

## Insecticidal Studies of O-(Alkyl Benzimidazolyl-2) Phosphorates and Phosphorothioates

P.C. VYAS, SUSHMA VYAS\*, P. VYAS and Y. CHAHAR

Department of Chemistry, University of Rajasthan  
Jaipur-302 004, India

The insecticidal activity of O-(alkyl benzimidazolyl-2)-phosphate and phosphorothioates have been evaluated against *Periplaneta americana* and the compounds are found to be strongly fatal for them. These compounds were synthesized by reacting the solution of 2-hydroxy alkyl benzimidazoles in acetone/tetrahydrofuran with phosphoryl chloride/thiophosphoryl chloride in the presence of potassium hydrogen carbonate. All the synthesized compounds were characterised by elemental analysis, TLC, IR, NMR and mass spectral studies.

### INTRODUCTION

The phosphorates and phosphorothioate derivatives containing benzimidazole substituent in place of  $R_1$ ,  $R_2$  or  $R_3$  on phosphorous atom exhibit toxicity towards insects and several benzimidazolylated phosphorus compounds possessing insecticidal and insecto fungicidal activity are known in the literature.<sup>1-4</sup> The action of these derivatives has been investigated especially against *periplaneta americana* by several workers.<sup>4,5</sup> The insecticidal activity of the organo-phosphorus moiety depends upon the electrophilic character of the substituent group bonded to phosphorus atom in the derivatives of the composition  $R_1 R_2 R_3 P(Z)$  (where  $R_1$ ,  $R_2$  and  $R_3$  are phenoxy or alkoxy or any other substituted group; or  $R_2$ ,  $R_3$  = chlorine,  $Z$  = O or S). In this communication we report the synthesis of O-(alkyl benzimidazolyl-2) phosphorates (Ia-f) or phosphorothioate (IIa-f) and their insecticidal activities carried out against *periplaneta americana*. (Table 1). These newly synthesized derivatives were characterized by elemental analysis, m. pt., chromatography, IR, NMR and mass spectral studies (Table 1).

### EXPERIMENTAL

Phosphoryl chloride (E. merck) was used. Thiophosphoryl chloride was prepared by the method described by Knotz.<sup>11</sup> 2-Hydroxy -(methyl/ethyl) benzimidazoles used for the synthesis of phosphorates and phosphorothioates were obtained by condensing *o*-phenylene diamine with glycolic acid, lactic acid respectively in 4 N-HCl aqueous solution according to the procedure described

TABLE 1  
PHYSICAL AND PERCENTAGE MORTALITY DATA OF O<sup>-</sup> (ALKYL) BENZIMIDAZOLYL -2 PHOSPHORATES (I<sub>a-f</sub>) AND PHOSPHOROTHIOATES (II<sub>a-f</sub>)

Sl. No.	R <sub>1</sub> R <sub>2</sub> R <sub>3</sub> P(O)/S			Yield %	M. pt. °C	R <sub>f</sub> Value	% Mortality of <i>Periplenata americana</i> for various conc., hours								
							0.005%			0.001%			0.0009%		
							24	48	72	24	48	72	24	48	72
I <sub>a</sub>	A	Cl	Cl	50	59	0.68	60	70	80	50	55	65	40	45	50
I <sub>b</sub>	B	Cl	Cl	48	66	0.67	80	90	95	65	70	75	50	55	60
I <sub>c</sub>	A	A	Cl	65	71	0.65	70	75	80	45	55	70	30	50	55
I <sub>d</sub>	B	B	Cl	64	72	0.61	75	100	—	50	65	90	40	60	70
I <sub>e</sub>	A	A	A	78	85	0.55	65	85	100	35	50	80	15	40	50
I <sub>f</sub>	B	B	B	78	75	0.51	70	85	100	40	60	90	30	40	60
II <sub>a</sub>	A	Cl	Cl	38	54	0.75	40	50	55	35	40	50	30	40	45
II <sub>b</sub>	B	Cl	Cl	45	65	0.71	60	65	70	55	60	65	35	40	50
II <sub>c</sub>	A	A	Cl	46	68	0.63	45	55	75	35	50	55	30	40	45
II <sub>d</sub>	B	B	Cl	60	81	0.61	55	65	90	50	60	75	40	45	60
II <sub>e</sub>	A	A	A	70	71	0.51	40	50	70	25	40	50	15	30	40
II <sub>f</sub>	B	B	B	71	85	0.48	50	65	80	30	55	70	20	40	50

A = O<sup>-</sup> (methyl) benzimidazolyl-2), B = O<sup>-</sup> (ethyl) benzimidazolyl-2), C = chlorine; IR<sup>7-10</sup> NH asym 2900-3500, sym -1410-1430 cm<sup>-1</sup>; P-O-C- asym 1010-1040, sym 940-980 cm<sup>-1</sup>; P-Cl sym 560-580, asym 480-540 cm<sup>-1</sup>; P = O 1260-1280 cm<sup>-1</sup>; P = S I, 740-840, II 610-650 cm<sup>-1</sup>; P-Cl sym 460-480 cm<sup>-1</sup>, asym 520-540 cm<sup>-1</sup>; NMR<sup>13</sup> δ PPM C<sub>6</sub>H<sub>4</sub> 6.5-7.51 (dm) -CH<sub>3</sub> 0.7-1.2 (MT), -CH 1.3-1.6(d), -NH 3.0-3.2(s) -CH<sub>2</sub> 3.4-3.5(dm).

by Phillips *et al.*<sup>6</sup>. Acetone, tetrahydrofuran, methylene dichloride and pet-ether were dried before use. Nitrogen, phosphorus, sulphur and chlorine content of these derivatives were determined by the procedure described by Vogel<sup>12</sup>. The carbon, hydrogen contents of O-(alkyl benzimidazolyl-2) phosphorates and phosphorothioate esters were determined by micro analytical combustion technique using colemann instrument model-33.

Purity of the samples were ascertained by running TLC in tetrahydrofuran, pet ether and DMF-acetone mixture and the spots corresponding to various derivatives were developed by keeping chromatographic plates in iodine chamber (brown spot), or by spraying with ammonium molybdate solutions. Melting points of the derivatives reported are uncorrected. The infrared spectra of these derivatives were recorded in KBr/nujol on Perkin Elmer 337 and 577 IR spectrometer. The NMR spectra were run in deuterated dimethyl formamide (DMF) or dimethyl sulphoxide (DMSO), deuterated chloroform (CDCl<sub>3</sub>) on Perkin Elmer R-12 B spectrometer using TMS as standard.

*Synthesis of O,O,O Tris (methyl/ethyl benzimidazolyl-2) phosphate (I<sub>e</sub> and I<sub>f</sub>):* Phosphoryl chloride (0.098 gm, 0.001 mole) dissolved in acetone was added

dropwise to a three necked flask containing 2-hydroxy (methyl/ethyl benzimidazole (0.444 gm/0.486 gm: 0.003 mole)) in (30 ml) dry acetone and potassium hydrogen carbonate (0.300 gm), fitted with a mechanical stirrer, reflux condenser and thermometer respectively, and kept in an ice bath. After mixing the reactants stirring was continued for 4 hrs. at 0° C. Thereafter the reaction mixture was refluxed for about 16 hrs. and kept over night. The solution containing the newly synthesized phosphorates were filtered through closed sintered funnel to separate potassium chloride (KCl) formed during this reaction. The product was concentrated to one fourth of its volume under reduced pressure in a 100 ml flask. The product was separated from the mother liquor as crystalline solids. These crystals were dried over phosphorus pentoxide. All the operation mentioned above were carried out under anhydrous conditions.

		P	N	C	H
I <sub>e</sub> C <sub>24</sub> H <sub>21</sub> N <sub>6</sub> PO <sub>4</sub> (m/z)(488)	Found %	6.40	17.16	59.05	4.28
	(Calcd)	(6.35)	(17.16)	(59.01)	(4.30)
I <sub>f</sub> C <sub>24</sub> H <sub>27</sub> N <sub>6</sub> PO <sub>4</sub> (m/z) (530)	Found %	5.85	15.72	61.01	5.08
	(Calcd)	(5.84)	(15.84)	(61.13)	(5.09)

*Synthesis of O, O<sup>-</sup> bis (methyl/ethyl benzimidazolyl-2)-phosphorochloridate (I<sub>c</sub> and I<sub>d</sub>):* To the ice cold solution of 2-hydroxy (methyl/ethyl) benzimidazoles (0.296 gm/0.324 gm 0.002 moles) in dry (30 ml) acetone and potassium hydrogen carbonate 0.200 gm), phosphoryl chloride 0.098 gm. 0.001 mole) in (20 ml) dry acetone, was added slowly with the help of dropping funnel. The reaction mixture was stirred for 4 hrs. The reaction mixture was refluxed for 10 hrs. The crystals of (I<sub>c</sub> and I<sub>d</sub>) O, O<sup>-</sup> bis (methyl/ethyl benzimidazolyl-2) phosphorochloridates were obtained according to the procedure adopted for tris derivatives as described earlier.

		P	N	Cl	C	H
I <sub>c</sub> C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> PO <sub>3</sub> Cl (m/z) (376)	Found %	8.25	17.79	9.47	49.47	4.28
	(Calcd)	(8.23)	(14.87)	(9.42)	(51.00)	(3.71)
I <sub>d</sub> C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> PO <sub>3</sub> Cl (m/z)(404)	Found %	7.68	13.82	8.75	53.41	3.68
	(Calcd)	(7.66)	(13.84)	(8.77)	(61.13)	(3.50)

*Synthesis of O<sup>-</sup> (methyl/ethyl-benzimidazolyl-2)-phosphorodichloridate (I<sub>a</sub> and I<sub>d</sub>):* These derivatives were prepared by taking 2-hydroxy (methyl/ethyl-benzimidazole) and phosphoryl chloride in 1:1 mole ratio (0.148/0.162 gm, 0.0.98 gm) respectively in the same manner as described for the synthesis of tris in derivatives (I<sub>e,f</sub>), reaction mixture was refluxed for 5 to 6 hrs.

		P	N	Cl	C	H	
I <sub>a</sub>	C <sub>8</sub> H <sub>7</sub> N <sub>2</sub> POCl <sub>2</sub> (m/z)(265)	Found %	11.70	10.54	26.76	36.20	2.66
		(Calcd)	(11.69)	(10.56)	(26.79)	(36.22)	(2.44)

		P	N	Cl	C	H	
I <sub>b</sub>	C <sub>9</sub> H <sub>9</sub> N <sub>2</sub> PO <sub>2</sub> Cl <sub>2</sub> (m/z)(279)	Found %	11.16	10.09	25.43	38.67	3.25
		(Calcd)	(11.11)	(10.03)	(25.44)	(38.70)	(3.50)

*Synthesis of O,O,O-tris (methyl/ethyl benzimidazolyl-2) phosphorothioate (II<sub>e</sub> and II<sub>f</sub>):* (0.444 gm/0.486 gm, 0.003 mole) in 40 ml dry acetone with a suspension potassium hydrogen carbonate (0.300 gm) was taken in a three necked flask kept in ice bath and fitted with a mechanical stirrer and thermometer. To this, thiophosphoryl chloride (0.104 gm, 0.001 mole) dissolved in (20 ml) dry acetone was added slowly with the help of dropping funnel. The stirring was continued for 3 hrs. there after, the reaction mixture was refluxed for 16 hrs. and the crystals of (II<sub>e,f</sub>) derivatives were obtained in the same manner as described for (I<sub>e,f</sub>).

		P	S	N	C	H	
II <sub>e</sub>	C <sub>24</sub> H <sub>21</sub> N <sub>6</sub> PO <sub>3</sub> S (m/z)(504)	Found %	6.15	6.36	16.67	57.16	4.16
		(Calcd)	(6.15)	(6.34)	(16.66)	54.14	(4.16)

		P	S	N	C	H	
II <sub>f</sub>	C <sub>27</sub> H <sub>27</sub> N <sub>6</sub> PO <sub>3</sub> S (m/z)(546)	Found %	5.67	5.88	15.40	59.35	4.93
		(Calcd)	(5.67)	(5.86)	(15.38)	(39.34)	(4.94)

*Synthesis of O,O-bis (methyl/ethyl) benzimidazolyl-2) phosphorochloridothioate (II<sub>c</sub> and II<sub>d</sub>), O<sup>-</sup> (methyl/ethyl), benzimidazolyl-2) phosphorodichloridothioate (II<sub>a</sub> and II<sub>b</sub>):* These were obtained by reacting 2-(hydroxy (methyl/ethyl) benzimidazoles with thiophosphoryl chloride (0.104 gm: 0.001 mole) by reacting in 2 : 1, 1:1 mole ratio respectively. Mixture was refluxed for 12 and 8 hrs. respectively and crystals of (II<sub>a</sub> and II<sub>d</sub>) were obtained as that of tris (II<sub>e,f</sub>) derivative.

		P	S	N	Cl	C	H	
II <sub>c</sub>	C <sub>16</sub> H <sub>14</sub> N <sub>4</sub> PO <sub>2</sub> SCl (m/z)(295)	Found %	7.95	8.20	14.23	9.07	48.92	3.56
		(Calcd)	(6.15)	(6.34)	(16.66)	(57.14)	(48.91)	(3.50)

		P	S	N	Cl	C	H	
II <sub>d</sub>	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> PSO <sub>2</sub> Cl (m/z)(418)	Found %	7.45	7.62	13.30	8.40	51.30	4.28
		(Calcd)	(7.37)	(7.60)	(13.31)	(8.40)	(34.16)	(2.56)

		P	S	N	Cl	C	H	
II <sub>a</sub>	C <sub>8</sub> H <sub>7</sub> N <sub>2</sub> PSOCl <sub>2</sub> (m/z)(218)	Found %	11.00	11.40	9.45	25.24	34.44	2.46
		(Calcd)	(11.03)	(11.38)	(9.96)	(25.26)	(34.16)	(2.56)

		P	S	N	Cl	C	H	
II <sub>b</sub>	C <sub>9</sub> H <sub>9</sub> N <sub>2</sub> PSOCl <sub>2</sub> (m/z)(295)	Found %	10.55	10.88	9.45	24.05	36.60	3.03
		(Calcd)	(10.50)	(10.84)	(9.49)	(24.01)	(36.60)	(3.03)

Insecticidal studies were carried out against *periplenta americana*. The percentage mortality was determined by Topical and Contact method.<sup>5</sup> The details are given in Table 1.

## RESULTS AND DISCUSSION

The reaction between phosphorylchloride/thiophosphorylchloride with 2-hydroxy alkyl benzimidazole lead to the formation of phosphate and phosphorothioate containing P-O-C bond. This was indicated by the disappearance of a broad absorption band in the region 3500-3200  $\text{cm}^{-1}$  assigned to -OH vibration in the spectra of 2-hydroxy - alkyl benzimidazoles from the spectra of phosphate/phosphorothioate esters containing O-alkyl benzimidazolyl-2 substituents. The P-O-C bond is characterized by the appearance of two absorption bands in the region 1010-1040 and 950-980  $\text{cm}^{-1}$  assigned as asymmetric and symmetric stretching vibrations in IR spectra of tris, bis and mono phosphorates and phosphothioates (I<sub>a-f</sub>, II<sub>a-f</sub>) (Table 1). The absorption band assigned to P-O-C asym, and sym vibration in the spectra of O,O,O tris- (ethyl) (benzimidazolyl-2) phosphate and phosphorothioate derivatives have been found to lie in the same region as reported by Thomas<sup>9</sup> for phosphorates and phosphorothioate esters. The P-Cl absorption bands at 560-580 and 500-540  $\text{cm}^{-1}$  and were however, not observed in the spectra of tris phosphate and phosphorothioate esters but for bis and mono-O-(alkyl-benzimidazolyl-2) substituted derivative, these bands were observed (I<sub>a-b</sub>, II<sub>a-d</sub>, II<sub>a,b</sub>).

The benzimidazolyl group is characterized by  $\nu$  asym. stretching vibration observed as a sharp absorption band of 3250-3050  $\text{cm}^{-1}$  and  $\delta$ NH stretching vibration at 1420  $\text{cm}^{-1}$  assigned vibration frequencies are present at nearly same region in the IR spectra of these phosphate and phosphorathioate esters. This confirmed that 1-NH group of imidzoloyl group is not involved in reaction with phosphoryl chloride or thiophosphorylchloride. The conspicuous absence of the absorption frequency (925-1500  $\text{cm}^{-1}$ ) assigned to P-N bond is supportive of above conclusions also. The other heterocyclic breathing modes of the imidazolyl ring observed in the IR spectra of 2-hydroxy-alkyl-benzimidazole are noticed unaltered in the spectra of these phosphorates and phosphorothioate esters.

Insecticidal studies were carried out against *Periplenta americana*. The percentage mortality was determined by *Topical and Contract* method.<sup>3,5</sup> The details are given in Table 1.

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