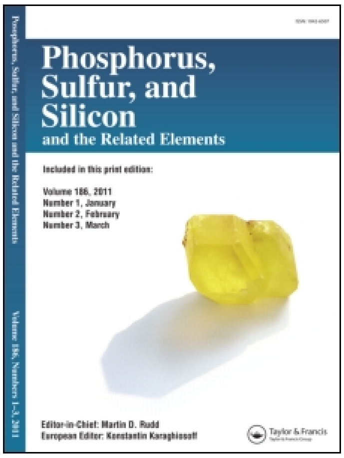

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ORGANO-PHOSPHORUS SCHIFF-BASES PART (IV): SYNTHESIS AND CHARACTERISTICS OF SOME PHOSPHATE SCHIFF-BASE COMPLEXES

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ORGANO-PHOSPHORUS SCHIFF-BASES PART (IV): SYNTHESIS AND CHARACTERISTICS OF SOME PHOSPHATE SCHIFF-BASE COMPLEXES

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Interaction of diphenylchlorophosphate with Schiff-bases(I-III) led to the formation of organo-phosphorus derivatives of type (IV-VI) and their metal complexes (VII-VIII) were prepared. The reaction products (IV-VI) were subjected to structural and mechanistic investigations.

Keywords: Schiff-base phosphate complexes; Organo phospate-Schiff-base complexes; Organo phosphate -Schiff-base derivatives; Phosphate Schiff-base complexes; Phosphate Schiff-base derivatives

INTRODUCTION

Although the synthesis of Schiff-bases has been reported and the coordination chemistry has been subjected to intensive study in the last twenty years, in marked contrast, little is known about the reaction of Schiff bases with halogenated organo-phosphorus compounds. Nurtidenov et al.(1) reported the formation of adducts in the reaction of azomethines with $RPCl_2$ in a 2:1 molar ration. Recently, I.M. AbdEllah, E.H. Ibrahim, E.H. and R.S. Farag prepared some organo-phosphorus Schiff-base derivatives by reacting diphenyl chlorophosphate and diphenyl chlorophosphine with some Schiff-bases.(2) Also, recent work has produced a useful study on the synthesis of phosphate and phosphine Schiff-base complexes.(3,4)

RESULTS AND DISCUSSION

In the present investigation a series of Schiff bases of types (I), (II) and (III) (Fig.1) were prepared essentially by the usual condensation reaction$^{(5)}$ between primary amine (p-toludene, propylenediamine, phenylenediamine) and aldehyde (anizaldehyde. N-N-P-dimethylaminobenzaldehyde). The products purified by repeated recrystallization from ethanol-diethylether mixture gave the corresponding Schiff bases (I-III).

$$R\text{-}CH{=}N\text{-}R'$$

(I)

Ia $R = C_6H_4\,OCH_3\text{-}p$, $R' = C_6H_4\,CH_3\text{-}p$

Ib $R = C_6H_4\,N(CH_3)_2\text{-}p$, $R' = C_6H_4\,CH_3\text{-}p$

$$R\text{-}CH = N - (CH_2)_3 - N = CH - R$$

(II)

IIa $R = C_6H_4\,N(CH_3)_2\text{-}p$

IIb $R = C_6H_4\,OCH_3\text{-}p$

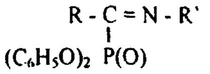
(III)

$R = C_6H_4\,OCH_3\text{-}p$

FIGURE 1 Reaction between primary amine and aldehyde to give Schiff base. (I-III)

It was found that the azomethine proton in Schiff-bases is subject to replacement reactions with halogen containing organo-phosphorus compounds. In general, interaction of diphenyl chlorophosphate with Schiff bases of types. I, II and III in the presence of a hydrogen ion acceptor such as triethylamine and in a dry inert solvent such as diethyl ether or benzene, produced the organo-phosphorus derivatives of types (IVa, b), (Va, b) and (VI) respectively. (Fig. 2).

The isolated products are crystalline substances, whose elemental analysis are consistent with structure IV-VI. The assignment of the isolated compounds was based on the bases of :

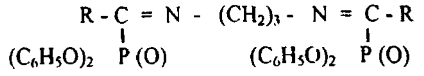


$$R-\underset{(C_6H_5O)_2\,P(O)}{C}=N-R'$$

(IV)

Iva $R = C_6H_4\,OCH_3$ - p $R' = C_6H_4\,CH_3$-p

Ivb $R = C_6H_4\,N\,(CH_3)_2$-p $R' = C_6H_4\,CH_3$-p

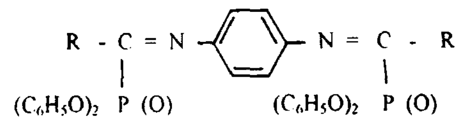


$$R-\underset{(C_6H_5O)_2\,P(O)}{C}=N-(CH_2)_3-N=\underset{(C_6H_5O)_2\,P(O)}{C}-R$$

(V)

Va $R = C_6H_4\,N\,(CH_3)_2$-p

Vb $R = C_6H_4\,OCH_3$-p



(VI)

$R = C_6H_4\,OCH_3$-p

FIGURE 2 Reaction between disheny1 chlorophosphate with Schiff bases (I-III) to produce organo-phosphorus derivatives of type (IVa, b), (Va,b) and (VI).

i. Elemental analysis (Table I.)

ii. IR spectra for compounds (IV-VI) showed the characteristic stretching vibrations for $_{\gamma}$ C = N, $_{\gamma}$ P = O stretching vibration and $_{\gamma}$ P-O-C stretching mode (6-8) as summarized in (Table II.).

iii. UV spectra for compounds (IV-VI) showed the characteristic absorption bands corresponding to the n-π* and π - π* transition in the ultraviolet region at λ = 265 nm and λ = 315 nm.

iv. ^{1}Hnmr spectra for compounds (IV-V), showed the aromatic proton signal at δ=7.5-8.0 ppm, while the azomethine proton signal at δ=8.3-9.0 ppm(9)in the spectra of the Schiff bases of type (I-III) disappeared from the spectra of the organo-phosphorus Schiff-base derivatives of type (IV-VI) due to the replacement of the azomethine proton by the organo phosphorus group. ^{1}Hnmr data are summarized in (Table III.)

v. Mass spectra of compound IVb were characterized by an intense peak at m/e 233 corresponding to the $(C_6H_5O)_2P(O)^+$ion and the Shiff base contain an

OH group an intense peak at m/e 250 appeared corresponding to $(C_6H_5O)_2$ P(O) OH which is very common in phenylphosphorus compounds containing more than one phenyl group attached to the phosphorus atom.(10) The proposed fragmentation pathway for compound (IVb & Vb) is given in Schemes (1) and (2). Attention was directed to the investigation of the chemical behavior of the phosphate Schiff-base derivatives towards some metal cations. The metal cations, selected for this purpose were Cr^{+3}, Fe^{+3}, Co^{+2}, Cu^{+2}, Pb^{+2}, and UO_2^{2+} ions.

TABLE I Elemental analysis data of compounds (IV - VI)

No. of compound	*m.p. °C*	*Yield %*	*Color*	*Molecular formula*	*Elemental analysis found/calc.*	
					N %	*P %*
					3.4	7.4
IVa	242	60	White	$C_{27}H_{24}NO_4P$	3.1	6.8
					5.5	6.2
IVb	166	75	Red	$C_{28}H_{27}N_2O_3P$	6.0	6.5
					6.0	7.5
Va	169	52	Brown	$C_{45}H_{48}N_4O_6P_2$	6.9	7.7
Vb	161	60	Pale-yellow	$C_{43}H_{40}N_2O_8P_2$	3.3	8.0
					3.1	7.1
VI	212	68	Yellow	$C_{46}H_{38}N_2O_8P_2$	3.4	7.6

TABLE II IR data of compounds (IV - VI)(6-8)

No. of compound	*Streching vibration in cm^{-1}*		
	C=N	*P=O*	*P-O-C*
IV a	1583	1141	1016
IV b	1600	1175	1024
Va	1597	1183	1083
Vb	1574	1200	1049
VI	1558	1158	1033

TABLE III ^{1}H n.m.r. data of schiff-bases and their phosphate derivatives.

No. of compound	*Chemical shifts (δ) in ppm*			
	CH = N	*Aromatic Protons*	*OCH$_3$*	*CH$_3$*
Ia	8.3	6.8 - 8.0	3.9	2.3
Ib	8.4	7.1 - 7.9	-	2.3
IIa	8.3	7.3 - 8.0	-	–
IIb	8.3	6.8 - 7.9	3.9	–
III	8.3	7.2 - 7.8	3.9	–
IVb		6.1 - 7.8	-	2.3
Vb		6.8 - 7.5	3.4	–

When a mixture of one mole of the organo-phosphate Schiff-base of type (IVb and Vb; in the Table 4 the two compound are shown as L) is dissolved in absolute ethanol, followed by dropwise addition of an alcoholic solution of one mole of metal ions to the above well stirred solution, a change in color is observed and a colored compound is precipitated (VII$_{a\text{-}f}$ - VIII$_{a\text{-}f}$) (Table IV.)

TABLE IV A mirtare of one mole organo-phosphate Schiff-base of type (IVb-Vb) with one male metal ions

		LMX$_n$			
		(VII$_{a\text{-}f}$- VIII$_{a\text{-}f}$)			
		L	**M**	x	n
VII	a	$C_{28}H_{27}N_2O_3P$ (IV b)	Cu	Br	2
	b	"	Fe	Cl	3
	c	"	Pb	CH_3COO	2
	d	"	UO_2	NO_3	2
	e	"	Cr	Cl	3
	f	"	Co	SCN	2
VIII	a	$C_{43}H_{40}N_2O_8P_2$(Vb)	Cu	Br	2
	b	"	Fe	Cl	3
	c	"	Pb	CH_3COO	2
	d	"	UO_2	NO_3	2
	e	"	Cr	Cl	3
	f	"	Cu	Cl	2

The products purified by recrystallization from ethanol gave analytical data compatable with the following proposed structures (VIIa-f - VIIIa-f) (Table V.).

TABLE V Analysis of organo-phosphorus Schiff-base metal complexes of type (VIIa-f- VIIIa-f)

No. of	*Reactants*		*Colour*	*m.p. °C*	*Yield %*	*Molecular formula*	*Elemental analysis found/culculated*		
	Ligand	*Metal*					*% N*	*% P*	*% M*
VII a	IVb (0.047gm; 0.001 M)	Cu Br_2 (0.22gm; 0.001 M)	Yellow	350	80	$C_{28}N_{27}N_2O_3P$ Cu Br_2	3.2 4.0	4.1 4.5	8.9 9.2
VIIb	IVb (0.47 gm; 0.001 M)	$FeCl_3$ (0.16 gm; 0.001 M)	Yello-wish	350	77	$C_{28}H_{27}N_2O_3P$ $FeCl_3$		4.6 4.9	8.5 8.0
VIIc	Ivb (0.47 gm; 0.001 M)	$(CH_3COO)_2$ $Pb.3H_2O$ (0.38 gm; 0.001 M)	White	350	75	$C_{32}H_{39}N_2O_{10}P$ Pb	4.2 4.4	3.4 3.6	24.1 24.4
VIId	IVb (0.47 gm; 0.001 M)	$UO_2(NO_3)$. $6H_2O$ (0.50 gm; 0.001 M)	Yellow	350	82	$C_{28}H_{39}N_4O_{15}PU$		2.8 3.2	
VIIe	IVb (0.47 gm; 0.001 M)	$CrCl_3$. $6H_2O$ (0.26 gm; 0.001 M)	Red	232	90	$C_{28}H_{39}N_2O_9PCrCl_3$	3.4 3.8	3.8 4.2	
VIIf	IVb (0.47 gm; 0.001 M)	$CO(SCN)_2$ (0.18 gm; 0.001 M)	Green	115	88	$C_{30}H_{39}N_4O_3PSCO$	9.8 8.7	4.6 4.8	8.7 9.1
VIIIa	IVb (0.77 gm; 0.001 M)	$CuBr_2$ (0.22 gm; 0.001 M)	Blue	205	80	$C_{43}H_{40}N_2O_8P_2CuBr_2$	2.6 2.8	5.8 5.9	5.9 6.3
VIIIb	IVb (0.77 gm; 0.001 M)	$Fecl_3$ (0.16 gm; 0.001 M)	Pale brown	350	92	$C_{43}H_{40}N_2O_8P_2FeCl_3$	2.4 3.0	6.2 6.6	6.8 5.9

TABLE V (continued)

No. of	Reactants		Colour	m.p. °C	Yield %	Molecular formula	Elemental analysis found/culculated		
	Ligand	Metal					% N	% P	% M
VIIIc	Vc (0.7 gm; 0.001 M)	$(CH_3COO)_2$ $Pb.3H_2O$ (0.38 gm; 0.001 M)	White	350	83	$C_{47}H_{52}N_2O_{15}P_2Pb$		4.9 5.4	17.5 17.9
VIIId	Vb (0.77 gm; 0.001 M)	$UO_2(NO_3)_2$ $6H_2O$ (0.50 gm; 0.001 M)	Yellow	350	75	$C_{43}H_{52}N_4O_{22}P_2U$	3.6 4.4	4.3 4.8	
VIIIe	Vb 0.77 gm; 0.001 M)	$CrCl_36H_2O$ (0.27 gm; 0.001 M)	Green	350	72	$C_{43}H_{52}N_2O_{14}OP_2Cr$ Cl_3	2.2 2.7	5.5 5.9	
VIIIf	Vb (0.77 gm; 0.001 M)	$CuCl_2$ (0.139 gm; 0.001 M)	Green	195-198	68	$C_{43}H_{40}N_2O_8P_2CuCl_2$		6.6 6.8	6.4 6.9

The assignments of the proposed structures (VII) - (VIII) were based on the following data.

i. The microanalytical data (Table V) which are in a good agreement with the proposed structure.

ii. The infrared spectra for the isolated products (VII - VIII) (Table VI) was detennined by comparison of the spectra of both organo-phosphate Schiff-base derivatives (IV, V) and their metal complexes (VII-VIII). The $_{\gamma}$C= N and $_{\gamma}$P = O stretching vibrations were shifted to lower frequencies upon coordination to metal cations with the appearance of another stretching mode corresponding to $_{\gamma}$N----M and $_{\gamma}$O ----M. The stretching vibration in the ligands are affected much less by the adduct formation.

The infrared spectra for compound (IVb) shows an absorption band at 1977 cm^{-1} characteristic for covalently bonded M-S-C≡N group.(1) Also the characteristic stretching vibration mode for the acetate group is observed in the infrared region 1205 cm^{-1}in the spectra of compounds (VIIc, VIIIc).

TABLE VI IR stretching vibrations of organo-phosphate Schiff-base complexes of type (VII$_{a-f}$ - VIII$_{a-f}$).

No of comp.	*Stretching vibration in cm^{-1}*					
	$\gamma C{=}N$			$\gamma p{=}o$		
	Free	*Coord.*	*Shift*	*Free*	*Coord.*	*Shift*
VIIa	1600	1588	12	1174	1164	10
VIIb	1600	1579	21	1174	1158	16
VIIc	1600	1574	26	1174	1166	8
VIId	1600	1583	17	1174	1166	8
VIIe	1600	1570	30	1174	1150	24
VIIf	1600	1574	26	1174	1154	20
VIIIa	1583	1558	25	1200	1141	59
VIIIb	1583	1566	17	1200	1166	34
VIIIc	1583	1549	34	1200	1190	10
VIIId	1583	1574	9	1200	1142	58
VIIIe	1583	1564	19	1200	1198	2
VIIIf	1583	1549	14	1200	1158	42

Further insight concerning the structure of these complex products was obtained from a consideration of conductometric and spectrometric studies. The conductometric titration is performed by titrating 25ml of 1×10^{-3} M Cu^{+2} ion solution with an increasing volume of 1×10^{-3} M complexing agent solution organo-phosphorus Schiff-base derivatives (Vb, VIIb) and the conductance recorded after stirring the solution for about 2 minutes.

The conductometric titration curves obtained by applying linear least square equation(12) are smooth straight lines for all the points, and the well defined breaks are coincident with the stoichiometric ration of complexes formed in solution and the results are in good agreement with the 1:1 and 2:1 molar ratio.

The spectrophotometric studies on the chelation of Cu^{++} with organophosphate Schiff-base derivatives of type (IVb, Vb); were carried out using the continuous variation method(13). The lack of correspondence between the spectra of the solutions containing Cu^{2+} ion and that of the free ligands used as a control, may be taken as evidence for complex formation between the organophosphate Schiff base compounds and the Cu^{2+} ion.

The spectrum of the free ligands of type (IVb, Vb) are characterized by two absorption bands at (210 and 260nm). The Cu^{2+} ion is characterised by one band at (270nm). The spectral change observed upon complexation is characterised by the appearance of a new band at a longer wavelength at (286 nm) for ligand IVb, and at (298nm) for ligand Vb, while the band of the free ligand at (260nm) had dissappeared completely. This may be attributed to the red shift of this band to a new band on complexation with Cu^{2+} for ligands (IVb and Vb).

On plotting the absorbance values of the prepared solutions measured at 298 nm against the mole fraction of metal, a curve was obtained which possesses two maximum at a metal mole fraction (0.42) for Vb indicting the formation of a 1:1 complex, but for ligand IVb the data obtained are in good agreement with 1:1 ligand to metal molar ratio complexes as indicated in (Table VII). (Fig. 3).

TABLE VII Continous variation data of ligands IV b, Vb with Cu^{2+}ion

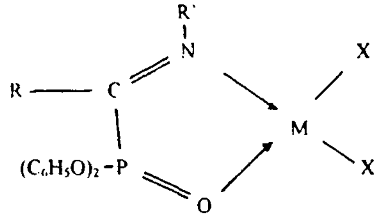
No.	*Ligand IV b*		*Ligand Vb*	
	Cu^{++} mole fraction	*Absorbance λ max = 286*	*Cu^{2+} mole fraction*	*Absorbance λ max = 288*
1	0.200	0058	0.0833	0005
2	0.233	0.516	0.1660	0.021
3	0.267	0.032	0.2500	0.047
4	0.300	0.206	0.3330	0.070
5	0.433	0.307	0.4160	0.120
6	0.467	0.267	0.5000	0.050
7	0.535	0.340	0.5830	0.233
8	0.567	0.294	0.6660	0.315
9	0.633	0.167	0.5700	0.520
10	0.667	0.162	–	–

From the above findings we propose that coordination occurs through the nitrogen of the Schiff-base and the phosphoryl oxygen to give structures IVb and Vb.

EXPERIMENTAL

Micro analytical determinations, were carried out by the micro analylical laboratory, Cairo University . Infra red spectra were recorded an a SHMADZU-440 spectrophotometer (KBr Technique), Ultraviolet spectra were recorded on Perkin

- Elmer Lambda - 3B UV- Visible spectrophotometer. ^1H nmr spectra were measured on a Varian -Em-360L, spectrophotometer using TMS as internal reference. Mass spectrometric measurments were carried out using SHIMADZU GC-MSGP 1000 Ex. Mass spectrometer with a direct inlet system.

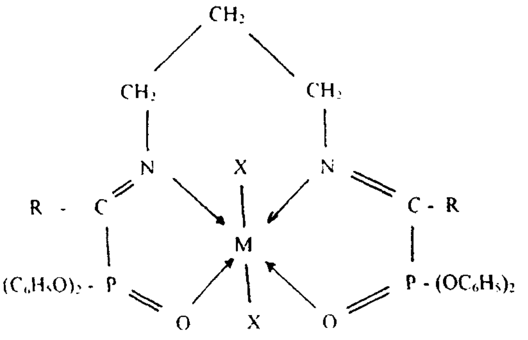


IVb I I

R = C_6H_4 $N(CH_3)_2$ -p

R' = C_6H_4 CH_3-p

X = Cl



Vb I I

R= $C_6H_4OCH_3$ -p

X= Cl

FIGURE 3 Coordination occurs through the nitrogen of the Schiff base and the phosphoryl oxygen to give (IVb) and (Vb) structures.

Preparation of compounds

The preparation and purification of Schiff bases, (I,II,III) as described previously$^{(5)}$, were prepared essentially by the usual condensation reaction between the primary amine & aldehydes heated at 100 °C for 10 minutes to give the corresponding imines. A solvent such as alcohol or acetic acid 5 ml may by used. The isolated compounds were purified from a suitable solvent.

Synthesis of organo-phosphorus Schiff-base dervatives (IVa,b), (Va,b) & (VI) General proceedure:

A solution of diphenyl chlorophosphate (0.1 mol) in dry benzene 100 ml was added dropwise to a well stirred solution of Schiff-base (0.1 mol) and triethyl amine (0.1 mol) in 100 ml. of dry benzene.

After complete addition, the reaction mixture was heated under reflux for two hours. The solid (tri ethyl amine hydrochloride) was filtered, and the filtrate was evaporated under vaccuo and the solid was recrystallized from ethanol. The data observed for compound (IVa -b) (Va-b) & (VI) are listed in (Table I).

Preparation of Metal complexes. (VIIa-f), (VIIIa-f).

A solution of metal halid (0.001) in dry ethanol (50ml) was added dropwise to a well stirred solution of the organo-phosphate-Schiff-base (IVb, Vb) (0.001 mole) in dry ethanol (50 ml) under anhydrous conditions.

After complete addition of the metal, the reaction mixtrue was heated under reflux for three hours. The solvent was evaporated under vaccou to give a solid compound which was recrystalized from ethanol. The data observed for compound (VIIa-f), (VIIIa-f) are listed in (Table V).

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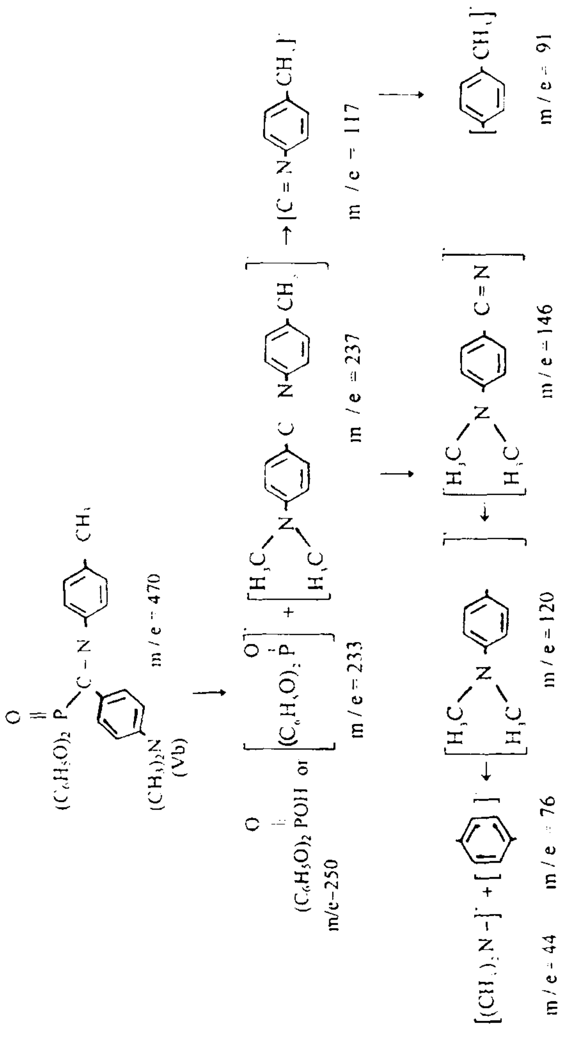
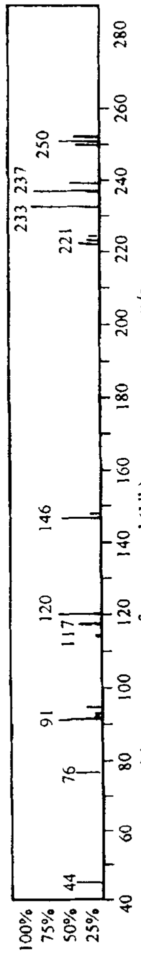
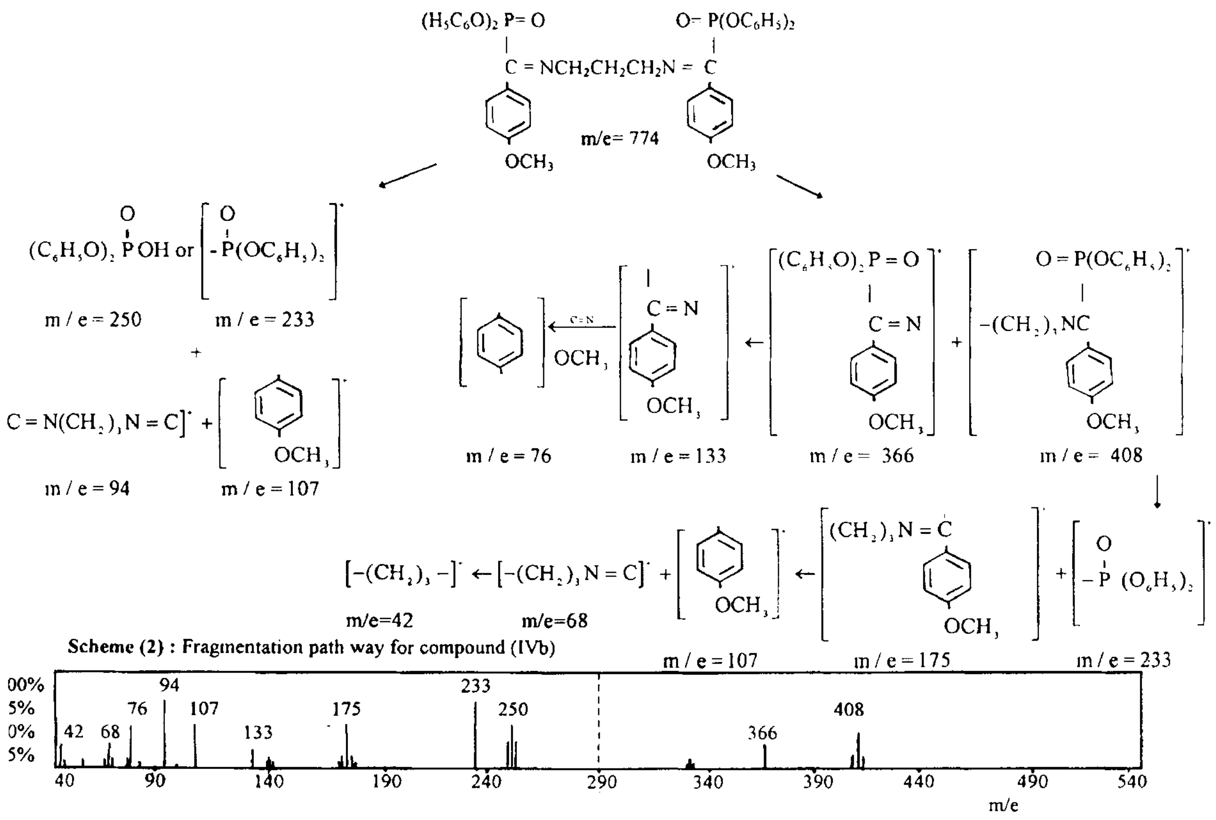


Scheme (1) : Fragmentation path way for compound (Vb).



Mass spectrum of compound (Vb)



Scheme (2) : Fragmentation path way for compound (IVb)