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Amines as leaving groups in nucleophilic aromatic substitution reactions. Part 5.[1] Substitution *vs.* *N*-oxide formation in the reaction of *N*-n-butyl-2,6-dinitroaniline with hydroxide ions

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A kinetic study of the reaction of *N*-n-butyl-2,6-dinitroaniline **1** with NaOH was carried out in 10% 1,4-dioxane–water at 25 °C, giving 2,6-dinitrophenol **2** and 7-nitro-2-n-propyl-1*H*-benzimidazole 3-oxide **3** in ratios depending on the HO^-concentration. The rate constant for the formation of **2** is second order in HO^- concentration while that of **3** is first order then, the relative amount of **2** : **3** formed increases with HO^-. A mechanism involving the formation of a σ complex by addition of HO^- to an unsubstituted position of the aromatic ring is proposed for 2,6-dinitrophenol formation. The mechanism suggested for the formation of the *N*-oxide requires the deprotonation of the substrate.

Introduction

Although amino groups are not generally considered as good leaving groups in nucleophilic aromatic substitution reactions,[2] there are many examples where an alkyl or dialkylamino group is replaced by a nucleophile.

Picramide and *N,N*-dimethylpicramide give picrate anions in aqueous sodium hydroxide,[3] while *N,N*-dimethylpicramide reacts in methanolic sodium methoxide to give the substitution product.[4]

Sekiguchi has reported that dialkylamino groups, such as dimethyl-, diethyl-, and *N*-methylbutyl-amino, piperidino and pyrrolidino groups, in 1-dialkylamino-2,4-dinitronaphthalene are easily replaced by primary amines and pyrrolidine in dimethyl sulfoxide (DMSO).[5] He also found that alkylamino groups in 2,4-dinitronaphthalene derivatives react in a similar way.[6] In 1990 he reported the amine–amine exchange reactions of 1-dialkylamino-2,4,6-trinitro- and 1-dialkylamino-2,4-dinitrobenzenes with various primary and secondary amines in DMSO.[7]

We have demonstrated that in aqueous solutions cyclic amines like pyrrolidine, piperidine and morpholine can act as leaving groups in aromatic nucleophilic substitution reactions of 1-amino-2,4-dinitrobenzenes,[8] and 1-amino-2,4,6-trinitrobenzenes.[1,9] Imidazole can also act as a leaving group in a reaction with hydroxide ions,[10] and n-butylamine[11] from 2,4,6-trinitrobenzene derivatives and piperidine and n-butylamine from 2,4-dinitrobenzene derivatives.[12]

In this paper we report on the kinetics of the reaction of *N*-n-butyl-2,6-dinitroaniline **1** in basic solution which, in addition to the substitution product of the alkyl amino group, 2,6-dinitrophenol **2**, gives a cyclization product, namely 7-nitro-2-n-propyl-1*H*-benzimidazole 3-oxide **3**.

Results

The reaction of *N*-n-butyl-2,6-dinitroaniline **1** with NaOH was studied in 10% 1,4-dioxane–water at 25 °C and 1 M ionic strength. The spectrum of **1** in neutral or acid media shows an absorption band at 442 nm. The reaction was followed by measuring the decrease in absorption at 442 nm in acid media. Under these conditions, two isosbestic points were observed at 375 and 260 nm (Fig. 1).

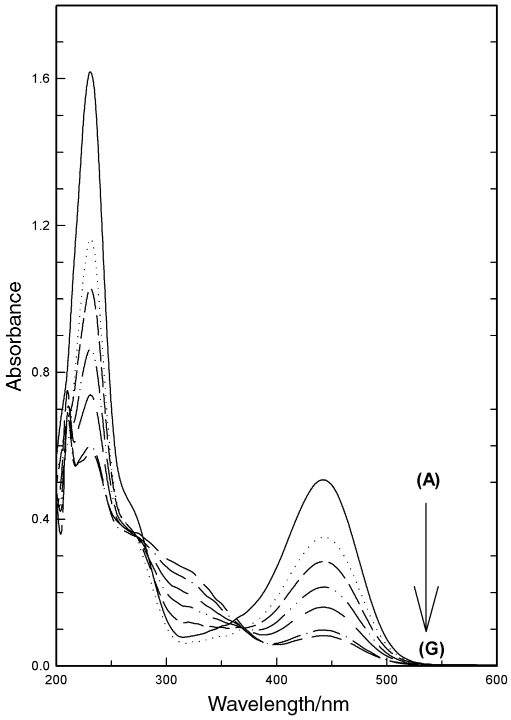

Fig. 1 Absorbance of **1** (7.78×10^{-5} M) in 10% 1,4-dioxane–water at 25 °C (A) and in acid media at different reaction times with 0.896 M NaOH; (B) 1 min; (C) 47 min; (D) 92.5 min; (E) 150 min; (F) 245 min; (G) 299 min.

Two products were formed: 2,6-dinitrophenol **2**, the substitution product and 7-nitro-2-n-propyl-1*H*-benzimidazole 3-oxide **3**, a cyclization product [eqn. (1)]. The isolation of these compounds was made from a reaction in 60% v/v 1,4-dioxane–water at reflux.[13]

In Table 1 are listed the observed rate constants, k_{obs}, the molar fractions of **2** and **3**, and the pseudo-first-order rate constants for the formation of the products, k_P and k_N, for **2** and **3** respectively.

It can be seen that the relative yields of the products depend on the HO^- concentration and that the relative amount of **2** is much lower at low than at high HO^- concentration.

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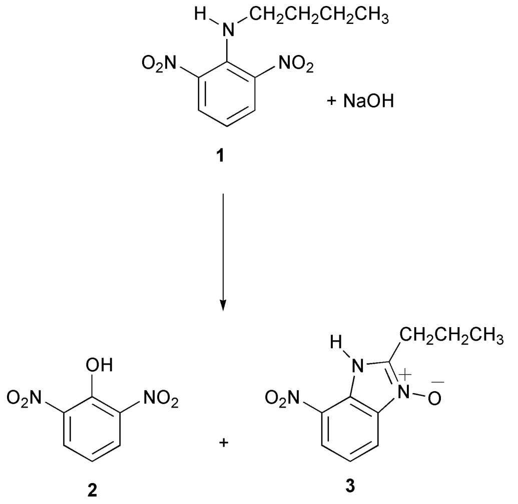
Table 1 Rate constants and product yield for the reaction of *N*-n-butyl-2,6-dinitroaniline **1** with NaOH at 25 °C in 10% 1,4-dioxane–water[a]

[NaOH]/M	$k_{obs}/10^{-4}$ s^{-1}	X_P[b]	$k_P/10^{-5}$ s^{-1}[c]	X_N[d]	$k_N/10^{-5}$ s^{-1}[e]
0.080	0.042	0.095	0.040	0.905	0.380
0.100	0.066	0.072	0.047	0.928	0.612
0.119	0.063	0.119	0.075	0.881	0.555
0.161	0.093	0.142	0.132	0.858	0.798
0.204	0.141	0.109	0.153	0.891	1.26
0.252	0.150	0.184	0.276	0.816	1.22
0.306	0.217	0.161	0.349	0.839	1.82
0.350	0.279	0.189	0.527	0.811	2.26
0.397	0.317	0.194	0.615	0.806	2.56
0.449	0.369	0.234	0.863	0.766	2.83
0.496	0.427	0.258	1.10	0.742	3.17
0.550	0.471	0.289	1.36	0.711	3.35
0.596	0.510	0.299	1.53	0.701	3.58
0.650	0.645	0.351	2.26	0.649	4.19
0.651	0.650	0.371	2.41	0.629	4.09
0.697	0.716	0.386	2.76	0.614	4.40
0.702	0.634	0.346	2.19	0.654	4.15
0.751	0.825	0.397	3.28	0.603	5.39
0.797	0.866	0.417	3.61	0.583	5.05
0.846	0.900	0.445	4.01	0.555	5.00
0.850	0.857	0.442	3.79	0.558	4.78
0.851	0.891	0.449	4.00	0.551	4.91
0.895	0.960	0.461	4.43	0.539	5.17
0.896	0.911	0.464	4.23	0.536	4.88
0.916	0.914	0.438	4.00	0.562	5.14
0.950	0.900	0.473	4.26	0.527	4.74
0.951	1.00	0.483	4.83	0.517	5.17
1.000	1.14	0.495	5.64	0.505	5.76
1.000[f]	1.13	[g]		[g]	
1.000[h]	0.900	[g]		[g]	
1.000[i]	1.13	[g]		[g]	
1.000[j]	1.100	[g]		[g]	

[a] Ionic strength I = 1 M (NaCl); $[\mathbf{1}]_0 = 8.00 \times 10^{-5}$ M. [b] Molar fraction of phenol **2**. [c] Pseudo-first-order rate constant for the formation of **2**. [d] Molar fraction of *N*-oxide **3**. [e] Pseudo-first-order rate constant for the formation of **3**. [f] $[\mathbf{1}]_0 = 2.01 \times 10^{-5}$ M. [g] Not determined. [h] $[\mathbf{1}]_0 = 4.00 \times 10^{-5}$ M. [i] $[\mathbf{1}]_0 = 6.00 \times 10^{-5}$ M. [j] $[\mathbf{1}]_0 = 1.00 \times 10^{-4}$ M.



(1)

The observed rate constant, k_{obs}, is independent of substrate concentration (Table 1) and is non-linearly correlated with NaOH concentration.

The non-linear plot of k_P, the pseudo-first-order observed rate constant for the formation of **2**, *vs.* [HO$^-$] (Fig. 2) was fitted by eqn. (2).

$$k_P = (5.20 \pm 0.09) \times 10^{-5}[\mathrm{HO}^-]^2 \qquad (2)$$

On the other hand, k_N, the pseudo-first-order observed rate constant for the formation of **3**, depends linearly on HO$^-$ concentration according to eqn. (3) (Fig. 3).

$$k_N = (2 \pm 1) \times 10^{-6} + (5.6 \pm 0.2) \times 10^{-5}[\mathrm{HO}^-] \qquad (3)$$

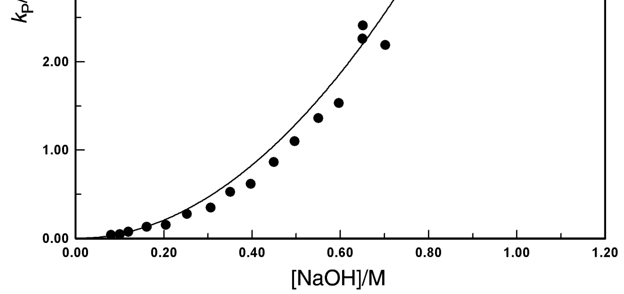


Fig. 2 Plot of k_P *vs.* [NaOH] for the formation of **2** from **1** at 25 °C. $[\mathbf{1}]_0 = 7.78 \times 10^{-5}$ M. Solvent 10% 1,4-dioxane–water. The line was drawn using eqn. (2).

Although we work at constant ionic strength, it is likely that the deviation of the activity coefficient of HO$^-$ from unity[14,15] may contribute to the small dispersion of the experimental data from a strictly second order dependence. Nevertheless, this should only affect slightly the numbers of the calculated parameters. The activity coefficient effect cannot be the main reason for the second order dependence because if that was the case, a similar deviation should be observed for k_N.

Table 2 Rate constants and product yield for the reaction of *N*-n-butyl-2,6-dinitroaniline **1** with NaOH at 25 °C in 60% 1,4-dioxane–water[a]

[NaOH]/M	$k_{obs}/10^{-6}\ s^{-1}$	X_P[b]	X_N[c]
0.021	1.64	0.010	0.990
0.042	3.20	0.003	0.998
0.063	4.54	0.000	1.000
0.080	5.72	0.003	0.997
0.098	7.20	0.020	0.980
0.119	8.00	0.010	0.990
0.140	10.0	0.009	0.991
0.161	11.2	0.006	0.994
0.182	12.4	0.006	0.994
0.203	14.0	0.001	0.990

[a] Ionic strength $I = 0.2$ M (NaCl); $[\mathbf{1}]_0 = 2.01 \times 10^{-5}$ M. [b] Molar fraction of phenol **2**. [c] Molar fraction of *N*-oxide **3**.

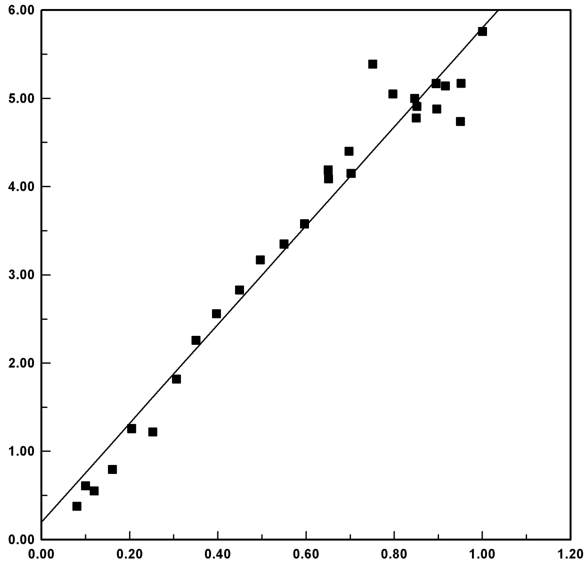


Fig. 3 Plot of k_N *vs.* [NaOH] for the formation of **3** from **1** at 25 °C. $[\mathbf{1}]_0 = 7.78 \times 10^{-5}$ M. Solvent 10% 1,4-dioxane–water. The line was drawn using eqn. (3).

We have also investigated the reaction of **1** with NaOH in 60% 1,4-dioxane–water at 25 °C. Under these conditions, only *N*-oxide **3** could be detected spectrophotometrically, within experimental error (Table 2). So, k_{obs} was taken as equal to k_N. The plot of k_N *vs.* HO^- (Fig. 4) can be fitted by eqn. (4).

$$k_N^{60} = (3 \pm 1) \times 10^{-7} + (6.7 \pm 0.1) \times 10^{-5}[HO^-] \qquad (4)$$

Another *N*-alkyl derivative of dinitroaniline, namely *N*-n-butyl-2,4-dinitroaniline **4**, behaves differently. The reaction of **4** in 20% 1,4-dioxane–water with NaOH 1 M at 25 °C gives only 2,4-dinitrophenol with a second order rate constant of 8×10^{-7} $M^{-1}\ s^{-1}$. The substitution product was also the only product found in 60% 1,4-dioxane–water at reflux.[13]

In order to investigate the role of the H in the amino group, we studied the reaction of *N*-n-butyl-*N*-methyl-2,6-dintroaniline **5** with NaOH 1 M in 10% 1,4-dioxane–water at 25 °C. No cyclization product was found and only 2,6-dinitrophenol **2** was formed with $k_{obs} = 1.56 \times 10^{-6}\ s^{-1}$. When this compound was heated at reflux in 60% 1,4-dioxane–water after 48 hours, no *N*-oxide was found and the only product formed was phenol (10%).

Discussion

We reported previously that the interaction of KOH with **1** in 30% DMSO-water at 25 °C could be described as shown in Scheme 1.[16]

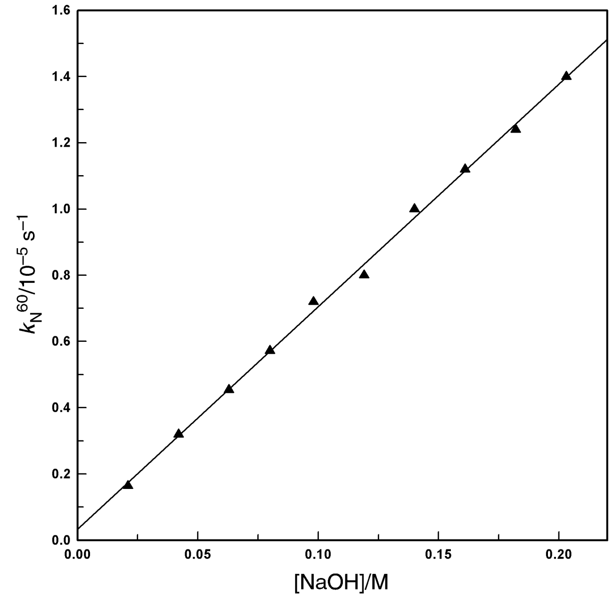
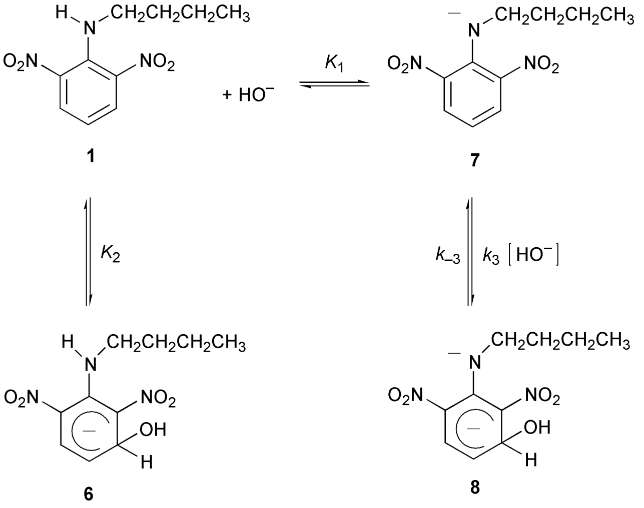


Fig. 4 Plot of k_N^{60} *vs.* [NaOH] for the formation of **3** from **1** at 25 °C. $[\mathbf{1}]_0 = 7.78 \times 10^{-5}$ M. Solvent 60% 1,4-dioxane–water. The line was drawn using eqn. (4).



Scheme 1

The values $K_1k_3 = 1.2 \times 10^3\ M^{-1}\ s^{-1}$ and $K_1K_3 = 41\ M^{-2}$ were calculated.[16]

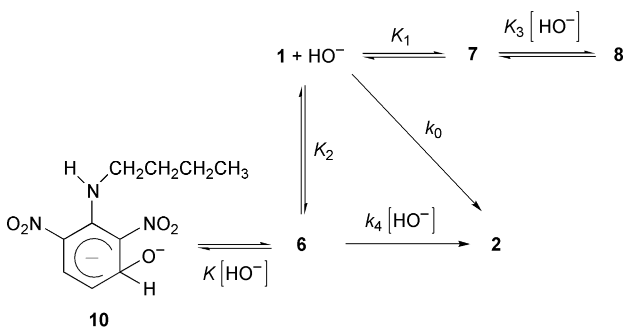
An acid base reaction such as that depicted in Scheme 1 to give **7**, was proposed before for 2,4- and 2,6-dinitroaniline with $NaCH_3O$ in DMSO–CH_3OH 75 : 25 v/v,[17] and for *N*-n-butyl-2,4,6-trinitroaniline **9** with n-butylamine in DMSO.[18]

We have also proposed the same type of ionization for *N*-n-butyl-2,4,6-trinitroaniline **9** with NaOH in 10% 1,4-dioxane–water, which gives 2,4,6-trinitrophenol as the only product.[19]

On the other hand, we have found that σ-complexes formed by addition of a nucleophile to unsubstituted ring positions of aromatic substrates favours the substitution of the leaving group in the reaction of some 2,4-dinitro and 2,4,6-trinitroanilines,[1,8,19] and *O*-ethyl *S*-(2,4,6-trinitrophenyl) thio- and dithiocarbonates.[20] Nucleophilic displacement of the leaving group by hydroxide within 3-hydroxy σ-complexes was also proposed previously for the reaction of 1-X-2,4,6-trinitrobenzene (X = NO_2, Cl or OMe) in water.[14]

Taking all these into consideration, we propose the mechanism shown in Scheme 2 for the substitution of n-butylamine in **1**.

The rate equation for the mechanism of Scheme 2 is given by eqn. (5).



Scheme 2

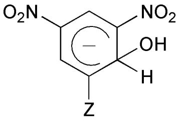
$$k_p = \frac{k_0[HO^-] + K_2k_4[HO^-]^2}{1 + (K_1 + K_2)[HO^-] + (K_1K_3 + K_2K)[HO^-]^2} \qquad (5)$$

Eqn. (5) can be reduced to eqn. (6) if the terms in the denominator are smaller than 1.

$$k_p = k_0[HO^-] + K_2k_4[HO^-]^2 \qquad (6)$$

The value of K_1 can be estimated from the pK_a of **1**. The pK_a of **9** was calculated as 13.60 from kinetic data.[19] Assuming that the difference in pK_a between **1** and **9** is the same as that for pK_{BH}^+ for 2,6-dinitroaniline and 2,4,6-trinitroaniline, *i.e.* 4.56,[21] we estimate a value of 18.16 for the pK_a of **1** and calculate $K_1 \approx 7 \times 10^{-5}$ M^{-1}.

K_2 was estimated as 6×10^{-7} M^{-1} from the ratio of the equilibrium constants for the formation of complexes **11a** and **11b** ($K_{11a} = 23$ M^{-1}, $K_{11b} = 10^{-6}$ M^{-1})[22] and the corresponding value for **9** (15 M^{-1}).[19] A value of $K \leq 1$ M^{-1} was estimated as was observed for trinitrobenzene derivatives.[1,20]



11a Z = NO_2
11b Z = H

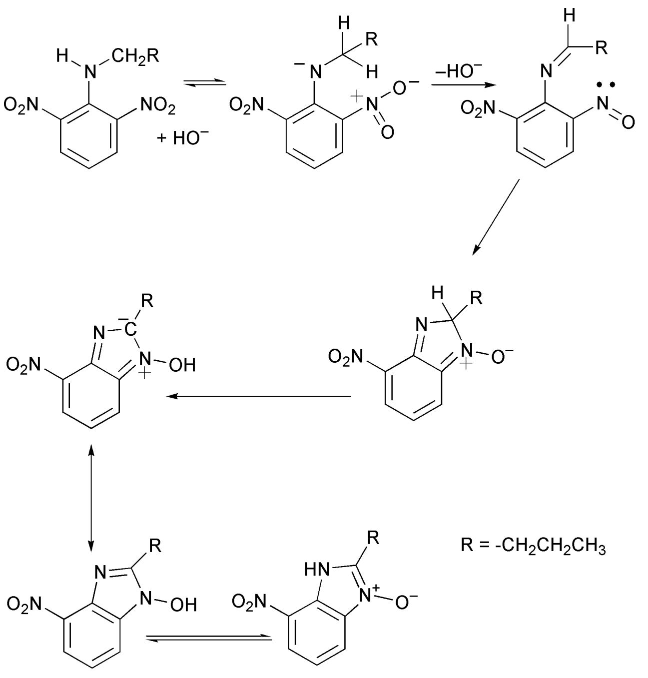
If K_3 corresponds to the addition of HO^- on the anion **7**, then the value should be smaller than K_2 since this represents the equilibrium constant for the addition of HO^- on **1** which is a neutral species. Therefore $K_1K_3 \ll K_1$ and eqn. (6) apply under all our experimental conditions.

The value of k_0 is also small compared with K_2k_4. For the reaction of 2,4,6-trinitro-1-piperidinobenzene and 1-morpholino-2,4,6-trinitrobenzene the ratios are 0.069 and 0.065 respectively,[1] while for 2,4,6-trinitro-1-pyrrolidinobenzene[1] and **9**,[19] the ratios are 0.218 and 0.221 respectively. From k_0 for the reaction of **9**, *i.e.* 0.00199 M^{-1} s^{-1},[19] and the ratio of the rate constants for the reaction of methoxide in methanol with 1-fluoro-2,4,6-trinitrobenzene and 1-fluoro-2,6-dinitrobenzene,[23] we estimate k_0 in Scheme 2 as 1.1×10^{-6} M^{-1} s^{-1} which gives a value of 0.021 for the ratio k_0/K_2k_4.

The importance of the formation of a σ complex intermediate is evident if one considers the rate constant for phenol formation for compounds **1** and **4**. The latter is about 70 times less reactive than the former in agreement with results reported which indicate that 2,4-dinitroanilines have less tendency to add bases than 2,6-dinitroanilines.[17]

A possible mechanism for the formation of **3** is shown in Scheme 3.†

The first step of the mechanism is the ionisation of substrate **1**; the absence of formation of *N*-oxide in the reaction of *N*-butyl-*N*-methyl-2,6-dinitroaniline **5** both in 10% and 60% 1,4-dioxane–water is a good proof of the need to generate a negative charge over the nitrogen of the amino group in order to give the cyclization product.



Scheme 3

The reduction of nitro to nitroso groups of benzene derivatives in basic solutions is a well documented reaction.[24]

The fact that when the reaction is carried out in 60% 1,4-dioxane–water at 25 °C no phenol is formed indicates that the transition state for the formation of **3** must be less polar than that leading to the phenol. The intermediates proposed in Scheme 3 are in agreement with these.

The presence of a second *o*-nitro group must have an important but yet not clear role in the formation of *N*-oxide because in the reaction of *N*-n-butyl-2,4-dinitroaniline **4** with NaOH both in 10% and 60%[13] 1,4-dioxane–water only the corresponding phenol was formed in spite of the fact that it was observed that proton loss is the major mode of reaction of 2,4-dinitroaniline and its *N*-alkyl derivatives with sodium methoxide in methanol.[17]

Experimental

Materials

N-n-Butyl-2,6-dinitroaniline **1**, *N*-n-butyl-2,4-dinitroaniline **4**, and 7-nitro-2-n-propyl-1*H*-benzimidazole 3-oxide **3** were available from previous work.[13]

N-n-Butyl-*N*-methyl-2,6-dinitroaniline was synthesised from 1-chloro-2,6-dinitrobenzene and *N*-n-butyl-*N*-methylamine. *N*-n-Butyl-*N*-methylamine was prepared as described previously;[25] a mixture of *N*-n-butyl-*N*-methylamine (62%) and n-butylamine (38%) identified and quantified by ^{1}H NMR was obtained. To 0.3270 g of 1-chloro-2,6-dinitrobenzene dissolved in 1.6 mL of *N*,*N*-dimethylformamide, 0.32 mL of the mixture of amines were added. After 5 h of stirring in the dark at room temperature, the reaction was poured over cold water and the precipitate was vacuum filtrated. A mixture of *N*-n-butyl-*N*-methyl-2,6-dinitroaniline **5**, *N*-n-butyl-2,6-dinitroaniline **1** and 1-chloro-2,6-dinitrobenzene was obtained. By column chromatography over silica gel compound **5** was isolated (mp 51–52.5 °C). It was identified by ^{1}H NMR.

1,4-Dioxane was purified as described previously.[10] Water purified in a Millipore Milli-Q apparatus was used throughout.

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† We thank Professor Scorrano for helpful suggestions in regard to this mechanism.

All of the inorganic reagents were of analytical-reagent grade and were used without further purification.

UV spectra and kinetic measurements were recorded on a Shimadzu UV-2101PC spectrophotometer and the change in absorbance during a kinetic run was measured on the same instrument. NMR spectra were recorded on a Brucker ACE 200 instrument.

Kinetic procedures

Reactions were initiated by adding the substrate dissolved in 1,4-dioxane to a solution containing all the other constituents. The reaction temperature was 25 ± 0.01 °C and NaCl was used throughout as compensating electrolyte. In the reactions in 10 or 20% v/v 1,4-dioxane–water the ionic strength was 1 M while for those in 60% v/v 1,4-dioxane–water, it was 0.2 M.

All kinetic runs were carried out under pseudo-first-order conditions, with substrate concentrations of about 2–8 $\times 10^{-5}$ M.

The reactions of **1** and **4** were followed by measuring the decrease in absorbance of 3 mL aliquots of the reaction solution taken at different reaction times and poured over 1 mL HCl 3 M at 442 nm for the reaction of compound **1** in 10% v/v 1,4-dioxane–water, 437 nm for **1** in 60% v/v 1,4-dioxane–water and 363 nm for **4** in 20% v/v 1,4-dioxane–water. The reaction of compound **5** was followed by measuring the increase in absorbance of the reaction mixture at 433 nm.

The yield of **2** and **3** was determined spectrophotometrically from the absorbance of solutions after ~10 half lives. For the reaction of **1** in 10% v/v 1,4-dioxane–water, the absorbance in basic media at 370 and 432 nm was recorded. At 370 nm the extinction coefficients are 2699 $cm^{-1} M^{-1}$ and 5552 $cm^{-1} M^{-1}$ for **2** and **3** respectively, while at 432 nm the extinction coefficient for **2** is 9080 $cm^{-1} M^{-1}$ and for **3** is 2477 $cm^{-1} M^{-1}$. On the other hand, in 60% v/v 1,4-dioxane–water, better results for the quantification of **2** and **3** were obtained in acid media. The absorbance of an aliquot of the reaction solution acidified as described for the kinetic measurements recorded at 297.5 and 346 nm were used. At 297.5 nm the extinction coefficients are 2084 $cm^{-1} M^{-1}$ and 7057 $cm^{-1} M^{-1}$ for **2** and **3** respectively and at 346 nm, the extinction coefficient of **2** is 4726.7 $cm^{-1} M^{-1}$ and of **3** is 1443.1 $cm^{-1} M^{-1}$. The wavelengths chosen in each case correspond to those where the greater difference in extinction coefficients for the two compounds were found.

In the case of the reactions of compounds **4** and **5**, the spectra of the solutions at infinity were compared with solutions of the corresponding phenols under the same reaction conditions.

Acknowledgements

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