

Synthesis and IR Spectra of O-ethyl/O,O-diethyl O/S Alkyl Benzimidazolyl-2 Phosphorothioates

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O-ethyl O/S alkyl benzimidazolyl-2-phosphorothioates and O,O-diethyl O/S alkyl benzimidazolyl-2 phosphorothioates derivatives have been synthesized by reacting O-ethylthiophosphorylchloride or O,O-ethylthiophosphorylchloride respectively with 2-hydroxy/mercapto alkyl benzimidazoles in various molar ratios. The potassium hydrogen carbonate/potassium carbonate was added as an acid scavenger in the above reactions. These O-ethyl/O,O-diethyl, O/S alkyl-benzimidazolyl-2 substituted phosphorothioate derivatives were characterized by elemental analysis, thin layer chromatographic and infrared spectral studies.

INTRODUCTION

Organophosphorus compounds possessing heterocyclic ring substituent containing nitrogen are now a days used as fumigant insecticides¹⁻³, pesticides⁴ and insectofungicides^{5,6}. Among nitrogen heterocycles benzimidazoles derivatives exhibit herbicidal, rodenticidal⁸ and fungicidal⁷ activities. The O-ethylthiophosphorylchloride or O,O-diethylthiophosphorylchloride react with 2-hydroxy/mercaptoalkylbenzimidazoles respectively and form phosphorothioate esters (RO) P(S) R'R'' [Where RO=O-ethyl, R'=Chlorine or 2 hydroxy/mercapto alkyl benzimidazoles (I_{a-h}); R''=O ethyl and R''=2 hydroxy/mercapto alkyl benzimidazoles (II_{a-d})] containing insecticidal organophosphorous and herbicidal as well as fungicidal benzimidazolyl moieties.

EXPERIMENTAL

O-Ethyl-Thiophosphoryl Chloride

O-Ethyl-thiophosphoryl chloride was prepared conveniently by allowing ethanol to react with thiophosphoryl chloride according to the method described in literature⁸. The PSCl₃ used in the reaction was obtained by direct combination of sulphur with PCl₃ in presence of anhydrous AlCl₃ according to the procedure described by Knotz⁹.

O,O-diethyl Thiophosphoryl Chloride

It was prepared according to the procedure described by Clemmenson¹⁰.

Synthesis of 2-Hydroxy/Mercapto Alkyl Benzimidazoles

These benzimidazoles derivatives used in the synthesis of phosphorothioate esters were prepared by condensation of O-phenylenediamine with

glycolic acid, lactic and mercaptoglycolic acid and mercaptolactic acid respectively in 4N-HCl solution as described by Philips *et. al.*¹¹. Solvents used in the reaction were dried according to the procedure described by Vogel¹². Nitrogen, phosphorus, sulphur and chlorine contents of the derivatives were determined by standard procedures¹². The carbon and hydrogen contents of reactants and O-ethyl/O,O-diethyl O/S benzimidazolyl-2-phosphorothioates were determined by micro analytical combustion technique using Colemann instrument model 33. Purity of reactants and products were ascertained by running thin layer chromatography in tetrahydrofuran or Pet-ether—DMF and acetone. Spots corresponding to various derivatives were determined by keeping chromatographic plates in iodine chamber (brown spot) or by spraying ammonium-molybdate solution for detection of phosphorothioates, (yellow spot). The infra red spectra of substituted benzimidazoles and phosphorothioates derivatives were recorded in KBr or nujol mull on Perkin Elmer 337 and 557 infrared spectrometer.

Synthesis of O-Ethyl O-Methyl/Ethyl Benzimidazolyl-2-Phosphorochloridothioate (I_{e, f})

O-Ethyl thiophosphorylchloride (0.001 mole; 0.179 gms) in dry acetone was added slowly with the help of dropping funnel to the fast stirring ice cold suspension of potassium hydrogen carbonate in the solution of 2-hydroxymethyl/ethyl benzimidazoles (0.001 mole, 0.148/0.162 gms) in acetone taken into a three necked flask fitted with mechanical stirrer and reflux condenser.

O-Ethyl-O,O-bis methyl/ethyl benzimidazolyl-2 phosphorothioate was synthesised by reacting O-ethylthiophosphoryl chloride and 2-hydroxy methyl/ethyl benzimidazoles in 1 : 2 molar ratio according to the procedure mentioned above (I_{e, f}). Similarly, for the preparation of O-ethyl/S, S-bis methyl/ethyl-phosphor/trithioate (I_{c, d}) and O-ethyl S-methyl/ethyl benzimidazolyl-2-phosphorochlorido-dithioate, O-ethylthiophosphorylchloride and 2-mercaptoalkyl benzimidazoles (alkyl=methyl, ethyl) were taken in 1 : 1, 1 : 2 molar ratios respectively. (I_{c, d}, I_{g, h})

The reaction mixture was refluxed for 12–14 hrs, there after cooled, kept overnight and the potassium chloride so formed in the reaction was filtered through closed sintered funnel under reduced pressure. The colored crystals of the phosphorothioate esters were obtained by keeping the filtrate in vacuum desiccator for three days.

Synthesis of O,O-diethyl-O/S Alkyl Benzimidazolyl 1–2 Phosphorothioate

Following above mentioned procedure II_{a–d} were prepared by reacting 2-hydroxy/mercaptoalkyl benzimidazoles (alkyl=methyl, ethyl) with O,O-diethyl thiophosphorylchloride in 1 : 1 stoichiometric ratio respectively

in acetone (II_{a,b})/tetrahydrofuran (II_{c,d}) in presence of potassium hydrogen carbonate as an acid scavenger and inert atmosphere.

The yield, elemental analysis, thin layer chromatography (R_f values), m.pt. data for these derivatives (I_{a-h} and II_{a-d}) are mentioned in Table 1.

RESULTS AND DISCUSSION

The composition of the derivatives reported are in agreement with the analytical data for the constituent elements (Table 1). The appearance of single clear spot for each derivative in the thin layer chromatogram is indicative of the formation of single product in these reactions. The R_f values for the mono substituted-chlorido-phosphorothioate esters (I_{e-h}) are higher than the disubstituted derivatives. (I_{a-d}) O-ethyl/O,O alkylbenzimidazolyl-2 phosphorothioates exhibits higher R_f value than the corresponding mercaptoalkylphosphorothioate ester derivatives. (I_{a-b}); (I_{c-d}); (II_{a-b}; II_{c-d}).

IR Spectra

The Absorption band assigned to ν_{asy} OH and δ_{asy} N-H in the IR spectra of 2-hydroxy alkyl benzimidazoles are observed at 3300-3500 and 3050-3200 cm^{-1} respectively. The absorption band assigned to ν_{asy} -OH was found to be absent in the IR spectra of phosphorothioate derivatives (I_{a-h}, II_{a-d}) prepared by reacting 2-hydroxy/mercapto-alkyl-benzimidazoles with O-ethyl/O,O-diethyl thiophorylchloride. The spectra of these derivatives contain strong and sharp absorption band assigned to ν_{asy} NH at 3090 cm^{-1} . Secondly the absorption band assigned to δ NH in the IR spectra of 2-hydroxy alkyl benzimidazoles was observed at 1410-1430 cm^{-1} in the IR spectra of O-ethyl/O,O-diethyl O-alkyl benzimidazolyl-2-phosphorothioates (I_{a-h}, II_{a-d}). Both these observations are supportive of fact that -OH group of 2-hydroxy-alkyl benzimidazoles is involved in reaction with P-Cl bond of O-ethyl/O,O-diethyl thiophosphoryl chloride. The imino group (-NH) of benzimidazolyl moiety remain intact and not involved in the reaction.

The absorption bands observed at (480-500 cm^{-1}) assigned to asymmetric stretching of P-Cl bond in the IR spectra of O-ethyl/O,O-diethyl thiophosphoryl chloride were found to be absent in the spectra of the O-ethyl/O,O-bis alkyl benzimidazolyl-2-phosphorothioate (I_{a-d}) and O,O-diethyl O-alkylbenzimidazolyl-2-phosphorothioates (II_{a-d}) (alkyl-methyl, ethyl). These observations for these derivatives confirms that P-Cl bond of O-ethylthio-phosphorylchloride reacted with -OH group of 2-hydroxy alkyl benzimidazoles to form phosphorothioate esters.

The infrared spectra of (I_{e-h}) of mono substituted O-ethyl, O-alkyl benzimidazolyl-2-phosphorochlorido-thioate showed the absorption bands due to ν_{asy} P-Cl bond in the some region as observed in the spectra of O-ethyl thiophosphoryl chloride esters at 480-500 cm^{-1} .

TABLE 1
 PHYSICAL DATA OF O-ETHYL/O,O-DIETHYL O/S-ALKYL BENZIMIDAZOLYL-2-PHOSPHOROTHIOATES

(RO)P(S)X ₁ X ₂	M.Pt. °C	Yield %	R _f value	Elemental Analysis Calcd/obsd %					
				Phosphorus	Sulphur	Nitrogen	Chloride	Carbon	Hydrogen
I _a A A	110	75	0.65	7.78 (7.21)	7.99 (7.44)	13.90 (13.03)	—	53.67 (53.73)	4.71 (4.73)
I _b B B	100	76	0.63	7.26 (7.21)	7.78 (7.44)	13.00 (13.03)	—	55.75 (55.81)	5.32 (5.35)
I _c C C	105	75	0.59	7.20 (7.14)	22.14 (21.12)	12.85 (12.90)	—	50.71 (49.77)	4.36 (4.38)
I _d D D	115	80	0.58	6.76 (6.71)	22.83 (22.78)	12.16 (12.12)	—	51.99 (51.95)	4.95 (4.98)
I _e A Cl	98	60	0.78	10.70 (10.67)	11.09 (11.02)	9.60 (9.64)	12.20 (12.22)	41.28 (41.31)	4.10 (4.13)
I _f B Cl	85	60	0.75	10.21 (10.18)	10.58 (10.51)	9.16 (9.20)	11.63 (11.66)	43.30 (43.35)	4.57 (4.60)
I _g C Cl	95	59	0.68	10.15 (10.11)	20.93 (20.88)	9.10 (9.14)	11.55 (11.58)	39.13 (39.15)	3.89 (3.92)
I _h D Cl	98	62	0.66	9.70 (9.67)	19.99 (19.97)	8.74 (8.74)	11.05 (11.08)	41.20 (41.19)	4.36 (4.37)
II _a A OEt	89	72	0.65	10.40 (10.33)	10.75 (10.66)	9.35 (9.33)	—	48.20 (48.00)	5.72 (5.66)
II _b B OEt	98	74	0.62	9.94 (9.87)	9.24 (10.19)	9.90 (8.91)	—	49.82 (49.68)	6.07 (6.05)
II _c C OEt	100	73	0.58	9.88 (9.81)	20.35 (20.25)	8.92 (8.86)	—	45.74 (45.56)	5.40 (5.38)
II _d D OEt	105	80	0.54	9.41 (9.39)	19.47 (19.39)	8.53 (8.48)	—	47.44 (47.27)	5.79 (5.75)

OR = O-Ethyl, A = 2-hydroxymethylbenzimidazolyl, B = 2-hydroxymethylbenzimidazolyl, C = 2-mercaptomethylbenzimidazolyl,
 D = mercaptoethylbenzimidazolyl, Cl = Chlorine.

P=S(I) and (II): A strong and sharp absorption band at 805–710 cm^{-1} and a medium intensity band at 610–620 cm^{-1} in the spectra of the derivatives ($\text{I}_{\text{a-h}}$, $\text{II}_{\text{a-d}}$) are assigned to ν_{asy} P=S, I and II. The frequencies due to P=S stretching vibrations reported in Table 2 are in accordance with those observed for phosphorothioate esters¹³.

TABLE 2
IR SPECTRAL DATA FOR O-ETHYL/O,O-DIETHYL O-ALKYL
BENZIMIDAZOLYL-2-PHOSPHOROTHIOATE (cm^{-1})

S.N.	N-H-bands		P-O-C bands		P-S-C band	P=S (I) (II)
	$\nu_{\text{N-H(asy,a)}}$	$\delta_{\text{N-H(sym)}}$	ν_{asy}	ν_{sym}		
I_{a}	3090	1430	1010	980		800 610
I_{b}	3090	1430	1010	980		805 615
I_{c}	3090	1430	1100	960	540	710 610
I_{d}	3090	1430	1100	960	540	710 610
I_{e}	3090	1420	1020	942		798 615
I_{f}	3090	1420	1026	939		805 615
I_{g}	3090	1420	1050	960	533	710 610
I_{h}	3090	1420	1050	960	540	710 610
II_{a}	3090	1420	1012	980		800 610
II_{b}	3090	1420	1010	980		800 610
II_{c}	3090	1410	1013	960	540	710 620
II_{d}	3090	1410	1013	950	555	710 620

In addition to these, spectra of phosphorothioate esters ($\text{I}_{\text{a-h}}$, $\text{II}_{\text{a-d}}$) exhibit absorption at 1010–1100 cm^{-1} and 930–980 cm^{-1} assigned to asymmetric stretching vibrations assigned to P-O-C ester linkage¹³. The absorption bands due to asymmetric vibration of P-S-C bond in the spectra of mono and di substituted S-alkyl-benzimidazolyl-2 phosphorothioate are observed at 530–540 cm^{-1} . The spectra of O,O-diethyl S-alkyl benzimidazolyl-2 phosphorodithioate ($\text{II}_{\text{c,d}}$) also show the absorption band due to P-S-C in the ν region 540–550 cm^{-1} . Mono-substituted O,

ethyl, S-alkyl benzimidazolyl-2-phosphorochlorodithioate ($I_{c,d}$) derivative showed the absorption at $480-500\text{ cm}^{-1}$ assigned to P-Cl vibration; whereas the spectra of bis derivative, O-ethyl-alkyl benzimidazolyl-2-phosphorotrithioate ($I_{g,h}$) did not show the above mentioned absorption frequencies.

The absorption frequencies due to P-O-C ester linkage were also observed in the spectra of these derivatives along with P=S in the regions mentioned above for II_{a-d} in O,O-diethyl O/S benzimidazolyl-2-phosphorothioate esters.

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