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Theoretical Calculations of Chemical Interactions. Part 4.† Aromatic Nucleophilic Substitutions and S_N2 Reactions of 4- and 6-Substituted 2-Nitroanisoles

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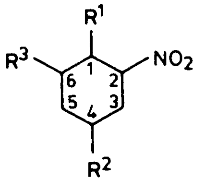
The reactions of 4-R- and 6-R-2-nitroanisoles (R = Me, Br) in neat cyclohexylamine and piperidine have been studied. The reactions with cyclohexylamine lead to the respective aromatic nucleophilic substitution products while the reactions with piperidine mainly yield the substituted nitrophenols. It was found that 6-R-2-nitroanisoles react faster than the respective 4-R-2-nitroanisoles. The absence of the expected primary steric effect is thought to be due to the spatial arrangement of the methoxide group, which adopts a conformation perpendicular to the ring plane when it is surrounded by two *ortho*-substituents. CNDO and INDO calculations for different conformations of the substrates give support to this assumption.

ortho-effects in aromatic nucleophilic substitution (ANS) have attracted interest.[1–4] Apart from the simple steric effect owing to a bulky substituent, other factors have been considered, such as: the steric inhibition of resonance,[4] the field effect,[5] the London forces,[1] and the intramolecular hydrogen bonds.[6,7]

As part of a more complete study on the reactivity of nitroanisoles,[8] we now report the reactions of 4-R- and 6-R-2-nitroanisoles (R = Me, Br) with piperidine and cyclohexylamine (**1**—**12**) in the neat amines.



(**1**) R^1 = OMe, R^2 = Me, R^3 = H
(**2**) R^1 = OMe, R^2 = H, R^3 = Me
(**3**) R^1 = OMe, R^2 = Br, R^3 = H
(**4**) R^1 = OMe, R^2 = H, R^3 = Br
(**5**) R^1 = NC_5H_{10}, R^2 = Me, R^3 = H
(**6**) R^1 = NHC_6H_{11}, R^2 = Me, R^3 = H
(**7**) R^1 = NC_5H_{10}, R^2 = H, R^3 = Me
(**8**) R^1 = NHC_6H_{11}, R^2 = H, R^3 = Me
(**9**) R^1 = NC_5H_{10}, R^2 = Br, R^3 = H
(**10**) R^1 = NHC_6H_{11}, R^2 = Br, R^3 = H
(**11**) R^1 = NC_5H_{10}, R^2 = H, R^3 = Br
(**12**) R^1 = NHC_6H_{11}, R^2 = H, R^3 = Br

This work allows the study of the differential effects operating from the 4- and 6-position. The present substituents have been chosen as they have similar van der Waals radii (2 Å)[9] and opposite electronic effects. Simple steric effects of these groups have already been reported in some other aromatic nucleophilic substitution reactions.[2] On the other hand, nitroanisoles are suitable substrates for studying competition between the aromatic nucleophilic substitution and S_N2 attack on the methoxide group.

To explain some unexpected kinetic results we have performed CNDO and INDO SCF-MO calculations for different conformations of the above-mentioned nitroanisoles and of 2,4- and 2,6-dinitroanisoles.

Results

The aforesaid substrates reacted very slowly with cyclohexylamine and piperidine hence a complete base catalysis study could not be carried out in any solvent and their reactivities had to be determined in neat amines at 30 °C (higher temperatures decompose the amines). Nitrophenols have not been detected in the reactions with cyclohexylamine, which cleanly lead to the expected aromatic nucleophilic substitution products. In contrast, the reactions in piperidine mainly yield the substituted nitrophenols and only in the case of (**3**) are both substitution processes competitive. The results are given in Table 1, where previous data for R = NO_2 have also been included.

Table 1. Reactions of 4-R- and 6-R-2-nitroanisoles in neat cyclohexylamine and piperidine at 30 °C: results are the first-order rate coefficients, $10^8\ k/s^{-1}$; [substrate] *ca.* 10^{-3}M

		Cyclohexylamine	Piperidine	
R		k_{ANS}	k_{ANS}	k_{S_N2}
4-Me[a]	(1)	4.34		1.12
6-Me	(2)	62.0		24.3
4-Br	(3)	175	41	22
6-Br	(4)	13 000		2 460
4-NO_2[b]		6 120[c]	491[d]	71[d]
6-NO_2[b]		60 000[c]	3 500[d]	64 100[d]

[a] The reaction was followed till 40% conversion. [b] Second-order rate coefficients, [amine] *ca.* 0.3M, 60 °C, benzene. [c] Reference 10. [d] Reference 8*a*.

For the more reactive compound, (**4**), the effect of amine concentration on the reaction rate can be studied in DMSO and the results are given elsewhere.[10] It was observed that the rate increases with the amine concentration and the plot of k_A *versus* [B] (not shown) has the typical shape of a base-catalysed reaction of the $k_{-1} \approx (k_2 + k_3[B])$ type. The reactions of (**3**) are virtually insensitive to the amine concentration;[10] since the reactions of Table 1 have been studied in neat amines it is reasonable to assume that, even when the reactions of some other substrates were subjected to base catalysis, they would be in the 'plateau' zone.

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† Part 3, N. S. Nudelman and P. MacCormack, *Tetrahedron*, 1984, **40**, 4227.

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Table 2. Energies and dipolar moments for different conformations of 4-R-2-nitroanisoles

Conformation	$-E_T$[a]	ΔE_T[b]	DM[c]
R = NO_2[d]			
PI	162.923 955	0	5.27
PII	162.922 540	+0.89	5.30
AI	162.921 076	+1.81	6.50
AII	162.887 354	+23.0	6.59
R = Me[d] **(1)**			
PI$_1$	125.709 402	0	5.83
PI$_2$	125.709 372	+0.02	5.86
AI$_2$	125.705 915	+2.19	6.86
R = Br[e] **(3)**			
PI	134.605 762	0	4.99
AI	134.600 875	+3.07	6.28

[a] Total energy, a.u. [b] Total energy differences referred to **PI**, kcal mol^{-1}. [c] Dipolar moment, debye. [d] INDO. [e] CNDO/3R.

Table 3. Energies and dipolar moments for different conformations of 6-R-2-nitroanisoles

Conformation	$-E_T$[a]	ΔE_T[b]	DM[c]
R = NO_2[d]			
PI	162.924 249	0	5.50
PII	162.922 898	+0.85	5.46
R = Me[d] **(2)**			
PI$_2$	125.710 761	0	5.82
PI$_1$	125.710 494	+0.17	5.80
SI$_3$	125.669 012	+26.2	4.20
AI$_3$	125.595 678	+72.2	6.65
AI$_2$	125.521 626	+119	6.74
AII$_3$	125.442 582	+168	5.94
AII$_2$	125.209 811	+314	6.35
R = Br[e] **(4)**			
AI	134.662 699	0	0.83
PI	134.609 395	+33.4	5.20
AII	134.208 660	+285	0.56

[a] Total energy, a.u. [b] Total energy differences referred to the more stable conformation, kcal mol^{-1}. [c] Dipolar moment, debye. [d] INDO. [e] CNDO/3R.

Method of Calculation.—Since the size of the molecules does not allow a complete optimization of the geometry, and crystallographic data of these compounds are not available, standard bond lengths and angles were used[11] for the SCF-MO calculations. The C–Br distance was taken as 1.87 Å according to the data of *p*-bromofluorobenzene.[12] A CNDO/3R program (QCPE No. 261) was used for molecules containing bromine and a CNDO/INDO (QCPE No. 141) for all the other cases.[13]

Tables 2 and 3 contain the data for 4-R- and 6-R-2-nitroanisoles, respectively. For molecules containing only one nitro group, this was located in the plane of the ring. Calculations were carried out for two extreme conformations of the methoxide group: **A** (for *anti*-coplanar) and **P** (for perpendicular) in Figure 1, and in a few cases for **S** (*syn*-coplanar). Depending on the positions of the methoxide hydrogen atoms, substructures **I** and **II** were generated (one or two hydrogen atoms heading up, respectively). The subscripts in Figure 1 refer to the conformation of the methyl group attached to the ring; 1 and 2 stand, respectively, for one or two hydrogen atoms located above the aromatic plane.

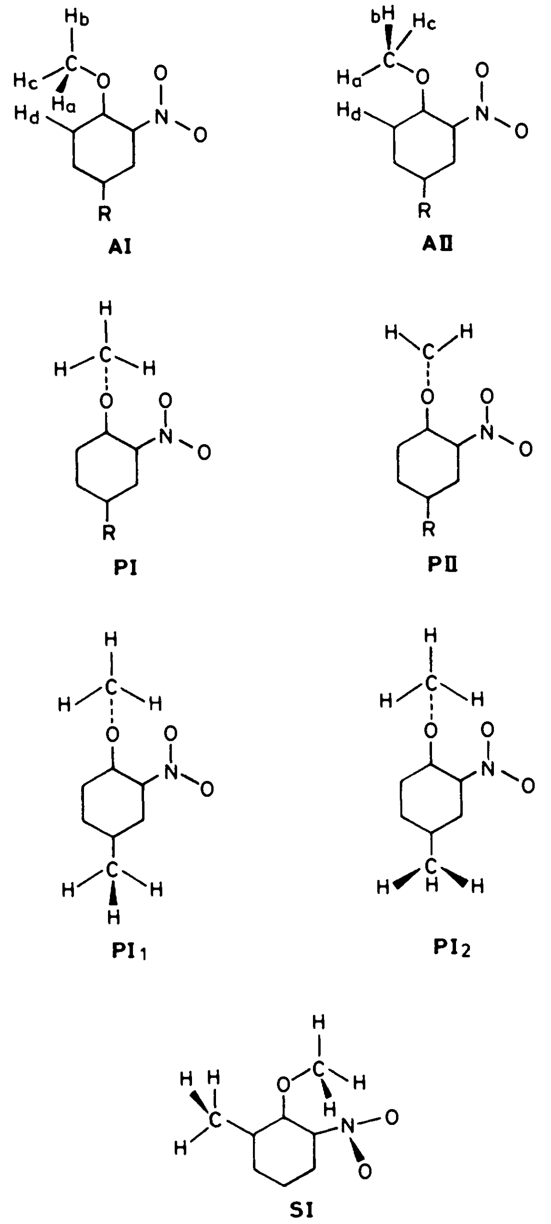

Figure 1. Conformations of 4-R- and 6-R-2-nitroanisoles

Discussion

As has been observed previously in reactions of nitroanisoles,[8,14,15] piperidine is more reactive than primary amines towards aliphatic carbon atoms, while the opposite behaviour is found in aromatic nucleophilic substitution. The steric requirements of piperidine compared with those of primary amines become important when a bulky substituent is located near the reaction centre (*i.e.*, the diminution in rate caused by the introduction of a methyl group in the 6-position of 2,4-dinitrochlorobenzene is 22-fold for aniline but 276-fold for piperidine).[16]

In spite of the expected primary steric effect we have observed that **(2)** reacts with cyclohexylamine about 15-fold faster than **(1)** (Table 1). (The possibility of a more reactive impurity contaminating the substrate was checked by means of diverse analyses and was rejected, see Experimental section.) Had a simple steric effect been operating a diminution in rate would have been observed, as had been reported previously for

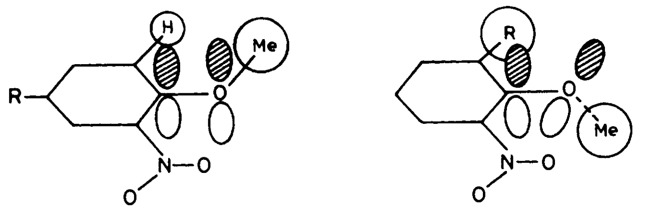

Figure 2. Orbital interactions in 4-R- and 6-R-2-nitroanisoles

the reactions of 1-X-2-nitro-6-methylbenzene (X = Cl,[2] Br[17]) with piperidine in benzene compared with those of 1-X-2-nitro-4-methylbenzene.[18]

The absence of primary steric effects, and even the increase in rate in the present case, can be understood by considering some substrate conformation features. Crystallographic studies of 2,4,6-trinitrophenetole show the ethoxide group is almost perpendicular to the aromatic ring.[19] However, when one of the *ortho*-positions is not substituted the methoxide group may be coplanar with the ring, as has been observed for bis-(2-methoxyphenyl)methanol[20] and 1,4-dimethoxybenzene.[21]

These studies[19-22] also show that the C$\hat{O}$C angle is *ca.* 120°, which would imply an sp^2 hybridization for the oxygen atom in the alkylphenyl ethers. Taking both facts into account, the loss of coplanarity would result in a decrease of resonance stabilization, as can be seen in Figure 2, which is what makes the 6-substituted compound more reactive, as is observed in Table 1.

Comparison of Tables 2 and 3 shows that the total energies of the 6-R compounds are always slightly higher than those of the 4-R and that the perpendicular conformation is almost always preferred. That the acceleration in rate is not due to a relief of steric strain in the 6-R when forming the zwitterionic intermediate is evident from the fact that in the case of R = Me and NO_2 the difference in energy, 1 kcal mol^{-1}, cannot account for the difference in rate; furthermore, for R = Br the energy of (**4**) is smaller than that of (**3**).

As can be seen in Table 2 the total energies calculated for different conformations of 4-R-2-nitroanisoles indicate that rotation of the methoxide group from **P** to **A** is free. Although for 2,4-dinitroanisole an energy difference of 23 kcal mol^{-1} between conformations **PI** and **AII** was found, this difference is not considered significant since it is well known that the INDO method minimizes the importance of conjugation compared with steric strain for substituents containing atoms with lone-pair electrons.[23,24] The experimental dipolar moment, 5.25 D,[25] agrees with the calculated value.

Table 3 gives the calculated energies and dipolar moments for several conformations of 6-R-2-nitroanisoles. The INDO-calculated dipolar moment for 2,6-dinitroanisole does not agree with the experimental value (3.31 D);[25] the difference might arise from the uncertainty in the degree of coplanarity of the 6-NO_2 group, in addition to the above-mentioned limitations of the INDO method[23,24] for this type of compound.

From the data in Table 3 it is clear that (**2**) exists mainly in the perpendicular conformation, which is in agreement with the observed spatial arrangements of hindered anisoles.[23d,26] In the case of (**4**), the *anti*-coplanar conformer, **AI**, was, unexpectedly, the more stable. The study of nuclear and electronic energies shows that in spite of the increase in nuclear repulsion on going from **PI** to **AI** (1.738 849 a.u.) the total energy diminishes, owing to an important diminution in the electronic energy caused by the interaction between the bromine atom and the H_a and H_c of the methyl group in **AI**. The electronic densities of bromine and hydrogen atoms are shown in Figure 3 for both conformations. For 2-methoxytrifluoropiperazine, Beer and Clark found a similar interaction between one hydrogen atom of the methyl group in the *syn*-conformation and the fluorine atom.[27] The decrease in energy due to this sort of interaction will also be important in the σ-zwitterionic intermediate, where, although the methoxide should be out of the plane, a strong interaction of the 6-Br atom with the amine proton is added. The bromine substituent exhibits the greater $k_{6\text{-R}}/k_{4\text{-R}}$ ratio (Table 1).

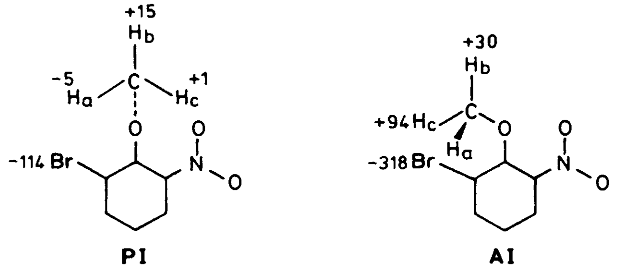

Figure 3. Net atomic charge for two conformations of 6-bromo-2-nitroanisole

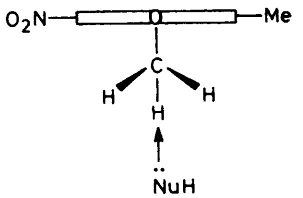

Figure 4. Geometry of 6-methyl-2-nitroanisoles for nucleophilic attack in S_N2-type reactions

The reactions with piperidine allows comparison of these substrates towards the S_N2 process, which, because of the steric requirements of piperidine, supersedes the aromatic nucleophilic substitution. Only for the 4-Br compound are both processes competitive.

From Table 1, it is again clear that primary steric effects are not important in the S_N2. In the reactions of different nitrophenyl esters of the toluene-*p*-sulphonic and mesitylenesulphonic acids with piperidine, Bunnett and Bussett have found that the methyl group at the *ortho*-position exerts a 'miserable effect' on the reaction rate, which has been ascribed to electronic factors.[28]

In the present case the forced non-coplanar conformations of the methoxide group in (**2**) favours the nucleophile attack on the methyl carbon (Figure 4), then the 6-R exhibits the greater reactivity. For the bromine-substituted compounds the increase in rate is about 100-fold and *ca.* 10^3-fold for the nitro-substituted compounds. This strong acceleration may be due to several effects operating together: the above-mentioned secondary steric effect, the stronger inductive effect exerted at the *ortho*-position and, in particular, a stabilizing field effect[5] arising from the developing negative charge on the oxygen atom and the well orientated C–Br (see neat atomic charges in Figure 3) and N–O dipoles.

Conclusion

The preceding results give evidence of the absence of primary steric effects in the studied aromatic nucleophilic substitution and S_N2 reactions as the 6-R-2-nitroanisoles are more reactive than the 4-R-isomers. Theoretical calculations show that 6-R-2-nitroanisoles adopt a conformation perpendicular to the ring plane, which is in agreement with crystallographic and spectroscopic results. This forced conformation is invoked to be responsible for the higher reactivity of 6-R-2-nitroanisoles. In the case of R = Br a strong interaction between the 6-Br and two methyl hydrogen atoms is observed.

Experimental

Cyclohexylamine and piperidine were kept over sodium wire, refluxed, and then fractioned over sodium; fractions of b.p. 134—135 °C and 106—106.5 °C, respectively, were used.

4-Methyl-2-nitroanisole (**1**) was obtained after treating 4-methyl-2-nitrophenol with dimethyl sulphate in basic medium according to the method described by De Vries;[29] b.p. 162 °C at 21 mmHg (lit.,[29] 155—157 °C at 13 mmHg). (**2**) Was prepared by nitration of 2-methylphenol according to Mraz[30] and further treatment of the potassium phenoxide with methyl iodide; b.p. 109—109.5 °C at 4 mmHg (lit.,[30] 134—137 °C at 17 mmHg). The purity of this compound was checked by careful g.l.c. and elemental analysis (Calculated for $C_8H_9NO_3$: C, 57.5; H, 5.4; N, 8.4. Found: C, 57.65; H, 5.7; N, 8.4%).

(**3**) Was prepared from *o*-nitrophenol by bromination[31] and further treatment with dimethyl sulphate; m.p. (ethanol) 85—85.5 °C (lit.,[32] 86 °C). (**4**) Was prepared by reducing 2,6-dinitrochlorobenzene with copper and hydrobromic acid,[33] Sandmeyer reaction of the obtained 2-chloro-3-nitroaniline, and further treatment of the 6-bromo-2-nitrochlorobenzene with sodium methoxide in methanol, m.p. (cyclohexane) 66—67 °C (lit.,[34] 66 °C). 6-Bromo-2-nitrophenol was prepared from 6-bromo-2-nitrochlorobenzene by reaction with sodium hydroxide in methanol.

The substitution products were prepared by heating the respective nitroanisoles or halogenonitrobenzenes with an excess of the appropriate amine; the products were separated by silica column chromatography using benzene–cyclohexane (9:1) as eluant. Products (**7**), (**8**), and (**10**)—(**12**) are not described in the literature.

(**5**): (1-piperidyl-2-nitro-4-methylcyclohexane), red oil (lit.,[35] b.p. 109—110 °C at 0.1 mmHg); δ_H ($CDCl_3$; 100 MHz) 1.62 (6 H, m, $CH_2[CH_2]_3CH_2$), 2.30 (3 H, s, ArCH_3), 2.95 (4 H, m, CH_2NCH_2), 7.02 (1 H, d, 6-H), 7.22 (1 H, dd, 5-H), and 7.52 (1 H, d, 3-H); *m/z* 220 (M^+, 27%), 219 (5), 203 (100), 173 (53), 172 (30), 158 (26), and 144 (22).

(**6**): m.p. (methanol) 125.5—126 °C (lit.,[36] red syrup); δ_H ($CDCl_3$; 100 MHz) 1.60 (10 H, m, $[CH_2]_5$), 2.24 (3 H, s, ArCH_3), 3.5 (1 H, br s, NHC*H*), 6.77 (1 H, d, 6-H), 7.22 (1 H, dd, 5-H), 7.95 (1 H, d, 3-H), and 8.0 (1 H, br s, NH, vanishes with DCl); *m/z* 234 (M^+, 60%), 217 (10), 199 (20), 191 (100), 152 (19), and 106 (30) (Calculated for $C_{13}H_{18}N_2O_2$: C, 66.6; H, 7.7; N, 12.0. Found: C, 66.5; H, 8.0; N, 11.9%).

(**7**): m.p. (methanol) 41—41.5 °C; δ_H ($CDCl_3$; 100 MHz) 1.60 (6 H, m, $CH_2[CH_2]_3CH_2$), 2.36 (3 H, s, ArCH_3), 2.95 (4 H, m, CH_2NCH_2), 7.00 (1 H, t, 4-H), 7.26 (1 H, dd, 5-H), and 7.40 (1 H, dd, 3-H); *m/z* 220 (M^+, 20%), 219 (8), 203 (100), 165 (12), 173 (30), 172 (77), and 144 (21) (Calculated for $C_{12}H_{16}N_2O_2$: C, 65.4; H, 7.3; N, 12.7. Found: C, 65.4; H, 7.5; N, 13.0%).

(**8**): red syrup, δ_H ($CDCl_3$; 60 MHz) 1.60 (10 H, m, $[CH_2]_5$), 2.35 (3 H, s, ArCH_3), 3.25 (1 H, br s, NHC*H*), 6.7 (1 H, br s, NH, vanishes with D_2O), 6.78 (1 H, t, 4-H), 7.30 (1 H, dd, 5-H), and 7.90 (1 H, dd, 3-H); *m/z* 234 (M^+, 46%), 217 (25), 204 (7), 199 (53), 191 (100), 152 (22), and 106 (30) (Calculated for $C_{13}H_{18}N_2O_2$: C, 66.6; H, 7.7; N, 12.0. Found: C, 66.5; H, 7.65; N, 11.75%).

(**9**): m.p. (light petroleum) 45—45.5 °C (lit.,[37] 45—45.5 °C).

(**10**): m.p. (methanol) 108—109 °C; δ_H ($CDCl_3$; 60 MHz) 1.6 (10 H, m, $[CH_2]_5$), 3.5 (1 H, br s, NHC*H*), 6.8 (1 H, d, 6-H), 7.40 (1 H, dd, 5-H), 8.1 (1 H, br s, NH, vanishes with D_2O), and 8.25 (1 H, d, 3-H); *m/z* 300/298 (M^+, 70%), 283/281 (10), 270/268 (5), 265/263 (20), 257/255 (100), 218/216 (20), 105 (58), and 55 (97) (Calculated for $C_{12}H_{15}BrN_2O_2$: C, 48.2; H, 5.05; Br, 26.7; N, 9.4. Found: C, 48.4; H, 5.2; Br, 26.8; N, 9.3%).

(**11**): m.p. (methanol) 41.5—42.5 °C; δ_H ($CDCl_3$; 100 MHz) 1.7 (6 H, br s, $CH_2[CH_2]_3CH_2$), 3.0 (4 H, br s, CH_2NCH_2), 6.92 (1 H, t, 4-H), 7.50 (1 H, dd, 5-H), and 7.80 (1 H, dd, 3-H); *m/z* 286/284 (M^+, 15%), 285/283 (10), 269/267 (100), 251/249 (5), 239/237 (34), 158 (45), and 130 (23) (Calculated for $C_{11}H_{13}BrN_2O_2$: C, 46.3; H, 4.6; Br, 28.0; N, 9.8. Found: C, 46.4; H, 4.8; Br, 27.8; N, 9.6%).

(**12**): red syrup, δ_H ($CDCl_3$; 100 MHz) 1.6 (10 H, m, $[CH_2]_5$), 3.6 (1 H, br s, NHC*H*), 6.2 (1 H, br s, NH, vanishes with DCl), 6.81 (1 H, t, 4-H), 7.74 (1 H, dd, 5-H), and 7.95 (1 H, dd, 3-H); *m/z* 300/298 (M^+, 35%), 283/281 (35), 270/268 (8), 265/263 (50), 257/255 (100), 218/216 (40), 105 (95), and 55 (88) (Calculated for $C_{12}H_{15}BrN_2O_2$: C, 48.2; H, 5.05; Br, 26.7; N, 9.4. Found: C, 48.5; H, 5.1; Br, 26.55; N, 9.6%).

Kinetic Procedures.—The reactions were studied spectrophotometrically.[37] Portions of the reaction mixtures were put in sealed bulbs and immersed in a thermostatically controlled vessel. Samples were taken at intervals, cooled, diluted, and the absorbances, *A*, were measured at appropriate wavelengths (410—440 nm). The overall pseudo-first-order rate coefficients for the disappearance of the substrates, k_T, were obtained from the slope of the linear regression analysis of $\ln(A_\infty - A_t)$ *versus* t, k_{ANS}, and k_{S_N2} were calculated from the k_T and the concentration ratios of the two reaction products, measured at different time intervals (t). These ratios were calculated by measuring the absorbances of the reaction mixtures diluted with benzene–piperidine and with methanol–hydrochloric acid solution (the absorbances of nitrophenols are negligible in this solvent).

Acknowledgements

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