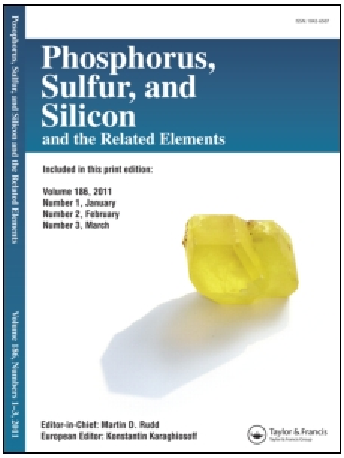

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Novel Synthetic Approach to Thiophosphinates Incorporating Different N-Heterocycles

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Novel Synthetic Approach to Thiophosphinates Incorporating Different N-Heterocycles

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Eight new cycloiminylidenamidothiophosphinates incorporating pyridine, pyrimidine, thiazole, and benzothiazole heterocycles were synthesized by phosphorylation of the quaternary iminium salts of the heterocycles by diphenylchlorophosphine followed by in situ sulfurization by elemental sulfur. Crystalline solid products were well characterized by elemental analysis and NMR spectroscopy.

Keywords Chlorodiphenylphosphine; cycloiminium salts; phosphorylation; thiophosphinates

INTRODUCTION

Organothiophosphinates are tetracoordinated phosphorus derivatives and have a significant place in the literature as ligands for metal complexes, catalysis, ion exchangers and synthons for biaryls.[1–6] Anchoring of phosphinate coupled molecules on titania particles[7] has recently attracted interest for their numerous applications such as self assembled monolayers,[8] ceramic membrane[9], optical write - read - erase devices[10].

A number of methods for the synthesis of the title compounds are available in the literature.[11,12] Recently, we have reported a facile route for the synthesis of organophosphorus derivatives in which the phosphorus exists in different coordination states, which include phospholes, organothiophosphates, and organothiophosphonates. Methods for the latter include phosphorylation of 2-aminocycloiminium halides with phosphorus trichloride and phenyldichlorophosphine,

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respectively, followed by in situ nucleophilic substitution and sulfurization.[13–18]

Extending this work, we now present the synthesis of novel organothiophosphinates by an analogous synthetic strategy using diphenylchlorophosphine as a phosphorylating agent. These thiophosphinates can be used as ligands for complexes as well as potential pesticides.

RESULTS AND DISCUSSION

The starting materials, N-alkylcycloiminium halides **(3)**, were synthesized by treating 2-amino-N-heterocycles **(1)** and appropriately substituted alkyl halides **(2)** in THF at room temperature.[13–15] The synthesized N-alkylcycloiminium halides[13–15] **(3)** were further allowed to react with chlorodiphenylphosphine (1 equivalent) in a methylene chloride/toluene mix (2:1) in the presence of two and a half equivalents of triethylamine at 0–5°C. The resulted diphenylphosphines **(4)** were subjected to sulfurizaton using one equivalent of elemental sulfur at ambient temperature and furnished the corresponding diphenylthiophosphinates **(5)** (Scheme 1).

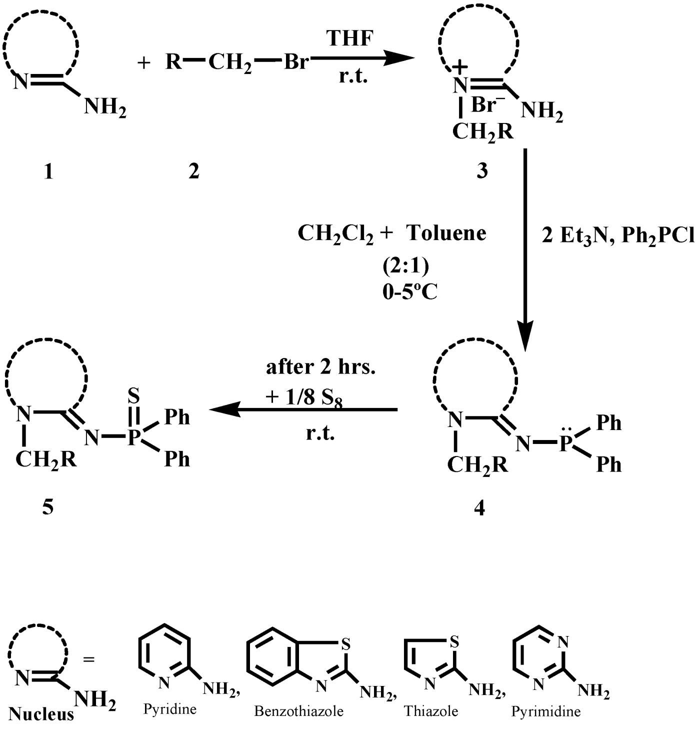
All synthesized thiophosphinates were obtained as white to creamy yellow crystalline solids, stable under a nitrogen atmosphere. All the products have been well characterized by elemental analysis, ^{31}P, and ^{1}H NMR spectroscopy.

Characterization

^{31}P NMR. The reactions were monitored by ^{31}P NMR spectroscopy of the reaction mixture. The solids (**5a–h**) show ^{31}P NMR signal between 49.19-80.87 ppm which were in good agreement with their tetra coordinated pentavalent nature[19] (Table I).

^{1}H NMR. The structures of cycloiminylidenamidothiophosphinates (**5a–h**) are confirmed by ^{1}H NMR studies (Table I). In the ^{1}H NMR all **NCH_3 (5a–d)** and NCH_2 (**5e–h)** protons absorbed as a singlet between 3.62–5.42 ppm. Three protons of **OCH_3 (5g)** were found at 3.69 ppm while three protons of OCH_2CH_3 **(5h)** and two protons of **OCH_2 (5h)** were found to absorb at 1.25 ppm and 4.22 ppm as triplet and quartet, respectively.

All aromatic and heterocyclic protons were found to absorb in their characteristic range at 6–9 ppm with expected multiplicities (Table I).



1-5	a	b	c	d	e	f	g	h
R	H	H	H	H	C_6H_5	C_6H_5	$COOCH_3$	$COOC_2H_5$
Nucleus	pyridine	benzothiazole	thiazole	pyrimidine	pyridine	pyrimidine	pyridine	thiazole

SCHEME 1

EXPERIMENTAL

All glassware used was washed with alkali followed by dilute acid then water and acetone sequentially and were dried in an electric oven for 4–6 h at a high temperature until just before use. Standard syringe techniques were used for the addition of chemicals. All solvents and reagents were freshly dried. Fine chemicals like 2-aminopyridine, 2-aminobenzothiazole, 2-aminothiazole,

TABLE I Physical and Spectral Data of the Compounds 5a–h

				Elemental analysis cal % (found %)				
Compd.	Mol. formula (mol. wt.)	Yield (%)	M.p. (°C)	C	H	N	^{31}P NMR	^{1}H NMR δ (ppm) J (Hz)
5a	$C_{18}H_{17}N_2PS$ (324.386)	68	122°C	66.65 (66.60)	5.28 (5.20)	8.64 (8.62)	80.39	3.82 (s, 3H, NCH_3); 6.29 (dt, 1H, $^3J_{HH} = 6.1$) $^4J_{HH} = 1.8$, H-5); 7.40 (unresolved m, 10H, $P(C_6H_5)_2$; 7.65 (dd, 1H, 3$J_{HH} = 6.1$, $^4J_{HH} = 1.8$, H-3); 7.83 (dd, 1H, $^3J_{HH} = 6.1$, $^4J_{HH} = 2.5$, H-4); 8.01 (dd, 1H, $^3J_{HH} = 6.1$, $^4J_{HH} = 2.5$, H-6)
5b	$C_{24}H_{21}N_2PS$ (400.484)	48	114°C	71.98 (71.97)	5.28 (5.26)	6.99 (6.91)	80.87	5.42 (s, 2H, NCH_2); 6.26 (dd, 1H, $^3J_{HH} = 6.18$, H-5); 7.46 (unresolved m, 15H, aromatic); 7.63 (d, 1H, $^3J_{HH} = 8.8$, H-3); 7.72 (unresolved m, 2H, H-4, H-6)
5c	$C_{20}H_{19}N_2PSO_2$(382.423)	72	134°C	62.82 (62.62)	5.01 (5.00)	7.32 (7.30)	68.57	3.69 (s, 3H, OCH_3); 4.74 (s, 2H, NCH_2); 6.31 (dt, 1H, $^3J_{HH} = 7.2$, $^4J_{HH} = 2.0$, H-5); 7.64 (unresolved m, 10H, P $(C_6H_5)_2$); 7.77 (dd, 1H, $^3J_{HH} = 7.8$, $^4J_{HH} = 2.01$, H-3); 7.86 (dd, 1H, $^3J_{HH} = 7.8$, $^4J_{HH} = 2.5$, H-4); 7.89 (dd, 1H, $^3J_{HH} = 7.8$, $^4J_{HH} = 2.5$, H-6)
5d	$C_{20}H_{17}N_2PS_2$(380.474)	65	162^{o}C	63.14 (63.10)	4.50 (4.42)	7.36 (7.33)	49.19	3.70 (s, 3H, NCH_3); 7.24 (t, 1H, $^3J_{HH} = 7.14$, H-6); 7.73 (d, 1H, $^3J_{HH} = 7.9$, H-7); 7.92 (t, 1H, $^3J_{HH} = 7.9$, H-5); 7.97 (d, 1H, $^3J_{HH} = 7.5$, H-4).

5e	$C_{16}H_{15}N_2PS_2$(330.414)	67	106°C	58.16 (58.00)	4.58 (4.56)	8.48 (8.44)	48.90	3.62 (s, 3H, NCH_3); 6.25 (dd, 1H, $^3J_{HH} = 6.4$, $^5J_{PH} = 1.65$, H-5); 6.75 (dd, 1H, $^3J_{HH} = 6.4$, $^5J_{PH} = 2.4$, H-4); 7.5 (unresolved m, 10H, P$(C_6H_5)_2$)
5f	$C_{19}H_{19}N_2PS_2O_2$(402.478)	71	102°C	56.70 (56.69)	4.76 (4.73)	6.96 (6.94)	49.73	1.25 (t, 3H, $^3J_{HH} = 6.42$, $OCH_2\mathbf{CH_3}$), 4.22 (q, 2H, $^3J_{HH} = 6.42$, OCH_2); 4.66 (s, 2H, NCH_2) ; 6.25 (d, 1H, $^3J_{HH} = 6.8$, H-5) ; 6.78 (d, 1H, $^3J_{HH} = 6.8$, H-4); 7.26–7.96 (unresolved, 10H, aromatic)
5g	$C_{17}H_{16}N_3PS$ (325.374)	58	122°C	62.75 (62.73)	4.96 (4.94)	12.91 (12.90)	78.50	3.75 (s, 3H, NCH_3) ; 6.68 (dd, 1H, $^3J_{HH} = 1.26$, H-5); 7.23 (unresolved m, 10H, arom); 7.67 (unresolved m, 2H, H-4, H-6)
5h	$C_{23}H_{20}N_3PS$ (401.472)	70	126°C	68.81 (68.80)	5.02 (5.00)	10.47 (10.45)	80.20	5.4 (s, 2H, NCH_2); 7.48 (dd, 1H, $^3J_{HH} = 6.96$, H-5) ; 7.82 (unresolved m, 15H, arom); 7.95 (unresolved m, 1H, H-6); 8.12 (d, 1H, $^3J_{HH} = 4.26$, H-4)

2-aminopyrimidine were procured from Aldrich and Merck and used without further purification. All the synthetic procedures were carried out in an inert atmosphere of nitrogen and due to the highly hygroscopic nature of the synthesized products. Elemental analyses were performed on Heraens Carlo Erba 1108 analyzer. ^{31}P NMR spectra were recorded on Jeol AL 300 at 121.50

MHz using 85% H_3PO_4 as an external standard. ^{1}H NMR spectra were recorded in $CDCl_3$ on Jeol AL300 at 300.4 MHz using TMS as a internal reference. Melting points were determined by standard capillary method on Electric Tempo Instrument and are uncorrected.

General Procedure for the Synthesis of N-alkyl-2-iminodiphenyl-thiophosphinate (5a–h)

Starting material N-alkyl cycloiminium halides (13 mmol) were stirred in minimum amount of 2:1 mix of dichloromethane (40 mL)/ toluene (20 mL). To this suspension one equivalent of chlorodiphenylphosphine (13 mmol) in the presence of two and a half equivalents of triethylamine (32.5 mmol) were added at 0–5°C. This reaction mixture was then allowed to come to room temperature. After 2 h of continuous stirring, one equivalent of elemental sulfur (13 mmol) was added at ambient temperature. After 48 h of stirring the solution was filtered; the solvent removed in vacuo; and the residue extracted with dried diethylether. Extraction was left in refrigerator whereupon a solid was separated out, which was dried under vacuum and recrystallized with hexane.

CONCLUSION

Eight diphenylthiophosphinates incorporating different N-cycloimines have been successfully synthesized and characterized. These novel organophosphorus molecules could be potential ligands for metal complexes and due to the presence of different heterocycle rings should be potentially bioactive molecules. Now, we are pursuing further research to find out the application of these phosphinates as ligands of transition metals, as well as their pesticidal properties.

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