

## Kinetics and Mechanism of the Benzylaminolysis of *O,O*-Dimethyl *S*-Aryl Phosphorothioates in Dimethyl Sulfoxide

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Kinetic studies of the reactions of *O,O*-dimethyl *Z*-*S*-aryl phosphorothioates with *X*-benzylamines have been carried out in dimethyl sulfoxide at 85.0 °C. The Hammett ( $\log k_2$  vs  $\sigma_X$ ) and Brønsted [ $\log k_2$  vs  $\text{p}K_a(\text{X})$ ] plots for substituent *X* variations in the nucleophiles are discrete with a break region between 4-Me and H, while the Hammett plots ( $\log k_2$  vs  $\sigma_Z$ ) for substituent *Z* variations in the leaving groups are linear. The sign of the cross-interaction constant ( $\rho_{XZ}$ ) is positive for both the strongly and weakly basic nucleophiles. Greater magnitude of  $\rho_{XZ}$  (= 2.54) value is observed with the weakly basic nucleophiles compared to with the strongly basic nucleophiles ( $\rho_{XZ}$  = 0.17). The deuterium kinetic isotope effects ( $k_H/k_D$ ) involving deuterated benzylamines [ $\text{XC}_6\text{H}_4\text{CH}_2\text{ND}_2$ ] are primary normal ( $k_H/k_D > 1$ ). The proposed mechanism is a stepwise with a rate-limiting leaving group expulsion from the intermediate involving a frontside nucleophilic attack with a hydrogen bonded, four-center-type transition state for both the strongly and weakly basic nucleophiles.

**Key Words** : Phosphoryl transfer reaction, Benzylaminolysis, Deuterium kinetic isotope effect, Discrete free energy correlation, *O,O*-Dimethyl *S*-aryl phosphorothioate

### Introduction

The various types of phosphoryl and thiophosphoryl transfer reactions are investigated experimentally (anilino-lysis,<sup>1</sup> pyridinolysis,<sup>2</sup> and benzylaminolysis<sup>3</sup>) and theoretically<sup>4</sup> by this lab. The kinetic studies on the benzylaminolyses of *O,O*-diethyl [**2**:  $(\text{EtO})_2\text{P}(=\text{O})\text{SC}_6\text{H}_4\text{Z}$ ]<sup>3b</sup> and *O,O*-diphenyl [**3**:  $(\text{PhO})_2\text{P}(=\text{O})\text{SC}_6\text{H}_4\text{Z}$ ]<sup>3a</sup> *Z-S*-aryl phosphorothioates with the leaving group *Z*-substituted thiophenoxide were carried out in dimethyl sulfoxide (DMSO) at 85.0 and 55.0 °C, respectively. In the present work, the kinetic studies of the reactions of *O,O*-dimethyl *Z-S*-aryl phosphorothioates [**1**:  $(\text{MeO})_2\text{P}(=\text{O})\text{SC}_6\text{H}_4\text{Z}$ ] with *X*-substituted benzylamines have been kinetically studied in DMSO at  $85.0 \pm 0.1$  °C (Scheme 1) to gain further information into the aminolysis mechanism and stereochemistry on the basis of the sign and magnitude of the cross-interaction constants (CICs;  $\rho_{XZ}$ ) and deuterium kinetic isotope effects (DKIEs;  $k_H/k_D$ ) involving  $\text{XC}_6\text{H}_4\text{CH}_2\text{ND}_2$ , as well as to compare with the kinetic results of the benzylaminolyses of **2** and **3**. The numbering of the substrates follows the sequence of the size of the two

ligands: **1**(MeO)<sub>2</sub>, **2**(EtO)<sub>2</sub>, and **3**(PhO)<sub>2</sub>.

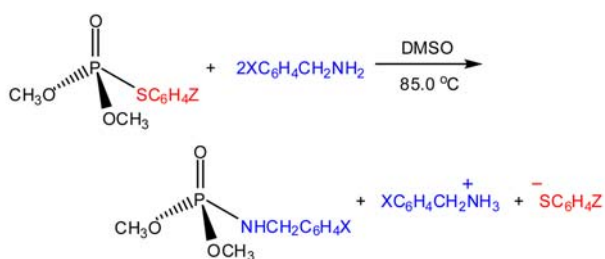
### Results and Discussion

The pseudo-first-order rate constants observed ( $k_{\text{obsd}}$ ) for all reactions obeyed eq. (1) with negligible  $k_0$  ( $\approx 0$ ) in DMSO. The clean second-order rate constants ( $k_2$ ) obtained as the slope of the plot of  $k_{\text{obsd}}$  against at least five concentrations of benzylamine are summarized in Tables 1 together with selectivity parameters ( $\rho_X$ ,  $\beta_X$ ,  $\rho_Z$ , and  $\rho_{XZ}$ ). The linear plots of eq. (1) suggest that there are no base-catalysis or noticeable side reactions and that the overall reaction is described by Scheme 1.

$$k_{\text{obsd}} = k_0 + k_2 [\text{XC}_6\text{H}_4\text{CH}_2\text{NH}_2] \quad (1)$$

The Brønsted  $\beta_X$  values are obtained by correlating  $\log k_2(\text{DMSO})$  with  $\text{p}K_a(\text{H}_2\text{O})$ . The  $\beta_X$  values listed in Table 1 seem to be less reliable since the  $\text{p}K_a$  values used are not those determined in DMSO, but rather in water. Using the  $\text{p}K_a$  values for the anilinium ions determined in DMSO, an approximate straight line is obtained when they are plotted against those determined in water.<sup>6</sup> Spillane and coworkers reported that the  $\beta_X$  value for the reactions of *N*-phenyl sulfamoyl chloride ( $\text{PhNHSO}_2\text{Cl}$ ) with *X*-anilines in DMSO is similar when determined using the  $\text{p}K_a$  values of anilines measured in water ( $\beta_X = 0.69$ ) and DMSO ( $\beta_X = 0.62$ ).<sup>7</sup> Accordingly, it may be inferred that the  $\beta_X$  values in Table 1 are considered to indicate the trends of changes with substituents, but not far from real values.

The Hammett (Fig. 1;  $\log k_2$  vs  $\sigma_X$ ) and Brønsted [Fig. 2;  $\log k_2$  vs  $\text{p}K_a(\text{X})$ ] plots for substituent *X* variations in the nucleophiles are discrete with a break region between *X* = 4-Me and H. The plots are divided into two blocks: block *a*



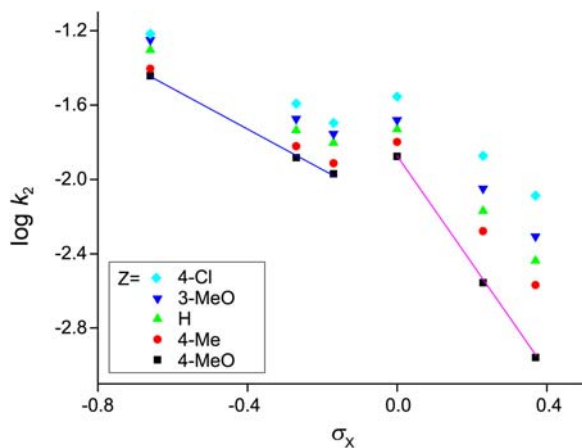
**X** = 4-NH<sub>2</sub>, 4-MeO, 4-Me, H, 4-Cl, 3-Cl; **Z** = 4-MeO, 4-Me, H, 3-MeO, 4-Cl  
**Scheme 1.** The studied reaction system.

**Table 1.** Second-Order Rate Constants ( $k_2 \times 10^3/\text{M}^{-1}\text{s}^{-1}$ ) and Selectivity Parameters<sup>a</sup> of the Reactions of *O,O*-Dimethyl *Z*-*S*-Aryl Phosphorothioates (**1**) with X-Benzylamines in DMSO at 85.0 °C

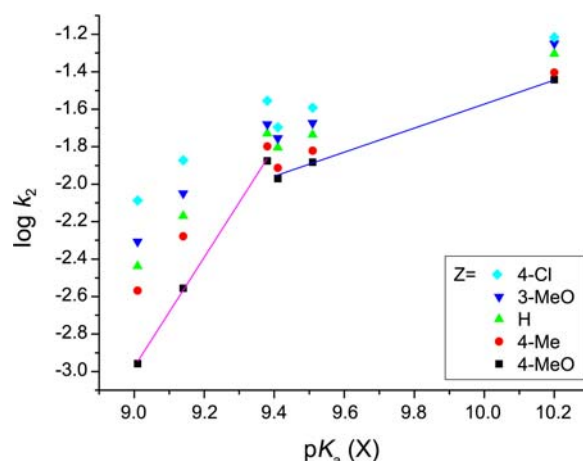
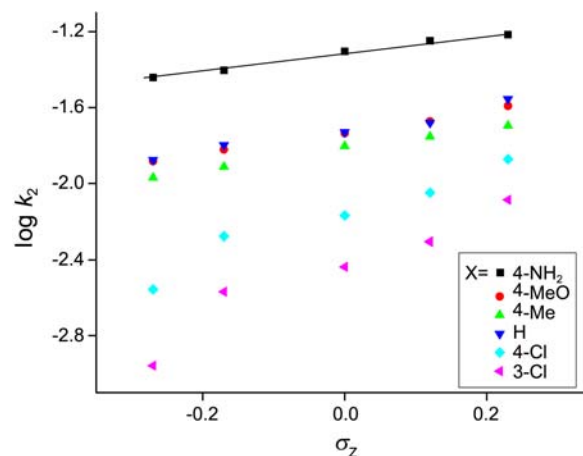
X \ Z	4-MeO	4-Me	H	3-MeO	4-Cl	$\rho_Z^h$
4-NH <sub>2</sub>	36.1 ± 0.12	39.4 ± 0.1	49.7 ± 0.1	56.4 ± 0.1	60.8 ± 0.1	0.46 ± 0.01
4-MeO	13.1 ± 0.05	15.1 ± 0.1	18.4 ± 0.1	21.2 ± 0.1	25.6 ± 0.1	0.58 ± 0.01
4-Me	10.7 ± 0.06	12.2 ± 0.1	15.7 ± 0.1	17.6 ± 0.1	20.1 ± 0.1	0.55 ± 0.01
H	13.3 ± 0.04	15.9 ± 0.1	18.6 ± 0.1	21.7 ± 0.1	27.9 ± 0.2	0.62 ± 0.02
4-Cl	2.78 ± 0.01	5.27 ± 0.01	6.76 ± 0.06	8.93 ± 0.02	13.4 ± 0.1	1.26 ± 0.08
3-Cl	1.10 ± 0.01	2.70 ± 0.01	3.65 ± 0.02	4.94 ± 0.01	8.18 ± 0.06	1.59 ± 0.12
$-\rho_X^{b,d}$	1.09 ± 0.02	1.05 ± 0.01	1.05 ± 0.03	1.05 ± 0.02	0.98 ± 0.01	$\rho_{XZ}^{b,i} =$
$\beta_X^{b,e}$	0.66 ± 0.02	0.63 ± 0.02	0.63 ± 0.01	0.63 ± 0.01	0.59 ± 0.03	0.17 ± 0.01
$-\rho_X^{c,f}$	2.93 ± 0.01	2.08 ± 0.01	1.91 ± 0.01	1.73 ± 0.01	1.44 ± 0.01	$\rho_{XZ}^{c,j} =$
$\beta_X^{c,g}$	2.91 ± 0.02	2.07 ± 0.02	1.90 ± 0.02	1.72 ± 0.03	1.43 ± 0.02	2.54 ± 0.07

<sup>a</sup>The  $\sigma$  values were taken from Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165. The  $\text{pK}_a$  values of the X-benzylammonium ions in water were taken from Blackwell, L. F.; Fischer, A.; Miller, I. J.; Topsom, R. D.; Vaughan, J. J. *Chem. Soc.* **1964**, 3588. The  $\text{pK}_a$  value of X = 4-NH<sub>2</sub> in DMSO was taken from Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456, 463. See ref. 5. <sup>b</sup>X = (4-NH<sub>2</sub>, 4-MeO, 4-Me); block a. <sup>c</sup>X = (H, 4-Cl, 3-Cl); block b. <sup>d</sup>Correlation coefficients (r) are better than 0.998. <sup>e</sup>r ≥ 0.996. <sup>f</sup>r ≥ 0.999. <sup>g</sup>r ≥ 0.998. <sup>h</sup>r ≥ 0.964. <sup>i</sup>r = 0.998. <sup>j</sup>r = 0.979.

with the strongly basic benzylamines (X = 4-NH<sub>2</sub>, 4-MeO, 4-Me) and block *b* with the weakly basic benzylamines (X = H, 4-Cl, 3-Cl). The magnitudes of the Hammett and Brønsted coefficients ( $\rho_X = -1.44$  to  $-2.93$  and  $\beta_X = 1.43$ – $2.91$ ) with block *b* are considerably greater than those with block *a* ( $\rho_X = -0.98$  to  $-1.09$  and  $\beta_X = 0.59$ – $0.66$ ). Although the rate with X = H (weaker nucleophile) is faster than those with X = 4-MeO and 4-Me (stronger nucleophiles), the rate increases as the nucleophile becomes stronger for each block, compatible with a typical nucleophilic substitution reaction with positive charge development at the nucleophilic nitrogen atom in the transition state (TS). The Hammett (Fig. 3;  $\log k_2$  vs  $\sigma_Z$ ) plots for substituent Z variations in the leaving groups show linear free energy correlations. The rate increases with a more electron-withdrawing substituent Z in the leaving groups, which is consistent with a typical nucleophilic substitution reaction with negative charge development at the thiophenoxy sulfur atom in the TS. In the benzylaminolyses of **2** and **3**, the free energy correlations with X showed biphasic concave downwards with a break point and those with Z showed linear.<sup>3</sup>

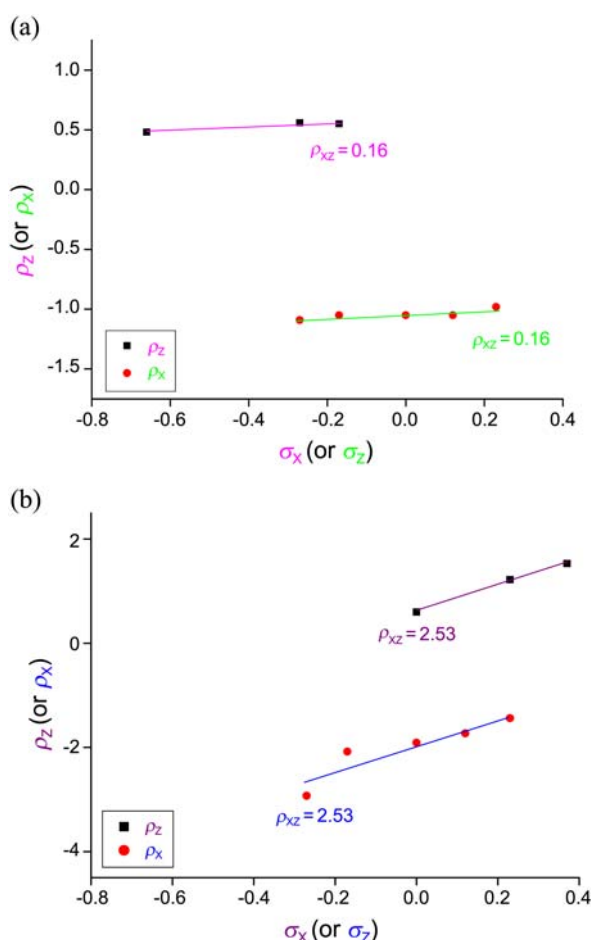
**Figure 1.** The Hammett plots ( $\log k_2$  vs  $\sigma_X$ ) of the reactions of *O,O*-dimethyl *Z*-*S*-aryl phosphorothioates (**1**) with X-benzylamines in DMSO at 85.0 °C.

The second-order rate constant of the studied substrate (**1**) with benzylamine ( $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ ) is  $18.6 \times 10^{-3} \text{M}^{-1}\text{s}^{-1}$ , while that with pyridine ( $\text{C}_5\text{H}_5\text{N}$ ) is  $5.49 \times 10^{-4} \text{M}^{-1}\text{s}^{-1}$  in DMSO at

**Figure 2.** The Brønsted plots [ $\log k_2$  vs  $\text{pK}_a(\text{X})$ ] of the reactions of *O,O*-dimethyl *Z*-*S*-aryl phosphorothioates (**1**) with X-benzylamines in DMSO at 85.0 °C.**Figure 3.** The Hammett plots ( $\log k_2$  vs  $\sigma_Z$ ) of the reactions of *O,O*-dimethyl *Z*-*S*-aryl phosphorothioates (**1**) with X-benzylamines in DMSO at 85.0 °C.

85.0 °C,<sup>20</sup> giving the rate ratio of  $k_{\text{BnA}}/k_{\text{Pyr}} = 34$ . Taking into account the greater basicity of benzylamine compared to pyridine ( $\text{p}K_{\text{a}} = 4-7$ ),<sup>8</sup> the rate ratio is reasonable, but not so great. In the aminolyses of **3**, on the contrary, the pyridinolysis rate is faster than the benzylaminolysis rate which is rationalized by the steric effects of large size of the two PhO ligands.<sup>3a</sup>

The cross-interaction constants (CICs;  $\rho_{\text{XZ}}$ ) are determined, where X and Z represent the substituents in the nucleophile and leaving group, respectively [eqs. (2)].<sup>9</sup> According to eq. (2b), the  $\rho_{\text{XZ}}$  values can be obtained from the slopes of the plots of  $\rho_{\text{X}}$  vs  $\sigma_{\text{Z}}$  and  $\rho_{\text{Z}}$  vs  $\sigma_{\text{X}}$  for block *a* (Fig. 4(a); X = 4-MeO, 4-Me, H) and *b* (Fig. 4(b); X = H, 4-Cl, 3-Cl), respectively. The sign and magnitude of the CICs have made it possible to correctly interpret the reaction mechanism and degree of tightness of the TS, respectively. In general, the  $\rho_{\text{XZ}}$  has a negative value (or sometimes a small positive value) in a concerted  $\text{S}_{\text{N}}2$  and a stepwise mechanism with a rate-limiting bond formation. On the contrary, it has a positive value for a stepwise mechanism with a rate-limiting leaving group departure from the intermediate. The magni-



**Figure 4.** Determination of  $\rho_{\text{XZ}} (= \partial\rho_{\text{X}}/\partial\sigma_{\text{Z}} = \partial\rho_{\text{Z}}/\partial\sigma_{\text{X}})$  by plotting  $\rho_{\text{Z}}$  (or  $\rho_{\text{X}}$ ) against  $\sigma_{\text{X}}$  (or  $\sigma_{\text{Z}}$ ) for the reactions of *O,O*-dimethyl *Z,S*-aryl phosphorothioates (**1**) with X-benzylamines in DMSO at 85.0 °C. The obtained  $\rho_{\text{XZ}}$  values by multiple regressions are: (a)  $\rho_{\text{XZ}} = 0.17 \pm 0.01$  with block *a* (X = 4-NH<sub>2</sub>, 4-MeO, 4-Me) and (b)  $\rho_{\text{XZ}} = 2.54 \pm 0.07$  with block *b* (X = H, 4-Cl, 3-Cl).

tude of  $\rho_{\text{XZ}}$  is inversely proportional to the distance between the nucleophile and leaving group in the TS.<sup>9</sup>

$$\log(k_{\text{XZ}}/k_{\text{HH}}) = \rho_{\text{X}}\sigma_{\text{X}} + \rho_{\text{Z}}\sigma_{\text{Z}} + \rho_{\text{XZ}}\sigma_{\text{X}}\sigma_{\text{Z}} \quad (2a)$$

$$\rho_{\text{XZ}} = \rho_{\text{X}}/\sigma_{\text{Z}} = \rho_{\text{Z}}/\sigma_{\text{X}} \quad (2b)$$

The positive sign of  $\rho_{\text{XZ}}$  values for both blocks suggests that the reaction proceeds through a stepwise mechanism with a rate-limiting leaving group expulsion from the intermediate, regardless of the nature of the substituent X, electron-donating or -withdrawing. The interaction between X and Z is much greater with block *b* (X = H, 4-Cl, 3-Cl) compared to with block *a* (X = 4-MeO, 4-Me, H), taking into account the magnitude of  $\rho_{\text{XZ}} = 2.54$  with block *b* and  $\rho_{\text{XZ}} = 0.17$  with block *a*. These results are consistent with the  $\beta_{\text{X}}$  values:  $\beta_{\text{X}} = 0.59-0.66$  with block *a* and  $\beta_{\text{X}} = 1.43-2.91$  with block *b*. It is known that the large magnitudes of the  $\rho_{\text{XZ}}$  values ( $|\rho_{\text{XZ}}| \geq 0.5$ ) are ascribed to the frontside nucleophilic attack.<sup>10</sup> Thus, the TS involving a frontside nucleophilic attack is proposed with block *b*.

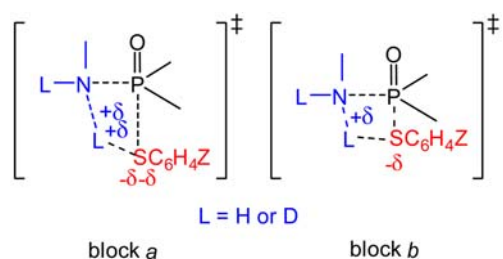
The DKIEs can be only secondary inverse ( $k_{\text{H}}/k_{\text{D}} < 1$ ) in a normal  $\text{S}_{\text{N}}2$  reaction, since the N-H(D) vibrational frequencies invariably increase upon going to the TS, given the increase in steric hindrance in the bond formation step; the greater the bond formation, the greater the steric congestion occurs, and the smaller the  $k_{\text{H}}/k_{\text{D}}$  value becomes.<sup>11</sup> In contrast, when partial deprotonation of the benzylamine occurs in a rate-limiting step by hydrogen bonding, the DKIEs are primary normal ( $k_{\text{H}}/k_{\text{D}} > 1$ ); the greater the extent of the hydrogen bond that occurs, the greater the  $k_{\text{H}}/k_{\text{D}}$  value becomes.<sup>12</sup> The DKIEs,  $k_{\text{H}}/k_{\text{D}}$ , involving deuterated benzylamines are summarized in Table 2. In the present work, the obtained primary normal DKIEs ( $k_{\text{H}}/k_{\text{D}} = 1.24-1.87 > 1$ ) for both blocks imply the partial deprotonation of the benzylamine, i.e., hydrogen bonding, in the TS. The real primary normal DKIE due to the hydrogen bond should be greater than the observed value, since the other hydrogen (deuterium) atom in the N-H(D) moiety, not involved in the hydrogen bond, yields the secondary inverse DKIE ( $k_{\text{H}}/k_{\text{D}} < 1$ ) due to the steric congestion.

The primary normal DKIEs ( $k_{\text{H}}/k_{\text{D}}$ ) with X = 4-MeO (block *a*) are greater than those with X = H and 4-Cl (block

**Table 2.** Deuterium Kinetic Isotope Effects ( $k_{\text{H}}/k_{\text{D}}$ ) of the Reactions of *O,O*-Dimethyl *Z,S*-Aryl Phosphorothioates (**1**) with X-Benzylamines in DMSO at 85.0 °C

X	Z	$k_{\text{H}} \times 10^3/\text{M}^{-1} \text{ s}^{-1}$	$k_{\text{D}} \times 10^3/\text{M}^{-1} \text{ s}^{-1}$	$k_{\text{H}}/k_{\text{D}}$
4-MeO	H	$18.4 \pm 0.01$	$11.0 \pm 0.04$	$1.67 \pm 0.01$
	4-Cl	$25.6 \pm 0.01$	$13.7 \pm 0.01$	$1.87 \pm 0.01$
H	H	$18.6 \pm 0.02$	$12.4 \pm 0.01$	$1.50 \pm 0.01$
	4-Cl	$27.9 \pm 0.2$	$19.3 \pm 0.1$	$1.45 \pm 0.01$
4-Cl	H	$6.76 \pm 0.06$	$5.47 \pm 0.01$	$1.24 \pm 0.01$
	4-Cl	$13.4 \pm 0.09$	$10.8 \pm 0.06$	$1.24 \pm 0.01$

<sup>a</sup>Standard error  $\{= 1/k_{\text{D}}[(\Delta k_{\text{H}})^2 + (k_{\text{H}}/k_{\text{D}})^2 \times (\Delta k_{\text{D}})^2]^{1/2}$  from Crumpler, T. B.; Yoh, J. H. *Chemical Computations and Errors*; John Wiley: New York, 1940; p 178.



**Scheme 2.** Hydrogen bonded, four-center-type TSs of block *a* with the strongly basic benzylamines involving late product-like TS and block *b* with the weakly basic benzylamines involving earlier TS.

*b*), suggesting (i) frontside nucleophilic attack with a hydrogen bonded four-center-type TS for both blocks and (ii) greater extent of the hydrogen bond with X = 4-MeO (block *a*) than with X = H and 4-Cl (block *b*) in the TS. At a glance, the magnitudes of  $k_{\text{H}}/k_{\text{D}}$  values are not consistent with the CIC values since the magnitudes of  $k_{\text{H}}/k_{\text{D}}$  values are generally proportional to the CIC values when the DKIEs are primary normal:  $k_{\text{H}}/k_{\text{D}} = 1.67\text{--}1.87$  (block *a*) >  $1.24\text{--}1.50$  (block *b*) while  $\rho_{\text{XZ}} = 2.54$  (block *b*) >  $0.17$  (block *a*). These results are substantiated by the TS variation with blocks as follows: (i) in block *a* with the strongly basic benzylamines, the degree of bond breaking is great (resulting in smaller  $\rho_{\text{XZ}} = 0.17$ ), and the negative charge development at the thiophenoxy sulfur atom is great and the extent of hydrogen bond is great (resulting in greater  $k_{\text{H}}/k_{\text{D}} = 1.67\text{--}1.87$ ) in the TS, i.e., late product-like TS (Scheme 2); (ii) in block *b* with the weakly basic benzylamines, the degree of bond breaking is small (resulting in greater  $\rho_{\text{XZ}} = 2.54$ ), and the negative charge development at the thiophenoxy sulfur atom is small and the extent of hydrogen bond is small (resulting in smaller  $k_{\text{H}}/k_{\text{D}} = 1.24\text{--}1.50$ ) in the TS, i.e., earlier TS than that that in block *a* (Scheme 2).

In summary, the authors herein propose the reaction mechanism as follows: (i) a stepwise mechanism with a rate-limiting leaving group departure from the intermediate on the basis of the positive sign of  $\rho_{\text{XZ}}$  for both blocks, the strongly and weakly basic benzylamines; (ii) a frontside nucleophilic attack involving a hydrogen bonded, four-center-type TS on the basis of the primary normal DKIEs for both blocks; (iii) late product-like TS for block *a* on the basis of the small magnitude of  $\rho_{\text{XZ}}$  and greater magnitudes of  $k_{\text{H}}/k_{\text{D}}$ ; (iv) earlier TS for block *b* on the basis of the large magnitude of  $\rho_{\text{XZ}}$  and smaller magnitudes of  $k_{\text{H}}/k_{\text{D}}$ .

### Experimental Section

**Materials.** The substrates were prepared as described previously.<sup>20</sup> GR grade dimethyl sulfoxide was dried over 4 Å molecular sieve and then used after three distillations under reduced pressure. The X-benzylamine nucleophiles, GR grade, were used after recrystallization (4-methylbenzylamine; mp 12–13 °C, recrystallized in ice bath) or distillation. For preparation of deuterated benzylamine, X-benzylamines were taken with ethyl ether and D<sub>2</sub>O. The mixture

was stirring for 24 hrs at room temperature. The deuterated benzylamines were isolated with ether and dried over anhydrous MgSO<sub>4</sub>. After numerous attempts, finally, X-benzylamines were isolated by solvent evaporation under reduced pressure and identified by <sup>1</sup>H-NMR.

**Kinetic Procedure.** Rates were measured conductometrically at 85.0 °C using a computer controlled conductivity bridge constructed in this lab. Pseudo-first-order rate constants,  $k_{\text{obsd}}$ , were measured by using curve-fitting method in ORIGIN program. Pseudo-first-order rate constants were determined with large excess of benzylamine; [Substrate] =  $5 \times 10^{-3}$  M and [X-BnA] = 0.10–0.25 M. Pseudo-first-order rate constants were reproducible within  $\pm 3\%$ .

**Product Analysis.** Dimethyl 4-methyl-*S*-phenyl phosphorothioate (0.05 M) were reacted with 4-methoxybenzylamine (0.5 M), in DMSO at 85.0 °C. After more than 15 half-lives, product was separated by using consecutive water and ethylacetate extraction process. Finally the product was isolated by column chromatography using ethylacetate/*n*-hexane (90%–10%) eluent. Analytical data of the products gave the following results:

(CH<sub>3</sub>O)<sub>2</sub>P(=O)NHCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>(4-OCH<sub>3</sub>). Light yellow, oily liquid (silicagel, 90% ethylacetate/*n*-hexane); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN),  $\delta$  2.19 (s, 1H), 2.58 (d, 6H,  $J = 11.2$  Hz), 3.77 (s, 3H), 33.94–3.97 (m, 2H), 6.89 (d, Arom. 2H,  $J = 8.4$  Hz), 7.25 (d, Arom. 2H,  $J = 8.8$  Hz); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>CN),  $\delta$  95.49, 114.76, 129.76 and 160.02 (C=C, aromatic, 6C, s/m), 55.94 (OCH<sub>3</sub>, 2C, s), 53.41 (CH<sub>2</sub>, 1C, m), 45.20 (OCH<sub>3</sub>, 1C, s); <sup>31</sup>P NMR (162 MHz, CD<sub>3</sub>CN),  $\delta$  22.18 (1P, d);  $m/z$  245 (M<sup>+</sup>).

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### References and Notes

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