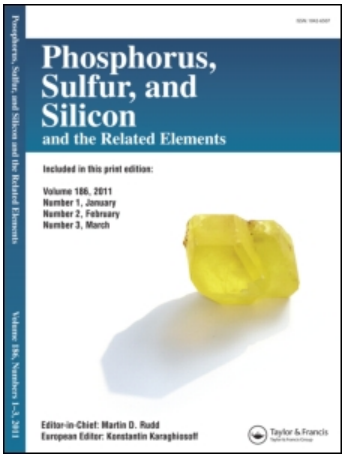

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Bioactive Heterocyclic Trithiophosphoric Esters: Synthesis and Bioactivity

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Bioactive Heterocyclic Trithiophosphoric Esters: Synthesis and Bioactivity

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Novel, heterocyclic derivatives of trithiophosphoric acid have been achieved through phosphorylation of quaternary salts of N-heterocycles with phosphorus trichloride, the iminohalophosphines, thus obtained in situ were subjected to nucleophilic substitution with mercaptans in organic solvents in the presence of HCl acceptors, preferably triethylamine. Synthesized derivatives exhibited potential insecticidal behavior against a polyphagous insect Plutella xylostella (Diamond Backmoth).

Keywords Heterocyclic organothiophosphate insecticides; phosphorylation; trithiophosphatic esters

INTRODUCTION

The organic trithiophosphates have been reported as important organophosphorus derivatives, which have been considered as defoliants,[1] insecticides,[1] and inhibitors of steel corrosion.[2] Tripathi et al.[3–5] have successfully used these esters as ligands for the synthesis of metal complexes of Sb, Sn, and so on. These authors also cited that interest in this chemistry as organo antimony derivatives of dithiophosphate ligands is a result of their potential bioactivity, such as antitumor.[6,7]

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In the literature, only few synthetic routes have been described for organotrithiophosphates. Bliznyuk et al.[8,9] and Mandelbaum et al.[10] have prepared these derivatives by treating dialkylchlorothiophosphate with thiophenols in presence of HCl acceptors.

In the present study, we have described a novel synthetic strategy and bioactivity of eleven such derivatives incorporating different heterocyclic rings. The amalgamation of trithiophospho moiety with heterocyclic ring was also expected to augment the bioactivity. In our previous publications,[11–13] we have reported the synthesis and bioactivity of different tris amidothiophosphates using different N-heterocycles as starting material and phosphorus trichloride as phosphorylating agent.

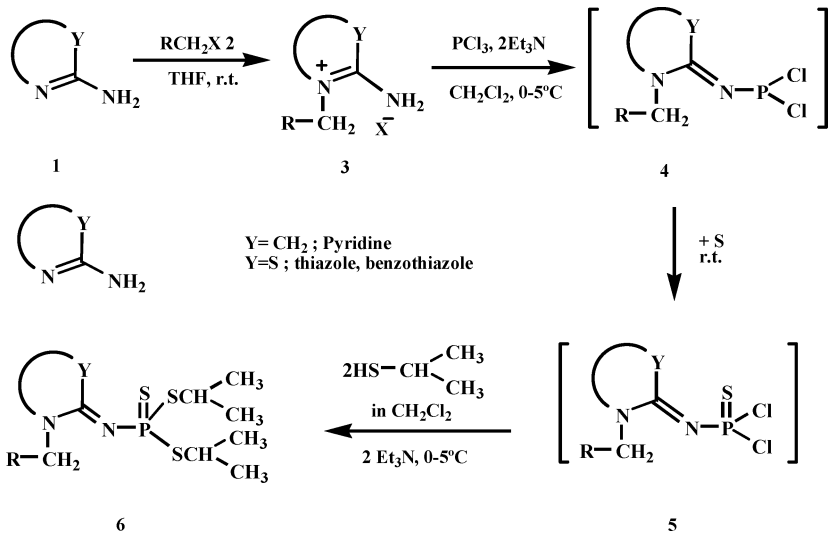
RESULTS AND DISCUSSION

N-Alkyl-2-aminopyridin/thiazole/benzothiazole (**1**) were reacted with different haloalkanes (**2**) in THF and generated the corresponding N-alkyl-2-aminopyridinium/thiazolium/benzothiazolium halides (**3**). These quaternary salts then were subjected to phosphorylation with phosphorus trichloride (one equivalent) in presence of a weak base triethylamine (two equivalents) in methylene chloride at 0–5°C and furnished the corresponding iminodichlorophosphines (**4**). This intermediate was oxidized in situ with elemental sulfur (1/8 equivalent) at ambient temperature and produced corresponding cycloiminylidenamidothiophosphoryl dichlorides (**5**), which on further substitution with 2-propanethiol (two equivalents) at 0–5°C gave the corresponding products **6** (Scheme 1).

All the synthesized products were white crystalline solids, having sharp melting points and were characterized by ^{1}H, ^{31}P and ^{13}C NMR techniques. All physical and spectral data have been reported in Tables I and II, respectively.

^{31}P NMR

The reaction course on monitoring showed a change in ^{31}P signal from 220 δppm (signal for PCl_3) to 146–158 δppm (signal for tricoordinated phosphorus) when phosphorus trichloride and triethylamine were added to corresponding salt solutions. But addition of sulfur shifted this signal in upfield region 38–80.6 δppm, which is characteristic for compounds containing phosphorus in tetracoordinated state thus confirming the completion of reaction. Pure solids **6a**–**k** have shown ^{31}P signal in the range 40–82.78 δppm (Table II).



1 3 4 5 6

1-6	a	b	c	d	e	f	g	h	i	j	k
R	$COOCH_2Ph$	$COOCH_2Ph$	$COOCH_2Ph$	$COOCH_2CH_3$	$COOCH_2CH_3$	$COOCH_3$	$COOCH_3$	C_6H_5	H	H	H
X	Br	Br	Br	Br	Br	Br	Br	Br	I	I	I
Heterocyclic ring	Thiazole	Benzothiazole	Pyridine	Pyridine	Thiazole	Pyridine	Thiazole	Pyridine	Thiazole	Benzothiazole	Pyridine

SCHEME 1

^{1}H NMR

All CH_3 protons of $SCH(\mathbf{CH}_3)_2$ moiety appeared as multiplet between 1.01–1.66 δppm, while both S**CH** protons gave two septates individually—between 3.01–3.55 δppm and 3.21–3.66 δppm, respectively. Position of both protons of S**CH** is different in space with respect to P=S, therefore gave signals separately. One S**CH** proton which is *cis* to sulfur got deshielded and appeared in downfield, while other one gave septate in comparatively upfield due to its *trans* position with respect to sulfur. All $N\mathbf{CH}_2$ and $N\mathbf{CH}_3$ protons of **6a**–**k** gave singlet in its expected characteristic region between 3.72–5.50 δppm.

In **6a**–**c**, two protons of $O\mathbf{CH}_2C_6H_5$ gave singlet between 4.76–4.90 δppm, and in **6d**, **6e** two protons of $O\mathbf{CH}_2CH_3$ gave quartet between 4.15–4.21 δppm. This is due to three-bond coupling with adjacent CH_3 protons, while CH_3 protons of $OCH_2\mathbf{CH}_3$ were found to absorb in the

TABLE I Physical Data of Compounds

Compound (S.N.)	Molecular formula (mol. weight)	M.P. (°C)	Yield (%)	Elemental analysis (%)		
				C	H	N
6a	$C_{18}H_{25}N_2S_4PO_2$ (460.65)	73	70	46.93 (46.81)	5.47 (5.43)	6.08 (6.01)
6b	$C_{22}H_{27}N_2S_4PO_2$ (510.71)	82	72	51.74 (51.73)	5.33 (5.32)	5.49 (5.43)
6c	$C_{20}H_{27}N_2S_3PO_2$ (454.62)	89	63	52.84 (51.90)	5.99 (5.90)	6.16 (6.11)
6d	$C_{15}H_{25}N_2S_3PO_2$ (392.55)	56	50	45.90 (45.45)	6.42 (6.48)	7.14 (7.01)
6e	$C_{13}H_{23}N_2S_4PO_2$ (398.58)	75	52	39.17 (39.12)	5.81 (5.80)	7.03 (7.00)
6f	$C_{14}H_{23}N_2S_3PO_2$ (378.52)	92	50	44.42 (44.40)	6.12 (6.11)	7.40 (7.39)
6g	$C_{12}H_{21}N_2S_4PO_2$ (384.55)	76	62	37.48 (37.42)	5.50 (5.50)	7.28 (722)
6h	$C_{18}H_{25}N_2S_3P$ (396.58)	92	80	54.52 (54.50)	6.35 (6.03)	7.06 (7.00)
6i	$C_{10}H_{19}N_2S_4P$ (326.51)	115	60	36.79 (36.76)	5.87 (5.80)	8.58 (8.50)
6j	$C_{14}H_2N_2S_4P$ (376.57)	83	60	44.65 (44.61)	5.62 (5.59)	7.44 (7.43)
6k	$C_{12}H_{21}N_2S_3P$ (320.48)	90	55	44.97 (44.92)	6.60 (6.59)	31.20 (30.20)

range 1.01–1.66 δppm merged with other methyl protons of SCH($\mathbf{CH_3}$)$_2$ moiety. In **6f**, **6g**, O$\mathbf{CH_3}$ protons gave singlet between 3.67–3.92 δppm. All the heterocyclic protons appeared in expected aromatic region with expected multiplicities together with the aromatic protons of phenyl group of $OCH_2\mathbf{C_6H_5}$ (**6a**–**c**).

^{13}C NMR

As was expected in ^{13}C NMR, SCH$\mathbf{CH_3}$ carbon gave singlet in most upfield region between 22.15–25.37 δppm, while both the S**CH** carbons gave singlet together between 37.49–55.86 δppm. N$\mathbf{CH_2}$ carbon in **6a**–**h** gave singlet between 48.23–112.54 δppm, while N$\mathbf{CH_3}$ carbon of **6i-k** gave singlet between 45-88–112.46 δppm. O$\mathbf{CH_2}$ carbons of **6a**–**e** appeared between 53.68–67.30 δppm, while O$\mathbf{CH_3}$ carbon of **6f–g** appeared between 52.58–65.36 δppm as singlet. Similarly CH_3 carbon of $OCH_2\mathbf{CH_3}$ in **6d**, **6e** gave singlet at 27.49 and 38.15 δppm, respectively.

TABLE II Spectral Data of Compounds

Compound (S.N.)	^{31}P NMR δ (ppm)	^{1}H NMR ($CDCl_3$) δ(ppm) J (Hz)	^{13}C NMR ($CDCl_3$) δ (ppm)
6a	51.62	1.18–1.47 (m, 12H, CH_3); 3.40 (sept., 1H, $^3J_{HH}$ =6.9, SCH); 3.59 (sept., 1H, $^3J_{HH}$ = 6.9, SCH); 4.76 (s, 2H, OCH_2) 5.22 (s, 2H, NCH_2); 6.64 (d, 1H, $^3J_{HH}$ =6.6,H-5); 6.99 (d, 1H, $^3J_{HH}$ =7.0, H-4); 7.26-7.40 (m, 5H, Arom)	25.32 (SCH**C**H$_3$); 42.50 (S**C**HCH$_3$); 48.23 (NCH_2); 67.94 (OCH_2); 107.20 (C-5); 126.87 (C-4); 134.50 (C-2); 166.53 (C=0)
6b	82.78	1.01–1.44 (m, 12H, CH_3); 3.38 (sept., 1H, $^3J_{HH}$ =6.9, SCH); 3.40 (sept., 1H, $^3J_{HH}$ =6.9, SCH); 4.90 (s, 2H, OCH2); 5.10 (s, 2H, NCH_2); 6.94 (d, 1H, $^3J_{HH}$ =7.8, H-7); 6.98-7.49 (m, 7H, H-5, H-6. Arom); 7.52 (d, 1H, $^3J_{HH}$ = 7.8 H-4)	22.72 (SCH**C**H$_3$); 37.49 (S**C**HCH$_3$); 48.78 (NCH_2) 53.68 (OCH_2); 101.54 (C-7); 106.12 (C-4); 107.58 (C-6); 126.34 (C-5); 141.29 (C-8); 154.91 (C-9); 171.85 (C-2); 176.68 (C=O)
6c	42.61	1.10–1.52 (m, 12H, CH_3); 3.18 (sept., 1H, $^3J_{HH}$ = 6.7, SCH); 3.49 (sept., 1H, $^3J_{HH}$ = 6.7, SCH); 4.78 (s, 2H, OCH_2); 5.10 (s, 2H, NCH_2); 7.23-7.67 (m, 9H, H-3, H-4, H-5, H-6, Arom)	25.29 (SCH**C**H$_3$); 54.29 (S**C**HCH$_3$); 67.30 (OCH_2); 112.06 (NCH_2); 118.44 (C_m); 127.22 (C-5); 127.26 (C_{para}); 127.33 (C-3); 140.26 (C-4); 140.29 (C-6); 141.82 (C_{ipso}); 165.60 (C=O)
6d	42.83	1.13–1.40 (m, 15H, CH_3); 2.73 (sept., 1H, $^3J_{HH}$ =6.7, SCH); 3.22 (sept., 1H, $^3J_{HH}$ = 6.7, SCH); 4.75 (s, 2H, NCH_2); 6.74 (dd, 1H, $^3J_{HH}$ =6.7, H-5); 7.57 (d, 1H, $^3J_{HH}$ =8.9, H-3); 7.63 (dd, 1H, $^3J_{HH}$ =8.0, H-4); 7.72 (d, 1H, $^3J_{HH}$ =8.7,H-6)	25.25 (SCH**C**H$_3$); 27.49 (OCH_2**C**H$_3$); 54.68 (S**C**HCH$_3$); 62.38 (OCH_2); 112.32 (NCH_2); 119.07 (C-5); 128.19 (C-3); 128.95 (C-4); 140.04 (C-6); 154.81 (C-2); 166.02 (C=O)
6e	51.72	1.20–1.43 (m, 15H, OCH_2**C**H$_3$, SCH**C**H$_3$) 3.25 (sept., 1H, $^3J_{HH}$ = 6.7, SCH); 3.33 (sept., 1H, $^3J_{HH}$ = 6.7, SCH); 4.15 (q, 2H, $^3J_{HH}$, 7.1, OCH_2); 4.18 (s, 2H, NCH_2); 7.03 (d, 1H, $^3J_{HH}$ = 7.1, H-5); 7.09 (d, 1H, $^3J_{HH}$ = 7.1, H-4)	24.90 (SCH**C**H$_3$); 38.15 (CH_2**C**H$_3$); 47.92 (SCHCH$_3$); 61.78 (OCH_2); 106.80 (C-5); 124.76 (C-4); 140.80 (C-2); 166.72 (C-O)
6f	50.81	1.17–1.46 (m, 12H, SCH**C**H$_3$); 3.27 (sept. 1H, $^3J_{HH}$ =6.9, SCH); 3.51 (sept., 1H, $^3J_{HH}$ =6.9, SCH); 3.67 (s, 3H, OCH_3); 4.54 (s, 2H, NCH_2); 6.43 (dd, 1H, $^3J_{HH}$ = 7.1, H-5); 7.08-7.26 (m, 2H, H-3, H-4); 7.22 (d, 1H, $^3J_{HH}$ =7.1,H-6)	25.11 (SCH**C**H$_3$); 47.76 (S**C**HCH$_3$) 52.58 (OCH_3); 106.86 (NCH_2); 125.04 (C-5); 128.76 (C-3); 137.42 (C-4); 166.34 (C=O)

(Continued on next page)

TABLE II Spectral Data of Compounds *(Continued)*

Compound (S.N.)	^{31}P NMR δ (ppm)	^{1}H NMR ($CDCl_3$) δ(ppm) J (Hz)	^{13}C NMR ($CDCl_3$) δ (ppm)
6g	41.88	1.09–1.39 (m, 12H, SCH**CH**$_3$); 3.27 (sept., 1H, $^3J_{HH}$ =6.9, SCH); 3.52 (Sept, 1H, $^3J_{HH}$ =6.9, SCH); 3.92 (s, 3H, OCH_3); 4.90 (s, 2H, NCH_2); 7.73 (d, 1H, $^3J_{HH}$ = 7.3, H-5); 7.74 (d, 1H, $^3J_{HH}$ = 7.3; H-4)	24.97 (SCH**CH**$_3$); 45.76 (S**CH**); 54.30 (NCH_2); 65.36 (OCH_3); 112.50 (C-5); 129.01 (C-4); 140.80 (C-2); 166.40 (C=O)
6h	47.70	1.14–1.66 (m, 12H, CH_3); 3.27 (sept., 1H, $^3J_{HH}$ = 6.9, SCH); 3.52 (sept., 1H, $^3J_{HH}$ = 6.9, SCH); 5.37 (s, 2H, NCH_2); 6.72 (dd, 1H, $^3J_{HH}$ = 7.1, H-5); 7.30 (d, 1H, $^3J_{HH}$ = 8.0, H-3); 7.40 (dd, 1H, $^3J_{HH}$ =8.0, H-4); 7.40 (dd, 1H, $^3J_{HH}$ =8.0, H-4); 7.26-7.41(m, 5H, Arom.); 7.70 (dd, 1H, $^3J_{HH}$ = 8.0, H-6)	25.37 (SCH**CH**$_3$); 55.86 (S**CH**CH_3); 112.54 (NCH_2); 119.81 (C-5) 129.00 (C-3); 129.20 (C-4) 138.74 (C-6); 141.01 (C-2)
6i	62.77	1.21–1.39 (m, 12H, SCH**CH**$_3$); 3.18 (sept., 1H, $^3J_{HH}$ =6.7, SCH); 3.43 (sept., 1H, $^3J_{HH}$ = 6.7, SCH); 3.55 (s, 3H, NCH_3); 6.29 (d, 1H, $^3J_{HH}$ =6.6, H-5); 6.70 (d, 1H, $^3J_{HH}$ =7.0, H-4)	23.66 (SCH**CH**$_3$); 38.85 (S**CH**CH_3) 58.49 (NCH_3); 117.30 (C-5); 131.08 (C-4)
6j	81.72	1.10–1.34 (m, 12H, SCH**CH**$_3$); 3.17 (sept., $^3J_{HH}$ = 6.7, SCH); 3.50 (sept., $^3J_{HH}$ =6.7, SCH); 5.50 (s, 3H, NCH_3); 7.10 (d, 1H, $^3J_{HH}$ =8.5, H-7); 7.24-7.38 (m, 2H, H-5, H-6); 7.58 (d, 1H, $^3J_{HH}$ = 8.5, H-4)	22.15 (SCH**CH**$_3$); 38.35 (S**CH**CH_3); 45.88 (NCH_3); 118.28 (C-5); 120.45 (C-3); 141.09 (C-4); 142.29 (C-6); 156.16 (C-2)
6k	39.88	1.11–1.41 (m, 12H, CH_3); 3.19 (sept., 1H, $^3J_{HH}$ =6.7, SCH); 3.52 (sept., 1H, $^3J_{HH}$ =6.7, SCH); 3.72 (s, 3H, NCH_3); 6.70 (dd, 1H, $^3J_{HH}$ =6.7, H-5); 7.53 (m, 2H, H-3, H-4); 7.68 (d, 1H, $^3J_{HH}$ =6.7, H-6)	25.32 (SCH**CH**$_3$); 41.86 (S**CH**CH_3); 112.46 (NCH_3); 119.24 (C-5); 119.42 (C-3); 140.06 (C-4); 141.24 (C-6); 155.12 (C-2)

TABLE III Percent Mortality of *Plutella Xylostella* 1,3,5,7 and 10 Days After the Treatment by Food Dipping Method

S. N.	Treatment	1 day		3 days		5 days		7 days		10 days	
		0.05	0.025	0.05	0.025	0.05	0.025	0.05	0.025	0.05	0.025
6a	N-Benzylethanoate-2-thiazolinylidenamido bis(S-isopropylthiol)thiophosphate	20.0 (51.29)	5.0 (12.92)	60.0 (91.24)	20.0 (50.01)	80.0 (106.19)	40.0 (73.39)	95.0 (116.72)	55.0 (86.84)	95.0 (116.72)	60.0 (91.14)
6d	N-(Ethoxy-2-oxoethyl)-2-pyridinylidenamido bis(S-isopropylthiol)thiophosphate	10.0 (35.58)	10.0 (36.40)	40.0 (73.80)	40.0 (73.60)	80.0 (106.2)	45.0 (78.12)	90.0 (113.29)	55.0 (86.84)	95.0 (116.69)	65.0 (95.14)
6h	N-Benzyl-2-pyridinylidenamido bis(S-isopropylthiol)thiophosphate	10.0 (25.78)	5.00 (22.20)	60.0 (91.14)	20.0 (51.56)	75.0 (102.55)	50.0 (82.75)	80.0 (106.33)	70.0 (98.76)	85.0 (109.87)	70.0 (98.76)
6k	N-Methyl-2-pyridinylinamido bis(S-isopropylthiol) thiophosphate	5.0 (22.2)	5.0 (22.20)	30.0 (60.40)	30.0 (60.40)	70.0 (98.82)	40.0 (72.33)	80.0 (106.38)	50.0 (81.78)	85.0 (109.78)	65.0 (94.21)
	Endosulfan	15.0 (43.98)		30.0 (62.70)		45.0 (78.35)		60.0 (91.01)		65.0 (94.94)	
	Control	0.0 (0.0)		0.0 (0.0)		0.0 (0.0)		0.0 (0.0)		0.0 (0.0)	
	*CD at 0.05%	5.70		4.17		4.84		2.80		2.70	

*CD = Critical difference.

C-2 carbon of heterocyclic ring absorbed at most downfield region between 134.50–171.85 δppm with minimum intensity due to its quaternary nature. Similarly all carbons of aromatic ring appeared according to their expected range.

Bioactivity

Four trithiophosphates—**6a**, **6d**, **6k**, **6h**—have been screened for insecticidal activity against *Plutella xylostella*. Two doses of 0.05% and 0.025% have been arbitrarily selected for inoculation observation of insect mortality; they have been recorded after one, three, five, seven, and ten days of their introduction to the insect food. The results have been analyzed statistically and reported in Table III (Fig. 1).

Compound **6a** was found to be most potent in both the concentrations and even has shown better insecticidal activity in comparison to endosulfan. Compound **6d** was at par with compound **6a,** and this was also found to be better than endosulfan.

Initially, except **6a**, all other synthesized products have shown low bioactivity after 1–3 days of treatment, but after 5 days, all compounds have shown appreciable activity. This enhancement of activity after 3 days of treatment could be explained due to auto oxidation of P═S bond to P═O bond in the course of time which is a reported factor.[14] Out of four compounds, **6a** and **6d** were found to be most bioactive. If we consider

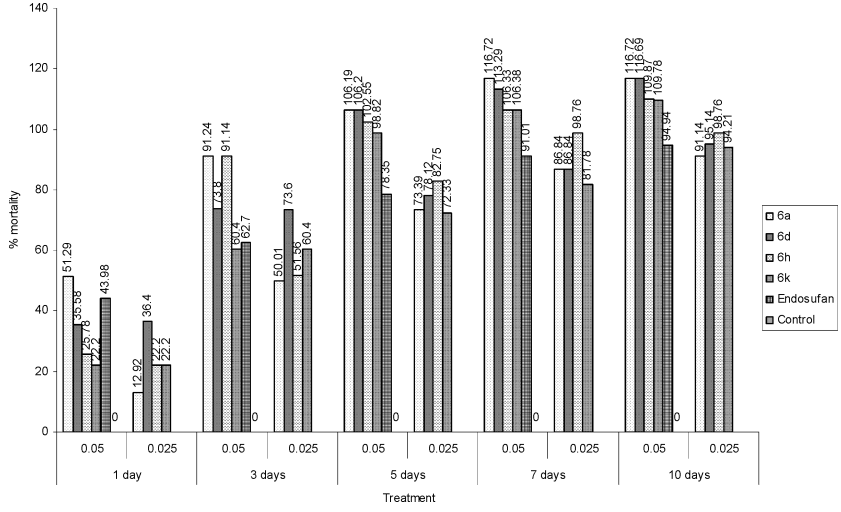


FIGURE 1 Percent mortality of Plutella xylostella 1, 3, 5, 7, and 10 days after the treatment.

structure versus reactivity relationship in both potent compounds **6a** and **6d**, bulky and electron withdrawing groups have been attached to NCH_2 moiety; these two factors were reported to be the prerequisite for a better insecticidal compound, which impaired the acetyl choline esterase activity in the insect[14] (Table III).

CONCLUSION

The present study has described a novel synthetic strategy for eleven trithiophosphoric esters incorporating three different heterocycles (pyridine, thiazole, and benzothiazole). Synthesized products **6a, 6d, 6h, 6k** exhibited strong insecticidal activity against a polyphagous pest *Plutella xylostella.* Even compound **6a** and **6d** were found to be better in comparison to an established insecticide endosulfan.

EXPERIMENTAL

All the reactions were carried out in an inert atmosphere under nitrogen. All solvents and reagents were used after drying freshly. Fine chemicals like 2-propanethiol, 2-aminopyridine, 2-amiothiazole, and 2-aminobenzothiazole were procured from Merck and used as such. Glasswares were also dried very well by putting them into oven at high temperature before using. Standard syringe technique was used for adding the solvents and reagents. Since all the synthesized products were highly hygroscopic in nature, we stored them under an inert atmosphere of nitrogen. Their melting points were determined by standard capillary method on electrictempo instrument. ^{31}P NMR spectra were recorded on Jeol AC300 at 121.50 MHz (Obset 156 KHz) using 85% H_3PO_4 as external standard and ^1H NMR spectra were recorded in Jeol AL 300 at 300.4 MHz (Obset 130 KHz) using TMS as internal standard.

General Procedure of Synthesis of N-Substituted-2-ylidenamido bis(S-isopropylthiol)thiophosphate (6a–k)

To the suspension of N-alkyl-2-pyridinium/thiazolium/benzothiazolium halides (10.12 mmol) in methylene chloride, addition of triethylamine (20.24 mmol) and phosphorus trichloride (10.12 mmol) was done at ambient temperature. After 24 h of stirring, 2-propanethiol (20.24 mmol) in methylene chloride was added dropwise in presence of triethylamine (20.24 mmol) at 0–5°C temperature. The stirring continued for the next 60–65 h. After that the solvent was dried under vacuo, and the residue was extracted with diethylether and left in refrigerator, whereupon a white solid was separated out that was filtered and dried.

Bioactivity

Two concentrations 0.05% (0.05 g was dissolved in 1–2 ml of acetone and was made up with distilled water up to 1000 ml) and 0.025% (0.025 g was dissolved in 1–2 ml of acetone and was made up with distilled water up to 1000 ml) of test compounds were given to the second instar larval stage of insect by food dipping method.[15,16] For control only acetone and water mixture have been used. For standard 0.05% solution of endosulfan was also prepared in similar way. Twenty insects were kept together in a separate container and four such replicates were prepared for each concentration of each compound. Percent mortality of each replicate were calculated and then converted into angular transformed values, which were then subjected to the statistical analysis of completely randomized design (CRD) technique.[17]

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