PERKIN 2

The kinetics and mechanism of the reaction of *p*-nitrocumyl bromide with azide ions in dimethyl sulfoxide. Evidence for a heterolytic reaction

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The reaction of *p*-nitrocumyl bromide 1 with azide ions in [$^2H_6$]dimethyl sulfoxide does not show the strong photochemical catalysis and inhibition by electron acceptors and radical traps characteristic of the reactions of the corresponding chloride in dipolar aprotic solvents and used as evidence for a $S_{RN}1$ reaction. Instead, the bromide reacts by a heterolytic mechanism that is approximately first-order with respect to both the substrate and the lithium azide. The results can be interpreted in terms of the preassociation mechanism proposed by Richard and Amyes for the reaction of *p*-nitrocumyl chloride with azide ions in aqueous trifluoroethanol but there is some evidence for the participation of the azide ion in heterolysis of the C–Br bond.

Introduction

The mechanisms for nucleophilic substitution in aliphatic and aromatic compounds are now known to include radical chain reactions ($S_{RN}1$)[1,2] with more limited evidence for non-chain electron transfer reactions.[3] There is at present considerable interest in defining the borderline between the heterolytic and electron transfer mechanisms of aliphatic[4–6] and aromatic[7–10] nucleophilic substitution. Both the interpretation and the results of some recent work have led to controversy.[2,7–11]

In aromatic nitration, the observation of chemically induced dynamic nuclear polarisation has proved helpful in distinguishing between heterolytic and electron transfer processes.[12] The value of this approach derives, in part, from the long relaxation time of the ^{15}N nucleus in the nitro group for this greatly aids the observation of such nuclear polarisation. We have therefore looked for ^{15}N nuclear polarisation in nitro groups present in the products of fast nucleophilic substitutions that might be made to occur through short chain or non-chain electron transfer reactions.[13] This work proved unsuccessful but the preliminary studies provided some unexpected observations concerning the reactions of azide ions and nitrite ions with *p*-nitrocumyl bromide and so the mechanisms of these reactions were investigated.

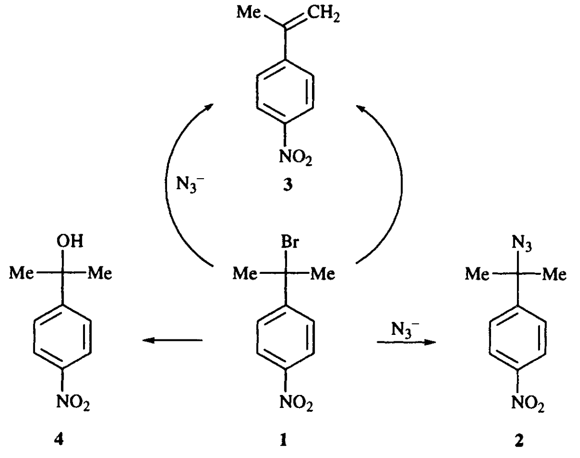
The reactions of *p*-nitrocumyl chloride with nucleophiles in dipolar aprotic solvents were studied in considerable detail by Kornblum and co-workers.[14–17] They provided convincing evidence that these reactions occur by the $S_{RN}1$ mechanism: the reactions are facilitated by the *para*-nitro substituent, are catalysed by light, and are inhibited by electron acceptors (*e.g. p*-dinitrobenzene) or radical scavengers (*e.g.* di-*tert*-butyl nitroxide†). As expected for this mechanism, the related displacement of the aliphatic nitro group from a chiral molecule [2-(*p*-nitrophenyl)-2-nitrobutane] by a range of nucleophiles in hexamethylphosphoramide shows a complete loss of optical activity at the reaction centre.[18]

In our studies, the substrate was changed to *p*-nitrocumyl bromide since this substrate is much more reactive than the corresponding chloride. However, the evidence below indicates that the substitutions then occur by a heterolytic reaction path.

Results

Products

p-Nitrocumyl bromide **1** (Scheme 1) (0.11 mol dm^{-3}) was mixed with a two-fold excess of lithium azide in dimethyl sulfoxide under an argon atmosphere at room temperature; after stirring for 3 h, the main product isolated was the corresponding azide **2** (yield 84%) together with 8% of the alkene **3** and 2% of the alcohol **4**. A similar reaction carried out for 9 h in the absence of the lithium azide gave 55% of the alkene **3** together with 10% of the alcohol **4**. Unreacted *p*-nitrocumyl bromide (21%) was also recovered. The reactions were then followed from the changes in the ^1H NMR spectrum using a 400 MHz instrument. From the integrals observed, it was possible to follow both the disappearance of the substrate and the formation of the three products (Fig. 1). The product composition obtained from the NMR spectrum under kinetic conditions is shown in Table 1. As might be expected, the proportion of the azide **2** formed increases with the initial concentration of the lithium azide.



Scheme 1

Kinetics

Unless indicated otherwise, the kinetics have been followed from the ^1H NMR signals of the methyl groups in the substrate and products. The alkene **3** is formed in part from a slow reaction with the solvent and, in the absence of azide ions, this reaction follows good first order kinetics, eqn. (1). The kinetics

$$\text{Rate} = k_1[\text{RBr}] \qquad (1)$$

of the reaction in the presence of azide ions would therefore be expected to follow a concurrent first order plus second order

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† The IUPAC name for the nitroxide radical is the aminoxyl radical.

Table 1 The reaction of *p*-nitrocumyl bromide (RBr) with lithium azide in [$^2H_6$]dimethyl sulfoxide at 30 °C. The variation of the product composition with the initial concentrations of the reactants. The lithium perchlorate is present to maintain the total salt concentration constant. The values in parentheses for the alkene **3** are calculated on the assumption that the lithium azide does not participate in the elimination reaction

Reactants			Products		
[RBr]/mol dm^{-3}	[LiN$_3$]/mol dm^{-3}	[LiClO$_4$]/mol dm^{-3}	[**2**] (%)	[**3**] (%)	[**4**] (%)
0.2	0.2	0.2	71	21 (13.8)	8
0.2	0.3	0.1	82	12 (6.8)	6
0.2	0.4	—	86	11 (4.1)	3
0.1	0.2	0.2	73	19 (7.9)	8

Table 2 The effect of the concentrations of the reactants and of various additives (X) on the rate coefficients [k_1, eqn. (1), k_2, eqn. (2)] for the reaction of *p*-nitrocumyl bromide (RBr) with lithium azide in [$^2H_6$]dimethyl sulfoxide at 30 °C

[RBr]/mol dm^{-3}	[LiN$_3$]/mol dm^{-3}	[LiClO$_4$]/mol dm^{-3}	X	[X]/mol dm^{-3}	$k_1/10^{-5}$ s^{-1}	$k_2/10^{-3}$ dm^3 mol^{-1} s^{-1}
0.2	—	0.4	—	—	4.87	—
0.2	0.2	0.2	—	—	—	4.25
0.2	0.3	0.1	—	—	—	3.74
0.2	0.4	—	—	—	—	3.96
0.1	0.2	0.2	—	—	—	4.12
0.2	0.4	—	*p*-DNB[a]	0.1	—	3.64
0.2	0.4	—	4-HT[b]	0.02	—	4.64
0.2	0.2	0.2	LiBr	0.2	—	3.85
0.2	0.4	—	H_2O	(5% v/v)	—	2.78

[a] *p*-Dinitrobenzene. [b] 4-HydroxyTEMPO (the 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxyl radical).

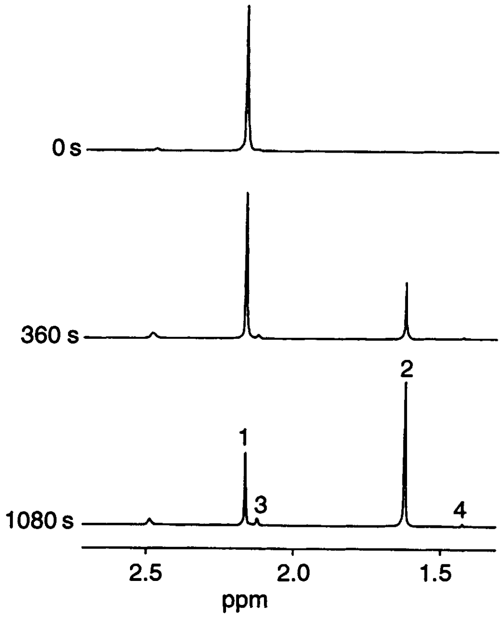


Fig. 1 The change in the ^1H NMR spectrum of the reaction mixture during the reaction of lithium azide (0.4 mol dm^{-3}) with *p*-nitrocumyl bromide (0.2 mol dm^{-3}) in [$^2H_6$]dimethyl sulfoxide at 30 °C. The numbers refer to the structures in Scheme 1.

kinetic form and were initially analysed in this way (see Experimental section). However, over the range of concentrations used, the reaction with azide ions is always predominant and the individual runs were found to follow second order kinetics [eqn. (2)] to a good approximation (correlation coefficients

$$\text{Rate} = k_2[\text{RBr}][\text{N}_3^-] \qquad (2)$$

>0.999). For our present purposes, this is an adequate representation of the kinetic form and the second order rate coefficients for the reaction of **1** with lithium azide are listed in Table 2. The range of concentrations used was limited by the solubility of the lithium azide and by the sensitivity of the NMR measurements. In varying the concentration of lithium azide, the total salt concentration was held constant by the addition of lithium perchlorate.

The relatively small variation of the second order rate coefficients with the initial concentrations of the reactants shows that the reaction is approximately first order with respect to both the substrate and the lithium azide. With the exception of water, none of the additives listed in Table 2 leads to a significant decrease in the rate of reaction. In one experiment, the reaction mixture was exposed to UV radiation for the first 5 min of the kinetic run; the first point taken after exposure showed a slight increase (11%) in the rate of reaction but later points showed no significant difference in the extent of reaction with or without the initial illumination.

Kinetic runs were also carried out using tetrabutylammonium azide and the results are listed in Table 3. This change in the cation reduces the rate of the underlying elimination reaction but slightly increases the rate of the substitution reaction.

The kinetic consequences of deuteriation in the methyl groups of the substrate are shown in Table 4. Because of the deuteriation, these runs were initially followed by ^2H NMR spectroscopy but this required a change to the unlabelled solvent (C_2H_6SO). As a check on possible solvent isotope effects, the runs were then repeated in the labelled solvent (C_2D_6SO) using the ^1H NMR signals of the *ortho* hydrogens to follow the reaction. As expected, deuteriation markedly decreases the rate of the underlying elimination reaction with the solvent ($k_H/k_D = 3.0$) but has a much smaller effect on the rate of the overall reaction.

One kinetic run was carried out on the reaction of *p*-nitrocumyl chloride (0.2 mol dm^{-3}) with lithium azide (0.4 mol dm^{-3}) in [$^2H_6$]dimethyl sulfoxide at 30 °C. The run was followed for about one half-life and gave a second-order rate coefficient (k_2) of 9.7 × 10^{-6} dm^3 mol^{-1} s^{-1}. Comparison with the kinetic run with *p*-nitrocumyl bromide under the same conditions (Table 2) gives $k_2^{Br}/k_2^{Cl} = 408$.

Discussion

Kornblum and co-workers[16,17] showed that the reaction of *p*-nitrocumyl chloride with azide ions in hexamethylphosphoramide had the characteristics of an $S_{RN}1$ reaction; the reaction

Table 3 Rate coefficients [k_1, eqn. (1), k_2, eqn. (2)] for the reaction of *p*-nitrocumyl bromide (0.2 mol dm^{-3}) with tetrabutylammonium azide (NR'_4N_3) in [$^2H_6$]dimethyl sulfoxide at 30 °C. These kinetic runs were followed from the signals for the *ortho* hydrogens in the aromatic ring

[NR'_4N_3]/mol dm^{-3}	[NR'_4ClO_4]/mol dm^{-3}	k_1/10^{-5} s^{-1}	k_2/10^{-3} dm^3 mol^{-1} s^{-1}
—	0.4	2.66	—
0.2	0.2	—	5.68
0.4	—	—	5.12

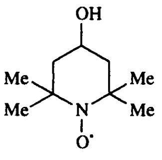
Table 4 Rate coefficients [k_1, eqn. (1), k_2, eqn. (2)] for the reaction of methyl labelled [$^2H_6$]*p*-nitrocumyl bromide (0.2 mol dm^{-3}) with lithium azide in dimethyl sulfoxide and [$^2H_6$]dimethyl sulfoxide at 30 °C

[LiN_3]/mol dm^{-3}	[$LiClO_4$]/mol dm^{-3}	Solvent	k_1/10^{-5} s^{-1}	k_2/10^{-3} dm^3 mol^{-1} s^{-1}	k_H/k_D
—	0.4	$C_2H_6SO^a$	1.79	—	
0.4	—	$C_2H_6SO^a$	—	3.89	
—	0.4	C_2D_6SO	1.61^b	—	3.02^{c,d}
0.4	—	C_2D_6SO	—	3.25^b	1.22^{c,d}

[a] Containing 0.5% C_2D_6SO and followed by ^2H NMR spectroscopy. [b] Followed by ^1H NMR spectroscopy using the signals for the *ortho* hydrogens of the aromatic ring. [c] Calculated from a direct comparison with the corresponding runs in Table 2. [d] These values are reduced by the presence of 6.3% of hydrogen in the methyl groups (see Experimental section).

was strongly catalysed by light[16] with quantum yields of up to 570 and was inhibited by dinitrobenzene.[17] They do not give details of the inhibition experiment with azide ion as the nucleophile but, in the typical example they quote (with nitrite ion as the nucleophile), the concentration of dinitrobenzene required to produce complete inhibition was 0.01 mol dm^{-3}. They also showed that radical traps (di-*tert*-butyl nitroxide, oxygen, galvinoxyl) were very effective in inhibiting the reactions of *p*-nitrocumyl chloride and α,*p*-dinitrocumene with nucleophiles but again no specific details are given of the reactions with azide ion as the nucleophile.

In contrast, in the analogous experiments on *p*-nitrocumyl bromide reported above, the catalysis by light was barely detectable and only a slight decrease (8%) in the reaction rate was detected in the presence of a much greater concentration of *p*-dinitrobenzene (0.1 mol dm^{-3}) (Table 2). In the presence of the radical trap‡ 4-hydroxyTEMPO (the 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxyl radical, 5), no retardation was observed and the rate of disappearance of the substrate was slightly increased (Table 2). The reaction of *p*-nitrocumyl bromide with azide ions in dimethyl sulfoxide does not therefore appear to occur by the $S_{RN}1$ mechanism.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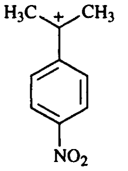
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$(N_3^-{\bullet}R^+{\bullet}Br^-)^‡$
7

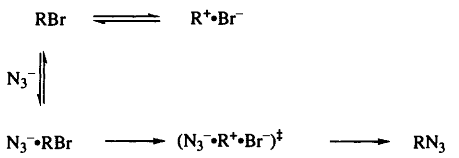
$PhSO_2CH{=}CHCH_2X$ X = Cl, Br
8

p-$MeC_6H_4SO_2CH{=}CHCMe_2X$ X = Cl, Br
9

The most obvious alternative mechanism, a conventional S_N1 ionisation of the tertiary bromide, is ruled out by the second order kinetics observed. The second order kinetics cannot come from a lithium catalysed S_N1 reaction because the kinetic form is retained when the lithium ion is replaced by the tetrabutylammonium ion (Table 3) and because the lithium ion concentration is constant within and between runs (Table 2). An S_N2C+ mechanism involving the reaction of the azide ions with an equilibrium concentration of the carbocation **6** derived from the heterolysis of **1** is ruled out by the absence of a significant common ion effect with added lithium bromide (Table 2). An azide catalysed elimination of hydrogen bromide followed by the back addition of hydrazoic acid is eliminated by the fact that deuteriation markedly retards the elimination reaction but has only a small effect on the concurrent substitution (Table 3). There was also no evidence of a fast reaction between hydrazoic acid and the alkene. We are left therefore with mechanisms in which the substitution occurs through the direct attack by azide ions on the substrate or on an ion pair derived from it.

The most direct analogy to these reactions in the literature is probably the work of Amyes and Richard[20] on the reaction of *p*-nitrocumyl chloride with azide ions in 50:50 (v/v) trifluoroethanol–water. They have provided evidence for a pre-association mechanism in which an encounter complex is formed between a substrate molecule and an azide ion followed by the heterolysis of the substrate and an effectively simultaneous reaction between the carbocation and the azide ion. They point out that the carbocation **6** is destabilised by the nitrogroup and that, in their system, the lifetime of the complex **7** is too short for this to be an intermediate. It is therefore a transition state but one in which the azide ion does not aid the ionisation of the substrate.

For the reaction of *p*-nitrocumyl chloride in 50:50 trifluoroethanol–water, the alkyl azide is formed at the expense of the solvolysis product and so the reaction with azide ions does not contribute to the overall rate. The reaction of *p*-nitrocumyl bromide in dimethyl sulfoxide has a very different kinetic form but the two can be fitted into the same mechanistic scheme if, in the absence of azide ions, the initial ionisation is considered to be reversible as shown in Scheme 2. This argument makes the reasonable assumption that dimethyl sulfoxide is a far less reactive solvent to carbocations than 50:50 trifluoroethanol–water.



Scheme 2

However, although the above arguments are consistent with the kinetic form of the reaction our results do not necessarily imply that azide ions play no part in facilitating the ionisation. The azide ion is a much more powerful nucleophile in dimethyl sulfoxide than in aqueous media because of the absence of hydrogen bonding.[21] There has recently been considerable discussion of possible nucleophilic participation by solvent molecules in the heterolysis of cumyl derivatives[22] and the above results provide two hints that some nucleophilic participation by azide ions may occur. The following arguments assume that

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‡ The rate of reaction of the 2,2,6,6-tetramethylpiperidinyloxyl radical with alkyl radicals is close to the diffusion-controlled limit.[19]

the substitution occurs in that fraction of the substrate that has undergone preassociation with azide ions and that there is no isotope effect on the preassociation stage.

One argument comes from the deuterium isotope effect observed for the azide reaction in C_2D_6SO (Table 4). When allowance is made for the concurrent elimination, this comes to a factor of 1.17 (1.08 per CD_3 group). Although *ca.* 6% H/D exchange occurred in the preparation of the labelled substrate (see Experimental section), this is a curiously low result for an S_N1 reaction. A value of 1.34 per CD_3 group has been given for the ionisation of *tert*-butyl chloride in 50% ethanol.[23]

The other hint of nucleophilic participation comes from the difference in the second order rate coefficients for the reactions of azide ions with *p*-nitrocumyl bromide and *p*-nitrocumyl chloride (a factor of 408). This is larger than expected for a simple heterolysis. For reaction with lithium azide in dimethylformamide, the k_2^{Br}/k_2^{Cl} ratio is 570 for the primary halides **8** but decreases to 164 for the tertiary halides **9**; this change has been related to the degree of ionisation of the halogen in the transition state.[24] The above argument assumes that the uncatalysed reaction of *p*-nitrocumyl chloride in dimethyl sulfoxide is predominantly heterolytic but, if this is not so, the rate of heterolysis of the chloro compound should be even slower and the argument from the high value of the k_2^{Br}/k_2^{Cl} is strengthened.

In the elimination reaction, the isotope effect of $k_H/k_D = 3.0$ (Table 4) suggests that the breaking of the C–H bond is at least partly rate-determining. From initial rates of formation of the alkene in different kinetic runs, it appears that some of the elimination occurs through reaction with lithium azide and this is supported by the difference between the observed and calculated percentages of the alkene at the end of the reaction (Table 1). The dual pathways for the formation of the alkene are shown in Scheme 1.

Other evidence for the relative preference of alkyl chlorides for electron transfer reactions has been observed recently[25] in the reactions of *p*-nitrobenzyl chloride and *p*-nitrobenzyl bromide with hydroxide ions in ethanol: the chloride yields dimeric products *via* an electron transfer process while the bromide yields the corresponding ethyl ether by what appears to be a conventional S_N2 reaction.

Experimental

Materials

Lithium azide was obtained from Eastman Kodak and lithium perchlorate was obtained from Aldrich; both salts were dried for 6 h under reduced pressure (35 °C, 0.1 mmHg). Cumene was obtained from BDH and *p*-nitrocumene from Lancaster Syntheses. Tetrabutylammonium hydroxide was obtained from Aldrich as a 40 wt.% aqueous solution. Tetrabutylammonium azide was prepared as previously described.[26] The product had mp 78–81 °C (lit.,[26] 80 °C) and was very hygroscopic; it was handled under dry nitrogen at all times. Tetrabutylammonium perchlorate was prepared by adding a twofold excess of aqueous sodium perchlorate (0.5 mol dm^{-3}) to aqueous tetrabutylammonium hydroxide (40 wt.%); after 10 min, the white solid was filtered off and washed with cold water. The residual water was removed by azeotropic distillation with toluene and the resulting solid was recrystallised from ethyl acetate and dried under reduced pressure (0.1 mmHg). The product had mp 218–220 °C (C, 56.1; H, 10.8; N, 3.9; Cl, 10.3. $C_{16}H_{36}NO_4Cl$ requires C, 56.2; H, 10.6; N, 4.1; Cl, 10.4%).

The dimethyl sulfoxide was the Merck AnalaR grade and was distilled from calcium hydride; [$^2H_6$]dimethyl sulfoxide (99.9 atom%) was obtained from Aldrich. Both sulfoxide solvents were dried with molecular sieves and handled under dry argon.

p-Nitrocumyl bromide

A mixture of *p*-nitrocumene (20.8 g), *N*-bromosuccinimide (21.85 g) and benzoyl peroxide (0.2 g) in carbon tetrachloride (150 cm^3) was heated under reflux for 1 h. The succinimide formed was then filtered off and the filtrate was evaporated to give a red-brown liquid which crystallised on standing. Recrystallisation of the solid from hexane at 5 °C gave 25.9 g of *p*-nitrocumyl bromide, mp 33–34 °C (yield 87%) (Found: C, 44.2; H, 4.1; N, 5.9; Br, 33.1. $C_9H_{10}NO_2Br$ requires C, 43.3; H, 4.1; N, 5.7; Br, 32.7%); $\delta_H(CDCl_3)$ 8.19 (2 H, d), 7.78 (2 H, d), 2.21 (6 H, s); $\delta_C(CDCl_3)$ 153.5, 146.9, 126.9, 123.5, 60.9, 35.1.

[$^2H_6$]*p*-Nitrocumyl bromide

This preparation started with a conventional Friedel–Crafts reaction between benzene (19.4 g) and [$^2H_8$]propan-2-ol (Aldrich, 4.94 g) to give [$^2H_7$]cumene (5.06 g). The ^1H NMR spectrum showed that the product had undergone *ca.* 5% H/D exchange in the methyl groups. The bulk of the cumene (4.12 g) was dissolved in acetic anhydride (25 cm^3) and a mixture of concentrated nitric acid (3 g, 70%) and acetic acid (10 cm^3) was added followed by sulfuric acid (98%, 1 cm^3). After being stirred for 3 h at 0 °C, the mixture was poured into ice–water. The aqueous solution was extracted with dichloromethane, and after a conventional work-up gave a mixture of the *ortho* and *para* isomers of [$^2H_7$]*p*-nitrocumene as a red-brown liquid (4.98 g, *ca.* 70% *para*).

This mixture of labelled nitrocumenes was dissolved in dimethyl sulfoxide (50 cm^3) and oxygen was bubbled through the solution with stirring at room temperature for 15 min. A solution of potassium *tert*-butoxide (0.51 g) in *tert*-butyl alcohol (20 cm^3) was then added slowly with vigorous stirring over a period of 10 min while the temperature was maintained at 20–35 °C. The stirring and the passage of oxygen through the reaction mixture were continued for 2 h. The reaction mixture was then poured onto ice, and the resulting solution was extracted with diethyl ether. After the etherial solution had been washed and dried (K_2CO_3), the solvent was removed and the product was purified by HPLC to give [$^2H_6$]*p*-nitrocumyl alcohol (2.76 g) as a colourless liquid.

A solution of this alcohol in dichloromethane (20 cm^3) was added to a stirred mixture of anhydrous zinc bromide (2 g) and dichloromethane (50 cm^3) at 0 °C through which a stream of hydrogen bromide was passing. The passage of the hydrogen bromide at 0 °C was maintained for 20 min and the mixture was then filtered twice, the second time after the addition of silicic acid (2 g). The filtrate was then concentrated by evaporation under reduced pressure to give a red-brown liquid which crystallised on standing. Recrystallisation of the product from hexane gave [$^2H_6$]*p*-nitrocumyl bromide, mp 34–35 °C (2.98 g) (Found: C, 43.0; H, 4.0; N, 5.2; Br, 32.2. $C_9D_6H_4NO_2Br$ requires C, 43.2; H, 4.0; N, 5.6; Br, 32.0%); $\delta_H(CDCl_3)$ 8.19 (2 H, d), 7.77 (2 H, d), 2.16–2.17 (0.38 H, m); $\delta_C(CDCl_3)$ 153.5, 146.9, 126.8, 123.4, 60.5, 35.1–34.2 (m). The small peak in the ^1H NMR spectrum (0.38 H) derives from the H/D exchange; this occurs mainly in the initial Friedel–Crafts reaction and corresponds to the presence of 6.3% of hydrogen in the methyl groups. The method used for the elemental analysis treats deuterium as hydrogen in calculating the percentage of hydrogen present.

Products

A solution of *p*-nitrocumyl bromide in dimethyl sulfoxide (20 cm^3, 0.11 mol dm^{-3}) was added to a solution of lithium azide in dimethyl sulfoxide (20 cm^3, 0.21 mol dm^{-3}) at room temperature under argon. After being stirred for 3 h, the reaction mixture was extracted with diethyl ether. The etherial solution was then washed with water and dried ($MgSO_4$). Removal of the solvent gave a yellow liquid (0.445 g) part of which (0.122 g) was purified by HPLC. Elution with 95% hexane–5% ethyl acetate gave *p*-nitrocumyl azide (0.100 g, 84%) (Found: C, 52.3; H, 5.1; N, 26.9. Calc. for $C_9H_{10}N_4O_2$: C, 52.4; H, 4.9; N, 27.2%); $\delta_H(CDCl_3)$ 8.23 (2 H, d), 7.62 (2 H, d), 1.68 (6 H, s); $\delta_C(CDCl_3)$ 152.0, 147.1, 126.2, 123.8, 63.3, 28.3. *p*-Nitro-α-methylstyrene was obtained as a second product (0.008 g, 8%) and was shown to be identical to a well characterised sample prepared independently by the reaction of *p*-nitrocumyl bromide with sodium nitrite.[13] A third product was obtained after elution with 50% hexane–50% ethyl acetate and shown to be *p*-nitrocumyl alcohol (0.002 g, 2%). This sample was shown to be identical to a sample of *p*-nitrocumyl alcohol prepared as described for [$^2H_6$]*p*-nitrocumyl alcohol above.

Kinetics

All solutions for kinetic runs were prepared under an atmosphere of dry argon. The kinetic runs were carried out using a Varian VXR-400 NMR spectrometer and those listed in Table 2 were followed from the integrals for the methyl protons in the substrate **1** and in the products **2**, **3** and **4**. The concentration of the substrate at a given time ($[RBr]_t$) was calculated from the initial concentration ($[RBr]_0$) by eqn. (3):

$$[RBr]_t = [RBr]_0\{I_1/(I_1 + I_2 + 2I_3 + I_4)\} \qquad (3)$$

where I_X stands for the integral for the methyl protons in the species X. The concentrations of the other species were calculated from analogous equations. This procedure could not be used in the presence of tetrabutylammonium salts (Table 3) and the integrals for the *ortho* protons of the aromatic ring were then used instead. For the reactions of the labelled substrate listed in Table 4, the kinetic runs were followed from either the integrals for the *ortho* protons in the aromatic ring or from the integrals for the methyl groups in the ^{2}H NMR spectra. Ten points were taken for each kinetic run normally covering two or more half-lives. A small amount of the alkene **3** appeared to be present at the start of reaction; the integral was too small to measure accurately and so the initial point was omitted from the calculation of the integrated rate coefficients.

Several attempts were made to analyse the kinetics on the basis of parallel first and second order reactions[27] but the results were not wholly satisfactory since the calculated first order component was then less than expected from the rate of the reaction of **1** with the solvent. Presumably, there is some unidentified distortion towards the end of each kinetic run that causes the runs to simulate almost perfect second order kinetics. The hydrazoic acid generated in the elimination reaction may perhaps decrease the reactivity of the azide ions by hydrogen bonding.

The comparison of the observed percentage of elimination with that expected from the equation for parallel first and second order reactions (Table 1) was carried out using GEAR, a program adapted by T. E. Beukelman and F. J. Weigert from the program HAVCHM.[28]

Acknowledgements

One of us (S. W. P.) thanks the EPSRC for a studentship.

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Paper 6/04725D
Received 5th July 1996
Accepted 8th August 1996