Pyridinolysis of *O*-Aryl Phenylphosphonochloridothioates in Acetonitrile

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The kinetics and mechanism of the reactions of Y-*O*-aryl phenylphosphonochloridothioates with X-pyridines are investigated in acetonitrile at 35.0 °C. The negative value of the cross-interaction constant, $\rho_{XY} = -0.46$, indicates that the reaction proceeds by concerted S_N2 mechanism. The observed k_H/k_D values involving *d*-5 pyridine (C_5D_5N) nucleophiles are greater than unity (1.05-1.11). The net primary deuterium kinetic isotope effects, $(k_H/k_D)_{net}$ = 1.28-1.35, excluding the increased pK_a effect of *d*-5 pyridine are obtained. The transition state with a hydrogen bond between the leaving group Cl and the hydrogen (deuterium) atom in the C-H(D) is suggested for the studied reaction system.

Key Words : *O*-Aryl phenylphosphonochloridothioates, Pyridinolysis, Cross-interaction constant, Deuterium kinetic isotope effect

Introduction

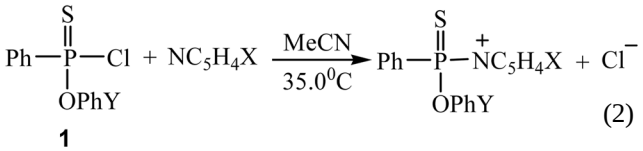
The kinetics and mechanism of phosphoryl transfer reactions have long been of interest. The nucleophilic substitution reactions of tetracoordinate phosphorus proceed mainly *via* two types of mechanism: (i) stepwise *via* a trigonal bipyramidal pentacoordinate (TBP-5C) intermediate and (ii) concerted *via* a TBP-5C transition state (TS).[1]

In our preceding papers,[2] we reported various aminolyses of phosphate derivatives and proposed a reaction mechanism mainly based on the deuterium kinetic isotope effects (KIEs) and the cross-interaction constants[3] ρ_{XY} in eqs. (1) where X and Y are the substituents in the nucleophiles and substrates, respectively.

$$\log(k_{XY}/k_{HH}) = \rho_X\sigma_X + \rho_Y\sigma_Y + \rho_{XY}\sigma_X\sigma_Y \quad (1a)$$

$$\rho_{XY} = \rho_X/\sigma_Y = \rho_Y/\sigma_X \quad (1b)$$

To extend this series of work, we have carried out kinetic studies of the reactions of Y-*O*-aryl phenylphosphonochloridothioates (**1**) with X-pyridines in MeCN at 35.0 °C, as shown by eq. (2). The purpose of this work is to clarify the mechanism by comparing the reactivities, the selectivity parameters, and the KIEs involving deuterated (*d*-5) pyridine (C_5D_5N) with those obtained in our previous studies.



1 (2)

X = 4-Me, 4-Bn, 3-Me, H, 3-MeO, 3-Ac
Y = 4-MeO, 4-Me, H, 3-Cl, 4-CN

Results and Discussion

The observed pseudo-first-order rate constants (k_{obsd}) for all the reactions obeyed eq. (3) with negligible k_o in MeCN.

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

X\Y	4-MeO	4-Me	H	3-Cl	4-CN	ρ_Y[d]
4-Me	85.5	99.6	106	152	195	0.38
4-Bn	40.6	43.2	46.8	61.9	80.6	0.32
3-Me	24.7	25.7	27.5	36.8	47.8	0.31
H	9. 28	10.4	11.2	14.4	17.5	0.29
3-MeO	3.82	4.31	4.64	5.77	6.57	0.24
3-Ac	0.339	0.351	0.369	0.392	0.438	0.11
$-\rho_X$[b]	4.35	4.39	4.40	4.62	4.75	ρ_{XY}[e] = −0.46
β_X[c]	0.87	0.88	0.88	0.93	0.95	

[a]σ values were taken from ref 4 and pK_a values of pyridines in water at 25 °C were taken from ref 5. [b]Correlation coefficients, r, were better than 0.994. [c]r ≥ 0.988. [d]r ≥ 0.988. [e]r = 0.990.

The second-order rate constants, k_2, obtained as the slope of the plot of k_{obsd} against pyridine concentrations, [X-Py], are summarized in Table 1 together with the selectivity parameters.

$$k_{obsd} = k_o + k_2[\text{X-Py}] \quad (3)$$

The rate was faster with a stronger nucleophile, $\rho_X < 0$, and also with a stronger electron-withdrawing substituent in the substrate, $\rho_Y < 0$, as normally observed for typical nucleophilic substitution reactions. The second-order rate constants ($k_2 \times 10^3/M^{-1}s^{-1}$) of the aminolyses of *O*-phenyl phenylphosphonochloridothioate [**1** with Y = H: (PhO)-PhP(=S)Cl] and diphenyl thiophosphinic chloride [**2**: Ph_2P-(=S)Cl] with pyridine (C_5H_5N), in MeCN at 35.0 °C, were 11.2 and 1.83,[2d] respectively (see Table 2). Figure 1 shows the natural bond order (NBO) charges and the geometries, calculated at the B3LYP/6-311+G(d,p) level.[6] The NBO charge on the reaction center P is 1.462 in **1** (with Y = H), and 1.236[2d] in **2**. These values are consistent with the expectations for the inductive effects of the ligands: the σ_I values of PhO and Ph are 0.40 and 0.12, respectively.[7] At a

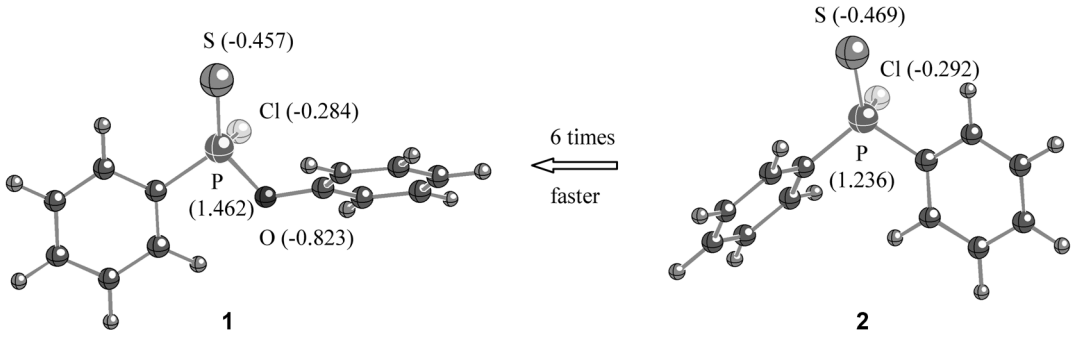


Figure 1. The B3LYP/6-311+G(d,p)[6] geometries and NBO charges of *O*-phenyl phenylphosphonochloridothioate [**1** with Y = H: (PhO)PhP(=S)Cl] and diphenyl thiophosphinic chloride [**2**: $Ph_2P(=S)Cl$][2d] in the gas phase.

glance, the reaction rates seem to be proportional to the positive charge on the reaction center P. However, it is well known that phosphoryl transfer reaction rates (especially for P=O systems) are strongly affected by steric hindrance.[2k,8] The P=O substrates are generally more reactive than their P=S counterparts for several reasons, the so-called "thio effect", which is mainly the electronegativity difference between O and S, favoring O over S.[1e,9] Further systematic investigation will clarify the major factor determining the reactivity of the studied reaction series (P=S systems).

The selectivity parameters of the reactions of **1**, **2**, **3** [diphenyl phosphinic chloride: $Ph_2P(=O)Cl$],[2d] and **4** [Y-aryl phenyl chlorophosphates: (YPhO)(PhO)P(=O)Cl][2a] with X-pyridines in MeCN are summarized in Table 2. In the case of the pyridinolysis of **2**, the Hammett and Brönsted plots are biphasic concave upwards with the breakpoint at 3-phenyl pyridine, which indicates a change in mechanism from a concerted S_N2 process with direct backside nucleophilic attack for less basic nucleophiles (X = 3-CN, 4-CN, 4-Ac, 3-Ac, 3-Cl, 3-MeO, and 3-Ph; $\rho_X = -2.28$ and $\beta_X = 0.38$) to a stepwise process with frontside attack for more basic nucleophiles (X = 4-MeO, 4-Me, 3-Me, H, and 3-Ph; $\rho_X = -7.84$ and $\beta_X = 1.53$).[2d] A concerted mechanism with backside nucleophilic attack is proposed for the pyridinolysis of **3** on the basis of the linear Brönsted plot with the β_X value of 0.68.[2d] The ρ_X (= −4.35 to −4.75) and β_X (= 0.87-0.95) obtained in the present study of **1** are somewhat larger than those obtained for **3** ($\rho_X = -3.86$ and $\beta_X = 0.68$) but are much smaller than those obtained for **2** with more basic nucleophiles ($\rho_X = -7.84$ and $\beta_X = 1.53$). The negative ρ_{XY} (= −0.46: Figure 2) for **1** implies that the reaction proceeds through a concerted S_N2 mechanism.[3] The magnitude of ρ_{XY} is inversely proportional to the distance between X and Y in the transition state (TS) for a concerted S_N2 mechanism.[3] We proposed an early TS for the pyridinolysis of **4** on the basis of considerably small values of ρ_X (= −0.86 to −1.00), β_X (= 0.16-0.18), and ρ_{XY} (= −0.15).[2a] Taking into account the greater values of ρ_{XY} (= −0.46), ρ_X, and β_X for **1** than for **4**, we can suggest that **1** has a later TS than **4** and, as a result, the TS of **1** has a greater extent of bond formation than that of **4**.

The observed KIEs, $(k_H/k_D)_{obsd}$, of the pyridinolysis of **1** with *d*-5 pyridine (C_5D_5N) are summarized in Table 3. The $(k_H/k_D)_{obsd}$ values of **1** are greater than unity (1.05-1.11),

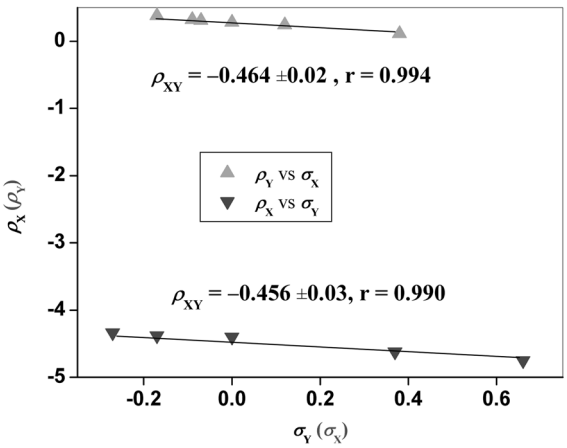


Figure 2. The ρ_{XY} (= $\partial\rho_X/\partial\sigma_Y = \partial\rho_Y/\partial\sigma_X$) plot of ρ_X *vs* σ_Y and ρ_Y *vs* σ_X for the reactions of Y-*O*-aryl phenylphosphonochloridothioates with X-pyridines in MeCN at 35.0 °C.

Table 2. Summary of Second-Order Rate Constants (k_2/M^{-1} s^{-1}), Deuterium Kinetic Isotope Effects (k_H/k_D involving *d*-5 Pyridine) and Selectivity Parameters for the Reactions of Y-*O*-Aryl Phenylphosphonochloridothioates [**1**: (YPhO)PhP(=S)Cl], Diphenyl Thiophosphinic Chlorides [**2**: $Ph_2P(=S)Cl$], Diphenyl Phosphinic Chlorides [**3**: $Ph_2P(=O)Cl$)], and Y-Aryl Phenyl Chlorophosphates [**4**: (YPhO)(PhO)-P(=O)Cl] with X-Pyridines in MeCN

substrate	$k_2 \times 10^3$[a]	$(k_H/k_D)_{obsd}$	$-\rho_X$	β_X	ρ_{XY}	ref
1	11.2[b]	1.05-1.11	4.34-4.75	0.87-0.95	−0.46	this work
2	1.83[c]	0.83[c]	7.84[d]/2.28[e]	1.53[d]/0.38[e]	–	2d
3	54.6[c]	0.78[c]	3.86	0.68	–	2d
4	266[b]	–	0.86-1.00	0.16-0.18	−0.15	2a

[a]At 35.0 °C. [b]X = Y = H. [c]X = H. [d]X = (4-MeO, 4-Me, 3-Me, H, 3-Ph). [e]X = (3-Ph, 3-MeO, 3-Cl, 3-Ac, 4-Ac, 4-CN, 3-CN).

Table 3. Deuterium Kinetic Isotope Effects (k_H/k_D) for the Reactions of Y-*O*-Aryl Phenylphosphonochloridothioates with *d*-5 Pyridine (C_5D_5N) in MeCN at 35.0 °C

Y	k_H ($\times 10^3/M^{-1}s^{-1}$)	k_D ($\times 10^3/M^{-1}s^{-1}$)	$(k_H/k_D)_{obsd}$	$(k_H/k_D)_{expd}$	$(k_H/k_D)_{net}$ [b]
4-MeO	9.28 ± 0.05	8.50 ± 0.07	1.09 ± 0.01[a]	0.82	1.33
4-Me	10.4 ± 0.09	9.88 ± 0.17	1.05 ± 0.02	0.82	1.28
H	11.2 ± 0.2	10.1 ± 0.1	1.11 ± 0.02	0.82	1.35
3-Cl	14.4 ± 0.2	13.6 ± 0.1	1.06 ± 0.02	0.81	1.31
4-CN	17.5 ± 0.1	16.5 ± 0.1	1.06 ± 0.01	0.80	1.33

[a]Standard error {$= 1/k_D[(\Delta k_H)^2 + (k_H/k_D)^2 \times (\Delta k_D)^2]^{1/2}$}.[12] [b]Net deuterium kinetic isotope effect.

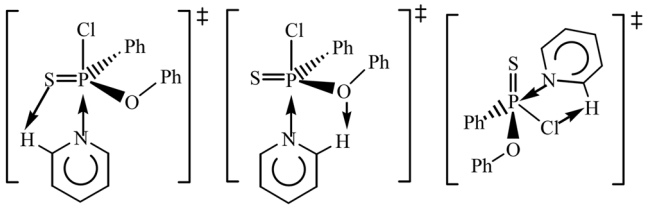
while those of **2** and **3** are less than unity (0.83 and 0.78, respectively).[2d] Perrin and his coworkers reported that the basicities of β-deuterated analogs of benzylamine, *N*,*N*-dimethylaniline and methylamine increase roughly by 0.02 pK_a units per deuterium, and that these effects are additive.[8] For the five deuterium atoms in *d*-5 pyridine, this gives an expected ΔpK_a of approximately +0.1 unit. For Y = H in **1**, considering the β_X value of 0.88, then

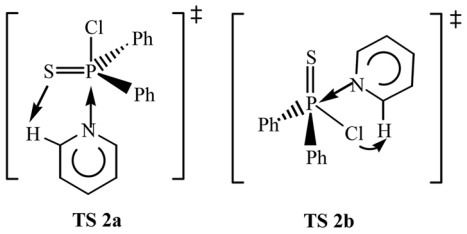
$$\log (k_H/k_D)_{expd} = -(\beta_X \times \Delta pK_a) = -(0.88 \times 0.1) = -0.088$$
$$\text{or } (k_H/k_D)_{expd} = 0.82 \quad (4)$$

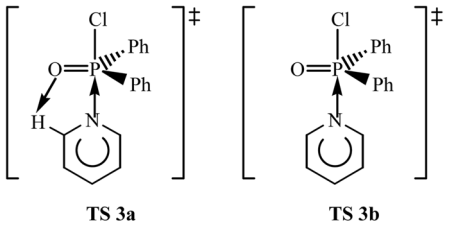
and the expected k_D value of *d*-5 pyridine is $k_{D,expd} = k_H/0.817 = 11.2 \times 10^{-3}/0.817 = 13.7 \times 10^{-3}$. However, the observed $k_{D,obsd}$ value of *d*-5 pyridine is 10.1×10^{-3} and the $(k_H/k_D)_{obsd}$ value is 1.11. Thus, the *net* deuterium KIE *excluding* the increased pK_a effect of *d*-5 pyridine for Y = H in **1**can be expressed as eq. (5).

$$(k_H/k_D)_{net} = (k_H/k_D)_{obsd}/(k_H/k_D)_{expd} = 1.11/0.82 = 1.35 \quad (5)$$

The $(k_H/k_D)_{net}$ value of **3** is less than unity, $(k_H/k_D)_{obsd}/(k_H/k_D)_{expd} = 0.78/0.85 = 0.92$ [larger than $(k_H/k_D)_{obsd} = 0.78$, but still less than unity],[2d] whereas those of **1** [$(k_H/k_D)_{obsd}/(k_H/k_D)_{expd}$ = 1.28-1.35: see Table 3] and **2** [$(k_H/k_D)_{obsd}/(k_H/k_D)_{expd} = 0.83/0.70 = 1.19$][2d] are greater than unity. The net KIE of less than unity, $(k_H/k_D)_{net} < 1$, implies a secondary inverse KIE while the net KIE of greater than unity, $(k_H/k_D)_{net} > 1$, implies a primary KIE.[10] The secondary inverse KIE is attributed to the increase of the out-of-plane bending vibrational frequencies of the C–H(D) bonds in the TS because of steric congestion of the hydrogen (deuterium) atom in the C–H(D) moiety in the bond-making step[11] as occuring in the pyridinolysis of **3** [$(k_H/k_D)_{net}$ = 0.92]. The primary KIE suggests that partial deprotonation of pyridine occurs by hydrogen bonding in the rate-determining step as occuring in the pyridinolysis of **1** [$(k_H/k_D)_{net}$ = 1.28-1.35] and **2** [$(k_H/k_D)_{net}$ = 1.19]. The real primary KIE would be larger than that obtained $(k_H/k_D)_{net}$, taking into account the secondary inverse KIE because of steric hindrance. The extent of hydrogen bond formation in TS would be greater for **1** than for **2**, since the magnitude of $(k_H/k_D)_{net}$ of **1** is greater than that of **2**. Thus, we can suggest the following possible TS structures of the pyridinolysis of **1**, **2**, and **3**.







The structure of **TS 3b** is attributed to backside nucleophilic attack resulting in the secondary inverse KIE [$(k_H/k_D)_{net}$ = 0.92] due to steric congestion of the hydrogen (deuterium) atom in the C–H(D) moiety. If a hydrogen bond between the P=O oxygen atom and the hydrogen (deuterium) atom in the C–H(D) moiety (**TS 3a**) is present, the primary normal KIE [$(k_H/k_D)_{net} > 1$] should result. Thus, considering the much greater electronegativity of the oxygen of P=O than the sulfur of P=S, a hydrogen bond between the sulfur of P=S and the hydrogen (deuterium) in the C–H(D) moiety in **TS 1a** and **TS 2a** would not be plausible. The structure of **TS 2b** is in line with the frontside nucleophilic attack that we proposed in an earlier paper.[2d] We can suggest that the primary KIE, $(k_H/k_D)_{net}$ = 1.19 in **2**, is attributed to the hydrogen bond between the leaving group Cl and the hydrogen (deuterium) atom in the C–H(D). Therefore, a plausible TS structure of the pyridinolysis of **1** could be **TS 1c** with the hydrogen bond between the leaving group Cl and the hydrogen (deuterium) atom in the C–H(D) moiety, the same as in **2**. However, at this point, **TS 1b** cannot be fully

neglected and further systematic work of P=S systems will clearly elucidate the reaction mechanism.

Experimental Section

Materials. GR grade pyridines, deuterated pyridine (C_5D_5N; 99 atom% D) and. HPLC-grade MeCN (water content is less than 0.005%) were used without further purification. The substrates, Y-*O*-Aryl Phenylphosphonochloridothioates, were prepared by the following single-step reaction. The equimolar starting materials of phenylthiophosphonic dichloride, substituted phenols, and triethyl amine were mixed and stirred in methylene chloride solvent for 2 hrs, all kept in an ice bath. GR grade phenylthiophosphonic dichloride (TCI, Japan), substituted phenols, and triethylamine (Aldrich) were used without further purification. The physical constants of the substrates were as follows:

***O*-(4-Methoxyphenyl) phenylphosphonochloridothioate.**[13] White solid; mp 48-50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ8.15 (dd, J = 16.7, 7.0 Hz, 2H), 7.68-7.62 (m, 1H), 7.59-7.54 (m, 2H), 7.26-7.21 (m, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H, OCH_3,); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4 (d, J = 2.2 Hz), 143.1 (d, J = 11.3 Hz), 135.1 (d, $J_{P\text{-}C}$ = 140.2 Hz), 133.3 (d, J = 3.8 Hz), 130.7 (d, J = 12.9 Hz), 128.5 (d, J = 16.7 Hz), 122.5 (d, J = 5.3 Hz), 114.5 (d, J = 1.5 Hz), 55.6 (s, OCH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ91.4 (s, 1P); IR (KBr, cm^{-1}) 3062 (C-H, aromatic), 2952 (-CH_3 Asym), 2839 (-CH_3 Sym), 1503 (C=C, Ar), 1441 (P-C, Ar), 1252, 1183, (P-O-C_6H_4), 832 (P=S); GCMS: m/z, 298 (M^+); Anal. Calcd for $C_{13}H_{12}O_2PSCl$: C, 52.27; H, 4.05; S, 10.73. Found: C, 52.35; H, 4.11; S, 10.87.

***O*-(4-Methylphenyl) phenylphosphonochloridothioate.**[14] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ8.15 (dd, J = 17.2, 7.2 Hz, 2H), 7.66-7.60 (m, 1H), 7.57-7.52 (m, 2H), 7.26-7.14 (m, 4H), 2.36 (s, 3H, CH_3,); ^{13}C NMR (100 MHz, $CDCl_3$) 147.4 (d, J = 12.1 Hz), 135.7 (d, J = 2.3 Hz), 135.1 (d, $J_{P\text{-}C}$ = 140.2 Hz), 133.2 (d, J = 3.8 Hz), 130.6 (d, J = 12.8 Hz), 130.1 (d, J = 2.3 Hz), 128.5 (d, J = 16.7 Hz), 121.2 (d, J = 5.3 Hz), 20.8 (s, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$) δ90.7 (s, 1P); IR (neat, cm^{-1}) 3056 (C-H, aromatic), 2920 (-CH_3 Asym), 2858 (-CH_3 Sym), 1503 (C=C, Ar), 1439 (P-C, Ar), 1385, 1191 (P-O-C_6H_4), 821 (P=S); GCMS: m/z, 282 (M^+); Anal. Calcd for $C_{13}H_{12}OPSCl$: C, 55.23; H, 4.28; S, 11.34, Found: C, 55.42; H, 4.38; S, 11.24.

***O*-Phenyl phenylphosphonochloridothioate.**[15] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ8.16 (dd, J = 16.6, 7.4 Hz, 2H), 7.68-7.60 (m, 1H), 7.57-7.52 (m, 2H), 7.41-7.26 (m, 5H), ^{13}C NMR (100 MHz, $CDCl_3$) 149.8 (d, J = 11.4 Hz), 135.2 (d, $J_{P\text{-}C}$ = 140.3 Hz), 133.4 (d, J = 2.2 Hz), 130.7 (d, J = 12.8 Hz), 129.6 (s), 128.6 (d, J = 16.7 Hz), 126.1 (s), 121.6 (d, J = 5.3 Hz); ^{31}P NMR (162 MHz,$CDCl_3$) δ90.3 (s, 1P); IR (neat, cm^{-1}) 3061 (C-H, Ar), 1494 (C=C, Ar), 1444 (P-C, Ar), 1196, 1124, (P-O-C_6H_4), 791 (P=S); GCMS: m/z, 268 (M^+); Anal. Calcd for $C_{12}H_{10}OPSCl$: C, 53.64; H, 3.75; S, 11.93, Found: C, 53.85; H, 3.91; S, 11.83.

***O*-(3-Chlorophenyl) phenylphosphonochloridothioate.** Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ8.12 (dd, J = 16.6, 6.0 Hz, 2H), 7.65-7.62 (m, 1H), 7.58-7.52 (m, 2H), 7.33-7.29 (m, 2H), 7.25-7.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 149.9 (d, J = 11.4 Hz), 134.8 (d, J = 2.3 Hz), 134.7 (d, $J_{P\text{-}C}$ = 140.3 Hz), 133.5 (d, J = 3.8 Hz), 130.6 (d, J = 12.9 Hz), 130.2 (d, J = 1.5 Hz), 128.6 (d, J = 16.6 Hz), 126.3 (d, J = 2.3 Hz), 122.2 (d, J = 5.3 Hz), 120.0 (d, J = 5.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 90.5 (s, 1P); IR (neat, cm^{-1}) 3063 (C-H, aromatic), 1585 (C=C, Ar), 1474 (P-C, Ar), 1198, 1112, (P-O-C_6H_4), 865 (P=S); GCMS: m/z, 302 (M^+); Anal. Calcd for $C_{12}H_9OPSCl_2$: C, 47.54; H, 2.99; S, 10.58, Found: C, 47.61; H, 3.08; S, 10.61.

***O*-(4-Cyanophenyl) phenylphosphonochloridothioate.**[16] White solid; mp, 100-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, J = 16.2, 7.9 Hz, 2H), 7.72 (d, J = 8.8 Hz, 2H), 7.69-7.67 (m, 1H), 7.62-7.57 (m, 2H), 7.44 (dd, J = 7.8, 3.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 152.7 (d, J = 11.4 Hz), 134.3 (d, $J_{P\text{-}C}$ = 140.3 Hz), 133.82-133.72 (3 peaks for 2C), 130.6 (d, J = 14.4 Hz), 128.7 (d, J = 17.5 Hz), 122.7 (d, J = 5.3 Hz), 117.9 (d, J = 1.5 Hz), 110.0 (CN); ^{31}P NMR (162 MHz, $CDCl_3$) δ90.3 (s, 1P); IR (KBr, cm^{-1}) 3090 (C-H, aromatic), 2232 (C≡N),1493 (C=C, Ar), 1439 (P-C, Ar), 1202, 1165, 1115 (P-O-C_6H_4), 850, (P=S); GCMS: m/z, 293 (M^+); Anal. Calcd for $C_{13}H_9ONPSCl$: C, 53.15; H, 3.09; S, 10.92, N, 4.77. Found: C, 52.74; H, 3.09; S, 11.44, N, 4.51.

Product analysis. *O*-Phenyl phenylphosphonochloridothioates was refluxed with excess 3-acetylpyridine for more than 15 half-lives at 35.0 °C in acetonitrile. Solvent was evaporated under reduced pressure. Diethyl ether was then added. An insoluble pale yellow gummy product was found. The product was washed several times with diethyl ether and thus isolated. The solvent was then removed under reduced pressure. The physical constants were as follows:

[3-$CH_3CO(NC_5H_4)P(=S)(OC_6H_5)(C_6H_5)]^+Cl^-$. Yellowish gummy substance; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.86 (d, J = 5.2 Hz, 1H), 8.45 (d, J = 7.6Hz, 1H), 8.07 (dd, J = 14.4, 7.6 Hz, 2H), 7.62-7.61 (m, 1H), 7.50-7.42 (m, 3H), 7.24-7.05 (m, 5H), 2.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ194.0 (–C=O, 1C), 151.3 (d, J = 10.0 Hz), 148.2, 145.2, 140.4, 135.9(d, $J_{P\text{-}C}$= 149.0 Hz), 133.7, 131.6 (d, J = 14.0 Hz), 130.9 (d, J = 12.2 Hz), 129.2 (d, J = 27.3 Hz), 128.1 (d, J = 22.4 Hz), 125.7, 124.4 (d, J = 2.5 Hz), 122.0 (d, J = 3.8 Hz), 26.0 (CH_3, 1C, s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 81.7 (1P, s); IR (KBr, cm^{-1}) 3064 (C-H, aromatic), 2930, 2867 (-CH_3), 1704 (C=O), 1491, 1442 (P-C, Ar), 1210, 1136 (P-O-C_6H_4), 714 (P=S); HRMS-EI m/z, M^+ Calcd. for positive ion, $C_{19}H_{17}O_2PSN^+$: 354.0718, Found: 354.0730.

Kinetic measurements. Conductometric rate measurements were carried out using self-made computer-aided automatic A/D converter conductivity bridges. The pseudo-first-order rate constants, k_{obsd}, were determined as previously described[2] using large excesses of nucleophiles, [Substrate] = 1×10^{-4} M, [X-Pyridine] = 0.05-0.13 M. The second-order rate constants, k_2, were also obtained as previously described[2] with at least five different concentrations of pyridine of more than two runs and were reproducible to within ± 3%.

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