# Nitrous Oxide as a Nucleophile in the Formation of a New Reactive Intermediate from Benzyl Cations in the Solvolysis of Benzyl Azoxytosylate

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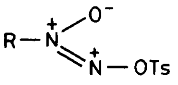
Rate and product analytical results of solvolysis of benzyl azoxytosylate in 1 : 1 (v/v) trifluoroethanol : water require two product-forming routes: one involves a long-lived intermediate (formed from benzyl cations and nitrous oxide) which is trappable by dilute nucleophiles and bases; the other involves either a very short-lived intermediate (the benzyl cation) which is not capable of being intercepted by solutes, or no intermediate at all.

The solvolysis of alkyl azoxytosylates, which constitutes a mechanistic link between solvolytic deamination and toluene-*p*-sulphonate solvolysis,[1,2] has been extended to the benzyl system, (**1a**), with a view to investigating the nature of electrophilic benzyl intermediates and probing further the mechanism of solvolysis of benzylic substrates.[3] The rates of reaction of (**1a**) have been measured in 97:3 (w/w) trifluoroethanol : water at four temperatures between 32 and 54 °C and activation parameters have been determined. The results [$\Delta H^{\ominus\ddagger} = 90\ (\pm 4)$ kJ mol$^{-1}$ and $\Delta S^{\ominus} = -35(\pm 8)$ J K$^{-1}$ mol$^{-1}$] are virtually identical with those obtained for the 2-adamantyl system, (**1b**), in the same solvent and are entirely compatible with a unimolecular rate-determining fragmentation, the mechanism proposed for the solvolysis of the 2-adamantyl, cyclohexyl, and bicyclo[2.2.2]octan-2-yl analogues.[2] The effects of electrolytes upon rates and products of reaction of (**1a**) in 1 : 1 (v/v) trifluoroethanol : water have also been investigated. In the absence of solutes, benzyl alcohol and benzyl trifluoroethyl ether are produced in the ratio 77 : 23 (±2) and, although sodium perchlorate gives rise to a kinetic salt effect, it does not affect this product ratio:† $PhCH_2OH : PhCH_2OCH_2CF_3$ = 76:24 (±3) at [$NaClO_4$] = 0.5 mol dm$^{-3}$.



(**1**)

R—OTs

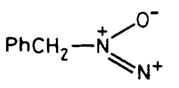
(**2**)

a; R = $PhCH_2$
b; R = 2-adamantyl

OTs = *p*-$MeC_6H_4SO_3$

$PhCH_2{-}O{-}\overset{+}{N}{\equiv}N$

(**3**)



(**4**)

$PhCH_2{-}N{=}\overset{+}{N}{=}O$

(**5**)

Sodium thiocyanate and iodide, powerful but non-basic nucleophiles,[4] introduce no second-order kinetic terms at constant ionic strength, but lead to the formation of benzyl thiocyanate and iodide whose yields increase with increasing concentration of nucleophile. The results for thiocyanate are included in Figure 1. The results exclude any significant route *via* an $S_N2$ mechanism. Clearly, an electrophilic intermediate is produced in or after the rate-determining step which is sufficiently long-lived to diffuse through the bulk solvent and

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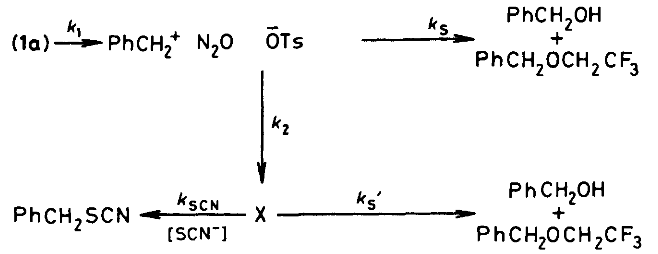
† Analyses were by reverse phase (C-18) h.p.l.c. using methanol–water with direct injection of reaction mixtures. Naphthalene was used as an internal standard to determine absolute rather than just relative yields.

be intercepted by nucleophilic solutes. However, extrapolation to infinite concentration of NaSCN by a (linear) double reciprocal plot of 1/[$PhCH_2SCN$] *vs.* 1/[NaSCN] leads to a limiting yield of only 45(±5)% $PhCH_2SCN$, so only about half of the total reaction goes through this long-lived intermediate. The remaining 55(±5)% of the reaction must, therefore, be *via* some species which is too short-lived to be intercepted by solutes and reacts entirely with solvent to give $PhCH_2OH : PhCH_2OCH_2CF_3 = 37(\pm 3) : 18(\pm 2)$, (67 : 33).

In view of the detection of 2-adamantyl toluene-*p*-sulphonate in the solvolysis of (**1b**)[1] and estimates of the lifetime of benzyl cation based upon studies in the 1-phenylethyl system,[5] a mechanism for the solvolysis of (**1a**) involving the benzyl cation as the short-lived intermediate and benzyl toluene-*p*-sulphonate (**2a**) as the long-lived intermediate X in Scheme 1 seemed reasonable. Indeed, benzyl toluene-*p*-sulphonate, a known compound with high electrophilic reactivity, is the exclusive organic product of thermolysis of (**1a**) in $CDCl_3$ at 66 °C, but its estimated lifetime is exceedingly short under the solvolytic conditions of reaction of (**1a**).[3] We have investigated the reactions of (**2a**) in 1 : 1 (v/v) trifluoroethanol : water with varying concentrations of NaSCN at the lower temperature of 25 °C; the results are shown in Table 1. Kinetic analysis of the reaction of (**1a**) according to the general mechanism in Scheme 1, applying the steady state approximation to the intermediate X = $PhCH_2OTs$, leads to the expression given in equation (1). A plot of (mol fraction $PhCH_2SCN)^{-1}$ against $[SCN^-]^{-1}$ is indeed linear and, from the gradient and intercept, the result $k_s'/k_{SCN} = 0.4$ mol dm$^{-3}$ is obtained. This is different from the value $k_{solv.}/k_{nuc.} = 0.08$ mol dm$^{-3}$ obtained from the kinetic study of (**2a**) itself (Table 1) and, therefore, rules out benzyl toluene-*p*-sulphonate as the long-lived intermediate X. It does not, however, rule out the general mechanism of Scheme 1, but leaves relatively few possibilities for the identity of the intermediate X.



**Scheme 1**

$$\frac{1}{\text{Mol fraction of } PhCH_2SCN} = \frac{k_s'(k_s + k_2)}{k_2 k_{SCN}[SCN^-]} + \frac{(k_s + k_2)}{k_2} \quad (1)$$

We have already noted that the very weakly nucleophilic toluene-*p*-sulphonate anion is able to compete with more strongly nucleophilic and preponderant solvent molecules, and trap the 2-adamantyl cation in the aqueous ethanolysis of (**1b**) simply by virtue of its close proximity to the nascent reactive electrophile.[1,2] In the same way, $N_2O$ is well positioned to intercept the benzyl cation after the initial fragmentation shown in Scheme 1 even though it also is only a weak nucleophile. We are not aware of nitrous oxide previously having been implicated as a nucleophile, although a precedent is the reversible departure of $N_2$ from aryldiazonium ions.[6] In principle, $PhCH_2^+$ could combine with $N_2O$ at

**Table 1.** Results of solvolysis of benzyl toluene-*p*-sulphonate (**2a**) in 1 : 1 (v/v) $CF_3CH_2OH : H_2O$ containing NaSCN at 25.0 °C, ionic strength maintained at 0.5 mol dm$^{-3}$ with $NaClO_4$.

| [NaSCN]/mol dm$^{-3}$ | $10^3 k_{obs.}$/s$^{-1}$ [a] |
|---|---|
| 0 | 2.61 |
| 0.04 | 3.55 |
| 0.08 | 5.08 |
| 0.16 | 7.52 |

[a] By linear regression using $k_{obs.} = k_{solv.} + k_{nuc.}[SCN^-]$, $k_{solv.} = 2.50 \times 10^{-3}$ s$^{-1}$ and $k_{nuc.} = 31.3 \times 10^{-3}$ dm$^3$ mol$^{-1}$ s$^{-1}$ ($r > 0.99$).

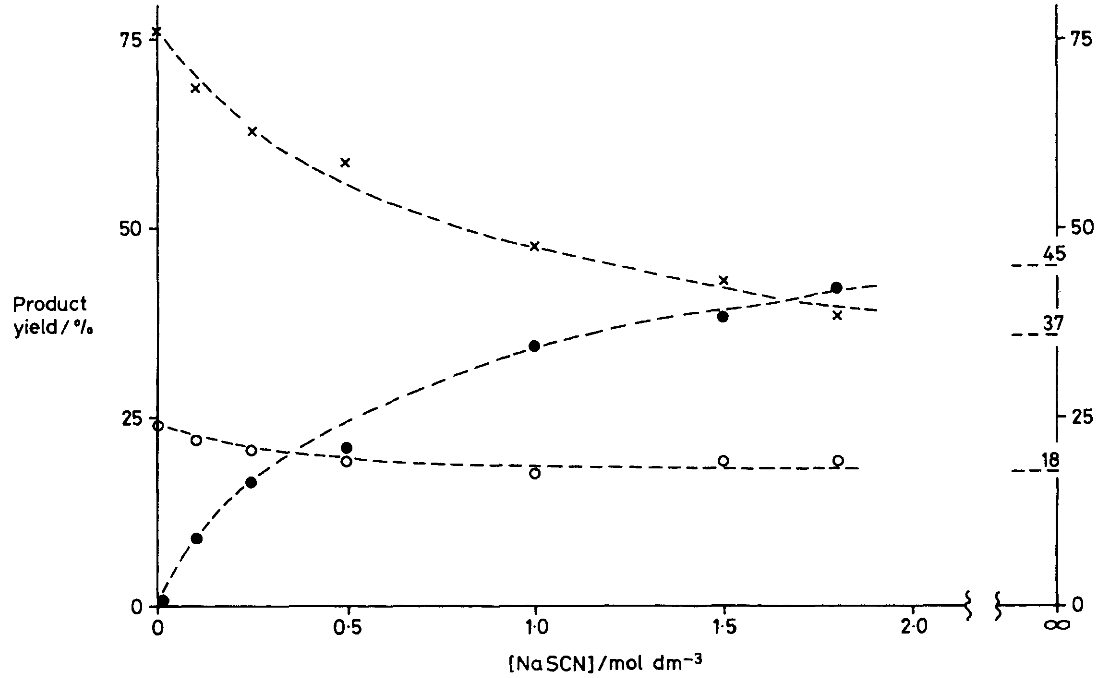


**Figure 1.** Product yields from solvolysis of (**1a**) in 1 : 1 (v/v) $H_2O : CF_3CH_2OH$ containing NaSCN × = $PhCH_2OH$; ○ = $PhCH_2OCH_2CF_3$; ● = $PhCH_2SCN$.

any of its three atoms to give alternative structures (**3**), (**4**), or (**5**) for the long-lived intermediate although linkage with the central nitrogen (to which the benzyl residue was originally bonded) seems the least likely. Direct evidence that combination occurs at the oxygen to give (**3**), a new type of reactive intermediate, is provided by the detection of benzaldehyde in the solvolysis of (**1a**) in the presence of bases. (We established that it is not an oxidation product of $PhCH_2OH$.) Proton abstraction and (concerted) loss of $N_2$ from (**3**) alone provides a reasonable mode of formation of benzaldehyde, a mechanism with ample precedent in the literature.[7] As the concentration of unbuffered sodium acetate in the medium is increased, the yield of benzaldehyde increases and graphical extrapolation to infinite concentration of base indicates a limiting yield of *ca.* 18% of the solvolysis product (the rest being $PhCH_2OH + PhCH_2OCH_2CF_3$ *via* solvent-induced $S_N2$ reactions of $PhCH_2ON_2^+$). [A complication which we have to take into account is the parallel acetate-catalysed reaction of trifluoroethanol with (**1a**) itself to give trifluoroethyl toluene-*p*-sulphonate and $PhCH_2N(O)NO^-$.] If the sodium acetate is buffered with acetic acid, the production of benzaldehyde is almost completely suppressed (detectable by h.p.l.c. but <1% at $[OAc^-]/[AcOH] = 4$).

An alternative to a short-lived intermediate which cannot be trapped by solutes is, in principle, possible and cannot on the present evidence be rigorously ruled out. If there is no barrier in the reaction with nucleophiles of the benzylic species produced by heterolysis of (**1a**), rebonding to a solvent molecule takes place in an uncoupled $S_N2$ process.[8] If no solvent molecule is appropriately placed at the instant of heterolysis of (**1a**), then rebonding to $N_2O$ takes place to give the long-lived intermediate. This alternative overall mechanism corresponds to parallel routes from (**1a**) with very closely related transition states followed in the proportions 55:45. One involves no real intermediate at all and the other involves only the (relatively) long-lived intermediate (**3**).

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