

## Eliminations from (*E*)-2,4-Dinitrobenzaldehyde *O*-Aryloximes Promoted by R<sub>3</sub>N in MeCN. Effects of β-Aryl Group and Base-Solvent on the Nitrile-Forming Transition-State

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Nitrile-forming eliminations from (*E*)-2,4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC<sub>6</sub>H<sub>4</sub>-2-X-4-NO<sub>2</sub> (**1a-e**) promoted by R<sub>3</sub>N in MeCN have been studied kinetically. The reactions are second-order and exhibit Brønsted β = 0.83-1.0 and |β<sub>lg</sub>| = 0.41-0.46. The results have been interpreted in terms of highly E1cb-like transition state with extensive C<sub>β</sub>-H bond cleavage and limited N<sub>α</sub>-OAr bond cleavage. Comparison with existing data reveals that the structure of the transition state changes from E2-central to highly E1cb-like either by the change of the β-aryl group from Ph to 2,4-dinitrophenyl under the same condition or by the base-solvent system variation from EtO<sup>-</sup>-EtOH to Et<sub>3</sub>N-MeCN for a given substrate (**1a-e**).

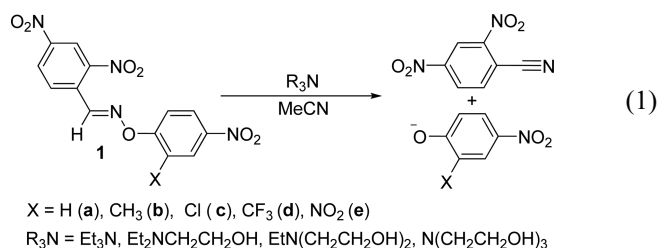
**Key Words** : Elimination, E2 and E1cb-like

### Introduction

Elimination reactions of (*E*)-benzaldehyde *O*-aryloximes have been extensively investigated under various conditions.<sup>1-6</sup> In all cases, the reactions proceeded by the E2 mechanism despite the fact that the reactants have *syn* stereochemistry, poor leaving, and an sp<sup>2</sup> hybridized β-carbon atom, all of which favor E1cb- or E1cb-like transition state.

Previously, we reported that elimination reactions of (*E*)-C<sub>6</sub>H<sub>5</sub>CH=NOC<sub>6</sub>H<sub>4</sub>-2-X-4-NO<sub>2</sub> (**2**) with R<sub>3</sub>N in MeCN proceeded by an E2 mechanism.<sup>1</sup> The transition state was shifted toward the E1cb corner by an electron-withdrawing β-aryl substituent and toward the E1 intermediate and the product by a stronger base in the reaction coordinate diagram. On the other hand, when the leaving group was changed from 2,4-dinitrophenoxide to picrate, the ρ value decreased but the β value increased. The results are in conflict with the prediction of the reaction coordinate diagram because both ρ and β values should be decreased with a better leaving group. The unusual changes in the transition-state structure noted with the leaving group variation have been interpreted as resulting from a large difference in the anion-stabilizing ability of the leaving groups. However, the validity of this interpretation remains to be verified.

To determine whether a change in mechanism could be realized by introducing an even more electron-withdrawing β-aryl substituent, we have now studied the reactions of (*E*)-2,4-dinitrobenzaldehyde *O*-aryloxime with R<sub>3</sub>N in MeCN (eq. 1). Comparison with the existing data for eliminations of (*E*)-C<sub>6</sub>H<sub>5</sub>CH=NOC<sub>6</sub>H<sub>4</sub>-2-X-4-NO<sub>2</sub> promoted by R<sub>3</sub>N-MeCN and of (*E*)-2,4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH=NOC<sub>6</sub>H<sub>4</sub>-2-X-4-NO<sub>2</sub> promoted by EtO<sup>-</sup>-EtOH reveals the effects of β-aryl group and base-solvent on the nitrile-forming transition state.



### Results

(*E*)-2,4-Dinitrobenzaldehyde *O*-aryloximes **1a-e** were prepared by reacting appropriate *O*-arylhydroxylamines with (*E*)-2,4-dinitrobenzaldehyde in ethanol as described previously.<sup>7-9</sup>

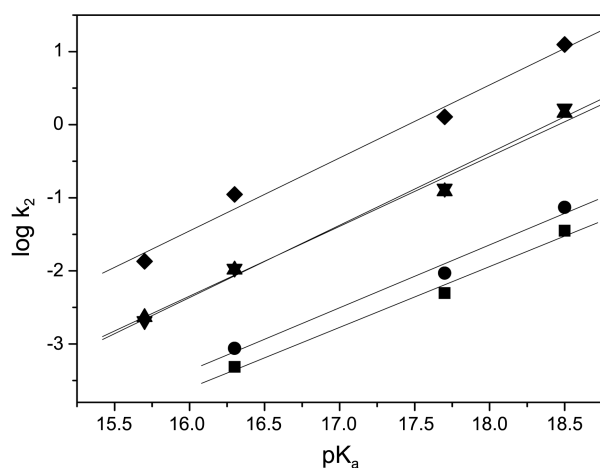
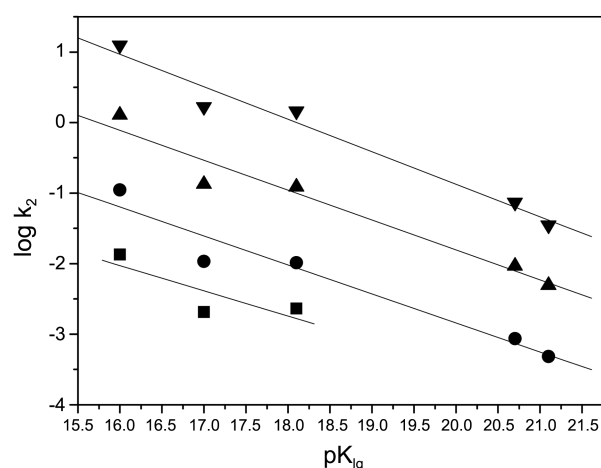
Reactions of **1a-e** with Et<sub>3</sub>N in MeCN produced 2,4-dinitrobenzonitrile and aryloxides. For all reactions, the yields of aryloxides determined by the comparing the absorbance of the infinity samples from the kinetic studies with those of the authentic aryloxides were in the range of 94-97%.

The rates of eliminations from **1a-e** promoted by R<sub>3</sub>N in MeCN were followed by monitoring the increase in the absorption at the λ<sub>max</sub> for the aryloxides. Excellent pseudo-first order kinetics plots, which covered at least three half-lives were obtained. The rate constants are summarized in Tables S1-4 in Supporting Information. The plots of *k*<sub>obs</sub> versus base concentration for the reaction of **1a-e** were straight lines passing through the origin, indicating that the reactions are second-order, first order to the substrate and first order to the base (Figure S1-9). The slopes are the overall second-order rate constants *k*<sub>2</sub>. Having established the second-order kinetics, the rate constants for the base-promoted eliminations from **1a**, **1b** with EtN(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>

**Table 1.** Rate Constants for Nitrile-Forming Elimination from (*E*)-2,4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH=NOC<sub>6</sub>H<sub>4</sub>-2-X-4-NO<sub>2</sub><sup>a</sup> Promoted by R<sub>3</sub>N in MeCN at 25.0 °C

Base <sup>b</sup>	pK <sub>a</sub> <sup>c</sup>	10 <sup>3</sup> k <sub>2</sub> , M <sup>-1</sup> s <sup>-1de</sup> When X is				
		CH <sub>3</sub> ( <b>1b</b> )	H( <b>1a</b> )	Cl ( <b>1c</b> )	CF <sub>3</sub> ( <b>1d</b> )	NO <sub>2</sub> ( <b>1e</b> )
N(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>3</sub>	15.7	-	-	2.32	2.06	13.5
EtN(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>	16.3	0.485	0.869	10.3	10.8	111
Et <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)	17.7	4.94	9.29	122	134	1278
Et <sub>3</sub> N	18.5	35.3	73.8	1446	1670	12499

<sup>a</sup>[Substrate] = 5.0 × 10<sup>-5</sup> M. <sup>b</sup>[R<sub>3</sub>N] = 8.0 × 10<sup>-4</sup> – 0.18 M. <sup>c</sup>Reference 10. <sup>d</sup>Average of three or more rate constants. <sup>e</sup>Estimated uncertainty, ± 3%.

**Figure 1.** Brønsted plots for the elimination from (*E*)-2,4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH=NOC<sub>6</sub>H<sub>4</sub>-2-X-4-NO<sub>2</sub> Promoted by R<sub>3</sub>N in MeCN at 25.0 °C [X = H (**1a**, ●), CH<sub>3</sub> (**1b**, ■), Cl (**1c**, ▲), CF<sub>3</sub> (**1d**, ▼), NO<sub>2</sub> (**1e**, ◆)].**Figure 2.** Plots log k<sub>2</sub> versus pK<sub>lg</sub> values of the leaving group for the elimination from (*E*)-2,4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH=NOC<sub>6</sub>H<sub>4</sub>-2-X-4-NO<sub>2</sub> Promoted by R<sub>3</sub>N in MeCN at 25.0 °C [R<sub>3</sub>N = N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub> (■), EtN(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub> (●), Et<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH) (▲), Et<sub>3</sub>N (▼)].

and **1c-e** with N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub> were determined at a single base concentration. The k<sub>2</sub> values were obtained by dividing the k<sub>obs</sub> by the base concentration. However, the rates for **1a** and **1b** with N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub> could not be determined because the rates were too slow to measure accurately. The k<sub>2</sub> values for eliminations from **1a-e** are summarized in Table 1.

Brønsted plots for eliminations from **1a-e** are depicted in Figure 1. Excellent correlations were obtained between the log k<sub>2</sub> and pK<sub>a</sub> values. The β values are in the range of 0.83-1.0 and remain within experimental errors with the

change in the leaving group (Table 2). Similarly, the rates of eliminations from **1a-e** promoted by EtN(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, Et<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH), and Et<sub>3</sub>N correlated well with the pK<sub>lg</sub> values of the leaving group (Figure 2). When N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub> was employed as the base, however, the Brønsted plot was too scattered to obtain a meaningful β<sub>lg</sub> value (β<sub>lg</sub> = -0.36 ± 0.25). Therefore, the |β<sub>lg</sub>| values determined with EtN(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, Et<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH), and Et<sub>3</sub>N have been used in the discussion. The |β<sub>lg</sub>| values are in the range of 0.41-0.46 and almost the same for all bases employed in this study (Table 3).

**Table 2.** Brønsted β Values for Elimination from (*E*)-2,4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH=NOC<sub>6</sub>H<sub>4</sub>-2-X-4-NO<sub>2</sub> Promoted by R<sub>3</sub>N in MeCN at 25.0 °C

	X = CH <sub>3</sub>	X = H	X = Cl	X = CF <sub>3</sub>	X = NO <sub>2</sub>
pK <sub>lg</sub> <sup>a</sup>	21.1 <sup>b</sup>	20.7	18.1	17.0	16.0
β	0.83 ± 0.09	0.86 ± 0.10	0.95 ± 0.08	0.99 ± 0.08	1.0 ± 0.09

<sup>a</sup>Reference 10. <sup>b</sup>Determined from the slope of the plot of σ vs pK<sub>a</sub>

**Table 3.** Brønsted β<sub>lg</sub> Values for Elimination from (*E*)-2,4-(NO<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH=NOC<sub>6</sub>H<sub>4</sub>-2-X-4-NO<sub>2</sub> Promoted by R<sub>3</sub>N in MeCN at 25.0 °C

R <sub>3</sub> N	N(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>3</sub>	EtN(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>	Et <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)	Et <sub>3</sub> N
pK <sub>a</sub> <sup>a</sup>	15.7	16.3	17.7	18.5
β <sub>lg</sub>	-	-0.41 ± 0.05	-0.42 ± 0.05	-0.46 ± 0.04

<sup>a</sup>Reference 10.

## Discussion

**Mechanism and Transition State Structure for Eliminations from 1 Promoted by R<sub>3</sub>N in MeCN.** Results of kinetic investigations and product studies reveal that the reactions of **1a-e** with tertiary amines produce the elimination products *via* an E2 mechanism. Since the reactions exhibited second-order kinetics, all but bimolecular pathway can be ruled out. In addition, an E1cb mechanism is negated by the substantial values of  $\beta$  and  $|\beta_{lg}|$ .<sup>11,12</sup>

For R<sub>3</sub>N-promoted eliminations from **1a-e**, the Brønsted  $\beta$  values are in the range of 0.83-1.0 and remain almost the same within experimental errors by the change in the leaving group. Similarly, little change in the  $|\beta_{lg}|$  values has been observed by the variation of the base strength (Table 4). The  $\beta$  values near unity and  $|\beta_{lg}| = 0.41$ -0.46 indicate extensive C $\beta$ -H bond cleavage and limited N $\alpha$ -OAr bond rupture in the transition state. Hence, it seems reasonable to locate the transition state near the middle left side of the More-O'Ferrall-Jencks diagram (A in Figure 3).

The results can be described by a zero  $p_{xy}$  interaction coefficient,  $p_{xy} = \partial\beta/\partial pK_{lg} = \partial\beta_{lg}/\partial pK_a$ .<sup>12-15</sup> The zero  $p_{xy}$  interaction coefficient is consistent with an E1cb-like transition state with little diagonal component. On the More-O'Ferrall-Jencks reaction coordinate diagram in Figure 3, a better leaving group would lower the bottom side of the diagram. Since the transition state with little diagonal component should have the energy surface with steeper curvature in the perpendicular than in the parallel direction, the transition state should be shifted from A to B, with increased N $\alpha$ -OAr bond cleavage and larger  $|\beta_{lg}|$  values as well as little change in the C $\beta$ -H bond rupture and nearly identical  $\beta$  values.<sup>12-15</sup> This prediction is borne out by the experimental results (Table 2). Similarly, a stronger base would lower the energy of the left side of the diagram. The transition state should remain nearly at the same position, with little change in the N $\alpha$ -OAr bond cleavage and identical  $|\beta_{lg}|$  values, as observed.<sup>12-15</sup>

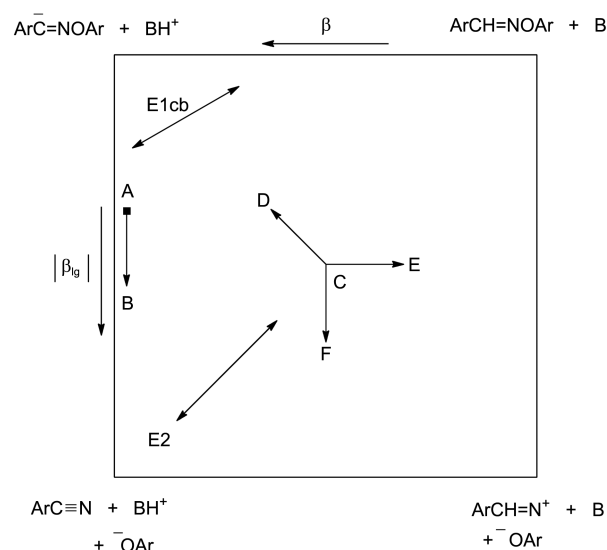
**Effect of  $\beta$ -Aryl Group on the Nitrile-Forming Transition State.** Earlier it was reported that the reactions of (*E*)-C<sub>6</sub>H<sub>5</sub>CH=NOC<sub>6</sub>H<sub>4</sub>-2-X-4-NO<sub>2</sub> (**2**) promoted by R<sub>3</sub>N-MeCN proceeded by the E2 central transition state with significant cleavages of C $\beta$ -H and N $\alpha$ -OAr bonds and extensive triple-bond formation (C in Figure 3).<sup>1</sup> When the  $\beta$ -aryl group was changed from phenyl to 2,4-dinitrophenyl, the rate of elimination increased by  $1.7 \times 10^4$  fold, Brønsted  $\beta$  value increased from 0.55 to 1.0, and  $|\beta_{lg}|$  value increased from 0.39 to 0.46, respectively (Table 4). This indicates a large increase in the C $\beta$ -H bond cleavage and a small increase in the N $\alpha$ -OAr bond rupture in the transition state.

On the More-O'Ferrall-Jencks reaction coordinate diagram in Figure 3, an electron-withdrawing  $\beta$ -aryl substituent will lower the energy of the carbanion intermediate in the upper left corner of the energy diagram.<sup>13</sup> Since the curvature of the energy surface in the diagonal direction is much steeper than that of parallel direction (see above), the transition state will then be shifted from C to A, because a larger effect is

**Table 4.** Effect of the  $\beta$ -Aryl Group on the Nitrile-Forming Eliminations from (*E*)-ArCH=NOC<sub>6</sub>H<sub>3</sub>-2,4-(NO<sub>2</sub>)<sub>2</sub> Promoted by R<sub>3</sub>N in MeCN at 25.0 °C

	Ar = Phenyl ( <b>2</b> ) <sup>a</sup>	Ar = 2,4-(NO <sub>2</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ( <b>1e</b> )
rel. rate	1	$1.7 \times 10^4$
$\beta$	$0.55 \pm 0.03$	$1.0 \pm 0.09$
$ \beta_{lg} $	$0.39 \pm 0.03$	$0.46 \pm 0.04$

<sup>a</sup>Reference 1.



**Figure 3.** Reaction coordinate diagram for nitrile-forming eliminations. The transition states for eliminations from **1e** and **2** are indicated as A and C, respectively. The effect of the change to a better leaving group on A is depicted by the shift from A to B, while the effects of the change to an electron-withdrawing substituent, a better leaving group, and a weaker base on C are shown by the shifts from C to D, C to E, and C to F, respectively.

expected in the direction where the curvature is smaller.<sup>13</sup>

It appears that the strongly electron withdrawing 2,4-dinitrophenyl group increases the C $\beta$ -H bond cleavage by stabilizing the negative charge density developed at the  $\beta$ -carbon, some of which transferred from the  $\beta$ -carbon the  $\alpha$ -nitrogen to form a partial triple bond and to increase the extent of N $\alpha$ -OAr bond rupture.

The 2,4-dinitrophenyl group seems to increase the acidity of the C $\beta$ -H and in part due to stabilize the transition state enormously by the negative charge stabilization at the  $\beta$ -carbon, thereby increasing the elimination rate by  $1.7 \times 10^4$  fold.

**Effect of Base-Solvent.** We reported that elimination from **1e** promoted by RO<sup>-</sup>-ROH proceeded *via* a central-E2 transition state.<sup>6</sup> Comparison of the transition state parameters for eliminations from **1e** reveals that there is a large difference in the transition state structure by the change in the base-solvent from RO<sup>-</sup>-ROH to R<sub>3</sub>N-MeCN (Table 5). The rate increased by 276-fold, despite the decrease in the basicity, the  $\beta$  value increased from 0.55 to 1.0 and  $|\beta_{lg}|$  value increased from 0.39 to 0.46 by the base-solvent variation. This indicates a large increase in the C $\beta$ -H bond cleavage and a modest increase in the N $\alpha$ -OAr bond rupture in the

**Table 5.** Effect of the Base-Solvent on the Nitrile-Forming Eliminations from (*E*)-2,4-(NO<sub>2</sub>)<sub>2</sub> C<sub>6</sub>H<sub>3</sub>CH=NOC<sub>6</sub>H<sub>3</sub>-2,4-(NO<sub>2</sub>)<sub>2</sub>

Base-solvent	RO <sup>-</sup> -ROH <sup>a</sup>	R <sub>3</sub> N-MeCN
p <i>K</i> <sub>a</sub>	19.2 <sup>b,c</sup>	18.5 <sup>d,e</sup>
rel. rate	1	276
$\beta$	0.55 ± 0.03	1.0 ± 0.09
$\beta_{lg}$	0.39 ± 0.03	0.46 ± 0.04

<sup>a</sup>Reference 6. <sup>b</sup>Reference 17. <sup>c</sup>RO<sup>-</sup> = EtO<sup>-</sup>. <sup>d</sup>Reference 10. <sup>e</sup>R<sub>3</sub>N = Et<sub>3</sub>N.

transition state. The result can be attributed to a solvent effect. Since the partial negative charge developed at the  $\beta$ -carbon in the transition state cannot be stabilized by solvation in aprotic MeCN, the transition state should be more sensitive to the change in the base strength to result in a larger  $\beta$  value. Moreover, the negative charge should be transferred from the  $\beta$ -carbon toward the  $\alpha$ -nitrogen to form partial triple bond and loosen the N <sub>$\alpha$</sub> -OAr bond for the maximum delocalization of the negative charge. If a larger amount of negative charge is transferred from the  $\beta$ -carbon, the extent of N <sub>$\alpha$</sub> -OAr bond cleavage should be larger too. This would predict a larger | $\beta_{lg}$ | value. Further, the faster rate of elimination in Et<sub>3</sub>N-MeCN can be attributed to the greater degree of triple bond formation in the transition state. The most interesting result from this study is the change of the transition state from central E2 to highly E1cb-like by the change in the base-solvent system from RO<sup>-</sup>-ROH to R<sub>3</sub>N-MeCN.

In conclusion, we have investigated the elimination reactions of **1a-e** promoted by R<sub>3</sub>N in MeCN. The reaction proceeded by an E2 mechanism *via* highly E1cb-like transition state. It appears that the strongly electron-withdrawing 2,4-dinitro group increased the acidity of the C <sub>$\beta$</sub> -H and in part due to stabilize the transition state enormously by the negative charge stabilization at the  $\beta$ -carbon. The most interesting result from this study is the change of the transition state from central E2 to highly E1cb-like by the change of the  $\beta$ -aryl group from Ph to 2,4-dinitrophenyl under the same condition and by the base-solvent system variation from RO<sup>-</sup>-ROH to R<sub>3</sub>N-MeCN for a given substrate (**1a-e**).

### Experimental Section

**Materials.** (*E*)-2,4-Dinitrobenzaloxime was synthesized as reported previously.<sup>7-9</sup> All of the (*E*)-2,4-dinitrobenzaldehyde *O*-aryloximes were prepared by the reactions of 2,4-dinitrobenzaldehyde with appropriately substituted *O*-arylhydroxylamines in the presence of catalytic amount of HCl. The spectral and analytical data of the compounds were consistent with the proposed structures. The yield (%), melting point (C), IR (KBr, C=N, cm<sup>-1</sup>), <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, *J* values are in Hz), and mass spectral data for the compounds are as follows. Chemical shifts are in ppm and *J* values in Hz.

**(*E*)-2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH=NOC<sub>6</sub>H<sub>4</sub>-4-NO<sub>2</sub> (**1a**):** Yield 68%; mp 181-182 °C; IR 1588 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.54 (d, *J* = 7.2 Hz, 2H), 8.32 (d, *J* = 7.2 Hz, 2H), 8.36 (d, *J* = 8.7 Hz,

1H), 8.65 (dd, *J* = 8.7, 2.4 Hz, 1H), 8.87 (s, 1H), 9.20 (s, 1H); HRMS-(EI); *m/z* calcd for C<sub>13</sub>H<sub>8</sub>N<sub>4</sub>O<sub>7</sub> 332.0393, found 332.0392.

**(*E*)-2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH=NOC<sub>6</sub>H<sub>3</sub>-2-CH<sub>3</sub>-4-NO<sub>2</sub> (**1b**):** Yield 71%; mp 168-170 °C; IR 1588 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  2.37 (s, 3H), 7.67 (d, *J* = 9.1 Hz, 1H), 8.16 (dd, *J* = 9.1, 2.7 Hz, 1H), 8.21 (s, 1H), 8.36 (d, *J* = 8.5 Hz, 1H), 8.65 (dd, *J* = 8.5, 2.1 Hz, 1H), 8.86 (s, 1H), 9.23 (s, 1H); HRMS-(EI); *m/z* calcd for C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>O<sub>7</sub> 346.0549, found 346.0549.

**(*E*)-2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH=NOC<sub>6</sub>H<sub>3</sub>-2-Cl-4-NO<sub>2</sub> (**1c**):** Yield 73%; mp 158-160 °C; IR 1586 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  7.86 (d, *J* = 9.2 Hz, 1H), 8.30 (dd, *J* = 9.2, 2.7 Hz, 1H), 8.37 (d, *J* = 8.6 Hz, 1H), 8.45 (s, 1H), 8.68 (dd, *J* = 8.6, 2.4 Hz, 1H), 8.88 (s, 1H), 9.32 (s, 1H); HRMS-(EI); *m/z* calcd for C<sub>13</sub>H<sub>7</sub>ClN<sub>4</sub>O<sub>7</sub> 366.0003, found 366.0004.

**(*E*)-2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH=NOC<sub>6</sub>H<sub>3</sub>-2-CF<sub>3</sub>-4-NO<sub>2</sub> (**1d**):** Yield 76%; mp 167-169 °C; IR 1598 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  8.02 (d, *J* = 9.6 Hz, 1H), 8.38 (d, *J* = 8.5 Hz, 1H), 8.51 (s, 1H), 8.62 (dd, *J* = 9.2, 2.7 Hz, 1H), 8.68 (dd, *J* = 8.5, 2.4 Hz, 1H), 8.88 (s, 1H), 9.30 (s, 1H); HRMS-(EI); *m/z* calcd for C<sub>13</sub>H<sub>7</sub>F<sub>3</sub>N<sub>4</sub>O<sub>7</sub> 400.0267, found 400.0267.

**(*E*)-2,4-(O<sub>2</sub>N)<sub>2</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC<sub>6</sub>H<sub>3</sub>-2,4-(NO<sub>2</sub>)<sub>2</sub> (**1e**):** Yield 69%; mp 165-167 °C; IR 1601 cm<sup>-1</sup>; <sup>1</sup>H NMR  $\delta$  8.08 (d, *J* = 9.2 Hz, 1H), 8.36 (d, *J* = 8.6 Hz, 1H), 8.60 (dd, *J* = 9.2, 2.7 Hz, 9.24), 8.69 (dd, 1H, *J* = 8.6, 2.0 Hz, 1H), 8.88 (m, 2H), 9.34 (s, 1H); HRMS-(EI); *m/z* calcd for C<sub>13</sub>H<sub>7</sub>N<sub>5</sub>O<sub>9</sub> 377.0244, found 377.0239.

Reagent-grade acetonitrile and tertiary amine were fractionally distilled from CaH<sub>2</sub>. The base-solvent solution was prepared by dissolving the appropriate amines to MeCN.

**Kinetic Studies.** Kinetics of eliminations from **1** were followed by monitoring the increase in the absorbance of the aryloxides at 400-426 nm with a UV-vis spectrophotometer as described.<sup>1,18</sup>

**Product Studies.** The product from the reaction of **1a** with Et<sub>3</sub>N in MeCN was identified by using more concentrated solution as described previously.<sup>19</sup> A solution of 0.5 g (1.51 mmol) of **1a** and an excess amount of base in the appropriate base (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-dinitrobenzonitrile with mp 103-105 °C (lit.<sup>20</sup> mp 104-105 °C). The yield of 2,4-dinitrobenzonitrile was 97%. 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 **1** were determined as reported earlier.<sup>6,19</sup> The solutions of **1** in MeCN were stable for at least two days when stored in the refrigerator.

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**Support Information Available.** Observed rate constants

for elimination from **1a-e** promoted by  $R_3N$  in MeCN, plots of  $k_{\text{obs}}$  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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