The Mechanisms of Nucleophilic Substitution Reactions of Aromatic Ethers with Amines in Benzene

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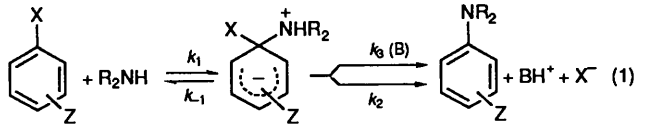
The variation of the second-order rate constants with nucleophile concentration has been determined for the following reactions of some aromatic ethers with primary and secondary amines in benzene: 6-methyl-2,4-dinitrophenyl- and 2,6-dinitrophenyl phenyl ethers with piperidine, n-butylamine, morpholine and benzylamine; 2-phenoxy-3,5-dinitropyridine with these four nucleophiles and aniline; and 2,4,6-trinitrophenyl 4-nitrophenyl ether with *N*-methylaniline. An attempt has been made to rationalise the kinetic forms of these and similar reactions of other aromatic ethers in benzene.

The gross mechanism of aromatic nucleophilic substitution reactions when primary and secondary amines are the nucleophiles is well established (see Scheme 1). Application of



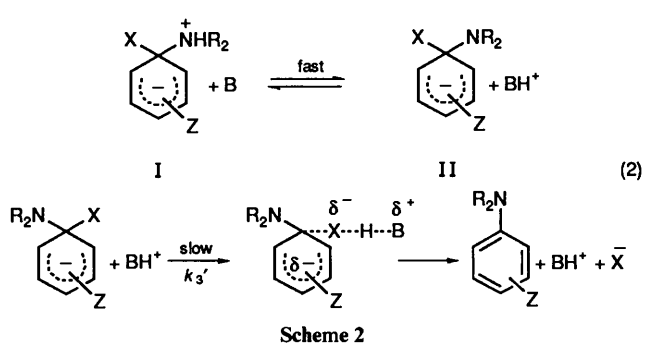
I

Scheme 1

the steady-state hypothesis gives eqn. (1), where k_A is the

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

observed second-second-order rate constant and B either a second molecule of the nucleophile or an added base. There is general agreement that in aprotic solvents such as cyclohexane and benzene the uncatalysed decomposition of the intermediate to products takes place unimolecularly *via* the hydrogen-bonded intermediate shown in Fig. 1, and that in dipolar aprotic solvents such as dimethyl sulphoxide and acetonitrile the mechanism of the base-catalysed path is that proposed by Bunnett and Davies[1] given in Scheme 2, often referred to as



Scheme 2

the special base–general acid (SB–GA) mechanism. In this mechanism there is a fast proton transfer between B and the first-formed intermediate to give its conjugate base followed by the slow, electrophilically assisted expulsion of the leaving group. There is controversy, however, as to whether this mechanism applies in protic solvents such as aqueous dioxane,[2] and Capon and Rees[3] have suggested that in aprotic solvents the catalysed

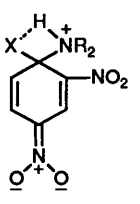


Fig. 1

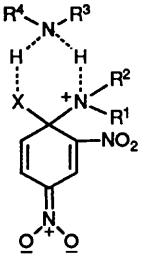


Fig. 2

reaction proceeds *via* a cyclic intermediate such as the one shown in Fig. 2.

Eqn. (1) allows three kinetic forms. If $k_{-1} \ll k_2 + k_3[B]$, then $k_A = k_1$ and the reaction is not base catalysed. If $k_{-1} \gg k_2 + k_3[B]$, then the equation has the form $k_A = k' + k''[B]$, and if no simplification of the equation can be made, plots of k_A *vs.* base concentration are curvilinear downwards. Frequently, however, in aprotic solvents a fourth kinetic form is observed in which plots of k_A *vs.* base concentration have upward curvatures. Several explanations of this abnormal behaviour have been given. Nudelman and Palleros[4] have suggested association of the nucleophile with the base prior to attack on the substrate followed by the base catalysed decomposition of the intermediate. Banjoko and Otiono[5] explained the third-order dependence on aniline concentration of the reaction of 2,4,6-trinitrophenyl phenyl ether with aniline in benzene by an initial attack of an aniline molecule on the substrate followed by the decomposition of the resulting intermediate *via* an eight-membered ring involving three aniline molecules. Ayediran, Bamkole, Hirst and Onyido[6] have proposed that in benzene, because of its low relative permittivity and consequent range of electrostatic forces, aggregates are formed within which mechanisms such as those proposed by Bunnett[1] can operate. They explain[7] the upward curving plots as being due to electrophilic catalysis of the expulsion of the leaving group by homo- and hetero-conjugates of the conjugate acid of the

nucleophile. They emphasize[8] that because of the range of electrostatic forces and the importance of hydrogen bonding in these solvents, several mechanisms can operate, the relative importance of which depends not only on the entities employed, but on their concentrations as well.

Recently[9] we observed that the reactions of 2,4-dinitrophenyl phenyl ether (but not of 1-fluoro-2,4-dinitrobenzene) with secondary amines in tetrahydrofuran (THF) and ethyl acetate were strongly catalysed by the nucleophile but were either not catalysed or showed only mild catalysis by 1,4-diazabicyclo-[2.2.2]octane (DABCO). This was explained by a second molecule of the nucleophile, hydrogen-bonded to the ethereal oxygen atom of the Meisenheimer complex, being most favourably situated for proton extraction, possibly to the exclusion of all other catalysts. It was pointed out that this should occur in aromatic substitution reactions of ethers in all solvents of low relative permittivity and gives a plausible mechanism for the formation of the cyclic transition states of Capon and Rees.[3] A further consequence was that values of the k_3/k_2 ratio should be high (for the kinetic form $k_A = k' + k''[B]$, when B is the nucleophile, $k''/k' = k_3/k_2$). It also enables the development of a rationale for the incidence of the upward curving plots obtained for ethers and other leaving groups which are good hydrogen-bond acceptors.

The formation of the zwitterionic intermediate **I** in Scheme 1 is accompanied by the formation of a hydrogen bond between the ammonio proton and the oxygen atoms of the *ortho*-nitro group. When the nucleophile is a secondary amine this is the hydrogen atom which is eliminated in the base catalysed step. If this hydrogen atom is relatively 'free', *i.e.* only weakly bonded to the *ortho*-nitro group then if there is a second molecule of the nucleophile anchored to the leaving group, both proximity and entropic effects will favour internal elimination over elimination by a third molecule of the nucleophile. Strong hydrogen-bonding, however, increases the possibility of the nucleophile attached to the leaving group becoming itself hydrogen-bonded to another molecule of the nucleophile and gives a reaction which is third rather than second order in the nucleophile. Bernasconi[10] has shown that when a series of amines form σ-complexes with the same substrate the ratio of the acidity constants of the complexes to those of the conjugate acids of the amines is approximately constant. Hence if the hydrogen-bond donor strength of the complexes increases with increasing acidity of the complexes, then for a given substrate, the strength of the *ortho*-nitro group hydrogen bond will increase with decreasing base strength of the nucleophile. Thus the reaction of secondary amines with aromatic ethers would be expected to have a greater tendency to exhibit a term third order in the nucleophile the more basic the ethereal oxygen atom, and for a given substrate, the weaker the nucleophile as a base. With primary amines the situation is obscured by the presence of a second ammonio proton and the result depends on the conformation the proton is forced to adopt because of the ammonio group/*ortho*-nitro group hydrogen bond. If this is favourable to attack by a molecule of the nucleophile attached to the oxygen atom of the leaving group a reaction second order in nucleophile concentration is promoted, and if the configuration is unfavourable, various paths are available which would give rise to a third-order component.

We have investigated the reactions in benzene of a series of aromatic phenyl ethers with piperidine and n-butylamine, morpholine and benzylamine, two sets of amine pairs where the primary and secondary amines have similar basicities in water[11] and acetonitrile,[12,*] and for the more reactive substrates with aniline and *N*-methylaniline. The results, together with those for 2-chloro-3,5-dinitropyridine with aniline are given in Table 1. The kinetic form of each of these reactions and those of other relevant reactions are summarised in Table 2.

Discussion

The following discussion is based on the kinetic form of the reactions. As this is determined by the relative magnitudes of several rate constants, it is possible that this is temperature dependent. The reactions of 6-methyl-2,4-dinitrophenyl phenyl ether with piperidine and morpholine and of 2-phenoxy-3,5-dinitropyridine with aniline were studied at different temperatures, but no significant change of form was observed.

Secondary Amines.—The reaction of 2,4-dinitrophenyl phenyl ether with morpholine in benzene is only very mildly catalysed by DABCO,[7] consequently the upward curvature of the plot of k_A *vs.* morpholine concentration is interpreted as being due to the decomposition of the intermediate to products taking place *via* a cyclic transition state containing three molecules of morpholine. As the reaction of this nucleophile with 6-methyl-2,4-dinitrophenyl phenyl ether and 2,6-dinitrophenyl phenyl ether has the same kinetic form we believe that the decomposition of their respective intermediates take place in a similar fashion.

When the substrates are 3,5-dinitro-2-phenoxypyridine and 2,4,6-trinitrophenyl phenyl ether, k_A has a linear dependence on the morpholine concentration. The introduction of an *ortho* aza or nitro group gives additional possibilities for resonance, lowering the electron density on the oxygen atoms of the original nitro group and consequently reducing the strength of the hydrogen bond formed with the ammonio proton of the intermediate **I**. This would favour a cyclic transition state which only contains two molecules of morpholine. Decomposition of the intermediate *via* a cyclic transition state, however, does not explain why the k_3/k_2 ratio increases with increased activation of the substrate. Alternatively the increased activation of the substrate reduces the basicity of the ethereal oxygen sufficiently to allow other mechanisms to compete successfully. Bernasconi[13] has given reasons why k_3/k_2 values should increase with increase of substrate activation for reactions in which the catalysed path takes place *via* the SB-GA mechanism and the uncatalysed one by the unimolecular mechanism. Kavalek and Stěrba[14] have shown experimentally that this increase does take place in the reactions of 4-substituted-2-nitrofluorobenzenes with piperidine in acetonitrile–benzene mixtures where reaction is believed to take place *via* these mechanisms.

Piperidine is a much stronger base than morpholine, hence the acidity of the ammonio hydrogen atoms of the intermediates which are formed in these reactions will be less, and consequently the strength of hydrogen-bonds formed with an *ortho* nitro group weaker, than the corresponding ones formed from morpholine. Thus piperidine would be expected to have a greater tendency to form cyclic transition states containing two rather than three molecules of the nucleophile. In contrast to the reaction with morpholine, a plot of k_A *vs.* nucleophile concentration for the reaction of 2,4-dinitrophenyl phenyl ether with piperidine is linear through the origin. When this reaction takes place in THF it is not catalysed by DABCO[9] and as the tendency towards hydrogen bonding to an ethereal oxygen atom would be expected to be greater in benzene than in THF, we explain the kinetic form in benzene as being due to the decomposition of the intermediate *via* a cyclic transition state containing two molecules of piperidine.

When the substrate is 2,6-dinitrophenyl phenyl ether, k_A has a curvilinear upwards dependence on the piperidine

* In benzene, however, the ability of the secondary amines to form ion pairs with 2,4-dinitrophenol is much greater than the primary ones. The relevant ion-pair formation constants are,[11] piperidine 4490, n-butylamine 110, morpholine 70 and benzylamine 17.

Table 1 Rate constants/dm^3 mol^{-1} s^{-1} for the reactions of some phenyl ethers with amines in benzene at 30 °C

Substrate	Nucleophile	Rate constant	[Nucleophile]						
6-Methyl-2,4-dinitrophenyl phenyl ether	Piperidine		[Piperidine]/10^{-1} mol dm^{-3}						
			4.0	6.0	8.0	10.0			
		10^5k_A	1.15	1.95	2.88	3.95			
		10^5k_A[a]	1.34	1.76	2.60	3.67			
		10^5k_A[b]	1.28	2.15	3.20	4.35			
	n-Butylamine		[n-Butylamine]/10^{-1} mol dm^{-3}						
			0.8	1.0	2.0	3.0	4.0	5.0	
		10^4k_A	1.50	1.70	2.94	4.70	6.03	7.41	
	Morpholine		[Morpholine]/10^{-1} mol dm^{-3}						
			4.0	6.0	8.0	10.0			
		10^6k_A	1.05	1.68	2.45	3.40			
		10^6k_A[a]	0.56	0.91	1.40	2.0			
	Benzylamine		[Benzylamine]/10^{-1} mol dm^{-3}						
			2.0	4.0	6.0	8.0	10.0		
		10^4k_A	0.56	0.92	1.16	2.20	3.30		
3,5-Dinitro-2-phenoxypyridine	Piperidine		[Piperidine]/10^{-2} mol dm^{-3}						
			2.0	3.0	4.0	5.0			
		$10k_A$	1.95	2.70	3.50	4.30			
	n-Butylamine		[n-Butylamine]/10^{-3} mol dm^{-3}						
			1.0	2.0	3.0	4.0	5.0		
		10^2k_A	4.54	5.30	6.0	6.50	7.54		
	Morpholine		[Morpholine]/10^{-3} mol dm^{-3}						
			6.0	8.0	10.0	20.0			
		10^3k_A	4.47	5.80	7.10	13.60			
	Benzylamine		[Benzylamine]/10^{-3} mol dm^{-3}						
			4.0	5.0	6.0	8.0	10.0		
		10^2k_A	1.10	1.13	1.24	1.55	1.74		
	Aniline		[Aniline]/10^{-2} mol dm^{-3}						
			8.0	10.0	15.0	20.0	30.0	40.0	50.0
		10^6k_A	1.90	2.25	3.20	4.10	6.25	8.30	10.4
			[Aniline]/10^{-1} mol dm^{-3}						
			1.0	2.0	3.0	4.0	5.0		
		10^6k_A[a]	2.65	3.45	4.73	7.20	12.5		
		10^6k_A[b]	1.80	3.80	6.70	11.0	18.7		
2-Chloro-3,5-dinitropyridine	Aniline		[Aniline]/10^{-2} mol dm^{-3}						
			2.0	4.0	6.0	8.0	10.0		
		10^3k_A	4.65	5.03	5.45	5.82	6.20		
2,4,6-Trinitrophenyl 4-nitrophenyl ether	*N*-Methylaniline		[*N*-Methylaniline]/10^{-2} mol dm^{-3}						
				2.0	3.0	4.0	5.0		
		10^4k_A		0.53	0.90	1.36	2.08		
2,6-Dinitrophenyl phenyl ether	Piperidine		[Piperidine]/10^{-1} mol dm^{-3}						
			2.0	3.0	4.0	5.0	6.0		
		10^4k_A	0.95	1.30	1.75	2.30	2.93		
	n-Butylamine		[n-Butylamine]/10^{-3} mol dm^{-3}						
			2.0	4.0	6.0	8.0	10.0		
		10^2k_A	2.34	2.65	2.98	3.35	3.70		
	Morpholine		[Morpholine]/10^{-1} mol dm^{-3}						
			2.0	3.0	4.0	5.0	6.0		
		10^5k_A	1.15	1.80	2.70	3.80	5.16		
	Benzylamine		[Benzylamine]/10^{-3} mol dm^{-3}						
			2.0	4.0	6.0	8.0	10.0		
		10^3k_A	1.50	2.33	3.18	4.05	4.98		

[a] At 20 °C. [b] At 40 °C.

concentration. The change in kinetic form can be attributed to two factors. Nudelman[15] has shown that the methoxy group in 2,6-dinitroanisole adopts a conformation perpendicular to the ring plane and she attributes the greater reactivity of 2,6- over 2,4-dinitroanisole with cyclohexylamine in benzene to this factor. A similar twisting would be expected to occur with the phenoxy ether, and in methanol where neither the reaction with n-butylamine of the 2,4-dinitro-[16] or 2,6-dinitrophenyl[17] phenyl ethers are base catalysed the 2,6- is the more reactive substrate. The twisting of the ether group from the plane of the

Table 2 Kinetic form of the reactions in Table 1 and of other relevant reactions in benzene. The curvatures refer to the shapes of the plots of k_A *vs.* nucleophile concentration

	Nucleophile				
Substrate	n-Butylamine	Benzylamine	Piperidine	Morpholine	Aniline
6-Methyl-2,4-dinitrophenyl phenyl ether	Linear $k''/k' = 52.4$	Upward curvature	Upward curvature	Upward curvature	
2,4-Dinitrophenyl phenyl ether	Normal curvature through origin[a]	Normal curvature through origin[a]	Linear through origin[b]	Upward curvature through origin[c]	
3,5-Dinitro-2-phenoxy-pyridine	Linear k''/k' 188	Linear k''/k' 195	Linear k''/k' 215	Linear 1126	Curvilinear upwards
2,4,6-Trinitrophenyl phenyl ether[d]	Not catalysed	Linear k''/k' 711	Linear k''/k' 578	Linear through origin	Linear *vs.* [aniline]^2
2,4,6-Trinitrophenyl 4-nitro-phenyl ether					Linear *vs.* [aniline]^2[e] and [*N*-methylaniline]^2
2,6-Dinitrophenyl phenyl ether	Linear k''/k' 86	Upward curvature	Upward curvature	Upward curvature	

[a] Data from ref. 9. [b] Data from F. Pietra, *Tetrahedron Lett.*, 1965, 2405. [c] Data from ref. 7. [d] Data from O. Banjoko and Khalil-Ur-Rahman, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1105. [e] Data from ref. 24.

2,6-dinitrophenyl moiety will increase the basicity of the ethereal oxygen atom, increasing the population of hydrogen-bonded species and thus increasing the likelihood of the attachment of a third molecule of the nucleophile. Furthermore, Nudelman[18] has shown that in 2,4-dinitrophenyl substrates, activation is due mainly to the mesomeric effect of the 4-nitro group. Hence in the σ-complex derived from the 2,6-substrate, the electron density on the oxygen atoms of at least one of the nitro groups will be greater than that on the corresponding group in the 2,4-isomer, leading to stronger *ortho*-nitro hydrogen bonding of the ammonio hydrogen atoms and to a greater propensity to a reaction third order in nucleophile concentration. The curvilinear upwards kinetic form observed for the 6-methyl substrate may also be attributed to the increase in basicity of the ethereal oxygen atom which occurs when a 6-methyl group is introduced into the 2,4-dinitrophenyl moiety of 2,4-dinitrophenyl phenyl ether.

The second-order rate constants for the reactions of piperidine with both 3,5-dinitro-2-phenoxypyridine and 2,4,6-trinitrophenyl phenyl ether increase linearly with increasing nucleophile concentration and the value of the k_3/k_2 ratio increases with increased activation of the substrate. This is the same behaviour as was observed for morpholine and the same rationale can be applied to the results.

Primary Amines.—The reactions of n-butylamine with 2,4-dinitrophenyl phenyl ether, its 6-methyl derivative, 3,5-dinitro-2-phenoxypyridine and those of benzylamine with the last two substrates have the same kinetic form as the corresponding reactions in acetonitrile.[19] The reactions of 2,4,6-trinitrophenyl phenyl ether with these two nucleophiles has not been investigated in this solvent. The change in kinetic form experienced by both n-butylamine and benzylamine when the substrate is changed from 2,4-dinitrophenyl phenyl ether to its 6-methyl derivative indicates a change in the condition of eqn. (1) from $k_{-1} \approx k_2 + k_3[B]$ to $k_{-1} \gg k_2 + k_3[B]$. This is readily explained[17,20] by the increased congestion at the reaction site imposing stereoelectronic effects which reduce both k_2 and k_3; the reduction in k_3 will take place irrespective of the mechanism of the base catalysed path.

The pattern of results of the reactions of n-butylamine with all four substrates is readily explicable on the SB–GA mechanism, as is that of benzylamine if it is assumed that electrophilic catalysis by the homoconjugate of the nucleophile is appreciable in the case of the 6-methyl substrate. However, it seems unlikely that appreciable catalysis by the bulky homoconjugate should occur at the crowded reaction centre of the 6-methyl reactant but not at the less congested one generated by 2,4-dinitrophenyl phenyl ether. The relative catalytic efficiencies of the benzylammonium ion and its homoconjugate towards the σ-complexes derived from the two substrates would have been expected to be the other way round. Moreover, as hydrogen bonding between the ethereal oxygen atoms of the σ-complexes generated by the two substrates and the nucleophiles has been demonstrated when these are secondary amines there is no reason why this should not occur when they are primary ones. On this reasoning the base-catalysed decomposition of the Meisenheimer complexes formed by both substrates should take place *via* cyclic transition states. When the substrate is 6-methyl-2,4-dinitrobenzene the difference in the transition states formed by n-butylamine and benzylamine arises from the greater acidity of the ammonio protons in the σ-complex formed by the latter. When the substrate is 2,4-dinitrophenyl phenyl ether the condition $k_{-1} \approx k_2 + k_3[B]$ gives a kinetic form which does not allow these differences to be observed.

Aniline is a much weaker base than either n-butylamine or benzylamine and it departs from σ-complexes much more readily than the other two making its reactions more prone to base catalysis.[21] Its amino hydrogen atoms are much more acidic and this leads to the base catalysis of the formation of Meisenheimer complexes from 2,4-dinitrobenzene derivatives in aprotic solvents.[22] This type of catalysis does not occur with 2,4,6-trinitrophenyl derivatives[22] and the results in Table 1 show that the reaction of aniline with 2-chloro-3,5-dinitropyridine in benzene is not base catalysed.* Hence we regard any strong base catalysis of the reactions of aniline with phenoxy esters containing these moieties as pertaining to the decomposition to products of the intermediates formed in these reactions. The greatly increased acidity of the amino hydrogen atoms should lead to a greater tendency to hydrogen bonding to ethereal oxygen and to form strong hydrogen bonds to the

* The slight linear increase of k_A with aniline concentration gives a value of k''/k' of 4.6, which by analogy with Bunnett's criteria[23] we do not regard as indicating true catalysis.

oxygen atoms of the *ortho* nitro groups present in the σ-complexes. Thus aniline should have a much greater proclivity than either n-butylamine or benzylamine to react *via* transition states containing three molecules of the nucleophile and for reaction to take place *via* this mechanism, even with highly activated substrates in which the basicity of the ethereal oxygen is reduced, such as 2,4,6-trinitrophenyl ethers.

The reactions of aniline with 2,4-dinitrophenyl phenyl ether and its 6-methyl derivative were too slow to be measured conveniently. Banjoko and Ezeani[24] have shown for the reactions in benzene of aniline with 2,4,6-trinitrophenyl phenyl ether and derivatives containing a nitro group in the 2-, 3- and 4-positions of the leaving group, that the second-order rate constant k_A has a linear dependence on [aniline]^2. The present results show a similar dependence on the nucleophile concentration for the 4′-nitro derivative when the nucleophile is the secondary amine, *N*-methylaniline. Banjoko also observed that with the exception of the 2′,6′-dinitro isomer, when the leaving group contained two nitro groups, k_A had a linear dependence on the aniline concentration, *i.e.* the transition state for the decomposition of the intermediate to products only contained two molecules of aniline. This is readily explicable as the introduction of a second nitro group will reduce the basicity of the ethereal oxygen atom in the σ-complex and decrease the population of the species hydrogen bonded to it and thus the likelihood of the attachment of a third molecule of the nucleophile. The results in Tables 1 and 2 also show, as would be expected, that the less activated 3,5-dinitro-2-phenoxypyridine has a curvilinear upwards dependence on the aniline concentration over a range of temperatures.

Experimental

Analytical grade benzene was shaken with iron(II) sulphate solution, dried over calcium chloride and distilled from sodium wire. The preparation and purification of all other materials and the spectrophotomeric method of following the reactions have been described previously.[17] In all cases good kinetics were obtained and all reactions went to completion.

Data for new products are as follows: N-(3,5-*dinitropyridyl*)-*piperidine*, m.p. 120–122 °C (Found: C, 47.6; H, 4.9; N, 22.3. $C_{10}H_{12}N_4O_4$ requires C, 47.6; H, 4.8; N, 22.2%); N-(3,5-*dinitropyridyl*)*butylamine*, m.p. 78–80 °C (Found: C, 45.2; H, 5.1; N, 23.4. $C_9H_{12}N_4O_4$ requires C, 45.0; H, 5.05; N, 23.2%); N-(3,5-*dinitropyridyl*)*morpholine*, m.p. 85–87 °C (Found: C, 42.6; H, 3.9; N, 21.95. $C_9H_{10}N_4O_5$ requires C, 42.5; H, 4.0; N, 22.0%); N-(6-*methyl*-2,4-*dinitrophenyl*)*benzylamine*, m.p. 134–136 °C (Found: C, 58.4; H, 4.4; N, 14.5. $C_{14}H_{13}N_3O_4$ requires C, 58.5; H, 4.6; N, 14.6%); N-(6-*methyl*-2,4-*dinitrophenyl*)*morpholine*, m.p. 105–107 °C (Found: C, 49.25; H, 4.7; N, 15.65. $C_{11}H_{13}N_3O_5$ requires C, 49.4; H, 4.9; N, 15.75%); N-(6-*methyl*-2,4-*dinitrophenyl*)*butylamine*, m.p. 70–72 °C (Found: C, 52.3; H, 5.85; N, 16.75. $C_{11}H_{15}N_3O_4$ requires C, 52.2; H, 6.0; N, 16.6%); N-(3,5-*dinitropyridyl*)*benzylamine*, m.p. 110–112 °C (Found: C, 52.4; H, 3.7; N, 20.4. $C_{12}H_{10}N_4O_4$ requires C, 52.55; H, 3.7; N, 20.4%); and N-(6-*methyl*-2,4-*dinitrophenyl*)*benzylamine*, m.p. 134–136 °C (Found: C, 58.4; H, 4.4; N, 14.5. $C_{14}H_{13}N_3O_4$ requires C, 58.5; H, 4.55; N, 14.6%).

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Paper 0/04512H
Received 5th *October* 1990
Accepted 28th *November* 1990