The mechanism of solvolysis of 2-adamantyl azoxytosylate: isotopic labelling, medium effect, and attempted deoxygenation studies

John K. Conner, Johanna Haider, M.N. Stuart Hill, Howard Maskill, and Monique Pestman

Abstract: Rates of solvolysis of 2-adamantyl azoxytosylate (**1**) have been measured over a range of temperatures in ethanoic acid, methanoic acid, 50:50 (v/v) trifluoroethanol:water, 80:20 (v/v) trifluoroethanol:water, 97:3 (w/w) trifluoroethanol:water, and 70:30 (v/v) ethanol:water. For comparison, rates of solvolysis of 2-adamantyl tosylate (**2**) have also been measured in 50:50, 80:20, and 90:10 (v/v) trifluoroethanol:water, and for both compounds, activation parameters have been determined. These and results published earlier allow a correlation of the two reactions and indicate that the *m* value for 2-adamantyl azoxytosylate solvolysis is only 0.46. This is one of the lowest *m* values for a reaction that is unambiguously an S_N1 solvolysis. We have also recorded the ^{17}O NMR spectrum of the 2-adamantyl tosylate formed from ^{17}O-labelled 2-adamantyl azoxytosylate in deuteriochloroform, and the millimeter-wave spectrum of the nitrous oxide evolved in the hydrolysis of ^{18}O-labelled 2-adamantyl azoxytosylate. These labelling studies have provided more detailed knowledge of the S_N1 fragmentation mechanism of **1** and exclude a mechanism of reaction via rearrangement to *N*-nitroso,*N*-(2-adamantyl),*O*-(*p*-toluenesulfonyl)hydroxylamine (**5**). Attempted deoxygenation of **1** to give 2-adamantyl diazotosylate (**8**) and a subsequent fragmentation proved unsuccessful.

Key words: nitrous oxide, carbenium ion, isotopic labelling, solvolysis, *m* value.

Résumé : On a mesuré les vitesses de solvolyse de azoxytosylate d'adamant-2-yle (**1**) à diverses températures, dans l'acide éthanoïque, l'acide méthanoïque, le trifluoroéthanol:eau (50:50, v/v), le trifluoroéthanol:eau (80:20, v/v), le trifluoroéthanol:eau (97:3, p/p) et l'éthanol:eau (70:30, v/v). Pour fins de comparaison, on a aussi mesuré les vitesses de solvolyse du tosylate d'adamant-2-yle (**2**) dans des mélanges (50:50, 80:20 et 90:10, v/v) de trifluoroéthanol:eau et, dans les cas des deux composés, on a déterminé les paramètres d'activation. Ces résultats couplés à d'autres publiés antérieurement permettent d'établir une corrélation entre les deux réactions et ils indiquent que la valeur *m* pour la solvolyse de l'azoxytosylate d'adamant-2-yle n'est que 0,46. Ceci correspond à l'une des valeurs de *m* les plus faibles pour une réaction qui est sans ambiguïté S_N1. On a aussi déterminé le spectre RMN du ^{17}O du tosylate d'adamant-2-yle formé à partir de l'azoxytosylate d'adamant-2-yle marqué au ^{18}O lors d'une réaction dans le chloroforme deutéré ainsi que le spectre d'onde à un millimètre de l'oxyde nitreux qui se dégage lors de l'hydrolyse de l'azoxytosylate d'adamant-2-yle marqué au ^{17}O. Ces études de marquage ont fourni des connaissances plus détaillées du mécanisme de fragmentation S_N1 du composé **1** et elles ont permis d'exclure un mécanisme réactionnel impliquant un réarrangement en *N*-nitroso-*N*-(adamant-2-yl)-*O*-(*p*-toluènesulfonyl)hydroxylamine (**5**). Il a été impossible de provoquer une désoxygénation du composé **1** pour donner du diazotosylate d'adamant-2-yle (**8**) et provoquer une fragmentation subséquente.

Mots clés : oxyde nitreux, ion carbénium, marquage isotopique, solvolyse, valeur *m*.

[Traduit par la rédaction]

Introduction

Mechanisms of reactions involving intermediate carbenium ions are amongst the earliest to have been investigated, and early proposals that some of the most deep seated of molecular rearrangements (e.g., amongst terpenoids) occur via such intermediates were some of the boldest (1). These proposals were accepted only after fierce debate and overwhelming evidence, and much of current organic chemistry reaction mechanisms vernacular originates from that Olympian period earlier this century. However, even though the principal features of substitution and elimination reactions that involve carbenium ions are well known, some details of the natures of these intermediates have been inferred from only indirect evidence or still remain obscure.

According to a frequently encountered model for S_N1 reactions (2*a*), the carbenium ion is generated in an initial rate-limiting step, then is captured by a nucleophile (which could be a

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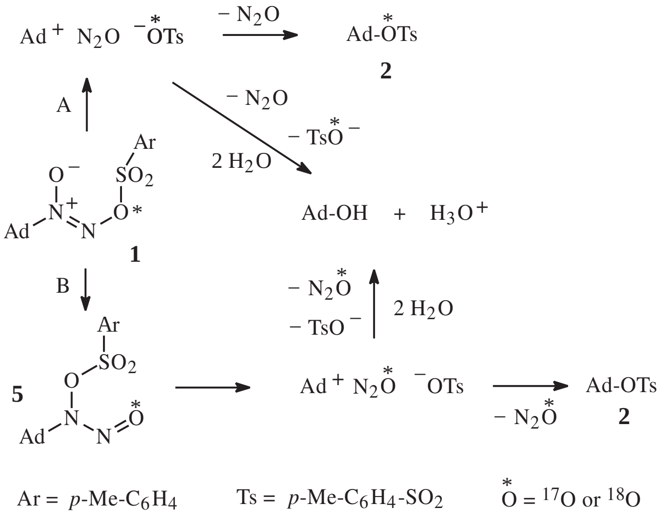
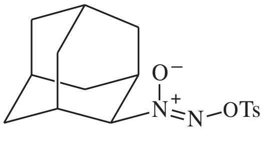
Scheme 1.



solvent molecule) in a subsequent product-forming step. In this simple model, the transition structure in the first step involves vestigial bonding between the developing trigonal electrophilic carbon and the nucleofuge. According to the more complete Winstein–Shiner ion-pair model (2*b*, 3), the rate-limiting step in the solvolysis of 2-adamantyl tosylate, for example, is not the initial ionization but the separation of the first-formed contact (or intimate) ion pair to give the solvent-separated ion pair. Clearly, this model requires that the contact ion pair undergoes internal return in competition with, but faster than, progression to the solvent-separated ion pair. In this model, the transition structure in the rate-limiting step of the solvolytic process involves a fully developed positive charge in the electrophilic fragment, and the solvent-separated ion pair is the main product-forming intermediate from 2-adamantyl tosylate.

Comparison of the effect of solvents upon the rate of solvolysis of a compound with the effect upon the rate of solvolysis of a standard compound may be quantified using the Winstein–Grunwald equation (4) (or an extended (5) or modified (6) version). An *m* value, the gradient of the log(k_{compound}) versus log(k_{standard}) correlation, close to unity means that the solvent effect for the solvolysis of the compound in question is the same as for the standard compound, and this is usually interpreted as evidence for very closely similar S_N1 solvolytic mechanisms. The original standard compound was *tert*-butyl chloride but 2-adamantyl tosylate is now regarded as more appropriate for substrates with arenesulfonate nucleofuges (7, 8). An *m* value appreciably lower than unity is usually interpreted as indicating that the reaction involves a low degree of charge separation in the transition structure (assuming there are other reasons for believing that the reaction is still an S_N1), or that the mechanism is not an S_N1 at all.

Recently, there has been an expansion in our knowledge of carbenium ion chemistry partly through developments in fast reaction methods pioneered by McClelland et al. (9), partly through new experimental techniques developed, for example, by Olah et al. (10) and Mayr and Patz (11) for preparing carbenium ions under nonnucleophilic conditions, partly through improved theoretical procedures for studying isolated carbenium ions themselves, for example, by Schleyer and co-workers (12), and partly due to better conceptual models for solvolytic and related reactions offered by Jencks and Richard (13). It is within this last context that the present project had its origins. Some years ago (14), we introduced the solvolysis of alkyl azoxyarenesulfonates as a heterolytic reaction, which is unambiguously unimolecular and allows the study of the S_N1 mechanism uncomplicated by competitive bimolecular substitution. The carbenium ions so formed are the same as when produced by other means, but their initial environment is different. We proposed a mechanism that is a link between the solvolysis of alkyl arenesulfonates on the one hand and nitrous acid induced deamination of primary alkylamines (and related reactions) on the other (14, 15). We also presented evidence that the initial fragmentation to give an ion pair and nitrous oxide is rate-determining (i.e., there is no internal



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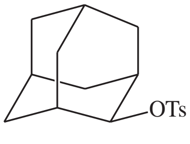

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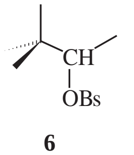

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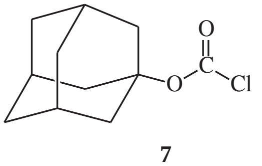

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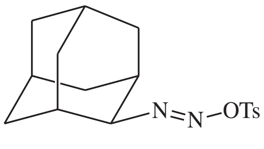

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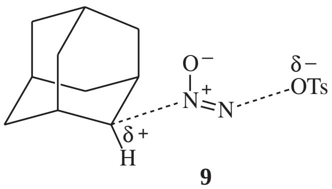

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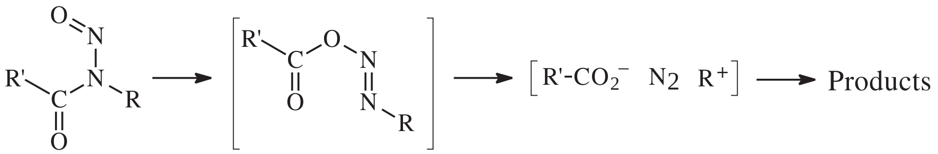
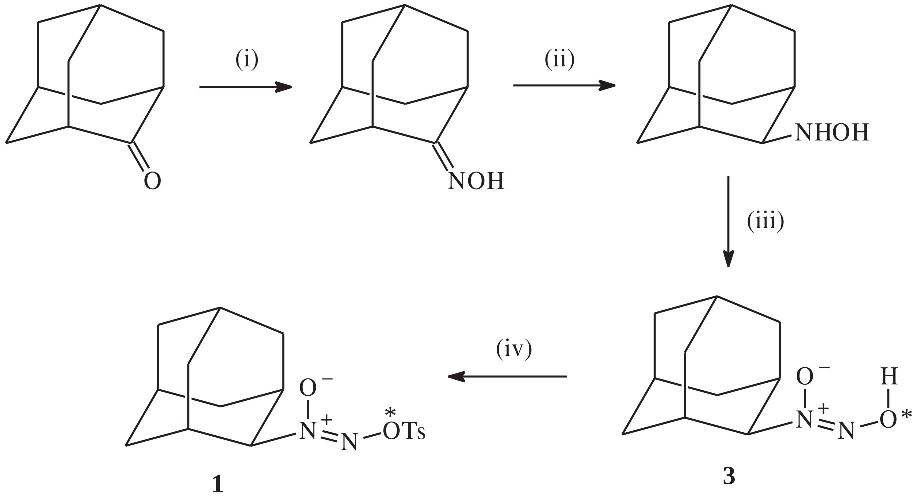
Scheme 2.



Scheme 3. (*i*) $NH_3OH^+Cl^-$, H_2SO_4, EtOH; (*ii*) NaH_3BCN, MeOH, HCl; (*iii*) $NaNO_2$, $H_3O^+Cl^-$, H_2O (using ordinary water or oxygen-labelled water as appropriate); (*iv*) TsCl, pyridine. The asterisk denotes the position of the ^{17}O or ^{18}O isotope when the nitrosation was carried out using labelled water.



return) and concerted (14, 16). In nonnucleophilic, weakly ionizing solvents such as chloroform or toluene, the initially formed ion pair collapses to give the covalent alkyl arenesulfonate whereas in ionizing nucleophilic media such as water, the carbocation is captured by a solvent molecule to give a solvolytic substitution product (17). These possibilities are illustrated for 2-adamantyl azoxytosylate (**1**) in Scheme 1, path A. An alternative mechanism for the decomposition of **1** is included in Scheme 1 path B, which is based (in part, see later) upon the probable mechanism for the isomerization of *N*-alkyl,*N*-nitrosoamides into alkyl diazocarboxylates prior to fragmentation in the nitrosoamide method of deamination and related reactions, Scheme 2 (18). In this route, there is an initial rearrangement of the substrate to give *N*-nitroso,*N*-(2-adamantyl),*O*-(*p*-toluenesulfonyl)hydroxylamine (**5**), possibly but not necessarily through a concerted cyclic mechanism, followed by the fragmentation step.

We now report a comparison of the decompositions in a range of solvents of 2-adamantyl azoxytosylate (**1**) and 2-adamantyl tosylate (**2**), the latter long having been regarded as an archetypal S_N1 substrate (19); we also compare the solvolyses of **1** and pinacolyl brosylate (3,3-dimethyl-2-butyl *p*-bromobenzenesulfonate, **6**) (19, 20), an S_N1 substrate that reacts with rate-limiting ionization, i.e., with no internal return, and 1-adamantyl chloroformate (**7**), an S_N1 substrate that also solvolyzes with liberation of a gas molecule (21). Additionally, we present oxygen isotope labelling results, which allow us to refine our earlier mechanistic proposal for the solvolysis of **1**. Finally, attempts to remove the pendant oxygen from **1**, which would lead to the previously unknown but presumably more unstable 2-adamantyl diazotosylate (**8**), are described. Compound **8**, which is analogous to the alkyl diazocarboxylate in Scheme 2 should, if formed, fragment to give a nitrogen-separated ion pair and thence either 2-adamantyl tosylate or solvent-derived products.

Results

The two substrates **1** and **2** were made by literature methods, see Scheme 3 for **1**, and all solvolytic media were prepared in conventional ways. Rate constants were already known for 2-adamantyl tosylate in many solvents, but to allow comparison with all our results for 2-adamantyl azoxytosylate, some new values were required. Rates of reaction of both substrates in all solvolytic media were investigated by our normal UV spectrophotometric methods (see experimental section) and activation parameters were calculated using the Eyring equation from rate constants measured over a temperature range of at least 30°C. Our results are shown in Table 1; Fig. 1 is a correlation of the rate results for the solvolyses of **1** and **2** in 11 solvents (gradient = 0.46, $R = 0.96$), and Fig. 2 is a correlation of the rate results for the solvolyses of **1** and pinacolyl brosylate (**6**) in just six solvents (gradient = 0.53, $R = 0.96$).

We also prepared samples of 2-adamantyl azoxytosylate specifically enriched with ^{17}O and with ^{18}O in the oxygen marked with an asterisk in Scheme 3 by reaction of tosyl chloride (22) with a specifically labelled sample of *N*-(2-adamantyl)hydroxydiazenium oxide (**3**), which in turn had been prepared by nitrosation of *N*-(2-adamantyl)hydroxylamine by a method based upon earlier work by Dahn and Ung-Truong (23). The ^{17}O NMR spectrum of the 2-adamantyl tosylate from the reaction of the labelled 2-adamantyl azoxytosylate in deuteriochloroform after more than 10 half-lives at 65°C unambiguously showed enhancement of the signal at δ_O 158.4 ppm

Table 1. Rate constants at 25°C and enthalpies and entropies of activation for the solvolysis of 2-adamantyl azoxytosylate (**1**) and 2-adamantyl tosylate (**2**).[a]

Compound	Solvent	Y_{OTs}[b]	$10^6 k_{25°C}$ (s^{-1})	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J K^{-1} mol^{-1})
1	50TFE	2.14	22.2	98	–5
	80TFE	1.95[c]	18.3	98	–6
	97TFE[d]	1.83	13.3	101	–1
	HCO_2H	3.04	19.4	105	16
	70E	0.47	3.56	107	10
	AcOH	–0.61	0.589	110	3
2	50TFE	2.14	2.98[e]	101	–12
	80TFE	1.95[c]	1.83	96	–32
	90TFE	1.9[c]	1.63	94	–41

[a] Rate constants at 25°C are by extrapolation from results at other temperatures, which in turn are means of several determinations and estimated to be reliable to 5%. The uncertainties in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are estimated to be 5 kJ mol^{-1} and 8 J K^{-1} mol^{-1}.

[b] Reference 8.

[c] Estimated from ref. 8.

[d] Less reliable results of $\Delta H^\ddagger = 89$ kJ mol^{-1} and $\Delta S^\ddagger = -35$ J K^{-1} mol^{-1} were reported earlier in ref. 14*b*.

[e] A result of 3.35×10^{-6} s^{-1} is reported in ref. 8.

Fig. 1. Graph of log k/s^{-1} for solvolysis of 2-adamantyl azoxytosylate **1** plotted against log k for solvolysis of 2-adamantyl tosylate **2**.

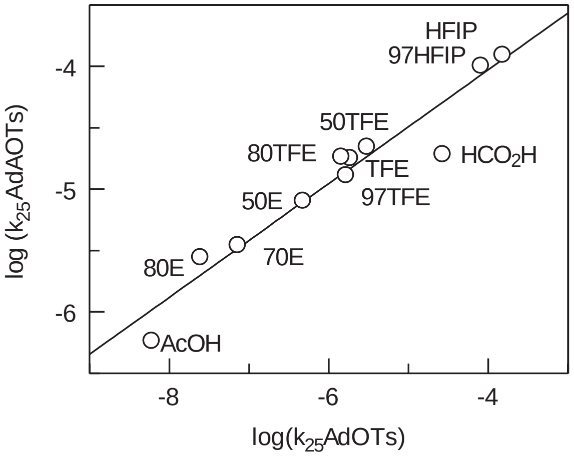
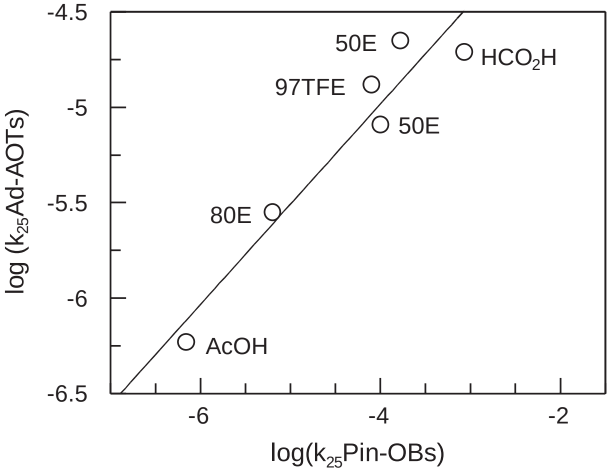


Fig. 2. Graph of log k/s^{-1} for solvolysis of 2-adamantyl azoxytosylate **1** plotted against log k for solvolysis of pinacolyl brosylate **6**.



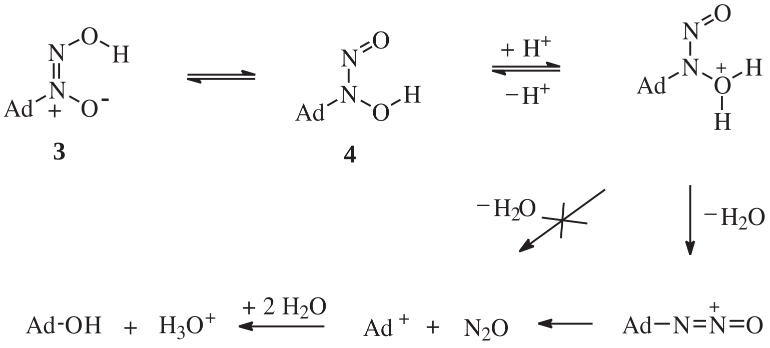
due to the sulfonyl oxygens; this compares with the signal at δ_O 157.5 ppm due to the sulfonyl bonded oxygens in the starting material. The millimeter-wave spectrum of the gas produced from the hydrolysis of the ^{18}O-labelled substrate was also recorded (24), which identified it unambiguously as nitrous oxide by the J 4←3 band at 96 512 MHz due to $N_2{}^{16}O$; there was no trace of the J 3←2 band at 71 155 MHz previously identified in the spectrum of N_2O containing the ^{18}O isotope (25).

Using a variety of reaction conditions and established deoxygenating agents (acetyl bromide (26), triethyl phosphite (27, 28), thionyl chloride (26), phosphorus trichloride (26, 29), triphenylphosphine (28), tri(*n*-butyl)phosphine (28*b*), and lithium metal (30)), we found no unambiguous evidence for the formation of 2-adamantyl tosylate from 2-adamantyl azoxytosylate under nonnucleophilic conditions.

Discussion

Isomerization of **3**, the product of nitrosation of *N*-(2-adamantyl)hydroxylamine, into **4** prior to the fragmentation in Scheme 4 has been identified as the first step in the mechanism of reaction of **3**; it involves a proton transfer either intermolecularly by protonation/deprotonation under the acidic conditions, or intramolecularly along a trajectory beginning in a strong hydrogen bond within **3** (25). In the next acid-catalysed step of this mechanism, the fragmentation is not concerted but stepwise via the oxodiazonium ion. In view of this preferred reaction of **3** via the *N*-nitroso tautomer, an intramolecular rearrangement of 2-adamantyl azoxytosylate (**1**) into the isomeric *N*-nitroso,*N*-(2-adamantyl),*O*-(*p*-toluenesulfonyl)hydroxylamine (**5**) via a cyclic transition structure is included as a preliminary to a credible alternative solvolytic mechanism for **1** in Scheme 1, path B. To distinguish between paths A and B in Scheme 1, we prepared 2-adamantyl azoxytosylate specifically labelled separately with ^{17}O and ^{18}O in the tosylated oxygen marked with an asterisk in Scheme 1. Clearly, if the mechanism follows path A, the labelled oxygen will end up in the 2-adamantyl tosylate in a nonnucleophilic medium whereas if the mechanism follows path B it will be lost as nitrous oxide. We have already shown that nitrous oxide

Scheme 4.



enriched with ^{18}O can be readily identified by observation of the J 3←2 rotational band at 71 155 MHz (25); its absence in the sample isolated in the present case established that the label is not in the nitrous oxide. To corroborate this negative evidence and now using ^{17}O enriched starting material **1** (25) we recorded an enhanced ^{17}O NMR signal at δ_O 158.4 ppm in the 2-adamantyl tosylate product (**2**). Clearly, the oxygen marked with an asterisk in 2-adamantyl azoxytosylate (**1**) in Scheme 1 ends up in the 2-adamantyl tosylate product (**2**), and not in the nitrous oxide, so path B via rearrangement to *N*-nitroso,*N*-(2-adamantyl),*O*-(*p*-toluenesulfonyl)hydroxylamine (**5**) in Scheme 1 may now be ruled out.

The logarithmic correlation of solvolytic rate constants at 25°C for 2-adamantyl azoxytosylate (**1**) and 2-adamantyl tosylate (**2**) is shown in Fig. 1. The nine points for aqueous alcoholic media constitute an excellent linear plot ($R > 0.99$), and the points for the two carboxylic acid solvents are noticeably off; omitting these two points has a negligible effect upon the gradient. Since 2-adamantyl tosylate is the standard compound for defining the solvent parameter Y(OTs), the gradient of this plot is the m value for 2-adamantyl azoxytosylate (**1**); the actual plot for **1** of log k/s^{-1} against Y(OTs) with the two carboxylic acid solvents omitted gives $m = 0.46$ ($R > 0.99$). Confidence in our earlier proposal that solvolysis of **1** involves rate-limiting fragmentation with formation of an ion pair separated by a molecule of nitrous oxide (14) is strengthened by our now having excluded the alternative mechanism for reaction of **1** via rearrangement through **5** (see above). Consequently, this very low m value for a reaction that is unambiguously an S_N1 indicates that the transition structure for this fragmentation has only a modest degree of dipolarity spread over four atoms, structure **9**. This is in accord with our conclusion from a double Hammett investigation of solvolyses of substituted benzyl azoxyarenesulfonates, i.e., that the bonds from the carbon to one nitrogen and from the other nitrogen to oxygen are about half broken in the transition structure (16). In contrast, the rate-limiting step in the solvolysis of **2** involves conversion of one type of ion pair into another (17, 31), i.e., ionization occurs in a prior (reversible) step, and the higher dipolarity in this transition structure arises from fully developed charges even though they are at only a small interionic separation. Our m value for **1** establishes that such a low result alone cannot be taken as a reliable indicator that a reaction of a simple secondary alkyl system is not an S_N1.

The deviations for the two carboxylic acids in the correlation of Fig. 1 indicate that the reactions of 2-adamantyl tosylate (**2**) in these solvents are faster than anticipated on the basis of their reactivity in aqueous alcohols. The most credible explanation on the basis of existing mechanistic understanding is that the bidentate carboxylic acid molecules are more effective than the aqueous alcohols at preventing internal return in the solvolysis of **2**. Internal return is also absent in the solvolysis of pinacolyl brosylate (**6**) but for a reason different to that for **1**. In the solvolysis of **6**, rearrangement is either concerted with the ionization or follows on so rapidly that internal return cannot compete (20). Consequently, in the correlation of pinacolyl brosylate with 2-adamantyl tosylate, points for carboxylic acids are also not on the line defined by reactions in aqueous ethanol (19). Low extents of internal return in the acetolysis and formolysis of 2-propyl brosylate (compared with trifluoroethanolysis) have been reported earlier (20). A fair correlation is obtained between the log k values for solvolyses of **1** and **6**, neither of which undergoes internal return, as shown in Fig. 2; the gradient (0.53) corresponds to an appreciably higher solvent effect for **6** than for **1**. This indicates a transition structure for the ionization of **6** with a higher degree of dipolarity than that in the ionization of **1**.

Another model for the reaction of **1** is 1-adamantyl chloroformate (**7**), although it is tertiary rather than secondary. A low m value determined over a wide range of solvents and appreciably positive $\Delta S^{\ddagger}$ values were reported by Kevill and colleagues (21); their solvolytic mechanism for **7** involves ionization to give the 1-adamantyl cation, carbon dixide, and chloride. Clearly, fragmentation in this system also cannot be followed by internal return to give covalent **7**, although the ions of the carbon dioxide separated ion pair can collapse to give 1-adamantyl chloride.

The newly determined activation parameters for the solvolysis of **1** shown in Table 1 are unexceptional except that they provide further supportive evidence that the reactions are S_N1 solvolyses, i.e., the enthalpies of activation are relatively high, and the entropies of activation are small (close to zero). In general terms, these and earlier results (14) show that the $\Delta S^{\ddagger}$ values are somewhat less negative than the corresponding results for **2**. We attribute this to a positive contribution to the overall entropy of activation arising from the nascent N_2O molecule in the reaction of **1** not found in the reaction of **2**. However, even this does not compensate in all cases for the substantial negative contribution to $\Delta S^{\ddagger}$ from the enhanced solvation that occurs due to the increased dipolarity in the transition state from **1**.

The original isolation of alkyl azoxyarenesulfonates as stable compounds was initially surprising in view of the instability of analogous compounds prepared by White et al. (18, 32), which fragment at low temperatures into cation, stable molecule, and anion. We reasoned that abstraction of the pendant oxygen atom of azoxytosylates such as **1** would give the corresponding diazotosylate (**8**) and that fragmentation of **8** would now liberate nitrogen (rather than nitrous oxide), and consequently be an easier reaction. We anticipated that **8**, if formed, would be too unstable to isolate under the deoxygenation reaction conditions and sought its expected decomposition product under non nucleophilic conditions, i.e., 2-adamantyl tosylate (17). Using a range of deoxygenating reagents, we found no firm evidence by TLC or NMR for the formation of **2** and conclude that **1** does not undergo an easy deoxygenation.

Experimental

Ethanoic acid was heated under reflux for 12 h with ethanoic anhydride, then fractionally distilled; trifluoroethanol was either stirred over molecular sieves for several days, then fractionally distilled, or heated under reflux over calcium hydride for 2 h, then fractionally distilled; spectroscopic grade absolute ethanol was used as supplied; methanoic acid was purified by standing over boric anhydride (B_2O_3) for several days followed by successive distillation from fresh B_2O_3 under reduced pressure until the separation of the OH and the CH signals in the ^{1}H NMR spectrum of the neat distillate became constant at ca. 3.158 ppm. Aqueous solvolytic media were prepared by mixing appropriate volumes of glass distilled water with either ethanol or trifluoroethanol except 97TFE, which was prepared by weight; the ethanoic acid was buffered with 0.15 mol dm^{-3} anhydrous sodium ethanoate, but all other solvents were unbuffered. Isotopically enriched water was purchased from Goss (10% enriched with ^{17}O) and from Aldrich (10% enriched with ^{18}O).

2-Adamantyl azoxytosylate (1) and 2-adamantyl tosylate (2)

2-Adamantyl azoxytosylate (**1**) (mp 111–112°C, lit. (14) 111–113°C) and 2-adamantyl tosylate (**2**) (mp 82–83°C, lit. (33) 82.7–83.7°C; δ_O 159.3 ppm (S=O, natural abundance)) were prepared as described previously (14*b*).

Isotopically labelled *N*-(2-adamantyl)hydroxydiazenium oxide (3) and the corresponding azoxytosylates

An ice-cold solution of sodium nitrite (0.20 g) in water (10% enriched with ^{18}O, 0.5 cm^3) was added dropwise over about 10 min to an ice-cold stirred solution of conc. hydrochloric acid (37%, 0.20 cm^3), *N*-(2-adamantyl)hydroxylammonium chloride (170 mg), and water (10% enriched with ^{18}O, 0.5 cm^3) in ethanol (3 cm^3). After about 20 min, the white crystalline product was filtered at the pump, washed with cold water, and dried under vacuum (143 mg; mp 134–135°C, lit. (14*b*) (unlabelled material) 137–139°C; δ_H 1.60–2.10 (m, 14H), 4.29 (s, 1H), 12.1 (br, 1H)). The ^{17}O-labelled analogue (148 mg, mp 135–136°C) was made in the same way from *N*-(2-adamantyl)hydroxylammonium chloride (167 mg) using 10% ^{17}O-enriched water and had an identical ^{1}H NMR spectrum.

Specifically labelled 2-adamantyl azoxytosylate (**1**)-^{17}O (δ_O 157.5 (S=O), 291.6 (N-O-S), 452.4 ppm (N-O)) and (**1**)-^{18}O were then made by our usual Tipson (14*b*, 22) method from **3**-^{17}O and **3**-^{18}O; both had melting points and ^{1}H NMR spectra identical with the unlabelled compound.

Decomposition of ^{17}O-labelled 2-adamantyl azoxytosylate

A sample (85 mg) of ^{17}O-labelled 2-adamantyl azoxytosylate (δ_O 157.5 (S=O)) was dissolved in a 1:4 mixture of chloroform:deuteriochloroform (4 cm^3) in an NMR tube and maintained at ca. 50°C in an oil bath for 10 h. The ^{1}H NMR spectrum indicated only about 10% conversion, so the temperature of the oil bath was raised to about 60°C, and the reaction was continued for a further 15 h by which time the conversion was about 40% by ^{1}H NMR, and the ^{17}O NMR spectrum showed a single strong but broad band centred at 158 ppm. After 4 days at this temperature, the ^{1}H NMR spectrum showed complete conversion to 2-adamantyl tosylate; there was no trace of the starting material, and the product showed a strong ^{17}O NMR signal at δ_O 158.4 ppm (S=O).

Decomposition of ^{18}O-labelled 2-adamantyl azoxytosylate

A gentle flow of nitrogen was passed through a stirred solution made up from aqueous perchloric acid (70%, 6.1 cm^3), water (24 cm^3), and ^{18}O-labelled 2-adamantyl azoxytosylate (85 mg, 0.25 mmol) in a flask fitted with a reflux condenser. The reaction was maintained at 69°C for 6 h, then for another 30 min as the reaction mixture cooled down; the gas flow passed through a KOH drying tower and a gas trap immersed in liquid nitrogen. The contents of the gas trap were then transferred at room temperature to a millimeter-wave spectrometer using standard vacuum line procedures, and predetermined regions of the spectrum were scanned. An intense absorption was recorded at 96 512 MHz due to the J 4←3 transition of $N_2{}^{16}O$; no absorption was detected in the region of 71 155 MHz previously identified as due to the J 3←2 transition of $N_2{}^{18}O$ (25).

Kinetics

Rates of solvolytic reactions were measured using either a Pye–Unicam SP8-300 spectrophotometer connected to an Apple microcomputer with in-house software for data collection (34) or a Cecil CE 5502 spectrophotometer connected to an Elonex PC using commercial data collection software. In the former case, rate constants were calculated also using in-house software (34); in the latter case, GraFit version 3.0 (Erithacus Software Ltd.) was used. In both cases, cell holders for up to four cells were thermostatted by circulating water, the cell-holder block temperature being measured with a fitted platinum resistance thermometer, and the system was programmed to record absorbance data automatically at predetermined time intervals. Rate constants were calculated from absorbance–time data collected over about three or four half-lives using standard computational techniques.

Attempted deoxygenations

(*i*) Four drops of triethyl phosphite (27, 28) were added to a solution of compound **1** (10 mg) in toluene (0.5 cm^3), and the reaction was monitored by TLC for 24 h. The temperature was then raised to 40°C but TLC showed only starting material after several days.

(*ii*) A solution of **1** (26 mg) in phosphorus trichloride (26, 29) (2 cm^3) was stirred at room temperature under nitrogen and protected from atmospheric moisture (SiO_2 tube). No change was detected by TLC after 24 h whereupon the reaction was worked up, and the isolated crystalline product was shown to be starting material by ^{1}H NMR and TLC. Further reactions with acetyl bromide (26) thionyl chloride (26), triphenylphosphine (28), tri(*n*-butyl)phosphine (28), and lithium wire (30), were also attempted but gave negative or ambiguous results.

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