Elimination Reactions of (*E*)- and (*Z*)-Benzaldehyde *O*-Pivaloyloximes. Transition-State Differences for the Syn and Anti Eliminations Forming Nitriles

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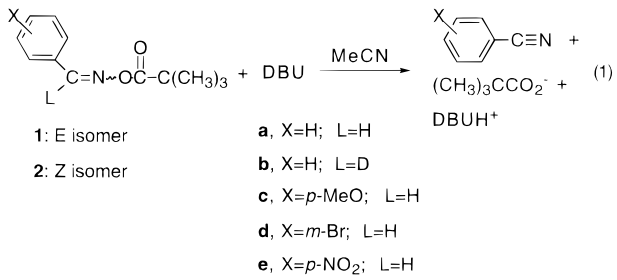
Elimination reactions of (*E*)- and (*Z*)-benzaldehyde *O*-pivaloyloximes **1** and **2** with DBU in MeCN have been investigated kinetically. The reactions are second order and exhibit substantial values of Hammett ρ and k_H/k_D values, and an E2 mechanism is evident. The rate of elimination from **2** is approximately 20 000-fold faster than that from **1**. For reactions of **1** with DBU in MeCN, a Hammett ρ value of 2.4 ± 0.1, k_H/k_D = 2.7 ± 0.3, $\Delta H^{\ddagger}$ = 12.5 ± 0.2 kcal/mol, and $\Delta S^{\ddagger}$ = −31.0 ± 0.6 eu have been determined. The corresponding values for **2** are ρ = 1.4 ± 0.1, k_H/k_D = 7.8 ± 0.3, $\Delta H^{\ddagger}$ = 8.8 ± 0.1 kcal/mol, and $\Delta S^{\ddagger}$ = −23.6 ± 0.4 eu, respectively. The results indicate that the nitrile-forming anti eliminations from **2** proceed via a more symmetrical transition state with a smaller degree of proton transfer, less negative charge development at the β-carbon, and greater extent of triple-bond formation than that for the syn elimination.

An excellent understanding of electronic effects and the effects of changes in reactant structure and reaction conditions on the structure of the E2 transition state for alkene- and alkyne-forming anti eliminations has evolved.[1−4] Similarly, the complementary syn eliminations have also been studied.[1−3] The results of these studies reveal that the anti elimination is more facile and proceeds through the transition state with less carbanionic character and smaller extents of C_β−H bond cleavage than the corresponding syn elimination reactions. In contrast, little is known about the differences between the syn and anti eliminations forming carbon−nitrogen triple bonds.

Previously, we reported that the elimination reactions of (*E*)-benzaldoxime derivatives proceed via an E2 mechanism under various conditions.[6−13] The influence of the reactant structures upon the transition state structures on the nitrile-forming syn elimination reactions have been thoroughly investigated.[5−12] However, virtually no study has been conducted on the nitrile-forming anti eliminations probably because of the difficulty involved in the synthesis of the (*Z*)-benzaldoxime derivatives. We have now synthesized the (*E*)- and (*Z*)-benzaldehyde *O*-pivaloyloximes and investigated their reactions with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in MeCN (eq 1).



(1)

These reactions enabled us to look into, for the first time, the transition-state differences for the syn and anti elimination reactions forming nitriles. The results of these studies are reported here.

Results

(*E*)-Benzaldehyde *O*-pivaloyloximes were available from previous studies.[13] (*Z*)-Benzaldehyde *O*-pivaloyloximes were synthesized in reasonable yields by reacting the (*Z*)-benzaldoximes[18] with pivaloyl chloride at −40 °C in pyridine solution. The reactions of **1a** and **2a** with DBU produced benzonitrile and pivaloate. The GC yields of the benzonitrile from the reactions of **1a** and **2a** with DBU were 89 and 92%, respectively. No trace of benzaldoxime could be detected by either GC or TLC.

Rates of eliminations from **1** and **2** were followed by monitoring the decrease in the absorption at the λ_{max} for the reactants in the range of 260−286 nm. Excellent pseudo-first-order kinetic plots that covered at least 2 half-lives were obtained. Reactions of **1a**−**c** with DBU were too slow to measure the infinity absorption values accurately. Therefore, a Guggenheim method was employed. The rate constants for DBU-promoted eliminations from **1** and **2** are listed in Tables 1 and 2. The k_2 values are constant for 2−8-fold variations in base concentration (entries 7 and 8 in Table 1 and entries 1−3 in Table 2).

The influence of the β-aryl substituents upon the elimination rates gave excellent correlations with σ values (Figure 1). Hammett ρ values are 2.4 ± 0.1 and 1.4 ± 0.1 for **1** and **2**, respectively.

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Table 1. Rate Constants for Eliminations from (*E*)-XC$_6$H$_4$CL=NOC(O)C(CH$_3$)$_3$[a] Promoted by DBU[b] in MeCN

entry	X	L	*T*, °C	[DBU], M	10^4k_2, M^{-1} s^{-1} [c]
1	H	H	25.0	0.101	7.64 ± 0.79
2	H	H	35.0	0.101	15.4 ± 0.91
3	H	H	45.0	0.101	30.6 ± 1.81
4	H	D	25.0	0.101	2.86 ± 0.05
5	*p*-MeO	H	25.0	0.101	2.01 ± 0.06
6	*m*-Br	H	25.0	0.101	55.0 ± 0.80
7	*p*-NO$_2$	H	25.0	0.101	640 ± 3
8	*p*-NO$_2$	H	25.0	0.0594	678 ± 4

[a] [Substrate] = (1−5) × 10^{-5} M. [b] DBU = 1,8-diazabicyclo-[5.4.0]undec-7-ene. [c] Average and standard deviation for two or more kinetic runs.

Table 2. Rate Constants for Eliminations from (*Z*)-XC$_6$H$_4$CL=NOC(O)C(CH$_3$)$_3$[a] Promoted by DBU[b] in MeCN

entry	X	L	*T*, °C	10^3[DBU], M	k_2, M^{-1} s^{-1} [c]
1	H	H	25.0	1.79	15.3 ± 0.3
2	H	H	25.0	6.44	15.3 ± 0.3
3	H	H	25.0	15.1	15.1 ± 0.6
4	H	H	15.0	6.44	8.88 ± 0.24
5	H	H	35.0	6.44	25.2 ± 1.5
6	H	H	45.0	6.44	41.9 ± 0.4
7	H	D	25.0	6.44	1.97 ± 0.04
8	*p*-MeO	H	25.0	6.44	6.32 ± 0.06
9	*m*-Br	H	25.0	6.44	45.7 ± 1.4
10	*p*-NO$_2$	H	25.0	2.00	199 ± 2

[a] [b] See footnotes in Table 1.

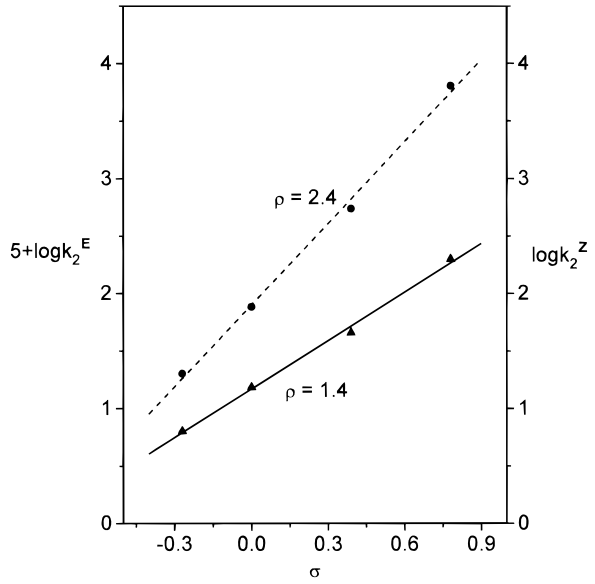

Figure 1. Hammett plots for eliminations from (*E*)- and (*Z*)-benzaldehyde *O*-pivaloyloximes **1** (●) and **2** (▲) promoted by DBU in MeCN at 25.0 °C.

Rates of elimination from **1** and **2** promoted by DBU−MeCN were measured at three or four temperatures spanning 20−30 °C. Arrhenius plots exhibited excellent linearity (plots not shown). Calculated enthalpies and entropies of activation are listed in Table 4.

From the rate coefficients for eliminations from **1a**, **2a**, and their deuterated analogues **1b** and **2b** the isotope effect values were calculated. The values are 2.7 ± 0.3 and 7.8 ± 0.3 for **1a** and **2a**, respectively (Table 4).

An ab initio calculation with the 6-31G basis set reveals that the structures of both **1** and **2** are planar and the lengths of the corresponding bonds are very similar, although the bond angles are appreciably different. In addition, **1** is more stable than **2** by 4.094 kcal/mol (Table S1 in the Supporting Information).

Table 3. Effect of Base Strength upon the Transition State for Elimination from (*E*)-XC$_6$H$_4$CL=NOC(O)C(CH$_3$)$_3$ Promoted by R$_3$N in MeCN

base	Et$_3$N[a]	DBU
pK_a	18.5	19.4[b]
rel rate	1	4200
ρ	1.6 ± 0.1	2.4 ± 0.1
k_H/k_D	3.7 ± 0.3	2.7 ± 0.3

[a] Reference 13. [b] Estimated from the pK_a = 11.5 for DBU and ΔpK_a = (pK_a)$_{MeCN}$ − (pK_a)$_{H_2O}$ = 7.9 for the 1,3-diphenylguanidine.[21]

Discussion

Mechanism of Eliminations from 1 and 2 Promoted by DBU in MeCN. Extensive studies of elimination reactions of (*E*)-benzaldehyde *O*-aryloximes have established that the reactions proceed by an E2 mechanism under various conditions.[6−12] More recently, the reactions of **1** with Et$_3$N in MeCN have also been shown to proceed by the same E2 mechanism via a cyclic transition state.[13] The results of the product and kinetic studies reveal that the reactions of **1** and **2** with DBU in MeCN proceed by a similar mechanism. Both reactions produced the elimination products exclusively. The absence of the benzaldoxime in the reaction product excludes the possibility of the attack of the base at the carbonyl group. Since the elimination reactions exhibit second-order kinetics and substantial k_H/k_D values, all but E2 and (E1cb)$_{irr}$ mechanisms can be ruled out.[4] The (E1cb)$_{irr}$ mechanism requires the formation of a carbanionic intermediate in the rate-determining step. Hence, the transition state for the (E1cb)$_{irr}$ mechanism should have more carbanionic character and a greater extent of C$_\beta$−H bond cleavage than those for an E2 mechanism. However, the observed ρ and k_H/k_D values for both reactions are similar to those observed for the nitrile-forming eliminations from (*E*)-benzaldoxime derivatives under comparable conditions.[6−13] Therefore, it seems reasonable to ascribe an E2 mechanism to the reactions of **1** and **2** with DBU in MeCN.[14,15]

Effect of Base Strength upon Nitrile-Forming Eliminations from 1. For nitrile-forming eliminations from **1**, the change of the base from Et$_3$N to DBU increased the rate by approximately 4200-fold, despite a moderate increase in basicity (Table 3). The unusual reactivity of the DBU as the base is well precedented in the literature and may be attributed to the resonance stabilization in both the base and conjugate acid.[16,17]

(14) A reviewer suggested an interesting possibility that k_H/k_D = 2.7 and ρ = 2.4 for the nitrile-forming syn elimination from **1** could result from significant internal return during proton transfer from carbon to nitrogen. We agree with the reviewer that this possibility cannot be ruled out by the experimental data. However, the $|\beta_{lg}|$ value for the closely-related eliminations from (*E*)-benzaldehyde *O*-benzoyloxime derivatives promoted by DBU in MeCN decreased from 0.56 ± 0.03 to 0.42 ± 0.04 as the β-aryl substituent is changed from *p*-MeO to *p*-NO$_2$. Similarly, the Hammett ρ value also decreased from 2.20 ± 0.11 to 1.90 ± 0.05 with the same variation of the substituent in the benzoyl group.[15] These results can be described by a negative $p_{yy'}$ interaction coefficient, $p_{yy'} = -\partial\beta_{lg}/\partial\sigma^- = -\partial\rho/\partial pK_{lg}$, that describes the interaction between the leaving group and the β-aryl substituent.[3] The negative $p_{yy'}$ coefficients are not consistent an E1cb mechanism for which $p_{yy'} = 0$ is expected but provide a strong support for the E2 mechanism.[3] Therefore, it seems reasonable to ascribe the same E2 mechanism to the eliminations from **1**.

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Table 4. Relative Rate, Hammett ρ, k_H/k_D, and Activation Parameters for the Syn and Anti Eliminations from (*E*)- and (*Z*)-$XC_6H_4CL{=}NOC(O)C(CH_3)_3$ Promoted by DBU in MeCN

compd	(*E*)-isomer	(*Z*)-isomer
rel rate	1	20 000
ρ	2.4 ± 0.1	1.4 ± 0.1
k_H/k_D	2.7 ± 0.3	7.8 ± 0.3
$\Delta H^{\ddagger}$, kcal/mol	12.5 ± 0.2	8.8 ± 0.1
$\Delta S^{\ddagger}$, eu	−31.0 ± 0.6	−23.6 ± 0.4

The Hammett ρ value increased from 1.6 to 2.4, indicating a significant increase in the negative charge development at the β-carbon in the transition state. On the other hand, the k_H/k_D value decreased from 3.7 to 2.7 with a stronger base. In view of the prediction that the k_H/k_D increases until it reaches a maximum value and then decreases as the extent of proton transfer increases, the decrease in the k_H/k_D value may be interpreted as either a greater or a smaller extent of proton transfer in the transition state.[18] However, the former interpretation seems more compatible with the larger ρ value observed with DBU. Therefore, the transition state for DBU-promoted eliminations from **1** appears to have more carbanionic-like character with increased negative charge development at the β-carbon and a greater extent of C_β−H bond cleavage than that for the Et_3N-promoted eliminations from the same substrate.

Transition-State Differences for the Syn and Anti Eliminations Forming Nitriles. It is generally accepted that the anti elimination is more facile than the syn elimination and proceeds via a more symmetrical transition state.[19] Thus, the alkyne-forming anti elimination of (*Z*)-*p*-nitro-β-chlorostyrene promoted by *t*-BuOK−*t*-BuOH proceeds at a 700-fold faster rate than the corresponding syn elimination.[1b] The much faster rate of anti elimination has been interpreted with a favorable overlap between the developing p orbitals at C_β and C_α in the transition state. In addition, the smaller k_H/k_D value for the latter was attributed to the greater extent of C_β−H bond cleavage in the transition state. In contrast, except for Hegarty's report that the OH^--promoted elimination from (*Z*)-*p*-nitrobenzaldehyde *O*-methyloxime proceeds 73-fold faster than that from the (*E*)-isomer,[5] nothing is known about the differences between the syn and anti eliminations forming nitriles.

The data presented in Table 4 reveal that the rate and the structure of the transition state change dramatically with the stereochemistry of the reactants. The anti/syn rate ratio calculated with the k_2 values of 7.64×10^{-4} and 15.3 M^{-1} s^{-1} for **1a** and **2a**, respectively, is approximately 20 000. The ratio is much larger than 700 observed for the *t*-BuOK-promoted eliminations from (*E*)- and (*Z*)-*p*-nitro-β-chlorostyrenes.[1b]

An ab initio calculation with the 6-31G basis set reveals that the structures of both **1** and **2** are planar and the lengths of the corresponding bonds in the two isomers are very similar, although the bond angles are appreciably different (Table S1). In addition, the (*E*)-isomer is more stable than the (*Z*)-isomer by 4.094 kcal/mol, probably due to the unfavorable steric interactions between the phenyl and the leaving group in the latter. Since the steric strain in **2** would undoubtedly decrease as the C_β−H and N_α−O bonds are stretched in the transition state, the unusually large anti/syn rate ratio for the nitrile-forming eliminations from **1** and **2** can most reasonably be attributed to both the higher energy of the reactant **2** and the favorable overlap between the developing p orbitals at the β-carbon and α-nitrogen atoms in the transition state.

The Hammett ρ value for the anti elimination is much smaller than that for the syn elimination, indicating a smaller extent of negative charge development at the β-carbon in the former transition state. In contrast, the k_H/k_D value is much larger for the former. Since the smaller isotope effect for the latter has been attributed to an extensive proton transfer past halfway (*vide supra*), this result should indicate a smaller extent of proton transfer near halfway in the former transition state. The activation parameters listed in Table 4 are consistent with this interpretation. The enthalpy of activation is smaller for the anti than for the syn elimination probably because less energy is required to cleave the C_β−H bond and more energy is liberated by the greater extent of triple bond formation in the transition state. In addition, the higher energy of **2** would also decrease the $\Delta H^{\ddagger}$. Finally, since the transition state for the anti elimination is less associated with respect to the base−proton bond, the entropy of activation should be less negative. Therefore, the transition state for the anti eliminations from **2** appears to be more symmetrical with a smaller degree of proton transfer, less negative charge development at the β-carbon, and a greater extent of triple bond formation than that for the corresponding syn eliminations.

Experimental Section

Materials. (*E*)-Benzaldehyde *O*-pivaloyloximes **1a**−**e** were available from the previous study.[13] (*Z*)-Benzaldoximes were synthesized by the isomerization of the corresponding (*E*)-isomer by the literature procedure.[20] All of the (*Z*)-benzaldehyde *O*-pivaloyloximes except for **2c** were prepared in reasonable yields by slowly adding (*Z*)-benzaldoximes (2.0 mmol) to the solution of pivaloyl chloride (0.27 g, 2.2 mmol) in 7.0 mL of pyridine at −40 °C. The solution was stirred for 5 min at −40 °C and poured into 70 mL of ice-water. The products were precipitated as needle crystals.

Synthesis of **2c** was carried out by the same procedure as above using a mixture of 20 mL of hexane−7.0 mL of pyridine as the solvent. When the reaction was completed, the hexane layer was separated, washed several times with cold water, dried over anhydrous $MgSO_4$, and then evaporated.

In most cases, the products were analytically pure and used without further purification. The spectral and analytical data of the compounds were consistent with the proposed structures. The yield (%), melting point (°C), NMR ($CDCl_3$), IR (KBr, C=O, cm^{-1}), and combustion analysis data for the new compounds are as follows. (*Z*)-$C_6H_5CH{=}NOC(O)C(CH_3)_3$ (**2a**): yield 59; mp 63−65; IR 1758; NMR δ 7.85−7.82 (m, 2H), 7.80 (s, 1H), 7.53−7.45 (m, 3H), 1.34 (s, 9H). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.83. Found: C, 70.18; H, 7.40; N, 6.84. (*Z*)-$C_6H_5CD{=}NOC(O)C(CH_3)_3$ (**2b**): yield 68; mp 63−65; IR 1758; NMR δ 7.86−7.83 (m, 2H), 7.54−7.46 (m, 3H), 1.34 (s, 9H). (*Z*)-*p*-$MeOC_6H_4CH{=}NOC(O)C(CH_3)_3$ (**2c**): yield 43; mp 33−35; IR 1752; NMR δ 7.82 (dd, 2H), 7.68 (s, 1H), 6.97 (dd, 2H), 3.87 (s, 3H), 1.36 (s, 9H). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.37; H, 7.25; N, 6.25. (*Z*)-*m*-$BrC_6H_4CH{=}NOC(O)C(CH_3)_3$ (**2d**): yield 82; mp 61−64; IR 1757; NMR δ 8.10 (s, 1H), 7.76 (s, 1H), 7.67 (d,

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1H), 7.64 (d, 1H), 7.37 (t, 1H), 1.35 (s, 9H). Anal. Calcd for $C_{12}H_{14}NO_2Br$: C, 50.72; H, 4.97; N, 4.93. Found: C, 50.48; H, 5.12; N, 4.89. (*Z*)-*p*-$NO_2C_6H_4CH{=}NOC(O)C(CH_3)_3$ (**2e**): yield 59; mp 55−56; IR 1765; NMR δ 8.47 (s, 1H), 8.29 (d, 2H), 7.94 (d, 2H), 1.32 (s, 9H). Anal. Calcd for $C_{12}H_{14}N_2O_4$: C, 57.59; H, 5.64; N, 11.20. Found: C, 57.51; H, 5.38; N, 11.18.

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was redistilled in vacuo prior to use and acetonitrile have been purified as described before.[13]

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 substrate at 254−282 nm under pseudo-first-order conditions employing at least a 100-fold excess of base as described before. In almost every case, plots of $-\ln (A_\infty - A_t/A_\infty - A_0)$ vs time were linear over at least 2 half-lives. The slope was the pseudo-first-order rate constants. However, reactions of **1a**−**c** were too slow to follow to completion conveniently. Therefore, a Guggenheim method was employed.

Product Studies. The yields of PhC≡N from the reactions of **1a** and **2a** with DBU were determined by GC as described previously.[13] The yields were 87 and 92% for **1a** and **2a**, respectively.

Control Experiments. The stability of **1** and **2** 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** and **2** during 6 months in the refrigerator. The solutions of **1** and **2** in MeCN were stable for at least 1 month when stored in the refrigerator.

Calculation. Structures of the reactants **1** and **2** were calculated on a Silicon Graphics workstation using the Gaussian 94, Revision A.1 quantum mechanical package developed by Pole and co-workers.[22] All structures were fully optimized using the 6-31G basis set.

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Supporting Information Available: Structures of (*E*)- and (*Z*)-benzaldehyde *O*-pivaloyloximes calculated by the Gaussian 94, Revision A.1, with 6-31G basis set (1 page). This information 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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