

Elimination Reactions of (*E*)-2,4-Dinitrobenzaldehyde *O*-Aryloximes Promoted by RO⁻/ROH Buffers in EtOH

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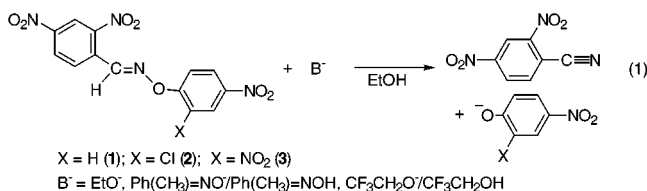
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Elimination reactions of (*E*)-2,4-dinitrobenzaldehyde *O*-aryloximes **1–3** promoted by EtO⁻, PhC(CH₃)=NO⁻/PhC(CH₃)=NOH, and CF₃CH₂O⁻/CF₃CH₂OH buffers in ethanol have been studied kinetically. The reactions produced 2,4-dinitrobenzotrile and aryloxides as the only products. The observed second-order kinetics, Brønsted β = 0.55–0.75, |β_{lg}| = 0.39–0.48 are consistent with the E2 mechanism. The Brønsted β decreased as the leaving group was made more nucleofugic and the |β_{lg}| increased with a weaker base. The result can be described by a positive interaction coefficient, $p_{xy} = \partial\beta/\partial pK_{lg} = \partial\beta_{lg}/\partial pK_{BH} > 0$, which provides additional support for the E2 mechanism.

Elimination reactions of (*E*)-benzaldehyde *O*-aryloximes have been extensively investigated under various conditions.^{1–7} In all cases, the reactions proceeded by the E2 mechanism despite the fact that the reactants have syn stereochemistry, poor leaving group, and sp² hybridized β-carbon atom, all of which favor the E1cb- or E1cb-like transition state.^{8–11}

In this work, we studied the reactions of (*E*)-2,4-dinitrobenzaldehyde *O*-aryloximes **1–3** with various oxyanion bases in ethanol (eq 1). We were interested in learning if a change to the E1cb mechanism could be realized by making the β-aryl substituent more electron-withdrawing and by making the solvent more protic. This substrate is the most strongly activated one studied so far in the (*E*)-benzaldehyde *O*-aryloxime series.



Results

(*E*)-2,4-Dinitrobenzaldehyde *O*-aryloximes **1–3** were prepared by the reactions of 2,4-dinitrobenzaldehydes

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with *O*-arylhydroxylamines as reported previously.^{1,12,13} The spectral and analytical data for the compounds were consistent with the proposed structures.

Reactions of (*E*)-2,4-dinitrobenzaldehyde *O*-aryloximes **1–3** with RONa–ROH buffers in EtOH produced 2,4-dinitrobenzotrile and aryloxides quantitatively. The rates of the reactions were followed by monitoring the increase in the absorption at the λ_{max} for the aryloxides in the range of 400–404 nm. Excellent pseudo-first-order kinetic plots which covered at least three half-lives were obtained. The pseudo-first-order rate constants are listed in Tables S1–S3 in the Supporting Information.

The pK_a values of trifluoroethanol and acetophenone oxime were determined by measuring the equilibrium constants for reactions between EtO⁻ and CF₃CH₂OH or PhC(CH₃)=NOH using *p*-nitrobenzyl cyanide as an indicator.^{14,15} The pK_a values of CF₃CH₂OH and PhC(CH₃)=NOH in EtOH are 17.64 ± 0.01 and 17.89 ± 0.01, respectively (Table 3).

Plots of k_{obs} for the EtO⁻-promoted eliminations from **1–3** against base concentration are straight lines passing through the origin (plots not shown). On the other hand, the same plots for the reactions with CF₃CH₂O⁻/CF₃CH₂OH and PhC(CH₃)=NO⁻/PhC(CH₃)=NOH buffers in EtOH showed straight lines with positive intercepts. Since the buffer solution contains significant amounts of both EtO⁻ and RO⁻, the rate equation can be expressed as k_{obs} = k₂^{EtO⁻}[EtO⁻] + k₂^{RO⁻}[RO⁻]. In this equation, the first term is a constant regardless of the buffer concentration because the buffer ratio is maintained to be 1.0. Therefore, the k₂^{RO⁻} values were determined from the slopes of the plots. The second-order rate constants for eliminations from **1–3** promoted by EtO⁻, CF₃CH₂O⁻/CF₃CH₂OH, and PhC(CH₃)=NO⁻/PhC(CH₃)=NOH buffers in EtOH are listed in Table 1.

Brønsted plots for eliminations from **1–3** are depicted in Figure 1. Excellent correlation was obtained between

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Table 1. Second Order Rate Constants for Eliminations from (*E*)-2,4-(O₂N)₂C₆H₃CH=NOC₆H₃-2-X-4-NO₂^a Promoted by RO⁻-ROH Buffer^{b,c} in EtOH at 25.0 °C

RO ⁻	pK _a	10 ⁻³ k ₂ ^{RO-} , M ⁻¹ s ⁻¹ ^d		
		X = H	X = Cl	X = NO ₂
EtO ⁻	19.18 ^e	1.25 ± 0.01	7.31 ± 0.09	45.3 ± 0.30
Ph(CH ₃)=NO ⁻	17.89 ^f	0.128 ± 0.06	1.27 ± 0.07	8.20 ± 0.02
CF ₃ CH ₂ O ⁻	17.64 ^f	0.0879 ± 0.0003	0.885 ± 0.004	6.63 ± 0.018

^a [Substrate] = 2 × 10⁻⁵ M. ^b Buffer ratio = 1.0. ^c [RO⁻] = 8.5 × 10⁻³–5.0 × 10⁻¹ M. ^d Determined from the slopes of the plots of log k_{obs} vs [RO⁻] (see text). ^e Reference 22. ^f This work.

Table 2. Brønsted β Values for Eliminations from (*E*)-2,4-(O₂N)₂C₆H₃CH=NOC₆H₃-2-X-4-NO₂ Promoted by RO⁻-ROH Buffer in EtOH at 25.0 °C

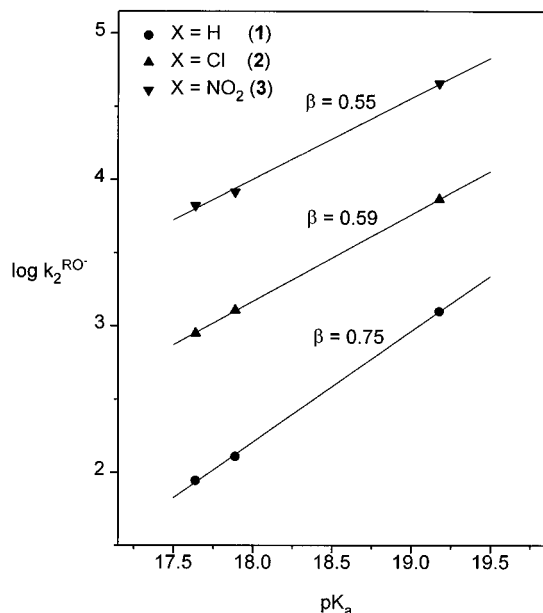
X	pK _{lg} ^a	β
H	12.02	0.75 ± 0.02
Cl	9.83	0.59 ± 0.01
NO ₂	8.08	0.55 ± 0.03

^a Reference 23.

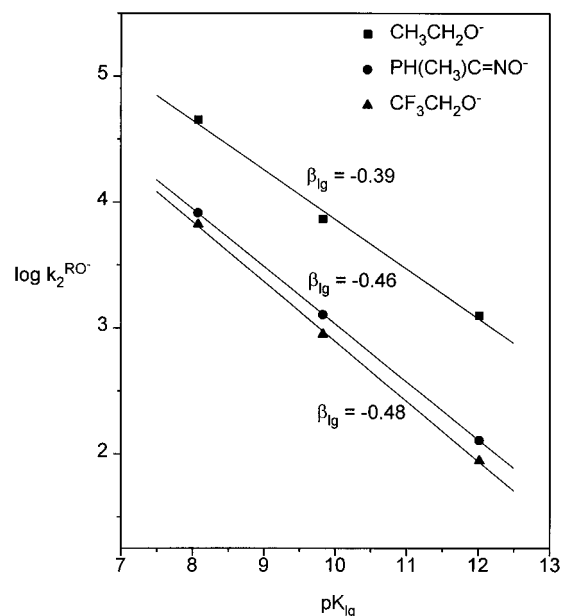
Table 3. Brønsted β_{lg} Values for Eliminations from (*E*)-2,4-(O₂N)₂C₆H₃CH=NOC₆H₃-2-X-4-NO₂ Promoted by RO⁻-ROH Buffer in EtOH at 25.0 °C

RO ⁻	pK _a	β _{lg}
EtO ⁻	19.18 ^a	-0.39 ± 0.03
PhC(CH ₃)=NO ⁻	17.89 ^b	-0.46 ± 0.01
CF ₃ CH ₂ O ⁻	17.64 ^b	-0.48 ± 0.01

^a Reference 22. ^b This work.

**Figure 1.** Brønsted plots for elimination reactions of (*E*)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2-X-NO₂ promoted by EtO⁻, PhC(CH₃)=NO⁻/PhC(CH₃)=NOH, and CF₃CH₂O⁻/CF₃CH₂OH buffers in EtOH at 25.0 °C. Buffer ratio = 1.0.

the log k₂^{RO-} and pK_a values. The β values for eliminations from **1–3** are 0.75 ± 0.02, 0.59 ± 0.01, and 0.55 ± 0.03, respectively (Table 2). Similarly, the elimination rates determined with different *O*-aryl substituents were correlated with the pK_{lg} values of the leaving group (Figure 2). The β_{lg} values for eliminations from **1–3** promoted by EtO⁻ and PhC(CH₃)=NO⁻ and CF₃CH₂O⁻ buffers are -0.39 ± 0.03, -0.46 ± 0.01, and -0.48 ± 0.01, respectively (Table 3).

**Figure 2.** Plots of log k₂^{RO-} vs pK_{lg} values of the leaving group for elimination reactions of (*E*)-2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2-X-NO₂ promoted by EtO⁻, PhC(CH₃)=NO⁻/PhC(CH₃)=NOH, and CF₃CH₂O⁻/CF₃CH₂OH buffers in EtOH at 25.0 °C. Buffer ratio = 1.0.

Discussion

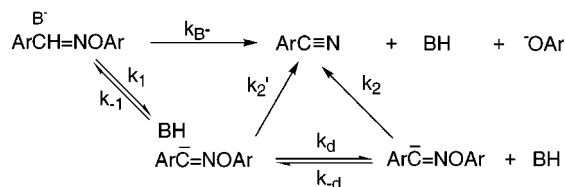
Mechanism and Transition State Structure for Eliminations from **1 to **3** Promoted by RO⁻-ROH Buffers.** Earlier it was established that the reactions of (*E*)-benzaldehyde *O*-aryloximes with OH⁻ in 60% DMSO(aq) or R₂NH in MeCN or MeONa in MeOH proceeded by a competing E2 and S_NAr mechanism.^{2,4–6} The yield of S_NAr product increased with base concentration, electron-withdrawing ability of the *O*-aryl group, and base strength. On the other hand, when tertiary amines were used or the electron-withdrawing ability of the β-aryl substituent was increased the E2 mechanism predominated.^{3,4,7} Therefore, the exclusive formation of the elimination products from **1–3** can be attributed to the strong electron-withdrawing ability of the β-aryl substituent.

Results of kinetic studies reveal that the reactions of **1–3** with EtO⁻-EtOH, PhC(CH₃)=NO⁻/PhC(CH₃)=NOH and CF₃CH₂O⁻/CF₃CH₂OH buffers proceed by an E2 mechanism. The observed general base catalysis with the Brønsted β values ranging from 0.55 to 0.75 rule out a mechanism in which either the breakdown of an ion-paired or hydrogen bonded carbanion (k₂') or free carbanion (k₂) is rate limiting because these mechanisms would exhibit either a specific base catalysis or Brønsted β value near unity (Scheme 1).^{10,16} A β value of ca. 1 is also expected for the internal return mechanism in which both k₁ and k₂ steps are rate limiting.¹⁶ In addition, the values of |β_{lg}| = 0.39–0.48 rule out a mechanism in which either k₁ [(E1cb)_{irr}] or k_d is rate limiting, for which a small or negligible leaving group effect is expected.¹⁶ On the other hand, the results are consistent with an E2 mechanism in which there is partial cleavage of the C_β-H and N_α-OAr bonds in the transition state.

The structures of the transition states may be assessed by the Brønsted β and β_{lg} values. The β values indicate

(16) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1987; pp 591–599.

Scheme 1



the extent of proton transfer in the transition state. For RO^- -promoted eliminations from **1–3**, values of $\beta = 0.55\text{--}0.75$ were determined (Table 2). This indicates moderate to extensive cleavage of the $\text{C}_\beta\text{--H}$ bonds in the transition states.

The β_{lg} values are usually taken as a qualitative measure of the extent of the leaving group cleavage. Hence the observed $|\beta_{\text{lg}}|$ values of $0.39\text{--}0.48$ for the nitrile-forming eliminations can be interpreted with significant extents of $\text{N}_\alpha\text{--OAr}$ bond cleavage in the transition states (Table 3). The combined results reveal that the nitrile-forming eliminations from **1–3** proceed by the concerted E2 mechanism via an E2-central transition state with significant cleavages of the $\text{C}_\beta\text{--H}$ and $\text{N}_\alpha\text{--OAr}$ bonds.

The structure–reactivity coefficients provide additional support for this conclusion. Table 2 shows that the Brønsted β values for RO^- -promoted eliminations from **1–3** decrease as the leaving group is made more nucleofugic. The results can be described by a positive p_{xy} interaction coefficient, $p_{xy} = \partial\beta/\partial pK_{\text{lg}} = \partial\beta_{\text{lg}}/\partial pK_{\text{BH}}$, that describes the interaction between the base catalyst and the leaving group.^{11,18} The observed increase in the $|\beta_{\text{lg}}|$ values as the catalyst is made less basic is another manifestation of this effect, i.e., $p_{xy} = \partial\beta_{\text{lg}}/\partial pK_{\text{BH}} > 0$ (Table 3).^{11,18} These changes in the β and $|\beta_{\text{lg}}|$ values can be described on the More–O’Ferrall–Jencks reaction coordinate diagram (Figure 3).¹⁸ A change to a better leaving group will raise the energy of the top edge of the diagram. The transition state will then move toward the right as depicted by a shift from A to B on the energy diagram, resulting in a decrease in β (Figure 3).¹⁸ Similarly, a weaker base will raise the energy of the left side of the diagram and shift the transition state from A to C to increase the extent of $\text{C}_\alpha\text{--OAr}$ bond cleavage (Figure 3).¹⁸ The positive p_{xy} coefficient is not consistent with an E1cb mechanism for which $p_{xy} = 0$ is expected, but provide additional support for the concerted E2 mechanism.^{11,18–21}

Effects of 2,4-Dinitro Substituents on the Nitrile-Forming Transition State. It was previously established that the MeONa -promoted elimination from (*E*)-benzaldehyde *O*-2,4-dinitrophenyloxime proceeded by the E2 mechanism via a symmetrical transition state.⁴ For the nitrile-forming eliminations from closely related compounds under comparable conditions, the rate increases by 5×10^5 fold, the Brønsted β value increases from 0.5 to 0.55, and the $|\beta_{\text{lg}}|$ decreases from 0.62 to 0.39, respectively, by the 2,4-dinitro substituent (Table 4). The

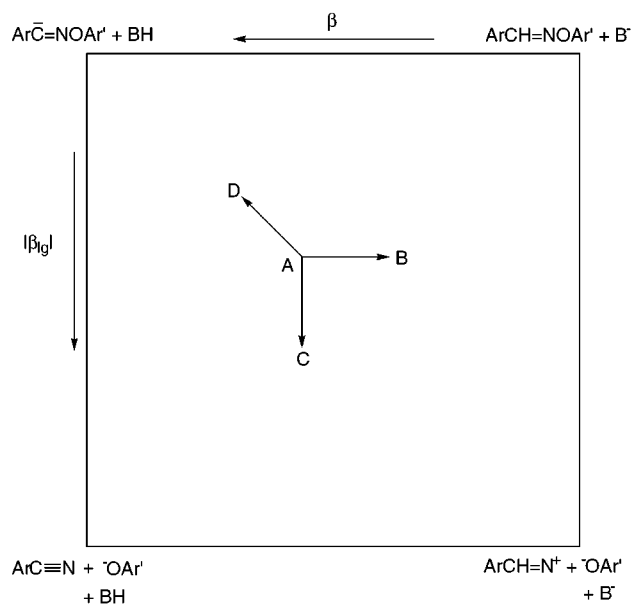


Figure 3. Reaction coordinate diagram for nitrile-forming eliminations. The effect of the change to a better leaving group, a weaker base, and an electron-withdrawing substituent are indicated by the shift of the transition state from A to B, A to C, and A to D, respectively.

Table 4. Transition State Parameters for Nitrile-Forming Eliminations from (*E*)- $\text{ArCH}=\text{NOC}_6\text{H}_3\text{2,4}(\text{NO}_2)_2$ Promoted by RO^- in ROH at 25.0 °C

	Ar = Ph ^a	Ar = 2,4-(NO ₂) ₂ C ₆ H ₃
base–solvent	MeONa–MeOH	EtONa–EtOH
pK_a	18.3 ^b	19.18 ^c
rel rate	1	5×10^5
β	0.5	0.55
β_{lg}	–0.62	–0.39

^a Reference 4. ^b Reference 27. ^c Reference 22.

results can be described by a positive p_{xy} interaction coefficient, $p_{xy} = \partial\beta/\partial\sigma$, that describes the interaction between the base catalyst and the β -aryl substituent.^{11,18} The positive p_{xy} interaction coefficient is consistent with an E2 mechanism and a predominantly diagonal reaction coordinate. On the More–O’Ferrall–Jencks reaction coordinate diagram in Figure 3, an electron-withdrawing β -aryl substituent will lower the energy of the carbanion intermediate in the upper left corner of the energy diagram.¹⁸ The transition state will then move toward the carbanion as depicted by a shift from A to D in Figure 3, with more proton transfer and a larger β value and less $\text{N}_\alpha\text{--OAr}$ bond cleavage and a smaller $|\beta_{\text{lg}}|$.²³

(22) Gaunti, G. *J. Chem. Soc., Perkin Trans. 2* **1981**, 327–330.

(23) A reviewer questioned the validity of using the More–O’Ferrall–Jencks diagram to compare two systems that differ by 10^5 in rate. It has been previously shown that the More–O’Ferrall–Jencks diagram could be successfully employed for the nitrile-forming syn elimination reactions with large difference in reactivity when the structures of the transition states are closely related, but fails to interpret results for reactions with only modest difference in reactivity if the transition state structures are very different.²⁴ Therefore, the qualitative nature of this interpretation should be emphasized because the two reactions were studied under different conditions.

(24) Cho, B. R.; Jang, W. J.; Bartsch, R. A. *J. Org. Chem.*, **1993**, *58*, 3901–3904.

(25) Estimated from the linear relationship between the pK_a values in H₂O and in EtOH.²⁶

(26) Uhm, I. W.; Hong, Y. J.; Kwon, D. S. *Tetrahedron*, **1997**, *53*, 5073–5082.

(17) Keeffe, J. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1983**, *105*, 265–279.

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(19) Gandler, J. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1982**, *104*, 1937–1951.

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It is conceivable that a strong electron-withdrawing β -aryl substituent may decrease the energy of the carbanion intermediate lower than that of the E2 transition state to induce a change in the reaction mechanism. However, no change in the reaction mechanism has been realized by the 2,4-dinitro substituents, despite 5×10^5 fold enhancement in rate. It appears that more stabilization energy is obtained by forming the partial triple bond than by delocalizing the negative charge at the β -carbon with the electron-withdrawing groups. Noteworthy is the relative insensitivity of the nitrile-forming transition state to the variation of the β -aryl substituent.

Experimental Section

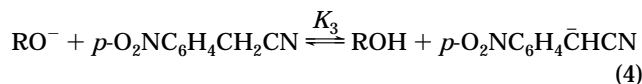
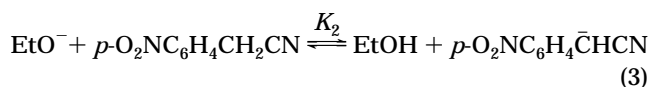
Materials. (*E*)-2,4-Dinitrobenzaldehyde *O*-aryloximes (**1–3**) were prepared by the reactions of 2,4-dinitrobenzaldehyde with appropriately substituted *O*-arylhydroxylamines in the presence of catalytic amount of HCl as described in the literature.^{1,12,13} The spectral and analytical data of the compounds were consistent with the proposed structures. The yield (%), melting point (°C), NMR (DMSO-*d*₆), IR (KBr, C=N, cm⁻¹), and combustion analysis data for the new compounds are as follows. 2,4-(NO₂)₂C₆H₃CH=NOC₆H₄-4-NO₂ (**1**): yield 70; mp 182–183; IR 1587; NMR δ 9.21 (s, 1H), 8.88 (s, 1H), 8.65 (dd, 1H), 8.36 (d, 1H), 8.32 (d, 2H), 7.54 (d, 2H). Anal. Calcd for C₁₃H₈N₄O₇: C, 47.00; H, 2.43; N, 16.86. Found: C, 46.87; H, 2.37; N, 16.56. 2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2-Cl-4-NO₂ (**2**): yield 70; mp 154–155; IR 1582; NMR δ 9.31 (s, 1H), 8.88 (d, 1H), 8.66 (dd, 1H), 8.42 (d, 1H), 8.36 (d, 1H), 8.29 (dd, 1H), 7.84 (d, 1H). Anal. Calcd for C₁₃H₇ClN₄O₇: C, 42.58; H, 1.93; N, 15.28. Found: C, 42.66; H, 1.87; N, 14.93. 2,4-(NO₂)₂C₆H₃CH=NOC₆H₃-2,4-(NO₂)₂ (**3**): yield 72; mp 163–168; IR 1601; NMR δ 9.36 (s, 1H), 8.89 (m, 2H), 8.70 (dd, 1H), 8.63 (dd, 1H), 8.38 (d, 1H), 8.10 (d, 1H). Anal. Calcd for C₁₃H₇N₅O₉: C, 41.39; H, 1.87; N, 18.57. Found: C, 41.20; H, 1.83; N, 18.60.

Ethanol was purified by reaction with magnesium and distillation. Solutions of EtONa–EtOH were prepared by adding clean pieces of sodium metal to anhydrous EtOH under nitrogen. The buffer solutions of PhC(CH₃)=NO⁻/PhC(CH₃)=NOH, CF₃CH₂O⁻/CF₃CH₂OH, and YC₆H₄O⁻/YC₆H₄OH (Y=H, *p*-Cl, *m*-Cl, *p*-CN) were prepared by adding appropriate amount of the conjugate acid to EtONa–EtOH. In all cases the buffer ratio was maintained to be 1.0.

p*K*_a Values. The p*K*_a values of the PhC(CH₃)=NOH and CF₃CH₂OH in ethanol were determined by measuring the equilibrium constant *K*₁ between ROH and EtO⁻ in ethanol using *p*-nitrobenzyl cyanide as an indicator.¹⁴ The *K*₂ value was determined by adding 1.0×10^{-4} M of *p*-nitrobenzyl cyanide to a solution containing 2.0×10^{-5} M of EtO⁻ in EtOH. The absorbance of the *p*-nitrobenzyl cyanide anion was measured at 530 nm and divided by its molar extinction coefficient ($\epsilon = 29400$) to obtain the anion concentration. The equilibrium constant *K*₂ was calculated with eq 6 using the *p*-nitrobenzyl cyanide anion concentration as described previously.¹⁵

To this solution was added $(4.6–13) \times 10^{-2}$ M of ROH in small increments, and the absorbances at 530 nm were measured. Utilizing the *K*₂ value determined as above and the *p*-nitrobenzyl cyanide anion concentration measured after addition of the ROH, the [EtO⁻] was calculated with eq 6. The *K*₁ values were calculated with eq 5 using the concentrations of [EtO⁻] calculated as above and [RO⁻] and [ROH] obtained from the relationship [RO⁻] = [EtO⁻]₀ - {[EtO⁻] + [*p*-O₂-NC₆H₄CHCN⁻]} and [ROH] = [ROH]₀ - [RO⁻]. The p*K*_a values of the ROH were then calculated with eq 8 using the

p*K*_a value of 19.18 for EtOH in EtOH²² and the *K*₁ value.



$$K_1 = [\text{RO}^-]/[\text{EtO}^-][\text{ROH}] \quad (5)$$

$$K_2 = [p\text{-O}_2\text{NC}_6\text{H}_4\text{C}^-\text{HCN}]/[\text{EtO}^-][p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{CN}] \quad (6)$$

$$K_3 = [\text{ROH}][p\text{-O}_2\text{NC}_6\text{H}_4\text{C}^-\text{HCN}]/[\text{RO}^-] \times [p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{CN}] \quad (7)$$

$$pK_a(\text{ROH}) = 19.18 - \log K_1 \quad (8)$$

Product Studies. The products of the reactions between **1–3** and EtO⁻, PhC(CH₃)=NO⁻/PhC(CH₃)=NOH, and CF₃CH₂O⁻/CF₃CH₂OH buffers in EtOH were identified by TLC and GC-MS. The products were 2,4-dinitrobenzoxime and aryloxides, which were stable under the experimental condition. The products were also identified by periodically monitoring the UV absorption of the reaction mixtures under the reaction condition. For all reactions the absorbance corresponding to the reactants decreased at 310–330 nm, and those for the products increased at 400–404 nm as the reactions proceeded. The UV spectra of the products were identical to those of the aryloxides. Clean isosbestic points were observed at 357, 339, and 354 nm for the reactions of **1**, **2**, and **3**, respectively. The yields of the aryloxides determined by comparing the UV absorptions of the infinity samples with those for the authentic aryloxides were in the range of 90–98%.

Kinetic Studies. Rates of the eliminations from **1–3** promoted by EtO⁻–EtOH, PhC(CH₃)=NO⁻/PhC(CH₃)=NOH, and CF₃CH₂O⁻/CF₃CH₂OH buffers in EtOH were followed using a stopped-flow spectrophotometer. Reactions were monitored by the increase in the absorption of the aryloxides at 400–404 nm under pseudo-first-order condition employing at least 50-fold excess of base. In almost every case, plots of $-\ln(A_\infty - A/A_\infty - A_0)$ vs time were linear over at least two half-lives. The slope was the pseudo-first-order rate constants. Freshly prepared buffer solutions were used in all kinetic runs.

Control Experiments. The stability of **1–3** and their solutions were determined by measuring the melting point and periodical scanning of the solutions with the UV spectrophotometer. No change in melting point or UV spectrum was detected for **1–3** during six months in the refrigerator. The solutions of **1** and **2** in EtOH were stable for at least three weeks when stored in the refrigerator.

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Supporting Information Available: Observed rate constants for eliminations from (*E*)-2,4-dinitrobenzaldehyde *O*-aryloximes (**1–3**) promoted by EtO⁻–EtOH, PhC(CH₃)=NO⁻/PhC(CH₃)=NOH, and CF₃CH₂O⁻/CF₃CH₂OH buffers in ethanol at 25.0 °C (2 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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