# Elimination Reactions of (*E*)-2,4,6-Trinitrobenzaldehyde *O*-Benzoyloximes Promoted by $R_2NH/R_2NH_2^+$ in 70 mol% MeCN (aq). Effects of the $\beta$ -Aryl Group and Leaving Group on Nitrile-Forming Transition States

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Elimination reactions of (E)-2,4,6- $(NO_2)_3C_6H_2CH=NOC(O)C_6H_4X$  (**3**) promoted by  $R_2NH/R_2NH_2^+$  in 70 mol% MeCN (aq) have been studied. The reactions produced elimination products and exhibited second-order kinetics. The  $\beta$  and  $|\beta_{lg}|$  values remained nearly the same for all leaving groups and bases. The results can be described by the negligible  $p_{xy}$  interaction coefficient,  $p_{xy} = \partial\beta/\partial pK_{lg} = \partial\beta_{lg}/\partial pK_{BH} \approx 0$ , which provides a strong support for the (E1cb)<sub>irr</sub> mechanism. For eliminations from (E)-ArCH=NOC (O)C<sub>6</sub>H<sub>4</sub>X (**1**, **3**) and (E)-2,4,6- $(NO_2)_3C_6H_2CH=NOAr'$  (**2**, **3**), the change of the  $\beta$ -aryl group (Ar) from 2,4-dinitrophenyl (**1**) to 2,4,6-trinitrophenyl (**3**) increased the rate by 270-fold without appreciable change in the transition state structure. On the other hand, the leaving group (OAr') variation from benzoate (**3**) to 4-nitrophenoxy (**2**) induced a change in reaction mechanism from (E1cb)<sub>irr</sub> to E2. These results have been attributed to the cyclic transition state for the nitrile-forming eliminations involving the benzoate leaving group.

Keywords: Elimination, E2 and (E1cb)<sub>irr</sub>, Mechanism, β-Aryl group and leaving group effect

## Introduction

During the last decades, there has been much interests in the structure–property relationship studies on the basepromoted nitrile-forming eliminations from (*E*)benzaldehyde *O*-benzoyloximes.<sup>1–7</sup> The main interest was how the structural features of such compounds, including *syn*-stereochemistry, poor leaving group, and an sp<sup>2</sup> hybridized  $\beta$ -carbon atom would influence the transition state structure. Most of the reactions proceeded by the E2 mechanism despite the above-mentioned factors favor E1cb- or E1cb-like transition state.<sup>8–11</sup>

Earlier, we reported that the eliminations from (E)-2,4- $(NO_2)_2C_6H_3CH=NOC(O)C_6H_4X$  (1) promoted by R<sub>2</sub>NH/ R<sub>2</sub>NH<sub>2</sub><sup>+</sup> in 70 mol% MeCN (aq).<sup>7</sup> The (E1cb)<sub>irr</sub> mechanism was proposed for this reaction based on the observation of the nitriles and benzoates as the only products as well as the 2nd-order kinetics and nearly identical values of the  $\beta$  and  $|\beta_{1g}|$  for the leaving group and base strength variations. We also investigated the elimination reactions of (E)-2,4,6- $(NO_2)_3C_6H_2CH=NOC_6H_4X$  (2) promoted by R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> in 70 mol% MeCN (aq),<sup>5</sup> with the expectation that the reaction may proceed by the E1cb mechanism because the  $pK_a$  values of benzoic acid and 4-nitrophenol in MeCN are identical<sup>12</sup> and the partial negative charge developed at the  $\beta$ -carbon in the transition state can be better stabilized by the 2,4,6-trinitrophenyl group. However, such expectation was not borne out by the experimental results; the reaction proceeded by the E2 mechanism.

In order to understand the origin of such dichotomy, it seemed crucial to conduct more systematic investigations using substrates having the same  $\beta$ -aryl group and different leaving group and the same leaving group and different  $\beta$ -aryl group. We, therefore, have investigated the reactions of (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC(O)C<sub>6</sub>H<sub>4</sub>X (**3**) with R<sub>2</sub>NH/R<sub>2</sub>NH<sub>2</sub><sup>+</sup> in 70 mol% MeCN (aq) (Eq. (1)). The effect of the  $\beta$ -aryl group was studied by comparing the transition state parameters for **1** and **3**. The influence of the leaving group was assessed by using the transition state parameters for **1** and **2**. The results of these studies are reported here.



X = H, Ar' = C(O)C<sub>6</sub>H<sub>4</sub>Y (1); NO<sub>2</sub>, Ar' = C<sub>6</sub>H<sub>4</sub>Y (2); NO<sub>2</sub>, Ar' = C(O)C<sub>6</sub>H<sub>4</sub>Y (3) Y = H (a), p-OCH<sub>3</sub> (b), m-Br (c), p- CF<sub>3</sub> (d)  $R_2NH = Bz(i-Pr)NH, i-Bu_2NH, i-Pr_2NH, 2,6-DMP$ 

### Results

All compounds (**3a–d**) were prepared in 45–85% yields by stirring the mixtures of appropriate benzoyl chlorides with (E)-2,4,6-trinitrobenzaldoxime in aqueous NaOH solution as before.<sup>1</sup>

When **3a** was reacted with i-Bu<sub>2</sub>NH/i-Bu<sub>2</sub>NH<sub>2</sub><sup>+</sup> in 70 mol% MeCN (aq), 2,4,6-dinitrobenzonitrile was obtained in 96% yield. The hydrolysis product, (*E*)-2,4,6-trinitrobenzaldehyde oxime, was not detected on TLC. The yields of benzoates were determined by comparing the UV absorptions of the infinity samples with those for the authentic benzoates. The yields were in the range of 95–97%.

The rates of the reactions were determined under pseudo-first-order conditions employing at least tenfold excess amount of the base. The decrease in the absorption at the  $\lambda_{max}$  of **3a-d** was monitored. Excellent pseudo-firstorder kinetics plots were obtained over three half-lives. The observed rate constants  $(k_{obs})$  are summarized in Tables S1-S4, Supporting Information. In all cases, the plots of  $k_{obs}$  vs. base concentration were straight lines passing through the origin. This outcome indicates that the reactions are overall second-order, first order to the substrate and first order to the base (Figure S1-S5). The secondorder rate constants  $(k_2)$  were obtained from the slopes of the plots. The  $k_2$  values are summarized in Table 1. The  $k_2$ value increased with basicity and the leaving group ability. There was an exception, however, the  $k_2$  value determined with *i*-Bu<sub>2</sub>NH was faster than those measured with Bz(*i*-Pr) NH, *i*-Pr<sub>2</sub>NH, and 2,6-DMP. This outcome can be attributed to the smaller steric effect of *i*-Bu<sub>2</sub>NH than those of the former.

Figure 1 shows the Brönsted plots for eliminations from **3a–d** promoted by  $R_2NH/R_2NH_2^+$  in 70 mol% MeCN (aq) at 25.0°C. The plots are straight lines, if the data for *i*-Bu<sub>2</sub>NH are excluded. The  $\beta$  values calculated from the slopes of these plots are in the range of 0.25–0.29. The

values remained nearly the same within experimental error for all of the leaving groups (Table 2).

Figure 2 shows the Brönsted  $\beta_{lg}$  plots for eliminations from **3a–d**. The  $k_2$  values correlated reasonably well with the leaving group  $pK_{lg}$  values. Here again, the data for *i*-Bu<sub>2</sub>NH were excluded (Figure 2). The  $|\beta_{lg}|$  values are in the range of 0.30–0.35 and (Table 3). The  $|\beta_{lg}|$  values are nearly the same for all of the leaving groups employed in this study (Table 3).

## Discussion

**Mechanism of Elimination from** 3. Earlier, we reported that the reactions of **2** with  $R_2NH/R_2NH_2^+$  in 70 mol% MeCN (aq) proceeded by the (E1cb)<sub>irr</sub> mechanism.<sup>7</sup> The mechanism of the reactions of **3** with  $R_2NH/R_2NH_2^+$  in 70 mol% MeCN (aq) was also investigated by the product



**Figure 1.** Brönsted plots for eliminations from (E)-2,4,6- $(NO_2)_3C_6H_2CH=NOC(O)C_6H_4Y$  promoted by  $R_2NH/R_2NH_2^+$  in 70 mol% MeCN (aq) at 25.0°C [Y = H (**3a**,  $\bullet$ ), *p*-OMe (**3b**,  $\blacksquare$ ), *m*-Cl (**3c**,  $\blacktriangle$ ), *p*-CF<sub>3</sub> (**3d**,  $\blacktriangledown$ )].

**Table 1.** Rate constants for eliminations from (E)-2,4,6- $(NO_2)_3C_6H_2CH=NOC(O)C_6H_4Y^a$  promoted by  $R_2NH/R_2NH_2^+$  in 70 mol% MeCN (aq)<sup>*b,c*</sup> at 25.0°C.

		$k_2, \mathrm{M}^{-1} \mathrm{s}^{-1f,g}$			
$R_2 NH^d$	pKa <sup>e</sup>	Y = H	Y = p-OMe	Y = m-Br	$Y = p - CF_3$
Bz(i-Pr)NH	16.8	2.79	1.43	6.29	7.12
<i>i</i> -Bu <sub>2</sub> NH	18.2	10.9	5.80	24.3	28.0
<i>i</i> -Pr <sub>2</sub> NH	18.5	7.29	3.66	13.9	17.2
2,6-DMP <sup><math>h</math></sup>	18.9	12.3	5.01	23.0	32.1

<sup>*a*</sup> [Substrate] =  $8.0 \times 10^{-5}$  M.

 $^{c}\mu = 0.1(Bu_4N^{+}Br).$ 

<sup>d</sup> [R<sub>2</sub>NH] =  $1.0 \times 10^{-3} - 2.0 \times 10^{-2}$  M.

<sup>e</sup> Ref. 12.

<sup>f</sup> Average of three or more rate constants.

<sup>*g*</sup> Estimated uncertainty,  $\pm 3\%$ .

<sup>h</sup> cis-2,6-Dimethylpiperidine.

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<sup>&</sup>lt;sup>b</sup>  $[R_2NH]/[R_2NH_2^+] = 1.0.$ 

**Table 2.** Brönsted  $\beta$  values for eliminations from (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC(O)C<sub>6</sub>H<sub>4</sub>Y promoted by R<sub>2</sub>NH/R<sub>2</sub>NH<sub>2</sub><sup>+</sup> in 70 mol% MeCN (aq) at 25.0°C.

	Y = p-OMe	Y = H	Y = m-Br	$\mathbf{Y} = p \text{-} \mathbf{C} \mathbf{F}_3$
$pK_{lg}^{a}$	21.3	20.7	19.5	19.2 <sup>b</sup>
β	$0.25\pm0.02$	$0.29\pm0.05$	$0.25\pm0.05$	$0.29\pm0.07$

<sup>a</sup> Ref. 12.

<sup>b</sup> Determined from the slope of the plot of  $\sigma$  vs. p $K_{a}$ .



**Figure 2.** Plots of log  $k_2$  vs.  $pK_{1g}$  values of the leaving group for the elimination from (E)-2,4,6- $(NO_2)_3C_6H_2CH=NOC(O)C_6H_4Y$  (**3a–d**). Promoted by  $R_2NH/R_2NH_2^+$  in 70 mol% MeCN (aq) at 25.0°C [ $R_2NH = Bz(i-Pr)NH$  ( $\blacksquare$ ), *i*-Bu<sub>2</sub>NH ( $\bullet$ ), *i*-Pr<sub>2</sub>NH ( $\blacktriangle$ ), 2,6-DMP ( $\bigtriangledown$ )].

**Table 3.** Brönsted  $\beta_{lg}$  values for eliminations from (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC(O)C<sub>6</sub>H<sub>4</sub>Y promoted by R<sub>2</sub>NH/R<sub>2</sub>NH<sub>2</sub><sup>+</sup> in 70 mol% MeCN (aq) at 25.0°C.

R <sub>2</sub> NH	Bz(i-Pr)NH	<i>i</i> -Bu <sub>2</sub> NH	<i>i</i> -Pr <sub>2</sub> NH	2,6-DMP <sup>a</sup>
pK <sub>a</sub> <sup>b</sup>	16.8	18.2	18.5	18.9
$\beta_{lg}$	-0.32	-0.32	-0.30	-0.35
	$\pm 0.03$	$\pm 0.03$	$\pm 0.04$	$\pm 0.06$

<sup>a</sup> cis-2,6-Dimethylpiperidine.

<sup>b</sup> Ref. 12.

and kinetic studies. The reactions produced nitriles and benzoates as the only products and exhibited 2nd-order kinetics, first order to the reactant, and first order to the base. The observation of the elimination products and 2ndorder kinetics rules out all but bimolecular  $\beta$ -elimination pathways (Scheme 1). The most likely mechanism for such a process is either E2 or E1cb. Of the three variants of the E1cb mechanisms, (E1cb)<sub>ip</sub>, (E1cb)<sub>R</sub>, and (E1cb)<sub>irr</sub>, the (E1cb)<sub>ip</sub> mechanism can be ruled out because it was observed only in aprotic solvent, not in highly aqueous medium such as 70 mol% MeCN (aq) employed in this study. The distinction between (E1cb)<sub>R</sub> and (E1cb)<sub>irr</sub> can be made using the rate equation. Assuming steady state for the intermediate, the rate equation for the E1cb mechanisms



expressed as  $k_{obs} = k_1 k_2 [B] / (k_{-1} [BH^+] + k_2)$ can be (Scheme 1).<sup>11</sup> For the  $(E1cb)_R$  mechanism, in which the first step must be reversible, *i.e.*,  $k_{-1}[BH^+] \gg k_2$ , the rate expression can be simplified to  $k_{obs} = k_1 k_2 [B] / k_{-1} [BH^+]$ . If  $[B]/[BH^+] = 1.0$ , the equation can further be simplified to  $k_{\text{obs}} = k_1 k_2 / k_{-1}$ . Because [B]/[BH<sup>+</sup>] = 1.0 was maintained throughout the reaction,  $k_{obs}$  should be a constant. In contrast,  $k_{obs}$  was linearly dependent on the base concentration (Figure S1–S5). Hence, the possibility of the (Elcb)<sub>R</sub> mechanism is clearly ruled out. On the other hand, the (E1cb)<sub>irr</sub> mechanism requires that the  $k_{-1}$  step is rate limiting, *i.e.*,  $k_{-1}[BH^+] \ll k_2$ . The rate equation should become  $k_{obs} =$  $k_1$ [B], which is identical to that of the E2 mechanism.<sup>13</sup> Hence, the distinction between the E2 and (E1cb)<sub>irr</sub> mechanisms cannot be made by the rate equation.

The  $|\beta_{1g}|$  values have often been used to distinguish the two mechanisms. The E2 and (E1cb)<sub>irr</sub> mechanisms predict significant and negligible degrees of the N<sub> $\alpha$ </sub>-OC(O)Ar bond cleavage, respectively. Hence, the  $|\beta_{1g}|$  value should be larger for the E2 than for the (E1cb)<sub>irr</sub> mechanism. However, the moderate  $|\beta_{1g}|$  values of 0.30–0.35 determined for this reaction do not provide a clear-cut evidence for either of these mechanisms.

The distinction between the two mechanisms has been made using the interaction coefficients,  $p_{xy} = \partial \beta / \partial p K_{lg} = \partial \beta_{lg} / \partial p K_{BH}$ , which describes the interaction between the base catalyst and the leaving group.<sup>11,14–17</sup> According to this formalism, the E2 mechanism predicts  $p_{xy} > 0$ , while the (E1cb)<sub>irr</sub> mechanism predicts  $p_{xy} \approx 0$ .

As shown in Table 2, the  $\beta$  values for eliminations from **3** are almost the same for all leaving groups. This effect can be ascribed to a negligible  $p_{xy}$  interaction coefficient,  $p_{xy} = \partial\beta/\partial pK_{lg} \approx 0.^{11,14-17}$  The similar  $|\beta_{lg}|$  values for all bases can also be interpreted with  $p_{xy} = \partial\beta_{lg}/\partial pK_{BH} \approx 0$  (Table 3). The negligible  $p_{xy}$  interaction coefficient provides a strong evidence for the (E1cb)<sub>irr</sub> mechanism.

The structures of the transition states have been assessed using the Brönsted  $\beta$  and  $|\beta_{1g}|$  values. The Brönsted  $\beta$  values indicate the extent of proton transfer in the transition state. For eliminations from **3a–d**, values of  $\beta = 0.25-0.29$  were determined (Table 2). This indicates a small degree of proton transfer in the transition state. The  $|\beta_{1g}|$  values are usually taken as the extent of the leaving group bond cleavage. Hence, the observed values of  $|\beta_{1g}| = 0.30-0.35$  (Table 3) are consistent with limited extent of the N<sub> $\alpha$ </sub>-OC(O)Ar bond rupture. Taken together, the elimination reactions of **3** promoted by R<sub>2</sub>NH/R<sub>2</sub>NH<sub>2</sub><sup>+</sup> in 70 mol% MeCN (aq) appear to proceed by the (E1cb)<sub>irr</sub> mechanism via a reactant-like transition state with limited extents of proton transfer and  $N_{\alpha}$ -OC(O)Ar bond cleavage.<sup>13</sup>

**Mapping of the Transition State.** The changes in the transition state parameters can be described on the More-O'Ferrall–Jencks reaction coordinate diagram (Figure 3).<sup>14</sup> For reactions of **3a** with 2,6-DMP, the values of  $\beta = 0.29$  and  $|\beta_{1g}| = 0.35$  indicate limited extents of proton transfer and N<sub>\alpha</sub>-OC(O)Ar bond cleavage. Hence, the transition state can be located near the right corner on the More-O'Ferrall–Jencks reaction coordinate diagram (A in Figure 3).

A change of the leaving group to a better one will increase the energy of the top edge of the diagram. The transition state (A) will remain at nearly the same position resulting in a negligible in  $\beta$  because there is no diagonal character on the horizontal coordinate.

Similarly, a change to a stronger base will raise the energy of the right edge of the diagram. The transition state (A) will then move toward the right edge resulting in a negligible in  $|\beta_{lg}|$  value. The nearly identical values of  $\beta$  and  $|\beta_{lg}|$  values for the leaving group and base strength variations are in good agreement with this prediction. This outcome provides strong support for the above conclusions.

Effect of  $\beta$ -Aryl Group on the Nitrile-Forming Transition State. When the  $\beta$ -aryl group was changed from 2,4dinitrophenyl to 2,4,6-trinitrophenyl, the rate of elimination



**Figure 3.** Reaction coordinate diagram for nitrile-forming eliminations from (*E*)-2,4,6-trinitrobenzaldehyde *O*-benzoyloximes. The transition state for eliminations from **3a** is indicated as A. A change to a better leaving group will have negligible influence on the position of the transition state resulting in a negligible  $\beta$  value. Similarly, a change to a stronger base will shift the transition state toward the right edge resulting in a negligible  $|\beta_{lg}|$  value. For comparison, the effects of the change to a stronger base and a better leaving group on the diagonal reaction coordinate are shown by the shifts from B to C and B to D, respectively.

reaction increased by 270-fold without appreciable changes in the  $\beta$  and  $|\beta_{lg}|$  values (Table 4). This outcome indicates that transition state structures are similar for both reactions, despite large rate difference. This result can be attributed to the cyclic transition state (TS1), in which the negative charge is delocalized through the intramolecular hydrogen bonding. This would stabilize the TS1, thereby rendering it less insensitive to the reactant structure variation. On the other hand, the partial negative charge developed at the  $\beta$ -carbon can be better stabilized by the more strongly electron-withdrawing 2,4,6-trinitrophenyl group, thereby increasing the rate.

Effect of Leaving Group on the Nitrile-Forming Transition State. The mechanism of eliminations from (E)-2,4,6- $(NO_2)_3CH$ =NOX changed from E2 to  $(E1cb)_{irr}$  by the leaving group variation from 4-nitrophenoxide to benzoate, despite their identical  $pK_{1g}$  values<sup>12</sup> (Table 4). Also, the rate of elimination and Brönsted  $\beta$  value decreased by threefold, whereas  $|\beta_{1g}|$  values remained nearly the same. This outcome indicates a smaller extent of proton transfer in the latter transition state and similar degree of the bond to the leaving group rupture in both transition states (Table 5).

These results can be interpreted with a cyclic transition state (TS1). In TS1, the negative charge developed at the  $\beta$ -carbon can be delocalized between the  $\beta$ -carbon and

**Table 4.** Effect of  $\beta$ -aryl group on the transition state parameters for eliminations from (*E*)-ArCH=NOC(O)C<sub>6</sub>H<sub>4</sub>-4-NO<sub>2</sub> promoted by R<sub>2</sub>NH/R<sub>2</sub>NH<sub>2</sub><sup>+</sup> in 70 mol% MeCN (aq) at 25.0°C.

	Ar = 2,4-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> <sup><i>a</i></sup>	$Ar = 2,4,6-(NO_2)_3C_6H_2$
Rel rate <sup>b</sup>	1	270
β	$0.32\pm0.02$	$0.29\pm0.05$
$\beta_{lg}$	$-0.31 \pm 0.01$	$-0.35 \pm 0.06$
$p_{xy}$	~0	~0
<sup>a</sup> Ref. 7.		

 ${}^{b}$  R<sub>2</sub>NH = 2.6-DMP.

**Table 5.** Effect of leaving group on the transition state parameters for eliminations from (E)-2,4,6- $(NO_2)_3$ CH—NOY promoted by  $R_3N/R_3NH^+$  and  $R_2NH/R_2NH_2^+$  in 70 mol% MeCN (aq).

Y	4-Nitrophenyl <sup>a</sup>	Benzoyl
Base	R <sub>3</sub> N/R <sub>3</sub> NH <sup>+</sup>	R <sub>2</sub> NH/R <sub>2</sub> NH <sub>2</sub> <sup>+</sup>
$pK_{lg}$	$20.7^{b,c}$	$20.7^{b,c}$
Rel rate	$3^d$	$1^e$
$p_{xy}$	>0	0
Mechanism	E2	(E1cb) <sub>irr</sub>
β	$0.88\pm0.11$	$0.29\pm0.05$
β <sub>lg</sub>	$-0.34 \pm 0.04$	$-0.30 \pm 0.04$

<sup>a</sup> Ref. 5.

<sup>*b*</sup>  $pK_a$  of the leaving group in MeCN.

<sup>c</sup> Ref. 12.

 $^{e}$  R<sub>2</sub>NH = *i*-Pr<sub>2</sub>NH (pK<sub>a</sub> = 18.5).

 $<sup>^{</sup>d}$  R<sub>3</sub>N = Et<sub>3</sub>N (pK<sub>a</sub> = 18.5).

carbonyl oxygen atoms, the latter of which can further stabilize TS1 by forming intramolecular hydrogen bond with the  $C_{\beta}$ -H proton.



Hence, the transition state should be less sensitive to the leaving group and base strength variations, and the  $(E1cb)_{irr}$  mechanism should be the favored. Because compound **2** cannot attain such a cyclic transition state (TS2), it is less likely for the negative charge at the  $\beta$ -carbon to be stabilized in a similar way. This would predict that the rate should be more sensitive to the base strength, a larger  $\beta$  is expected, and the reaction should follow E2 mechanism where the transition state energy can be minimized by breaking the  $C_{\beta}$ -H and  $N_{\alpha}$ -OAr bonds and forming partial C=N bond concertedly.

# Conclusion

We have studied the elimination reactions of (*E*)-2,4,6trinitrobenzaldehyde *O*-benzoyloximes promoted by R<sub>2</sub>NH/ R<sub>2</sub>NH<sub>2</sub><sup>+</sup> in 70 mol% MeCN (aq). The reaction proceeded by the (E1cb)<sub>irr</sub> mechanism via a cyclic transition state, which is insensitive to the reactant structure variations and favors the (E1cb)<sub>irr</sub> mechanism. The increase in the reaction rate without affecting the transition state structure by the change to a strongly electron-withdrawing β-aryl group provided additional support for the cyclic transition state.

### **Experimental**

Materials. (E)-2,4,6-Trinitrobenzaldoxime was synthesized as reported previously.<sup>1</sup> All of the (E)-2,4,6trinitrobenzaldehyde O-benzoyloximes 1a-d were prepared in reasonable yields by adding appropriate benzoyl chlorides (0.6 mmol) to the solution of (E)-2,4,6trinitrobenzaldoxime (0.14 g, 0.5 mmol) in 0.4 N NaOH (aq) solution at 0°C. The solution was stirred for 20 -30 min at 10°C and poured into 10 mL of cold water. The products were recrystallized from ethanol. It was difficult to obtain HRMS and elemental analysis results of 1 because the compounds decomposed upon standing. However, the NMR data of the compounds were consistent with the proposed structures. The yield (%), melting point (°C), IR (KBr, C=O, cm<sup>-1</sup>), <sup>1</sup>H NMR (400 MHz, acetone- $d_6$ , J values are in Hz), and <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) spectral data for the new compounds are as follows.

(*E*)-2,4,6-( $O_2N$ )<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC(O)C<sub>6</sub>H<sub>5</sub> (3a). Yield 85%; mp 190°C; IR 1762; <sup>1</sup>H NMR  $\delta$  7.61–7.63 (m 2H), 7.73–7.75 (m,1H), 8.14–8.16 (m, 2H), 9.32 (s,2H), 9.39 (s,1H); <sup>13</sup>C NMR  $\delta$  124.0, 125.0, 127.0, 129.1, 129.5, 134.3, 148.4, 149.2, 152.9, 162.2.

(E)-2,4,6-( $O_2N$ )<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC(O)C<sub>6</sub>H<sub>4</sub>-*p*-OMe(3b).Yield 73%; mp 216°C; IR 1772; <sup>1</sup>H NMR  $\delta$  3.93 (s, 3H),7.11 (d, J = 9.16, 2H), 8.10 (d, J = 9.16, 2H), 9.31 (s, 2H),9.34 (s, 1H); <sup>13</sup>C NMR  $\delta$  55.6, 114.4, 118.8, 124.0, 125.1,131.7, 148.3, 149.2, 152.2, 161.8, 163.9.

(*E*)-2,4,6-( $O_2N$ )<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC(O)C<sub>6</sub>H<sub>4</sub>-*m*-Br (3c). Yield 57%; mp 240°C; IR 1782; <sup>1</sup>H NMR  $\delta$  7.60 (t, *J* = 8.08, 1H), 7.93 (d, *J* = 8.08, 1H), 8.15 (d, *J* = 7.68, 1H), 8.30 (s, 1H), 9.33 (s, 2H), 9.45 (s, 1H); <sup>13</sup>C NMR  $\delta$  122.1, 124.0, 124.9, 128.6, 129.3, 131.2, 131.8, 137.0, 148.4, 149.2, 153.4, 161.0.

(*E*)-2,4,6-( $O_2N$ )<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC(O)C<sub>6</sub>H<sub>4</sub>-*p*-CF<sub>3</sub> (3d). Yield 45%; mp 288°C; IR 1744; <sup>1</sup>H NMR  $\delta$  7.83 (d, J = 8.2, 2H), 8.19 (d, J = 7.88, 2H), 9.28 (s, 2H), 9.40 (s, 1H); <sup>13</sup>C NMR  $\delta$  110.0, 124.3, 125.6, 130.1, 130.5, 132.3, 132.6, 134.6, 149.2, 151.2, 153.7, 166.2.

Reagent grade acetonitrile and secondary amine were fractionally distilled from CaH<sub>2</sub>. The solutions of R<sub>2</sub>NH/  $R_2NH_2^+$  in 70 mol% MeCN (aq) were prepared by dissolving equivalent amount of R<sub>2</sub>NH and R<sub>2</sub>NH<sub>2</sub><sup>+</sup> in 70 mol% MeCN (aq). In all cases, the ionic strength was maintained to 0.1 M with Bu<sub>4</sub>N<sup>+</sup>Br<sup>-</sup>.

**Kinetic Studies.** Reactions of **3** with  $R_2NH/R_2NH_2^+$  in 70 mol% MeCN (aq) were followed by monitoring the decrease in the absorbance of the substrate at 258–280 nm with a UV–vis spectrophotometer as described previously.<sup>3,4</sup>

**Product Studies.** The product of eliminations from **3a** promoted by *i*-Bu<sub>2</sub>NH/*i*-Bu<sub>2</sub>NH<sub>2</sub><sup>+</sup> in 70 mol % MeCN (aq) was identified as described.<sup>6</sup> A solution of 0.54 g (1.51 mmol) of **3a** and an excess amount of base in 70 mol % MeCN (aq) (10 mL) was stirred for 5 h at room temperature. The solvent was removed *in vacuo* and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed thoroughly with water until all of the amine, ammonium salt, and aryloxide were completely removed. The product was 2,4,6-trinitrobenzonitrile with mp 133–134°C (lit.<sup>18</sup> mp 134–135°C). The yield of 2,4,6-trinitrobenzonitrile was 96%. Also, the yields of aryloxides determined by comparing the UV absorptions of the infinity samples with those for the authentic aryloxides were in the range of 95–97%.

**Control Experiments.** The stabilities of **3a–d** were determined as reported.<sup>4,6</sup> The solutions of **3** in MeCN were stable for at least 5 weeks when stored in the refrigerator.

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**Supporting Information.** Observed rate constants for elimination from **3a–d** promoted by  $R_2NH/R_2NH_2^+$  in 70 mol% MeCN (aq), plots of  $k_{obs}$  vs. base concentration, and NMR spectra for all compounds are available on

request from the correspondence author (11 pages). E-mail: sypyun@pknu.ac.kr.

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