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K^+ Ion Catalysis in Nucleophilic Displacement Reaction of Y-Substituted-Phenyl Picolinates with Potassium Ethoxide: Effect of Substituent Y on Reactivity and Transition State Structure

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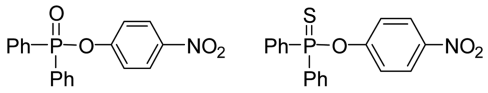
Pseudo-first-order rate constants (k_{obsd}) have been measured spectrophotometrically for the nucleophilic substitution reaction of Y-substituted-phenyl picolinates (**7a-f**) with potassium ethoxide (EtOK) in anhydrous ethanol at 25.0 ± 0.1 °C. The plot of k_{obsd} *vs*. [EtOK] curves upward while the plot of $k_{obsd}/[EtO^-]_{eq}$ *vs*. $[EtO^-]_{eq}$ is linear with a positive intercept in all cases. Dissection of k_{obsd} into k_{EtO^-} and k_{EtOK} (*i.e*., the second-order rate constants for the reactions with the dissociated EtO^- ion and ion-paired EtOK, respectively) has revealed that the ion-paired EtOK is more reactive than the dissociated EtO^-. The σ^o constants result in a much better Hammett correlation than σ^- constants, indicating that the reaction proceeds through a stepwise mechanism in which departure of the leaving group occurs after the rate-determining step (RDS). K^+ ion catalyzes the reaction by increasing the electrophilicity of the reaction center through formation of a cyclic transition state (TS). The catalytic effect decreases as the substituent Y becomes a stronger electron-withdrawing group (EWG). Development of a positive charge on the N atom of the picolinyl moiety through resonance interactions is responsible for the decreasing K^+ ion catalysis.

Key Words : Aryl picolinates, Metal-ion catalysis, Hammett plot, Electrophilicity, Nucleofugality

Introduction

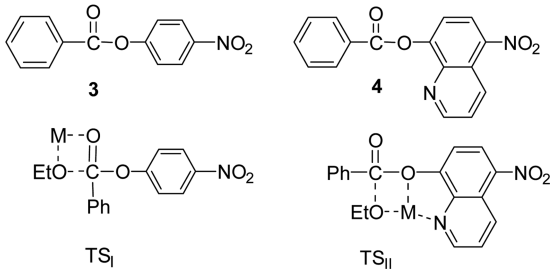
Nucleophilic substitution reactions of esters with amines have intensively been investigated due to their importance in biological processes as well as in synthetic applications.[1-4] The reactions have been reported to proceed through a concerted mechanism or *via* a stepwise pathway, in which the rate-determining step (RDS) is dependent on the basicity of the incoming amine and the leaving group.[2-4] In general, the RDS changes from breakdown of a tetrahedral intermediate ($T^{\pm}$) to its formation as the amine becomes more basic than the leaving group by 4 to 5 pK_a units.[2-4]

Reactions of esters with anionic nucleophiles have also been carried out intensively to investigate the reaction mechanism.[5-7] Interestingly, alkali metal ions have been reported to behave as a Lewis acid catalyst or as an inhibitor in nucleophilic substitution reactions of esters with alkali-metal ethoxides (EtOM; M = K, Na, Li) depending on the nature of the electrophilic center (*e.g*., P=O, P=S, SO_2, C=O).[8-12] Buncel *et al*. have reported that the reaction of 4-nitrophenyl diphenylphosphinate (**1**) with EtOM is catalyzed by M^+ ions and the catalytic effect increases as the size of M^+ ions decreases (*e.g*., $K^+ < Na^+ < Li^+$).[8] In contrast, we have shown that the corresponding reaction of 4-nitrophenyl diphenylphosphonothioate (**2**) is inhibited by Li^+ ion but is catalyzed by K^+ ion and the K^+ ion complexed by 18-crown-6-ether (18C6), indicating that the role of M^+ ions is dependent on the electronic nature of the reaction centers (*e.g*., P=O *vs*. P=S).[9]

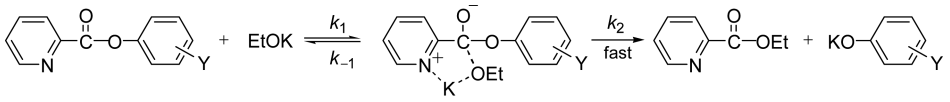


1 **2**

Alkali metal ions have also been reported to catalyze the reactions of 4-nitrophenyl benzoate (**3**) and 5-nitro-8-quinolyl benzoate (**4**) with EtOM (M = K, Na, Li) in anhydrous ethanol.[10] The catalytic effect decreases in the order $K^+ > Na^+ > Li^+$ for the reaction of **3** but in the order $Na^+ > K^+ > Li^+$ for the reaction of **4**.[10] Thus, M^+ ions have been reported to catalyze the reactions of **3** and **4** by increasing either the electrophilicity of the reaction center through TS_I or the nucleofugality of the leaving group *via* TS_{II} on the basis of the contrasting M^+ ion effects.[10]



In contrast, we have reported that the rate of reactions of 4-nitrophenyl salicylate (**5**) with EtOM decreases steeply as

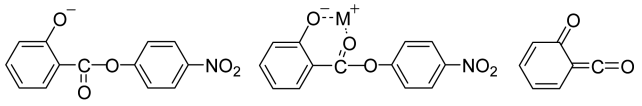


7a-f

Y = 4-NO_2(**7a**), 4-CN(**7b**), 4-COMe(**7c**), 4-COOEt(**7d**), 4-Cl(**7e**), H(**7f**).

Scheme 1

the concentration of EtOM increases.[11] More interestingly, addition of inert salts such as LiSCN and KSCN to the reaction mixture causes a significant decrease in reactivity.[11] Thus, M^+ ions have been suggested to act as a strong inhibitor by forming a cyclic complex **5**M, which inhibits the subsequent reaction to produce α-oxoketene **6**.[11]



5 **5M** **6**

M^+ ions has been reported to catalyze the reaction of 4-nitrophenyl picolinate (**7a**) with EtOM and the catalytic effect increases in the order $Li^+ > K^+ > Na^+$.[12] M^+ ions would catalyze the reaction by increasing either the electrophilicity of the reaction center or the nucleofugality of the leaving group. However, the enhanced nucleofugality would be effective only for reactions in which leaving-group departure occurs in the RDS but would be ineffective for reactions in which departure of the leaving group occurs after the RDS. Thus, detailed information on the reaction mechanism is necessary to investigate the role of M^+ ions. Our study has now been extended to the reaction of Y-substituted-phenyl picolinates (**7b-f**) with EtOK in anhydrous ethanol to investigate the reaction mechanism including the nature of RDS. We wish to report that the reaction proceed through a stepwise mechanism in which expulsion of the leaving group occurs after the RDS and that K^+ ion catalyzes the reaction by increasing the electrophilicity of the reaction center as shown in Scheme 1.

Results and Discussion

The kinetic study was performed spectrophotometrically under pseudo-first-order conditions in which the concentration of EtOK was in large excess over that of substrates **7b-f**. All the reactions in this study obeyed pseudo-first-order kinetics and proceeded with quantitative liberation of Y-substituted-phenoxide ion. Pseudo-first-order rate constants (k_{obsd}) were calculated from the equation, $\ln (A_\infty - A_t) = -k_{obsd}t + C$. The correlation coefficient for the linear plots of $\ln (A_\infty - A_t)$ *vs*. t was better than 0.9995 in all cases. It is estimated from replicate runs that the uncertainty in the k_{obsd} values is less than ± 3%. The kinetic conditions and results are summarized in Table 1.

As shown in Figure 1, the plots of k_{obsd} *vs*. [EtOK] curve upward for the reactions of 4-cyanophenyl picolinate (**7b**) and 4-acetylphenyl picolinate (**7c**) with EtOK. Similarly

Table 1. Kinetic Data for the Reactions of Y-Substituted-Phenyl Picolinates (**7b-f**) with EtOK in Anhydrous Ethanol at 25.0 ± 0.1 °C

[EtOK]/ mM	k_{obsd}/s^{-1}				
	7b	**7c**	**7d**	**7e**	**7f**
1.15	0.44	0.130	0.122	0.0500	0.0139
2.25	1.14	0.343	0.320	0.147	0.0402
3.98	2.48	0.779	0.741	0.359	0.102
5.44	3.86	1.22	1.17	0.573	0.172
6.64	5.11	1.61	1.55	0.781	0.234
7.85	6.52	2.04	2.00	0.900	0.299
8.97	7.85	2.45	2.40	1.23	0.364
9.96	9.10	2.82	2.78	1.43	0.425

curved plots were obtained for the reactions of the other aryl picolinates **7d-f** (Figures not shown). Such upward curvature is typical for nucleophilic substitution reactions of esters with alkali-metal ethoxide (EtOM), in which alkali-metal ion behaves as a Lewis acid catalyst and the ion-paired EtOM is more reactive than the dissociated EtO^-. In fact, we have previously reported that M^+ ions catalyze the reaction of 4-nitrophenyl picolinate (**7a**) with EtOM (M = K, Na, and Li).[12]

Dissection of k_{obsd} into k_{EtO^-} and k_{EtOK}. To examine the above idea that K^+ ion catalyzes the reaction, the k_{obsd} values have been dissected into k_{EtO^-} and k_{EtOK} (*i.e*., the second-order rate constants for the reactions with the dissociated EtO^- ion and ion-paired EtOK, respectively). It was reported that EtOK exists as dimers or other aggregates in a high

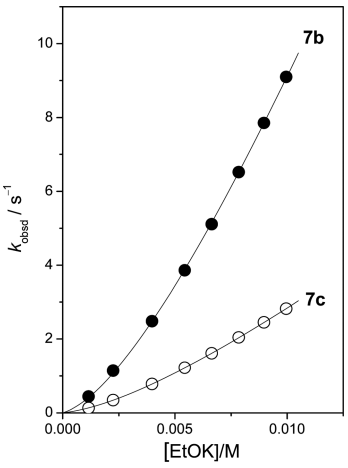
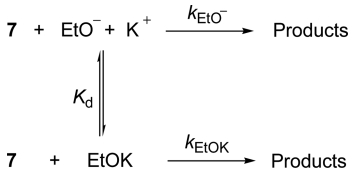


Figure 1. Plots of k_{obsd} *vs*. [EtOK] for the reaction of 4-cyanophenyl picolinate **7b** (●) and 4-acetylphenyl picolinate **7c** (○) with EtOK in anhydrous EtOH at 25.0 ± 0.1 °C.



Scheme 2. Reactions of **7** with the dissociated EtO^- and ion-paired EtOK.

concentration (*e.g.*, [EtOK] > 0.1 M).[13] However, EtOK was suggested to exist mainly as the dissociated and ion-paired species in a low concentration (*e.g.*, [EtOK] < 0.1 M).[13] Since [EtOK] << 0.1 M in this study, one might expect that both the dissociated EtO^- and ion-paired EtOK would react with substrates **7a-f** as shown in Scheme 2.

Thus, Eq. (1) can be derived on the basis of the kinetic results and the reactions proposed in Scheme 2. Under pseudo-first-order kinetic conditions (*e.g.*, [EtOK] >> [**7**]), k_{obsd} can be expressed as Eq. (2). It is noted that the dissociation constant $K_d = [EtO^-]_{eq}[K^+]_{eq}/[EtOK]_{eq}$, and $[EtO^-]_{eq} = [K^+]_{eq}$ at equilibrium. Accordingly, Eq. (2) can be converted to Eq. (3). The $[EtO^-]_{eq}$ and $[EtOK]_{eq}$ values can be calculated from the reported K_d value of 11.1×10^{-3} M for EtOK[14] and the initial concentration of EtOK using Eqs. (4) and (5).

$$\text{Rate} = k_{EtO^-}[EtO^-]_{eq}[\mathbf{7}] + k_{EtOK}[EtOK]_{eq}[\mathbf{7}] \quad (1)$$

$$k_{obsd} = k_{EtO^-}[EtO^-]_{eq} + k_{EtOK}[EtOK]_{eq} \quad (2)$$

$$k_{obsd}/[EtO^-]_{eq} = k_{EtO^-} + k_{EtOK}[EtO^-]_{eq}/K_d \quad (3)$$

$$[EtOK] = [EtO^-]_{eq} + [EtOK]_{eq} \quad (4)$$

$$[EtO^-]_{eq} = [-K_d + (K_d^2 + 4K_d[EtOK])^{1/2}]/2 \quad (5)$$

One might expect that the plot of $k_{obsd}/[EtO^-]_{eq}$ *vs.* $[EtO^-]_{eq}$ would be linear if the reaction proceeds as proposed in Scheme 2. In fact, the plots shown in Figure 2 exhibit excellent linear correlations with positive intercepts, indicating that the derived equations based on the reactions proposed in Scheme 2 are correct. Accordingly, one can calculate the k_{EtO^-} and k_{EtOK}/K_d values from the intercept and the slope of the linear plot, respectively. The k_{EtOK} value can be calculated from the above k_{EtOK}/K_d values and the reported K_d value for EtOK.[14] In Table 2 are summarized the calculated k_{EtO^-} and k_{EtOK} values for the reactions of **7a-f**.

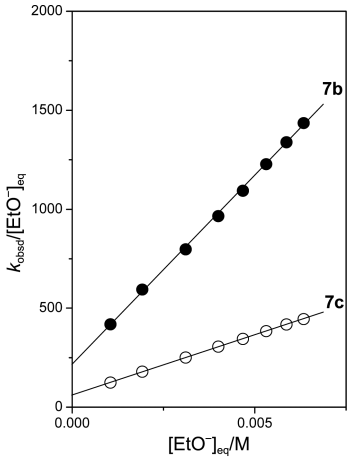


Figure 2. Plots of $k_{obsd}/[EtO^-]_{eq}$ *vs.* $[EtO^-]_{eq}$ for the reactions of 4-cyanophenyl picolinate (**7b**, ●) and 4-acetylphenyl picolinate (**7c**, ○) with EtOK in anhydrous EtOH at 25.0 ± 0.1 °C.

Table 2. Summary of Second-Order Rate Constants (k_{EtO^-} and k_{EtOK}) Calculated form Ion-pairing Treatment of the Kinetic Data for the Reactions of Y-Substituted-Phenyl Picolinates (**7a-f**) with EtOK in Anhydrous Ethanol at 25.0 ± 0.1 °C[a]

	Y	$k_{EtO^-}/M^{-1}s^{-1}$	$k_{EtOK}/M^{-1}s^{-1}$	k_{EtOK}/k_{EtO^-}
7a	4-NO_2	486	3370	6.93
7b	4-CN	215	2110	9.81
7c	4-COMe	61.5	673	10.9
7d	4-COOEt	49.7	678	13.6
7e	4-Cl	11.1	377	34.0
7f	H	1.43	114	79.7

[a]The kinetic data for the reaction of **7a** were taken from ref. 12.

As shown in Table 2, the k_{EtOK} value is much larger than the k_{EtO^-} value in all cases. This supports the preceding idea that the ion-paired EtOK is more reactive than the dissociated EtO^-. It is noted that both the k_{EtO^-} and k_{EtOK} values decrease as the substituent Y becomes a weaker electron-withdrawing group (EWG), *e.g.*, k_{EtO^-} decreases from 486 $M^{-1}s^{-1}$ to 61.5 and 1.43 $M^{-1}s^{-1}$ as the substituent Y changes from 4-NO_2 to 4-COMe and H, in turn. In contrast, the k_{EtOK}/k_{EtO^-} ratio (*i.e.*, the catalytic effect exerted by K^+ ion) increases as the substituent Y becomes a weaker EWG.

Deduction of Reaction Mechanism. K^+ ion would catalyze the reaction of **7a-f** by increasing the nucleofugality of the leaving Y-substituted-phenoxide or by increasing the electrophilicity of the reaction center. However, enhanced nucleofugality of the leaving group cannot be a cause of the K^+ ion catalysis for reactions in which departure of the leaving group occurs after the rate-determining step (RDS).

If the current reaction proceeds through a concerted mechanism, a partial negative charge would develop at the O atom of the leaving group. Since such negative charge could be delocalized to the subsituent Y through resonance interactions, Hammett correlation with σ^- constants should result in a better correlation than σ^o constants. In contrast, if the current reaction proceeds through a stepwise mechanism, departure of the leaving group would not be advanced in the transition state (TS). Because EtO^- is much more basic and a poorer nucleofuge than Y-substituted-phenoxide. Accordingly, no negative charge would develop on the O atom of the leaving group if the reaction proceeds through a stepwise mechanism. In this case, σ^o constants should give a better Hammett correlation than σ^- constants.

To deduce the reaction mechanism, Hammett plots have been constructed using σ^- and σ^o constants. As shown in Figure 3(a), σ^o constants result in a much better linear correlation than σ^- constants (the inset) for the reaction with the dissociated EtO^-. A similar result is demonstrated in Figure 3(b) for the reaction with the ion-paired EtOK. These results indicate that no negative charge develops on the O atom of the leaving group. This is contrary to the expectation if

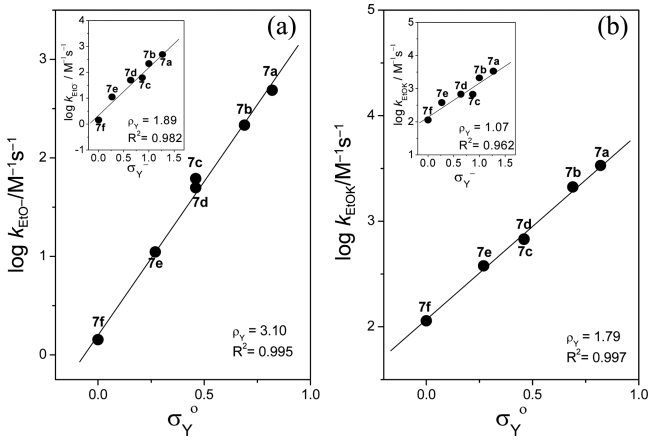


Figure 3. Hammett correlations of log k_{EtO^-} (a) and log k_{EtOK} (b) with σ_Y^o and σ_Y^- (inset) for the reactions of Y-substituted-phenyl picolinates (**7a-f**) in anhydrous ethanol at 25.0 ± 0.1 °C.

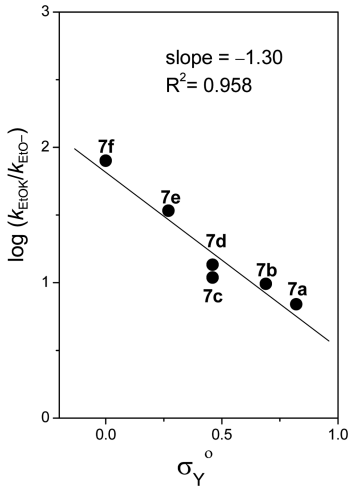
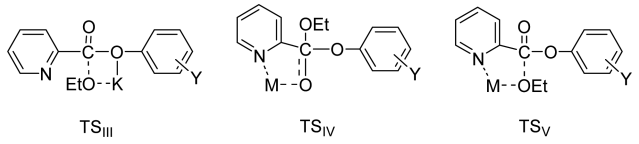


Figure 4. Plot showing K^+ ion effect on the substituent Y for the reactions of Y-substituted-phenyl picolinates (**7a-f**) with EtOK in anhydrous ethanol at 25.0 ± 0.1 °C.

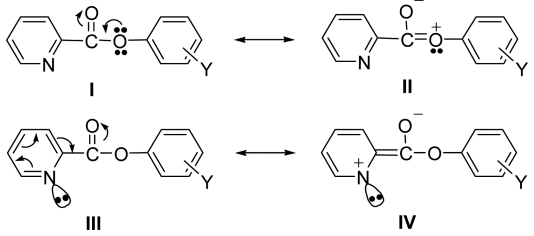
departure of the leaving group is involved in the RDS either for a concerted mechanism or for a stepwise pathway. Thus, one can conclude that the current reaction proceeds through a stepwise mechanism in which expulsion of the leaving group occurs after the RDS.

TS Structures and Role of K^+ Ion. Three different TS structures are plausible to explain the catalytic effect exerted by K^+ ion. TS_{III} could increase the nucleofugality of the leaving group, while TS_{IV} and TS_V could enhance the electrophilicity of the reaction center. Since expulsion of the leaving group occurs after the RDS in this study, the reaction cannot be catalyzed by increasing the nucleofugality of the leaving group through TS_{III}. One can also exclude a possibility that K^+ ion catalyzes the reaction through TS_{IV}, in which the K^+ and EtO^- ions in TS_{IV} are not ion-paired species. This is because the current reaction is catalyzed by the ion-paired EtOK but not by the dissociated K^+. Thus, one can conclude that K^+ ion catalyzes the reaction of **7a-f** by increasing the electrophilicity of the reaction center through a TS structure similar to TS_V.



The effect of the leaving-group substituent Y on the catalytic effect exerted by K^+ ion (*i.e.*, the k_{EtOK}/k_{EtO^-} ratio) is illustrated in Figure 4. One can see that the k_{EtOK}/k_{EtO^-} ratio decreases linearly as the substitutent Y in the leaving group becomes a stronger EWG, although the correlation coefficient of the linear plot is not very good (R^2 = 0.958). The k_{EtOK}/k_{EtO^-} ratio should have resulted in a good correlation with the electronic nature of the substituent Y, if the reaction is catalyzed by increasing the nucleofugality of the leaving group through TS_{III}. In contrast, if the reaction is catalyzed by increasing the electrophilicity through TS_V, the correlation of k_{EtOK}/k_{EtO^-} ratio with the electronic nature of the substituent Y would not be excellent because of the long distance between the substituent Y and the N atom of the picolinyl moiety of TS_V. Thus, the poor correlation shown in Figure 4 clearly supports the proposed TS structure (*i.e.*, TS_V) and reaction mechanism.

It is noted that the slope of the linear plot in Figure 4 is –1.30. Such a large slope indicates that the catalytic effect is strongly dependent on the electronic nature of the substituent Y. The dependence of the k_{EtOK}/k_{EtO^-} ratio on the substituent Y can be explained by the resonance structures as modeled by I ↔ II and by III ↔ IV. It is evident that the contribution of the resonance structure II would decrease as the substituent Y becomes a stronger EWG. In contrast, the resonance structure IV would become a major contributor with increasing electron-withdrawing ability of the substituent Y. In this case, the positively charged N atom of the resonance structure IV inhibits formation of TS_V. This idea accounts nicely for the kinetic result that K^+ ion catalysis decreases as the substituent Y becomes a stronger EWG.



Conclusions

The kinetic study on the reaction of **7a-f** with EtOK has allowed us to conclude the following: (1) Dissection of k_{obsd} into k_{EtO^-} and k_{EtOK} has revealed that the ion-paired EtOK is more reactive than the dissociated EtO^-. (2) The Hammett plots correlated with σ^o constants result in much better linearity than those correlated with σ^- constants, indicating that the reaction proceeds through a stepwise mechanism in which expulsion of the leaving group occurs after the RDS.

(3) K^+ ion catalyzes the reaction by increasing the electrophilicity of the reaction center through TS_Y. (4) The catalytic effect decreases as the substituent Y becomes a stronger EWG. (5) Development of a positive charge on the N atom through resonance interactions is responsible for the decreasing K^+ ion catalysis.

Experimental Section

Materials. Y-Substituted-phenyl picolinates (**7a-f**) were readily prepared by adding Y-substituted-phenol to the solution of picolinyl chloride in the presence of triethylamine in anhydrous diethyl ether as reported previously.[12] The crude products were purified by column chromatography (silica gel, methylene chloride/*n*-hexane 50/50). Their purity was checked by their melting points and ^{1}H NMR spectra.

Kinetics. The kinetic study was carried out with a UV-vis spectrophotometer for slow reactions (*e.g.*, $t_{1/2} > 10$ s) or a stopped-flow spectrophotometer for fast reactions (*e.g.*, $t_{1/2} \leq 10$ s) equipped with a constant temperature circulating bath to maintain the temperature in the reaction cell at 25.0 ± 0.1 °C. The reaction was followed by monitoring the appearance of Y-substituted-phenoxide ion. All reactions were carried out under pseudo-first-order conditions in which EtOK concentration was at least 20 times greater than the substrate concentration. The stock solution of EtOK was prepared by dissolving freshly cleaned potassium metal in anhydrous ethanol under nitrogen and stored in the refrigerator. The concentration of EtOK was determined by titration with potassium hydrogen phthalate. The anhydrous ethanol was further dried over magnesium and was distilled under N_2 just before use.

All solutions were prepared freshly just before use under nitrogen and transferred by gas-tight syringes. Typically, the reaction was initiated by adding 5 μL of a 0.01 M solution of the substrate in CH_3CN by a 10 μL syringe to a 10 mm quartz UV cell containing 2.50 mL of the thermostatted reaction mixture made up of anhydrous ethanol and aliquot of the EtOK solution.

Product Analysis. Y-Substituted-phenoxide ion was liberated quantitatively and identified as one of the products by comparison of the UV-vis spectrum at the end of reaction with the authentic sample under the experimental condition.

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