# Kinetic Study on $S_NAr$ Reactions of 1-(Y-Substituted-phenoxy)-2,4-dinitrobenzenes with Azide Ion: Effect of Changing Nucleophile from Hydroxide to Azide Ion on Reaction Mechanism and Reactivity

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Second-order rate constants ($k_{N3-}$) for $S_NAr$ reactions of 1-(Y-substituted-phenoxy)-2,4-dinitrobenzenes (**2a–2h**) with $N_3^-$ in 80 mol % $H_2O$/20 mol % DMSO at 25.0 ± 0.1 °C have been measured spectrophotometrically. The Brønsted-type plot is linear with $\beta_{lg} = -0.38$. The Hammett plots correlated with $\sigma_Y^o$ and $\sigma_Y^-$ constants exhibit highly scattered points. In contrast, the Yukawa–Tsuno plot results in an excellent linear correlation with $\rho_Y = 1.02$ and $r = 0.51$, indicating that a negative charge develops partially on the O atom of the leaving Y-substituted-phenoxy moiety in the transition state. Accordingly, the reactions have been concluded to proceed through a stepwise mechanism, in which expulsion of the leaving group occurs in the rate-determining step. Comparison of $k_{N3-}$ with the $k_{OH-}$ values reported previously for the corresponding reactions with $OH^-$ has revealed that $N_3^-$ is only 6- to 26-fold less reactive than $OH^-$ toward substrates **2a–2h**, although the former is over 11 $pK_a$ units less basic than the latter. Solvation and polarizability effects have been suggested to be responsible for the unusual reactivity shown by $N_3^-$ and $OH^-$. Effects of changing nucleophile from $OH^-$ to $N_3^-$ on reaction mechanism and reactivity are discussed in detail.

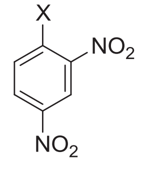
**Keywords:** $S_NAr$ reaction, 1-Phenoxy-2,4-dinitrobenzene, Rate-determining step, Hammett plot, Yukawa–Tsuno plot

## Introduction

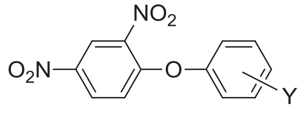
Numerous studies on nucleophilic substitution reactions of activated aromatic compounds with various nucleophiles have been carried out due to their importance not only in biological process but also in synthetic applications.[1–10] In fact, nucleophilic aromatic substitution ($S_NAr$) reactions of aromatic compounds activated by one or more powerful electron-withdrawing groups (*e.g.*, $NO_2$, $SO_2CF_3$, $F_3CSO{=}NSO_2CF_3$, etc.) have been reported to be useful in organic synthesis including improved methods of stereoselective reaction,[7] in preparation of electrophilic derivatives of water soluble polymers as well as poly(aryl ethers),[8] and in some possible environmental remediation protocols.[9]

$S_NAr$ reactions have generally been understood to proceed through a stepwise mechanism, *i.e.*, nucleophilic attack at the position bearing a leaving group to form a σ-bonded adduct, commonly referred to as a Meisenheimer complex, followed by expulsion of the leaving group.[1–6] There is a similarity between nucleophilic substitution reactions of carboxylic esters and $S_NAr$ reactions of activated aromatic compounds possessing a leaving group, *e.g.*, nucleophilic addition step rehybridizes the electrophilic center from $sp^2$ to $sp^3$ to yield a tetrahedral intermediate and expulsion of the leaving group in the subsequent step regenerates the $sp^2$ center. However, a fundamental difference in $S_NAr$ reactions is loss of aromaticity on formation of a Meisenheimer complex and restoration of aromaticity on expulsion of the leaving group.

The rate-determining step (RDS) in $S_NAr$ reactions has been reported to be dependent on reaction conditions (*e.g.*, reaction medium, type of nucleophile and leaving group, etc.).[2,3,10] We have shown that expulsion of the leaving group from the Meisenheimer complex occurs in the RDS for $S_NAr$ reactions of 1-fluoro-2,4-dinitrobenzene (**1a**) with secondary amines in MeCN.[10a] In contrast, expulsion of the leaving group has been reported to occur after the RDS for the corresponding reactions carried out in $H_2O$ and for those with primary amines in MeCN or for those of other 1-X-2,4-dinitrobenzenes, *e.g.*, X = Cl (**1b**), Br (**1c**), and I (**1d**), with primary and secondary amines not only in MeCN but also in $H_2O$.[10b]



X = F (**1a**), Cl (**1b**), Br (**1c**), I (**1d**)



Y = 4-Me (**2a**), H (**2b**), 4-Cl (**2c**), 3-Cl (**2d**), 4-COMe (**2e**), 4-CN (**2f**), 4-CHO (**2g**), 4-$NO_2$ (**2h**)

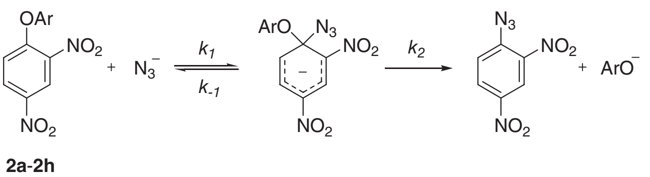
$S_NAr$ reactions with anionic nucleophiles have also been carried out.[10d] We have recently reported that $S_NAr$ reactions of 1-(Y-substituted-phenoxy)-2,4-dinitrobenzenes (**2a–2h**) with alkali-metal ethoxides ($EtO^-M^+$; $M^+ = Li^+, Na^+, K^+$) in anhydrous ethanol proceed through a stepwise mechanism with a Meisenheimer complex, in which expulsion of the leaving group occurs after the RDS, on the basis of the kinetic results that $\sigma^o$ constants resulted in a much better Hammett correlation than $\sigma^-$ constants.[10d] A similar result has been reported for the reactions of **2a–2h** with $OH^-$ in 80 mol % $H_2O$/20 mol % DMSO.[10e]

Our study has now been extended to $S_NAr$ reactions of **2a–2h** with $N_3^-$ to obtain further information on the reaction mechanism (Scheme 1). Azide ion has been reported to be highly regioselective in epoxide-ring opening to give α-azidoalcohols.[11] Azide ion is also known to be useful in synthesis of 1,2,3-triazoles from epoxides and in cycloaddition of [3+2] azide-alkyne and azide-nitrile which leads to triazoles and tetrazoles, respectively.[11,12] Although $N_3^-$ is a weak base, it is known to be an excellent nucleophile especially toward polarizable substrates.[13,14] We have compared the kinetic results obtained from the current $S_NAr$ reactions with those reported previously for the corresponding reactions with $OH^-$[10e] to investigate effects of changing nucleophile from strongly basic $OH^-$ to weakly basic $N_3^-$ on reaction mechanism and reactivity.

## Results and Discussion

The kinetic study was carried out under pseudo-first-order conditions with the nucleophile concentration in excess (≥20-fold) over the substrate concentration. All the reactions in this study obeyed first-order kinetics with quantitative liberation of Y-substituted-phenoxide ion and/or its conjugate acid (*i.e.*, Y-substituted-phenol). Pseudo-first-order rate constants ($k_{obsd}$) were calculated from the equation $\ln (A_\infty - A_t) = -k_{obsd}t + C$. The second-order rate constants ($K_{N3}-$) were calculated from the slope of linear plots of $k_{obsd}$ vs. [N3−]. The $K_{N3}-$ values calculated in this way and relevant $pK_a$ values are summarized in Table 1 for the reactions of **2a–2h** with N3− together with the $k_{OH}$ _values reported previously for the corresponding reactions with $OH^-$ for comparison. It is estimated from replicate runs that the uncertainty in the rate constants is less than ±3%.

**Deduction of Reaction Mechanism.** As shown in Table 1, the second-order rate constant for the reactions of **2a–2h** with $N_3^-$ increases as the basicity of the leaving group decreases, *e.g.*, $K_{N3}-$ increases from $0.137 \times 10^{-3}/M^{-1}s^{-1}$ to $0.924 \times 10^{-3}$ and $1.99 \times 10^{-3}/M^{-1}s^{-1}$ as the $pK_a$ of the conjugate acid of the leaving Y-substituted-phenoxide ion decreases from 10.19 to 8.05 and 7.14, in turn. A similar result is shown for the corresponding reactions with $OH^-$, although hydroxide ion is up to 26-fold more reactive than azide ion. The difference in reactivity of $N_3^-$ and $OH^-$ will be discussed in detail in the following section.



Scheme 1. $S_NAr$ reactions of **2a–2h** with $N_3^-$.

To deduce reaction mechanism, Brønsted-type plots have been constructed. As shown in Figure 1, the Brønsted-type plot for the reactions with $N_3^-$ is linear with $\beta_{lg} = -0.38$. The plot for the corresponding reactions with $OH^-$ is also linear with $\beta_{lg} = -0.16$. It is noted that a $\beta_{lg}$ value of $-0.3 \pm 0.1$ is typical for reactions reported previously to proceed through a stepwise mechanism with formation of an intermediate being the RDS.[10,15,16] In fact, the $S_NAr$ reactions of **2a–2h** with $OH^-$ were suggested to proceed through a stepwise mechanism with a Meisenheimer complex, in which expulsion of the leaving group occurs after the RDS, on the basis of a linear Brønsted-type plot with $\beta_{lg} = -0.16$.[10e] Thus, one might propose that the $S_NAr$ reactions of **2a–2h** with $N_3^-$ proceed also through a stepwise mechanism with formation of a Meisenheimer complex being the RDS.

To examine validity of the above proposal, Hammett plots for the reactions of **2a–2h** with $N_3^-$ have been constructed using $\sigma^o$ and $\sigma^-$ constants in Figure 2. It is well-known that useful

**Table 1.** Summary of second-order rate constants for the reactions of 1-(Y-substituted-phenoxy)-2,4-dinitrobenzenes (**2a–2h**) with $N_3^-$ and $OH^-$ in 80 mol % $H_2O$/20 mol % DMSO at 25.0 ± 0.1 °C.[a]

| | Y | $pK_a^{Y\text{-}PhOH}$ | $10^3k_{N3}-/M^{-1}s^{-1}$ | $10^3k_{OH}-/M^{-1}s^{-1}$ |
|---|---|---|---|---|
| **2a** | 4-Me | 10.19 | 0.137 | 3.62 |
| **2b** | H | 9.95 | 0.175 | 4.05 |
| **2c** | 4-Cl | 9.38 | 0.357 | 5.77 |
| **2d** | 3-Cl | 9.02 | 0.495 | 6.50 |
| **2e** | 4-COMe | 8.05 | 0.924 | 8.56 |
| **2f** | 4-CN | 7.95 | 1.53 | 11.4 |
| **2g** | 4-CHO | 7.66 | 1.19 | 7.70 |
| **2h** | 4-NO2 | 7.14 | 1.99 | 12.1 |

[a] The kinetic data for the reactions with $OH^-$ were taken from Ref. 10e.

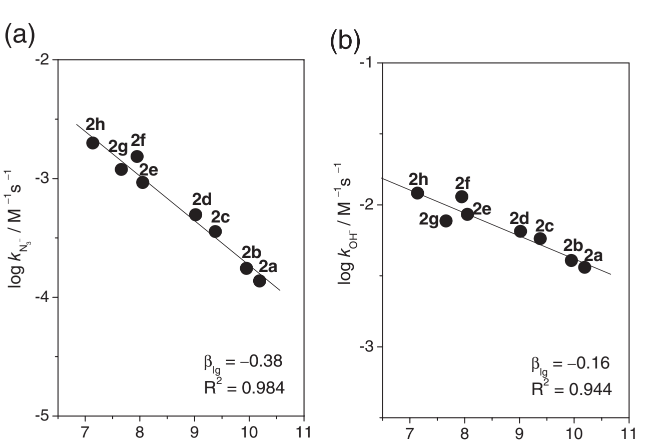


**Figure 1.** Brønsted-type plots for the $S_NAr$ reactions of 1-(Y-substituted-phenoxy)-2,4-dinitrobenzenes (**2a–2h**) with (a) $N_3^-$ and (b) $OH^-$ in 80 mol % $H_2O$/20 mol % DMSO at 25.0 ± 0.1 °C. The identity of points is given in Table 1.

information on reaction mechanism including the RDS can be obtained from Hammett plots correlated with $\sigma^o$ and $\sigma^-$ constants. If the reactions of **2a–2h** with $N_3^-$ proceed through a stepwise mechanism in which expulsion of the leaving group occurs after the RDS (*i.e.*, $k_{-1} << k_2$), no negative charge would develop on the O atom of the leaving Y-substituted-phenoxy moiety in the transition state (TS). In this case, $\sigma^o$ constants should result in a better Hammett correlation than $\sigma^-$ constants. In contrast, if the reactions proceed through a concerted mechanism or via a stepwise pathway with expulsion of the leaving group being the RDS (*i.e.*, $k_{-1} >> k_2$), a negative charge would develop partially on the O atom of the leaving group in the TS. In this case, $\sigma^-$ constants should result in a better Hammett correlation than $\sigma^o$ constants. This is because the negative charge developing on the O atom of the leaving Y-substituted-phenoxy moiety can be delocalized to the substituent Y through resonance interactions.

As shown in Figure 2, the Hammett plot correlated with $\sigma_Y{}^o$ constants for the reactions with $N_3^-$ results in a poorer correlation coefficient ($R^2 = 0.968$). A slightly better Hammett correlation is demonstrated when $\sigma_Y{}^-$ constants are used ($R^2 = 0.984$). However, both Hammett plots exhibit highly scattered points. This is in contrast to our previous report that $\sigma_Y{}^o$ constants result in a much better Hammett correlation ($R^2 = 0.991$) than $\sigma_Y{}^-$ constants ($R^2 = 0.941$) for the reactions of **2a–2h** with $OH^-$.[10e] Thus, one cannot obtain conclusive information on the reaction mechanism from these poorly correlated Hammett plots.

To obtain more decisive information on the reaction mechanism for the reactions of **2a–2h** with $N_3^-$, Yukawa–Tsuno plot has been constructed. The Yukawa–Tsuno equation (Eq. (1)) was originally derived to account for the kinetic results obtained from solvolysis of benzylic systems in which a positive charge develops partially at the reaction center.[17,18] However, we have shown that Eq. (1) is highly effective to clarify ambiguities in reaction mechanisms for $S_NAr$ reactions of **2a–2h** with amines as well as for nucleophilic substitution reactions of esters with various nucleophiles (*e.g.*, neutral amines as well as anionic nucleophiles such as $OH^-$, $N_3^-$, and $CN^-$).[15,19]

$$\log k^Y/k^H = \rho_Y\left[\sigma_Y^o + r\left(\sigma_Y^- - \sigma_Y^o\right)\right] \qquad (1)$$

As shown in Figure 3, the Yukawa–Tsuno plot results in an excellent linear correlation with $\rho_Y = 1.02$ and $r = 0.51$. It is noted that the $r$ value in Eq. (1) represents resonance demand of the reaction center or extent of the resonance contribution, while the term $(\sigma_Y{}^- - \sigma_Y{}^o)$ is the resonance substituent constant that measures the capacity for π-delocalization of the π-electron acceptor substituent.[17,18] Thus, the $r$ value of 0.51 found for the reactions of **2a–2h** with $N_3^-$ is a clear indication that a negative charge develops partially on the O atom of the leaving group which can be delocalized to the substituent Y through resonance interactions. This is possible only for reactions in which expulsion of the leaving group occurs in the RDS either in a concerted mechanism or in a stepwise pathway with the second step (*i.e.*, expulsion of the leaving group) being the RDS.

However, one can exclude a possibility that the $S_NAr$ reactions of **2a–2h** with $N_3^-$ proceed through a concerted mechanism. This is because $S_NAr$ reactions are generally understood to proceed through a stepwise mechanism with a Meisenheimer complex. Thus, the current $S_NAr$ reactions are concluded to proceed through a stepwise mechanism, in which expulsion of the leaving group from a Meisenheimer complex occurs in the RDS. This mechanism is clearly in contrast to the mechanism proposed based on the linear Brønsted-type plot with $\beta_{lg} = -0.38$ (*i.e.*, a stepwise mechanism in which expulsion of the leaving group occurs after the RDS).

**Effect of Changing Nucleophile from $OH^-$ to $N_3^-$ on Reaction Mechanism and Reactivity.** It is generally understood that expulsion of the leaving group from a Meisenheimer complex occurs rapidly after the RDS to regain the lost aromaticity.[2–6] In fact, we have recently reported that the $S_NAr$

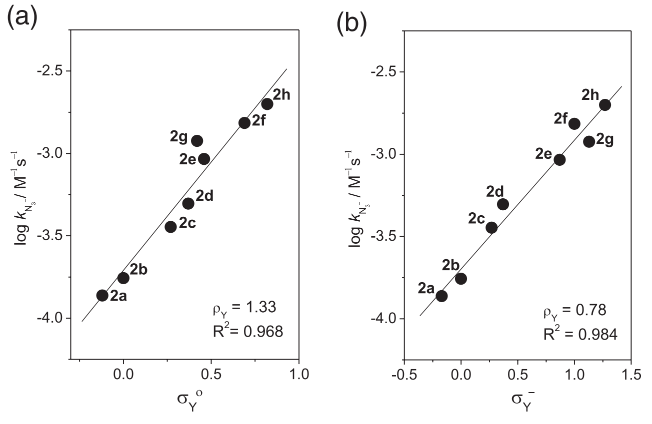


**Figure 2.** Hammett plots correlated with (a) $\sigma_Y^o$ and (b) $\sigma_Y^-$ constants for the $S_NAr$ reactions of 1-(Y-substituted-phenoxy)-2,4-dinitrobenzenes (**2a–2h**) with $N_3^-$ in 80 mol % $H_2O$/20 mol % DMSO at 25.0 ± 0.1 °C.

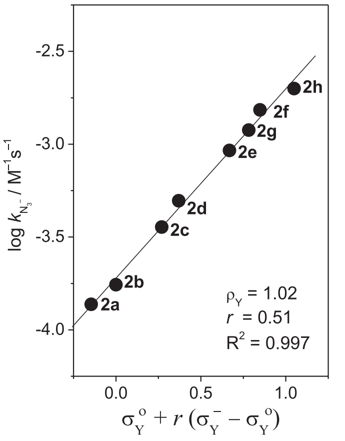
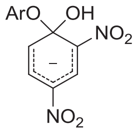


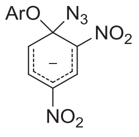
**Figure 3.** Yukawa–Tsuno plot for the $S_NAr$ reactions of 1-(Y-substituted-phenoxy)-2,4-dinitrobenzenes (**2a–2h**) with $N_3^-$ in 80 mol % $H_2O$/20 mol % DMSO at 25.0 ± 0.1 °C.

reactions of **2a–2h** with $OH^-$ and $C_2H_5O^-$ proceed through a stepwise mechanism, in which expulsion of the leaving group occurs after the RDS, on the basis of excellent Hammett correlations with $\sigma^o$ constants.[10d,e] However, expulsion of the leaving group has been concluded to occur in the RDS for the current $S_NAr$ reactions of **2a–2h** with $N_3^-$ on the basis of the linear Yukawa–Tsuno plot with $\rho_Y = 1.02$ and $r = 0.51$. This demonstrates clearly that modification of nucleophile from $OH^-$ to $N_3^-$ changes the RDS from formation of an anionic Meisenheimer complex to its breakdown.

To account for such a change in the RDS upon modification of nucleophile from strongly basic $OH^-$ to weakly basic $N_3^-$, Meisenheimer complexes have been depicted as $MC_{OH}$– and $MC_{N3}$– for the reactions with $OH^-$ and $N_3^-$, respectively. It is noted that $OH^-$ is much more basic and a poorer nucleofuge than all the Y-substituted-phenoxides employed in this study, while $N_3^-$ is less basic and a better nucleofuge than the aryloxides. This explains why expulsion of the leaving group occurs after the RDS for the reactions with $OH^-$ (*i.e.*, $k_{-1} << k_2$) but in the RDS for the corresponding reactions with $N_3^-$ (*i.e.*, $k_{-1} >> k_2$).



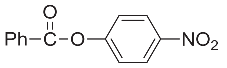
$MC_{OH^-}$



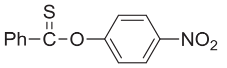
$MC_{N3^-}$

It is noted that $N_3^-$ is only 6–26 times less reactive than $OH^-$, although the former is over 11 $pK_a$ units less basic than the latter (Table 1). Thus, one can suggest that $N_3^-$ is significantly more reactive (or $OH^-$ exhibits unusually lower reactivity) than would be expected from its basicity. This argument is consistent with the report that $N_3^-$ deviates positively from the linear Brønsted-type plot for the reactions of 4-nitrophenyl acetate with a series of aryloxides, while $OH^-$ exhibits negative deviation significantly from the linear Brønsted-type plot.[13] Jencks *et al.* have attributed the decreased reactivity shown by strongly basic $OH^-$ to solvation effect because $OH^-$ is known to be strongly solvated in $H_2O$ through H-bonding interactions.[13] In contrast, one might expect that weakly basic $N_3^-$ would be weakly solvated in the current reaction medium. Thus, one can suggest that solvation effect is one plausible reason why $N_3^-$ is only up to 26-fold less reactive than $OH^-$ although the former is over 11 $pK_a$ units less basic than the latter.

Another possibility that might account for the high reactivity of $N_3^-$ (or unusually low reactivity of $OH^-$) compared with its basicity is polarizability effect. Azide ion is known to be highly polarizable and to exhibit significantly enhanced reactivity toward polarizable electrophiles.[13,14] In contrast, hydroxide ion is a nonpolarizable base and often exhibits unusually low reactivity toward polarizable electrophiles.[14] In fact, we have previously reported that $k_{N3-}$ increases from 0.00234 to 11.0/$M^{-1}s^{-1}$ (*i.e.*, $4.7 \times 10^3$-fold increase) on changing the substrate from 4-nitrophenyl benzoate (**3a**, a C═O centered electrophile) to *O*-4-nitrophenyl thionobenzoate (**3b**, a C═S centered electrophile).[14] In contrast, $k_{OH}$– decreases from 4.20 to 0.470/$M^{-1}s^{-1}$ on changing electrophile from **3a** to **3b**.[14] It is noted that $OH^-$ is $1.8 \times 10^3$-fold more reactive than $N_3^-$ toward **3a**. On the contrary, $N_3^-$ is ca. 23-fold more reactive than more basic $OH^-$ toward the polarizable substrate **3b**.[14]



**3a**



**3b**

It is noted that the electrophilic center of substrates **2a–2h** is highly polarizable due to the polarizable π-electrons in the benzene ring. Thus, one can suggest that the high reactivity exerted by $N_3^-$ toward polarizable substrates **2a–2h** is due to strong interactions between polarizable $N_3^-$ and substrates **2a–2h**, while the unusually decreased reactivity of $OH^-$ is caused by weak interactions between nonpolarizable $OH^-$ and polarizable substrates. This is in accord with the hard–soft acids and bases (HSAB) principle.[20]

## Conclusions

The current study has allowed us to conclude the following: (1) The Brønsted-type plot for the reactions of **2a–2h** with $N_3^-$ is linear with $\beta_{lg} = -0.38$. (2) The Hammett plot correlated with $\sigma_Y^-$ constants results in a slightly better correlation than that correlated with $\sigma_Y^o$ constants. In contrast, the Yukawa–Tsuno plot exhibits an excellent linear correlation with $\rho_Y = 1.02$ and $r = 0.51$, indicating that a negative charge develops partially on the O atom of the leaving Y-substituted-phenoxy moiety in the TS. (3) The $S_NAr$ reactions with $N_3^-$ are concluded to proceed through a stepwise mechanism, in which expulsion of the leaving group occurs in the RDS. This is in contrast to the reaction mechanism reported previously for the corresponding reactions with $OH^-$. The difference in basicity of the nucleophile is responsible for the difference in the reaction mechanism. (4) Azide ion is only 6- to 26-fold less reactive than hydroxide ion toward substrates **2a–2h**, although the former is over 11 $pK_a$ units less basic than the latter. (5) Solvation and polarizability effects are responsible for the unusual reactivity shown by $N_3^-$ and $OH^-$.

## Experimental Section

**Materials.** Substrates **2a–2h** were prepared from the reaction of 1-fluoro-2,4-dinitrobenzene with the respective Y-substituted-phenol in anhydrous ether in the presence of triethylamine as reported previously.[10c] The crude product was purified through column chromatography. The purity of **2a–2h** was checked by means of the melting point and $^1H$ NMR characteristics. Other chemicals used in this study were of the highest quality available. Doubly glass distilled water was further boiled and cooled under nitrogen just before use. Due to low solubility of **2a–2h** in pure $H_2O$, 80 mol % $H_2O$/20 mol % DMSO was used as the reaction medium.

**Kinetics.** The kinetic study was performed using a UV–Vis spectrophotometer equipped with a constant temperature circulating bath to maintain the reaction temperature at 25.0 ± 0.1 °C. The reaction was followed by monitoring the appearance of the leaving Y-substituted-phenoxide ion. All the reactions were carried out under pseudo-first-order conditions in which nucleophile concentrations were at least 20 times greater than the substrate concentration. All solutions were prepared freshly just before use under nitrogen and transferred by gas-tight syringes. The reaction was initiated by adding 5 μL of a 0.01 M solution of the substrates **2a–2h** in $CH_3CN$ by a 10-μL syringe to a 10-mm quartz UV cell containing 2.50 mL of the thermostatted reaction mixture made up of solvent and aliquot of the $NaN_3$ stock solution.

**Product Analysis.** Y-Substituted-phenoxide ion (and/or its conjugate acid) was liberated quantitatively and identified as one of the products by comparison of the UV–Vis spectrum at the end of reaction with the authentic sample under the experimental condition.

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