

## Elimination Reactions of (*E*)-2,4,6-Trinitrobenzaldehyde *O*-Aryloximes Promoted by R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> in 70 mol % MeCN(aq). Effect of β-Aryl Group the Nitrile-Forming Transition-State

Sang Yong Pyun,<sup>\*</sup> Woong Sub Byun,<sup>†</sup> and Bong Rae Cho<sup>‡\*</sup>

Department of Chemistry, Pukyong National University, Pusan 608-737, Korea. \*E-mail: sypyun@pknu.ac.kr

<sup>†</sup>Department of Chemistry, Konkuk University, Seoul 143-70, Korea

<sup>‡</sup>Department of Chemistry, Korea University, Seoul 136-701, Korea. \*E-mail: chobr@korea.ac.kr

Received March 16, 2011, Accepted April 19, 2011

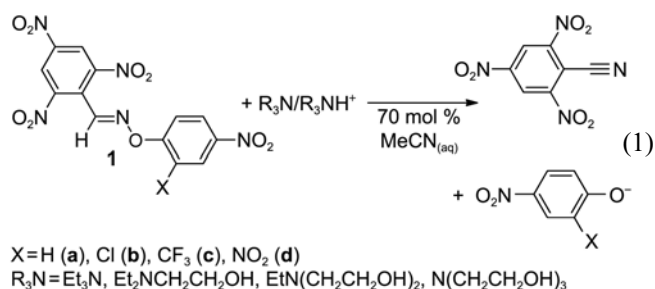
Nitrile-forming eliminations from (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC<sub>6</sub>H<sub>4</sub>-2-X-4-NO<sub>2</sub> (**1**) promoted by R<sub>3</sub>NH/R<sub>3</sub>NH<sup>+</sup> in 70 mol % MeCN(aq) have been studied kinetically. When X = NO<sub>2</sub>, the reactions exhibited second-order kinetics as well as Brønsted β = 0.63 and |β<sub>lg</sub>| = 0.34-0.46, and an E2 mechanism is evident. As the leaving group was made poorer (X = H, Cl, and CF<sub>3</sub>), Brønsted β value increased from 0.63 to 0.85-0.89 without much change in the |β<sub>lg</sub>| value E2, indicating that structure of the transition state changed to an E1cb-like with extensive C<sub>β</sub>-H bond cleavage, significant negative charge development at the β-carbon, and limited C<sub>α</sub>-OAr bond cleavage.

**Key Words :** Elimination, E2 and E1cb-like, β-Aryl group effect

### Introduction

Base-promoted elimination reactions of (*E*)-benzaldehyde *O*-aryloximes have been extensively investigated under various conditions.<sup>1-6</sup> We have employed mono-substituted phenyl and 2,4-dinitrophenyl groups as the β-aryl group and 4-nitrophenoxy, 2,4-dinitrophenoxy, and picrate as the leaving group, and HO<sup>-</sup> in 60% DMSO(aq), RO<sup>-</sup> in ROH, R<sub>2</sub>N<sup>-</sup> in MeCN, and R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> in 70 mol % MeCN(aq) as the base-solvent system, respectively. In all cases, the reactions proceeded by the E2 mechanism despite the fact that the reactants have *syn* stereochemistry, poor leaving, and sp<sup>2</sup> hybridized β-carbon atom, all of which favor E1cb- or E1cb-like transition state. Very recently, we discovered an (E1cb)<sub>irr</sub> mechanism for the reaction 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>5</sub> (**2a**) with R<sub>2</sub>NH in MeCN.<sup>7</sup> The result has been attributed to the strong electron withdrawing ability of β-aryl group and the poor leaving group ability the benzoate.

The result is somewhat surprising, since MeCN is a poor anion solvating solvent that stabilizes E2 transition state with maximum charge dispersal. We were interested in learning whether the occurrence of in the (E1cb)<sub>irr</sub> mechanism might be due to the strongly anion-stabilizing β-aryl group in **2a**. To provide a better insight the nitrile-forming transition state, we have now studied the reactions of (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC<sub>6</sub>H<sub>4</sub>-4-X (**1a-d**) with R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> in 70 mol % MeCN(aq) (eq. 1). Since the pK<sub>a</sub> values of benzoic acid and 4-nitrophenol are identical in MeCN,<sup>8</sup> a similar mechanism should be anticipated, if the above interpretation could be applied. Herein, we report the similarities and differences in the nitrile-forming eliminations from **1a-d** and **2a**.



### Results

(*E*)-2,4,6-Trinitrobenzaldehyde *O*-aryloximes **1a-d** were prepared by reacting appropriate *O*-arylhydroxylamines with (*E*)-2,4,6-trinitrobenzaldehyde in ethanol as described previously.<sup>9-11</sup>

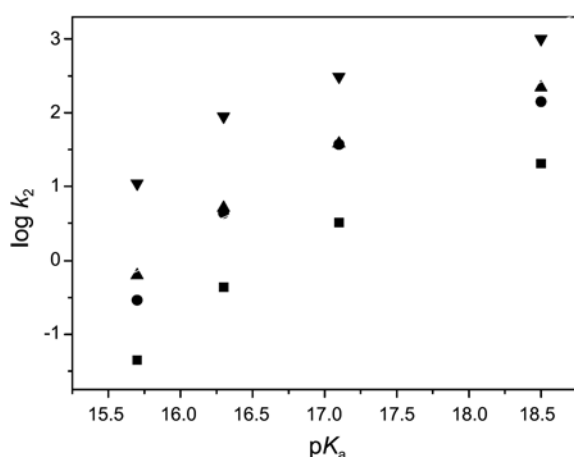
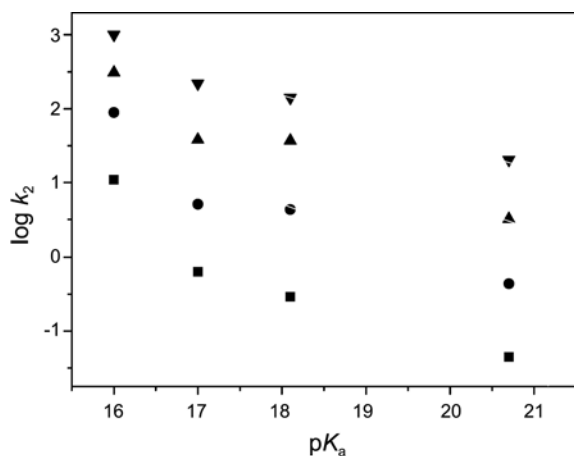
The reactions of **1a** with Et<sub>3</sub>N/Et<sub>3</sub>NH<sup>+</sup> in 70 mol % MeCN(aq) produced 2,4,6-trinitrobenzonitrile in 94%. No trace of (*E*)-2,4,6-trinitrobenzaldehyde oxime could be detected by TLC. For all reactions, the yields of aryloxides determined by the comparing the absorbance of the infinity samples from the kinetic studies with those of the authentic aryloxides were in the range of 95-98%.

The rates of elimination reactions were followed by monitoring the increase in the absorption at the λ<sub>max</sub> for the leaving groups in the range of 400-426 nm. Reactions were followed under pseudo-first order conditions employing at least a ten-fold excess of base. Plots of ln(A<sub>∞</sub>-A<sub>t</sub>) versus time were linear over at least three half-lives of the reaction. The rate constants (k<sub>obs</sub>) are the averages of more than triplicate runs and the correlation coefficients are better than 0.995 in all cases. The rate constants are summarized in Tables S1-4 in Supporting Information. The plots of k<sub>obs</sub> versus base

**Table 1.** Rate constants for eliminations from (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC<sub>6</sub>H<sub>3</sub>-2-X-4-NO<sub>2</sub><sup>a</sup> promoted by R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> in 70 mol % MeCN(aq)<sup>b,c</sup> at 25.0 °C

R <sub>3</sub> NH <sup>d</sup>	pK <sub>a</sub> <sup>e</sup>	k <sub>2</sub> , M <sup>-1</sup> s <sup>-1,f,g</sup>			
		X = H ( <b>1a</b> )	X = Cl ( <b>1b</b> )	X = CF <sub>3</sub> ( <b>1c</b> )	X = NO <sub>2</sub> ( <b>1d</b> )
N(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>3</sub>	15.7	0.0451 ± 0.002	0.291 ± 0.005	0.633 ± 0.006	11.0 ± 0.4
EtN(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>	16.3	0.436 ± 0.009	4.32 ± 0.05	5.12 ± 0.05	90.0 ± 1.4
Et <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH)	17.7	3.21 ± 0.03	37.2 ± 0.3	38.1 ± 0.4	307 ± 6
Et <sub>3</sub> N	18.5	20.2 ± 0.3	142 ± 4	218 ± 3	998 ± 5

<sup>a</sup>[Substrate] = 4.0 × 10<sup>-5</sup> M. <sup>b</sup>[R<sub>3</sub>NH]/[R<sub>3</sub>NH<sup>+</sup>] = 1.0. <sup>c</sup>μ = 0.1 (Bu<sub>4</sub>N<sup>+</sup>Br). <sup>d</sup>[R<sub>3</sub>NH] = 4.0 × 10<sup>-4</sup> - 5.0 × 10<sup>-2</sup> M. <sup>e</sup>pK<sub>a</sub> in MeCN taken from Reference 8. <sup>f</sup>Average of three or more rate constants. <sup>g</sup>Estimated uncertainty, ± 3%.

**Figure 1.** Brønsted plots for the elimination from (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</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> promoted by R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> in 70 mol % MeCN(aq) at 25.0 °C [X = H (**1a**, ■), Cl (**1b**, ●), CF<sub>3</sub> (**1c**, ▲), NO<sub>2</sub> (**1d**, ▼)].**Figure 2.** Plots log *k*<sub>2</sub> versus p*K*<sub>lg</sub> values of the leaving group for the elimination from (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</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> promoted by R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> in 70 mol % MeCN(aq) 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 (▼)].

concentration for the reaction of **1a-c** 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 S1-6). The slopes are the overall second-order rate constants *k*<sub>2</sub>. The rate constant for eliminations from **1d** were determined at a single base concentration and the *k*<sub>2</sub>

**Table 2.** Brønsted β values for elimination from (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</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> promoted by R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> in 70 mol % MeCN(aq) at 25.0 °C

	X = H	X = Cl	X = CF <sub>3</sub>	X = NO <sub>2</sub>
p <i>K</i> <sub>lg</sub> <sup>a</sup>	20.7	18.1	17.0	16.0
β	0.88 ± 0.11	0.89 ± 0.14	0.85 ± 0.09	0.63 ± 0.12

<sup>a</sup>p*K*<sub>a</sub> in MeCN taken from Reference 8.

values were obtained by dividing the *k*<sub>obs</sub> by the base concentration. The *k*<sub>2</sub> values are summarized in Table 1.

The plots of *k*<sub>2</sub> values for **1a-d** against the p*K*<sub>a</sub> values of the base are depicted in Figure 1. The rate data show linear Brønsted correlation with scattered points. The β values are in the range of 0.63-0.89 and decrease as the leaving group ability of the aryloxy increase, although no clear trend is observed for **1a** and **1b** (Table 2). Similarly, the elimination rates determined with different leaving groups correlated reasonably well with the leaving group p*K*<sub>lg</sub> values (Fig. 2). The |β<sub>lg</sub>| values are in the range of 0.34-0.46 and decrease as the p*K*<sub>a</sub> value of the base increase (Table 3).

## Discussion

**Mechanism of Eliminations from 1.** Results of kinetic investigations and product studies reveal that the reactions of **1a-d** with R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> in 70 mol % MeCN(aq) proceed by the E2 mechanism. The reactions produced the elimination products exclusively. Since the reactions exhibited second-order kinetics, all but bimolecular pathway can be ruled out. The (E1cb)<sub>R</sub>, (E1cb)<sub>ip</sub>, and internal return mechanisms were ruled out by the observed general base catalysis with the Brønsted β ranging from 0.63 to 0.89 because such mechanisms would exhibit either a specific base catalysis or Brønsted α values near unity.<sup>12</sup> In addition, the possibility that the values

**Table 3.** Brønsted β<sub>lg</sub> values for elimination from (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</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> promoted by R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> in 70 mol % MeCN(aq) at 25.0 °C

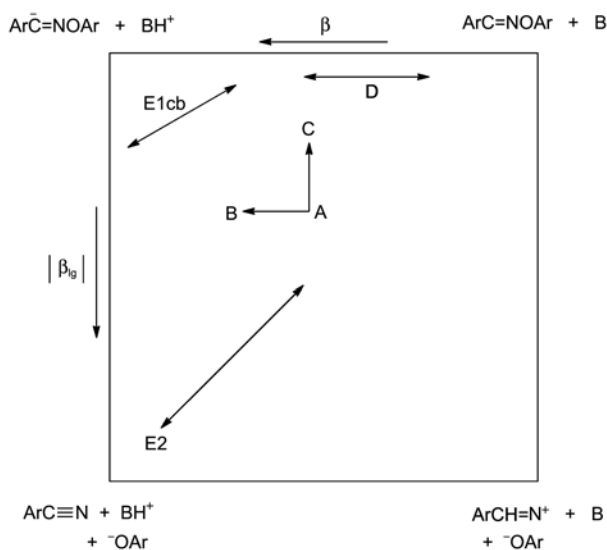
R <sub>3</sub> N	N (CH <sub>2</sub> CH <sub>2</sub> OH) <sub>3</sub>	EtN (CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>	Et <sub>2</sub> N (CH <sub>2</sub> CH <sub>2</sub> OH)	Et <sub>3</sub> N
p <i>K</i> <sub>a</sub> <sup>a</sup>	15.7	16.3	17.7	18.5
β <sub>lg</sub>	-0.46 ± 0.12	-0.44 ± 0.12	-0.38 ± 0.07	-0.34 ± 0.04

<sup>a</sup>Reference 8.

of  $|\beta_{lg}| = 0.34\text{--}0.46$  might be due to the  $(E1cb)_{irr}$  mechanism<sup>13</sup> is negated by the interaction coefficients, i.e.,  $p_{xy} = \partial\beta/\partial pK_{lg} = \partial\beta_{lg}/\partial pK_{BH} > 0$  (*vide infra*).

**Mapping of the E2 Transition State.** The structure of the transition state may be assessed by the Brønsted  $\beta$  and  $|\beta_{lg}|$  values. The Brønsted  $\beta$  values indicate the extent of proton transfer in the transition state. For  $R_3N$ -promoted eliminations from **1d**, the value of  $\beta = 0.63$  was determined (Table 2). This indicates more than half proton transfer in the transition state. The  $|\beta_{lg}|$  values are usually taken as the extent of the leaving group cleavage. However, it should be noted that the values of  $|\beta_{lg}|$  are not restricted to 0-1. In fact, for reactions involving loss of arenesulfonate in the rate-determining step, they range up to nearly 3.<sup>14</sup> For ketene-forming eliminations from aryl *p*-nitrophenylacetates, the maximum values of  $|\beta_{lg}| = 1.34$  was reported.<sup>15,16</sup> Therefore, the measured values of  $|\beta_{lg}| = 0.34\text{--}0.46$  for  $R_3N$ -promoted eliminations from **1** can most reasonably be interpreted with a limited extent of  $N_\alpha$ -OAr bond cleavages in the transition state. The combined results reveal that the nitrile-forming elimination from **1d** proceeds by the E2 mechanism with significant  $C_\beta$ -H bond cleavage and limited  $N_\alpha$ -OAr bond cleavage. Hence, it seems reasonable to locate the transition state at A in the More-O'Ferrall-Jencks diagram (Fig. 3).

This conclusion is supported by the interaction coefficients. Table 2 shows that the  $\beta$  values for **1** decrease, as the leaving groups are made less basic. This effect corresponds to a positive  $p_{xy}$  interaction coefficient,  $p_{xy} = \partial\beta/\partial pK_{lg}$ , which describes the interaction between the base catalyst and leaving group.<sup>12,13</sup> The observed increase in the  $|\beta_{lg}|$  values as the catalyst is less basic is another manifestation of this effect, i.e.,  $p_{xy} = \partial\beta_{lg}/\partial pK_{BH} > 0$  (Table 3). On the More-O'Ferrall-Jencks energy diagram in Figure 3, a change to a



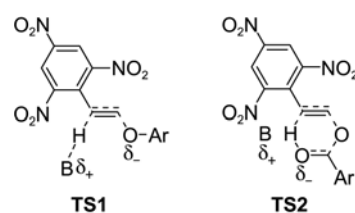
**Figure 3.** Reaction coordinate diagram for nitrile-forming eliminations from (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOAr. The transition states for eliminations from **1d** and **2a** are indicated as A and D, respectively. The effect of the change to a poorer leaving group and a stronger base for eliminations from **1a-d** are shown by the shifts of the transition state from A to B and A to C, respectively.

poorer leaving group will raise the energy of the bottom edge of the diagram shifting the transition state toward the product and E1cb intermediate. The transition state will then move toward the left as depicted by a shift from A to B on the energy diagram, resulting in an increase in  $\beta$  (Fig. 3).<sup>12,17,18</sup> Similarly, a stronger base will raise the energy of the right side of the energy diagram and shift the transition state from A to C to decrease the extent of  $N_\alpha$ -OAr bond cleavage and  $|\beta_{lg}|$  (Fig. 3).<sup>12,17,18</sup> The positive  $p_{xy}$  interaction coefficient are not consistent with an E1cb mechanism for which  $p_{xy} = 0$  is expected, but provide additional support for the E2 mechanism.<sup>12,17,18</sup>

**Effect of the Leaving Group on the Nitrile-Forming Transition State.** Table 4 compares the transition state parameters for the eliminations of (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC(O)Ph<sup>7</sup> and (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC<sub>6</sub>H<sub>4</sub>-4-NO<sub>2</sub> determined under comparable conditions. The two reactions proceeded at comparable rates. However, Brønsted  $\beta$  and  $|\beta_{lg}|$  values were significantly larger for **1a-d**, indicating greater extents of  $C_\beta$ -H and  $N_\alpha$ -OAr cleavage in the transition state. Moreover, **1a-d** react by the E2 mechanism, whereas **2a** reacts by the  $(E1cb)_{irr}$  mechanism. The dichotomy between these two reactions can be explained by assuming *syn*-transition state for **1a-d** and cyclic transition state for **2a** (Chart 1).

In TS2, the carbonyl oxygen atom can participate in the hydrogen bonding with the B-H proton to help stabilize the negative charge developed at the  $\beta$ -carbon in the  $(E1cb)_{irr}$  transition state. On the other hand, aryloxide leaving group in TS1 cannot provide such stabilizing effect and the *syn*-transition state appears to be the favored alternative.

In conclusion, we have studied the reactions of (*E*)-2,4,6-trinitrobenzaldehyde *O*-aryloxime with  $R_3NH/R_3NH^+$  in 70 mol % MeCN(aq). The reactions proceeded by an E2 mechanism. The structure of the transition state changes from E2-central (**1d**) to E1cb-like (**1a-c**) as the leaving is made poorer. The  $(E1cb)_{irr}$  mechanism observed in the



**Chart 1**

**Table 4.** Transition state parameters for nitrile-forming eliminations from **1a** and **2a** under comparable conditions

Compounds	<b>1a</b>	<b>2a</b>
base-solvent	$R_3N/R_3NH^+$ in 70 mol % MeCN(aq)	$R_2NH$ in MeCN
$pK_a$ (AH)	20.7 <sup>a,b</sup>	20.7 <sup>a,b</sup>
rel rate	1.8 <sup>d</sup>	1 <sup>d</sup>
$\beta$	0.88 ± 0.11	0.40 ± 0.03 <sup>e</sup>
$\beta_{lg}$	-0.34 ± 0.04	-0.18 ± 0.01 <sup>e</sup>

<sup>a</sup> $pK_a$  of the leaving group in MeCN. <sup>b</sup>Reference 8. <sup>c</sup>Base was Et<sub>3</sub>N. <sup>d</sup>Base was *i*-Pr<sub>2</sub>NH. <sup>e</sup>Reference 7.

elimination from **2a** appears to be due to the participation of the carbonyl oxygen atom in the leaving group in the 6-membered hydrogen bonding that stabilized the carbanion intermediate.

### Experimental Section

**Materials.** (*E*)-2,4,6-Trinitrobenzaldehyde was synthesized as reported previously.<sup>9-11</sup> All of the (*E*)-2,4,6-trinitrobenzaldehyde *O*-aryloximes were prepared by the reactions of 2,4,6-trinitrobenzaldehyde with appropriately substituted *O*-arylhydroxylamines in the presence of catalytic amount of HCl. HRMS and elemental analysis results for **1d** could not be performed because they decomposed after several hours. However, the NMR 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, CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub>, *J* values are in Hz), and <sup>13</sup>C NMR (100 MHz, spectral data for the new compounds are as follows.

**(*E*)-2,4,6-(O<sub>2</sub>N)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC<sub>6</sub>H<sub>4</sub>-4-NO<sub>2</sub> (**1a**):** Yield 68%; mp 152-153 °C; IR 1650; <sup>1</sup>H NMR δ 7.21 (d, *J* = 9.60, 2H), 8.25 (d, *J* = 9.60, 2H), 9.01 (s, 1H), 9.15 (s, 2H); <sup>13</sup>C NMR δ 114.3, 123.4, 125.9, 126.3, 143.6, 145.7, 148.3, 150.2, 162.6; 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 377.0242.

**(*E*)-2,4,6-(O<sub>2</sub>N)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC<sub>6</sub>H<sub>3</sub>-2-Cl-4-NO<sub>2</sub> (**1b**):** Yield 62%; mp 155-156 °C; IR 1658; <sup>1</sup>H NMR δ 7.35 (d, *J* = 9.24, 1H), 8.13-8.16 (dd, *J* = 9.24, 2.72, 1H), 8.33 (d, *J* = 2.72, 1H), 9.14 (s, 1H), 9.17 (s, 2H); <sup>13</sup>C NMR δ 114.7, 120.9, 123.5, 123.9, 126.0, 126.3, 143.3, 147.3, 147.2, 148.5, 150.3, 158.4; HRMS-(EI); *m/z* calcd for C<sub>13</sub>H<sub>6</sub>ClN<sub>5</sub>O<sub>9</sub> 410.9854, found 410.9863.

**(*E*)-2,4,6-(O<sub>2</sub>N)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC<sub>6</sub>H<sub>3</sub>-2-CF<sub>3</sub>-4-NO<sub>2</sub> (**1c**):** Yield 71%; mp 141-142 °C; IR 1655; <sup>1</sup>H NMR δ 7.49 (d, *J* = 9.24, 1H), 8.39-8.43 (dd, *J* = 9.24, 2.72, 1H), 9.13 (s, 1H), 9.19 (s, 2H); <sup>13</sup>C NMR δ 115.6, 117.2, 117.6, 117.9, 118.2, 120.5, 123.4, 123.6, 125.9, 129.1, 142.7, 147.9, 148.6, 150.2, 159.8; HRMS-(EI); *m/z* calcd for C<sub>14</sub>H<sub>6</sub>F<sub>3</sub>N<sub>5</sub>O<sub>9</sub> 445.0118, found 445.0124.

**(*E*)-2,4,6-(O<sub>2</sub>N)<sub>3</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> (**1d**):** Yield 41%; mp 161-163 °C; IR 1645; <sup>1</sup>H NMR δ 7.62 (d, *J* = 9.60, 1H), 8.44-8.46 (dd, *J* = 9.24, 2.76 1H), 8.91 (d, *J* = 2.76 1H), 9.22 (s, 3H); <sup>13</sup>C NMR δ 107.1, 110.0, 119.7, 122.0, 124.3, 129.4, 136.5, 138.1, 149.2, 151.2, 157.5.

Reagent grade acetonitrile and tertiary amines were fractionally distilled from CaH<sub>2</sub>. The solutions of R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> in 70 mol % MeCN(aq) were prepared by dissolving equivalent amount of R<sub>3</sub>N and R<sub>3</sub>NH<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 **1** with R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> in 70 mol % MeCN(aq) were followed by monitoring the increase in the absorbance of the leaving aryloxide at 400-426 nm with a UV-vis spectrophotometer as described previously.<sup>1,15</sup>

**Product Studies.** The product of eliminations from **1a**

promoted by Et<sub>3</sub>N/Et<sub>3</sub>NH<sup>+</sup> in 70 mol % MeCN(aq) was identified by as described.<sup>19</sup> The product was 2,4,6-trinitrobenzonitrile with mp 135-156 °C (lit.<sup>20</sup> mp 134-135 °C). The yield of 2,4,6-trinitrobenzonitrile was 94%. Also, the yields of aryloxides from the reactions of **1** determined by the comparing the UV absorptions of the infinity samples with those of the authentic aryloxides were in the range of 95-98%.

**Control Experiments.** The stabilities of **1** were determined as reported earlier.<sup>6,19</sup> The solutions of **1a-c** in MeCN were stable for at least two days when stored in the refrigerator. However, the solution of **1d** was stable for only 3 hours.

**Acknowledgments.** This research was supported by NRF grants (2010-0018921 and 2010-0020209).

**Support Information Available.** Observed rate constants for elimination from **1a-d** promoted by R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> in 70 mol % MeCN(aq), plots of *k*<sub>obs</sub> vs base concentration, and NMR spectra for all new compounds are available on request from the correspondence author (11 pages).

### References

1. Cho, B. R.; Kim, K. D.; Lee, J. C.; Cho, N. S. *J. Am. Chem. Soc.* **1988**, *110*, 6145-6148.
2. Cho, B. R.; Lee, J. C.; Cho, N. S.; Kim, K. D. *J. Chem. Soc. Perkin Trans II* **1989**, 489-492.
3. Cho, B. R.; Min, B. K.; Lee, C. W.; Je, J. T. *J. Org. Chem.* **1991**, *56*, 5513-5517.
4. Cho, B. R.; Jung, J.; Ahn, E. K. *J. Am. Chem. Soc.* **1992**, *114*, 3425-3429.
5. Cho, B. R.; Je, J. T. *J. Org. Chem.* **1993**, *58*, 6190-6193.
6. Cho, B. R.; Cho, N. S.; Song, K. S.; Son, K. N.; Kim, Y. K. *J. Org. Chem.* **1998**, *63*, 3006-3009.
7. Cho, B. R.; Pyun, S. Y. *Bull. Korean Chem. Soc.* **2010**, *31*, 1043-1046.
8. Coetzee, J. F. *Prog. Phys. Org. Chem.* **1965**, *4*, 45-92.
9. Hegarty, A. F.; Tuohy, P. J. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1313-1317.
10. Tamura, Y.; Minamikawa, J.; Sumoto, K.; Fujii, S.; Ikeda, M. *Synthesis* **1977**, 1-17.
11. Bumgardner, C. L.; Lilly, R. L. *Chem. Ind. (London)* **1962**, *24*, 599-560.
12. Gandler, J. R. *The Chemistry of Double Bonded Functional Groups*; Patai, S., Ed.; John Wiley and Sons: Chichester, 1989; vol. 2, part 1, pp 734-797.
13. Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1987. (a) pp 214-218. (b) pp 591-616. (c) pp 640-644.
14. Hoffman, R. V.; Shankweiler, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 5536-5539.
15. Tagaki, W.; Kobayashi, S.; Kurihara, K.; Kurashima, K.; Yoshida, Y.; Yano, J. *J. Chem. Soc., Chem. Commun.* **1976**, 843-845.
16. Cho, B. R.; Kim, Y. K.; Maing Yoon, C. O. *J. Am. Chem. Soc.* **1997**, *119*, 691-697.
17. Jencks, W. P. *Chem. Rev.* **1985**, *85*, 511-527.
18. Gandler, J. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 1937-1951.
19. Cho, B. R.; Chung, H. S.; Pyun, S. Y. *J. Org. Chem.* **1999**, *64*, 8375-8378.
20. Sitzmann, M. E.; Dacons, J. C. *J. Org. Chem.* **1973**, *38*, 4363-4365.

## Supporting Information

Elimination Reactions of (*E*)-2,4,6-Trinitrobenzaldehyde *O*-Aryloximes Promoted by R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> in 70 mol % MeCN(aq). Effect of β-Aryl Group the Nitrile-Forming Transition-StateSang Yong Pyun,<sup>\*</sup> Woong Sub Byun,<sup>†</sup> and Bong Rae Cho<sup>\*\*</sup>

Department of Chemistry, Pukyong National University, Pusan 608-737, Korea. \*E-mail: sypyun@pknu.ac.kr

<sup>†</sup>Department of Chemistry, Konkuk University, Seoul 143-70, Korea<sup>\*\*</sup>Department of Chemistry, Korea University, Seoul 136-701, Korea. \*E-mail: chobr@korea.ac.kr

Received March 16, 2011, Accepted April 19, 2011

**Table S1.** Observed Rate Constants 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>X (**1a-d**)<sup>a</sup> Promoted by Et<sub>3</sub>N/Et<sub>3</sub>NH<sup>+</sup><sup>b,c</sup> 70 mol % MeCN(aq) at 25.0 °C

Entry	10 <sup>2</sup> [buffer], M	10 <sup>2</sup> k <sub>obs</sub> , s <sup>-1 d,e</sup>			
		<b>1a</b>	<b>1b</b>	<b>1c</b>	<b>1d</b>
1	0.04				39.1
2	0.06	1.21	9.56	9.15	
3	0.08	1.66	14.5	13.5	
4	0.1	2.07	16.8	18.8	
5	0.2	4.56	30.3	39.7	
6	0.4	8.06			
7	0.6	11.5			
8	0.8	15.4			
	1.0	19.5			
	1.2	28.0			
	1.4	29.2			

<sup>a-e</sup>See footnotes under Table S1.**Table S2.** Observed Rate Constants 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>X (**1a-d**)<sup>a</sup> Promoted by Et<sub>2</sub>NCH<sub>2</sub>OH/Et<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>OH<sup>+</sup><sup>b,c</sup> 70 mol % MeCN(aq) at 25.0 °C

Entry	10 <sup>2</sup> [buffer], M	10 <sup>2</sup> k <sub>obs</sub> , s <sup>-1 d,e</sup>			
		<b>1a</b>	<b>1b</b>	<b>1c</b>	<b>1d</b>
1	0.06	-	4.70	4.04	18.4
2	0.08	-	5.32	9.20	-
3	0.1	0.699	6.72	5.64	-
4	0.2	-	9.92	9.42	-
5	1.0	3.84	-	-	-
6	1.6	5.84	-	-	-
7	3.0	9.64	-	-	-
8	5.0	16.7	-	-	-

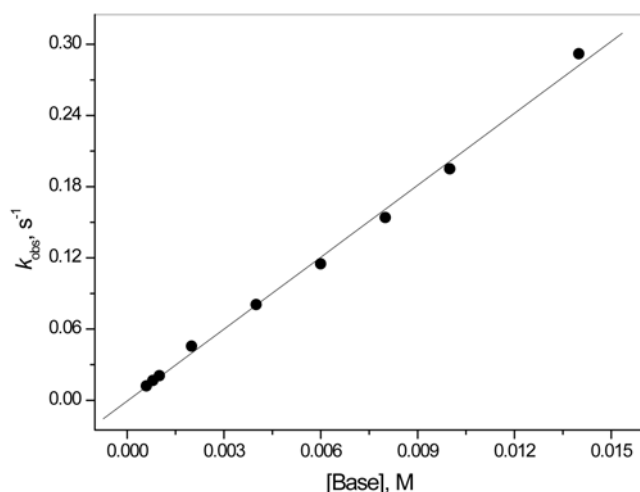
<sup>a-e</sup>See footnotes under Table S1.**Table S3.** Observed Rate Constants for Eliminations from (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC(O)C<sub>6</sub>H<sub>4</sub>X (**1a-d**)<sup>a</sup> Promoted by EtN(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>/EtNH(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub><sup>+</sup><sup>b,c</sup> 70 mol % MeCN(aq) at 25.0 °C

Entry	10 <sup>2</sup> [buffer], M	10 <sup>2</sup> k <sub>obs</sub> , s <sup>-1 d,e</sup>			
		<b>1a</b>	<b>1b</b>	<b>1c</b>	<b>1d</b>
1	0.06	-	-	-	5.4
2	0.1	0.943	1.49	1.49	-
3	1.0	0.585	5.08	6.69	-
4	1.6	0.743	7.59	9.90	-
5	3.0	1.45	13.6	16.1	-
6	5.0	2.24	22.6	27.0	-

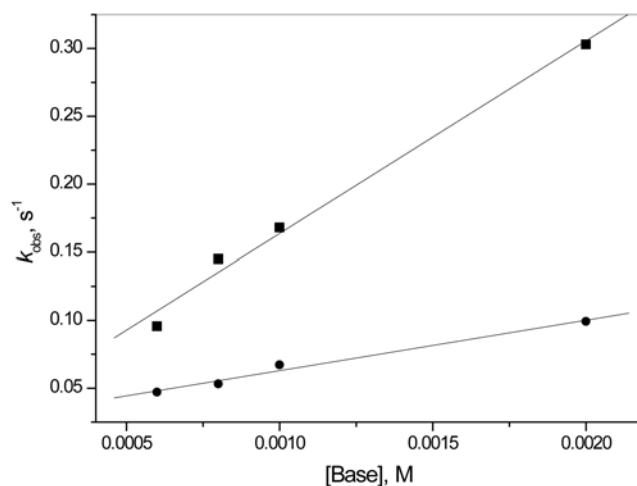
<sup>a-e</sup>See footnotes under Table S1.**Table S4.** Observed Rate Constants for Eliminations from (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC(O)C<sub>6</sub>H<sub>4</sub>X (**1a-d**)<sup>a</sup> Promoted by N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub>/NH(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub><sup>+</sup><sup>b,c</sup> 70 mol % MeCN(aq) at 25.0 °C

Entry	10 <sup>2</sup> [buffer], M	10 <sup>2</sup> k <sub>obs</sub> , s <sup>-1 d,e</sup>			
		<b>1a</b>	<b>1b</b>	<b>1c</b>	<b>1d</b>
1	0.06	-	-	-	1.10
2	0.1	-	0.228	0.102	-
3	1.0	0.114	0.451	0.655	-
4	1.6	0.155	0.624	0.982	-
5	3.0	0.204	1.01	1.89	-
6	5.0	0.301	1.65	3.20	-

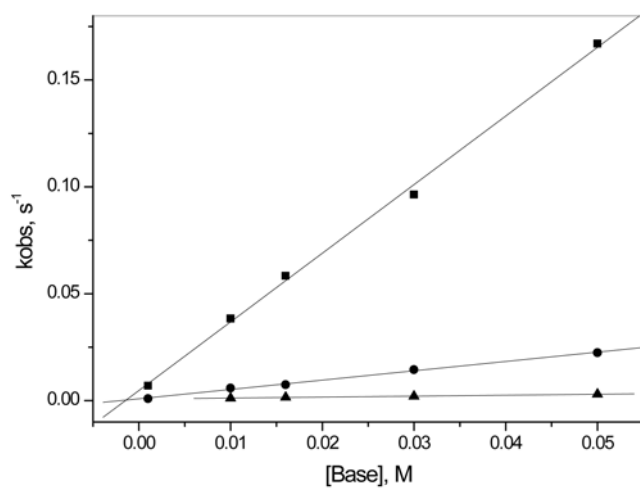
<sup>a-e</sup>See footnotes under Table S1.



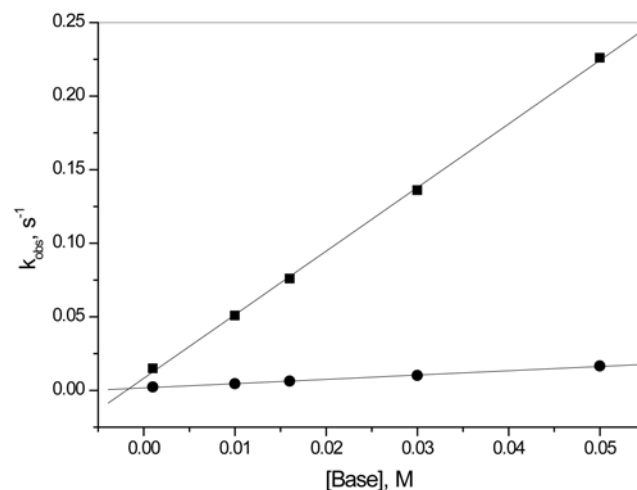
**Figure S1.** Plots of  $k_{obs}$  vs base concentration for eliminations from (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC<sub>6</sub>H<sub>5</sub>-4-NO<sub>2</sub> (**1a**) Promoted by Et<sub>3</sub>N/Et<sub>3</sub>NH<sup>+</sup> 70 mol % MeCN(aq) 25 °C, [R<sub>3</sub>N]/[R<sub>3</sub>NH<sup>+</sup>] = 1.0,  $\mu$  = 0.10 M (Bu<sub>4</sub>N<sup>+</sup>Br<sup>-</sup>).



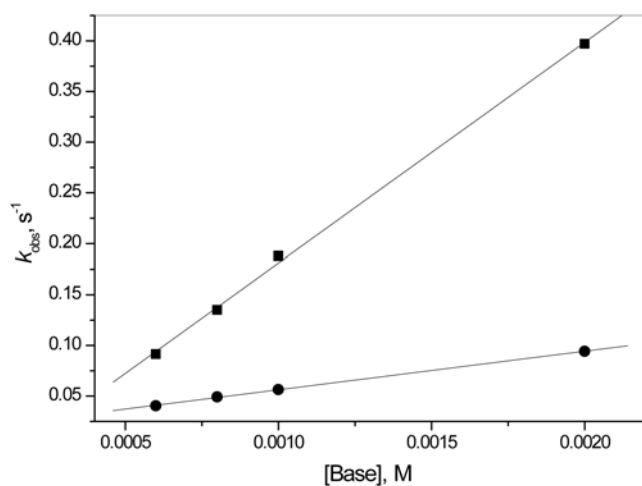
**Figure S3.** Plots of  $k_{obs}$  vs base concentration for eliminations from (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC(O)C<sub>6</sub>H<sub>3</sub>-2-Cl-4-NO<sub>2</sub> (**1b**) Promoted by R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> 70 mol % MeCN(aq) 25 °C, [R<sub>3</sub>N]/[R<sub>3</sub>NH<sup>+</sup>] = 1.0,  $\mu$  = 0.10 M (Bu<sub>4</sub>N<sup>+</sup>Br<sup>-</sup>). [R<sub>3</sub>N = Et<sub>3</sub>N (■), Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH (●)].



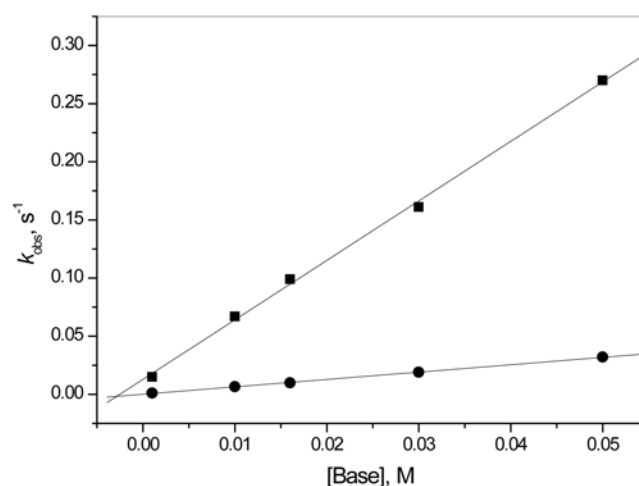
**Figure S2.** Plots of  $k_{obs}$  vs base concentration for eliminations from (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC(O)C<sub>6</sub>H<sub>4</sub>-4-NO<sub>2</sub> (**1a**) Promoted by R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> 70 mol % MeCN(aq) 25 °C, [R<sub>3</sub>N]/[R<sub>3</sub>NH<sup>+</sup>] = 1.0,  $\mu$  = 0.10 M (Bu<sub>4</sub>N<sup>+</sup>Br<sup>-</sup>). [R<sub>3</sub>N = Et<sub>2</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH) (■), EtN(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub> (●), N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub> (▲)].



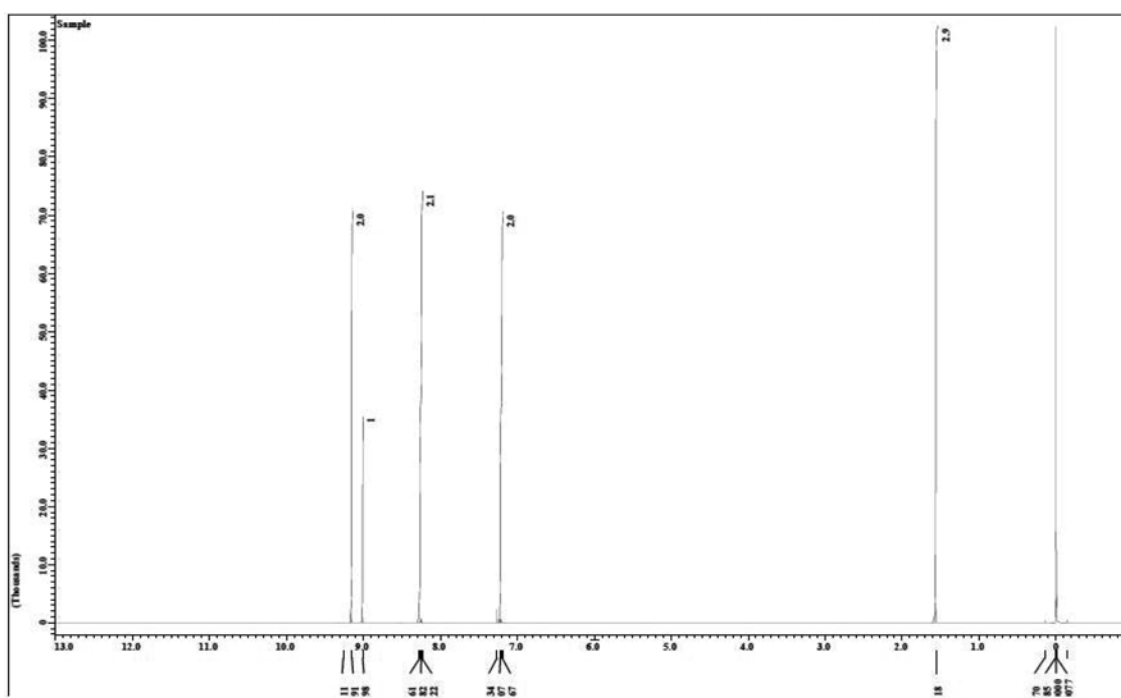
**Figure S4.** Plots of  $k_{obs}$  vs base concentration for eliminations from (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC(O)C<sub>6</sub>H<sub>3</sub>-2-Cl-4-NO<sub>2</sub> (**1b**) Promoted by R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> 70 mol % MeCN(aq) 25 °C, [R<sub>3</sub>N]/[R<sub>3</sub>NH<sup>+</sup>] = 1.0,  $\mu$  = 0.10 M (Bu<sub>4</sub>N<sup>+</sup>Br<sup>-</sup>). [R<sub>3</sub>N = EtN(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub> (■), N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub> (●)].



**Figure S5.** Plots of  $k_{obs}$  vs base concentration 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>3</sub>-2-CF<sub>3</sub>-4-NO<sub>2</sub> (**1c**) Promoted by R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> 70 mol % MeCN(aq) 25 °C, [R<sub>3</sub>N]/[R<sub>3</sub>NH<sup>+</sup>] = 1.0,  $\mu$  = 0.10 M (Bu<sub>4</sub>N<sup>+</sup>Br<sup>-</sup>). [R<sub>3</sub>N = Et<sub>3</sub>N (■), Et<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH (●)].



**Figure S6.** Plots of  $k_{obs}$  vs base concentration 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>3</sub>-2-CF<sub>3</sub>-4-NO<sub>2</sub> (**1c**) Promoted by R<sub>3</sub>N/R<sub>3</sub>NH<sup>+</sup> 70 mol % MeCN(aq) 25 °C, [R<sub>3</sub>N]/[R<sub>3</sub>NH<sup>+</sup>] = 1.0,  $\mu$  = 0.10 M (Bu<sub>4</sub>N<sup>+</sup>Br<sup>-</sup>). [R<sub>3</sub>N = EtN(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub> (■), N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub> (●)].



**Figure S7.** <sup>1</sup>H-NMR spectrum of (*E*)-2,4,6-(NO<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>CH=NOC<sub>6</sub>H<sub>4</sub>-4-NO<sub>2</sub> (CDCl<sub>3</sub>).

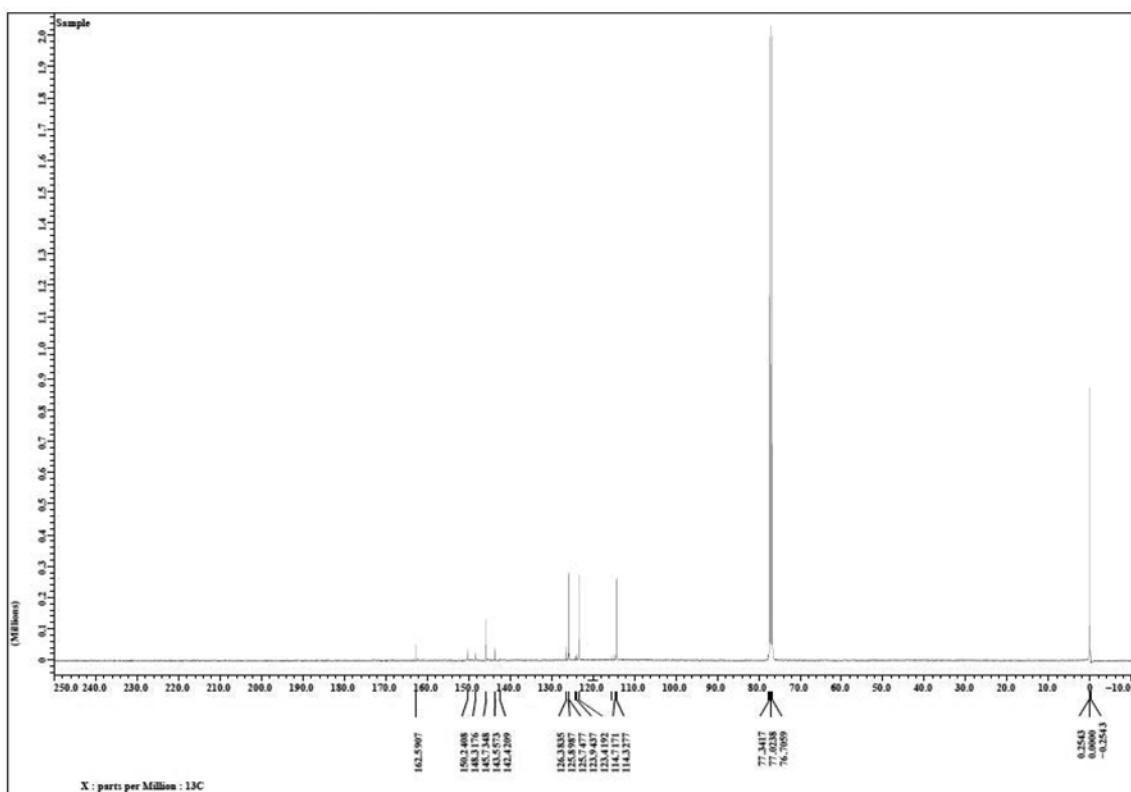


Figure S8.  $^{13}\text{C}$ -NMR spectrum of  $(E)$ -2,4,6-( $\text{NO}_2$ ) $_3\text{C}_6\text{H}_2\text{CH}=\text{NOC}_6\text{H}_4$ -4- $\text{NO}_2$  ( $\text{CDCl}_3$ ).

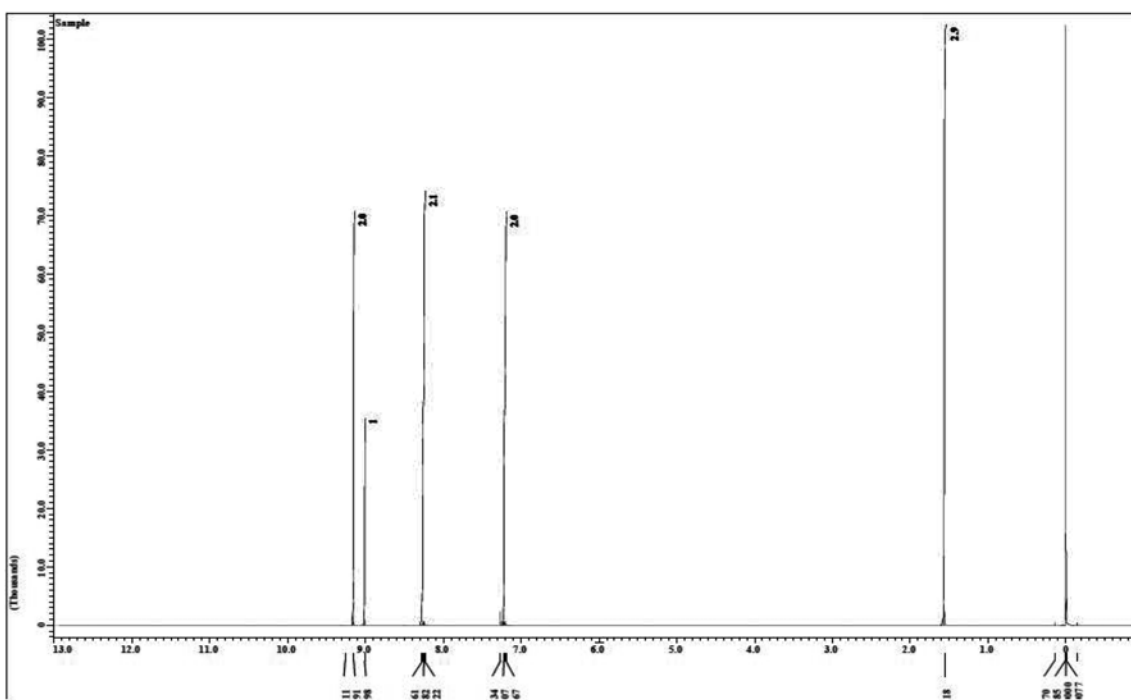


Figure S9.  $^1\text{H}$ -NMR spectrum of  $(E)$ -2,4,6-( $\text{NO}_2$ ) $_3\text{C}_6\text{H}_2\text{CH}=\text{NOC}_6\text{H}_3$ -2- $\text{Cl}$ -4- $\text{NO}_2$  ( $\text{CDCl}_3$ ).



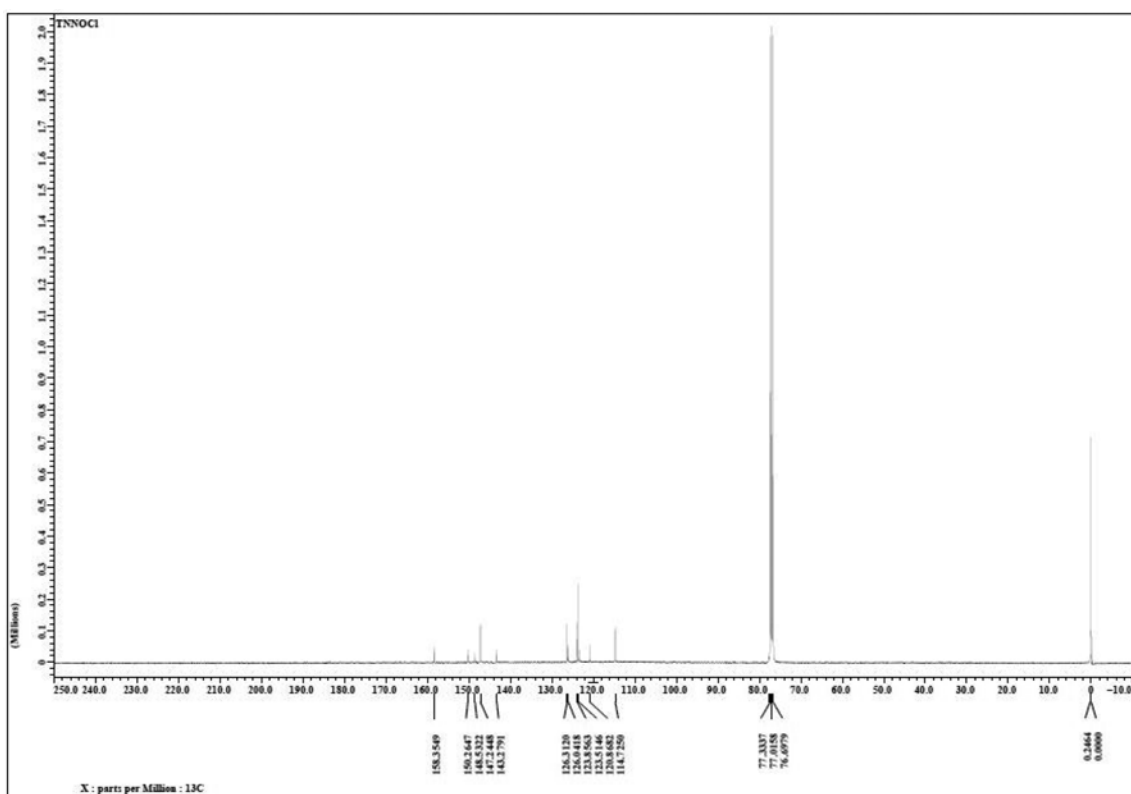


Figure S10.  $^{13}\text{C}$ -NMR spectrum of (*E*)-2,4,6-( $\text{NO}_2$ ) $_3\text{C}_6\text{H}_2\text{CH}=\text{NOC}_6\text{H}_3\text{-2-Cl-4-NO}_2$  ( $\text{CDCl}_3$ ).

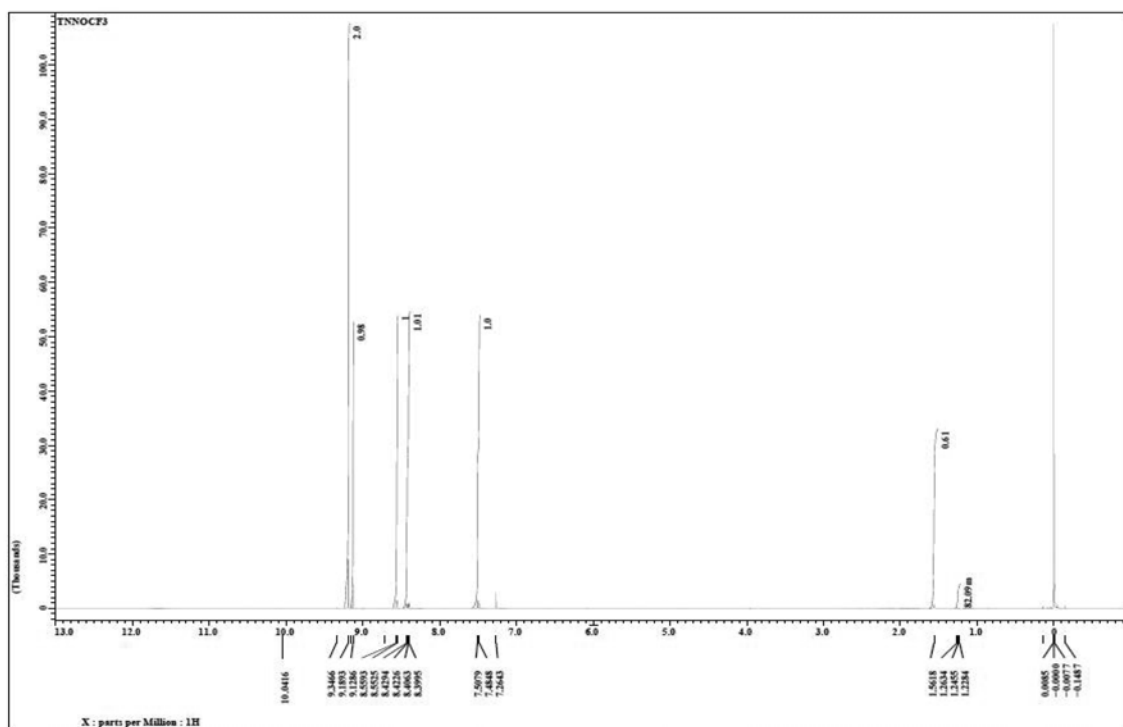
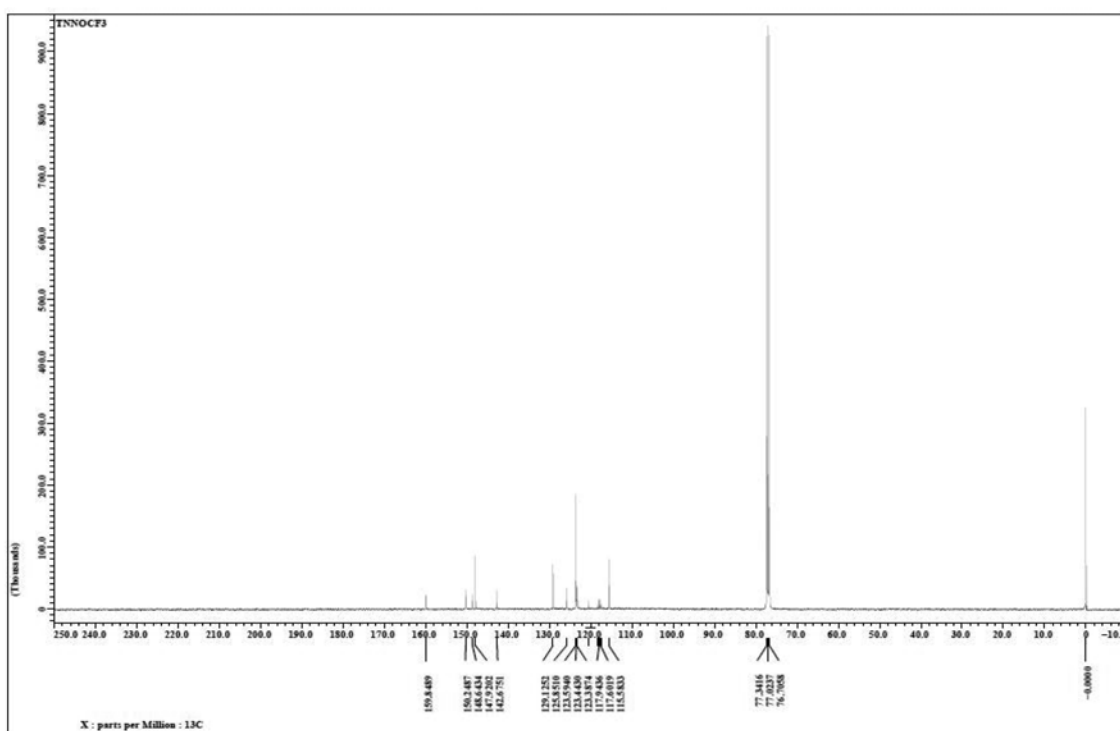
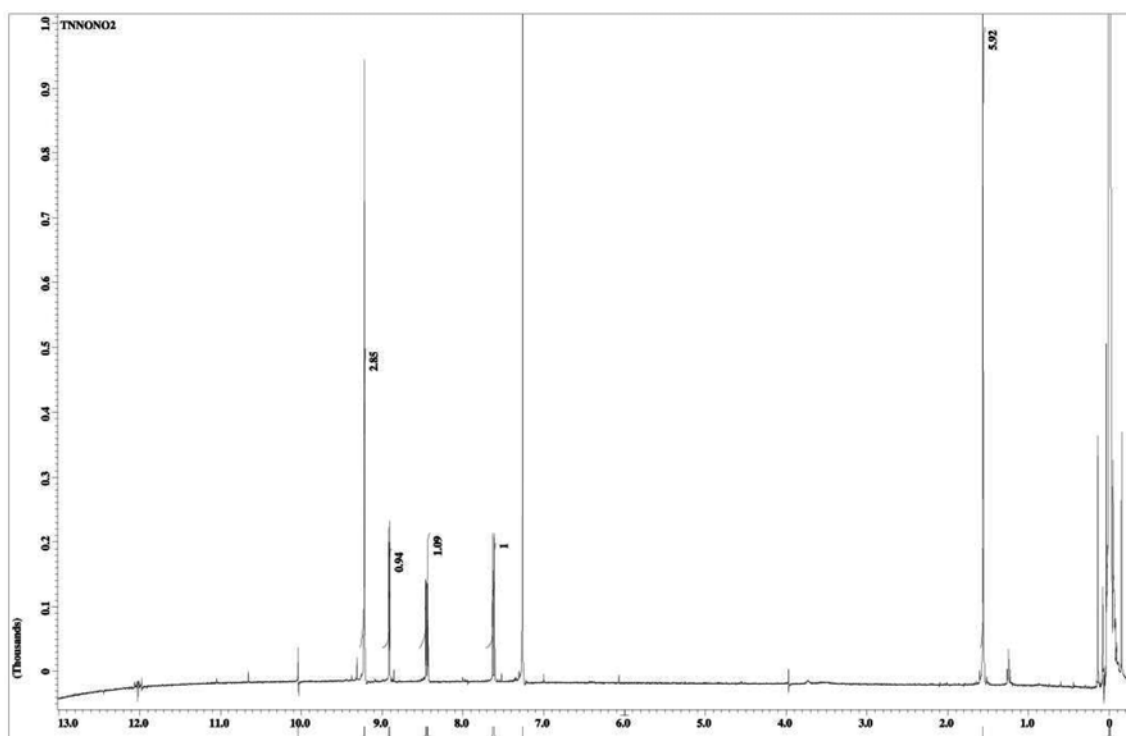


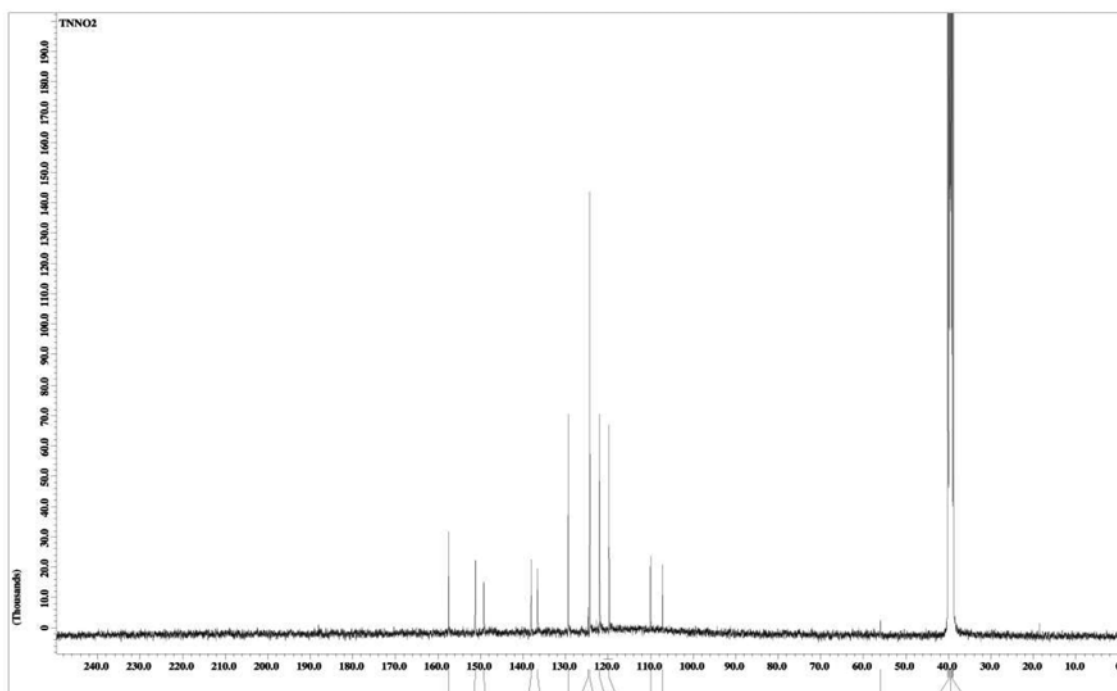
Figure S11.  $^1\text{H}$ -NMR spectrum of (*E*)-2,4,6-( $\text{NO}_2$ ) $_3\text{C}_6\text{H}_2\text{CH}=\text{NOC}_6\text{H}_3\text{-2-CF}_3\text{-4-NO}_2$  ( $\text{CDCl}_3$ ).



**Figure S12.**  $^{13}\text{C}$ -NMR spectrum of  $(E)$ -2,4,6-( $\text{NO}_2$ ) $_3\text{C}_6\text{H}_2\text{CH}=\text{NOC}_6\text{H}_3$ -2- $\text{CF}_3$ -4- $\text{NO}_2$  ( $\text{CDCl}_3$ ).



**Figure S13.**  $^1\text{H}$ -NMR spectrum of  $(E)$ -2,4,6-( $\text{NO}_2$ ) $_3\text{C}_6\text{H}_2\text{CH}=\text{NOC}_6\text{H}_3$ -2,4-( $\text{NO}_2$ ) $_2$  ( $\text{CDCl}_3$ ).



**Figure S14.**  $^{13}\text{C}$ -NMR spectrum of (*E*)-2,4,6-( $\text{NO}_2$ ) $_3\text{C}_6\text{H}_2\text{CH}=\text{NOC}_6\text{H}_3-2,4-(\text{NO}_2)_2$  ( $\text{DMSO}-d_6$ ).