Solvolysis of 2-Adamantyl *ONN*-Azoxytoluene-*p*-sulphonate.† A New Reaction

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Summary The first secondary alkyl azoxyarenesulphonate 2-adamantyl azoxytosylate, has been made and shown to have the *Z* configuration about the nitrogen–nitrogen double bond, rates of solvolysis and activation parameters in aqueous ethanol, aqueous trifluoroethanol and aqueous hexafluoropropan-2-ol have been determined and a solvolytic mechanism involving unimolecular fragmentation and carbonium ion intermediates is proposed

Although the primary alkyl compounds (**1**) have been known for some years [1,2] we are not aware of any investigations into the mechanisms of the solvolytic decomposition of these or any other alkyl azoxyarenesulphonates This is surprising because such solvolyses would constitute an important link[2] between two reaction types which proceed *via* carbonium ion intermediates but which otherwise show quite distinctive characteristics solvolytic deamination type reactions of alkylamines on the one hand[3,4] [equation (1)] and solvolysis of alkyl arenesulphonates (and halides) on the other[5,6] [equation (2)]

$$\text{R–NH}_2 \rightarrow [\text{R–N=N–X}] \xrightarrow[\text{HY}]{-\text{N}_2} \text{RX, RY plus elimination and rearrangement products} \qquad (1)$$

$$\text{X} = \text{OH, ArNH, R}'\text{CO}_2\text{, R} = \text{alkyl}$$

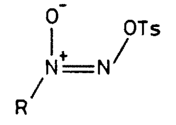
$$\text{R–X} \underset{(\leftarrow)}{\rightleftharpoons} [\text{R}^+\text{X}^-] \xrightarrow[-\text{HX}]{\text{HY}} \text{RY plus elimination and rearrangement products} \qquad (2)$$

$$\text{X} = \text{hal , ArSO}_3\text{, R} = \text{alkyl}$$

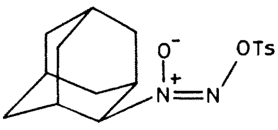
An important aspect of such a link, if it could be realized, is that it would make available for the first time a reaction in which a deaminative fragmentation is amenable to kinetic investigation,[2] equation (3) This has not been

$$\text{R–}\overset{\overset{\text{O}^-}{|}}{\text{N}^+}\text{=N–OSO}_2\text{Ar} \xrightarrow[-\text{ArSO}_3\text{H,N}_2\text{O}]{\text{HX, HY}} \text{RX, RY (plus, according to R, elimination and rearrangement products)} \qquad (3)$$

possible previously because in the more usual solvolytic deaminations, a rapid heterolytic fragmentation always follows at least one much slower step involved in the generation of the labile azo-intermediate We have recently prepared 2-adamantyl azoxytosylate (**2**)[7] and determined its structure Crystals were obtained from ether–light petroleum (b p 40—60 °C) at −70 °C, m p = 111—113 °C (decomp)



(1) R = Me, Bu^n, Bu^t, PhCH$_2$
Ts = *p*-MeC$_6$H$_4$SO$_2$–



(2)

Crystal data $C_{17}H_{22}N_2O_4S$, $M_r = 350\ 43$, monoclinic, space group $P2_1/c$, $a = 10\ 30(2)$, $b = 11\ 68(2)$, $c = 14\ 39(2)$ Å $\beta = 98\ 50(1)°$, $U = 1713$ Å^3, $Z = 4$ $D_c = 1\ 36$ g cm^{-3} $D_m = 1\ 33$ g cm^{-3} Mo K_α radiation ($\lambda = 0\ 71069$ Å, $\mu = 1\ 68$ cm^{-1}) 1455 reflexions (*hk*0—9) with $\theta < 22°$ were collected on a STADI-2 diffractometer of which 568 with $I > 3\sigma(I)$ were used The structure was refined by full matrix techniques (SHELX 76)[8] to $R = 0\ 091$ Despite high thermal motion of atoms in the adamantyl unit the structure is established as (**2**) having the *Z* configuration about the nitrogen–nitrogen double bond ‡

Our initial kinetics results confirm that indeed solvolysis of (**2**) has a first-order rate law and shows other characteristics of unimolecular heterolytic fragmentation implicating carbonium ion intermediates This new reaction therefore represents another probe for investigating the properties and reactions of these very important reaction intermediates

Table Rates of solvolysis of 2 adamantyl azoxytosylate at 25 °C [a]

Solvent[b]	10^5k/s^{-1}	$\Delta H^{\ominus\ddagger}$/kJ mol^{-1}	$\Delta S^{\ominus\ddagger}$/J K^{-1} mol^{-1}
97TFE[c]	2 33	89	−36
97HFIP	10 7	88	−26
50E	0 789	109	+24

[a] Four rate constants were measured between about 32 and 69 °C in each solvent In all cases these are means of several values obtained by monitoring the u v absorbance at 240 nm by our previously described methods (ref 9) Standard deviations on individual rate constants were ⩽ 1% and the error on each mean was ⩽ ∓ 3% Rate constants quoted at 25 °C and the activation parameters were obtained by Eyring plots estimated uncertainties are ∓ 2 kJ mol^{-1} and ∓ 10 J K^{-1} mol^{-1} in $\Delta H^{\ominus\ddagger}$ and $\Delta S^{\ominus\ddagger}$ respectively [b] 97TFE = trifluoroethanol water 97 3 by weight 97HFIP = hexafluoropropan 2 ol water 97 3 by weight 50E = ethanol water 1 1 by weight [c] Additionally the rate of solvolysis of (**2**) in 97TFE at 41 7 °C was measured by simultaneous monitoring of the decrease in u v absorbance and the increase in electrical conductance The mean rate constants by the two methods are $15\ 8_5 \times 10^{-5}$ and $15\ 7_6 \times 10^{-5}$ s^{-1} respectively

Rates of solvolysis (Table) are faster in the more highly ionizing, less nucleophilic media and the standard entropies of activation are typical of S_N1 reactions

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† Alternative name 2-(*p*-tolylsulphonyloxy-*NNO*-azoxy)adamantane

‡ The atomic co ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre University Chemical Laboratory, Lensfield Rd , Cambridge CB2 1EW Any request should be accompanied by the full literature citation for this communication

We have also established by g.l.c. that the principal products (perhaps the only ones) are the substitution products derived from the solvents: ethers and adamantan-2-ol. Neither adamantane nor adamantanone are formed to any appreciable extent (<1%).

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