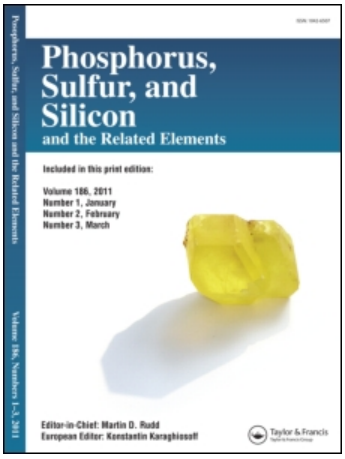

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One-Pot Synthesis and Fungicidal Activity of Pyrimidinylidenamido- and Thiazolinylidenamidomonothiophosphoric Esters

Neelima Gupta[a]; Vijaya Kabra[a]; Varsha Saxena[a]; Sama Jain[a]; Kalpana Bhatnager[b]
[a] University of Rajasthan, Jaipur, India [b] A.R.S., Jaipur, India

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ONE-POT SYNTHESIS AND FUNGICIDAL ACTIVITY OF PYRIMIDINYLIDENAMIDO- AND THIAZOLINYLIDENAMIDOMONOTHIOPHOSPHORIC ESTERS

Neelima Gupta,[a] *Vijaya Kabra,*[a] *Varsha Saxena,*[a] *Sama Jain,*[a] *and Kalpana Bhatnager*[b]
University of Rajasthan, Jaipur, India[a] *and A.R.S., Jaipur, India*[b]

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A novel one-pot synthesis of four new classes of amidothiophosphoric esters and trisamidothiophosphoric esters is developed. (1-Alkyl-2-pyrimidinylidenamido)bis(diethylamido)thiophosphates, (1-alkyl-2-pyrimidinylidenamido)bis (O-2/4-methylphenyl)thiophosphates, (3-alkyl-2-thiazolinylidenamido)bis (diethylamido)thiophosphate and (3-alkyl-2-thiazolinylidenamido)bis(O-2/4-methylphenyl)thiophosphates are obtained from the nucleophilic substitution and oxidation of N-alkyl-2-cycloiminylidenaminodichlorophosphines generated in situ from the reaction of the corresponding N-alkyl-2-aminocycloiminium halide with phosphorus trichloride and triethylamine. The synthesized thiophosphoric esters have been investigated for fungicidal properties.

Keywords: Alkylidenamidothiophosphates; amidothiophosphoric esters; trisamidothiophosphoric esters; fungicidal activity

Functionalized halophosphines have been used widely as precursors for the synthesis of a variety of organophosphorus compounds having phosphorus in different oxidation states;[1,2] including phosphoric esters, thiophosphoric esters, and amidophosphoric esters; a number of representatives of which are known for their insecticidal and fungicidal properties.[3–6] Synthesis of amidophosphoric, amidothiophosphoric,

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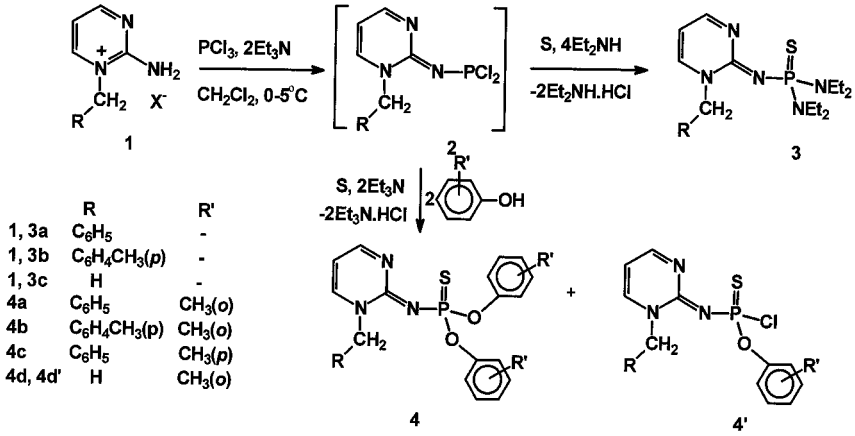
Address correspondence to Vijaya Kabra, University of Rajasthan, Department of Chemistry, Jaipur 302 004, India. E-mail: sgkabra@sancharnet.in

and trisamidophosphoric ester derivatives has been reported from the reaction of 2-aminopyridine with dimethylphosphoric chloride, diethylthiophosphoric chloride, and bis(phenylamido)phosphoric chloride respectively.[7] Alternatively, trisamidophosphoric esters have been prepared from the reaction of amidophosphoric dichloride with amines[8,9] or oxidation of tris-amidophosphorus.[8] Dehydrosulfuration of $(OR)_2P(S)NHCSNHPh$ yielded $(OR)_2P(S)N{:}C{:}NPh$; the latter on further reaction with 2-bromoethylamine hydrobromide gave imidazolidinylidenamidothiophosphoric esters.[10] Alkylidenamido-bis(amido) phosphoric esters have been obtained from the reaction of bis(dimethylamino)chlorophosphine with ketoximes[11] or the substitution of chlorines from alkylidenamidophosphoric dichloride with amines.[12,13]

Recently, a novel class of halophosphines, namely N-alkyl-2-cycloiminylidenaminodichlorophosphines has been reported as an intermediate during the synthesis of anellated diazaphospholes.[14–16] In view of the electrophilic as well as nucleophilic nature of the phosphorus of the halophosphine moiety,[17] the chlorine atoms of these aminodichlorophosphines may undergo substitution accompanied by the oxidation of phosphorus[18] to form a novel class of alkylidenamidothiophosphates incorporating a variety of nitrogen heterocycles. A novel one-pot synthesis of four new classes of amidothiophosphoric esters and trisamidothiophosphoric esters namely, (1-alkyl-2-pyrimidinylidenamido)bis(diethylamido)thiophosphates, (1-alkyl-2-pyrimidinylidenamido)bis(O-2/4-methylphenyl)thiophosphates, (3-alkyl-2-thiazolinylidenamido)bis(diethylamido)thiophosphate, and (3-alkyl-2-thiazolinylidenamido)bis(O-2/4-methylphenyl)thiophosphates from N-alkyl-2-cycloiminylidenaminodichlorophosphines generated in situ from the reaction of corresponding N-cycloiminium salt with phosphorus trichloride is reported here. Fungicidal properties of these thiophosphates have been investigated against *Fusarium oxysporium* and *Alternaria cymopsidies*.

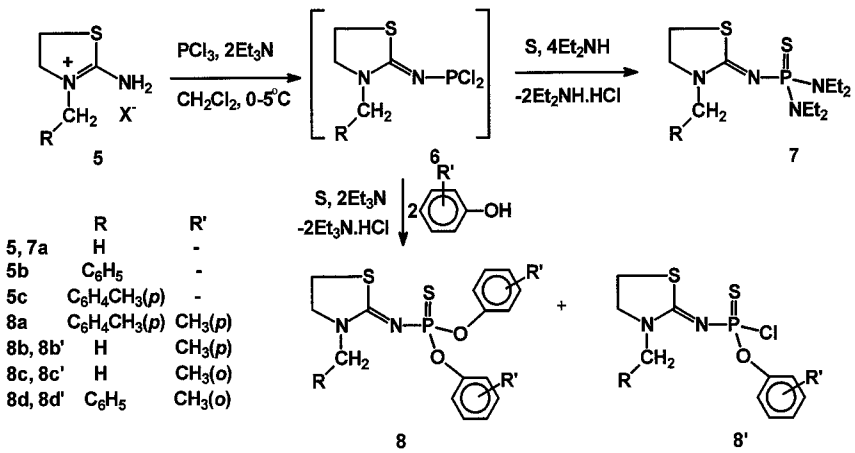
RESULTS AND DISCUSSION

(1-Alkyl-2-pyrimidinylidenamino)dichlorophosphine **2a–c** is generated in situ ($\delta\ ^{31}P \sim 191$) from the reaction of 1-alkyl-2-aminopyrimidinium halide **1a–c** with phosphorus trichloride (1 equivalent) and triethylamine (2 equivalents) in methylene chloride at 0–5°C. Further addition of a four-fold amount of diethylamine and equimolar amount of sulfur results in the formation of (1-alkyl-2-pyrimidinylidenamido) bis(diethylamido)thiophosphates **3a–c** (Scheme 1).



SCHEME 1

Analogously, from the reaction of 2-amino-3-methylthiazolinium iodide **5a** with phosphorus trichloride (1 equivalent) and triethylamine (2 equivalent) followed by reaction with diethylamine (**4** equivalents) and simultaneous oxidation with sulfur (3-methyl-2-thiazolinylidenamido)bis(diethylamido)thiophosphate **7a** is obtained (Scheme 2).



SCHEME 2

The reaction of **1a** or **1b** with *o*-cresol (2 equivalents) and **1a** or **5c** with *p*-cresol (2 equivalents) and triethylamine (2 equivalents)

TABLE I Physical and Spectral Data of Compounds **1**, **3**, **4**, **5**, **7**, **8**

Cpd.	m.p. (°C)	Yield (%)	Mol. form. (mol. wt.)	^{31}P-NMR ($CDCl_3$)	^{1}H-NMR δ ppm (J Hz)
1a	158–159	85	$C_{11}H_{12}N_3Br$ (266.1)	—	5.61 (s, 2H, N—CH_2); 6.73 (t, 1H, $^3J_{HH}$ = 8.5 Hz, 5-H); 7.22 (br s, 5H, C_6H_5); 8.58 (d, 2H,$^3J_{HH}$ = 8.5 Hz, 4-H, 6-H); 8.88 (br s, 2H, NH_2)
1b	178–180	78	$C_{12}H_{14}N_3Cl$ (235.7)	—	2.29 (s, 3H, *p*-CH_3); 5.67 (s, 2H, N—CH_2); 6.82 (dd, 1H, $^3J_{HH}$ = 8.5, 5.7 Hz, 5-H); 7.06 (d, 2H, $^3J_{HH}$ = 7.1 Hz, *m*-H); 7.31 (d, 2H, $^3J_{HH}$ = 7.1 Hz, *o*-H); 8.37 (dd, 1H, $^3J_{HH}$ = 8.5, $^4J_{HH}$ = 2.8 Hz, 4-H); 8.58 (dd, 1H, $^3J_{HH}$ = 5.7, $^4J_{HH}$ = 2.8 Hz, 6-H); 9.36 (br s, 2H, NH_2)
1c	233–235	87	$C_5H_8N_3I$ (237.0)	—	3.56 (s, 3H, N—CH_3); 6.73 (t, 1H, $^3J_{HH}$ = 7.1 Hz, 5-H); 8.43 (d, 2H, $^3J_{HH}$ = 7.1, 4-H, 6-H); 8.74 (br s, 2H, NH_2)
3a	123–124	55	$C_{19}H_{30}N_5SP$ (391.5)	66.4	0.99 (t, 12H, $^3J_{HH}$ = 7.1 Hz, NCH_2CH_3); 3.03 (dq, 8H, $^3J_{HH}$ = 7.1, $^3J_{PH}$ = 19.8 Hz, NCH_2CH_3); 4.96 (s, 2H, $NCH_2C_6H_5$); 6.04 (dd, 1H, $^3J_{HH}$ = 7.1, 4.5 Hz, 5-H); 7.01 (br s, 5H, C_6H_5); 7.30 (d, 1H, $^3J_{HH}$ = 7.1 Hz, 4-H); 8.30 (d, 1H, $^3J_{HH}$ = 4.5 Hz, 6-H)
3b	122–123	46	$C_{20}H_{32}N_5SP$ (405.5)	66.2	0.99 (t, 12H, $^3J_{HH}$ = 7.1 Hz, NCH_2CH_3); 2.25 (s, 3H, *p*-CH_3); 3.04 (dq, 8H, $^3J_{PH}$ = 17.3, $^3J_{HH}$ = 7.1 Hz, NCH_2CH_3); 5.03 (s, 2H, NCH_2); 6.10 (dd, 1H, $^3J_{HH}$ = 7.1, 5.7 Hz, 5-H); 7.11 (s, 4H, C_6H_4); 7.28 (d, 1H, $^3J_{HH}$ = 7.1 Hz, 4-H); 8.34 (unresolved d, 1H, 6-H)
3c	124–125	50	$C_{13}H_{16}N_5SP$ (305.3)	65.0	1.0 (t, 12H, $^3J_{HH}$ = 7.1 Hz, NCH_2CH_3); 3.06 (dq, 8H, $^3J_{HH}$ = 5.7, $^3J_{PH}$ = 19.8 Hz, NCH_2CH_3); 3.40 (s, 3H, N—CH_3); 6.12 (dd, 1H, $^3J_{HH}$ = 5.7, $^3J_{HH}$ = 4.5 Hz, 5-H), 7.51 (d, 1H, $^3J_{HH}$ = 5.7 Hz, 4-H); 8.39 (d, 1H, $^3J_{HH}$ = 4.5 Hz, 6-H)
4a	99–100	45	$C_{25}H_{24}N_3O_2SP$ (461.5)	58.5	2.30 (s, 6H, *o*-CH_3); 4.99 (s, 2H, N—CH_2); 6.38(dd, 1H, $^3J_{HH}$ = 6.6, 4.2 Hz, 5-H); 6.98 (d, 2H, $^3J_{HH}$ = 7.3 Hz, 3′-H of OC_6H_4); 7.04 (dd, 2H, $^3J_{HH}$ = 7.6, 6.8 Hz, 5′-H of OC_6H_4); 7.09 (t, 2H, $^3J_{HH}$ = 6.5 Hz, 4′-H of OC_6H_4); 7.12 (d, 2H, $^3J_{HH}$ = 6.8 Hz, 6′-H of OC_6H_4); 7.29 (unresolved, 2H, *m*-H of C_6H_5); 7.33 (dd, 1H, $^3J_{HH}$ = 5.6, $^4J_{HH}$ = 2.9 Hz, *p*-H of C_6H_5); 7.42 (d, 2H, $^3J_{HH}$ = 8.1 Hz, *o*-H of C_6H_5); 7.68 (dd, 1H, $^3J_{HH}$ = 6.6, $^4J_{HH}$ = 2.7 Hz, 4-H); 8.54 (dd, 1H, $^3J_{HH}$ = 4.8, $^4J_{HH}$ = 2.9 Hz, 6-H)
4b	105–107	44	$C_{26}H_{26}N_3O_2SP$ (475.5)	58.8	2.34 (s, 9H, *o*-CH_3 & *p*-CH_3); 4.97 (s, 2H, N—CH_2); 6.42 (unresolved, 1H, 5-H); 6.89–7.27 (m, 12H, C_6H_4); 7.42 (d, 1H, $^3J_{HH}$ = 5.7 Hz, 4-H); 8.56 (unresolved, 1H, 6-H)
4c	89–90	40	$C_{25}H_{24}N_3O_2SP$ (461.5)	58.7	2.25 (s, 6H, *p*-CH_3); 5.10 (s, 2H, N—CH_2); 6.43 (dd, 1H, $^3J_{HH}$ = 7.1, 5.7 Hz, 5-H); 6.91–7.47 (m, 13H, OC_6H_4, C_6H_5); 7.59 (d, 1H, $^3J_{HH}$ = 7.1 Hz, 4-H); 7.69 (d, 1H, $^3J_{HH}$ = 5.7 Hz, 6-H)

4d	—	—	$C_{19}H_{20}N_3O_2SP$ (385.4)	58.6	2.37 (s, 6H, *o*-CH_3); 3.49 (s, 3H, N—CH_3); 6.41 (unresolved, 1H, 5-H); 7.01–7.54 (unresolved m, 8H, OC_6H_4); 7.81 (d, 1H, $^3J_{HH}$ = 6.7 Hz, 4-H); 8.62 (d, 1H, $^3J_{HH}$ = 6.9 Hz, 6-H)
4d′	—	—	$C_{12}H_{13}N_3OSPCl$ (313.7)	61.4	2.42 (s, 3H, *o*-CH_3); 3.56 (s, 3H, N—CH_3); 6.79 (unresolved, 1H, 5-H); 7.01–7.54 (m, 4H, OC_6H_4); 7.84 (d, 1H, $^3J_{HH}$ = 6.8 Hz, 4-H); 8.74 (d, 1H, $^3J_{HH}$ = 7.1 Hz, 6-H)
5a	155–156	96	$C_4H_9N_2SI$ (244.1)	—	2.80 (s, 3H, N—CH_3); 3.59 (t, 2H, $^3J_{HH}$ = 7.1 Hz, 5-H); 4.18 (t, 2H, $^3J_{HH}$ = 7.1 Hz, 4-H); 9.90 (s, 2H, NH_2)
5b	107–108	83	$C_{10}H_{13}N_2SBr$ (273.2)	—	3.13 (t, 2H, $^3J_{HH}$ = 8.0 Hz, 5-H); 3.90 (t, 2H, $^3J_{HH}$ = 8.0 Hz, 4-H); 4.91 (s, 2H, N—CH_2); 7.21 (br s, 5H, C_6H_5); 10.11 (br s, 2H, NH_2)
5c	220–222	89	$C_{11}H_{15}N_2SBr$ (287.2)	—	1.85 (s, 3H, *p*-CH_3); 2.80 (t, 2H, $^3J_{HH}$ = 7.5 Hz, 5-H); 3.23 (t, 2H, $^3J_{HH}$ = 7.5 Hz, 4-H); 4.12 (s, 2H, NCH_2); 7.46 (br s, 4H, *o*-H & *m*-H); 10.06 (s, 2H, NH_2)
7a	49–50	56	$C_{12}H_{27}N_4S_2P$ (322.5)	66.8	1.05 (t, 12H, $^3J_{HH}$ = 7.1 Hz, NCH_2CH_3); 2.93 (t, 2H, $^3J_{HH}$ = 7.1 Hz, 5-H); 2.97 (s, 3H, N—CH_3); 3.20 (q, 8H, $^3J_{HH}$ = 7.1 Hz, NCH_2CH_3); 3.58 (t, 2H, $^3J_{HH}$ = 7.1 Hz, 4-H)
8a	95–97	40	$C_{25}H_{27}N_2O_2S_2P$ (454.6)	60.6	2.29 (s, 6H, $OC_6H_4CH_3$); 2.32 (s, 3H, $NCH_2C_6H_4CH_3$); 3.12 (t, 2H, $^3J_{HH}$ = 7.6 Hz, 5-H); 3.49 (t, 2H, $^3J_{HH}$ = 7.6 Hz, 4-H); 4.52 (s, 2H, NCH_2); 6.95 (d, 2H, $^3J_{HH}$ = 7.3 Hz, *o*-H of $NCH_2C_6H_4$); 6.98 (d, 2H, $^3J_{HH}$ = 7.3 Hz, *m*-H of $NCH_2C_6H_4$); 7.07 (dd, 4H, $^3J_{HH}$ = 8.3, $^4J_{PH}$ = 3.4 Hz, *o*-H of OC_6H_4); 7.15 (dd, 4H, $^3J_{HH}$ = 8.3, $^4J_{PH}$ = 1.5 Hz, *m*-H of OC_6H_4)
8b	—	—	$C_{18}H_{21}N_2O_2S_2P$ (392.5)	61.3	2.26 (s, 6H, *p*-CH_3); 2.99 (s, 3H, NCH_3); 3.23 (unresolved triplet, 2H, 5-H), 3.65 (unresolved triplet, 2H, 4-H), 7.08–7.14 (m, 8H, C_6H_4)
8b′	—	—	$C_{11}H_{14}N_2OS_2PCl$ (320.8)	64.8	2.33 (s, 3H, *p*-CH_3), 3.05 (s, 3H, NCH_3); 3.32 (t, 2H, $^3J_{HH}$ = 8.0 Hz, 5-H); 3.74 (t, 2H, $^3J_{HH}$ = 8.0 Hz, 4-H); 7.15 (d, 2H, $^3J_{HH}$ = 8.3 Hz, *m*-H); 7.22 (dd, 2H, $^3J_{HH}$ = 8.28 Hz, $^4J_{PH}$ = 1.9 Hz, *o*-H)
8c	—	—	$C_{18}H_{21}N_2O_2S_2P$ (392.5)	60.2	2.32 (s, 6H, *o*-CH_3); 2.93 (s, 3H, NCH_3); 3.21 (t, 2H, $^3J_{HH}$ = 7.6 Hz, 5-H); 3.63 (t, 2H, $^3J_{HH}$ = 7.6 Hz, 4-H); 7.09–7.47 (m, 8H, C_6H_4)
8c′	—	—	$C_{11}H_{14}N_2OS_2PCl$ (320.8)	63.7	2.36 (s, 3H, *o*-CH_3); 3.00 (s, 3H, NCH_3); 3.31 (t, 2H, $^3J_{HH}$ = 7.6 Hz, 5-H); 3.72 (t, 2H, $^3J_{HH}$ = 7.6 Hz, 4-H); 7.09 –7.47 (m, 4H, C_6H_4)
8d	—	—	$C_{24}H_{25}N_2O_2S_2P$ (468.6)		2.24 (s, 6H, *o*-CH_3); 3.11 (t, 2H, $^3J_{HH}$ = 7.7 Hz, 5-H); 3.21 (t, 2H, $^3J_{HH}$ = 7.7, 4-H); 4.49 (s, 2H, NCH_2); 7.02–7.37 (m, 13H, C_6H_5, OC_6H_4)
8d′	—	—	$C_{17}H_{18}N_2OS_2PCl$ (396.9)	61.2	2.29 (s, 3H, *o*-CH_3); 3.44 (t, 2H, $^3J_{HH}$ = 7.6 Hz, 5-H); 3.57 (t, 2H, $^3J_{HH}$ = 7.6 Hz, 4-H); 4.54 (s, 2H, NCH_2); 7.02–7.37 (m, 9H, C_6H_5, OC_6H_4)

[a] ^{1}H-NMR of **1** and **5** in $CDCl_3$ + DMSO-d_6 and **3**, **4**, **7** and **8** in $CDCl_3$.

in place of diethylamine under similar conditions affords (1-benzyl-2-pyrimidinylidenamido)bis(O-2-methylphenyl) thiophosphate **4a**, {1-(4-methylbenzyl)-2-pyrimidinylidenamido}bis(O-2-methylphenyl) thiophosphate **4b**, (1-benzyl-2-pyrimidinylidenamido)bis(O-4-methylphenyl) thiophosphate **4c**, and {3-(4-methylbenzyl)-2-thiazolinylidenamido}bis(O-4-methylphenyl)thiophosphate **8a** respectively (Schemes 1 and 2).

The products thus obtained are stable cream to yellow crystalline solids characterized by elemental analysis and NMR spectroscopy (Table I). The ^{31}P NMR signal of **3** and **5** appears at $\delta \sim 66$, which is in the range of trisamidothiophosphates.[19] The ^{31}P NMR signals of **4a–c** and **8a** in the range δ 58–61 is again characteristic for tetracoordinated pentavalent phosphorus compounds.[19,20] However, the reaction of **2c** generated from **1c** with *o*-cresol and sulfur is not complete and a monosubstituted product **4d′** also is obtained in addition to **4d**, as revealed by the appearance of two signals at δ 61.5 and 58.6 in the ^{31}P NMR spectrum of the isolated product. In ^{1}H NMR spectrum a singlet at δ 2.37 is assigned to the six protons of the two methyl groups of cresol corresponding to **4d** and the singlet at δ 2.42 to three protons of one 2-methyl substituent of **4d′**. Similarly, the products isolated from the reactions of **6a** with *p*-cresol and **6a**,**b** with *o*-cresol also are found to be mixtures of mono-(**8b′–d′**) and disubstituted (**8b–d**) compounds (Scheme 2), separation of which could not be accomplished by recrystallization. In the case of the 4-methyl substituent, disubstituted product (**8b**) is obtained in larger amount (85%); while in the case of the 2-methyl substituent, the major component (71–63%) of the product mixture is monosubstituted (**8c′** and **8d′**), indicating that the steric crowding plays an important role on the completion of reaction.

FUNGICIDAL PROPERTIES

The products **3**, **4**, **7**, and **8** have been screened for fungicidal properties against two fungi, namely *Fusarium oxysporium* and *Alternaria cymopsidies* at two concentrations of 100 and 500 ppm, and the results in terms of the radial growth and statistical analysis are given in Table II. All the compounds tested for both test fungi have been found to show significant fungicidal properties in terms of the reduced radial growth wth reference to the control average growths of 84–85% at two concentrations of 5% and 1%. More significant results have been obtained at 5% concentration. Among the trisamodothiophosphate derivatives, those (**3a**,**b**) with bulkier benzyl or *p*-methylbenzyl substituent at endocyclic nitrogen show stronger fungitoxic activity against both fungi.

TABLE II Fungicidal Activity of the Compounds **3**, **4**, **7**, **8**

	Average Radial Growth in mm (range)			
	Fusarium oxysporium		*Alternaria cymopsidies*	
Cpd.	100 ppm	500 ppm	100 ppm	500 ppm
3a	60.72 (47.5–82.5)	25.83 (25.0–27.0)	60.83 (47.5–82.5)	16.67 (15.0–19.0)
3b	59.17 (57.5–60.0)	24.50 (23.5–25.0)	78.67 (70.0–87.5)	17.50 (15.0–20.0)
3c	49.17 (45.0–52.5)	42.33 (35.0–55.0)	72.50 (60.0–82.5)	69.17 (60.0–77.5)
4a	64.17 (60.0–67.5)	45.00 (37.5–50.0)	75.00 (75.0–75.0)	51.67 (50.0–55.0)
4c	25.00 (25.0–25.0)	22.67 (21.0–25.0)	86.50 (82.5–90.0)	66.67 (62.5–72.5)
7a	49.17 (40.0–57.5)	39.17 (35.0–45.0)	71.67 (70.0–72.5)	70.83 (67.5–75.0)
8a	28.00 (25.0–30.0)	16.40 (15.0–17.5)	60.00 (47.5–70.0)	34.67 (29.0–45.0)
8b	63.33 (60.0–65.0)	26.67 (22.5–30.0)	44.17 (35.0–50.0)	12.50 (10.0–15.0)
Acetone (Solvent)	80.00 (75.0–85.0)	80.00 (75.0–85.0)	84.17 (77.5–90.0)	84.17 (77.5–90.0)
Control	84.17 (80.0–87.5)	84.17 (80.0–87.5)	85.00 (80.0–90.0)	85.00 (80.0–90.0)

GM 56.29, 40.67, 69.90, 43.57.
F cal (9.20) 21.35, 66.28, 6.42, 83.96.
SEM± 2.29, 1.59, 2.90, 1.70.
CD 5% 6.76, 4.70, 8.56, 5.01.
CV% 12.87, 12.39, 13.13, 12.33.

However, in the case of amidothiophosphates **4** and **8**, the fungitoxic activity is more significant against *Fusarium oxysporum* than *Alternaria cymopsidies*.

EXPERIMENTAL

All reactions were carried out under nitrogen atmosphere using Schlenk techniques. Solvents were distilled and dried using standard procedures and commercial reagents were freshly distilled under nitrogen atmosphere before use. Melting points were determined by capillary method and are uncorrected. NMR data were recorded on FT NMR spectrometer Jeol FX-90Q at 89.5 MHz (^{1}H NMR) and 36.23 MHz (^{31}P NMR) or Bruker WM-400 at 399.65 MHz (^{1}H NMR), 161.7 MHz (^{31}P NMR) or Bruker DRX-300 at 300.13 MHz (^{1}H NMR) and 121.5 MHz (^{31}P NMR) with reference to TMS (internal) or 85% H_3PO_4 (external). Elemental analyses were carried out on Heraeus Carlo Erba 1108 analyzer.

N-Alkyl-2-aminopyrimidinium Halides (1a–c) and N-Alkyl-2-amino/thiazolinium Halides 5a–c. General Procedure

To a solution of 2-aminopyrimidine (2.853 g, 30 mmol) or 2-aminothiazoline (3.064 g, 30 mmol) in tetrahydrofuran (60 mL) was added

an equimolar amount of benzyl bromide (3.6 mL), *p*-methylbenzyl chloride (4.0 mL)/*p*-methylbenzyl bromide (5.552 g) or methyl iodide (1.9 mL) and the resulting mixture was stirred at room temperature for 5–10 days. White or cream colored solid thus separated was filtered, washed with diethyl ether, and used without further purification.

(1-Alkyl-2-pyrimidinylidenamido)bis(diethylamido)-thiophosphate (3a–c). General Procedure

To a suspension of 1-alkyl-2-aminopyrimidinium bromide (10 mmol) in methylene chloride (30 mL) was added phosphorus trichloride (1.0 mL, 10 mmol) at 0–5°C. A solution of triethylamine (2.8 mL, 20 mmol) in methylene chloride (10 mL) was added dropwise with stirring. The reaction mixture was brought to room temperature and the stirring was continued for 4–5 h. To this was added sulfur powder (320 mg, 10 mmol) followed by dropwise addition of a solution of diethylamine (4.2 mL, 40 mmol) in methylene chloride (10 mL) while maintaining the temperature at 0–5°C and the resulting mixture was stirred overnight at room temperature. Solvent was removed under reduced pressure and the residue extracted with diethyl ether (3 × 50 mL). On leaving the combined and concentrated extract in refrigerator, **3a–c** separated as creamish white solid, which was filtered washed with hexane and dried.

3a	Yield 55%;	%Calc C 58.28	H 7.22	N 17.88
		%Found 58.08	7.18	17.95
3b	Yield 46%;	%Calc C 59.18	H 7.89	N 17.26
		%Found 59.03	7.92	17.45
3c	Yield 50%;	%Calc C 49.49	H 8.30	N 22.20
		%Found 49.37	8.33	22.17

(1-Alkyl-2-pyrimidinylidenamido)bis(O-2/4-methylphenyl)thiophosphates (4a–d). General Procedure

Phosphorus trichloride (1.8 mL, 20 mmol) was added to a well-stirred suspension of 1-alkyl-2-aminopyrimidinium halide (20 mmol) in methylene chloride (50 mL) at 0–5°C. A solution of triethylamine (5.6 mL, 40 mmol) in methylene chloride (10 mL) was added dropwise slowly with constant stirring. The reaction mixture was brought to room temperature and the stirring was continued for 5 h. To this was added sulfur powder (640 mg, 20 mmol) and triethylamine (5.6 mL,

40 mmol) followed by dropwise addition of a solution of *o*- or *p*-cresol (4.2 mL, 40 mmol) in methylene chloride (10 mL) over 15–20 min while maintaining the temperature at 0–5°C. The resulting reaction mixture stirred overnight at room temperature. Solvent was removed under reduced pressure and the residue extracted with diethyl ether (2 × 50 mL). On leaving the combined and concentrated extract in refrigerator, **4a–c** deposited as light yellow crystalline solid, which was filtered washed with hexane and dried. However, the product obtained from the reaction of **1c** with *o*-cresol was found to be a mixture of (1-methyl-2-pyrimidinylidenamido)bis(O-2-methylphenyl)-thiophosphate (**4d**, 25%) and (1-methyl-2-pyrimidinylidenamido)-(O-2-methylphenyl)thiophosphoric chloride (**4d′**, 75%).

4a	Yield 45%;	%Calc C 65.06	H 5.24	N 9.10
		%Found 65.27	5.21	9.06
4b	Yield 44%;	%Calc C 65.66	H 5.51	N 8.83
		%Found 65.79	5.47	8.77
4c	Yield 40%;	%Calc C 65.06	H 5.24	N 9.10
		%Found 65.19	5.28	9.17

Bis(diethylamido)(3-methyl-2-thiazolinylidenamido)thiophosphate (7a)

To a suspension of 2-amino-3-methylthiazolinium iodide (3.904 g, 16 mmol) in methylene chloride (30 mL) was added phosphorus trichloride (1.4 mL, 16 mmol) at 0–5°C. A solution of triethylamine (4.4 mL, 32 mmol) in methylene chloride (10 mL) was added dropwise with stirring. The reaction mixture was brought to room temperature and the stirring was continued for 4 h. To this was added sulfur powder (512 mg, 16 mmol) followed by dropwise addition of a solution of diethylamine (6.6 mL, 64 mmol) in methylene chloride (10 mL) while maintaining the temperature at 0–5°C and the resulting mixture was stirred overnight at room temperature. Solvent was removed under reduced pressure and the residue extracted with diethyl ether (3 × 50 mL). On leaving the combined and concentrated extract in refrigerator, **7a** separated as creamish white solid, which was filtered washed with hexane and dried.

7a	Yield 56%;	%Calc C 44.69	H 8.37	N 17.36
		%Found 44.75	8.28	17.11

(3-Alkyl-2-thiazolinylidenamido)bis(O-2/4-methylphenyl)thiophosphate (8a–d) and (3-Alkyl-2-thiazolinylidenamido)(O-2/4-methylphenyl)-thiophosphoric Chloride (8b′–d′). General Procedure

Phosphorus trichloride (0.9 mL, 10 mmol) was added to a well-stirred suspension of 3-alkyl-2-aminothiazolinium halide (10 mmol) in methylene chloride (40 mL) at 0–5°C. A solution of triethylamine (2.8 mL, 20 mmol) in methylene chloride (10 mL) was added dropwise with constant stirring. The reaction mixture was brought to room temperature and the stirring was continued for 6 h. To this was added sulfur powder (320 mg, 10 mmol) and triethylamine (2.8 mL, 20 mmol) followed by dropwise addition of a solution of *o*- or *p*-cresol (2.1 mL, 20 mmol) in methylene chloride (10 mL) over 15–20 min while maintaining the temperature again at 0–5°C. The resulting reaction mixture was stirred overnight at room temperature. Solvent was removed under reduced pressure and the residue extracted with diethyl ether (2 × 50 mL). On leaving the combined and concentrated extract in refrigerator, white to pale crystalline solid deposited, which was filtered washed with hexane and dried. Except **8a**, the product was found to be a mixture of **8** and **8′**.

8a	Yield 40%;	%Calc C 62.21	H 5.60	N 5.80
		%Found 62.34	5.54	5.71

Fungicidal Activity

A standard method to evaluate the fungitoxic properties of the compounds was adopted here. Using the poison food technique, the two pathogens, *Fusarium oxysporium* and *Alternaria cymopsidies*, were isolated from the *Cumin* (*Cuminum cyminum*) and *cluster bean* (*Cymopsis tetragonal*) crops, respectively on 2% sterile potato-dextrose agar (PDA) medium. Test compounds were added to this in two concentrations (100 ppm and 500 ppm). This poisoned medium was poured into petriplates (90 mm diameter) and was inoculated by inoculum disk of 3 mm diameter cut from the margin of a 6-day old culture of the test pathogen and incubated at 26°C. Each experiment was replicated three times and a suitable control without the test compound was also maintained. The radial growth of the mycelium was measured in mm after 6 days.

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