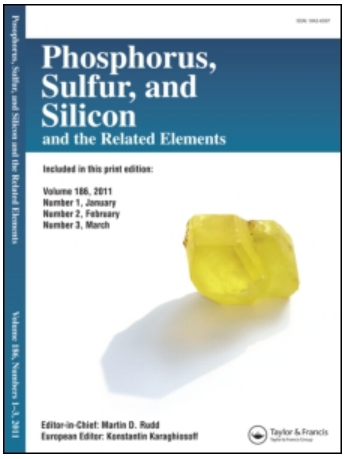

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Synthesis and Biological Activity of Some Novel *O*-Phosphorylated Benzoxazole Derivatives

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Synthesis and Biological Activity of Some Novel *O*-Phosphorylated Benzoxazole Derivatives

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The phosphorylation of 2-(2′-hydroxyphenyl) benzoxazole has been accomplished with phosphorus oxychloride in a 1:1, 2:1, and 3:1 molar ratio in the presence of a base to yield O-phosphorylated benzoxazole derivatives. Their structures were confirmed by elemental analyses and IR, ^{1}H NMR, and ^{31}P NMR spectral studies. These compounds have been screened for their insecticidal activity against Periplenata americana *and were found to be quite active in this respect.*

Keywords Benzoxazole; insecticidal activity; phosphorylation

INTRODUCTION

Organophosphoric esters and related compounds are well known for their broad-spectrum biocidal activity and superiority to organochlorine pesticides.[1–3] Phosphorylated heterocycles have gained importance in a variety of fields, viz. pesticides, insecticides, fungicides, bactericides, and even as growth regulators.[4–5] Liu-Zhao-Jie and Li-Min[6] reported phosphorylation reactions of benzoxazolone. In the present communication, we report the synthesis, characterization, and biological activity of some novel O-phosphorylated benzoxazole derivatives.

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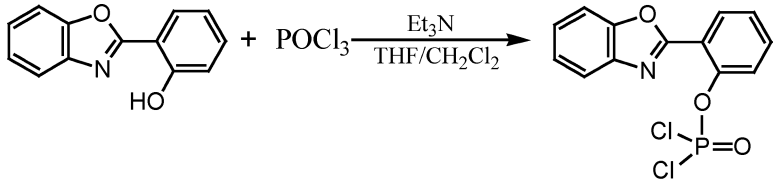
RESULTS AND DISCUSSION

The reactions of 2-(2′-hydroxyphenyl)benzoxazole with phosphorus oxychloride (1:1, 2:1, and 3:1 molar ratio) in the presence of a stochiometric amount of triethylamine in THF/methylene chloride resulted in the formation of corresponding O-phosphorylated benzoxazole derivatives. In this manner, O-(phenylbenzoxazolyl-2-) phosphorodichloridate (1), O,O-bis(phenylbenzoxazolyl-2-) phosphorochloridate (2), and O,O,O-tris(phenylbenzoxazolyl-2-) phosphorate (3) were obtained (Schemes 1, 2, and 3). The physical and analytical data of the compounds are given in Table I.



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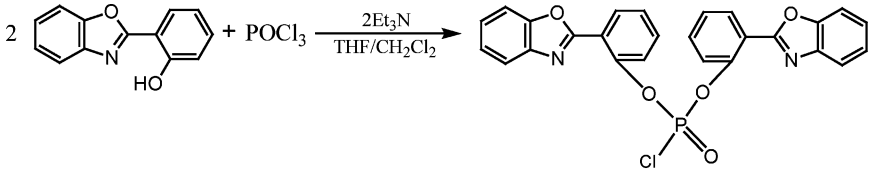
SCHEME 1



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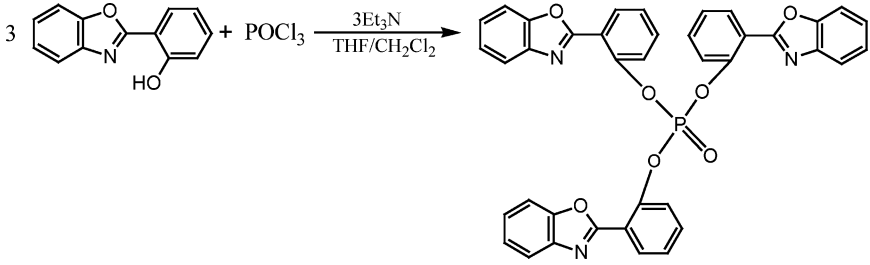
SCHEME 2



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SCHEME 3

TABLE I Physical Properties and Analytical Data of O-Phophorylated Benzoxazole Derivatives

S. No.	Compound Color & State	M.P. °C	Elemental Analysis, % Found (Calcd.) C	H	N	Cl	P
1	$(C_{13}H_8NO_2)P(O)(Cl_2)$	210	47.52	2.41	4.23	21.56	9.38
	Brownish cream solid		(47.59)	(2.46)	(4.27)	(21.61)	(9.44)
2	$(C_{13}H_8NO_2)_2P(O)(Cl)$	220	62.06	3.16	5.52	7.01	6.12
	Creamish solid		(62.10)	(3.20)	(5.57)	(7.05)	(6.16)
3	$(C_{13}H_8NO_2)_3P(O)$	230	69.09	3.52	6.16	—	4.52
	Creamish white solid		(69.13)	(3.57)	(6.20)		(4.57)

IR Spectra

The formation of O-phosphorylated benzoxazole derivatives was indicated by the disappearance of the ν(O–H) absorption band at 3400–3300 cm^{-1} present in 2-(2′-hydroxyphenyl)benzoxazole. In O-(phenylbenzoxazolyl-2-)phosphorodichloridate characteristic stretching vibrations ν(P—O—C),[7] ν(P═O)[8], and ν(P—Cl)[9] appear at 1200–1100 cm^{-1}, 1285–1270 cm^{-1}, and 530–510 cm^{-1} respectively. In O,O,O-tris(phenylbenzoxazolyl-2-)phosphorate chracteristic stretching vibrations, ν(P—O—C) and ν(P═O) appear at 1140–1130 cm^{-1} and 1290–1280 cm^{-1}, respectively (Table II).

^{1}H NMR Spectra

The ^{1}H NMR spectrum of 2-(2′-hydroxyphenyl) benzoxazole shows an OH proton signal at ~δ10.5 ppm, and aromatic protons were observed at ~δ7.9–8.0 ppm. The OH proton signal at ~δ10.5 ppm disappeared in O-phosphorylated benzoxazole derivatives.

TABLE II IR Spectral Data (cm^{-1}) of O-Phosphorylated Benzoxazole Derivatives

S. No.	Compounds	ν(P—O—C)	ν(P═O)	ν(P—Cl)
1	$(C_{13}H_8NO_2)P(O)(Cl_2)$	1100 980	1285	610 530
2	$(C_{13}H_8NO_2)_2P(O)(Cl)$	1130 970	1290	530
3	$(C_{13}H_8NO_2)_3P(O)$	1140 980	1280	—

TABLE III Insecticidal Activity of O-Phosphorylated Benzoxazole Derivatives Against *P. Americana*

S. No.	Compounds	Concentration (μg/cm^2) 20 % Mortality			Concentration (μg/cm^2) 40 % Mortality			Concentration (μg/cm^2) 60 % Mortality		
		24 h	48 h	72 h	24 h	48 h	72 h	24 h	48 h	72 h
1	$(C_{13}H_8NO_2)P(O)(Cl_2)$	50	54	56	60	65	67	65	70	72
2	$(C_{13}H_8NO_2)_2P(O)(Cl)$	52	56	58	65	68	72	70	74	76
3	$(C_{13}H_8NO_2)_3P(O)$	56	60	62	68	70	74	76	80	82
4	Malathion (standard)	58	62	65	70	72	75	78	82	88

^{31}P NMR Spectra

All O-phosphorylated benzoxazole derivatives have been characterized by the down field ^{31}P NMR signal at $\sim\delta$ 70–90 ppm.

Biological Activity

All the newly synthesized O-phosphorylated benzoxazole derivatives were screened for their insecticidal activity against *Periplenata americana*. Malathion was used as a standard insecticide to compare the activity of these compounds. The percent mortality was determined by contact as well as an oral feeding method. The effect of O-phosphorylated benzoxazole derivatives of different concentrations (20, 40, and 60 μg/cm^2) was investigated on the mortality rate of *P. americana*. The average percent mortality of *P. americana* was recorded after 24, 48, and 72 h, taking three different concentrations (20, 40, and 60 μg/cm^2) of these derivatives. Results of the insecticidal activity have been compared with conventional insecticide, Malathion taken as standards. The bioassay data are presented in Table III. From these results, it was observed that all the newly synthesized compounds were found to be significant active against *P. americana*. O,O,O-tris(phenylbenzoxazolyl-2-)phosphorate has been found to show stronger insecticidal activity than O,O-bis(phenylbenzoxazolyl-2-) phosphorochloridate and O-(phenylbenzoxazolyl-2-)phosphorodichloridate.

EXPERIMENTAL

All commercial reagents and solvents were dried and distilled by common methods before use. 2-(2′-hydroxyphenyl)benzoxazole was purchased from Aldrich, and $POCl_3$ was purchased from Fluka.

Melting points were determined by the capillary method and are uncorrected. All operations involving phosphorus compounds were carried out in dry equipment under a nitrogen atmosphere. IR spectra were recorded on a Perkin-Elmer 577 grating spectrometer in KBr discs in the region 4000–200 cm^{-1}. NMR spectra were recorded on JEOL FX-90Q spectrophotometer using $CDCl_3$ as a solvent. Nitrogen was estimated by Kjeldahl's method. Phosphorus was estimated as ammonium phosphomolybdate. Chlorine was estimated volumetrically by Volhard's method.

Synthesis of O-(phenylbenzoxazolyl-2-) phosphorodichloridate (1)

In a fast stirring solution of 2-(2′-hydroxyphenyl) benzoxazole (0.001 mole) and Et_3N (0.001 mole) in dry THF/CH_2Cl_2, a solution of $POCl_3$ (0.001 mole) in dry THF was added dropwise. The reaction mixture was then filtered through a closed sintered funnel into another round-bottom flask and then relfuxed under a nitrogen atomsphere for 14–15 h. Then it was cooled and filtered through a closed sintered funnel. The filtrate was then concentrated to 1/4of its volume and kept for crystallization in a vaccum for 2 days. It was recrystallized from dry ethanol (yield 40%).

Synthesis of O,O-Bis(phenylbenzoxazolyl-2-) phosphorochloridate (2)

In a fast stirring solution of 2-(2′-hydroxyphenyl) benzoxazole (0.002 mole) and Et_3N (0.002 mole) in dry THF/CH_2Cl_2, a solution of $POCl_3$ (0.001 mole) in dry THF was added dropwise. Then the reaction was carried out in a manner similar to what was previously described. The product was filtered, concentrated, and recrystallized from dry ethanol (yield 42%).

Synthesis of O,O,O-Tris(phenylbenzoxazolyl-2-) phosphorate (3)

In a fast-stirring solution of 2-(2′-hydroxyphenyl) benzoxazole (0.003 mole) and Et_3N (0.003 mole) in dry THF/CH_2Cl_2, a solution of $POCl_3$ (0.001 mole) in dry THF was added dropwise by a droping funnel. Then the reaction was carried out in a similar manner as previously described. The product was recrystallized from dry ethanol (yield 42%).

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