Pyridinolysis of *O,O*-Diphenyl *S*-Phenyl Phosphorothiolates in Acetonitrile

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Received March 10, 2008

The reactions of *O,O*-diphenyl Z-*S*-phenyl phosphorothiolates with X-pyridines have been studied kinetically in acetonitrile at 35.0 °C. The Hammett plots for substituent (Z) variations in the leaving group (log k_2 *vs.* σ_Z) are biphasic concave downwards with breaks at Z = H. The large magnitudes of ρ_X (ρ_{nuc}), β_X (ρ_{nuc}), and the cross-interaction constant, ρ_{XZ}, suggest frontside nucleophilic attack toward the leaving group. The sign reversal of ρ_Z from positive in $\sigma_Z \leq 0$ to negative in $\sigma_Z \geq 0$ is interpreted as the change in mechanism from concerted to stepwise with rate-limiting expulsion of the leaving group. The anomalous negative sign of ρ_Z for leaving groups with electron-withdrawing substituents is interpreted as the intramolecular ligand exchange process of the leaving group from the equatorial position in the intermediate to the apical position in the TS.

Key Words : *O,O*-Diphenyl *S*-phenyl phosphorothiolate, Pyridinolysis, Cross-interaction constants, Frontside attack, Negative ρ_Z (ρ_{Lg})

Introduction

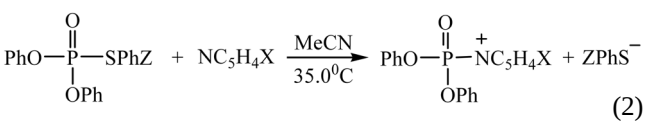
Phosphoryl transfers from phosphate monoesters and diesters proceed concertedly with a single transition state (TS)[1] or stepwise with a trigonal bipyramidal pentacoordinate (TBP-5C) intermediate.[2] The nucleophile attacks the backside toward the leaving group in most phosphoryl transfers, *i.e.*, the attacking and the leaving groups occupy apical positions [ap(Nu)-ap(Lg)]. However, when the nucleophile attacks frontside toward the leaving group, *i.e.*, when the nucleophile and the leaving groups occupy apical and equatorial positions [ap(Nu)-eq(Lg)], or equatorial and apical positions [eq(Nu)-ap(Lg)], respectively, the configuration is retained.[3] When backside and frontside nucleophilic attacks occur simultaneously, the relative importance of each reaction pathway leads to products with inversion or retention of the configuration, depending on the nucleophile, the leaving group, and the reaction conditions.[3a]

In our preceding papers,[4] we reported various aminolyses of phosphate derivatives and proposed a reaction mechanism mainly based on the deuterium kinetic isotope effects and the cross-interaction constants,[5] ρ_{ij}, in eqs. (1) where i and j are the substituents in the nucleophiles, leaving groups and/or substrates, respectively.

$$\log(k_{ij}/k_{HH}) = \rho_i\sigma_i + \rho_{jj} + \rho_{ij}\sigma_i\sigma_j \quad (1a)$$

$$\rho_{ij} = \rho_i/\sigma_j = \rho_j/\sigma_i \quad (1b)$$

Extending this series of work, we have carried out kinetic studies of the reactions of *O,O*- diphenyl Z-*S*-phenyl phosphorothiolates with X-pyridines in MeCN at 35.0 °C.



(2)

X = 4-MeO, 4-Me, H, 3-MeO, 4-Ac, 3-Ac
Z = 4-Me, H, 4-Cl, 3-Cl

The purpose of this work is to clarify the mechanism by comparing the reactivities, the selectivity parameters, and the magnitudes of the cross-interaction constants with those obtained in our previous studies.

Results and Discussion

The observed pseudo-first-order rate constants (k_{obsd}) for all the reactions obeyed eq. (3) with negligible k_0 in MeCN. The second-order rate constants, k_2, obtained as the slope of the plot of k_{obsd} against pyridine concentrations, [Py], are summarized in Table 1 along with the selectivity parameters. Clean second-order kinetics according to eq. (3) were obtained with no base-catalysis or noticeable side reactions.

$$k_{obsd} = k_0 + k_2[Py] \quad (3)$$

The second-order rate constants ($k_2 \times 10^3/M^{-1}s^{-1}$) of the aminolyses of diphenyl chlorophosphate [$(PhO)_2P(=O)Cl$],[4h] *O,O*-diphenyl *S*-phenyl phosphorothiolate [$(PhO)_2P(=O)$-SPh], and diphenyl isothiocyanophosphate [$(PhO)_2P(=O)$-

Table 1. Second-Order Rate Constants ($k_2 \times 10^3/M^{-1}s^{-1}$) and Selectivity Parameters[a] for the Reactions of *O,O*-Diphenyl Z-*S*-Phenyl Phosphorothiolates with X-Pyridines in MeCN at 35.0 °C

X \ Z	4-Me	H	4-Cl	3-Cl	ρ_Z[d]	ρ_Z[e,f]
4-MeO	590	1090	513	467	1.57	−1.04
4-Me	183	284	77.8	68.3	1.12	−1.75
H	28.3	44.2	11.0	8.70	1.14	−1.98
3-MeO	17.5	34.8	5.89	3.85	1.76	−2.66
4-Ac	2.63	3.42	2.08	1.60	0.67	−0.90
3-Ac	0.245	0.375	0.231	0.201	1.09	−0.75
$-\rho_X$[b]	4.64	4.76	4.43	4.51	ρ_{XZ}[d,g] = −0.70	ρ_{XZ}[d,h] = +0.76
β_X[c]	0.93	0.95	0.88	0.89		

[a] σ values were taken from ref 6 and pK_a values of pyridines in water at 25 °C were taken from ref 7. [b] Correlation coefficients, r, were better than 0.956. [c] r 0.963. [d] Z = 4-Me and H. [e] Z = H, 4-Cl, and 3-Cl. [f] r 0.955. [g] r = 0.956. [h] r = 0.951.

NCS][4j] with pyridine (C_5H_5N) were 135 at 25.0 °C, 38.8 at 25.0 °C (see Table 3), and 3.02 at 55.0 °C, respectively, in MeCN. This may imply that the sequence of leaving group mobilities is Cl > SPh > NCS. A similar sequence was obtained for the anilinolyses of benzoyl chloride (PhCOCl),[8] k_2 = 81.8 $M^{-1}s^{-1}$ at 35 °C, and *S*-phenyl thiobenzoate (PhCOSPh),[9] k_2 = 0.0174 $M^{-1}s^{-1}$ at 55 °C, in MeOH.

Figure 1 shows the natural bond order (NBO) charges, calculated at the B3LYP/6-311+G(d,p) level,[10] on reaction center P, 2.140 [$(PhO)_2P(=O)SPh$] , 2.230 [$(PhO)_2P(=O)Cl$], and 2.455 [$(PhO)_2P(=O)NCS$]. The NBO charges on reaction center P are consistent with the expectations for the inductive effects of the leaving groups: σ_I values of SPh, Cl, and NCS are 0.31, 0.47, and 0.56, respectively.[11] If the rate is proportional to the positive charge on reaction center P, the rate sequence should be $(PhO)_2P(=O)NCS$ > $(PhO)_2P(=O)Cl$ > $(PhO)_2P(=O)SPh$, inconsistent with the obtained results. These kinetic results imply that the studied reaction system rate does not depend on the magnitude of the positive charge on reaction center P but mainly depend on the leaving group mobility.

In the present work, the rate was faster with a stronger nucleophile, *i.e.*, ρ_X < 0, as normally observed for a typical nucleophilic substitution reaction. However, the Hammett plots for substituent (Z) variations in the leaving group (log k_2 *vs.* σ_Z) were biphasic concave downwards with breaks at Z = H as shown in Figure 2. Moreover, the ρ_Z values were strikingly largely *negative*, ρ_Z = (–0.75 to –2.66), for leaving groups with electron-withdrawing substituents (σ_Z 0; Z = H, 4-Cl and 3-Cl), *i.e.*, a better leaving group retards the rate in contrast to normal nucleophilic substitution reactions. The negative slope (ρ_Z < 0) may imply either development of positive charge or, alternatively, a reduction of negative charge at the S atom of the leaving group, SPhZ, in the TS.

In the case of the reaction of cumyl arenesulfonates [$C_6H_5C(CH_3)_2OSO_2C_6H_4Z$] with X-anilines in MeCN,[12] the ρ_Z values gradually decreased from a positive value to a negative value as the nucleophiles got weaker. This rather unusual phenomenon was rationalized by a strong interaction between the nucleophile and the leaving group due to their close proximity in the TS, which in turn was a result of the frontside nucleophilic attack; thus, a large magnitude ρ_{XZ} (= –0.75) value was obtained. If the reactions proceed through a direct backside displacement, ρ_Z should be positive and cannot have a negative value, in contrast to the large negative ρ_Z value observed. Comparing the present work with the anilinolysis of cumyl arenesulfonates (ρ_{XZ} = –0.75), both reactions have comparably large magnitudes of ρ_{XZ} values (ρ_{XZ} = –0.70 and +0.76 for leaving groups with electron-donating and electron-withdrawing substituents, respectively, in the present work), strongly suggesting frontside nucleophilic attack for the present work.

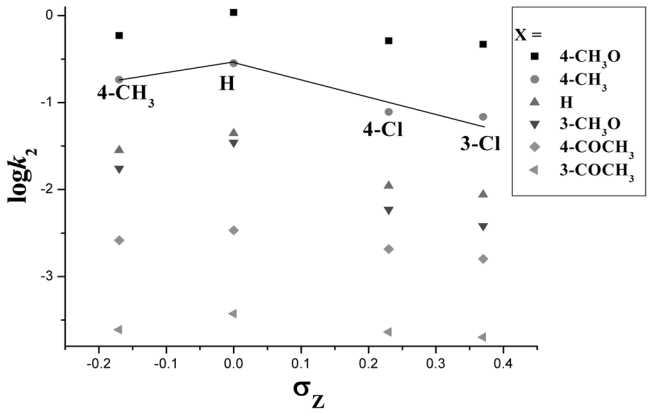


Figure 2. The Hammett plots for the reactions of *O*,*O*-diphenyl Z-*S*-phenyl phosphorothiolates with X-pyridines in MeCN at 35.0 °C.

Selectivity parameters of the reactions of Y-aryl phenyl chlorophosphates, *O*,*O*-diphenyl Z-*S*-phenyl phosphorothiolates, Y-aryl phenyl isothiocyanophosphates, and Z-aryl bis(4-methoxyphenyl) phosphates with X-pyridines in MeCN are summarized in Table 2. The pyridinolysis of Y-aryl phenyl chlorophosphates was proposed to proceed concertedly with an early TS [ap(Nu)-ap(Lg)] in which the extent of both bond formation and leaving group departure is small, based on the small magnitudes of ρ_X (= −0.86 to −1.00) and β_X (= 0.16-0.18), and small negative ρ_{XY} (= –0.15).[4h] In the pyridinolysis of Y-aryl phenyl isothiocyanophosphates,[4j] the Hammett plots were biphasic concave upwards for substituent (X) variations in the nucleophile, interpreted as a change in the direction of nucleophilic attack

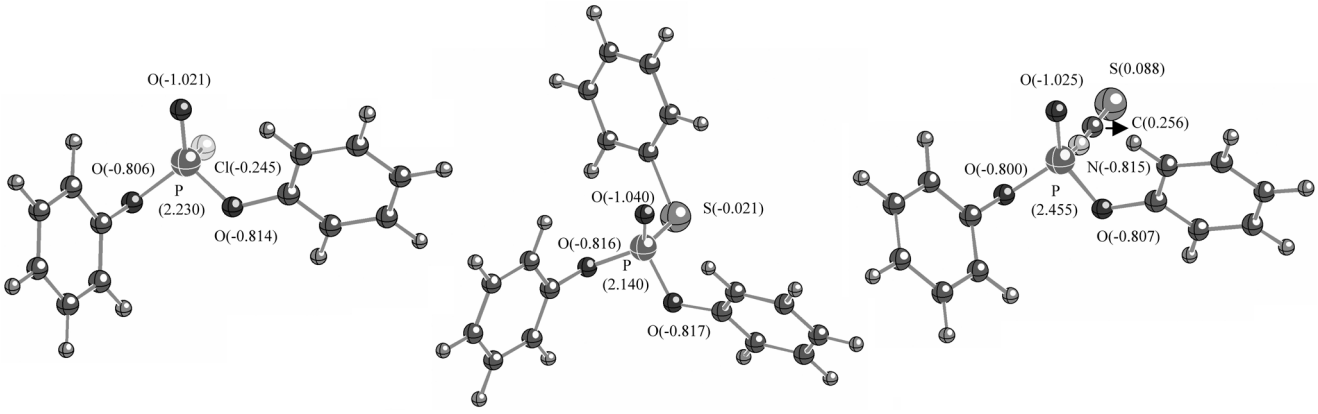


Figure 1. The B3LYP/6-311+G(d,p)[10] geometries and NBO charges of *O*,*O*-diphenyl *S*-phenyl phosphorothiolate [$(PhO)_2P(=O)SPh$], diphenyl chlorophosphate [$(PhO)_2P(=O)Cl$], and diphenyl isothiocyanophosphate [$(PhO)_2P(=O)NCS$] in the gas phase.

Table 2. Summary of Selectivity Parameters for the Reactions of Y-Aryl Phenyl Chlorophosphates, *O,O*-Diphenyl Z-*S*-Phenyl Phosphorothiolates, Y-Aryl Phenyl Isothiocyanophosphates, and Z-Aryl Bis(4-methoxyphenyl) Phosphates with X-Pyridines in MeCN

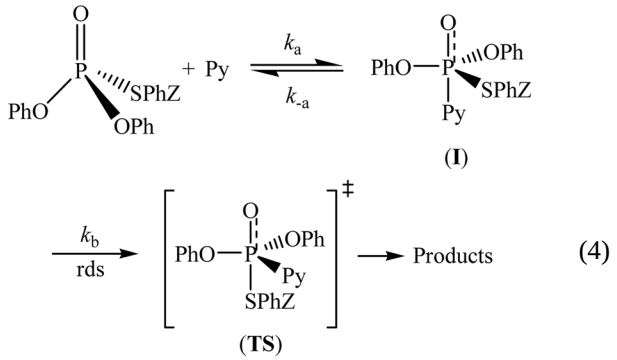
substrate	$-\rho_X$	β_X	ρ_{XY} or ρ_{XZ}	ref
(YPhO)(PhO)P(=O)Cl	0.86-1.00	0.16-0.18	$\rho_{XY} = -0.15$	4h
$(PhO)_2P(=O)SPhZ$	4.43-4.76	0.88-0.95	$\rho_{XZ} = -0.70$[a] $\rho_{XZ} = +0.76$[a]	This work
(YPhO)(PhO)P(=O)NCS	5.38-6.14[b] 0.33-0.90[c]	1.13-1.28[b] 0.08-0.22[c]	$\rho_{XY} = -1.42$,[d] -1.81[e] $\rho_{XY} = +3.16$,[f] $+1.40$[g]	4j
$(4\text{-MeOPhO})_2P(=O)(OPhZ)$	0.53-0.89[h] 1.11-1.96[i]	0.09-0.14[h] 0.22-0.39[i]	$\rho_{XZ} = +0.97$;[j] $+0.18$[k] $\rho_{XZ} = -1.98$,[l] -0.81[m]	4i

[a]See Table 1. [b]X = (4-MeO, 4-Me, 3-Me, H, 3-Ph). [c]X = (3-Ac, 3-Cl, 4-Ac, 4-CN). [d]X = (4-MeO, 4-Me, 3-Me, H, 3-Ph) and Y = (4-MeO, 4-Me, H). [e]X = (4-MeO, 4-Me, 3-Me, H, 3-Ph) and Y = (H, 3-MeO, 4-Cl). [f]X = (3-Ac, 3-Cl, 4-Ac, 4-CN) and Y = (4-MeO, 4-Me, H). [g]X = (3-Ac, 3-Cl, 4-Ac, 4-CN) and Y = (H, 3-MeO, 4-Cl). [h]X = (4-NH_2,4-Me, 4-Bn, 3-Me) and Z = (4-Cl, 3-Cl, 3-CN, 4-CN, 4-NO_2). [i]X = (3-Cl, 3-Ac, 4-Ac, 3-CN, 4-CN) and Z = (4-Cl, 3-Cl, 3-CN, 4-CN, 4-NO_2). [j]X = (4-NH_2,4-Me, 4-Bn, 3-Me) and Z = (4-Cl, 3-Cl, 3-CN). [k]X = (4-NH_2,4-Me, 4-Bn, 3-Me) and Z = (3-CN, 4-CN, 4-NO_2). [l]X = (3-Cl, 3-Ac, 4-Ac, 3-CN, 4-CN) and Z = (4-Cl, 3-Cl, 3-CN). [m]X = (3-Cl, 3-Ac, 4-Ac, 3-CN, 4-CN) and Z = (3-CN, 4-CN, 4-NO_2).

from backside for weaker basic pyridines [smaller magnitudes of ρ_X (= −0.33 to −0.90) and β_X (= 0.08-0.22)] to frontside for stronger basic pyridines [larger magnitudes of ρ_X (= −5.38 to −6.14) and β_X (= 1.13-1.28)]. Biphasic concave downwards Hammett plots for substituent (Y) variations in the substrate are interpreted to indicate a mechanistic change at the breakpoint (Y =H; $\sigma_Y = 0$) from a concerted ($\rho_{XY} < 0$) to a stepwise mechanism with rate-limiting expulsion ($\rho_{XY} > 0$) of the NCS group from a TBP-5C intermediate, based on the sign of ρ_{XY}.[4j] We also reported the reactions of Z-aryl bis(4-methoxyphenyl) phosphates with X-pyridines.[4i] With more basic phenolate leaving groups, the mechanism changes from a concerted process with a frontside nucleophilic attack for less basic pyridines [larger magnitudes of ρ_X (= −1.11 to −1.96), β_X (= 0.28-0.39), and ρ_{XZ} = −1.98] to a stepwise process with rate-limiting formation of a TBP-5C intermediate for more basic pyridines [smaller magnitudes of ρ_X (= −0.53 to −0.89), β_X (= 0.09-0.14), and ρ_{XZ} = 0.97]. With less basic phenolate leaving groups, the reaction proceeds concertedly through a direct backside attack for more basic pyridines [smaller magnitudes of ρ_X (= −0.53 to −0.89), β_X (= 0.09-0.14), and ρ_{XZ} = 0.18], and a frontside attack for less basic pyridines [larger magnitudes of ρ_X (= −1.11 to −1.96), β_X (= 0.28-0.39), and $\rho_{XZ} = -0.81$].[4i]

The obtained ρ_X (= −4.43 to −4.76) and β_X (= 0.88-0.95) in the present work are much larger than those obtained in Z-aryl bis(4-methoxyphenyl) phosphates [ρ_X (= −1.11 to −1.96), β_X (= 0.28-0.39)], and somewhat smaller than those in Y-aryl phenyl isothiocyanophosphates [ρ_X (= −5.38 to −6.14) and β_X (= 1.13-1.28)] for frontside nucleophilic attacks. Thus, there is no doubt that the nucleophile attacks frontside toward the leaving group in the present work.

The anomalous negative sign of ρ_Z values for the leaving groups with electron-withdrawing substituents can be substantiated on the following basis. In the case of the frontside nucleophile attack, the attacking nucleophile occupies the apical position and the leaving group occupies the equatorial position, [ap(Nu)-eq(Lg)], rather than eq(Nu)-ap(Lg) in a TBP-5C intermediate,[13] since pyridine is less bulky than PhO and/or ZPhS. It can undergo an intramolecular ligand exchange process by Berry-type pseudorotation (or turnstile rotation);[14] the nucleophile occupies the equatorial position and the leaving group occupies the apical position, [eq(Nu)-ap(Lg)], in the TS, eq. (4).



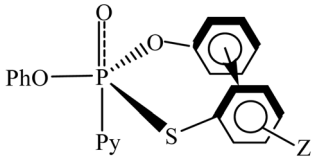
(4)

For the rate-limiting breakdown of intermediate to products, the overall observed second-order rate constant, k_2, can be given as follows:

$$k_2 = (k_a/k_{-a})k_b = Kk_b \ (k_{-a} \gg k_b) \quad (5)$$

$$\rho_Z = (d\log k_2/d\sigma_Z) = (d\log K/d\sigma_Z) + (d\log k_b/d\sigma_Z) \quad (6)$$

The first term on the right-side of eq. (6) is absolutely positive, so the second term should be large and negative in order to obtain the negative sign on the ρ_Z values. When a thiophenolate leaving group with an electron-withdrawing substituent occupies the equatorial position in a TBP-5C intermediate, the π-cloud of the phenyl ring in the "electron-poor" leaving group interacts strongly with the π-cloud of the phenyl ring in the adjacent "electron-rich" phenoxy group by through-space interaction, (**1**). Thus, the π-electron charge transfer from the phenoxy group to the leaving group with electron-withdrawing substituents occurs effectively and the strong through-space interaction stabilizes the intermediate.



1 (Z = electron-withdrawing group)

In contrast, when a thiophenolate leaving group with an electron-withdrawing substituent occupies the equatorial position in the TS by Berry-type pseudorotation (or turnstile rotation) (eq. 5), the through-space interaction between the π-clouds of two phenyl rings no longer exists. If the decrement of the negative charge in the leaving group due to the Berry-type pseudorotation (or turnstile rotation) is sufficiently larger than the negative charge development in the leaving group due to the leaving group departure, then the negative charge of the leaving group is greatly reduced from intermediate to TS. As a result, the second term on the right-side of eq. (6) has a large negative value and the sign of ρ_Z in eq. (6) is negative. This is consistent with rate-limiting expulsion of the leaving group. Thus, when the electron-withdrawing ability of the leaving group is greater, the through-space interaction is stronger, a TBP-5C intermediate is more stabilized, the energy barrier to cross over the TS is greater, the rate is slower, and $\rho_Z < 0$ is obtained. This suggestion is supported by the activation parameters in Table 3. Activation enthalpy (11.0 kcal) for a leaving group with an electron-withdrawing substituent (Z = 4-Cl) is much larger than that (1.1 kcal) for a leaving group with an electron-donating substituent (Z = 4-Me).

In the case of a leaving group with an electron-donating substituent (Z = 4-Me), if the thiophenolate leaving group occupies the equatorial position in the intermediate, the interaction between the π-cloud of the phenyl ring in the "electron-rich" leaving group and the π-cloud of the phenyl ring in the adjacent "electron-rich" phenoxy group by through-space interaction is so unfavorable that a TBP-5C intermediate with ap(NX)-eq(LZ) can be excluded. Thus, we suggest that the reaction for the poor leaving groups (Z = 4-Me-H) proceeds through a concerted mechanism with a frontside nucleophilic attack followed by a fast intramolecular ligand exchange process to yield products.

The sign of ρ_{XZ} can be positive or negative whether the reaction proceeds through a concerted S_N2 mechanism or a stepwise mechanism regardless of the rate-limiting step.[4] However, the magnitude of ρ_{XZ} is inversely proportional to the distance between the nucleophile and the leaving group in the TS regardless of the sign of the cross-interaction constant. The obtained large magnitudes of ρ_{XZ} (= –0.70 and 0.76) are also ascribed to a frontside nucleophilic attack in which the nucleophile and the leaving group occupy close proximity in the TS. The sign reversal of ρ_{XZ} from positive in $\sigma_Z \leq 0$ to negative in $\sigma_Z \geq 0$ may indicate the mechanism change from concerted to stepwise with rate-limiting expulsion of the leaving group.

Table 3. Activation Parameters[a] for the Reactions of *O,O*-Diphenyl Z-*S*-Phenyl Phosphorothiolates with X-Pyridines in MeCN at 35.0 °C

Z	X	Temp /°C	$k_2 \times 10^3$ /$M^{-1}s^{-1}$	$\Delta H^{\neq}$ /kcal mol^{-1}	$-\Delta S^{\neq}$ /cal $mol^{-1}K^{-1}$
4-Me	4-Me	25.0	169	1.1 ± 0.1[b]	59 ± 1
		35.0	183		
		45.0	201		
H	H	25.0	38.8	2.1 ± 0.2	58 ± 1
		35.0	44.2		
		45.0	51.7		
4-Cl	3-Ac	25.0	0.0115	11.0 ± 0.7	40 ± 2
		35.0	0.231		
		45.0	0.395		

[a]Calculated by Eyring equation. [b]Standard deviation.

Experimental Section

Materials. Aldrich GR grade pyridines were used without further purification. HPLC-grade MeCN (water content is less than 0.005%) was used without further purification. *O,O*-Diphenyl Z-*S*-phenyl phosphorothiolates were prepared by the following single step reaction. Diphenyl chlorophosphate was reacted with Z-substituted thiophenol for 6-12 hours in the presence of triethylamine in methylene chloride on an ice bath with constant stirring as reported.[4a] Aldrich GR Grade diphenyl chlorophosphate, substituted thiophenols and triethylamine were used without further purification. The physical constants of the substrates after column chromatography (silicagel/ethylacetate + *n*-hexane) were as follows:

***O,O*-Diphenyl *S*-(4-Methylphenyl) Phosphorothiolate.** Liquid. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.40-7.10 (m, 14H), 2.33 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 120.36-150.29, 20.17; ν_{max} (neat), 3071-3040, 2924, 2876, 1594, 1491, 1285 (P=O str.), 1165 (P-O-Ph), 693 (C-S str.); EI-MS *m/z* 356 (M^+).

***O,O*-Diphenyl *S*-Phenyl Phosphorothiolate.**[16] Liquid. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.17-7.54 (m, 15H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 114.33-150.46; ν_{max} (neat), 3060 (C-H, str. aromatic), 1503, 1496, 1447, 1279 (P=O str.), 1171 (P-O-Ph), 687 (C-S str.); EI-MS *m/z* 343 (M^+).

***O,O*-Diphenyl *S*-(4-Chlorophenyl) Phosphorothiolate.** Liquid. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.19-7.45 (s, 14H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 120.49-150.30; ν_{max} (neat), 3076-3055 (C-H, str. aromatic), 1594, 1491, 1399, 1312 (P=O str.), 1160 (P-O-Ph), 698 (C-S str.); EI-MS *m/z* 376 (M^+).

***O,O*-Diphenyl *S*-(3-Chlorophenyl) Phosphorothiolate.** Liquid. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.22-7.45 (m, 14H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 120.37-150.35; ν_{max} (neat), 3064 (C-H, str. aromatic), 1596, 1499, 1277, 1215 (P=O str.), 1153 (P-O-Ph), 690 (C-S str.); EI-MS *m/z* 376 (M^+).

Kinetic Measurements. Rates were measured conductometrically as described previously.[3] For the present work, [substrate] = 1×10^{-3} M and [Py] = 0.1-0.5 M were used. We tried at least five concentrations of pyridines. Pseudo-first-order rate constant values were the average of three runs that were reproducible within ± 3%.

Calculation. The B3LYP/6-311+G(d,p)[10] geometries and NBO charges of *O,O*-diphenyl *S*-phenyl phosphorothiolate and diphenyl isothiocyanophosphate in the gas phase were calculated by using super computing center IBM system in KISTI.

Product Analysis. *O,O*-Diphenyl *S*-phenyl phosphorothiolate was refluxed with excess 4-acetylpyridine and 4-methoxypyridine for more than 15 half-lives at 35.0 °C in acetonitrile separately. Acetonitrile was evaporated under reduced pressure. Diethylether was then added. An insoluble white product that melted at room temperature was found. The product was washed several times with acetonitrile and isolated with diethylether. The solvent was then removed under reduced pressure. The physical constants were as follows:

$[4\text{-}CH_3CO(NC_5H_4)P(=O)(OC_6H_5)_2]^+SC_6H_5^-$. White gel (mp. 23.0 °C), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.21 (m, 6H), 7.31-7.33 (m, 6H), 7.37-7.38 (m, 1H), 7.48-7.51 (m, 2H), 7.72-7.73 (m, 2H), 8.80-8.82 (d, 2H), 2.64 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 118-189 (aromatic-C, 23C, w), 189.07 (–C=O, 1C, w), 24.31 (CH_3, 1C, s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.21 (1P, s).

Acknowledgements. This work was supported by Inha University Research Grant.

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