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Mechanism of Elimination from (E)-2,4-Dinitrobenzaldehyde O-pivaloyloxime Promoted by R₂NH/R₂NH₂⁺ Buffer in 70% MeCN(aq)

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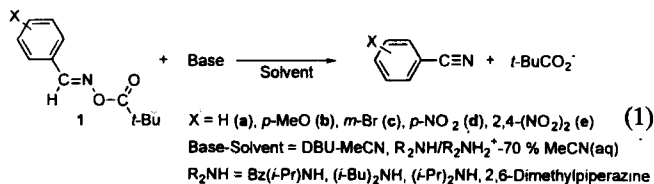[‡]*Department of Chemistry, Korea University, 1-Anamdong, Seoul 136-701, Korea*
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Elimination reactions of (E)-2,4-dinitrobenzaldehyde O-pivaloyloxime promoted by R₂NH/R₂NH₂⁺ buffer in 70% MeCN(aq) have been studied kinetically. The reaction exhibited second order kinetics and general base catalysis with Brönsted β=0.45. The Hammett ρ value decreased from 2.3 to 1.6 as the base-solvent system was changed from DBU in MeCN to R₂NH/R₂NH₂⁺ buffer in 70% MeCN(aq). From these results an E2 mechanism is proposed.

Introduction

Recently, we reported that elimination reactions of (E)- and (Z)-benzaldehyde O-pivaloyloximes promoted by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in MeCN proceed by an E2 mechanism.[1] The rate of syn-elimination from the (E)-isomer was approximately 20,000-fold slower than that of anti-elimination from the (Z)-isomer. The transition state for the former was more E1cb-like than the latter with greater extent of proton transfer, more negative charge development at the β-carbon, and smaller extent of triple-bond formation than that for the latter. We were interested in learning if a change to the E1cb mechanism could be realized by using a stronger electron-withdrawing substituent and more protic solvent. For this purpose we have studied the reactions of (E)-2,4-dinitrobenzaldehyde O-pivaloyloxime 1e with DBU in MeCN and R₂NH/R₂NH₂⁺ buffer in 70% MeCN(aq) (eq. 1). This substrate is the most strongly activated one studied so far in the (E)-benzaldehyde O-pivaloyloxime series.[1,2]

$$X = H \text{ (a)}, p\text{-MeO (b)}, m\text{-Br (c)}, p\text{-NO}_2 \text{ (d)}, 2,4\text{-(NO}_2)_2 \text{ (e)} \quad (1)$$

Base-Solvent = DBU-MeCN, R₂NH/R₂NH₂⁺-70 % MeCN(aq)

R₂NH = Bz(*i*-Pr)NH, (*i*-Bu)₂NH, (*i*-Pr)₂NH, 2,6-Dimethylpiperazine

Results and Discussion

Reactions of (E)-2,4-dinitrobenzaldehyde O-pivaloyloxime with DBU in MeCN and R₂NH/R₂NH₂⁺ buffer in 70% MeCN(aq) produced 2,4-dinitrobenzonitrile quantitatively. The rates of elimination from 1e were followed by monitoring the decrease in the absorption of the reactant at 270 nm. Excellent pseudo-first-order kinetic plots which covered at least 3 half-lives were obtained. The k_{obs} values are summarized in Table 1. On the other hand, the rates of the reactions of 1a-d were too slow to follow to completion. Therefore, initial rate method was employed.[3] The observed rate

Table 1. Observed rate constants for eliminations from (E)-2,4-dinitrobenzaldehyde O-pivaloyloxime promoted by i-Pr$_2$NH/i-Pr$_2$NH$_2$. [b,c] in 70 mol % MeCN(aq) at 25.0 °C

10^2 [buffer], M	10^4 k_{obs}, s^{-1} [d]
0.197	0.625±0.05
0.388	1.10±0.08
0.759	1.58±0.07
1.11	2.16±0.03
1.64	2.86±0.04
2.53	4.60±0.07
3.90	7.28±0.02
6.701	0.3±0.3

[a] [Substrate]=5.0×10^{-5} M. [b] Buffer ratio=1.0. [c] Ionic strength=0.1 (Bu$_4$N$^+$Br$^-$). [d] Average rate constant and standard deviation for three kinetic runs.

Table 2. Second-order rate constants for eliminations from (E)-XC$_6$H$_4$CH=NOC(O)C(CH$_3$)$_3$ [3a] promoted by R$_2$NH/R$_2$NH$_2$ [b,c] in 70 mol % MeCN(aq) at 25.0 °C

X	R$_2$NH [d]	pK_a [e]	10^2 k_2, M^{-1} s^{-1} [f]
p-MeO	i-Pr$_2$NH	18.5	0.00188±0.00045
H	i-Pr$_2$NH	18.5	0.00348±0.00023
m-Br	i-Pr$_2$NH	18.5	0.00838±0.00014
p-NO$_2$	i-Pr$_2$NH	18.5	0.0273±0.0003
2,4-NO$_2$	DBU [g]	19.4 [h]	32.5±1.7
2,4-NO$_2$	Bz(i-Pr)NH	16.8	0.352±0.017
2,4-NO$_2$	i-Bu$_2$NH	18.2	1.27±0.02
2,4-NO$_2$	i-Pr$_2$NH	18.5	1.87±0.08
2,4-NO$_2$	2,6-DMP [i]	18.9	3.27±0.06

[a] [Substrate]=5.0×10^{-5} M. [b] Buffer ratio=1.0. [c] Ionic strength=0.1 (Bu$_4$N$^+$Br$^-$). [d] [Base]=3.9×10^{-2}-1.1×10^{-1} M. [e] Reference 4 except otherwise noted. [f] Average rate constant and standard deviation for three kinetic runs. [g] DBU was used as the base. [h] Reference 1. [i] cis-2,6-dimethylpiperidine.

constants were divided by the base concentration to obtain the second order-rate constants k_2. The k_2 values are summarized in Table 2.
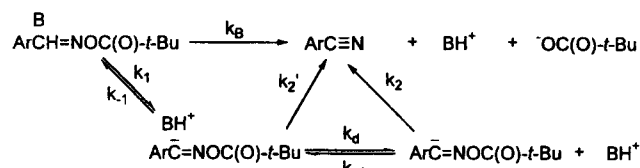
Figure 1 shows that the k_2 value for elimination from **1e** promoted by DBU in MeCN falls on a single line in the Hammett plot with the literature data for **1a-d**, which have been shown to react by the E2 mechanism.[1] This result indicates that the reaction mechanism is not changed by the introduction of the 2,4-dinitro substituents and that the elimination reactions from **1a-e** proceed by the common E2 mechanism.

It is conceivable that a change to a more protic solvent may stabilize the carbanion intermediate by hydrogen bonding, which may in turn change the reaction mechanism to E 1cb.[4] To assess this possibility, we have investigated elimination reactions of **1e** with R$_2$NH/R$_2$NH$_2^+$ buffer in 70% MeCN(aq). Figure 2 shows that the plot of k_{obs} vs buffer concentration is a straight line passing through the origin, i. e., $k_{obs}=k_2$[buffer], indicating that the elimination reaction is second-order.[5] The most likely mechanism for this bimolecular process is either E2 or E1cb. If the reaction proceeds via a carbanion intermediate, the rate equation can be expressed as $k_{obs}=k_1k_2$[B]/(k_{-1}[BH$^+$]+k_2) (Scheme 1).[6-8] The
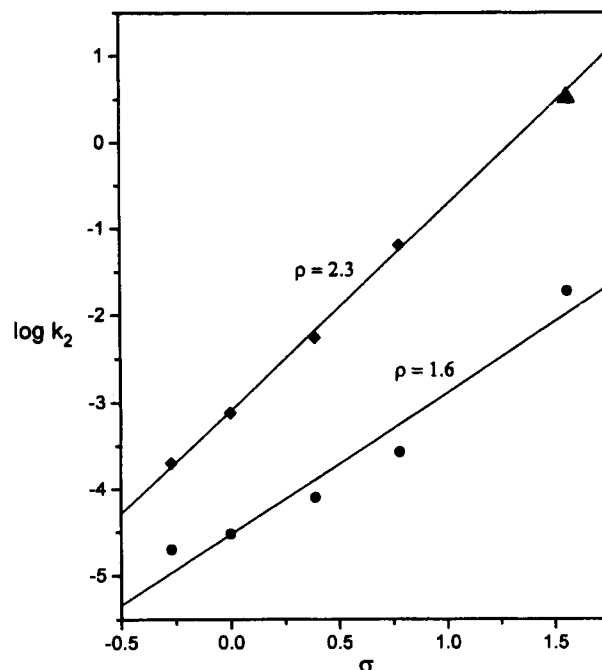
Figure 1. Hammett plots for elimination from (E)-benzaldehyde O-pivaloyloxime promoted by DBU in MeCN (◆) and i-Pr$_2$NH/i-Pr$_2$NH$_2^+$ in 70 mol % MeCN(aq) (●) at 25.0 °C. The rate data for the DBU-promoted elimination from (E)-2,4-dinitrobenzaldehyde O-pivaloyloxime (▲) falls on a single line with the literature data for other derivatives (◆).

(E1cb)$_R$ mechanism requires that the first step must be reversible, i.e., k_{-1}[BH$^+$]>>k_2, and the rate expression can be simplified to $k_{obs}=k_1k_2$[B]/k_{-1}[BH$^+$]. This would predict that
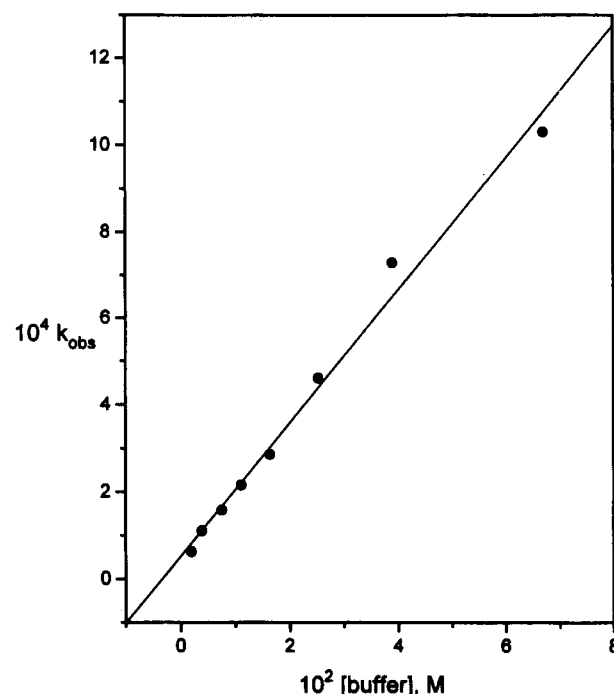
Figure 2. Plot of k_{obs} vs buffer concentration for the reaction of (E)-2,4-dinitrobenzaldehyde O-pivaloyloxime with i-Pr$_2$NH/i-Pr$_2$NH$_2^+$ in 70 mol % MeCN(aq) at 25.0 °C.

B
ArCH=NOC(O)-*t*-Bu $\xrightarrow{k_B}$ ArC≡N + BH⁺ + ⁻OC(O)-*t*-Bu

k_1 ⟍ ⟍ k_{-1}

BH⁺

k_2' / ⟍ k_2

ArC̄=NOC(O)-*t*-Bu $\underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}}$ ArC̄=NOC(O)-*t*-Bu + BH⁺

Scheme 1.

the k_{obs} should remain constant regardless of the buffer concentration because [B]/[BH⁺]=1.0 is maintained throughout the reaction. Therefore, the (E1cb)$_R$ mechanism is ruled out by the linear dependence of the k_{obs} values on the buffer concentration (Figure 2).

The Bronsted plot for eliminations from **1e** is linear with excellent correlation (Figure 3). The observed general base catalysis with the Brönsted β value of 0.45 rules out a mechanism in which either the breakdown of an ion-paired or hydrogen bonded carbanion (k_2') or free carbanion (k_2) is rate limiting, and the internal return mechanism in which both k_1 and k_2 steps are rate limiting, because these mechanisms would exhibit either a specific base catalysis or Brönsted β value near unity (Scheme 1).[6-8]

On the other hand, if the reactions proceed by the (E1cb)$_{irr}$ mechanism, i.e., k_{-1}[BH⁺]≪k_2' or k_2, the rate equation should become $k_{obs}=k_1$[B], which is kinetically indistinguishable from the E2 mechanism.[6-8] The distinction between these two mechanisms has been made by the interaction coefficient. Figure 1 shows that the Hammett β value for eliminations from **1a-e** decreases from 2.3 to 1.6 as the basicity of the promoting base is decreased. The result can be described by a positive $p_{xy'}$ coefficient, $p_{xy'}=\partial\rho/\partial pK_a$,, that describes the interaction between the base catalyst and the
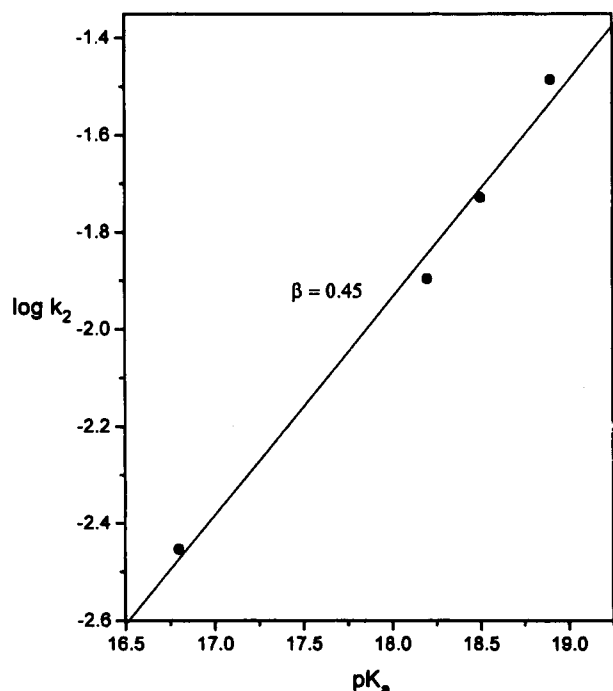
β-aryl substituent.[2,7,9,10] The positive $p_{xy'}$ coefficient is not consistent with an E1cb mechanism for which $p_{xy'}<0$ is expected, but provides a strong support for the concerted E2 mechanism. All of these results indicate that the elimination reactions of **1a-e** with R₂NH/R₂NH₂⁺ buffer in 70% MeCN (aq) proceed by the E2 mechanism.

It is well established that the transition state for the syn elimination has more carbanionic character than the anti elimination because of the poorer overlap of the developing p-orbitals.[1,7,11,12] In addition, the pivaloates are among the poor leaving groups, which would increase the negative charge density at the β-carbon in the transition state.[1,2,6-8] Moreover, the 2,4-dinitro substituents and the sp² hybridized β-carbon atom should provide additional stabilization for the negative charge developed at the β-carbon. All of these factors favor the E1cb or E1cb-like transition state for the elimination from **1e**. However, in no case has such transition state been observed in the nitrile-forming eliminations.[13] It appears that more stabilization energy is obtained by forming partial triple bond than by stabilizing the carbanion with electron-withdrawing substituents and protic solvent. These results underline the importance of the orbital overlap in the nitrile-forming transition state.

Experimental

Materials. (E)-Benzaldehyde O-pivaloyloximes **1a-d** were available from the previous study.[1,2] (E)-2,4-dinitrobenzaldehyde O-pivaloyloximes **1e** was synthesized by the reaction of (E)-2,4-dinitrobenzaldehydeoxime with pivaloyl chloride as described elsewhere.[1,2] Yield 45%, mp 125-127 °C, IR (KBr, C=O, cm⁻¹) 1746; NMR (CDCl₃) δ 9.03 (s, 1H), 8.99 (d, 1H), 8.54 (d, 1H), 8.40 (d, 1H), 1.34 (s, 9H). Anal. Calcd for C₁₂H₁₃N₃O₆: C, 48.81; H, 4.44; N, 14.24; O, 32.51. Found: C, 48.78; H, 4.40; N, 14.34; O, 32.48

Buffer solutions were prepared by dissolving equivalent amount of R₂NH and R₂NH₂⁺ in 70% MeCN(aq). In all cases, the ionic strength was maintained to be 0.1 M with Bu₄N⁺Br⁻.

Kinetic studies. All of the reactions were followed using a UV-vis spectrophotometer with thermostated cuvette holders. Reactions were monitored by the decrease in the absorption of the substrates at 260-420 nm under pseudo-first-order condition employing at least 100-fold excess of the base. For reactions of **1e** with DBU in MeCN and R₂NH/R₂NH₂⁺ in 70% MeCN(aq), plots of -ln (A_t-A_∞/A_0-A_∞) vs time were linear over at least 2 half-lives. The slope was the pseudo-first-order rate constants. On the other hand, the rates of the reactions of **1a-d** were too slow to follow to completion. Therefore, initial rate method was employed.[3]

Product Studies. The yield of PhC≡N from the reaction of **1a** with *i*-Pr₂NH/*i*-Pr₂NH₂⁺ in 70% MeCN(aq) was determined by GC as described previously.[1,2] The yield was 88%. To determine the yield of the elimination reaction from **1e**, 2 mmol of **1e** was reacted with 10 equiv of *i*-Pr₂NH/*i*-Pr₂NH₂⁺ in 15 mL 70% MeCN(aq) for 5 hrs at room temperature. After evaporation of the solvent, the product was taken up in CH₂Cl₂ and washed thoroughly with water until all of the amine, ammonium salt, and the pivaloate were completely removed. The yield of 2,4-dinitrobenzonitrile was 0.41 g (91%).

Figure 3. Brönsted plot for elimination from (E)-2,4-dinitrobenzaldehyde O-pivaloyloxime promoted by R₂NH/R₂NH₂⁺ in 70 mol % MeCN(aq) at 25.0 °C.

Control Experiments. The stability of **1a-e** was determined as reported earlier.[1,2] The solutions of **1a-e** in 70% MeCN(aq) were stable for at least a month when stored in a refrigerator.

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