Observation of an Unusually Large Rate Acceleration Caused by a Homoallylic Double Bond in the Solvolyses of an Unstrained Secondary Adamantyl Tosylate

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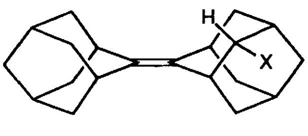
The solvolysis of 2-adamantylideneadamantyl tosylate **1c** in aqueous solvent mixtures shows a sensitivity to the ionizing power of the solvent (*m* value) of 0.66 ± 0.01, 0.65 ± 0.01 and 0.66 ± 0.02 for mixtures of methanol, ethanol and acetone respectively. **1c** reacts 4 × 10^5 faster than 2-adamantyl tosylate in 80:20 v/v ethanol–water, this rate acceleration is caused by a reduction in the enthalpy of activation ($\Delta H^\ddagger$ = 19.2 kcal mol^{-1} for **1c** *vs.* 26.9 kcal mol^{-1} for 2-adamantyl tosylate).

We have been interested in the mechanism of electrophilic addition to congested olefins, where the normal product-forming steps are retarded due to steric inhibition. Congested olefins such as adamantylideneadamantane (Ad=Ad) allow several aspects of the proposed mechanism to be probed. These include the structural characterization of reactive intermediates, such as bromonium,[1,2] iodonium,[2] and thiiranium ions,[3] reversibility of addition,[4] and reactivity of intermediates.[5] We were intrigued by the ease with which several electrophilic reagents (such as PhSCl,[6] NCS[7] and PhSeCl†) give a homoallylic chlorination product **1b** when treated with Ad=Ad **1a**.



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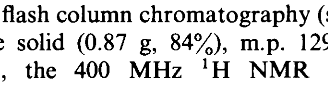
a X = H
b X = Cl
c X = OTs
d X = Br
e X = OH
f X = OMe
g X = OEt
h X = OAc
i X = OPr^i



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Clearly, there is a large stabilizing interaction to allow the electrophilic chlorination[7] of an apparently non-activated CH_2 group. One of the possible intermediates on the pathway to the chlorination product is the homoallylic carbenium ion **2**. We therefore decided to probe the degree of stabilization inferred by the double bond in the Ad=Ad skeleton using the solvolysis reaction of the homoallylic tosylate **1c**. We chose the tosylate **1c** because a large amount of work has previously focused on the use of 1- and 2-adamantyl systems (especially 2-adamantyl tosylate) for the establishment of extended Grunwald–Winstein relationships, such as Y_{OTs}.[9] Thus, by measuring the relative reactivity of **1c** and comparing it with the rates of solvolysis of 2-adamantyl tosylate we can gain an insight into the magnitude of the stabilizing interaction at the transition state, and how this quantity varies as the nature of the solvent is varied.

Experimental

Materials and Methods.—Ethanol and methanol were dried by distillation from their respective magnesium alkoxide salts. Acetic acid was purified by heating to reflux with acetic anhydride containing toluene-4-sulfonic acid, followed by subsequent fractional distillation. Propan-2-ol was dried by distillation from calcium hydride. De-ionized water was further purified by use of a 'Milli-Q ultra pure water' system. All NMR spectra were run on a Bruker AMX-400 spectrometer, using either $CDCl_3$ or CD_2Cl_2 as solvent and as the internal reference. All melting points are uncorrected.

(1R*,2R*)-2-*Bromo*-4-*tricyclo*[3.3.1.$1^{3,7}$]*decylidenetricyclo*-[3.3.1.$1^{3,7}$]*decane* **1d**. 2-Tricyclo[3.3.1.$1^{3,7}$]decylidenetricyclo-[3.3.1.$1^{3,7}$]decane **1a**[10] (0.8 g, 3.0 mmol) and *N*-bromosuccinimide (0.65 g, 3.6 mmol) in 1,2-dichloroethane (50 cm^3) were heated to reflux overnight. After cooling, the reaction mixture was washed with water, dried ($MgSO_4$), filtered and the volatiles were removed under reduced pressure. The residue was purified by flash column chromatography (silica, hexanes) to give a white solid (0.87 g, 84%), m.p. 129–130 °C (lit.,[7] 130.5–131.5 °C), the 400 MHz ^1H NMR spectrum was identical to that reported in the literature.[7]

(1R*,2R*)-2-*Tosyl*-4-*tricyclo*[3.3.1.$1^{3,7}$]*decylidenetricyclo*-[3.3.1.$1^{3,7}$]*decane* **1c**. Compound **1d** (0.4 g, 1.2 mmol) and silver tosylate (0.44 g, 1.6 mmol)[11] were stirred in dry toluene (10 cm^3) in the dark at 5 °C for 4 days. The solid silver salts were removed by filtration and washed with toluene (10 cm^3). The combined filtrates were evaporated to dryness under reduced pressure (1 mmHg) at room temperature. The residue was sonicated with dry hexane (3 × 10 cm^3) to remove unchanged **1d**. The solid was dissolved in dichloromethane and any insoluble material was removed by filtration. Removal of the volatiles gave an analytically pure white solid (0.46 g, 90%), m.p. 147–148 °C (decomp.) (Found C, 73.7; H, 8.0. Calc. for $C_{27}H_{34}O_3S$: C, 73.9; H, 7.8%); δ_H(400 MHz; CD_2Cl_2) 1.36–1.48 (2 H, m), 1.49–1.65 (6 H, m), 1.70–1.92 (11 H, m), 2.02–2.14 (3 H, m), 2.30 (1 H, br s), 2.44 (3 H, s, Ar-CH_3), 2.64 (1 H, br s), 2.80 (2 H, br s), 4.35 (1 H, br t, CH-O), 7.36 (2 H, m) and 7.59 (2 H, m); δ_C(100 MHz; CD_2Cl_2, −5 °C) 21.6, 27.2, 28.5, 28.7, 30.4, 30.8, 32.2, 32.6, 32.7, 33.1, 36.0, 37.0, 37.1, 38.6, 39.4 (2 C), 39.5, 39.9, 86.2, 127.8, 129.1, 130.0, 134.3, 137.8 and 144.9.

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† We find that in contrast to the report in the literature;[8a] the reaction of phenylselenenyl chloride with adamantylideneadamantane gives an almost quantitative yield of **1b**. In a footnote, L. Lopez *et al.*,[8b] communicated a similar result.

Table 1 Observed first-order rate constants ($k_1 \times 10^3$ s^{-1}) for the solvolysis of **1c** in aqueous solvent mixtures at 25 °C[a,b]

Solvent composition (% co-solvent)	Methanol	Ethanol	Propan-2-ol	Acetone
100	6.10 ± 0.03	0.75 ± 0.06	0.075 ± 0.001	
90	19.7 ± 0.2	3.77 ± 0.06	1.12 ± 0.02	0.28 ± 0.01
80	50.8 ± 0.2	9.68 ± 0.08	2.98 ± 0.05	1.7 ± 0.1
70		19.3 ± 0.1	5.5 ± 0.1	4.9 ± 0.1
60		36.6 ± 0.6	9.2 ± 0.2	15.3 ± 0.7
50		69.2 ± 0.4	16.3 ± 0.2	45 ± 2
40			35.5 ± 0.4	

[a] The quoted values are the mean and the s.d. from at least three independent kinetic runs. [b] The measured value for acetic acid was 1.14 ± 0.03 × 10^{-3} s^{-1}.

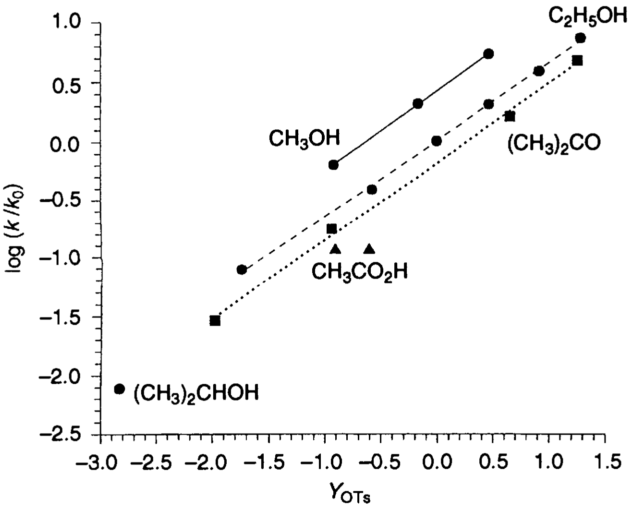

Fig. 1 Correlation of logarithms of solvolysis rates for **1c** with Y_{OTs}, taken from ref. 12. The rate constant k_0 refers to 80% ethanol–water. Two values are used for the Y_{OTs} of acetic acid [ref. 12(b)]. Displayed lines are the calculated fits to the Grunwald–Winstein equation for each aqueous solvent mixture for which Y_{OTs} values are established.

Solvolysis Kinetics.—Solvolysis kinetics for the alcoholic solvents were followed using a Cary-3E UV–VIS spectrophotometer equipped with the Cary six cell peltier constant temperature accessory. Reactions were initiated by injection of a stock solution of **1c** in dichloromethane (2 mm^3; 91 mmol dm^{-3}) into an equilibrated solvent mixture (3 cm^3; 30 min), the change in absorbance at 235 nm was followed as a function of time. Because of the background absorbance of acetic acid, kinetics were followed at 273 nm using a higher final substrate concentration (30 mm^3 of stock solution injected). Solvolysis data in acetone–water mixtures were acquired using an indicator technique, where all manipulations were performed with syringe techniques under an inert atmosphere to negate the effects of atmospheric CO_2. The kinetic solution (3 cm^3) containing bromothymol blue (2.6 × 10^{-5} mol dm^{-3}) was allowed to equilibrate at 25 °C for 20 min, then a 9.1 mmol dm^{-3} solution of **1c** (3 mm^3) in dichloromethane was added. The decrease in absorbance of the basic form of the indicator (622 nm) was followed. In all cases it was checked that the decrease in absorbance was kept between 20 and 30% of the maximum. First-order rate constants for these solvolyses were determined by non-linear least squares fitting to a standard first-order equation. All fitted data exhibited clean first-order kinetics for at least the four half-lives for which the absorbance data was monitored.

Solvolysis Products.—Compound **1c** (*ca.* 20 mg) was added to the solvent (10 cm^3) and the reaction was allowed to proceed for at least ten half-lives. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography; the yield of product was always > 85%. All products of the solvolysis reactions had ^{1}H NMR spectra that were consistent with the proposed structures.

Partition Ratios.—Compound **1c** (*ca.* 8 mg) was added to aqueous ethanol (30 cm^3) and the reaction was allowed to proceed for at least 10 half-lives. The products were extracted from the aqueous solvent using dichloromethane (2 × 10 cm^3). The organic extracts were dried, and concentrated under reduced pressure to give a white solid residue. This residue was dissolved in $CDCl_3$ (0.6 cm^3) and the ratio of ether:alcohol product was calculated from the integral of the respective peaks in the ^{1}H NMR spectrum. Because, during storage **1c** slowly reacts with atmospheric moisture to afford the alcohol **1e**, all ratios (**1g**:**1e**) were calibrated using the measured integrals from a 100% ethanol solution. Repeat measurements for two solvent mixtures allow an estimate of the accuracy of these measurements of ±0.04.

Results

The observed rate constants for the solvolysis of **1c** in aqueous solvent mixtures are shown in Table 1. The data from Table 1 is shown graphically in Fig. 1, in the standard format, where $\log(k/k_0)$ is plotted against Y_{OTs}.[12]

Using the standard Grunwald–Winstein equation all aqueous solvent mixtures display the same sensitivity to solvent ionizing power (*m* value) within experimental error. The *m* values are 0.66 ± 0.01; 0.65 ± 0.01;* 0.66 ± 0.02† for mixtures of methanol, ethanol and acetone respectively. The effect of temperature on the rate constant for the reaction of **1c** in 80% v/v ethanol–water is shown in Table 2. The activation parameters for the solvolysis reaction were calculated using the Eyring equation, $\ln(k_{obs}/T) = \ln(k_B/h) - \Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R$, the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are listed in footnote *b* to Table 2. The partition ratios k_E/k_W for the capture of the intermediates involved in the solvolysis of **1c**, 2-adamantyl tosylate and 2-adamantyl perchlorate as a function of the solvent composition are listed in Table 3. The ratio was calculated according to eqn. (1).[13]

$$\frac{k_E}{k_W} = \frac{[\mathrm{ROEt}][\mathrm{HOH}]}{[\mathrm{ROH}][\mathrm{EtOH}]} \qquad (1)$$

The magnitude of the calculated rate accelerations for the solvolysis of **1c** when compared to 2-adamantyl tosylate

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* Using the Y_{OTs} values from reference 18(*c*) an *m* value of 0.636 ± 0.005 is obtained, and a Y_{OTs} value for 100% ethanol of 1.778 can be extrapolated from the data in this paper.

† A Y_{OTs} value of −0.16 can be interpolated from our data for 70% v/v acetone–water.

Table 2 Observed first-order rate constants ($k_1 \times 10^3$ s^{-1}) for the solvolysis of **1c** in 80:20 v/v, ethanol–water^{a,b} at various temperatures

T/°C	k_{obs}
45.0	70 ± 1
35.0	27.4 ± 0.4
25.0	9.68 ± 0.08
15.0	2.77 ± 0.02

[a] The quoted values are the mean and the s.d. from at least three independent kinetic runs. [b] A linear least-squares fit of the solvolysis data to the Eyring equation furnished the following values for the activation parameters; $\Delta H^‡ = 19.2 \pm 0.5$ kcal mol^{-1} and $\Delta S^‡ = -3.4 \pm 1.8$ cal K^{-1} mol^{-1}.

Table 3 Comparison of partition ratios (k_E/k_W) observed in the solvolysis of **1c** in aqueous ethanol, with those for 2-adamantyl tosylate and 2-adamantyl perchlorate

Solvent (% ethanol)	**1c**^{a,b}	2-Adamantyl tosylate^c	2-Adamantyl perchlorate^d
90	0.43	0.49	0.64
80	0.37^e	0.49	0.52
70	0.45	0.53	0.52
60	0.56^f	0.57^g	0.55
50	0.61		0.62

[a] Single determination at 25 °C, except where noted. [b] k_E/k_W is a dimensionless ratio of second-order rate constants [see eqn. (1)]. [c] Ref. 34, at 100 °C. [d] Ref. 36, at 25 °C. [e] A repeat measurement gave a value of 0.45. [f] A repeat measurement gave a value of 0.60. [g] T = 75 °C.

Table 4 Calculated rate accelerations for the solvolysis of **1c** compared with 2-adamantyl tosylate at 25 °C^a

Solvent	Rate acceleration
Methanol	2.1×10^6
Ethanol	1.7×10^6
80% Ethanol	$^b4.0 \times 10^5$
Propan-2-ol	$^c3.7 \times 10^6$
90% Acetone	$^c1.1 \times 10^6$
Acetic acid	2.0×10^5

[a] Rate constants for 2-adamantyl tosylate taken from ref. 19. [b] Using the value for the solvolysis rate constant in ref. 18*c* a value of 4.5×10^6 is obtained. [c] Rate constant for 2-adamantyl tosylate estimated from the published Y_{OTs} value for 1-adamantyl tosylate [ref. 12(*b*)] and the rate constant for 2-adamantyl tosylate in 80:20 v/v ethanol–water (ref. 19).

Table 5 Observed chemical shifts for the two upfield CH$_2$ resonances in the ^{13}C NMR spectra of adamantylideneadamantane derivatives^{a,b}

Compound	X	δ^c
1c	OTs	30.8, $32.7^{d,e}$
1e	OH	30.7, 32.6
1f	OMe	31.5, 33.4^d
1g	OEt	31.2, 33.1
1h	OAc^f	
1i	OPr^i	31.3, 33.1

[a] Carbon NMR spectra were run at 100.6 MHz. [b] No other CH$_2$ resonance occurred at less than 37.0 ppm. [c] Spectra run in CDCl$_3$ unless stated. [d] Run in CD$_2$Cl$_2$. [e] Spectrum acquired at −5 °C. [f] Hydrolysis promoted by hydroxide furnished an alcohol which had an identical NMR spectra to that of **1e**.

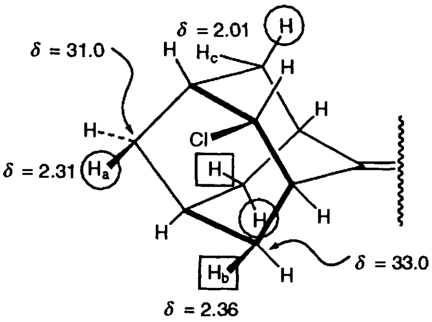

Fig. 2 Assigned chemical shifts for the chloro-substituted adamantyl ring in compound **1b**, shifts are quoted downfield from (CH$_3$)$_4$Si

are presented in Table 4. The products from the reactions in various solvents were determined by both ^{1}H and ^{13}C NMR spectroscopy. For all solvents used in this study the only stereoisomer observed (within experimental error) was the pseudo-equatorial isomer, thus all reactions proceeded with >95% retention of configuration. The assignment of the configuration of all the 2-substituted adamantylideneadamantanes is based on chemical shifts in the ^{13}C NMR spectrum. Using a DEPT pulse sequence[14] we observe only two methylene carbon resonances that occur with chemical shifts of less than 35 ppm. That two CH$_2$ carbons are shielded relative to the seven remaining CH$_2$ groups is explained by the γ-gauche effect.*[15] For the 2-chloro compound the two resonances occur at 31.0 and 33.0 ppm. The assignment was also confirmed by 2-D correlation spectra, the ^{1}H–^{1}H double quantum filtered COSY spectrum allowed the unambiguous assignment (among others) based on chemical shifts and coupling patterns for the protons shown in Fig. 2. The ^{13}C–^{1}H heteroCOSY showed that the two upfield CH$_2$ resonances were correlated with the protons shown in Fig. 2. The appearance of the protons H$_a$ (double quintet), H$_b$ (double quartet) and H$_c$ (doublet triplet) in the ^{1}H NMR spectrum is readily explained by the assignments shown in Fig. 2. Each proton is split by a large geminal coupling and by two smaller couplings to the adjacent methine protons, H$_a$ also has two long range 'W' couplings (protons circled in Fig. 2), while H$_b$ has one long range coupling (shown by a box), and H$_c$ has no long range couplings. The shielded CH$_2$ resonances in the carbon NMR spectra of the products are listed in Table 5.

Discussion

When comparing the rate accelerations for the intramolecular participation of the double bond for **1c** it is necessary to try and compare results under as similar conditions as possible. Thus, we have limited our investigation to solvent mixtures for which there is a large amount of data in the literature for the solvolyses of either 1- or 2-adamantyl tosylate. The effect of solvent on solvolytic reactions as analysed in the extended Grunwald–Winstein analysis,[9] is a function of two parameters, *i.e.* nucleophilicity (N) and 'ionizing power' (Y). In this respect observation of small m values (< 1) are indicative of reaction in which the sensitivity to the ionizing ability of the solvent has been reduced, this is normally interpreted in terms of a nucleophilic involvement at the transition state,[17] or with either σ- or π-type participation occurring during the ionization of the starting material.[18] We assume for these crowded adamantyl-based systems that solvent nucleophilic assistance to ionization is negligible (*i.e.* $l \approx 0$).

As can be seen from the data in Table 4, there is clear evidence for a large rate enhancement, and the product studies show that the solvolysis reactions proceed with >95% retention of configuration. These observations, taken with the measured values for m of around 0.66, indicate that π-participation by the proximal double bond into the nascent p-orbital at the

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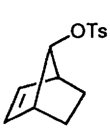
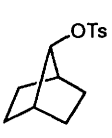
* For the 2-methyl substituted isomers, we have shown that for the 2-axial methyl compound there is only one upfield CH$_2$ (33.7 ppm), while the 2-equatorial isomer has two upfield CH$_2$ (31.2 and 33.0 ppm). These assignments have also been confirmed by 2-D NOESY experiments.[16]

developing carbenium ion is occurring. We can be confident of the magnitude of this effect (especially in ethanol–water mixtures) as we have been able to measure the rate constants for **1c** directly, and although the rate constants for the comparison compound(s) generally require an extrapolation of rate constants from higher temperatures, these measurements have been independently performed by different workers.[18c,19] The variation in solvolytic rate constant for **1c** and 2-adamantyl tosylate corresponds to a difference in free energy of activation ($\delta\Delta G^{\ddagger}$) of approximately 7.6 kcal mol^{-1} in 80% v/v ethanol–water at 25 °C. From the data for 2-adamantyl tosylate where $\Delta H^{\ddagger} = 26.9$ kcal mol^{-1} and $\Delta S^{\ddagger} = -3$ cal K^{-1} mol^{-1},[*,19] and our data for **1c** where $\Delta H^{\ddagger} = 19.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -3.4$ cal K^{-1} mol^{-1}, it can be seen that the rate acceleration (within experimental error) is due to a reduction in the enthalpy of activation caused by π-participation from the homoallylic double bond.

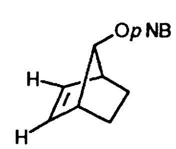
If we compare this effect with those for other homoallylic solvolyses reported in the literature, we find that the largest reported rate acceleration for a homoallylic double bond is approximately 10^{11} for the acetolysis of the 7-*anti*-norborenyl tosylate **3a** compared to its saturated analogue **3b**.[21]



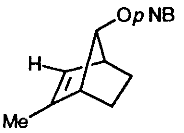
3a



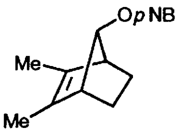
3b



4a



4b

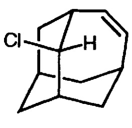


4c

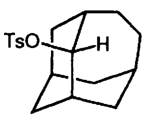
Here, both ends of the homoallylic double bond are symmetrically disposed to the reaction centre. Thus, the rate acceleration caused by participation should be equally dependent on the electronic nature of both carbon atoms of the alkene. This has been shown for unsubstituted **4a**, 2-methyl **4b** and 2,3-dimethyl-7-*anti*-norborenyl 4′-nitrobenzoates **4c**, where the relative rates of solvolysis in 70% v/v dioxane–water at 140 °C were 1 : 13.3 : 148 respectively.[22]

The observed rate accelerations with a non-symmetrically aligned alkene are in general much smaller in magnitude. Harris *et al.* followed the solvolyses of **5a** and **5b** and extrapolated a rate acceleration for the assisted solvolysis of 3×10^5 at 70 °C in a solvent of 70% aqueous acetone for the tosylate leaving group.[23] However, based on the value of the Grunwald–Winstein parameter *m* of 0.86, for the solvolysis of **5b**, it was argued that this solvolysis reaction was assisted by either neighbouring carbon or solvent participation at the transition state.[23] Consequently, Harris *et al.* choose **5c** as their model compound, and they extrapolated a rate ratio of 3×10^7 for the *exo*-tosylate **5d** when compared to the *endo*-tosylate **5c**.

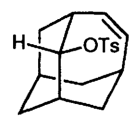
In their paper Harris *et al.* used a factor of 5×10^5 to correct for the different leaving groups (Cl$^-$ *vs.* TsO$^-$) in their study. This ratio was taken from studies on the solvolysis of 1-adamantyl tosylate and 1-adamantyl chloride in 80:20 v/v ethanol–water.[12b,24] However, Bentley and Roberts showed that this ratio ($k_{\text{1-AdOTs}}/k_{\text{1-AdCl}}$) decreases as the percentage of water in the aqueous–organic solvent mixture increases, *i.e.* as the transition state is stabilized more effectively by the solvent, the dependence of the solvolytic rate constant on nucleofugacity decreases.[25] Consequently, where the possibility for a stabilizing interaction exists (*i.e.* homoallylic participation) a smaller β_{lg} is anticipated.† Therefore, the rate accelerations calculated by Harris *et al.* probably overestimate the magnitude of the interaction between the homoallylic double bond and the electron-deficient reaction centre at the transition state, in the *exo*-homoadamant-4-en-2-ol system.



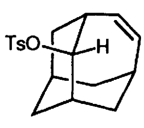
5a



5b

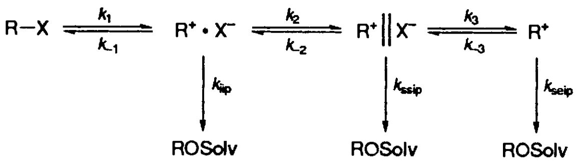


5c



5d

For a more detailed analysis of the effect of the homoallylic double bond in **1c** we must consider the nature of the transition states for the solvolysis reactions of both **1c** and 2-adamantyl tosylate. In general there are three ion-pairs that are considered to be important in nucleophilic substitution reactions categorized as S_N1[26] ($D_N + A_N$).[27] These intermediates are shown in Scheme 1, along with their respective rate constants for the reaction with solvent. Where k_{iip}, k_{ssip} and k_{seip} represents the rate constants for the reaction of solvent with the intimate ion-pair, the solvent separated ion-pair and the solvent equilibrated ion-pair respectively.



Scheme 1

The solvolysis of 2-adamantyl (and 1-adamantyl) derivatives are now almost universally accepted as the standard reactions for the analysis of solvolytic rates as the nature of the solvent is changed, using either an extended or a standard Grunwald–Winstein analysis.[9,‡] However, there are still features of the solvolysis of 2-adamantyl derivatives which remain controversial. These include the degree of σ-participation, the mechanism of internal return, and the nature of the product-forming steps (*via* k_{ssip} or k_{seip}). Two key experiments allow a clearer understanding of the nature of the transition state for the solvolysis of 2-adamantyl tosylate.

Firstly, in 80:20 v/v ethanol–water, and acetic acid, a large amount of scrambling occurs between the ester and sulfonyl oxygen atoms during the solvolysis of 2-adamantyl tosylate.[29] The clear implication is that 2-adamantyl tosylate undergoes significant internal return (*i.e.* $k_{-1} > 0$, Scheme 1), and that the rate limiting step for the solvolysis reaction occurs after the initial ionization (k_1) which leads to the formation of an intimate ion-pair. The assumption made in this analysis is that any oxygen scrambling occurs at the stage of the intimate ion-pair. However, recently the possibility that a concerted process is responsible for the observed exchange has been proposed.[30]

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[*] Grob *et al.*[20] measured the activation parameters for 2-adamantyl tosylate as $\Delta H^{\ddagger} = 27.1$ kcal mol^{-1} and $\Delta S^{\ddagger} = -2.4$ cal K^{-1} mol^{-1}.

[†] We are currently investigating the rates of solvolysis of **1b** and **1d**.

[‡] The 3,3-dimethylbutan-2-ol system has also been suggested as a basis for the definition of a solvent polarity/nucleophilicity scale by the group of Shiner.[28]

Table 6 Proposed Y_{OTs} values for aqueous mixture of propan-2-ol, based on the solvolysis of **1c** at 25 °C[a]

Solvent composition (% co-solvent)	Y_{OTs}
100	-2.829[b]
90	-1.05
80	-0.41
70	0.00
60	0.34
50	0.71
40	1.22

[a] Using an m value of 0.66, a Y_{OTs} value of 2.829 for 100% propan-2-ol, and the equation $\log(k/k_o) = m \times (Y_{\mathrm{OTs}} - 2.829)$; where k_o is the rate constant for solvolysis in 100% propan-2-ol. [b] Ref. 12(*b*).

Secondly, dominant retention of configuration is observed in the solvolysis reactions of 5-methyl-[31] and 5-deuterio-[32] substituted 2-adamantyl derivatives, while complete retention is observed for *cis*-5-fluoro- and *trans*-5-trimethylstannyl-2-adamantyl tosylate.[33] This strongly suggests that either σ-participation is stabilizing the secondary carbenium ion, and/or that the leaving group is assisting in the delivery of the nucleophile, presumably by acting as a general base (at the stage of the solvent separated ion-pair, *i.e.* product formation occurs through the k_{ssip} channel in Scheme 1). Karton and Pross measured the product ratios for the aqueous ethanolysis of 1- and 2-adamantyl derivatives,[34] from this data they calculated the relative selectivities for the reactive intermediate with ethanol and water (k_E/k_W). From this data and a previous proposal by Harris *et al.*[35] it was argued that the product-forming reactions of 2-adamantyl tosylate occur at the stage of the solvent separated ion-pairs. Ta-Shma and Rappoport in a recent review also supported this argument, that k_E/k_W values of < 1 are diagnostic for systems in which product formation occurs from the solvent separated ion-pairs.[13] Shown in Table 3 are the selectivities (k_E/k_W) for **1c**, 2-adamantyl tosylate[34] and 2-adamantyl perchlorate.[36] Clearly, our data is very similar to the data of both Karton and Pross, and Kevill *et al.* given the differences in both the temperature and the leaving groups involved. That the observed ratios are so similar has implications for the solvolysis of 2-adamantyl derivatives, either the products from the solvolysis of **1c** arise from a solvent separated ion-pair or the observed ratio corresponds to the inherent reactivity patterns of the adamantyl ring system towards either water or ethanol, and not the reactivity of the various solvent separated ion-pairs.

The presumed carbenium ion derived from **1c** should be more stable than that generated from 2-adamantyl tosylate, given the difference in free energy of activation for solvolysis of approximately 7.6 kcal mol^{-1}. If retention of configuration (for 2-adamantyl systems) is caused by trapping at the stage of the solvent separated ion-pair, then when $< 100\%$ retention is found, capture by solvent on the opposite face, or diffusional separation of the solvent separated ion-pair is competitive with this process. However, as the intermediate formed during the solvolysis of **1c** should have a longer lifetime, we expect that diffusional separation of the solvent-separated ion-pair would now be faster than capture by solvent, therefore, the reaction should proceed through fully solvated ions. Unfortunately, we were unable to test for the occurrence of solvent equilibrated ions during the solvolysis of **1c** using the phenomenon of common ion rate depression because of the large UV absorbance of the tosylate anion in the region where the absorbance changes during the course of reaction.

As the rate of solvolysis of **1c** is much faster than either 1- or 2-adamantyl tosylate, we can readily calculate Y_{OTs} values for less reactive solvent systems. Thus, using our data for the solvolysis of **1c**, an assumed m value of 0.66, and the Y_{OTs} value for propan-2-ol,[12b] we propose the values shown in Table 6 for the 'solvent ionizing parameter' Y_{OTs} in aqueous propan-2-ol mixtures.

Conclusions.—There is a large rate acceleration of around six orders of magnitude for the solvolysis of adamantylideneadamantyl tosylate compared with 2-adamantyl tosylate. The rate acceleration is caused by a reduction in the enthalpy of activation, as π-participation of the proximal double bond occurs into the nascent p-orbital at the developing carbenium ion centre. These solvolytic reactions probably proceed through solvent equilibrated ions.

Acknowledgements

We gratefully acknowledge the financial support of Simon Fraser University and the Natural Sciences and Engineering Research Council of Canada. In addition we acknowledge the Natural Sciences and Engineering Research Council of Canada for providing funds to purchase the spectrophotometer used in this work.

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Paper 3/07647D
Received 31*st December* 1993
Accepted 15*th February* 1994