Elimination Reactions of Aryl Furylacetates Promoted by R2NH-R2NH2+ in 70 mol % MeCN(aq). Effects of β–Aryl on the Ketene-Forming Transition-State

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Ketene-forming elimination from 2-X-4-nitrophenyl furylacetates (**1a-d**) promoted by R2NH-R2NH2+ in 70 mol % MeCN(aq) has been studied kinetically. When X = Cl and NO2, the reactions exhibited second-order kinetics as well as Brönsted β = 0.37-0.54 and $|β_{lg}|$ = 0.31-0.45. The Brönsted β decreased with a poorer leaving group and $|β_{lg}|$ increased with a weaker base. The results are consistent with an E2 mechanism. When the leaving group was changed to a poorer one [X= H (**1a**) and OCH3 (**1b**)], the reaction mechanism changed to the competing E2 and E1cb mechanisms. A further change to the E1cb mechanism was realized for the reaction of **1a** with *i*-Pr2NH/*i*-Pr2NH2+ in 70 mol % MeCN-30 mol % D2O. By comparing the kinetic results in this study with the existing data for ArCH2C(O)OC6H3-2-X-4-NO2, the effect of the β-aryl group on the ketene-forming elimination was assessed.

Key Words : Elimination, E2 and E1cb Mechanism, β–Aryl Group effect

Introduction

Extensive studies of the structure-reactivity relationships in the ketene-forming elimination reactions have led to the qualitative understanding of the relationship between the reactant structure and the mechanism.[1-11] Earlier, we reported that the ketene-forming elimination reactions from *O*-aryl phenylacetates (**3**) promoted by R2NH-R2NH2+ in 70 mol % MeCN(aq) proceeded by an E2 mechanism,[11a] while the reactions of *O*-aryl thienylacetates (**2a-c**) proceeded by a competing E2 and E1cb mechanism under the same condition.[11g] The results have been attributed to the higher acidity of the Cβ-H bond in the latter,[12] which would stabilize the carbanion intermediate such that the E1cb mechanism can compete with the E2. Alternatively, the smaller aromatic resonance energy of the thiophene than that of benzene may also have contributed to the stability of the carbanion.[13] To assess the relative importance of Cβ-H bond acidity and the aromatic resonance energy of the β-aryl group on the ketene-forming eliminations, we have now studied the reactions of aryl furylacetates (**1**) with R2NH-R2NH2+ in 70 mol % MeCN(aq) (eq 1). Since the pK_a values of 2-methylfuran and toluene are identical,[12] whereas the aromatic resonance energy of furan is much lower than that of benzene,[13] this seemed to be an ideal system for such a purpose. We have investigated the reaction mechanism under various conditions. By comparing with the existing data for eliminations of ArCH2C(O)OC6H3-2-X-4-NO2 [Ar = thiophene (**2**), phen-

yl (**3**)] with R2NH-R2NH2+ in 70 mol % MeCN(aq), the effect of β-aryl group was assessed.

Results

Aryl furylacetates **1a-d** were synthesized by the reaction between 2-furylacetic acid, substituted phenols, 2-chloro-1-methylpyridinium iodide, and Et3N in CH2Cl2 as reported previously.[11a,14] The spectral and analytical data for the new compounds were consistent with the proposed structures.

For the reactions of **1a-d** with R2NH-R2NH2+ in 70 mol % MeCN(aq), the yields of aryloxides determined by comparing the UV absorption of the infinity samples of the kinetic runs with those of the authentic aryloxides were in the range
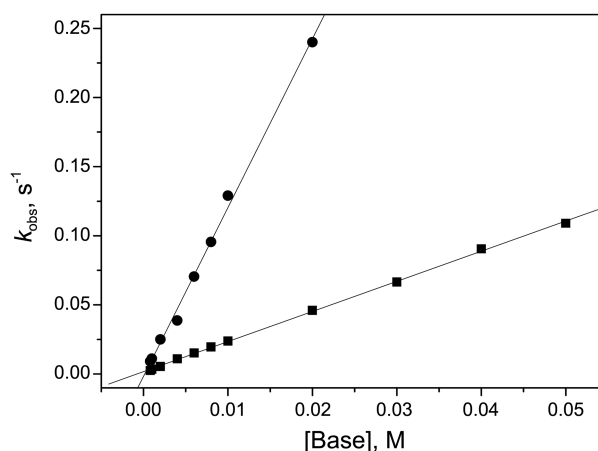

Figure 1. Plots of k_{obs} *versus* base concentration for eliminations from 2-chloro-4-nitrophenyl furylacetate (**1c**, ■) and 2,4-dinitrophenyl furylacetate (**1d**, ●) promoted by R2NH-R2NH2+ in 70 mol % MeCN(aq) at 25.0 °C, [*i*-Pr2NH]/[*i*-Pr2NH2+] = 1.0, μ = 0.10 M (Bu4N+Br−).
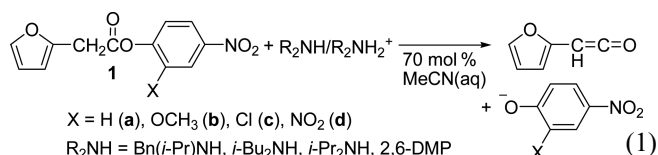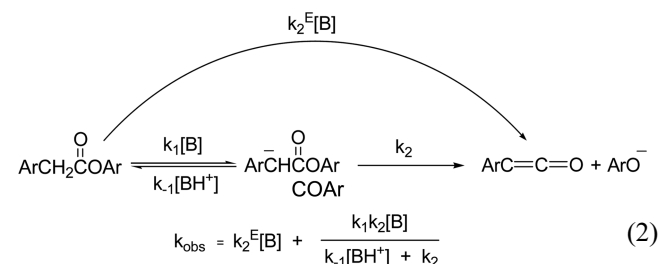

X = H (**a**), OCH3 (**b**), Cl (**c**), NO2 (**d**)
R2NH = Bn(*i*-Pr)NH, *i*-Bu2NH, *i*-Pr2NH, 2,6-DMP

(1)

Table 1. Rate constants for ketene-forming elimination from $ArCH_2C(O)OC_6H_3$-2-X-4-NO_2 (Ar = furyl)[a] promoted by R_2NH-$R_2NH_2^+$ in 70 mol % MeCN(aq) at 25.0 °C

R_2NH[b]	pK_a[c]	$10^2 k_2^E$, $M^{-1} s^{-1d,e}$			
		X = H (**1a**)	X = OMe (**1b**)	X = Cl (**1c**)	X = NO_2 (**1d**)
Bn(*i*-Pr)NH	16.8	0.217	0.254	36.0	309
i-Bu$_2$NH	18.2	0.766	0.686	120	1054
i-Pr$_2$NH	18.5	1.62	1.26	218	1220
2,6-DMP[f]	18.9	3.52	3.83	443	1935

[a][Substrate] = 5.0×10^{-5} M. [b][R_2NH] = 8.0×10^{-4} - 5.0×10^{-2} M. [c]Reference 15. [d]Average of three or more rate constants. [e]Estimated uncertainty, ± 3%. [f]*cis*-2,6-Dimethylpiperidine.

of 94-98%. The rates of elimination reactions were followed by monitoring the increase in the absorption at the λ_{max} for the aryloxides in the range of 400-434 nm. Excellent pseudo-first order kinetics plots, which covered at least three half-lives were obtained. The rate constants are summarized in Tables S1-S4 in Supporting Information. For the reactions of **1c** and **1d** with R_2NH-$R_2NH_2^+$ in 70 mol % MeCN(aq), the plots of k_{obs} versus base concentration 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 (Figures 1, S8 and S9). The slopes are the overall second-order rate constants k_2^E. Values k_2^E for eliminations from **1c** and **1d** were summarized in Table 1.

In contrast to the reactions of **1c** and **1d**, the plots of k_{obs} versus base concentration for the reactions of **1a** and **1b** were curves at low base concentration and straight lines at higher base concentration (Figures 2 and S1-S7). The data were analyzed with a nonlinear regression analysis program by assuming that the reaction proceeds by concurrent E2 and E1cb mechanisms (eq. 2).[11a,11d] By utilizing the computer program, the k_2^E, k_1, and k_{-1}/k_2 values that best fit with Eq. (2) were calculated, and the plots were dissected into the E2 and E1cb components. In all cases, the correlations between the calculated and the experimental data were excellent. The calculated k_2^E values are included in Table 1 and k_1 and k_{-1}/k_2 values are summarized in Table 2. The k_1 increased and k_{-1}/k_2 decreased with a stronger base. For a given base, k_1 decreased and k_{-1}/k_2 ratio increased as the leaving group was changed to a poorer one.

$$ArCH_2COAr \underset{k_{-1}[BH^+]}{\overset{k_1[B]}{\rightleftharpoons}} Ar\bar{C}HCOAr \overset{k_2}{\longrightarrow} ArC{=}C{=}O + ArO^-$$

$$k_{obs} = k_2^E[B] + \frac{k_1 k_2[B]}{k_{-1}[BH^+] + k_2} \tag{2}$$

The k_2^E values for **1a-d** showed excellent correlations with the pK_a values of the promoting bases on the Brönsted plots (Figure 3). The β values are in the range of 0.37-0.54 and
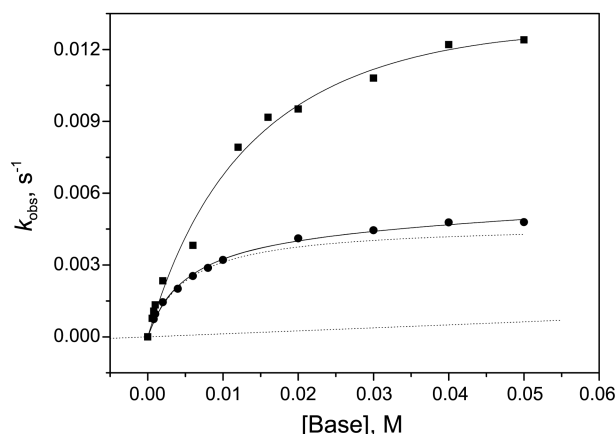
Figure 2. Plots of k_{obs} versus base concentration for eliminations from 4-nitrophenyl furylacetate (**1a**) promoted by R_2NH-$R_2NH_2^+$ in 70 mol % MeCN(aq) (●) and 70 mol % MeCN-30 mol % D_2O (■) at 25.0 °C, [*i*-Pr$_2$NH]/[*i*-Pr$_2$NH$_2^+$] = 1.0, μ = 0.10 M (Bu$_4$N$^+$Br$^-$). The closed circles (●) and squares (■) are the experimental data, and the solid line shows the fitted curve by using eq. 2 (see text). The curve for the reaction in 70 mol % MeCN(aq) is dissected into the E2 and E1cb reaction components (dashed lines). Calculated values of k_2^E, k_1, and k_{-1}/k_2 for **1a** and **1b** are summarized in Tables 1 and 2.

Table 2. The k_1 and k_{-1}/k_2 values for elimination from $ArCH_2C(O)$-OC_6H_3-2-X-4-NO_2 (Ar = furyl, **1a-d**)[a] promoted by R_2NH-$R_2NH_2^+$ in 70 mol % MeCN(aq) at 25.0 °C

R_2NH[b]	k_1, $M^{-1}s^{-1c-e}$		k_{-1}/k_2, M^{-1c-e}	
	X = H (**1a**)	X = OMe (**1b**)	X = H (**1a**)	X = OMe (**1b**)
Bn(*i*-Pr)NH	0.260	0.238	967	1920
i-Bu$_2$NH	0.728	0.319	880	636
i-Pr$_2$NH	0.922(1.13)[f]	0.602	196(67.9)[f]	300
2,6-DMP[g]	1.77	1.19	381	594

[a][Substrate] = 5.0×10^{-5} M. [b][R_2NH] = 8.0×10^{-4}-5.0×10^{-2} M. [c]Calculated from k_{obs} by using eq. 2. [d]The slopes of the plots of log k_1 versus pK_a of the base for **1a** and **1b** are 0.38 ± 0.04 and 0.29 ± 0.12, respectively. [e]The slopes of the plots of log k_{-1}/k_2 versus pK_a of the base for **1a** and **1b** are −0.17 ± 0.12 and −0.27 ± 0.07, respectively. [f]Solvent was 70 mol % MeCN-30 mol % D_2O. [g]*cis*-2,6-Dimethylpiperidine.

Table 3. Brönsted β values for elimination from $ArCH_2C(O)$-OC_6H_3-2-X-4-NO_2 (Ar = furyl) promoted by R_2NH-$R_2NH_2^+$ in 70 mol % MeCN(aq) at 25.0 °C

	X = H (**1a**)	X = OMe (**1b**)	X = Cl (**1c**)	X = NO_2 (**1d**)
pK_{lg}[a]	20.7	20.6	18.1	16.0
β	0.54 ± 0.12	0.51 ± 0.1	0.49 ± 0.07	0.37 ± 0.02

[a]Reference 16.

decrease with a better leaving group (Table 3).

When the reaction of **1a** with *i*-Pr$_2$NH/*i*-Pr$_2$NH$_2^+$ was conducted in 70 mol % MeCN-30 mol % D_2O, the k_{obs} values were larger than those measured in 70 mol % MeCN(aq) (Figure 2 and Table S2), and the rate data could be fitted with the E1cb mechanism, that is, the 2nd term in Eq. (2). Calculated values of k_1 and k_{-1}/k_2 for this reaction are
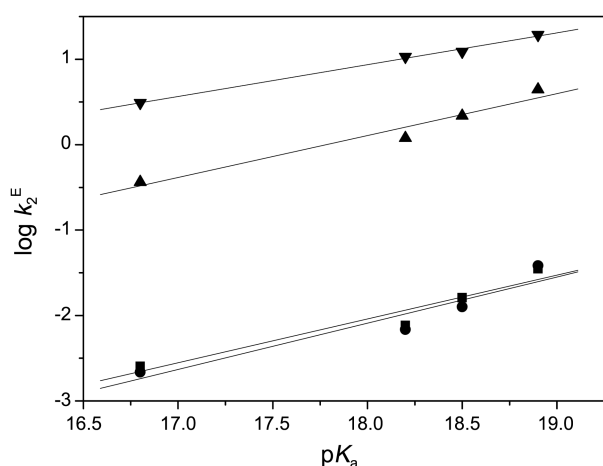
Figure 3. Brönsted plots for the elimination from $ArCH_2C(O)$-OC_6H_3-2-X-4-NO_2 (Ar = furyl) promoted by R_2NH-$R_2NH_2^+$ in 70 mol % MeCN(aq) at 25.0 °C at 25.0 °C [X = H (**1a**, ●), OMe (**1b**, ■), Cl (**1c**, ▲), NO_2 (**1d**, ▼)].
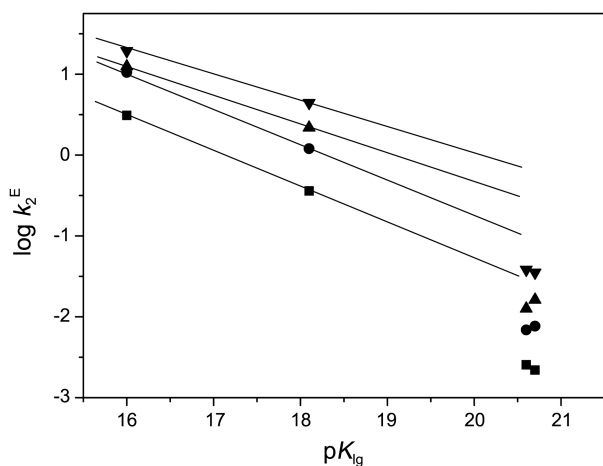
Figure 4. Plots log k_2 *versus* pK_{lg} values of the leaving group for the elimination from $ArCH_2C(O)OC_6H_3$-2-X-4-NO_2 (Ar = furyl, **1a-d**) promoted by R_2NH-$R_2NH_2^+$ in 70 mol % MeCN(aq) at 25.0 °C. [R_2NH = Bn(i-Pr)NH (■), i-Bu_2NH (▲), i-Pr_2NH (●), 2,6-DMP (▼)].

summarized in Table 2.

The plots of the logk_2^E *versus* the leaving group pK_{lg} values are depicted in Figure 4. As reported for **2a** and **2b**,[11g] the data for **1a** and **1b** showed large negative deviation from the straight lines. Therefore, the β_{lg} values were calculated without the date for **1a** and **1b**. The β_{lg} values are in the range 0.31-0.45 and decrease as the pK_a value of the base increase (Table 4).

Table 4. Brönsted β_{lg} values for Eelimination from $ArCH_2C(O)$-OC_6H_3-2-X-4-NO_2 (Ar = furyl) promoted by R_2NH-$R_2NH_2^+$ in 70 mol % MeCN(aq) at 25.0 °C

R_2NH	Bn(i-Pr)NH	i-Bu_2NH	i-Pr_2NH	2,6-DMP[b]
pK_a[a]	16.8	18.2	18.5	18.9
β_{lg}	-0.45	-0.45	-0.36	-0.31

[a]Reference 15. [b]*cis*-2,6-Dimethylpiperidine.

To provide additional evidence for the reaction mechanism, the H-D exchange experiment was conducted by mixing **1a** with i-Pr_2NH/i-$Pr_2NH_2^+$ in 70 mol % MeCN-30 mol % D_2O at −10 °C. The reactant was recovered immediately after mixing. The NMR spectrum indicated that approximately 35% of furfuryl C-H bond of **1a** was converted to the C-D bond.

Discussion

Mechanism of Eliminations from 1. Results of kinetic investigations and product studies reveal that the reaction of **1c** and **1d** with R_2NH-$R_2NH_2^+$ in 70 mol % MeCN(aq) proceed by an E2 mechanism. The reactions produced elimination product and exhibited second-order kinetics, thereby ruling out all but bimolecular pathway. The $(E1cb)_R$, $(E1cb)_{ip}$, and internal return mechanisms, which would exhibit either a specific base catalysis or Brönsted β values near unity,[16,17] were negated by the observed general base catalysis with the Brönsted β ranging from 0.37 to 0.54. Moreover, the β values increased with a poorer leaving group. This effect corresponds to a positive interaction coefficient, *i.e.*, $p_{xy} = \partial\beta/\partial pK_{lg}, = \partial\beta_{lg}/\partial pK_{BH} > 0$, which describes the interaction between the base catalysis and the leaving group.[17,18] The positive interaction coefficient provides additional support for an E2 mechanism in which the C_β-H and C_α-OAr bonds are partially cleaved in the transition state.

When the leaving group was changed to a poorer one (**1a** and **1b**), the plots of k_{obs} *versus* the base concentration were curves (Figures 2 and S1-S7). The result could be explained with a competing E2 and E1cb mechanism, as explained below. First, the rate date fitted well with Eq. (2) and the shapes of dissected lines were typical for an E2 and E1cb mechanisms. Second, the calculated values of k_2^E, k_1, and k_{-1}/k_2 are consistent with the competing mechanism; (i) The calculated k_2^E values for **1a** and **1b** and the experimentally measured k_2^E values for **1c** and **1d** show excellent correlation on the Brönsted plots (Figure 3), as expected for the E2 mechanism. (ii) The increase in the k_1 value with a stronger base is in good agreement with the deprotonation step of the E1cb mechanism. (iii) The decrease in the k_{-1}/k_2 ratio with a stronger base can be attributed to the decreased acidity of the $R_2NH_2^+$ which would reduce k_{-1}.

It is interesting to note that the k_2^E values for **1a** and **1b** showed large negative deviation in Figure 4. This outcome could be explained, if the extent of the C_α-OAr bond cleavage is smaller than those for **1c** and **1d**. Since the β values for **1a** and **1b** are larger than those for **1c** and **1d**, the transition state of the E2 pathway would be skewed toward the E1cb-like with greater extend of proton transfer and smaller degree of cleavage of the C_α-OAr bond. This would destabilize the transition state as a result of the smaller extent of double bond formation due to the inefficient charge transfer from the β- to α-carbon and retard the rate. This result underlines the unusual sensitivity of the ketene-forming transition state to the reactant structure in the borderline between the E2 and E1cb.

The mechanistic diversity of the ketene-forming elimination was further demonstrated in the reaction of **1a** with *i*-Pr$_2$NH/*i*-Pr$_2$NH$_2^+$ in 70 mol % MeCN-30 mol % D$_2$O. There is convincing evidence in support of the mechanism change from the competing E2 and E1cb to E1cb under this condition. First, the k_{obs} values measured in the deuterated solvent could be fitted to the 2nd term of Eq. (2), indicating an exclusive E1cb mechanism (Figure 2). Second, the larger k_1 value in the deuterated solvent is also consistent because the basicity of R$_2$NH would increase in the poorer solvating D$_2$O.[19] Third, since the k_2 value should be almost the same in the two solvents, the 3-fold smaller k_{-1}/k_2 value in the deuterated solvent predicts that $k_{-1}^{H2O}/k_{-1}^{D2O} \approx 3.0$ (Table 2). Since all of the R$_2$NH$_2^+$ should be converted to R$_2$ND$_2^+$ in the deuterated solvent, the large primary isotope effect is not unexpected. Fourth, the smaller k_{-1}^{D2O} would increase the 2nd term of Eq. (2) more in the deuterated than in undeuterated solvent to make the k_{obs} values larger. If it becomes the predominant term, a change of the mechanism would occur. Fifth, the partial H-D exchange of the furfuryl C-H bond in the recovered starting material from the reaction of **1a** with *i*-Pr$_2$NH/*i*-Pr$_2$NH$_2^+$ in 70 mol % MeCN-30 mol % D$_2$O provides additional support for the E1cb mechanism.

Effect of β-Aryl Group on the Ketene-Forming Transition State. Table 5 compares the rates and transition state parameters for the eliminations from ArCH$_2$C(O)OC$_6$H$_3$-2-X-4-NO$_2$. The relative rate of E2 reaction changed from 1.0 to 10 to 1.2 as the β-aryl group was varied from furyl (**1a**) to thienyl (**2**) to phenyl (**3**). Since the pK_a values of 2-methyl furan, 2-methylthiophene, and toluene in DMSO are 43, 42, and 43, respectively,[12] the faster rate observed for **2** can be attributed to the higher acidity of the C$_β$-H bond. However, b and |β$_{lg}$| values of **1a**, **2**, and **3** are almost the same within experimental errors, indicating that structure of the E2 transition states are not significantly influenced by the β-aryl group. In addition, the k_1 value is larger for **2** than that for **1a** is consistent with the higher acidity of the C$_β$-H bond. The larger k_{-1}/k_2 value for **2** is as expected for the E1cb mechanism. Although the lower basicity of the conjugate base of **2** would reduce both k_{-1} and k_2, the effect should be more pronounced for the slower step (k_2). This would predict a larger k_{-1}/k_2. The most interesting result from this study is that **1a** and **2**, but not **3**, showed mechanistic changes from E2 to a competing E2 and E1cb. While the change of the mechanism for **2** can be attributed to the higher acidity of the C$_β$-H bond of **2** (see above), the difference between **1a** and **3** cannot be explained similarly because the acidities of their C$_β$-H bonds are the same. Alternatively, the negative charge density developed at the β-carbon can better be stabilized by the furyl than phenyl group because of the smaller aromatic resonance energy.[13] This would stabilize the carbanion intermediate for **1a** such that the E1cb mechanism can compete with E2. A similar explanation can be applied to the competing E2 and E1cb mechanisms for **2**, although the higher acidity of the C$_β$-H bonds would undoubtedly contribute to the carbanion stability.

In conclusion, we have studied the elimination reactions of

Table 5. Transition state Parameters for ketene-forming eliminations from ArCH$_2$C(O)OC$_6$H$_4$-4-NO$_2$ Promoted by R$_2$NH-R$_2$NH$_2^+$ buffers in 70 mol % MeCN(aq) at 25.0 °C

	Ar = furyl (**1a**)	Ar = thienyl (**2**)[a]	Ar = phenyl (**3**)[b]
rel. rate (k_2^E)[c]	1.0	10	1.2
β	0.54 ± 0.12	0.64 ± 0.09	0.77 ± 0.03
β$_{lg}$	-0.45	-0.49 ± 0.01	-0.43
k_1	0.26	0.53	
k_{-1}/k_2	967	2100	

[a]Reference 11g. [b]Reference 11a. [c]R$_2$NH = Bn(*i*-PrNH).

aryl furylacetates (**1a-d**) promoted by R$_2$NH-R$_2$NH$_2^+$ in 70 mol % MeCN(aq). The reactions of **1c** and **1d** proceeded by a concerted E2 mechanism. The mechanism changed to the competing E2 and E1cb mechanisms as the leaving group was changed to a poorer one [X = H (**1a**) and OCH$_3$ (**1b**)]. For elimination from **1a** with *i*-Pr$_2$NH/*i*-Pr$_2$NH$_2^+$, a further change to the E1cb mechanism was realized in 70 mol % MeCN-30 mol % D$_2$O. When the β-aryl groups was changed from phenyl to thienyl to furyl, the structure of the E2 transition state remained almost the same although k_2^E value changed according to the acidity of the C$_β$-H bond. Noteworthy is the mechanistic diversity observed in the ketene-forming eliminations from **1** by the changes in the leaving group and the base-solvent system.

Experimental Section

Materials. Aryl furylacetates **1a-d** were prepared from 2-furanacetic acid and substituted phenols in the presence of Et$_3$N and 2-chloro-1-methylpyridinium iodide in CH$_2$Cl$_2$ as previously reported.[11a,14] The yield (%), IR (KBr, C=O, cm^{-1}), ^{1}H NMR (400 MHz, CDCl$_3$, J values are in Hz), and ^{13}C NMR (100 MHz), and mass spectral data for the new compounds are as follows.

2-(4-Nitrophenyl)furylacetate (1a): Yield 75%; IR 1760 cm^{-1}; ^{1}H NMR δ 3.98 (s, 2H), 6.37 (m, 2H), 7.29 (d, J = 9.24, 2H), 7.41 (s, 1H), 8.25 (d, J = 9.24, 2H); ^{13}C NMR δ 34.1, 108.8, 110.8, 122.4, 125.2, 142.6, 145.5, 146.2 ,155.2, 167.0; LRMS (EI); *m/z* 247 [M$^+$] (64), 109 (12), 108 (79), 81 (100) ,82 (34), 63 (6), 53 (46), 50 (5).

2-(2-Methoxy-4-nitrophenyl)furylacetate (1b): Yield 78 %; IR 1774 cm^{-1}; ^{1}H NMR δ 3.90 (s, 3H), 3.99 (s, 2H), 6.38 (m, 2H), 7.20 (d, J = 8.56, 1H), 7.41 (d, J = 1.72, 1H), 7.83 (d, J = 2.4, 1H), 7.88 (dd, J = 2.4, 8.56, 1H); ^{13}C NMR δ 33.7, 56.5, 107.7, 108.7, 110.7, 116.4, 123.1, 142.5, 144.9, 146.4, 146.5, 151.6, 166.5; LRMS (EI); *m/z* 277 [M$^+$] (14), 108 (99), 81 (100), 53 (27).

2-(2-Chloro-4-nitrophenyl)furylacetate (1c): Yield 58 %; IR 1780 cm^{-1}; ^{1}H NMR δ 4.03 (s, 2H), 6.37 (m, 2H), 7.35 (d, J = 8.88, 1H), 7.42 (d, 1.72, 1H), 8.15 (dd, J = 2.72, 8.88, 1H), 8.33 (d, J = 2.72, 1H); ^{13}C NMR δ 33.7, 109.0, 110.8, 123.2, 124.3, 125.9, 128.2, 142.7, 145.9, 151.9, 166.1; LRMS (EI); *m/z* 281 [M$^+$] (42), 109 (14), 108 (29), 82 (64), 81 (100), 63 (11), 53 (53).

2-(2,4-Dinitrophenyl)furylacetate (1d): Yield 49%; IR

1745 cm^{-1}; ^{1}H NMR δ 4.08 (s, 2H), 6.39 (m, 1H), 7.42 (m, 1H), 7.50 (d, J = 9.06, 1H), 8.51 (dd, J = 2.72, 9.06, 1H), 8.96 (d, J = 2.72, 1H); ^{13}C NMR δ 33.6, 109.3, 110.8, 121.3, 121.8, 126.7, 129.1, 131.6, 142.8, 145.4, 148.4, 166.3; LRMS (EI); m/z 292 [M$^+$] (23), 125 (9), 108 (27), 82 (40), 81 (100), 53 (38).

Reagent grade acetonitrile and secondary amine were fractionally distilled from CaH$_2$. The base-solvent solutions were prepared by dissolving equivalent amount of R$_2$NH and R$_2$NH$_2^+$ in 70 mol % MeCN(aq). In all cases, the ionic strength was maintained to 0.1 M with Bu$_4$N$^+$Br$^-$.

Kinetic Studies. Reactions of **1a-d** with R$_2$NH/R$_2$NH$_2^+$ in 70 mol % MeCN(aq) were followed by monitoring the increase in the absorbance of aryloxides at 400-434 nm with a UV-vis spectrophotometer as described.[11a-11e]

Product Studies. The products of eliminations from **1a-d** promoted by R$_2$NH/R$_2$NH$_2^+$ in 70 mol % MeCN(aq) were identified as reported.11a The yields of aryloxides determined by comparing the UV absorptions of the infinity samples with those for the authentic aryloxides were in the range of 94-98%.

H-D Exchange Experiment. To determine whether the β-furfuryl protons of **1a** undergo H-D exchange, **1a** (0.047 g, 0.19 mmol) was reacted with i-Pr$_2$NH/i-Pr$_2$NH$_2^+$ (0.05 M, 5 mL) in 70 mol % MeCN-30 mol % D$_2$O at −10 °C. The reaction was quenched by adding dilute HCl(aq) immediately after mixing. The recovered reactant was isolated by extracting the products with ethyl acetate followed by the silca gel column chromatography using ethyl acetate/hexane = 1/4 as eluent. The proton NMR spectrum of the recovered reactant from **1a** was identical to that of the substrate except that the integration at δ 3.98 decreased by approximately 35%.

Control Experiments. The stabilities of **1a-d** were determined as reported.[11b-11d] The solutions of **1** in MeCN were stable for at least two weeks when stored in the refrigerator.

Support Information Available. Observed rate constants for elimination from **1a-d** promoted by R$_2$NH/R$_2$NH$_2^+$ in 70 mol % MeCN(aq), plots of k_{obs} *versus* base concentration, and spectroscopic and analytical data for the new compounds are available on request from the correspondence author (20 pages).e-mail:sypyun@pknu.ac.kr.

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