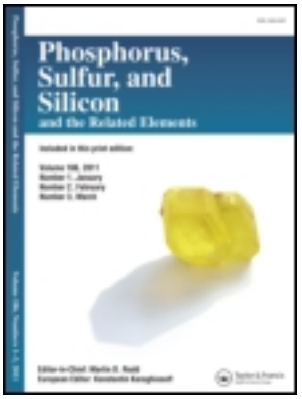

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Synthesis, Structures, and Fungitoxicity of Novel Organophosphorus Compounds

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SYNTHESIS, STRUCTURES, AND FUNGITOXICITY OF NOVEL ORGANOPHOSPHORUS COMPOUNDS

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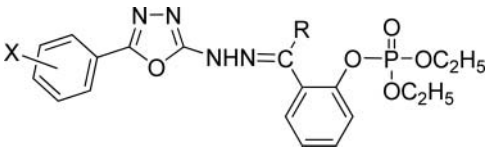
GRAPHICAL ABSTRACT



Abstract *A series of biologically active organophosphorus compounds have been synthesized by the reactions of O,O-diethylchlorophosphate with Schiff bases derived from 5-(phenyl/substituted phenyl)-2-hydrazino-1,3,4-oxadiazole and salicylaldehyde/2-hydroxyacetophenone. The compounds have been characterized on the basis of analyses and spectral (IR, ^{1}H, ^{13}C NMR) data. Fungicidal activities of these derivatives against* Colletotrichum falcatum, Fusarium oxysporum*, and* Curvularia pallescence *have been evaluated. All compounds showed moderate to significant antifungal activity.*

Keywords Organophosphorus derivatives; IR; NMR; fungicidal properties

INTRODUCTION

One of the most important groups of pesticides is the organophosphorus compounds.[1] Their pesticidal value is rated high especially because they have wide spectrum of action on plant pests, are readily metabolized, and have little residual toxicity. A few recent studies[2–5] from our laboratory have shown that on the basis of suitable logic organic molecules, incorporating phosphorus may be designed such that they may be less dangerous in use without losing their value as effective pesticides. One of the useful properties of phosphorus compounds is their relatively low stability and rapid metabolic breakdown in plants, animals, organisms, soil, and in other components of the environment, with the formation of products that are safe for human beings and domestic animals.[6] Another important feature of these compounds is the high selectivity of their action. The discovery of the mechanism

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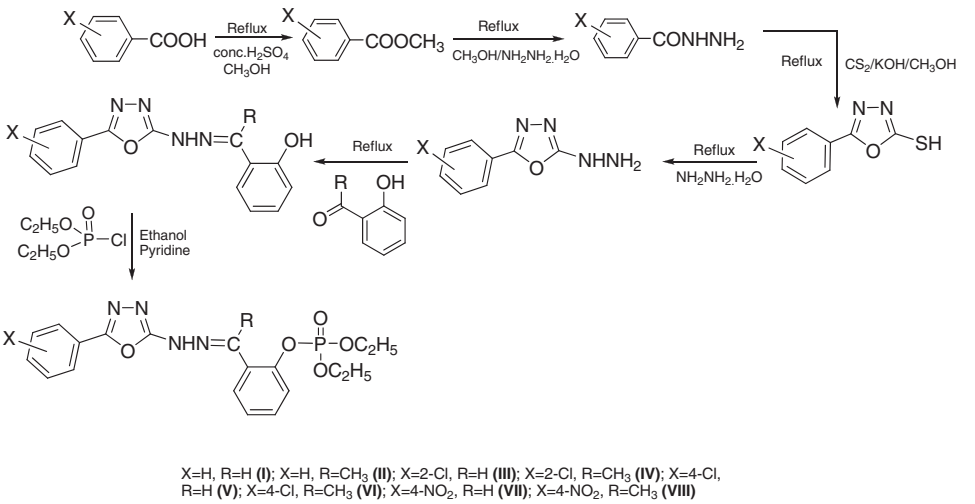
of action[6,7] of organophosphorus compounds makes it possible to develop the fundamental principles of the direct synthesis of new substances and to establish the cause of their selective action on an organism. Organophosphorus compounds containing P—O—C and P—S—C bonds show exciting pesticidal properties.[8] Studies on organophosphorus derivatives could constitute a new and promising field of application in the national economy. The present study was therefore undertaken to evaluate the antifungal efficacy of some newly synthesized organophosphorus compounds against various important fungal pathogens of sugarcane.

RESULTS AND DISCUSSION

Reactions of O,O-diethylchlorophosphate with Schiff bases derived from 5-(phenyl/substituted phenyl)-2-hydrazine-1,3,4-oxadiazole and salicylaldehyde/2-hydroxyacetophenone have been carried out in methanol in the presence of pyridine and a variety of organophosphorus derivatives have been isolated according to Scheme 1.



X=H, R=H **(I)**; X=H, R=CH_3 **(II)**; X=2-Cl, R=H **(III)**; X=2-Cl, R=CH_3 **(IV)**; X=4-Cl, R=H **(V)**; X=4-Cl, R=CH_3 **(VI)**; X=4-NO_2, R=H **(VII)**; X=4-NO_2, R=CH_3 **(VIII)**

Scheme 1 Synthetic route of O,O-diethylchlorophosphate derivatives containing Schiff bases derived from 5-(phenyl/substituted phenyl)-2-hydrazino-1,3,4-oxadiazole and salicylaldehyde/2-hydroxy acetophenone.

The methods used for the preparation and isolation of these compounds gave materials of good purity as supported by their analyses and thin layer chromatography. The elemental analyses and physical properties of the organophosphorus derivatives are given in Table 1. The organophosphorus derivatives are found to be soluble in dimethylformamide, tetrahydrofuran, and dimethylsulfoxide.

Infrared Spectra

The infrared spectral bands of the ligands and their corresponding complexes are given in Table 2. A comparison of characteristic infrared absorption bands of Schiff bases with those of the corresponding organophosphorus derivatives gives information regarding the structures of the compounds. The infrared spectra of the Schiff bases show bands at *ca.*

Table 1 Physical and analytical data of organophosphorus compounds

Compounds	Reflux time (h)	Yield (%)	Color	Decom. temp. (°C)	Found (calcd) (%)			
					C	H	N	Cl
[{$(C_2H_5O)_2PO$}$C_{15}H_{11}N_4O$] **(I)**	24	64	Cream	188–192	54.70 (54.04)	5.02 (5.06)	13.31 (13.46)	—
[{$(C_2H_5O)_2PO$}$C_{16}H_{13}N_4O$] **(II)**	23	59	Light yellow	168–173	55.76 (55.61)	5.27 (5.39)	12.91 (13.02)	—
[{$(C_2H_5O)_2PO$}$C_{15}H_{10}N_4OCl$] **(III)**	22	61	Light brown	178–182	55.53 (55.62)	4.31 (4.47)	12.22 (12.43)	7.61 (7.66)
[{$(C_2H_5O)_2PO$}$C_{15}H_{12}N_4OCl$] **(IV)**	26	66	Light yellow	163–167	51.41 (51.68)	4.68 (4.77)	11.96 (12.05)	7.47 (7.63)
[{$(C_2H_5O)_2PO$}$C_{15}H_{10}N_4OCl$] **(V)**	23	59	Light brown	170–173	50.56 (50.62)	4.41 (4.47)	12.31 (12.43)	7.64 (7.86)
[{$(C_2H_5O)_2PO$}$C_{15}H_{12}N_4OCl$] **(VI)**	24	63	Light yellow	164–168	51.47 (51.68)	4.67 (4.77)	11.93 (12.05)	7.44 (7.63)
[{$(C_2H_5O)_2PO$}$C_{15}H_{10}N_5O_3$] **(VII)**	23	60	Yellow	182–187	49.41 (49.46)	4.29 (4.37)	15.09 (15.18)	—
[{$(C_2H_5O)_2PO$}$C_{15}H_{12}N_5O_3$] **(VIII)**	21	62	Yellow	158–162	50.46 (50.53)	4.58 (4.66)	14.16 (14.73)	—

Table 2 Infrared spectral bands of Schiff bases and their corresponding organophosphorus derivatives

Compound	ν(N−H)	ν(C=N)	ν(C−O−C)	ν(P=O)	ν(P−O−C)
I	3150 m	1620 s, 1570 m	1360 m, 1280 s	1260 m	1020 s
II	3145 m	1610 s, 1580 m	1350 m, 1285 s	1265 m	1025 s
III	3160 m	1615 s, 1510 m	1355 m, 1275 s	1258 m	1030 s
IV	3150 m	1610 s, 1575 m	1352 m, 1278 s	1260 m	1020 s
V	3155 m	1620 s, 1570 m	1348 m, 1280 s	1262 m	1025 s
VI	3160 m	1618 s, 1580 m	1350 m, 1282 s	1265 m	1030 s
VII	3150 m	1620 s, 1565 m	1350 m, 1280 s	1260 m	1010 s
VIII	3145 m	1610 s, 1580 m	1355 m, 1278 s	1255 m	1015 s

1620–1610 and 1580–1565 cm^{-1} that may be assigned[7–9] to ν(C=N; azomethine group) and ν(C=N; ring), respectively. All these bands are present almost at the same position in their corresponding organophosphorus derivatives indicating the non-involvement of these groups in the bond formation. All Schiff bases and their corresponding organophosphorus derivatives show band at *ca.* 3150 cm^{-1} assignable[10] to ν(N—H). The ν(C—O—C) bands in the Schiff bases occur at *ca*. 1350 cm^{-1} (asymmetric) and at *ca.* 1280 cm^{-1}(symmetric), which remain unaltered in the spectra of the complexes indicating[11–13] the non-coordination of oxygen atom of the oxadiazole ring. The infrared spectra of these Schiff bases show strong band at *ca.* 3400 cm^{-1} due to ν(O—H). However, this band disappears in the spectra of their corresponding complexes indicating[14] the coordination of the phenolic oxygen to phosphorus. The ν(P—O—C) band appears[4,5] at *ca.* 1025 cm^{-1}. In addition, all phosphate derivatives show bands at *ca*.1260 cm^{-1} due to ν(P=O).[15–17]

Proton Magnetic Resonance Spectra

The proton magnetic resonance spectra of the derivatives have been recorded in dimethyl sulfoxide (DMSO)-d_6 (Table 3). The line intensities were determined by planimetric integration. The Schiff bases and their corresponding organophosphorus derivatives show signal at *ca*. δ ~7.20 due to NH proton. The signals (multiplet) due to aromatic ring protons appear in region *ca*. δ 7.40–7.65. The signals due to ethoxy group appear at *ca*. δ 2.10–2.28 (triplet, CH_3) and at *ca*. δ 3.18–3.40 (quartet, CH_2) in the spectra of all organophosphorus derivatives. The spectra of all Schiff bases show a signal at *ca*. δ 10.50, which disappear in their corresponding organophosphorus derivatives indicating the deprotonation of phenolic proton and formation of bond between oxygen and phosphorus. The signal, because of the methyl group, appears at *ca.* δ 1.98 (singlet, CH_3). A signal, because of the azomethine proton (—CH=N—), appears at *ca.* δ 8.12–8.22 in the spectra of Schiff bases and their corresponding organophosphorus derivatives.

^{13}C Magnetic Resonance Spectra

The ^{13}C NMR spectral data of organophosphorus compounds are given in Table 3. For O,O-diethyl group, two signals appear at *ca.* δ 58.1–59.2 (CH_2) and δ 14.1–15.0 (CH_3). For oxadiazole ring carbons, two signals appear at *ca.* 160–166 ppm, while for imine carbon a signal appears at *ca*. δ 154.7–155.6. For phenyl ring, a number of signals appear.

Representative ^{1}H and ^{13}C NMR spectra for compounds **I** and **V** are shown in the Supplementary Materials (Figures S2–S5; posted online only).

Antifungal Activity

Sugarcane, a major source of sugar and important cash crop, is extensively grown worldwide. Diseases are one of the major constraints in the profitable cultivation of sugarcane. About 100 diseases of sugarcane caused by virus, fungi, bacteria, phytoplasma, and nematodes have been reported from different parts of the world. Among fungal diseases, red rot by *Colletotrichum falcatum*, wilt caused by *Fusarium monliforme* and *Fusarium oxysporum*, and leaf spots caused by *Curvularia lunata* and *Curvularia pallescence* are the main diseases responsible for loss in sugarcane production.[6]

The organophosphorus derivatives containing Schiff bases of 5-(phenyl/substituted phenyl)-2-hydrazino-1,3,4-oxadiazole show promising results inhibiting the mycelia

Table 3 ^{1}H NMR and ^{13}C NMR data (scale, ppm) of organophosphorus derivatives containing Schiff bases derived from 5-(phenyl/substituted phenyl)-2-hydrazino-1,3,4-oxadiazole and salicylaldehyde/2-hydroxyacetophenone

	^{1}H NMR					^{13}C NMR				
Compound	N=CH−	Aromatic ring	−NH	$-C_2H_5$	$-CH_3$	Aromatic ring	Oxadiazole ring	Imine carbon	$-CH_3$	$-CH_2$
I	8.12 (s)	7.40–7.58 (m)	7.20 (s)	3.28 (q; $J = 7.0$ Hz)), 2.15 (t; $J = 7.1$ Hz)	—	115.0, 120.2, 121.2, 127.1, 128.1, 128.2, 130.1, 136.1, 137.2, 148.1	161.2, 166.5	154.7	14.1	58.6
II	—	7.45–7.60 (m)	7.20 (s)	3.30 (q; $J = 7.1$ Hz), 2.20 (t; $J = 7.1$ Hz)	1.80 (s)	114.9, 121.2, 123.0, 127.8, 128.4, 130.0, 132.1, 135.5, 137.0, 150.0	161.8, 165.1	155.6	14.6	58.3
III	8.20 (s)	7.45–7.55 (m)	7.20 (s)	3.20 (q; $J = 7.1$ Hz), 2.25 (t; $J = 7.0$ Hz)	—	114.0, 118.2, 120.6, 122.5, 123.0, 127.5, 128.3, 128.9, 135.1, 135.9, 138.2, 149.0	160.9, 166.8	154.7	15.0	57.9
IV	—	7.44–7.58 (m)	7.24 (s)	3.40 (q; $J = 7.0$ Hz), 2.28 (t; $J = 7.0$ Hz)	1.95 (s)	114.2, 118.3, 120.8, 122.5, 123.6, 127.4, 128.0, 128.8, 135.2, 136.0, 138.6, 148.8	160.4, 165.3	155.6	14.9	59.0
V	8.18 (s)	7.48–7.60 (m)	7.25 (s)	3.18 (q; $J = 7.1$ Hz), 2.18 (t; $J = 7.1$ Hz)	—	115.0, 122.2, 122.8, 127.4, 127.1, 128.9, 133.1, 135.8, 137.2, 149.0	161.9, 166.8	154.7	14.3	58.7
VI		7.42–7.58 (m)	7.28 (s)	3.38 (q; $J = 7.1$ Hz), 2.28 (t; $J = 7.0$ Hz)	1.98 (s)	114.9, 123.1, 124.0, 127.8, 128.2, 129.3, 132.1, 135.6, 138.4, 150.2	160.7, 166.1	155.6	14.8	58.1
VII	8.22 (s)	7.48–7.65 (m)	7.20 (s)	3.25 (q; $J = 7.0$ Hz), 2.10 (t; $J = 7.0$ Hz)	—	115.2, 122.2, 122.9, 126.6, 127.5, 131.0, 135.1, 137.8, 142.1, 151.3	161.2, 166.4	154.7	14.3	59.2
VIII	—	7.46–7.58 (m)	7.00 (s)	3.18 (q; $J = 7.1$ Hz), 2.25 (t; $J = 7.0$ Hz)	1.92 (s)	114.9, 121.2, 123.1, 127.1, 127.9, 132.0, 135.6, 138.4, 143.2, 151.3	160.9, 165.8	155.6	14.6	58.8

growth of all the test fungi. Best result was obtained with O,O-diethylphosphate derivative containing 2-(1{(5-(4-chlorophenyl)-[1,3,4] oxadiazole-2-yl]-hydrazono}-ethyl]-phenol **(VI)**. This compound showed activity upto 77.8% against *C. falcatum*, 71.2% against *F. oxysporum*, and 69.8% against *C. Pallescence* at 1000 ppm concentration. Other derivatives also showed antifungal activity against all test fungi from 37.8% to 70.2% at 1000 ppm concentration. A graphical representation of the results is presented in Table S1 and Figure S1 (Supplementary Materials; posted online only).

EXPERIMENTAL

The reaction of O,O-diethylchlorophosphate was carried out under anhydrous conditions. Special precautions were taken to exclude moisture from the apparatus and chemicals as the starting materials (O,O-diethylchlorophosphate) and reactions were susceptible to hydrolysis. Glass apparatus with interchangeable joints were used throughout the work. All the organic solvents used were of analytical reagent grade. The solvents were purified and dried using the method described in the literature.[2] O,O-diethylchlorophosphate was prepared by adding a solution of pyridine, absolute ethanol, and benzene dropwise to an ice-cooled solution of phosphorus oxychloride in benzene at temperature below 20 °C.[3] After 3 h of stirring, the pyridine hydrochloride was filtered off. The product, after distillation, was obtained as colorless liquid (bp 60–63 °C/2.5 mm Hg). The details of analysis and physical measurements were the same as reported earlier.[2]

For antifungal activity, all the compounds were tested against all test fungi by the food poison technique[4] at three concentrations (10, 100, and 1000 ppm). For this, the desired amount of chemical was dissolved in 0.5 mL of solvent and mixed with the culture medium on the basis of the volume of medium in each Petri plate (80 mm diameter). Oatmeal agar medium was used for all test fungi. In controls, the same amount of medium containing the requisite amount of solvent was poured in place of test chemicals. A mycelia disk (5 mm diameter) obtained from the periphery of two-week old cultures was taken and transferred to the center of each Petri plate. Plates were incubated for seven days at 28 ± 2 °C. Each treatment was repeated three times, and the inhibition was recorded relative to percent mycelia inhibition calculated using, the formula:

$$[(dc - dt)/dc] \times 100$$

where *d*c is the average diameter of the mycelia colony of the control and *d*t is the average diameter of the mycelia colony of the treatment.

Reactions of O,O-diethylchlorophosphate with Schiff bases: O,O-diethylchlorophosphate (0.01 mol) was added to a solution of the appropriate Schiff base (0.01 mol) in methanol (25 mL) in the presence of pyridine (5 mL), and reaction mixture was refluxed for *ca*. 21–26 h. The precipitate, thus obtained, was filtered off. The compound was recrystallized from methanol.

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