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Pyrimidin-/Thiazol-/Thiazolin-ylidenamidothiophosphoric Dichlorides

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ABSTRACT: *Nine new amidodichlorothiophosphorus(V) derivatives incorporating pyrimidine, thiazole, and thiazoline rings were obtained by sulfurization of the corresponding aminodichlorophosphines generated in situ from the reaction of the respective N-alkyl-2-aminocycloiminium halide with PCl_3 in the presence of triethylamine. These pyrimidin-/thiazol-/thiazolin-ylidenamidothiophosphoric dichlorides were isolated as stable crystalline solids and are well characterized by elemental analysis, NMR, and mass spectroscopy.*
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INTRODUCTION

Dichlorothiophosphorus(V) derivatives have found a significant place in literature [1] as versatile synthons for obtaining a wide variety of important organophosphorus compounds ranging from deoxynucleoside/nucleotide esters [2–4], phosphorus containing crown ethers [5,6], functionalized phosphorus macrocycles [7], dithioxo-λ^5-phosphorane [8], thiophosphoramide esters having flame retardant properties [9] to the compounds having insecticidal and nematocidal properties [10–13]. A number of methods for the sulfurization of dichlorophosphorus(III) compounds to form dichlorothiophosphorus(V) compounds are available in literature. Elemental sulfur has been used in solution, or in a sealed tube at temperature above 100°C, for the sulfurization of dichlorophosphites to give dichlorothiophosphates [14–16]. The sulfurization of *N*-dichlorophosphinotriphenylphosphazene has been achieved by treatment with elemental sulfur [17]. The sulfurization of alkylphosphonous dichloride with elemental sulfur has been carried out in an exothermic reaction in the presence of anhydrous aluminium chloride as catalyst [18]. The oxidation of bisdichlorophosphinylphenylamine has also been carried out by the addition of sulfur in the presence of aluminium chloride at 150°C [19]. However, during the sulfurization of cycloalkanephosphonic acid dichloride, quantitative yields could be obtained by using Sn(IV) or Ti(IV) chloride as a catalyst in place of aluminium chloride [20,21]. In some cases, for the oxidation of dichlorophosphites, thiophosphoryl chloride at 125–155°C [22] or sulfur monochloride at 15–20°C have been used as sulfurizing agent [23]. In an isomerization reaction, dichlorothiophosphites have been converted into thiophosphonic acid dichlorides by heating at ~300°C [24–27].

Recently we have developed a facile method for the preparation of *N*-alkylcycloiminylidenaminodichlorophosphines from the reaction of *N*-alkyl-2-aminocycloiminium halides with phosphorus trichloride in the presence of triethylamine [28–30]. We now report the sulfurization of these precursors with elemental sulfur at room temperature, leading to cycloiminylidenamidothiophosphoric dichlorides. These compounds can be used as synthons for preparing amidothiophosphate

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derivatives, which are expected to be potential pesticides.

RESULTS AND DISCUSSION

N-Alkyl-2-aminopyrimidin(thiazol/thiazolin)ium halides **1** react with 1 equivalent of phosphorus trichloride and 2 equivalents of triethylamine at 0–5°C in methylene chloride to generate the corresponding aminodichlorophosphines **2** ($\delta^{31}P = 146–192$) [29,30]. The intermediate pyrimidinylidenaminodichlorophosphines **2a–d** have been isolated for the first time. The reaction was completed in 4–6 h as revealed by disappearance of the ^{31}P NMR signal for phosphorus trichloride in the reaction mixture. Thereafter, the oxidation of **2** with elemental sulfur at ambient temperature afforded the corresponding cycloiminylidenamidothiophosphoric dichlorides **3** in good yields (Scheme 1).

In case of **1a–d**, the intermediate pyrimidinylidenaminodichlorophosphines **2a–d** were isolated by carrying out the reaction in toluene. Cycloiminylidenamidothiophosphoric dichlorides **3a–h** were obtained as creamish white to pale yellow, crystalline, sharp melting solids, stable under nitrogen atmosphere, except **3i** which was obtained as syrupy mass.

All the products have been well characterized by elemental analysis, NMR spectroscopy (Table 1), and mass spectrum in one case (**3c**).

^{31}P NMR

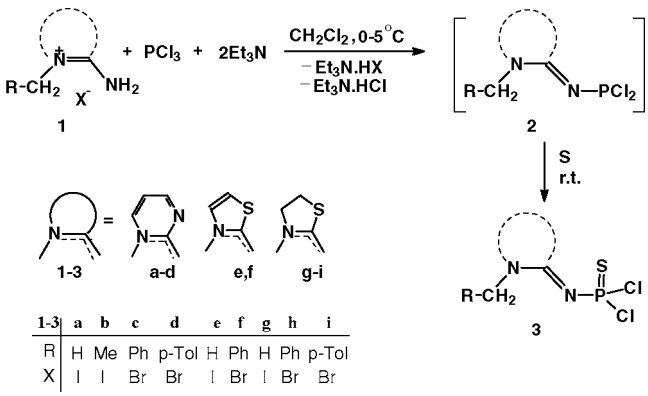
The ^{31}P NMR chemical shift of **2a–d** at δ 179–192 is in the range characteristic for halophosphine derivatives [31]; however, in comparison to other reported analogous aminodichloropshosphine derivatives [28–30] the phosphorus is much deshielded because of the presence of one additional iminium ring nitrogen in the conjugative position. ^{31}P NMR signal of the cycloiminylidenamidothiophosphoric dichlorides **3a–i** appears at δ 50.6–68.9, the range for a four-coordinate, pentavalent phosphorus [32].

^{1}H NMR

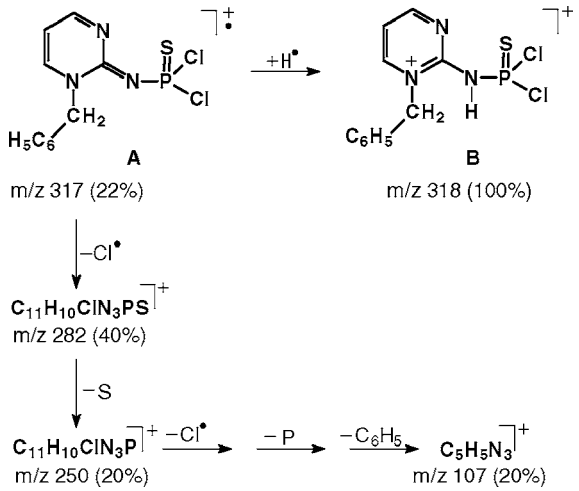
The structures of the cycloiminylidenaminodichlorophosphines **2a–d** and of the cycloiminylidenamidothiophosphoric dichlorides **3a–i** are confirmed by ^{1}H NMR studies (Table 1). As compared to that in **1a–d**, the *N*-methylene or methyl protons in **2a–d** become shielded by $\Delta\delta$ 0.13–0.41 ppm as a result of dichlorophosphinylation. However, sulfurization of phosphorus of **2** does not cause any remarkable shielding effect on $N{-}CH_2/CH_3$ protons in **3**.

Mass Spectrum

The mass spectrum of one representative **3c** has been recorded where, in accordance with the nitrogen rule, the molecular ion peak is observed at *m/z* 317 (22%). However, the (M + 1) peak (*m/z* 318) forms the base peak in the spectrum because of the possible acceptance of one proton by iminium nitrogen to give more stable species **B** (Scheme 2). This peak is accompanied by (M + 1) + 2 (*m/z* 320, 70%) and (M + 1) + 4 (*m/z* 322, 14%) peaks, consistent with the presence of two chlorine atoms. Initial fragmentation takes place by the loss of one chlorine atom from the molecular ion, when the fragment ion (*m/z* 282, 40%) having one chlorine atom is accompanied by the +2 peak (*m/z* 284, 16%). During further fragmentation, loss of sulfur atom (*m/z* 250, 20%) is favored over the loss of second chlorine atom.



SCHEME 1



SCHEME 2 Mass spectral fragmentation of **3c**.

TABLE 1 Physical and NMR Data of Compounds **2** and **3**

	mp (°C)	*Yield (%)*	*Mol. Formula (mol. wt.)*	*Found %*[a]			$\delta^{31}P$ *(CDCl₃)*	$\delta^{1}H$; *J (Hz)*[b]
				C	*H*	*N*		
2a	Syrupy		$C_5H_6Cl_2N_3P$ (210.01)	–	–	–	179.0	3.23 (s, 3H, NCH_3), 7.10–7.40 (m, 3H, H-4, H-5 & H-6)
2b	140–142	65	$C_6H_8Cl_2N_3P$ (224.03)	32.02 (32.16)	3.35 (3.59)	18.45 (18.75)	179.0	1.52 (t, 3H, $^3J_{HH} = 7.1$, NCH_2CH_3); 4.21 (q, 2H, $^3J_{HH} = 7.1$, NCH_2CH_3); 6.81 (dd, 1H, $^3J_{HH} = 7.1$, 4.3, H-5); 7.95 (ddd, 1H, $^3J_{HH} = 7.1$, $^4J_{HH} = 3.5$, $^5J_{PH} = 2.1$, H-6); 8.86 (unresolved dd, 1H, H-4)
2c	128–129	70	$C_{11}H_{10}Cl_2N_3P$ (286.09)	46.10 (46.17)	3.41 (3.52)	14.52 (14.68)	191.8	5.38 (s, 2H, NCH_2), 6.80 (dd, 1H, $^3J_{HH} = 5.7$, 4.3, H-5); 7.47 (s, 5H, C_6H_5); 7.97 (unresolved m, 1H, H-6); 8.82 (dd, 1H, $^3J_{HH} = 4.3$, $^4J_{HH} = 2.1$, H-4)
2d	130–131	68	$C_{12}H_{12}Cl_2N_3P$ (300.13)	47.96 (48.02)	4.01 (4.03)	13.92 (14.00)	191.7	2.34 (s, 3H, $C_6H_4CH_3$-*p*); 5.26 (s, 2H, NCH_2), 6.65 (dd, 1H, $^3J_{HH} = 7.1$, 4.3, H-5); 7.22 (s, 4H, $C_6H_4CH_3$-*p*); 7.79 (ddd, 1H, $^3J_{HH} = 7.1$, $^4J_{HH} = 3.5$, $^5J_{PH} = 2.1$, H-6); 8.71 (unresolved m, 1H, H-4)
3a	108–110	60	$C_5H_6Cl_2N_3PS$ (242.06)	24.71 (24.80)	2.41 (2.49)	17.24 (17.35)	68.9	3.74 (s, 3H, NCH_3); 6.75 (dd, 1H, $^3J_{HH} = 6.3$, 4.4, H-5); 7.98 (unresolved t, 1H, H-6); 8.75 (unresolved d, 1H, H-4).
3b	115–117	72	$C_6H_8Cl_2N_3PS$ (256.24)	28.03 (28.12)	3.09 (3.15)	16.31 (16.39)	50.6	1.39 (t, 3H, $^3J_{HH} = 8.5$, NCH_2CH_3); 4.15 (q, 2H, $^3J_{HH} = 8.5$, NCH_2CH_3); 6.75 (dd, 1H, $^3J_{HH} = 5.7$, 4.3, H-5); 7.93 (ddd, 1H, $^3J_{HH} = 5.7$, $^4J_{HH} = 2.8$, $^5J_{PH} = 2.1$, H-6); 8.81 (dd, 1H, $^3J_{HH} = 5.7$, $^4J_{HH} = 2.8$, H-4)
3c	110–112	75	$C_{11}H_{10}Cl_2N_3PS$ (318.16)	41.39 (41.52)	3.11 (3.17)	13.14 (13.20)	68.8	5.36 (s, 2H, NCH_2); 6.82 (dd, 1H, $^3J_{HH} = 5.7$, 4.3, H-5); 7.49 (s, 5H, C_6H_5); 7.96 (ddd, 1H, $^3J_{HH} = 5.7$, $^4J_{HH} = 2.8$, $^5J_{PH} = 2.1$, H-6); 8.87 (dd, 1H, $^3J_{HH} = 5.7$, $^4J_{HH} = 2.8$, H-4)
3d	115–116	70	$C_{12}H_{12}Cl_2N_3PS$ (332.19)	43.20 (43.38)	3.55 (3.64)	12.60 (12.65)	53.2	2.37 (s, 3H, $C_6H_4CH_3$-*p*); 5.25 (s, 2H, NCH_2); 6.71 (dd, 1H, $^3J_{HH} = 6.3$, 4.3, H-5); 7.24 (d, 2H, $^3J_{HH} = 7.7$, *m*-H); 7.32 (d, 2H, $^3J_{HH} = 7.7$, *o*-H); 7.83 (unresolved m, 1H, H-6); 8.70 (unresolved d, 1H, H-4)
3e	85–86	70	$C_5H_7Cl_2N_2PS_2$ (261.1)	22.86 (22.99)	2.65 (2.70)	10.68 (10.73)	57.9	1.34 (t, 3H, $^3J_{HH} = 7.2$, NCH_2CH_3); 3.98 (q, 2H, $^3J_{HH} = 7.2$, NCH_2); 6.60 (dd, 1H, $^3J_{HH} = 4.7$, $^5J_{PH} = 1.7$, H-5); 6.91 (dd, 1H, $^3J_{HH} = 4.7$, $^5J_{PH} = 1.7$, H-4)
3f	56–58	73	$C_{10}H_9Cl_2N_2PS_2$ (323.6)	37.02 (37.11)	2.76 (2.80)	8.52 (8.66)	52.5	5.07 (s, 2H, NCH_2); 6.51 (d, 1H, $^3J_{HH} = 4.0$, H-5); 6.84 (d, 1H, $^3J_{HH} = 4.0$, H-4); 7.19–7.32 (m, 5H, C_6H_5)

(*Continued*)

TABLE 1 Continued

	mp (°C)	Yield (%)	Mol. Formula (mol. wt.)	Found %[a] C	H	N	$\delta^{31}P$ ($CDCl_3$)	δ ^1H; J (Hz)[b]
3g	81–83	65	$C_4H_7Cl_2N_2PS_2$ (249.1)	19.15 (19.28)	2.77 (2.83)	11.19 (11.25)	55.5	3.05 (s, 3H, NCH_3); 3.34 (bd, 1H, H-5); 3.7 (bd, 1H, H-4)
3h	95–97	67	$C_{10}H_{11}Cl_2N_2PS_2$ (325.2)	36.90 (36.93)	3.35 (3.41)	8.55 (8.61)	53.4	3.29 (t, 2H, $^3J_{HH} = 7.1$, H-5); 3.60 (t, 2H, $^3J_{HH} = 7.1$, H-4); 4.71 (s, 2H, NCH_2); 7.31 (s, 5H, C_6H_5)
3i	Syrupy		$C_{11}H_{13}Cl_2N_2PS_2$ (339.1)	–	–	–	54.7	2.32 (s, 3H, $C_6H_4CH_3$-*p*); 3.20 (t, 2H, $^3J_{HH} = 7.5$, H-5); 3.29 (t, 2H, $^3J_{HH} = 7.5$, H-4); 4.66 (s, 2H, NCH_2); 7.09–7.21 (m, 4H, $CH_2C_6H_4CH_3$-p)

[a]Values in parentheses represent calculated values.
[b]**2a–d, 3b, 3h** on Jeol FX 90Q; **3a,c–g** on Brucker DPX 300; and **3i** on Brucker WM400 spectrometer.

EXPERIMENTAL

Solvents and commercial reagents were distilled and dried by common methods before use. All experiments were carried out in dry nitrogen atmosphere using Schlenk technique. Melting points were determined by capillary method and are uncorrected. NMR spectra were recorded on a JEOL FX 90 Q (^{31}P NMR at 36.23 MHz, ^1H NMR at 89.55 MHz), Brucker DPX 300 (^{31}P NMR at 121.5 MHz, ^1H NMR at 300.13 MHz), or Brucker WM 400 (^{31}P NMR at 161.7 MHz, ^1H NMR at 399.65 MHz) spectrometer. The chemical shifts refer to 85% H_3PO_4 (external) for ^{31}P NMR and TMS (internal) for ^1H NMR. The FAB mass spectrum was recorded on Jeol SX 102 mass spectrometer. *N*-Alkyl-2-aminocycloiminium salts **1** were prepared by reported [29] or analogous method.

*N-Alkyl-2-pyrimidinylidenamino-dichlorophosphines (**2a–d**)*

To a well stirred suspension of *N*-alkyl-2-aminopyrimidinium halide (20 mmol) in toluene (30 ml) was added phosphorus trichloride (1.75 ml, 20 mmol) with stirring. A solution of triethylamine (5.6 ml, 40 mmol) in toluene (10 ml) was added slowly with continuous stirring. After stirring for 20–22 h at room temperature, the reaction mixture was filtered, residue washed with toluene, and solvent was removed from the filtrate in vacuo. The residue thus obtained was extracted with diethyl ether (2 × 50 ml). Combined ether extracts were concentrated to 15–20 ml and left in refrigerator, whereupon creamish white to yellow solid (**2**) deposited, which was filtered and dried. **2a** was obtained as syrupy mass.

*N-Alkyl-2-pyrimidin-/thiazol-/thiazolin-ylidenamidothiophosphoric Dichlorides (**3a–i**)*

N-Alkyl-2-aminocycloiminium halide **1** (20 mmol) was suspended in methylene chloride (40 ml) and phosphorus trichloride (1.75 ml, 20 mmol) was added slowly with stirring at 0–5°C, followed by a solution of triethylamine (5.6 ml, 40 mmol) in methylene chloride (10 ml). After 5–6 h of stirring, the reaction mixture was brought to room temperature and sulfur powder (640 mg, 20 mmol) was added to it. The resulting mixture was left for overnight stirring, the solvent was removed in vacuo, and residue extracted with diethyl ether (2 × 50 ml). The combined ether extracts were concentrated and left in refrigerator, whereupon cream to pale yellow solid (**3**) separated, which was filtered and dried. However, **3i** was obtained as syrupy mass and could not be crystallized.

3c: Mass spectrum (FAB): *m/z* 322 [(M + 1) + 4, 14%], *m/z* 321 (M + 4, 15%), *m/z* 320 [(M + 1) + 2, 70%], *m/z* 319 (M + 2, 30%), *m/z* 318 (M + 1, 100%), *m/z* 317 (M^+, $C_{11}H_{10}Cl_2N_3PS$, 22%), *m/z* 284 ($C_{11}H_{10}N_3ClPS$, 16%), *m/z* 282 ($C_{11}H_{10}ClN_3PS$, 40%), *m/z* 252 ($C_{11}H_{10}ClN_3P$, 8%), *m/z* 250 ($C_{11}H_{10}ClN_3P$, 20%), *m/z* 107 ($C_5H_5N_3$, 20%).

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