Eliminations from (*E*)-*O*-Arylbenzaldoximes Promoted by Tertiary Amines in Acetonitrile. Effects of Aryl Substituents, Base Strength, and Leaving Group upon the Nitrile-Forming Transition State

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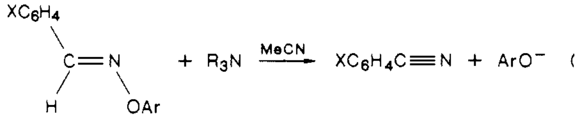
Abstract: Elimination reactions of (*E*)-*O*-(2,4-dinitrophenyl)benzaldoximes (**1**) and (*E*)-*O*-picrylbenzaldoximes (**2**) with R_3N in MeCN have been investigated. The reactions are quantitative, producing only benzonitriles and aryloxides. The observation of second-order kinetics, $\beta = 0.43–0.81$, and $|\beta_{lg}| = 0.39–0.73$ is consistent with an E2 mechanism. For reactions of **1** with R_3N in MeCN, the β and ρ values increased significantly with electron-withdrawing aryl substitutents and stronger bases respectively. The corresponding changes in the β and ρ values for **2** were in the same direction but much less. When the leaving group was changed from 2,4-dinitrophenoxide to picrate, however, β increased and ρ decreased. Changes in transition-state parameters with alteration in the reactant structure are interpreted as resulting from variation in a nitrile-forming transition state.

Extensive studies of structure–reactivity relationships in β-elimination reactions have led to a qualitative understanding of the relationship between the structure of the E2 transition state and changes in reactant structure or reaction conditions.[1,2] Results from these studies have usually been interpreted with the aid of More O'Ferral–Jencks (MOFJ) reaction coordinate diagrams.[3-11]

Very recently we reported a kinetic investigation of the nitrile-forming elimination reactions of (*E*)-*O*-arylbenzaldoximes promoted by OH^- in 60% DMSO(aq).[12] The reaction proceeded via an E2 central type of transition state with similar extents of C_β–H and N_α–OAr bond cleavage and extensive negative charge development on the leaving group. The influence of a change to a poorer leaving group was rationalized with the shift of the transition state in the horizontal direction in the reaction coordinate diagram. However, the observed changes in transition-state structure with aryl-substituent variation were too small to interpret with the reaction coordinate diagram.

It occurred to us that the influence of reactant structure upon the transition state for nitrile-forming eliminations could be more clearly understood if the reactivity of the compound were changed to a greater extent. Accordingly, we have investigated the reactions of (*E*)-*O*-arylbenzaldoximes, in which the leaving groups are 2,4-dinitrophenoxide (**1**) and picrate (**2**), with tertiary amines in MeCN (eq 1). It was expected that the poor anion-solvating abilities of a dipolar aprotic solvent might destabilize the charged transition state more than the neutral reactant, rendering the former more susceptible to the changes in the reactant structure.



(1)

	Ar	X	R_3N
1	2,4-dinitrophenyl	**a** H	Et_3N
2	picryl	**b** *p*-CH_3O	$Et_2NCH_2CH_2OH$
		c *m*-Br	$EtN(CH_2CH_2OH)_2$
		d *p*-NO_2	$N(CH_2CH_2OH)_3$

In this study, we have determined the transition-state differences for eliminations from **1** wrought by the change in base–solvent system from OH^-–60% DMSO(aq) to Et_3N–MeCN. The influence of aryl substituents, base strength, and leaving group variations upon the nitrile-forming transition state was studied. The results of these studies are reported here.

Results

(*E*)-*O*-(2,4-Dinitrophenyl)benzaldoximes (**1**) and (*E*)-*O*-picrylbenzaldoximes (**2**) were prepared by reactions of (*E*)-benzaldoximes with aryl halides as reported previously.[12]

Reactions of **1** and **2** with R_3N in MeCN produced benzonitrile and aryloxides quantitatively. The rates of eliminations from **1** and **2** promoted by R_3N in MeCN were followed by monitoring the increase in the absorption at the λ_{max} for the aryloxides. Second-order rate constants for reactions of **1** and **2** with R_3N in MeCN are given in Table I.

Hammett plots for eliminations from **1** and **2** are shown in Figures 1 and 2. The influence of β-aryl substituents (**a**–**d**) upon the elimination rates gave excellent correlations with σ. Hammett ρ values are listed in Tables II and IV.

Rates of elimination from **1a** and **2a** promoted by Et_3N in MeCN were measured at three temperatures spanning 20 °C. The Arrhenius plots were linear with excellent correlation. The calculated enthalpies and entropies of activation are presented in Tables II and V.

The ρ_{lg} and β_{lg} values, which are calculated from the rate data and δ^- and pK_{lg} values,[14] are included in Tables II and III.

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Table I. Rate Constants for Eliminations from (*E*)-*O*-Arylbenzaldoximes[a] Promoted by R_3N in MeCN at 25.0 °C

		10^4k_2,[e] $M^{-1}\,s^{-1}$				10^2k_2,[e] $M^{-1}\,s^{-1}$			
base[b]	pK_a[c]	**1a**	**1b**	**1c**	**1d**	**2a**	**2b**	**2c**	**2d**
Et_3N	18.5[d]	7.56[f]	1.34	45.8	841	139[g]	63.1	279	771
$Et_2NCH_2CH_2OH$	17.7	1.24	0.297	7.08	79.4	24.4	8.67	42.5	115
$EtN(CH_2CH_2OH)_2$	16.3	0.573	0.176	2.51	19.9	3.45	1.58	6.38	12.1
$N(CH_2CH_2OH)_3$	15.7	0.114	0.0581	0.638	3.89	1.00	0.488	1.92	3.62

[a] [Substrate] = $5.0 \times 10^{-4} - 1.00 \times 10^{-4}$ M. [b] [Base] = $1.0 \times 10^{-3} - 1.0 \times 10^{-1}$ M. [c] Estimated from $(pK_a)_w$[15] and $pK_a(MeCN-H_2O) = 7.8$ for Et_3N[14] except where otherwise noted. [d] Reference 14. [e] Estimated uncertainty ±5%. [f] $k_2 = 1.5 \times 10^{-3}$ at 35.0 °C and 3.32×10^{-3} at 45.0 °C. [g] k_2 = 2.43 at 35.0 °C and 5.54 at 45.0 °C.

Table II. Effect of Base-Solvent upon Nitrile-Forming Eliminations from (*E*)-$ArCH{=}NOC_6H_3$-2,4-$(NO_2)_2$.

	(*E*)-$ArCH{=}NOC_6H_3$-2,4-$(NO_2)_2$	
	^-OH-60% DMSO(aq)[a]	Et_3N-MeCN
pK_a	18.3	18.5
rel rate	1	1.0×10^{-4}
ρ	0.20 ± 0.45	2.6 ± 0.2
β	0.49 ± 0.14	0.57 ± 0.12
ρ_{lg}	1.4 ± 0.1	2.6
β_{lg}	−0.59 ± 0.01	−0.65
$\Delta H^{\ddagger}$, kcal/mol	14.5 ± 0.1	13.9 ± 0.8
$\Delta S^{\ddagger}$, eu	−6.4 ± 0.1	−28.1 ± 2.2
$\Delta G^{\ddagger}$, kcal/mol	16.4 ± 0.1	22.3 ± 1.8

[a] Reference 12.

Table III. Effect of Aryl Substituents upon Brønsted β and β_{lg} Values for Eliminations from (*E*)-$XC_6H_4CH{=}NOAr$ Promoted by R_3N in MeCN at 25.0 °C

	β		
X	Ar = 2,4-dinitrophenyl	Ar = picryl	β_{lg}[a]
p-CH_3O	0.43 ± 0.09	0.71 ± 0.07	−0.73
H	0.57 ± 0.12	0.72 ± 0.04	−0.65
m-Br	0.60 ± 0.10	0.74 ± 0.06	−0.56
p-NO_2	0.75 ± 0.12	0.81 ± 0.04	−0.39

[a] The base was Et_3N.

Table IV. Effect of Base Strength upon Hammett ρ Values for Eliminations from (*E*)-$XC_6H_4CH{=}NOAr$ Promoted by R_3N in MeCN at 25.0 °C

		ρ	
base	pK_a[a]	Ar = 2,4-dinitrophenyl	Ar = picryl
Et_3N	18.5	2.6 ± 0.2	1.0 ± 0.1
$Et_2NCH_2CH_2OH$	17.7	2.3 ± 0.1	1.0 ± 0.1
$EtN(CH_2CH_2OH)_2$	16.3	2.0 ± 0.1	0.81 ± 0.08
$N(CH_2CH_2OH)_3$	15.7	1.8 ± 0.1	0.81 ± 0.06

[a] See footnotes in Table I.

Table V. Effect of the Leaving Group upon Eliminations from (*E*)-$XC_6H_4CH{=}NOAr$ Promoted by R_3N in MeCN at 25.0 °C

	Ar = 2,4-dinitrophenyl	Ar = picryl
pK_{lg}[a]	16.0	11.0
rel rate	1	1.8×10^3
ρ[c]	2.0 ± 0.1	1.0 ± 0.1
β[d]	0.57 ± 0.12	0.72 ± 0.04
$\Delta H^{\ddagger}$,[d] kcal/mol	13.9 ± 0.8	12.4 ± 1.6
$\Delta S^{\ddagger}$,[d] eu	−28.1 ± 2.2	−16.3 ± 2.0
$\Delta G^{\ddagger}$,[d] kcal/mol	22.3 ± 1.8	17.3 ± 2.8

[a] See footnotes in Table II. [b] X = H, and base = Et_3N. [c] Base was Et_3N. [d] X = H.

Brønsted plots for eliminations from **1** and **2** are depicted in Figures 3 and 4. The β values are summarized in Table III.

Discussion

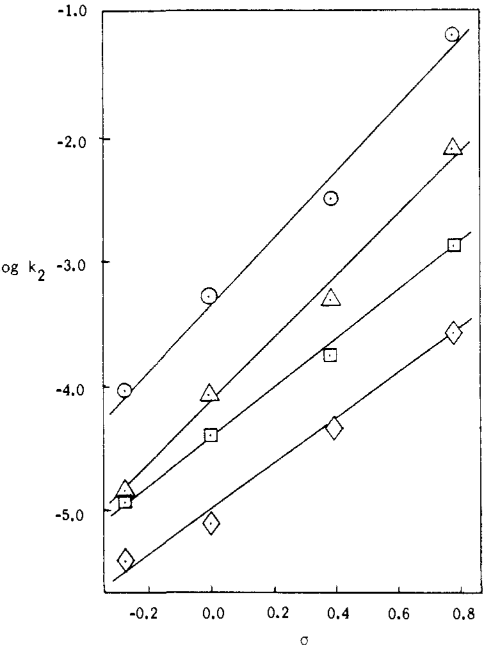

Figure 1. Hammett plots for eliminations from (*E*)-*O*-(2,4-dinitrophenyl)benzaldoximes (**1**) promoted by R_3N in MeCN at 25.0 °C. Bases are the following: Et_3N (⊙), Et_2NEtOH (△), $EtN(EtOH)_2$ (⊡), and $N(EtOH)_3$ (◇).

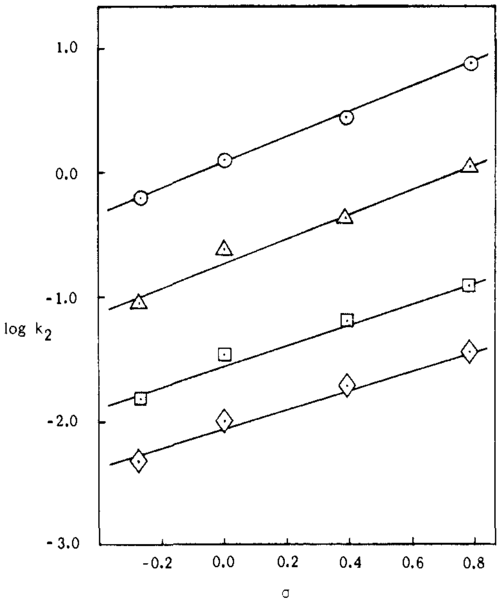

Figure 2. Hammett plots for eliminations from (*E*)-*O*-picrylbenzaldoximes (**2**) promoted by R_3N in MeCN at 25.0 °C. Bases are the following: Et_3N (⊙), Et_2NEtOH (△), $EtN(EtOH)_2$ (⊡), and $N(EtOH)_3$ (◇).

Transition State for Elimination from 1 Promoted by Et_3N in MeCN. Results of the kinetic investigations and product studies clearly establish that the reactions of **1** and **2** with Et_3N in MeCN proceed via an E2 mechanism. Since the reactions produced benzonitrile and aryloxides as the only products and exhibited second-order kinetics, all but bimolecular pathways can be ruled

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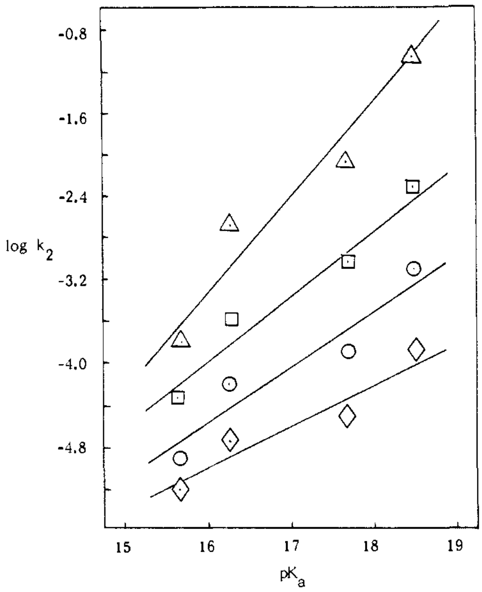

Figure 3. Brønsted plots for eliminations from (*E*)-$XC_6H_4CH{=}NOC_6H_3$-2,4-$(NO_2)_2$ (**1**) promoted by R_3N in MeCN at 25.0 °C. Aryl substituents are the following: X = *p*-NO_2 (▲), *m*-Br (▣), H (⊙), and *p*-CH_3O (◆).

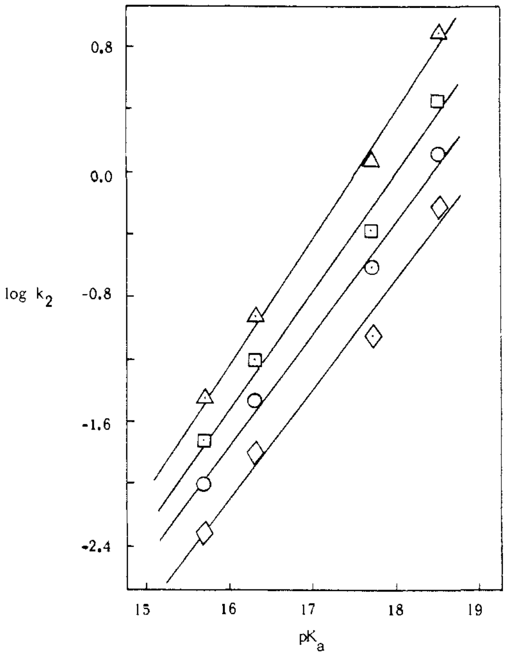

Figure 4. Brønsted plots for eliminations from (*E*)-$XC_6H_4CH{=}NO(Pic)$ (**2**) promoted by R_3N in MeCN at 25.0 °C. Aryl substituents are the following: X = *p*-NO_2 (▲), *m*-Br (▣), H (⊙), and *p*-CH_3O (◆).

out. In addition, an E1cB mechanism is negated by the substantial values of β and β_{lg} (Table II).[2]

Comparison of transition-state parameters for base-promoted eliminations from **1** (Table II) reveals that the transition state changes significantly when the base–solvent is varied from OH^-–60% DMSO(aq) to Et_3N–MeCN even though the base strength remains nearly the same. The Hammett ρ and ρ_{lg} values for Et_3N-promoted elimination from **1** are both 2.6, which are much larger than those for the OH^--promoted eliminations for the same substrate. Thus, the carbanionic character of the transition state increases significantly with this variation of base–solvent system.

The Brønsted β and β_{lg} values indicate the extents of C_β–H and N_α–OAr bond rupture in the transition state. For Et_3N-promoted elimination from **1**, values of $\beta = 0.57$ and $\beta_{lg} = -0.65$ were determined. This indicates significant cleavage of both the C_β–H and N_α–OAr bonds in the transition state. Moreover, the values are similar to those obtained from OH^--promoted elimination for the same substrate. Along with similar enthalpies of activation for both base-solvent combination (Table II), these results indicate similar extents of C_β–H and N_α–OAr bond cleavage and triple-bond formation in both transition states.

The combined results reveal that the extents of C_β–H and N_α–OAr bond cleavage and the triple-bond formation are similar, but the transition-state carbanionic character increases significantly when the base-solvent system is changed from OH^-–60% DMSO(aq) to Et_3N–MeCN. Thus, it appears that the structure of the transition state for the Et_3N-promoted elimination from **1** is highly symmetrical with similar extents of C_β–H and N_α–OAr bond cleavage, similar negative charge distribution on the β-carbon and the leaving group, and extensive triple-bond character.

The change in the transition-state carbanionic character with this base–solvent system variation can be attributed to a solvent effect. Since the partial negative charge developed on the β-carbon in the transition state can not be stabilized by solvation in the poorly anion-solvating medium MeCN, the transition state should be more sensitive to the electron-withdrawing ability of the aryl substituent. Furthermore, the negative charge should be distributed between the β-carbon and the leaving group as much as possible in order to achieve maximum charge dispersal. Therefore, it seems reasonable to expect that the ρ and ρ_{lg} values should show parallel increases with the base–solvent system variation.

For elimination from **1**, the enthalpy of activation remains nearly constant, but the entropy of activation decreases considerably when the base–solvent is changed from OH^-–60% DMSO(aq) to Et_3N–MeCN (Table II). The large negative entropy of activation with Et_3N–MeCN as the base–solvent system is typical for reactions of this charge type[6] and can be attributed to the large degree of solvent reorganization that is necessary to solvate the charged transition state. Thus, the 10^4-fold retardation in rate results from an entropic factor.

Effects of Aryl Substituent, Base Strength, and Leaving Group Variations upon a Nitrile-Forming Transition State. For elimination from **1** promoted by R_3N in MeCN, Brønsted β increases and $|\beta_{lg}|$ decreases substantially with enhancement of the electron-withdrawing ability of the β-aryl substituent (Table III). This indicates a significant increase in C_β–H bond cleavage and an appreciable decrease in the N_α–OAr bond rupture in the transition state. This result is in contrast with the negligible substituent effect observed for OH^--promoted elimination from the same substrate.[12]

The pronounced influence of the aryl substituent upon the transition-state structure for the Et_3N-promoted elimination can be attributed to both the increased carbanionic character at the β-carbon in the transition state and a solvent effect. The negative charge density developed on the β-carbon is much higher than that for the OH^--promoted elimination. Moreover, it can not be stabilized by solvation in MeCN (vide supra). Therefore, the structure of the transition state for Et_3N-promoted elimination is anticipated to be more susceptible to the electron-withdrawing ability of the aryl substituent.

A distinct change in the transition-state carbanionic character is also observed in eliminations from **1** with base strength variation. Thus, the Hammett ρ values decrease systematically as the base strength becomes weaker (Table IV), indicating a gradual decrease in the transition-state carbanionic character with a weaker base.

When the leaving group is changed from 2,4-dinitrophenoxide to picrate, ρ decreases from 2.6 to 1.0 but β increases from 0.57 to 0.72 (Table V). These results indicate a large decrease in carbanionic character at the β-carbon but a significant increase in the C_β–H bond cleavage in the transition state as the leaving group becomes better.

The unusual changes in the transition-state structure noted with the leaving group variation may be rationalized as resulting from a large difference in the anion-stabilizing ability of the leaving groups. The pK_a values of picric acid and 2,4-dinitrophenol in MeCN are 11.0 and 16.0, respectively.[14] Thus, picrate would stabilize the negative charge much better than 2,4-dinitrophenoxide. Moreover, the partial negative charge developed on the β-carbon in the transition state cannot be stabilized by solvation

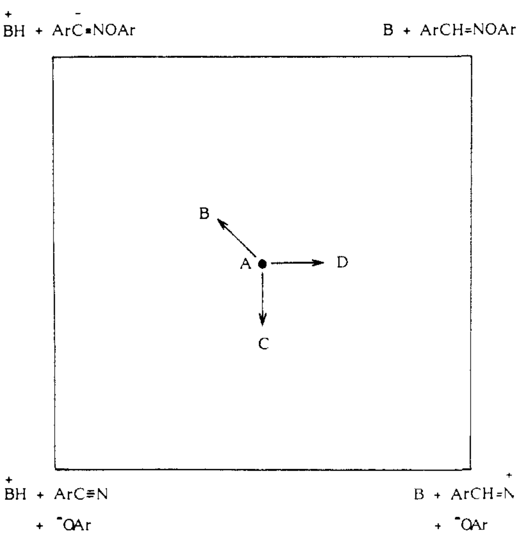

Figure 5. More O'Ferrall–Jencks reaction coordinate diagram for elimination reactions of (*E*)-*O*-2,4-dinitrophenylbenzaldoximes (**1**) promoted by R_3N in MeCN. Energy contours are omitted. Effects of aryl substituents (A → B), base strength (A → C), and leaving group (A → D) variations upon the transition-state position are shown by solid lines (see text).

in MeCN. Therefore, the charge density on the β-carbon in the transition state for **2a** would be transferred to the picrate leaving group to a much greater extent than that for **1a**. Accordingly, the C_β–H bond could be broken more, and little negative charge would remain on the β-carbon in the former transition state.

The large increase in the entropy of activation with the leaving group variation is consistent with this view. Since most of the negative charge is delocalized on the rather bulky picrate leaving group, the transition state for **2a** would be better solvated by MeCN than that for **1a**, in which some of the negative charge is localized on the β-carbon. Therefore, less solvent reorganization would be required to solvate the former, and the entropy of activation should increase.

For R_3N-promoted eliminations from **2**, the β increases with the electron-withdrawing ability of the aryl substituent, and the ρ decreases with a weaker base (Tables III and IV). The trends are similar to those noted for **1**, but the magnitude of the change is much less.

The changes in transition-state structure with aryl substituent and base strength can readily be interpreted with a reaction coordinate diagram.[3,16] As previously mentioned, the transition state for elimination from **1** promoted by Et_3N–MeCN appears to be highly symmetrical with significant cleavage of the C_β–H and N_α–OAr bonds. Therefore, it can be located near the center of the diagram (A in Figure 5). An increase in the electron-withdrawing ability of the aryl substituents would lower the energy of the ElcB intermediate, shifting the transition state from A to B as depicted in Figure 5. This corresponds to an increase in C_β–H bond cleavage and a decrease in N_α–OAr bond rupture, as observed.

Similarly, change of the base to a weaker one should lower the energy of the right edge of the diagram. This is expected to shift the transition state toward the product and the E1 intermediate. Assuming similar effects for parallel and perpendicular motions, the effect of the change to a weaker base would be to shift the transition state directly downward to point C, decreasing the carbanionic character at the β-carbon. The prediction is borne out by the decrease in ρ value with a weaker base.

The changes in the transition-state structure for **2** with the aryl substituent and base strength variations can also be interpreted similarly except that the magnitude of the change is much less than that for **1**.

In contrast, the effect of the leaving group variation upon the nitrile-forming transition state cannot be interpreted with the reaction coordinate diagram. A change to a better leaving group is expected to lower the energy of the lower edge of the diagram (Figure 5). This would shift the transition state toward the reactant and the E1 intermediate. If similar effects are assumed for the parallel and perpendicular motions, the transition state would move from A to D as depicted in Figure 5. This corresponds to decreased C_β–H bond cleavage and diminished carbanionic character on the β-carbon. However, this prediction is in conflict with our result.

Thus, it appears that the reactions of (*E*)-*O*-arylbenzaldoximes with tertiary amines in MeCN proceed via an E2 central type of transition state with significant cleavage of C_β–H and N_α–OAr bonds and extensive triple-bond formation. The structure of the transition state for more reactive **2** changes only slightly with the variation of the β-aryl substituents and base strength. The influence of the structural variations in the reactants upon the transition-state structure becomes more evident for less reactive **1**. When the leaving group is changed from 2,4-dinitrophenoxide to picrate, unusual changes in the transition state occur, probably due to the large differences in the anion-stabilizing abilities of the leaving groups in the poor anion-solvating solvent MeCN.[17]

Experimental Section

NMR spectra were recorded on EM-360 or Brucker AM-200 spectrometers. Chemical shifts are reported to the nearest 0.1 ppm with TMS as an internal standard. IR spectra were recorded with Perkin-Elmer Model 710 B spectrophotometer. UV spectra were taken with a Cary 17-D spectrophotometer with thermostated cuvette holders. Elemental analyses were performed by Korea Advanced Institute of Science and Technology, Seoul, Korea.

Materials. (*E*)-*O*-Arylbenzaldoximes were prepared by reactions of benzaldehydes with *O*-arylhydroxylamines[18-20] or (*E*)-benzaldoximes with appropriate aryl halides.[21] The physical, spectral, and analytical data for these compounds were consistent with the proposed structures.[22] The melting point (°C), NMR (benzal C–H, ppm), and IR (C=N, cm^{-1}) of the new compounds are as follows: $C_6H_4CH{=}NO(Pic)$ (**2a**) (172–173/8.5/1615); *p*-$CH_3OC_6H_4CH{=}NO(Pic)$ (**2b**) (135–136/8.8/1600); *m*-$BrC_6H_4CH{=}NO(Pic)$ (**2c**) (161–163/8.5/1630); *p*-$NO_2C_6H_4CH{=}NO(Pic)$ (**2d**) (158–160/8.6/1610).

Reagent-grade MeCN was distilled from CaH_2. The tertiary amines were purified by literature method.[23] The base–solvent solution was prepared by adding the appropriate amines to MeCN.

Kinetic Studies of Eliminations from 1 and 2. Kinetics of eliminations from **1** and **2** were followed by monitoring the increase in the absorbance of the aryloxides with time as described previously.[12]

Product Studies of Eliminations from 1 and 2. The products of eliminations from **1** and **2** promoted by Et_3N in MeCN were determined as described previously.[12] The products were benzonitrile and aryloxides.

Control Experiments. The stability of solutions of **1** and **2** in MeCN was determined by periodical scanning of the solution with the UV spectrophotometer. No change in the UV spectrum was detected during 1 month.

Acknowledgment. This investigation was supported by a grant from the Korea Science and Engineering Foundation.

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