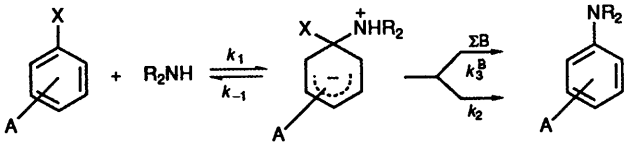
The Mechanism of Aromatic Nucleophilic Substitution Reactions in Protic Solvents. The Reactions of Aniline, *N*-Methylaniline, n-Butylamine, and Piperidine with some Nitroaryl Phenyl Ethers in Methanol

Thomas A. Emokpae,[a] Jack Hirst*[,b] and Patrick U. Uwakwe[a]
[a] *Department of Chemistry, University of Lagos, Nigeria*
[b] *Department of Chemistry, Queen's University, Kingston, Ontario*

In methanol, the reactions of aniline with 2-phenoxy-3,5-dinitropyridine, phenyl 2,4,6-trinitrophenyl ether, and 4-nitrophenyl 2,4,6-trinitrophenyl ether and the last-named substrate with *N*-methylaniline are general-base catalysed. The reaction of 2,6-dinitrophenyl phenyl ether with n-butylamine is not base catalysed, but its reaction with piperidine is specific-base catalysed. The results are discussed in terms of the mechanism of aromatic nucleophilic substitution reactions in protic solvents.

Many aromatic nucleophilic substitution reactions in which primary and secondary amines are the nucleophiles, are general-base catalysed. The overall mechanism of these reactions is believed to be that given in Scheme 1 where A denotes

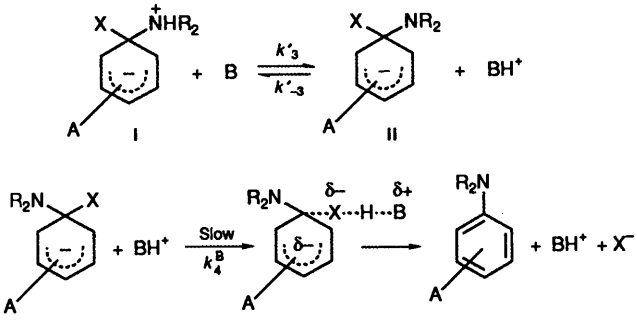


Scheme 1.

a generalised substituent, ΣB represents total base in solution, and when the only added base is the amine, $\Sigma k_3^B[B] = k_3^A[\text{amine}]$. Application of the steady state hypothesis gives equation (1) where k_A is the observed second order rate constant.

$$k_A = \frac{k_1(k_2 + \Sigma k_3^B[B])}{k_{-1} + k_2 + \Sigma k_3^B[B]} \quad (1)$$

Bunnett and Davis[1] proposed that the mechanism of the base-catalysed decomposition was that given in Scheme 2. In



Scheme 2.

this mechanism there is a fast proton transfer from the first formed intermediate to give its conjugate base, followed by a slow electrophilically catalysed expulsion of the leaving group. On this interpretation k_3^B (Scheme 1) = $k_4^B K_B$, where K_B = [II][BH^+]/[I][B]. Originally the mechanism given in Scheme 2 was believed to apply to reactions in both protic and dipolar solvents, the SB–GA (specific base–general acid) mechanism. Bernasconi *et al.*,[2] however, have interpreted the general-base catalysis in protic solvents as due to a rate-limiting proton transfer between the intermediates **1** and **2** in Scheme 2. Their arguments against the SB–GA mechanism are as follows (see Scheme 3).

Treatment of MH and M^- as steady-state intermediates gives equation (2). In protic solvents (SOH) where the only

$$k_A = \frac{k_1k_2(k_{-3p} + k_4) + k_1k_{3p}k_4}{(k_{-1} + k_2)(k_{-3p} + k_4) + k_{3p}k_4} \quad (2)$$

added base is the nucleophile, equations (3)–(5) apply, where

$$k_{3p} = k_{3p}^{os}[OS^-] + k_{3p}^{\wedge}[R_2NH] \quad (3)$$

$$k_{-3p} = k_{-3p}^{os} + k_{3p}^{\wedge}[R_2NH_2^+] \quad (4)$$

$$k_4 = k_4^{os} + k_4^{\wedge}[R_2NH_2^+] \quad (5)$$

OS^- is produced by the equilibrium

$$R_2NH + SOH \rightleftharpoons R_2NH_2^+ + OS^-$$

k_{3p}^{os} and $k_{3p}^{\wedge}$ are the rate constants for deprotonation of MH by OS^- and the amine respectively, k_{-3p}^{os} and $k_{-3p}^{\wedge}$ refer to protonation of M^- by the solvent and $R_2NH_2^+$ respectively, k_4^{os} refers to the uncatalysed expulsion of the leaving group X and $k_4^{\wedge}$ to its loss electrophilically assisted by $R_2NH_2^+$.

The rate-limiting proton transfer mechanism requires the loss of the leaving group from M^- to be much faster than reprotonation of M^- to give MH, *i.e.* $k_4 \gg k_{-3p}$. Under this condition deprotonation of MH becomes rate limiting and equation (2) becomes equation (6). Comparison of equation (6)

$$k_A = \frac{k_1(k_2 + k_{3p})}{(k_{-1} + k_2 + k_{3p}} = \frac{k_1(k_2 + k_{3p}^{os}[OS^-] + k_{3p}^{\wedge}[R_2NH])}{k_{-1} + k_2 + k_{3p}^{os}[OS^-] + k_{3p}^{\wedge}[R_2NH])} \quad (6)$$

with equation (1) gives $k_3^{\wedge} = k_{3p}^{\wedge}$; $k_3^{os} = k_{3p}^{os}$.

For the SB–GA mechanism the departure of the leaving group is slow and rate limiting, $k_4 \ll k_{-3p}$, hence equation (2) becomes equation (7), where $K_{3p} = k_{3p}/k_{-3p}$, or equation (8).

$$k_A = \frac{k_1[k_2 + k_4K_{3p}]}{k_{-1} + k_2 + k_4K_3} \quad (7)$$

$$k_A = \frac{k_1(k_2 + k_{4^A}K_{3p^A}[R_2NH] + k_{4^{OS}}K_{3p^{OS}}[OS^-])}{k_{-1} + k_2 + k_{4^A}K_{3p^A}[R_2NH] + k_{4^{OS}}K_{3p^{OS}}[OS^-]} \quad (8)$$

Comparison with equation (1) gives $k_{3^A} = k_{4^A}K_{3p^A}$: $k_{3^{OS}} = k_{4^{OS}}K_{3p^{OS}}$. As this reaction shows general-base catalysis, the expulsion of the leaving group is strongly electrophilically catalysed, *i.e.* $k_{4^A}[k_2NH_2^+]$ in equation (5) is large.

A variation on this mechanism involves loss of the leaving group without electrophilic catalysis, *i.e.* $k_{4^A} = 0$ or is very small. Equation (8) becomes equation (9). The reaction no

$$k_A = k_1(k_2 + k_{4^{OS}}K_{3p^{OS}}[OS^-])/(k_{-1} + k_2 + k_{4^{OS}}K_{3p^{OS}}[OS^-]) \quad (9)$$

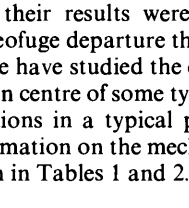
longer shows general base catalysis, but specific base (SB) catalysis.

Bernasconi *et al.*[2] have noted that in protic solvents there is evidence that catalysis of alkoxide ion expulsion from Meisenheimer complexes is weak, or occurs only with acids considerably more acidic than $R_2\overset{+}{N}H_2$. When the nucleofuge is a much better leaving group such as phenoxide, catalysis would not be expected on theoretical grounds as proton transfer from $R_2\overset{+}{N}H_2$ to ^-OPh is thermodynamically unfavourable. It should be noted that the amines referred to above are relatively strong bases such as n-butylamine and piperidine.

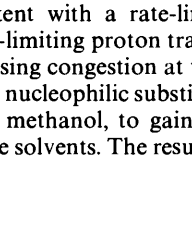
Using rates obtained from measurements on the decomposition of Meisenheimer complexes, with 'suitable extrapolation', Bernasconi showed that when the leaving group is phenoxide, $k_4 \gg k_{-3p}$ (Scheme 3), not $k_4 \ll k_{-3p}$ as required by the SB–GA mechanism. When the leaving group is a much poorer one such as methoxide the evidence against the SB–GA mechanism is less compelling, the strongest evidence being that in 60% aqueous dioxane the reaction of 2,4-dinitroanisole with piperidine shows specific-base catalysis while the reaction with n-butylamine is general-base catalysed.

Subsequent evidence shows that the reactions of some 5-substituted 2-methoxy-3-nitrothiophenes with piperidine in methanol[3] and the pyrrolidino- and piperidino-demethoxylation of the 4-methoxy-2,6-diphenylpyridinium ion in methanol[4] proceed by SB–GA mechanisms while the reaction of the 2,4,6-triphenylpyrylium ion with amines in methanol[5] and the Smiles rearrangement of 2-(*p*-nitrophenoxy)ethylamine in water[6] take place by a rate-limiting proton transfer mechanism. Bunnett and Cartano[7] studied the reactions of pyrrolidine and piperidine with 2,4-dinitrophenyl- and 2,4-dinitro-6-methylphenyl phenyl ethers in 60% aqueous dioxane and concluded that their results were more consistent with a rate-limiting nucleofuge departure than with a rate-limiting proton transfer.

We have studied the effect of increasing congestion at the reaction centre of some typical aromatic nucleophilic substitution reactions in a typical protic solvent, methanol, to gain more information on the mechanism in these solvents. The results are given in Tables 1 and 2.



(1)



(2) R = H, $R^1 = NO_2$
(3) $R = R^1 = NO_2$
(4) $R = R^1 = H$

Discussion

The second-order rate constants k_A for the reactions of 2-phenoxy-3,5-dinitropyridine **1** and 2,4,6-trinitrophenyl phenyl ether **2** increase linearly with increasing nucleophile concentration, *i.e.* $k_A = k' + k''$[nucleophile].

The addition of aniline hydrochloride leads to a slight increase in k_A for the reactions of 2-phenoxy-3,5-dinitropyridine and 2,4,6-trinitrophenyl phenyl ether with aniline and this, together with the data in Table 2 shows that under the experimental conditions employed, the concentration of methoxide ion produced by the solvolysis of aniline is too small appreciably to catalyse the reaction. The addition of the hydrochloride of the nucleophile does result in a substantial reduction in the rate constants for the reactions of 2,4,6-trinitrophenyl 4-nitrophenyl ether **3** with aniline and *N*-methylaniline. We do not believe, however, that this reduction indicates catalysis by methoxide ion in the absence of amine hydrochloride.

The effect of amine hydrochloride on the ratio k''/k' $\{=k_3^A/k_2$, equation (1) for the condition $k_{-1} \gg k_2 + \Sigma k_3^B[B]\}$ varies from substrate to substrate. In the case of 2-phenoxy-3,5-dinitropyridine, addition of 0.1 mol dm^{-3} aniline hydrochloride has only a small effect, increasing the ratio from 103 ± 36 to 158 ± 18, whereas for 2,4,6-trinitrophenyl phenyl ether the addition of 0.02 mol dm^{-3} hydrochloride reduces the ratio from 840 ± 300 to 338 ± 74. When the leaving group is 4-nitrophenoxy, both the reaction with aniline and that with *N*-methylaniline have low values of k''/k', 35 ± 0.5 and 31 ± 0.5, respectively. According to Bunnett's[8] criteria this could signify no catalysis and the linear increase of k_A with increasing nucleophile concentration could be an example of 'linear accelerations of unknown origin'.[8] The addition of 0.1 mol dm^{-3} hydrochloride, however, results in a large increase in k''/k' to 338 ± 60 and 208 ± 22, respectively.

Inspection of the individual values of k' and k'' shows that in all cases the addition of hydrochloride has little effect on k''; the variation is due almost entirely to changes in k'. In terms of Scheme 1, $k' = k_1k_2/k_{-1}$ and $k'' = k_1k_3^A/k_{-1}$. Hence addition of hydrochloride has little effect on k_3^A for all substrates, gives a slight decrease in k_2 when the substrate is 2-phenoxy-3,5-dinitropyridine, a $2\frac{1}{2}$-fold increase when it is the 2,4,6-trinitrophenyl phenyl ether, and reductions of approximately 13- and 8-fold for the reactions of 4-nitrophenyl 2,4,6-trinitrophenyl ether with aniline and *N*-methylaniline, respectively. A tentative explanation of these results is as follows. The mechanism of the uncatalysed path in protic solvents is usually discussed in terms of the unimolecular decomposition of an internally hydrogen-bonded intermediate as in Fig. 1, while

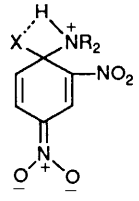


Fig. 1.

Bernasconi[2] has advocated a rate-limiting departure of the leaving group from MH (Scheme 3) followed by fast loss of a proton. The following discussion is applicable to either mechanism, if it is assumed that in the presence of relatively large concentrations of hydrochloride, acid-catalysed departure of the leaving group can compete with the hydrogen bonded mode of decomposition.

Bernasconi[9] has pointed out that a factor leading to the reduction of k_2 and k_3^B in Scheme 1 is steric hindrance by *ortho*-

Table 1. Rate constants for the reactions of some phenyl ethers (**1**–**4**)[a] with amines in methanol at 30 °C, and values of k' and k'' in the equation $k_A = k' + k''$[nucleophile].

Reaction	$[PhNH_2]/10^{-2}$ mol dm^{-3}	$k_A/10^{-4}$ dm^3 mol^{-1} s^{-1}	k'/dm^3 mol^{-1} s^{-1}	k''/dm^3 mol^{-1} s^{-1}
1–$PhNH_2$	2.0	1.05	3.47×10^{-5}	3.57×10^{-3}
	4.0	1.80		
	6.0	2.55		
	8.0	3.23		
	10.0	4.00		
1–$PhNH_2$–$PhNH_3^+Cl^-$[b]	2.0	1.06	2.59×10^{-5}	4.10×10^{-3}
	4.0	1.95		
	6.0	2.70		
	8.0	3.54		
	10.0	4.35		
2–$PhNH_2$	0.6	120	1.92×10^{-3}	1.61
	0.8	148		
	1.0	182		
	2.0	330		
	3.0	510		
2–$PhNH_2$–$PhNH_3^+Cl^-$[c]	0.6	148	4.79×10^{-3}	1.62
	0.8	180		
	1.0	210		
	2.0	360		
	3.0	541		
3–$PhNH_2$	0.5	260	2.23×10^{-2}	77.1
	1.0	300		
	2.0	381		
	3.0	455		
	4.0	530		
3–$PhNH_2$–$PhNH_3^+Cl^-$[b]	1.0	75	1.67×10^{-3}	56.4
	2.0	130		
	3.0	185		
	4.0	240		
	5.0	295		
	6.0	360		
3–PhNHMe	4.0	2.15	9.60×10^{-5}	2.98×10^{-3}
	6.0	2.74		
	8.0	3.35		
	10.0	3.93		
3–PhNHMe–$PhNMeH_2^+Cl^-$[b]	4.0	1.15	1.24×10^{-5}	2.58×10^{-3}
	6.0	1.68		
	8.0	2.19		
	10.0	2.70		
4–piperidine–piperidineH^+Cl^-[b]	5.0	0.0130	1.15×10^{-7}	2.34×10^{-5}
	10.0	0.0243		
	15.0	0.0361		
	20.0	0.0480		
4–Bu^nNH_2–$Bu^nNH_3^+Cl^-$[b]	5.0	20.4	1.93×10^{-3}	2.02×10^{-3}
	10.0	21.4		
	15.0	21.9		
	20.0	23.6		

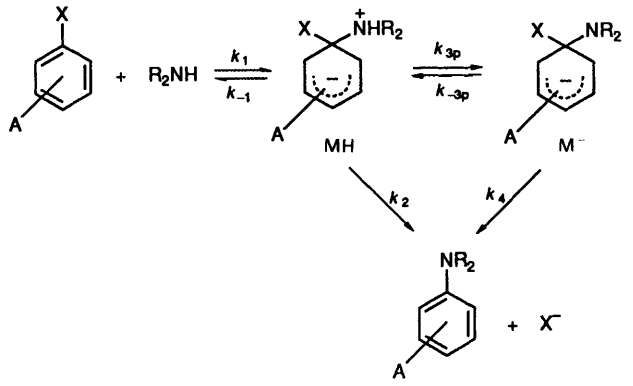
[a] [Substrate] = (5–35) $\times 10^{-5}$ mol dm^{-3}. [b] 0.1 mol dm^{-3}. [c] 0.02 mol dm^{-3}.

substituents to the resonance which occurs in the product (Fig. 2). The reaction of 2,4-dinitrophenyl phenyl ether with piperidine in 10% dioxane–90% water is catalysed by hydroxide ions[10] while the corresponding reaction with pyrrolidine is not;[11] in dimethyl sulphoxide the σ-adduct corresponding to **II** in Scheme 2 (M^- in Scheme 3) formed by the reaction of pyrrolidine with 2,4-dinitro-1-naphthyl ethyl ether decomposed to products 11 000 times faster than the corresponding adduct formed by piperidine.[12] Bunnett[12] has attributed the difference between the nucleophiles to steric interactions forced by the difference in conformation between the two amino groups in the σ-adduct as they release the nucleofuge. A similar reason has been given[13] to account for the difference in behaviour of the two amines with 2-methoxy-3-nitrothiophene in methanol; the reaction with piperidine is base catalysed whereas that with pyrrolidine is not. When the nucleophile is a primary aliphatic amine, if the effect exists at all, it is very much less than for piperidine. Thus in dimethyl sulphoxide the anionic σ-complex

Table 2. Effect of amine concentration,[a] at constant [methoxide], on the rate constants for the reactions of some phenyl ethers (**1**–**4**) with amines in methanol at 30 °C.

Reaction	[Amine]/ 10^{-2} mol dm^{-3}	[AmineH$^+$Cl$^-$]/ 10^{-2} mol dm^{-3}	$k_A/10^{-4}$ dm^3 mol^{-1} s^{-1}
1–$PhNH_2$–$PhNH_3^+Cl^-$	4.0	4.0	1.87
	6.0	6.0	2.62
	8.0	8.0	3.33
	10.0	10.0	4.31
1–$PhNH_2$–$PhNH_3^+Cl^-$	4.0	2.0	1.83
	6.0	3.0	2.58
	8.0	4.0	3.26
	10.0	5.0	4.05
2–$PhNH_2$–$PhNH_3^+Cl^-$	0.6	0.6	133
	0.8	0.8	154
	1.0	1.0	192
	2.0	2.0	355
3–$PhNH_2$–$PhNH_3^+Cl^-$	1.0	1.0	142
	2.0	2.0	175
	3.0	3.0	210
	4.0	4.0	253
	5.0	5.0	284
3–PhNHMe–$PhNMeH_2^+Cl^-$	4.0	4.0	1.52
	6.0	6.0	2.05
	8.0	8.0	2.44
	10.0	10.0	2.85
4–piperidine–piperidineH$^+$Cl$^-$	6.0	6.0	0.0240
	8.0	8.0	0.0238
	10.0	10.0	0.0243
	15.0	15.0	0.0240

[a] Ionic strength maintained at 0.1 mol dm^{-3} by addition of NaCl as required.



Scheme 3.

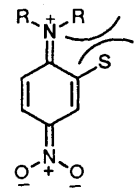


Fig. 2.

formed between n-butylamine and 2,4,6-trinitrophenetole decomposes with a rate constant of 8.3 dm^3 mol^{-1} s^{-1}, whereas the corresponding complex formed with piperidine remains in solution for several hours with little decomposition.[14] In the present system the considerable crowding that exists at the reaction centre is shown by the X-ray analysis[15] of one of the products, 2,4,6-trinitrodiphenylamine, which shows that the dihedral angle between the trinitrophenyl and phenyl rings is 52° and that the two *ortho* nitro groups are twisted from the plane of the benzene ring by 22 and 39° respectively.

In the present series, when the substrate contains the 3,5-dinitropyridine group, rate reductions arising from the above effect should be minimal. Any stabilization of the intermediate in Scheme 1 (MH in Scheme 3) by hydrogen-bonding between the oxygen atoms of the *ortho*-nitro group and the amino-hydrogen atoms of the added anilinium ions would be counterbalanced by a similar effect in the transition state of its decomposition and the effect of aniline hydrochloride on k_2 would be small. When the substrate contains the 2,4,6-trinitrophenyl moiety, the congestion at the reaction site is increased considerably and this will be augmented by hydrogen bonding between the *ortho*-nitro groups and added anilinium ions. Thus if a steric/stereoelectronic effect operates k_2 would be expected to be reduced by the addition of anilinium ions as is found with the 4-nitrophenoxy leaving group. When the leaving group is phenoxy the difference in pK values (pK_a H_2O, phenol 9.95, anilinium ion 4.62) constitutes a thermodynamic driving force for electrophilic catalysis. Hence the addition of aniline hydrochloride has two opposing effects resulting in a slight increase in k_2. The pK_a of 4-nitrophenol in water is 7.14, hence the driving force for catalysis by anilinium ions is considerably reduced. If this is a correct interpretation of the effect of aniline hydrochloride on k_2, it has implications for the mechanism of the base catalysed path. If this takes place by a rate-limiting proton transfer mechanism, the addition of anilinium ions will have little effect on k'', as is observed, but should result in a decrease in magnitude of k'' if it takes place by the SB–GA mechanism.

The reactions of n-butylamine and piperidine with the 3,5-dinitropyridine and trinitrophenyl substrates were too fast to measure by the techniques available to us, so the reactions of 2,6-dinitrophenyl phenyl ether (**4**) were studied instead. With this substrate, although the total activation is decreased compared to the phenyl 2,4,6-trinitrophenyl ether, the two compounds have the same degree of congestion at the reaction centre. The rate constants for the reaction of n-butylamine increase slightly with increasing nucleophile concentration, but the low value of 1.05 for the k''/k' ratio indicates that the reaction is not base catalysed.[8] This change in the position of the rate-limiting step between the 2,4,6-trinitrophenyl/aniline and 2,6-dinitrophenyl/n-butylamine systems is in accord with the usual effect of change of basicity of the nucleophile on the mechanism of aromatic nucleophilic substitution reactions. Thus the reaction of 1-fluoro-2,4-dinitrobenzene with n-butylamine in acetonitrile is not base catalysed,[16] whereas the corresponding reaction with aniline is catalysed.[17]

The reaction with piperidine is strongly catalysed, $k''/k' = 203$, and the data in Table 2 show that it is specific- not general-base catalysis. The piperidinodephenoxylation of 2,4-dinitrophenyl phenyl ether in methanol is base catalysed,[18] but the results do not distinguish between specific- and general-base catalysis; as the reaction shows general-base catalysis when the solvent is either 10[10] or 60%[7] dioxane–water it should exhibit this type of catalysis in methanol. Thus the change from general-base catalysis in the 2,4,6-trinitrophenyl/aniline and 2,4-dinitrophenyl/piperidine systems to specific-base catalysis in the 2,6-dinitrophenyl/piperidine system is not due to electronic effects but is associated with increased crowding at the reaction centre in the latter case.

The observation of specific-base catalysis means that in Scheme 3, $k_4 \ll k_{-3p}$ and k_4[A] is approximately zero, *i.e.* the reaction takes place *via* a relatively fast proton transfer to a base

followed by a rate limiting loss of the nucleofuge, which is not electrophilically assisted by the conjugate acid of the base. As mentioned earlier, this lack of catalysis is to be expected as there is no thermodynamic driving force for it. This has implications for the other two reactions for which general-base catalysis can be interpreted as being due to either the SB–GA or the rate-limiting proton transfer mechanisms. If the 2,4-dinitrophenyl phenyl ether–piperidine reaction takes place by the SB–GA mechanism, this implies that the switching of a nitro group from the 4- to the 6-position brings about a change in conditions from one in which the loss of the leaving group requires electrophilic assistance to one in which it does not. This could be due to steric hindrance to the approach of the electrophile to the leaving group, unless this approach is no more sensitive to steric effects than the reprotonation of M^- in Scheme 3. Crampton[19] has shown that although the reprotonation of the complex M^- formed from 1,3,5-trinitrobenzene and piperidine by the piperidinium ion in dimethyl sulphoxde is subject to strong steric retardation, this diminishes rapidly with increasing the protic content of the solvent, and in 30% Me_2SO–70% H_2O there is little difference in the rate constants for proton transfer from the pyrrolidinium and piperidinium ions to the complexes formed by their conjugate bases with trinitrobenzene.[20] If, however, the 2,4-dinitrophenylphenyl ether reaction takes place by a rate-limiting proton transfer, this implies that the switch of a nitro group from the 4- to the 6-position is accompanied by a change from $k_4 \gg k_{-3p}$ to $k_4 \ll k_{-3p}$ (Scheme 3). This is easily accounted for by significant stereo-electronic retardation of the loss of the leaving group by the piperidine moiety from the Meisenheimer complex formed by the attack of piperidine on the crowded reaction centre.

The implications for the reaction of aniline with 2,4,6-trinitrophenyl phenyl ether are less clear cut. Stereoelectronic effects leading to reductions in the rate of the loss of the leaving group from the Meisenheimer complexes formed from 2,4,6-trinitrophenetole and primary acyclic amines are much less than those for piperidine, but thre is no evidence as to whether this holds for aniline and its *N*-methyl derivative, or whether the magnitude of the effect is sufficient to bring about the condition $k_4 \ll k_{-3p}$ in Scheme 3. If this condition does hold, the difference in basicity between phenoxide and the anilines could constitute a driving force for the SB–GA mechanism to operate.

Experimental

All substrates and products were prepared by standard methods and had melting points in accordance with literature values. Aniline was distilled over zinc dust and then over potassium hydroxide pellets in a stream of nitrogen. It was stored in dark bottles and redistilled immediately before use. *N*-Methylaniline was purified *via* the acetyl derivative. AnalaR grade piperidine was refluxed with sodium wire for 24 h and then distilled. AnalaR grade n-butylamine was distilled from potassium hydroxide pellets. The hydrochlorides of n-butylamine, piperidine, and *N*-methylaniline were prepared by passing dry hydrogen chloride through a solution of the amine in dry ether; aniline hydrochloride was prepared from aniline and concentrated hydrochloric acid. All hydrochlorides were purified by recrystallisation from ethanol–ether mixtures.

Kinetic measurements on the slower reactions were made using a pipette technique[21] in which aliquots of the reaction mixture were pipetted into volumetric flasks containing methanol (1.0 mol dm^{-3} in sulphuric acid) and the absorbance measured at the appropriate wavelength. Faster reactions were followed in the thermostatted cell compartment of a Pye Unicam SP 600 spectrophotometer. The concentrations of the nucleophiles were at least ten times those of the substrates and the reactions were followed to 60–70% completion. In all cases good first-order kinetics were obtained and the absorbances of the reaction mixtures at infinite time agreed with the calculated values.

References

1 J. F. Bunnett and G. T. Davies, *J. Am. Chem. Soc.*, 1960, **82**, 665.
2 C. F. Bernasconi, R. H. de Rossi and P. Schmid, *J. Am. Chem. Soc.*, 1977, **99**, 4090.
3 G. Consiglio, C. Arnone, D. Spinelli and R. Noto, *J. Chem. Soc., Perkin Trans. 2*, 1981, 642.
4 R. Aveta, G. Doddi and G. Illuminati, *J. Am. Chem. Soc.*, 1983, **105**, 5661.
5 G. Doddi, G. Illuminati, M. Mecozzi and P. Nunziante, *J. Org. Chem.*, 1983, **48**, 5268.
6 A. C. Knipe, J. Lourd-Keast and N. Sridhar, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1885.
7 J. F. Bunnett and A. Cartano, *J. Am. Chem. Soc.*, 1981, **103**, 4861.
8 J. F. Bunnett and R. H. Garst, *J. Am. Chem. Soc.*, 1965, **87**, 3875.
9 C. F. Bernasconi and R. H. de Rossi, *J. Org. Chem.*, 1976, **41**, 44.
10 J. F. Bunnett and C. F. Bernasconi, *J. Am. Chem. Soc.*, 1965, **87**, 5209.
11 J. F. Bunnett and D. H. Hermann, *Biochemistry*, 1970, **9**, 816.
12 J. F. Bunnett, S. Sekiguchi and L. A. Smith, *J. Am. Chem. Soc.*, 1981, **103**, 4865.
13 G. Consiglio, C. Arnone, D. Spinelli and R. Noto, *J. Chem. Soc., Perkin Trans. 2*, 1982, 721.
14 M. R. Crampton and P. J. Rowledge, *J. Chem. Soc., Perkin Trans. 2*, 1984, 573.
15 V. Dijakovic, W. Nowacki, A. Edenharter, P. Engel, B. Ribar and R. Halasi, *Cryst. Struct. Commun.*, 1973, **2**, 411.
16 D. Ayediran, T. O. Bamkole and J. Hirst, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1396.
17 J. Kavalek, J. Haasova and V. Sterba, *Collect. Czech. Chem. Commun.*, 1972, **32**, 3333.
18 D. Ayediran, T. O. Bamkole, J. Hirst and I. Onyido, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1580.
19 M. R. Crampton and C. Greenhalgh, *J. Chem. Soc., Perkin Trans. 2*, 1983, 1175.
20 C. F. Bernasconi, M. C. Muller and P. Schmid, *J. Org. Chem.*, 1979, **44**, 3189.
21 T. O. Bamkole, C. W. L. Bevan and J. Hirst, *Niger. J. Sci.*, 1968, **2**, 11.

Paper 0/01443E
Received 2nd *April* 1990
Accepted 15th *June* 1990