Aminolysis of 2,4-Dinitrophenyl and 3,4-Dinitrophenyl 2-Thiophenecarboxylates: Effect of *ortho*-Nitro Group on Reactivity and Mechanism

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Second-order rate constants (k_N) have been measured spectrophotometrically for reactions of 3,4-dinitrophenyl 2-thiophenecarboxylate (**2**) with a series of alicyclic secondary amines in 80 mol % H_2O/20 mol % dimethyl sulfoxide at 25.0 °C. The Bronsted-type plot exhibits a downward curvature for the aminolysis of **2**. The curved Bronsted-type plot is similar to that reported for the corresponding reactions of 2,4-dinitrophenyl 2-thiophenecarboxylate (**1**). The reactions of **1** and **2** have been suggested to proceed through the same mechanism, *i.e.*, through a zwitterionic tetrahedral intermediate ($T^{\pm}$) with a change in the rate-determining step. Substrate **2** is less reactive than **1** toward weakly basic amines (*e.g.*, $pK_a < 10.4$) but becomes more reactive as the basicity of amines increases further. Dissection of k_N into the microscopic rate constants has revealed that the reaction of **2** results in a smaller k_2/k_{-1} ratio but larger k_1 than the corresponding reaction of **1**. Steric hindrance exerted by the *ortho*-nitro group has been suggested to be responsible for the smaller k_1 value found for the reactions of **1**.

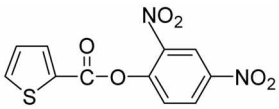
Key Words : Aminolysis, Bronsted-type plot, Steric hindrance, Reaction mechanism, *ortho*-Effect

Introduction

Aminolysis of esters has been understood to proceed through a concerted or a stepwise mechanism.[1-7] Many factors have been reported to influence the reaction mechanism (*e.g.*, the basicity of the attacking amines and the leaving group, the nature of solvent, and the type of the nonleaving group).[1-7] Aminolysis of aryl benzoates has been reported to proceed through a stepwise mechanism with a change in the rate-determining step (RDS) in aqueous medium.[5] The RDS has been suggested to change from breakdown of the zwitterionic tetrahedral intermediate ($T^{\pm}$) to its formation as the amine becomes more basic than the nucleofuge or the leaving group becomes less basic than the amine by 4 to 5 pK_a units.[5] However, the reactions performed in MeCN have been concluded to proceed through a concerted mechanism.[6] The medium change from H_2O to CH_3CN has been suggested to force the reaction to proceed concertedly by decreasing the stability of $T^{\pm}$ in the aprotic solvent.[6] On the other hand, we have recently shown that aminolysis of aryl cinnamates proceeds through a concerted mechanism while the corresponding reaction of aryl benzoates proceeds through a stepwise mechanism with a change in the RDS,[7] implying that the effect of changing the nonleaving group is also significant to determine reaction mechanism.

Linear free energy relationships of various types (*e.g.*, Bronsted and Hammett correlations) have most commonly been used to investigate reaction mechanisms.[8] It is generally known that the nucleophilicity of amines increases with increasing the amine basicity while the nucleofugality increases with decreasing the basicity of the nucleofuge. However, Gresser and Jencks have found that 2,4-dinitrophenyl phenyl carbonate is less reactive than 3,4-dinitrophenyl phenyl carbonate toward quinuclidines,[1d] although 2,4-dinitrophenoxide is less basic than 3,4-dinitrophenoxide by *ca.* 1.3 pK_a units. Since the nitro group at the *ortho*-position would cause steric hindrance, Gresser and Jencks have proposed that steric effect is responsible for the reversed reactivity order.[1d] However, such steric effect has been found to be absent for aminolysis of 2,4-dinitrophenyl diphenylphosphinate and diphenylphosphinothioates,[9] indicating that steric effect is dependent on the nature of the electrophiles.

We have recently performed a kinetic study on aminolysis of 2,4-dinitrophenyl 2-thiophenecarboxylate (**1**) and concluded that the reaction proceeds through $T^{\pm}$ with a change in the RDS on changing the basicity of amines.[10] The kinetic study has now been extended to reactions of 3,4-dinitrophenyl 2-thiophenecarboxylate (**2**) with a series of alicyclic secondary amines. The kinetic data in the current study have been compared with those reported for the corresponding reactions of **1** to investigate the effect of changing the nucleofuge from 2,4-dinitrophenoxide to 3,4-dinitrophenoxide on the reactivity and reaction mechanism (*i.e.*, an *ortho*-substituent effect) in a microscopic rate constant level.



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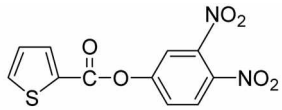

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Results and Discussion

The current aminolysis of **2** proceeded with quantitative liberation of 3,4-dinitrophenoxide ion under pseudo-first-

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order conditions (*e.g.*, the concentration of amines was at least 20 times greater than that of the substrate **2**). The reactions were followed by monitoring the appearance of 3,4-dinitrophenoxide at 410 nm. All reactions obeyed first-order kinetics. Pseudo-first-order rate constants (k_{obsd}) were determined from the equation. $\ln(A - A_t) = -k_{obsd}t + C$. The plots of k_{obsd} *vs.* the amine concentration were linear passing through the origin, indicating that general base catalysis by a second amine molecule is absent and the contribution of H_2O and/or OH^- ion from the hydrolysis of amines to k_{obsd} is negligible. Thus, the rate equation can be given as eq. (1). The apparent second-order rate constants (k_N) were determined from the slope of the linear plots of k_{obsd} *vs.* the amine concentration. Generally five different amine concentrations were used to determine k_N values. It is estimated from replicate runs that the uncertainty in the rate constants is less than 3%. The k_N values determined in this way are summarized in Table 1 together with those reported for the corresponding reactions of **1** for comparison purpose.

$$\text{rate} = k_{obsd}[\mathbf{2}], \text{ where } k_{obsd} = k_N[\text{amine}] \quad (1)$$

Effect of *ortho*-Nitro Group on Reactivity and Mechanism. As shown in Table 1, the second-order rate constant for the reaction of **2** decreases as the basicity of amines decreases, *i.e.*, k_N decreases from 152 $M^{-1}s^{-1}$ to 10.1 and 0.080 $M^{-1}s^{-1}$ as the pK_a of amines decreases from 11.02 to 8.65 and 5.95, respectively. A similar result is shown for the corresponding reactions of **1**. Interestingly, **2** is less reactive than **1** when the attacking amines are weakly basic (pK_a < 10.4) but becomes more reactive as the amine basicity increases further.

The effect of amine basicity on reactivity is illustrated in Figure 1. The Bronsted-type plots are curved downwardly for the reactions of **2**, when k_N and pK_a are statistically corrected using p and q (*i.e.*, $p = 2$ except $p = 4$ for piperazinium ion and $q = 1$ except $q = 2$ for piperazine).[11] A similar result is demonstrated for the corresponding reactions of **1**, although the slopes are slightly different, *i.e.*, the slope of the Bronsted-type plots decreases from 0.83 to 0.34 and from 0.74 to 0.34 for the reactions of **2** and **1**, respectively, as the amine basicity increases.

It has generally been understood that a change in the RDS occurs as the attacking amine becomes more basic than the leaving group by 4 to 5 pK_a units.[1-5] The pK_a at the center of Bronsted curvature has been defined as pK_a^o.[1d,12] The pK_a^o value for the reactions of **1** has been reported to be 9.1, which is *ca.* 5 pK_a units larger than the pK_a of the conjugate acid of the leaving 2,4-dinitrophenoxide (pK_a = 4.11). Thus, the curved Bronsted-type plot obtained for the aminolysis of **1** has been taken as evidence for a change in RDS of a stepwise reaction.[10] As shown in Figure 1, the pK_a^o value for the reactions of **2** is 10.4, which is *ca.* 5 pK_a units larger than the pK_a of the conjugate acid of the leaving 3,4-dinitrophenoxide (pK_a = 5.42). Accordingly, one can suggest that the current aminolysis of **2** also proceeds through $T^{\pm}$ as shown in Scheme 1 and the RDS changes at pK_a = 10.4.

To examine the above argument a plot of log k_N for the reactions of **1** *vs.* log k_N for the corresponding reactions of **2** has been constructed. As shown in Figure 2, an excellent linear correlation is obtained (*e.g.*, $R^2 = 0.9992$) with a slope of 1.29. Such a good linear plot suggests that the reactions of **1** and **2** proceed through the same mechanism. The slope of 1.29 is consistent with the fact that the reactions of **2** exhibit

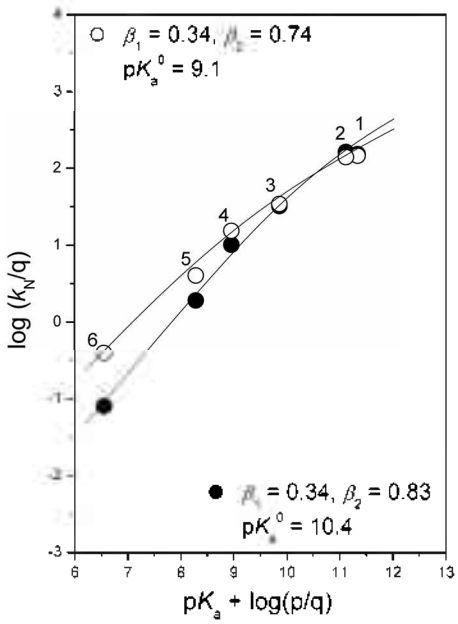
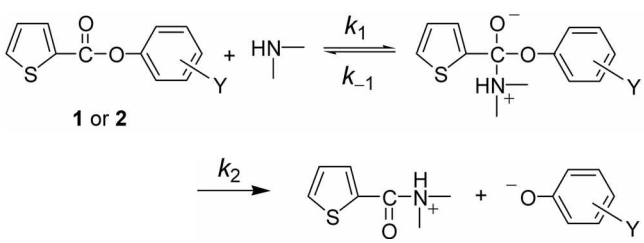


Figure 1. Bronsted-type plots for the reactions of 2,4-dinitrophenyl 2-thiophenecarboxylates **1** (○) and 3,4-dinitrophenyl 2-thiophenecarboxylates **2** (●) with secondary alicyclic amines in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C. The identity of points is given in Table 1.

Table 1. Summary of Second-order Rate Constants (k_N, $M^{-1}s^{-1}$) for the Reactions of 3,4-Dinitrophenyl 2-Thiophenecarboxylates (**2**) and 2,4-Dinitrophenyl 2-Thiophenecarboxylates (**1**) with Secondary Alicyclic Amines in 20 mol % DMSO at 25.0 ± 0.1 °C[a]

Entry	Amines	pK_a	k_N/$M^{-1}s^{-1}$	
			2	**1**
1	piperidine	11.02	152	145
2	3-methylpiperidine	10.80	162	139
3	piperazine	9.85	64.1	68.2
4	morpholine	8.65	10.1	15.3
5	1-formylpiperazine	7.98	1.76	4.04
6	piperazinium ion	5.95	0.080	0.397

[a]The data for the reactions of **1** were taken from ref. 10.



Scheme 1

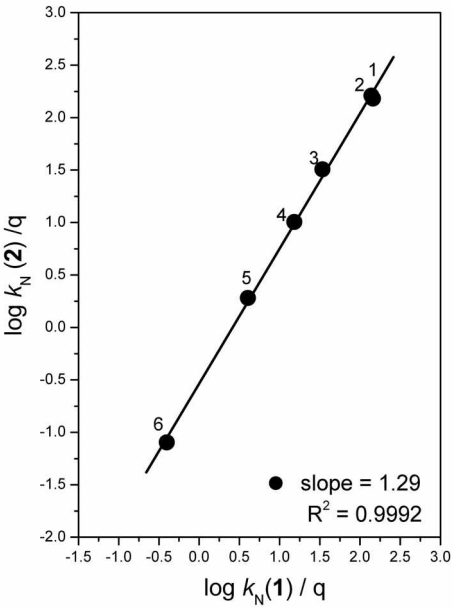


Figure 2. Plot of log k_N for the reactions of 2,4-dinitrophenyl 2-thiophenecarboxylates (**1**) *vs.* log k_N for the reactions of 3,4-dinitrophenyl 2-thiophenecarboxylates (**2**) in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C. The identity of numbers is given in Table 1.

a larger slope than those of **1** in the Bronsted-type plots (see Figure 1). Accordingly, one can suggest that shifting the NO_2 group from the *ortho*-position to the *meta*-position of the leaving group does not alter the reaction mechanism but influences the reactivity and the Bronsted coefficient.

Determination of Microscopic Rate Constants. On the basis of the mechanism proposed above, the curved Bronsted-type plot for the aminolysis of **2** has been analyzed using a semiempirical equation (eq. 2).[1d,12] The parameters β_1 and β_2 represent the slope of the curved Bronsted plot for the reactions with strongly basic and weakly basic amines, respectively. Here k_N° refers to the k_N value at pK_a°. The parameters determined from the fitting of eq. (2) to the experimental points are $\beta_1 = 0.34$, $\beta_2 = 0.83$, and $pK_a^\circ = 10.4$ for the reactions of **2**. The β_1 value for the reactions of **2** is the same as that reported for the reactions of **1**, while β_2 is slightly larger for the reactions of **2** ($\beta_2 = 0.83$) than for those of **1** ($\beta_2 = 0.74$).

$$\log (k_N/k_N^\circ) = \beta_2(pK_a - pK_a^\circ) - \log (1 + \alpha)/2$$
$$\text{where } \log \alpha = (\beta_2 - \beta_1)(pK_a - pK_a^\circ) \quad (2)$$

The k_N values for the reactions of **2** have been dissected into their microscopic rate constants through eqs. (3)-(10) as shown below. The apparent second-order rate constant k_N can be expressed as eq. (3) by applying the steady-state conditions to the intermediate on the basis of the proposed mechanism.

$$k_N = k_1k_2/(k_{-1} + k_2) \quad (3)$$

The k_2/k_{-1} ratios associated with the aminolysis of **2** have been determined using eqs. (4)-(9). Eq. (3) can be simplified to eq. (4) or (5). Then, β_1 and β_2 can be expressed as eqs. (6) and (7), respectively.

$$k_N = k_1k_2/k_{-1}, \text{ when } k_2 << k_{-1} \quad (4)$$

$$k_N = k_1, \text{ when } k_2 >> k_{-1} \quad (5)$$

$$\beta_1 = d(\log k_1)/d(pK_a) \quad (6)$$

$$\beta_2 = d(\log k_1k_2/k_{-1})/d(pK_a)$$
$$= \beta_1 + d(\log k_2/k_{-1})/d(pK_a) \quad (7)$$

Eq. (7) can be rearranged as eq. (8). Integral of eq. (8) from pK_a° results in eq. (9). Since $k_2 = k_{-1}$ at pK_a°, the term $(\log k_2/k_{-1})_{pKa^\circ}$ is zero. Therefore, one can calculate the k_2/k_{-1} ratios for the aminolysis of **2** from eq. (9) using $pK_a^\circ = 10.4$, $\beta_1 = 0.34$, and $\beta_2 = 0.83$. The k_1 values have been determined from eq. (10) using the k_N values in Table 1 and the k_2/k_{-1} ratios calculated above. The k_2/k_{-1} ratios and k_1 values are summarized in Table 2.

$$\beta_2 - \beta_1 = d(\log k_2/k_{-1})/d(pK_a) \quad (8)$$

$$(\log k_2/k_{-1})_{pKa} = (\beta_2 - \beta_1)(pK_a - pK_a^\circ) \quad (9)$$

$$k_N = k_1k_2/(k_{-1} + k_2) = k_1/(k_{-1}/k_2 + 1) \quad (10)$$

Table 2. Summary of Microscopic Rate Constants (k_1 and k_2/k_{-1} Ratios) for the Reactions of 2,4-Dinitrophenyl 2-Thiophenecarboxylates (**1**) and 3,4-Dinitrophenyl 2-Thiophenecarboxylates (**2**) with Alicyclic Secondary Amines in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1°C[a]

Entry	Amines	pK_a	$10^2\ k_2/k_{-1}$		k_1/ $M^{-1}s^{-1}$	
			1	**2**	**1**	**2**
1	piperidine	11.02	773	282	164	206
2	3-methylpiperidine	10.80	631	220	161	236
3	piperazine	9.85	200	53.8	102	183
4	morpholine	8.65	87.1	19.5	32.9	62.0
5	1-formylpiperazine	7.98	47.0	9.15	12.6	21.0
6	piperazinium ion	5.95	9.55	1.30	4.55	6.24

[a]The data for the reactions of **1** were taken from ref. 10.

Effect of *ortho*-Nitro Group on Microscopic Rate Constants. As shown in Table 2, the k_2/k_{-1} ratio decreases as the amine basicity decreases for both reactions of **1** and **2**. The k_2 value has been suggested to be independent of the basicity of amines, since the N atom of the aminium moiety of $T^\pm$ cannot provide a push to expel the leaving aryloxide from $T^\pm$ due to the lack of an electron pair on its nitrogen atom.[1d,13] On the other hand, the k_{-1} value would increase as the amine basicity decreases. Thus, one can expect that the k_2/k_{-1} ratio would decrease as the amine basicity decreases. In fact, as shown in Table 2, the k_2/k_{-1} ratio decreases as the amine basicity decreases.

In Figure 3 is illustrated the effect of amine basicity on the k_2/k_{-1} ratio. The plots of log k_2/k_{-1} *vs.* pK_a of the conjugate acid of amines are linear for the reactions of **1** and **2**, although the slope of the linear plots is slightly larger for the reactions of **2** (*i.e.*, $\beta_{-1} = 0.49$) than for those of **1** (*i.e.*, $\beta_{-1} = 0.40$).

The reaction of **2** would results in a smaller k_2 value than

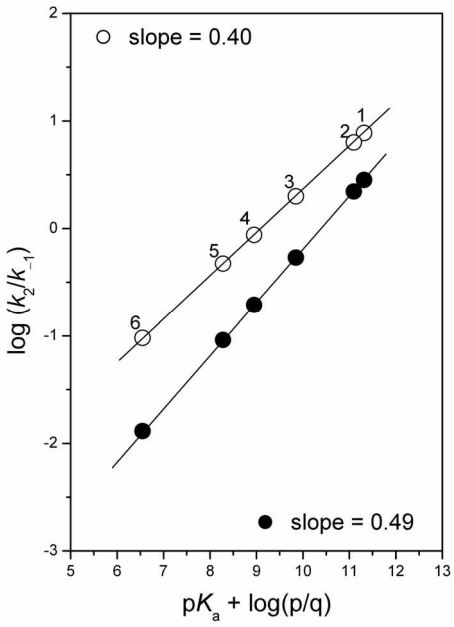


Figure 3. Plots of log k_2/k_{-1} versus pK_a for the reactions of 2,4-dinitrophenyl 2-thiophenecarboxylates **1** (○) and 3,4-dinitrophenyl 2-thiophenecarboxylates **2** (●) with secondary alicyclic amines in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C. The identity of points is given in Table 2.

that of **1** for a given amine, since 3,4-dinitrophenoxide is more basic and a poorer nucleofuge than 2,4-dinitrophenoxide. On the other hand, the k_{-1} value would be little influenced by the basicity of the leaving group. Thus, one might expect that the k_2/k_{-1} ratio is smaller for the reaction of **2** than for the corresponding reaction of **1**. In fact, Table 2 and Figure 3 show that the k_2/k_{-1} ratio is smaller for the reaction of **2** than for the reaction of **1** for a given amine.

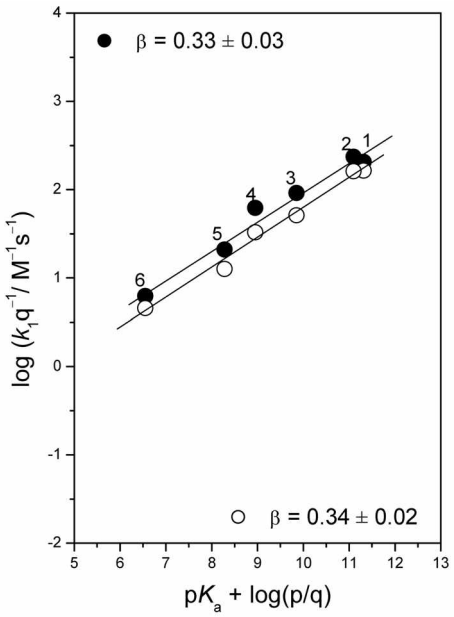


Figure 4. Bronsted-type plots for the reactions of 2,4-dinitrophenyl 2-thiophenecarboxylates **1** (○) and 3,4-dinitrophenyl 2-thiophenecarboxylates **2** (●) with secondary alicyclic amines in 80 mol % H_2O/20 mol % DMSO at 25.0 ± 0.1 °C. The identity of points is given in Table 2.

Table 2 shows that k_1 increases with increasing amine basicity for the reactions of **1** and **2**. The effect of amine basicity on k_1 is illustrated in Figure 4. The plots of log k_1 *vs.* pK_a of the conjugate acid of amines are linear. Interestingly, the reaction of **2** exhibits a slightly larger k_1 value than that of **1** for a given amine. This result is unexpected, since the C=O bond of **2** would be less electrophilic than that of **1** on the basis of the fact that 3,4-dinitrophenoxide is more basic than 2,4-dinitrophenoxide. Accordingly, the difference in basicity between the two nucleofuges cannot account for the k_1 values determined for the reactions of **1** and **2**.

The steric hindrance exerted by the *ortho*-NO_2 in substrate **1** would be significant for the nucleophilic attack process (or when the k_1 step is the RDS). This idea is consistent with the fact that k_1 is smaller for the reactions of **1** than for the corresponding reactions of **2**, and the reactions of **1** with strongly basic piperidine and 3-methylpiperidine result in smaller k_N values than for the corresponding reactions of **2** when the k_1 step is the RDS. However, the steric hindrance appears to be insignificant when the k_2 step is the RDS, since the reactions of **1** with weakly basic amines result in larger k_N values than for the corresponding reactions of **2** (note that the k_2 step is the RDS when pK_a < 10.4). Thus, one can suggest that steric hindrance is mainly responsible for the fact that the reaction of **1** results in a smaller k_N value than the corresponding reaction of **2** when pK_a > 10.4 (or k_1 is smaller for the former reactions than for the latter ones regardless of the amine basicity).

Conclusions

The current study has allowed us to conclude the following: (1) Aminolyses of **1** and **2** proceed through $T^{\pm}$ with a change in the RDS. (2) Substrate **2** is less reactive than substrate **1** toward weakly basic amines (pK_a < 10.4) but becomes more reactive as the basicity of amines increases further. (3) Dissection of k_N into the microscopic rate constants has revealed that aminolysis of **2** results in smaller k_2/k_{-1} ratio as expected, however unexpectedly, the k_1 value is larger for the reaction of **2** than the corresponding reaction of **1**. (4) The steric effect of the *ortho*-NO_2 is significant when the k_1 is the RDS but insignificant when the k_2 process is the slow step. (5) The steric hindrance exerted by the *ortho*-NO_2 is mainly responsible for the fact that the reaction of **1** results in a smaller k_N value than the corresponding reaction of **2** when pK_a > 10.4 (or k_1 is smaller for the former reactions than for the latter ones regardless of the amine basicity).

Experimental Section

Materials. Substrate **2** was readily prepared from the reaction of 3,4-dinitrophenol and 2-thiophenecarbonyl chloride in the presence of triethylamine in anhydrous ether. The purity of **2** was confirmed by its melting point and ^1H

NMR spectrum. Due to the low solubility of **2** in pure H_2O, 20 mol % DMSO/80 mol % H_2O was used as the reaction medium. Doubly glass distilled water was further boiled and cooled under nitrogen just before use.

Kinetics. The kinetic studies were performed at 25.0 ± 0.1 °C with a Scinco S-3100 UV-Vis spectrophotometer equipped with a constant temperature circulating bath for slow reactions (*e.g.*, $t_{1/2} \geq 10$ s) or with an Applied Photophysics Stopped-flow spectrophotometer for fast reactions (*e.g.*, $t_{1/2} < 10$ s). The reactions were followed by monitoring the appearance of 3,4-dinitrophenoxide ion at 410 nm. All the reactions were carried out under pseudo-first-order conditions in which the amine concentration was at least 20 times greater than that of the substrate **2**.

Products Analysis. 3,4-Dinitrophenoxide ion was liberated quantitatively and identified as one of the reaction products by comparison of the UV-vis spectra after the completion of the reactions with those of the authentic samples under the same reaction conditions.

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