadamantanol. [f]Yield of 1-(1-adamantyl)propene-1-*d*.

TABLE III

Products of solvolysis[a] of 1-(1-adamantyl)propyl-2,2-d_2 sulfonate esters at 25 °C from ^{2}H-NMR analysis

Solvent[b]	Lvg Grp[c]	% Sub[d]	% Elim[e]
98H	OPms	87.6	12.4
90H	OPms	84.7	15.2
97T	OTs	83.5	16.4
80T	OTs	74.8	25.2
90E	OBs	57.7	42.3
70E	OBs	60.9	39.1

[a]See footnote to Table II. [b,c]See footnotes to Table I. [d]Yield of both unrearranged and rearranged substitution; the dmr peaks were not separated. [e]Yield of 1-(1-adamantyl)propene-2-*d*.

the more highly substituted nature of the alkene formed. The ratio of elimination to total substitution for the α-*d* ester divided by the same ratio for the β-d_2 ester, gives an estimate of the primary isotope effect on the elimination fraction. These numbers are as follows: 98H, 6.7; 80H, 3.4; 97T, 11.3; 80T, 2.5; 90E, 5.1; 70E, 2.4. The numbers in the more aqueous solvents, 2.4–3.4, are all similar to the value of 2.5 which gave the best fit for the primary isotope effect on the elimination from the ion pair (r^b_{5e}) in the earlier work; however, the values of 5.1 and 6.7, while not large for primary effects are nevertheless larger than any other observed values for hydron elimination from an alkyl carbenium ion. The value for 97T, 11.3, must involve experimental error. The large values, 5.5–6.7, found in the less polar solvents may be due to elimination of the proton by the leaving group.

TABLE IV

Solvolysis rate constants[a] and isotope effects for 1-(1-adamantyl)propyl sulfonate esters at 25°C

Solvent[b]	Lvg gp[c]	k_H[d]	$k_H/k_{\alpha d}$	$k_H/k_{\beta d2}$	k/k_{AdEt}[e]
90H	OPms	423.8	1.162	1.339	9.7
80H	OPms	191.7	1.185	1.345	5.0
97T	OTs	131.5	1.177	1.412	4.4
80T	OTs	122.5	1.179	1.411	3.7
90E	OBs	2.181	1.211	1.641	–
80E	OBs	6.669	1.213	1.649	13
70E	OBs	15.2	1.203	1.597	10.8

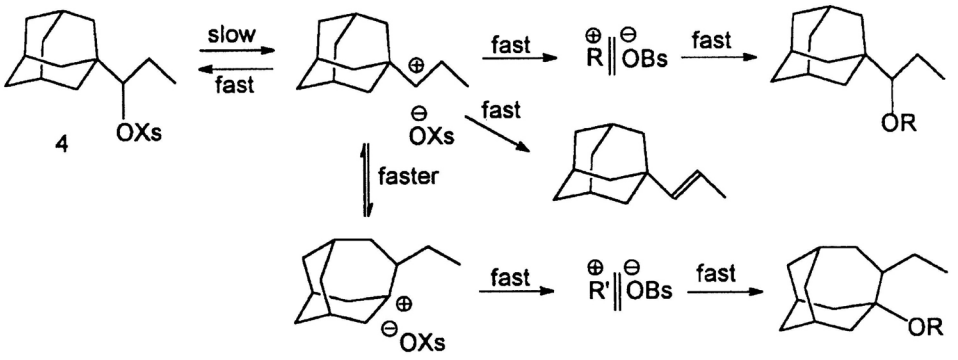
[a,b,c,d] See footnotes to Table I. [e]Rate relative to 1-(1-adamantyl)ethyl sulfonate in the same solvent.

Despite the fact that these solvolyses give very large proportions of elimination, the β-d_2 effects on the solvolysis rate, shown in Table IV, are all below 1.7. The fact that they are smaller than the beta isotope effect on the elimination fraction means that elimination is not dominantly rate-determining. However, the fact that the β-d_2 effects are larger than ≈1.46, the expected secondary effect on the reversible formation of the tight ion-pair,[7] means that the elimination must be partly rate-determining. Thus we can conclude that the tight ion-pair undergoes some internal return but that internal return is not dominant, so that both ionization and elimination are partly rate-determining. In the solvolyses of the lower homolog, the elimination fractions were small and internal return was found to be about 1 to 2 times faster than the sum of the other reactions of the ion pair. In the present case, the fact that the elimination fraction is large means that elimination from the intimate ion pair is proportionately faster and that internal return is reduced.

The α-*d* effects, shown in Table IV, generally parallel the β-d_2 effects but cover a much smaller range, 1.162–1.213. Thus they are all between the value of ≈1.16, characteristic of rate determining formation of the intimate ion pair, and ≈1.23 characteristic of reversible formation of the intimate ion pair.[7] This is qualitatively consistent with the behavior of the β-d_2 effects. However, as we will see below, the β-d_2 effects are too far from their maximum values to require much internal return while some the α-*d* effects are quite near their maximum values, which makes a satisfactory quantitative fit, using the expected single step isotope effects previously applied, difficult.

We have used the steady state treatment, which so successfully fit the results from the 1-(1-adamantyl)propyl sulfonate esters, **4**,[7] to fit the present results. This treatment is based on the mechanism, outlined in Scheme 2, which involves the formation of the intimate ion pair, which can undergo

four different reactions: 1) rapid and reversible formation of the rearranged ion, 2) internal return to the covalent reactant, 3) elimination to the unrearranged alkene, 4) solvent separation to give unrearranged substitution; the rearranged cation-ion pair undergoes solvent separation to give rearranged substitution. It should be noted that this is one of the simplest mechanisms that could be used to fit the results; specifically ignored are the possibility of any elimination or rearrangement of the solvent separated ion pairs. The steady state equations use the isotope effects on the individual rate constants and the ion pair partitioning ratios to calculate product proportions and isotope effects on the solvolysis rates. The simplex procedure



Scheme 2.

is used to determine the partitioning ratios which give the best fit of the calculated isotope effects and yields to the observed values. Since the fitting procedure uses the same single step isotope effects to fit the data from each solvent, and since the isotope effects on the elimination fraction were so different in 97T and 98H (see above) the results from these solvents were not included in the simplex fitting procedure. There were a total of 40 observations to fit by the adjustment of the four branching ratios of the competing reactions of the intimate ion pairs; however this involves only three adjustable parameters in each solvent (15 altogether) since the yields of products must add up to 100%.

In fitting the results to the mechanism shown in Scheme 2, we used the isotope effects on the individual steps that best fit the solvolyses of 1-(1-adamantyl)ethyl sulfonates[7], with the following exceptions: 1) the alpha-d and beta-d_2 effects on the ionization step, 1.164 and 1.230 respectively, were those found in the present work for the solvolysis of 3,3-dimethyl-2-pentyl sulfonates; these values are slightly larger than 1.155 and 1.20 used previously, and 2) the beta isotope effect on the elimination step, selected by

the program to give the best fit, was 2.80 instead of 2.5 found for the lower homolog. The average deviation between the calculated and observed values of the product yields (expressed as fractions) was ±0.03 well within the error in the NMR determinations. The β-d_2 effects were fit very well; the average deviation was only ±0.005 and the largest deviation was 0.012. The α-*d* isotope effects were fit less well; the average deviation was ±0.016 and the largest was 0.032. The fit to the observed alpha-*d* effects could be brought to within experimental error by using effects on the ionization step and the elimination step 1–2% larger.

The internal return values ranged from 0.34 to 0.44 times the total rate of product formation from the ion pairs, in accord with the qualitative analysis given above (internal return values for the lower homolog ranged from ≈1 to ≈2). The rates relative to the lower homolog, shown in Table IV, range from ≈4 to ≈13; this is reasonable in that the additional β-methyl group is expected to increase the ionization rate by a factor of ≈ 4–8 (solvolysis rate ratio, **5/1**) and the reduced internal return would add another factor of ≈ 2–3.

The fit is certainly reasonable, especially in view of the approximation that a single average isotope effect applies to the hydron elimination reaction, which the product yields show is not quite the case. Thus the interpretation that the secondary *t*-butyl carbinyl sulfonate esters react by rate determining ionization to form the secondary cation-ion pair followed by rapid Wagner-Meerwein rearrangement, and that the secondary adamantyl carbinyl sulfonate esters react with significant proportions of internal return is further reinforced. The utility of the steady state treatment, correlating isotope effects and product yields with single step isotope effects and branching ratios, in evaluating mechanistic postulates is again demonstrated.

EXPERIMENTAL

Melting points and boiling points are uncorrected. ^{1}H-NMR spectra were recorded on Varian T60, Varian HR220 and Varian EM 360 spectrometers. Chemical shifts, δ values, are recorded in parts per million (ppm) from tetramethylsilane (TMS). ^{2}H-NMR spectra were recorded on a Varian HR 220 spectrometer; chemical shifts are recorded in parts per million from TMS, with deuterochloroform, δ = 7.27, used as an external standard. Mass spectra were obtained with a Hewlett-Packard Model 5992A gc/ms System.

Spectrophotometric Determination of Solvolysis Rates, Solvent Preparation and Calculation of Rate Constants. The procedures used were the same as those described earlier.[11–14]

2,2-Dimethyl-3-pentanol-3-d

This compound was prepared by the reduction of 3 g of 2,2-dimethyl-3-pentanone with 0.92 g of lithium aluminum deuteride following the usual procedure. The prod-

uct was distilled and 1.91 g of the alcohol was collected at 132–135 °C (740 torr), yield 62%. ^{1}H-NMR (CCl_4) δ: 1.0 (t, 3H), 1.1 (s, 9H), 2.4 (m, 2H).

2,2-Dimethyl-3-pentanone-4,4-d_2

This compound was prepared by mixing 12 g of 2,2-dimethyl-3-pentanone, 40 mL of tetrahydrofuran, freshly distilled from $LiAlH_4$, and 40 mL D_2O with a catalytic amount of anhydrous K_2CO_3 and refluxing for three days. The tetrahydrofuran was removed by distillation and the residue was extracted with diethyl ether. After removal of the ether by distillation, mass spectral analysis indicated only 84% of exchange of the methylene hydrogens. The procedure was repeated and mass spectral analysis of the product indicated 98% exchange of the methylene hydrogens.

2,2-Dimethyl-3-pentanol-4,4-d_2

This compound was prepared from 5.2 g (0.046 mol) of the corresponding ketone by reduction with 0.512 g (0.012 mol) of $LiAlH_4$ using the usual procedure. The product was distilled and collected at 132–134°C (740 torr). Yield 3.7 g, 67%. ^{1}H-NMR (CCl_4) δ: 0.89 (s, 9H), 0.98 (s, 3H), 1.46 (d, 1H), 3.06 (s, 1H).

cis-*4,4-Dimethyl-2-pentene Oxide*

A sample of 9.4 g (0.57 mol) of *m*-chloroperbenzoic acid (MCPBA) in methylene chloride (caution, dissolve slowly to avoid an explosively high concentration of the peracid)[15] was added dropwise to a stirred, refluxing solution of 5.01 g (0.051 mol) of *cis*-4,4-dimethyl-2-pentene (Chemical Samples Co., Columbus Ohio) and 10.6 g (0.10 mol) of Na_2CO_3 in 200 mL of methylene chloride. After the addition was complete, reflux was continued for three more hours. The reaction mixture showed no positive starch iodide test indicating that all of the MCPBA had been consumed. The reaction mixture was washed with 200 mL of water twice and the organic layer dried with Na_2SO_4. The methylene chloride was removed by careful distillation through a 30 cm vigreaux column. The desired epoxide was collected at 110–120°C, 4.5 g, yield 77%. ^{1}H-NMR (CCl_4) δ: 1.0 (s, 9H), 1.4 (d, 3H), 2.45 (d, 1H), 2.80 (p, 1H).

*Threo-2,2-dimethyl-3-pentanol-4-*d

To mixture of 0.073 g (0.0017 mol) of $LiAlD_4$ in dry tetrahydrofuran cooled to 0 °C was added slowly, with stirring, 0.782 g (0.0069 mol) of *cis*-4,4-dimethyl-2-pentene oxide dissolved in 20 mL of anhydrous tetrahydrofuran. After addition, the mixture was allowed to warm and then refluxed for 24 hours. The mixture was quenched with a 10% solution of ammonium chloride and extracted with ether. The ether layer was dried and the ether removed by fractional distillation. The residue contained a mixture of the unreacted epoxide and the desired alcohol which was isolated by preparative glc. Analysis by ^{1}H- and ^{2}H-NMR showed that the alcohol product was 98% deuterated in the beta position and 5% deuterated in the alpha position (di-reduction). ^{1}H-NMR ($CDCl_3$) δ: 0.84 (s, 9H), 0.97 (d, 3H), 1.22 (m, 1H), 1.54 (m, 1H), 3.02 (s, 1H). ^{2}H-NMR ($CDCl_3$) δ: 1.59 (s, 1D), 3.2 (s, 0.05 D).

trans-*4,4-Dimethyl-2-pentene Oxide*

This compound was prepared by the same procedure used for the preparation of the *cis* isomer; 10 g (0.102 mol) of *trans*-4,4-dimethyl-2-pentene (Chemical samples Co., Columbus Ohio) was treated with 20.7 g (0.12 0 mol) of MCPBA in methylene

chloride, yielding 8.2 g (0.72 mol), 70%, of the desired epoxide. ^{1}H-NMR (CCl_4) δ: 0.85 (s, 9H), 1.2 (d, 3H), 2.30 (d, 1H), 2.70 (m, 1H).

*Erythro-2,2-dimethyl-3-pentanol-4-*d

This compound was prepared by the same procedure used in the preparation of the threo isomer. A sample of 0.756 g (0.0066 mol) of *trans*-4,4-dimethyl-2-pentene oxide was reduced with 0.0732 g (0.0017 mol) of $LiAlD_4$ yielding 0.42 g (0.0035 mol), 53%, of the desired alcohol. Analysis by ^{1}H- and ^{2}H-NMR showed the alcohol to be 99% isotopically pure. ^{1}H-NMR ($CDCl_3$) δ: 0.86 (s, 9H), 0.95 (d, 3H), 1.17 (m, 1H), 1.54 (m, 1H), 3.05 (d, 1H). ^{2}H-NMR ($CDCl_3$) δ: 1.50(s).

2,2-Dimethyl-3-pentanol-5,5,5-d_3

This compound was prepared from ethyl-2,2,2-d_3 iodide and isobutyraldehyde by a grignard reaction using the usual procedure; 10.34 g (0.065 mol) of ethyl-2,2,2-d_3 iodide and 6.4 g (0.076 mol) of isobutyraldehyde gave 4.3 g (0.0377 mol), 57%, of the desired product. ^{1}H-NMR (CCl_4) δ: 0.84 (s, 9H), 1.02 (m, 1H), 1.42 (d, 1H), 2.68 (s, 1H), 2.95 (q, 1H).

2,2-Dimethyl-3-pentyl p-*Bromobenzenesulfonates (Brosylates) and Variously Deuterated Analogs*

These sulfonate esters were prepared according to the Tipson procedure.[16] Typically, 2 g (0.017 mol) of alcohol were treated with 5 g (0.02 mol) of *p*-bromobenzene sulfonyl chloride were mixed with a minimum amount of dry pyridine and allowed to stand in a refrigerator for several days. After workup and recrystallization, yields were typically 4 g (0.012 mol), 70%, and mp's were in the range of 41–42 °C. Parent H ester, ^{1}H-NMR (CCl_4) δ: 0.84 (s, 12H), 1.55 (m, 1H), 4.28 (q, 1H), 7.63 (q, 4H). Alpha-*d* ester, ^{1}H-NMR (CCl_4) δ: 0.88 (s, 12H), 1.61 (m, 2H), 7.68 (q, 4H). Beta-d_2 ester, ^{1}H-NMR (CCl_4) δ: 0.90 (s, 12H), 4.31 (s, 1H), 7.67 (q, 4H). Erythro-β-*d* ester, ^{1}H-NMR (CCl_4) δ: 0.86 (s, 12H), 1.47 (m, 1H), 4.28 (d, 1H), 7.62 (q, 4H). Threo-β-*d* ester, ^{1}H-NMR (CCl_4) δ: 0.86 (s, 12H), 1.59 (m, 1H), 4.27 (s, 1H), 7.62 (q, 4H). Gamma-d_3 ester, ^{1}H-NMR ($CDCl_3$) δ: 0.84 (s, 9H), 1.59 (m, 2H), 4.28 (q, 1H), 7.68 (q, 4H).

Ethyllithium

This compound was prepared from 24 g (0.22 mol) ethyl bromide and 3.0 g (0.44 mol) lithium wire. The lithium was rolled flat with a stainless steel rolling pin. The thin lithium sheets were washed in an erlenmeyer flask containing anhydrous ethyl ether. The lithium was transferred to a 1 L, 3-neck flask containing 500 mL of anhydrous argon. After the addition of ether, the flask, containing an addition funnel, reflux condenser, and gas inlet tube, was flushed with argon. Freshly distilled ethyl bromide was added slowly to the reaction mixture which was kept at 0 °C with an ice bath. After addition, the reaction mixture was warmed to room temperature and stirred for 4 h. The reaction mixture was then filtered under argon. The concentration of the alkyl lithium solution was determined by titration. A 10 mL aliquot of solution was hydrolyzed by adding 10 mL of distilled water and titrated with standard acid. A second 10 mL aliquot was mixed with 1 mL of benzyl chloride. The mixture was then hydrolyzed with water and titrated with standard acid. The difference between the two titers gave the concentration of the alkyl lithium reagent which varied in several preparations from 0.5 to 0.6 molar.

1-(1-Adamantyl)propanone

This compound was prepared following the method of Heathcock.[17] A sample of 10 g (0.055 mol) of 1-adamantane carboxylic acid (Aldrich) was dissolved in 200 mL of anhydrous ether in a 1 L flask and the flask flushed with argon gas. Ethyl lithium (0.0122 mol) was added slowly and the reaction mixture stirred for 2 h. A solution of 2 N sulfuric acid was added until all of the lithium salt was dissolved. The ether layer was separated and the water layer extracted with additional ether. The ether layers were combined and washed successively with a 3 N solution of sodium hydroxide, water and saturated NaCl solution. The ether was removed by distillation and the ketone purified by vacuum distillation, b.p. 114 °C (0.5 torr); yield 5.8 g (0.03 mol), 55%. ^{1}H-NMR (CCl_4) δ: 1.0 (t, 3H), 1.8 (m, 12H), 2.0 (m, 3H), 2.4 (q, 2H).

1-(1-Adamantyl)propanone-2,2-d_2.

This compound was prepared by exchange of 1-(1-adamantyl)propanone in deuterium oxide. The ketone, 5 g (0.03 mol) was added to a mixture of 50 mL of dioxane, 10 mL D_2O (0.5 mol) and 1 g of Na_2CO_3 and refluxed for 24 h. The dioxane-D_2O azeotrope (80% dioxane, 20% D_2O, b.p. 88–89°C) was then removed by distillation. When the distillation of the azeotrope was complete and only dioxane (b.p. 101°C) and the ketone remained, 50 mL of dioxane and 10 mL D_2O (0.5 mol) was added and the exchange repeated for a second and again for a third time. The dioxane-ketone mixture was distilled to a small volume and allowed to cool. The addition of water to the mixture caused the ketone to precipitate. The solid was removed by filtration, dried and the ketone checked for deuterium content by NMR. Yield 4.1g (0.02 mol). ^{1}H-NMR (CCl_4) δ: 1.0 (s, 3H), 1.8 (m, 12H), 2.0(m, 3H).

1-(1-Adamantyl)propanol[18]

This compound was prepared from 6 g (0.032 mol) of 1-(1-adamantyl)propanone by reduction with 0.6 g (0.014 mol) $LiAlH_4$. Recrystallization of the alcohol from hexane yielded 5.2 g (0.026 mol), 80%. ^{1}H-NMR (CCl_4) δ: 1.0 (t, 3H), 1.7 (m, 14H), 2.0 (m, 3H), 2.9 (d, 1H).

*1-(1-Adamantyl)propanol-1-*d

This compound was prepared from 3.0 g (0.016 mol) of 1-(1-adamantyl)propanone by reduction with 0.3 g (0.007 mol) $LiAlHD_4$. Recrystallization of the alcohol from hexane yielded 2.7 g (0.013 mol), 80%. ^{1}H-NMR (CCl_4) δ: 1.0 (t, 3H), 1.7 (m, 14H), 2.0 (m, 3H).

1-(1-Adamantyl)propano1-2,2-d_2

This compound was prepared from 3.0 g (0.017 mol) 1-(1-adamantyl)propanone-2,2-d_2 by reduction with 0.3 g (0.0^{1}08 mol) $LiAlH_4$. Recrystallization from hexane gave 2.8 g (0.014 mol), 84%. ^{1}H-NMR (CCl_4) δ: 1.0 (s, 3H), 1.7 (m, 12H), 2.0 (m, 3H), 2.9 (s, 1H).

1-(1-Adamantyl)propano1-1,2,2-d_3

This compound was prepared from 2.0 g (0.01 mol) 1-(1-adamantyl)propanone-2,2-d_2 by reduction with 0.2 g (0.005 mol) $LiAlD_4$. Recrystallization from hexane gave 1.5 g (0.0075 mol), 75%. ^{1}H-NMR (CCl_4) δ: 1.0 (s, 3H), 1.7 (m, 12H), 2.0 (m, 3H).

1-(1-Adamantyl)propyl p-*Bromobenzenesulfonate, 1-(1-Adamantyl)propyl-1-*d p-*Bromobenzenesulfonate, 1-(1-Adamantyl)propyl-2,2-*d_2 p-*Bromobenzenesulfonate, and 1-(1-Adamantyl)propyl-1,2,2-*d_3 p-*Bromobenzenesulfonate*

These sulfonate esters were prepared according to the Tipson procedure.[16] A sample of typically 1 g (0.005 mol) of alcohol with 1.7 g (0.006 mol) of recrystallized benzenesulfonyl chloride were dissolved in 50 mL of pyridine and kept in the refrigerator for 24 hr. After the addition of 2 mL of water the solution was stirred in an ice bath. The solution was then poured into 100 mL of water and returned to the ice bath. The crystals were then filtered, dried and recrystallized from 30–60 °C petroleum ether. Yields were generally 55–65%. ^{1}H-NMR (CCl_4) of the parent ester δ: 1.0 (t, 3H), 1.7 (m, 14H), 2.0 (m, 3H), 4.0 (t, 1H), 7.6 (s, 4H). For the 1-*d* ester: 1.0 (t, 3H), 1.7 (m, 14H), 2.0 (m, 3H), 7.6 (s, 4H). For the 2,2-d_2 ester: 1.0 (s, 3H), 1.7 (m, 12H), 2.0 (m, 3H), 4.0 (s, 1H), 7.6 (s, 4H). For the 1,2,2-d_3 ester: 1.0 (s, 3H), 1.7 (m, 12H), 2.0 (m, 3H), 7.6 (s, 4H).

1-(1-Adamantyl)propyl p-*Toluenesulfonate, 1-(1-Adamantyl)propyl-1-*d p-*Toluenesulfonate, and 1-(1-Adamantyl)propyl-2,2-*d_2 p-*Toluenesulfonate*

These sulfonate esters were prepared according to the procedure describe above for the benzenesulfonates. The yields were 50–60%. ^{1}H-NMR (CCl_4) of the parent ester δ: 1.0 (t, 3H), 1.7 (m, 14H), 2.0 (m, 3H), 2.4 (s, 3H), 4.1 (t, 1H), 7.4 (q, 4H). For the 1-*d* ester δ: 1.0 (t, 3H), 1.7 (m, 14H), 2.0 (m, 3H), 2.4 (s, 3H), 7.4 (q, 4H). For the 2,2-d_2 ester δ: 1.0 (t, 3H), 1.7 (m, 12H), 2.0 (m, 3H), 2.4 (s, 3H), 4.1 (s, 1H), 7.4 (q, 4H).

*1-(1-Adamantyl)propyl Pentamethylbenzenesulfonate, 1-(1-Adamantyl)propyl-1-*d *Pentamethylbenzenesulfonate, and 1-(1-Adamantyl)propyl-2,2-*d_2 *Pentamethylbenzenesulfonate*

These sulfonate esters were prepared according to the procedure describe above for the benzenesulfonates. The yields were 35–50%. ^{1}H-NMR (CCl_4) of the parent ester δ: 1.0 (t, 3H), 1.7 (m, 14H), 2.0 (m, 3H), 2.3 (s, 9H), 2.6 (s, 6H), 4.2 (t, 1H). For the 1-*d* ester δ: 1.0 (t, 3H), 1.7 (m, 14H), 2.0 (m, 3H), 2.3 (s, 9H), 2.6 (s, 6H). For the 2,2-d_2 ester δ: 1.0 (t, 3H), 1.7 (m, 12H), 2.0 (m, 3H), 2.3 (s, 9H), 2.6 (s, 6H), 4.2 (s, 1H).

Pentamethylbenzenesulfonyl Chloride

This compound was prepared by the method of Gregoriou.[19]

Product Determinations

Products from solvolysis of the deuterated sulfonate esters were determined from the ^{2}H-NMR spectra taken on spent solvolysis reaction mixtures made up to be 0.1 molar in reactant and 0.12 molar in 2,6-lutidine with the Varian HR 220 spectrometer using the previously described procedure.[7]

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SAŽETAK

Mehanizam solvolize 2,2-dimetil-3-pentil- i 1-(1-adamantil)propil-sulfonata

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Izmjerene su konstante brzine solvolize, izračunani alfa- i beta-deuterijski izotopni efekti te iskorištenja produkata pri solvolizi nekih 1-(1-adamantil)propil-sulfonatnih estera, **4**, u otapalima etanol-voda, trifluoretanol-voda te heksafluorizopropanol-voda. Za usporedbu, slična su mjerenja provedena i pri solvolizi 2,2-dimetil-3-pentil-sulfonata, **5**. Kod estera **5**, alfa-d- i beta-d_2 izotopni efekti se malo mijenjaju s promjenom otapala i to u rasponu 1,164–1,165, odnosno 1,215–1,241, a nastaje vrlo malo nepregrađenih produkata. Zaključeno je da mehanizam uključuje stvaranje sekundarnoga kationskog ionskog para u stupnju koji određuje brzinu reakcije, nakon čega slijedi brzo pregrađivanje. Kod adamantil-analoga, **4**, alfa-d efekti mijenjaju se s promjenom otapala od 1,162 do 1,213, a beta-d_2-efekti od 1,339 do 1,649. Nepre-

građeni produkti te produkti pregrađeni po Wagner-Meerweinu (povećanje prstena) nastali su u znatnom iskorištenju. »Steady state«-postupak, koji je i ranije korišten za 1-(1-adamantil)etil-estere, primijenjen je i na rezultate adamantil-analoga, **4**. Mehanizam koji uključuje djelomično reverzibilnu ionizaciju do intimnog ionskog para, nakon čega slijedi kompetitivna eliminacija te odjeljivanje otapalom, rezultirajući produktima supstitucije, prilično dobro odgovara dobivenim rezultatima.