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Syntheses and characterisation of new diazaphospholes and phosphonic acids

Chava V N Rao*, Ch Rama Teerdha, Ashvin K Aggarwal and V Ram Manohar

PG Department of Chemistry, AG & SG Siddhartha College of Arts & Science, Vuyyuru, Krishna Dt. A.P., India

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ABSTRACT

Synthesis of diazaphospholes (1- 8) were accomplished by the condensation of 1, 2 -ethylene diamine with phosphorus oxychloride and the intermediate compound in situ treated with water or indole or 5-bromoindole. Synthesis of phosphonic acids and its derivatives (9-14) were obtained by reacting phosphorus oxychloride with indole or 5-bromoindole in presence of triethylamine. All these compounds were (1-14) colourless to brown coloured solids. These compounds structures were elucidated with the help of spectral data – IR, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR, MASS and Elemental analysis.

Keywords: Diazaphospholes, Phosphonic acids, Indole, 5-bromoindole, 1, 2-ethylene-diamine.

INTRODUCTION

Phosphorous compounds play a vital role in the growth, sustenance and reproduction of life. Several phosphate esters are important precursors in the bio-synthesis of many macro molecules of life [1]. Some of the esters and thioesters of phosphoric acid are well known agrochemicals, used as effective pesticides [2,3]. Many cyclic and acyclic organo–phosphorus compounds having a nitrogen atom are known to exhibit anti tumour activity [4-6]. Recent development in the applications of phosphorous compounds in the nano-technology was found promising applications in the pharmacy [7]. Some diazaphospholes and certain phosphinyl carbamates have been demonstrated to possess insecticidal, bactericidal, antiviral, antitumor and anti-carcinogenic activity [8]. Organophosphorus compounds are ubiquitous in nature and have applications in the field of agriculture, medicine, and industry as some of them are important pesticides, bactericides, and antibiotics. Phosphorus analogues of α-pyrones act as HIV protease inhibitors. There exists growing interest in organo phosphorus heterocyclic compounds since extensive use as pesticides in agriculture, as stabilizers in polymers and as lubricant oil additives has been found [9]. Unsymmetrical substituted N-heterocyclic phosphenium ions were also reported [10].

Diazaphospholes and diazaphosphorinanes are considered as important compounds due to their applications in chemistry and medicine [11-13]. So far, few structures and coupling constant

assignments of these compounds have been reported [14,15]. Stereochemistry, P–C coupling constants in 1, 3, 2-benzodiazaphospholes [16] and 2-oxo-, 2-thio-diazaphosphorinanes also has been reported [17]. Phosphorus–hydrogen coupling constants in some diazaphospholes with three coordinated phosphorus atoms were studied [18] to further investigate this area.

The structural and theoretical study of 1*H*-3, 5-di-phenyl-1, 2, 4-diazaphosphole in the solid state was reported [19]. A theoretical comparison of the chemical shifts of three related heterocycles,1H-pyrazoles, 1*H*-1,2,4-triazoles and 1*H*-1,2,4-diazaphospholes were also reported [20].

In view of the exhibition of potential bioactivity of these molecular skeletons, their phosphorus structural analogues 2- substituted diazaphospholes, phosphonic acids and phosphonic acid esters were synthesised and characterised with spectral studies in this paper.

MATERIALS AND METHODS

Infrared spectra (ν max in cm^{-1}) were recorded as KBr pellets on Perkin - Elmer FT-IR 1000 spectra photometer. The wave numbers of the spectra were calibrated by using a standard poly styrene film. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Brucker Avance II 400 NMR spectra Meter operating at 400 MHz for ^{1}H, 100 MHz for ^{13}C and 161.89 MHz for ^{31}P. NMR data were recorded in $CDCl_3$ or CD_3OD or DMSO-d_6 and were referenced to TMS as an internal standard (^{1}H and ^{13}C) and 85% H_3PO_4 as an external standard (^{31}P) NMR. Elemental analyses were recorded on Flash 1112 Thermo Finnegan. Mass spectra were recorded on Agilent Technology 1200 Series, LCMS, Triple Quad 6410. 1,2-ethylene diamine, indole, bromoindole were procured from SD fine Chemicals Ltd.

In a 250 ml round bottom flask phosphorus oxychloride 33 gms (0.215 moles) in 50 ml toluene was taken and 1, 2-ethylenediamine 10 gm (0.1666 moles) in toluene was added slowly at -12 ^{0}C for a period of 30 min with stirring. Then 7.23gms (0.07145 moles) triethyl amine was added in toluene slowly at the same temperature for about 20 min. Stirring was continued with a rise in temperature to 50 ^{0}C over a period of 2 hours. The reaction was monitored with TLC for every 30 min. After completion of reaction, the reaction mixture was put into a beaker containing crushed ice. A light brown colour solid was obtained. It was collected and rectrystalised from ethyl acetate. This solid contained two compounds and they were separated and isolated from silica gel column with n- hexane and ethyl acetate (9:1 and 7:3) as eluents. They were 2-oxo-$2\lambda^5$-[1, 3, 2] diazaphospholidin-2-ol (1) with mp (90 ^{0}C) and $2\lambda^5$-[1, 3, 2] diazaphospholidine -2, 2, 2-triol (2) with mp (98 ^{0}C).

In a 250 ml round bottom flask phosphorus oxychloride 33 gms (0.215 moles) in 50 ml toluene was taken and 1,2-ethylenediamine 10 gm (0.1666 moles) in toluene was added slowly at -12 ^{0}C for a period of 30 min with stirring. Then 30 ml triethyl amine in toluene was added slowly at the same temperature. Stirring was continued with a rise in temperature to 50^{0} C over a period of 2 hours. The reaction was monitored with TLC for every 30 min. After completion of the reaction cool it to 15 ^{0}C, and indole 8 gm (0.0689 moles) in 15ml toluene was slowly added to this reaction mixture at 20 ^{0}C for about 20min. through an addition funnel. Stirring was continued for 2 hours more with TLC for every 30 min. After completion of the reaction, reaction mixture was put into a beaker containing crushed ice and charged n-hexane 25ml to that beaker under stirring to remove the un-reacted indole. A light brown colour solid was obtained. It was collected and rectrystalised from ethyl acetate. This solid contained three compounds and they were separated and isolated from silica gel column with n- hexane and ethyl acetate (8:2 and

7:3) as eluents. 1-(2-oxo-2λ^5-[1,3,2] diazaphospholidin-2-yl)-1*H*-indole (3) with mp 102 ^{0}C and 2-indol-1-yl-2λ^5-[1,3,2] diazaphospholidine- 2, 2- diol (5) with mp 119 ^{0}C and 2-(3 –Chloro-indol-1-yl)- 2λ^5-[1, 3, 2] diazaphospholidine-2,2- diol (6) with mp 107 ^{0}C were obtained.

In a 250 ml round bottom flask phosphorus oxychloride 33 gms (0.215moles) in 50 ml toluene was taken and 1,2-ethylenediamine 10 gm (0.1666 moles) in toluene was added slowly at -12 ^{0}C for a period of 20 min with stirring. Then triethyl amine in toluene was added slowly at the same temperature. Stirring was continued with a rise in temperature to 50^0 C over a period of 2 hours. The reaction was monitored with TLC for every 30 min. After completion of the reaction cool it to 15 ^{0}C. 5 - bromoindole 8 gm (0.04060 moles) in 15ml toluene was slowly added for about 20 min through an addition funnel. Stirring was continued for 2 hours more and cheked TLC for every 30 min. After completion of reaction, the reaction mixture was put into a beaker containing crushed ice and charged n-hexane 25 ml to that beaker under stirring to remove the un-reacted 5-bromo indole. A light brown colour solid was obtained. It was collected and rectrystalised from ethyl acetate. This solid contained three compounds and they were separated and isolated from silica gel column with n- hexane and ethyl acetate (9:1, 8:2 and 7:3) as eluents. These were 5-Bromo-1-(2-oxo-2λ^5-[1,3,2] diazaphospholidin -2-yl)-1*H*-indole (4), 2-(5-bromo-indol-1-yl)- 2λ^5-[1,3,2] diazaphospholidine - 2,2-diol (7) and 2-(5-bromo-3-chloro-indol-1-yl)-2λ^5-[1,3,2] diazaphospholidine - 2, 2-diol (8). This compound 4, 7 and 8 melts at 109 ^{0}C, 127 ^{0}C and 134 ^{0}C respectively.

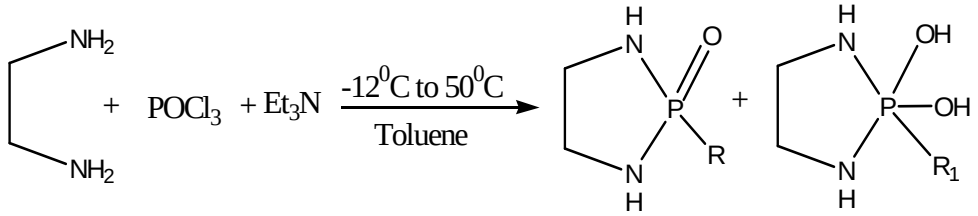
In a 250 ml round bottom flask phosphorus oxychloride 20 gm (0.1307 moles) in toluene was taken and indole 10 gm (0.8536 moles) in toluene was added slowly at -10 ^{0}C for a period of 30 min with stirring. Then triethyl amine in toluene was added slowly at the same temperature. Stirring was continued with a rise in temperature to 30 ^{0}C over a period of 2 hours. The reaction was monitored with TLC for every 30 min. After completion of the reaction, the reaction mixture was put into a beaker containing crushed ice and charged n-hexane 25 ml to that beaker under stirring to remove the un-reacted indole. A light brown colour solid was obtained. It was collected and rectrystalised from ethyl acetate. This solid contained three compounds and they were separated and isolated by silica gel column with n- hexane and ethyl acetate (9:1, 8:2 and 7:3) as eluents. Indol-1-yl-phosphonicacid (9) with mp 125 ^{0}C, Bis-indol-1-yl-phosphonicacid (10) with mp 113 ^{0}C and 1, 1', 1''phosphoryltris (1*H*-indole) (11) with mp 105 ^{0}C were isolated.

In a 250 ml round bottom flask phosphorus oxychloride 15 gm (0.0980 moles) in toluene was taken and 5-bromo indole 10 gm (0.5072 moles) in toluene was added slowly at -10 ^{0}C for a period of 30 min. with stirring. Then triethyl amine in toluene was added slowly at the same temperature. Stirring was continued with a rise in temperature to 30 ^{0}C over a period of 2 hours. The reaction was monitored with TLC for every 30 min. After completion of the reaction, the reaction mixture was put into a beaker containing crushed ice and charged n-hexane 25 ml to that beaker under stirring to remove the un-reacted 5-bromo indole. A light brown colour solid was obtained. It was collected and rectrystalised from ethyl acetate. This solid contained three compounds and they were separated by and isolated from silica gel column with n- hexane and ethyl (8:2, 7:3 and 1:1) acetate as eluents. (5-bromo indol-1-yl) –Phosphonic acid (12) with mp is125 ^{0}C, Bis (5-bromo-indol-1-yl)-phosphonic acid (13) with mp (113 ^{0}C) and 1, 1', 1''phosphoryltris (5-bromo-1*H*-indole) (14) with mp (140 ^{0}C).

RESULTS AND DISCUSSION

Syntheses of the first set of compounds (1-8) were accomplished in a two step process. The synthetic route involves the condensation of 1, 2 -ethylene diamine with phosphorus oxychloride

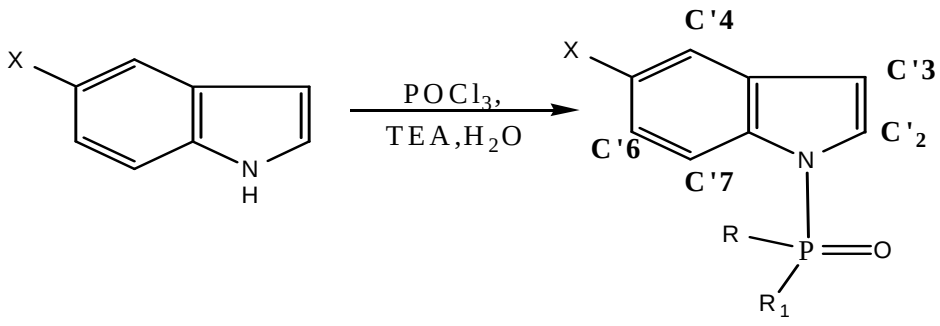
in presence of triethyl amine in dry toluene to yield the intermediate monochloride and trichloride. These intermediates *in situ* were mixed with water or indole or 5-bromoindole to get the final products. The compound (7) 2-(5-bromo 3-chloro indole) - $2\lambda^5$ – [1,3,2] benzodiazaphosphole 2,2-diol was formed as one of the products. This compound was formed due to chlorination of the indole ring with $POCl_3$ taken as one of the reactants in this reaction [21]. The reaction scheme is shown below.



1, 3, 4 2,5,6,7,8

Compound No	R	Compound No	R_1
1	OH	2	OH
3	Indole	5	Indole
4	5-bromo indole	6	3-ChloroIndole
		7	5-bromoindole
		8	3-chloro-5-bromo indole

The second set of six compounds (9-14) were synthesised by condensing indole or 5-bromoindole with phosphorus oxychloride in presence of triethylamine to yield phosphonic acids and its derivatives. This reaction scheme is shown below.



9-14

Compound No	R	R_1	X
9	OH	OH	H
10	OH	indole	H
11	indole	indole	H
12	OH	OH	Br
13	OH	5-bromoindole	Br
14	5-bromoindole	5-bromoindole	Br

These compounds were colourless or light brown substances with melting points in the range of 98 – 140^{0}C and presented in the Table -1 along with other physical characteristics.

IR spectra of these compounds were presented in Table -1. All these compounds had shown all the important absorption frequencies in the expected region. P =O (1197–1245 cm $^{-1}$), P –OH (949–1105 cm^{-1}), HO-P=O (1616-1621 cm^{-1}), P-N-C (695-1212cm^{-1}), O-H (3221-3425 cm^{-1}), N-H (3424-3443cm^{-1}) groups were obtained in the ranges reported in the brackets. All these values were in the ranges reported in the literature [8,22].

Table 1: Physical, I R and ^{31}P NMR spectral data of Diazaphospholes, Phosphonic acids

Comp. No	Molecular Formula	M.P. ^{0}C	Yield %	Elemental Analysis (Cald.) /Found			IR in cm $^{-1}$						^{31}P NMR ppm
				C	H	N	P=O	P-OH	HO-P=O	P-N-C	N-H	C-Br	
1	$C_2H_7N_2O_2P$	90	35	(19.68) 20.12	(5.78) 5.26	(22.95) 23.41	1225	1261	1612	1130,724	3302	-	1.699
2	$C_2H_9N_2O_3P$	98	27	(17.15) 17.51	(6.48) 6.19	(20.00) 20.35	-	1258	-	1130,712	3290	-	-
3	$C_{10}H_{14}N_3O_2P$	102	33	-	-	-	1197	-	-	1125,697	3330	-	-
4	$C_{10}H_{12}N_3OP$	109	25	-	-	-	1212	-	-	1122,697	3315	691	-
5	$C_{10}H_{11}BrN_3OP$	119	23	-	-	-	-	1274	-	1124,712	3312	-	-
6	$C_{10}H_{13}ClN_3O_2P$	107	15	-	-	-	-	1197	-	1121,714	3392	-	-
7	$C_{10}H_{13}BrN_3O_2P$	121	22	-	-	-	1214	1255	1624	1112,725	-	712	-
8	$C_{10}H_{12}BrClN_3O_2P$	137	27	-	-	-	-	1213	-	1115,695	3415	697	1.128
9	$C_8H_8NO_3P$	125	31	(48.74) 48.65	(4.09) 4.15	(7.11) 7.21	1128	1213	1613	1115,730	-	-	- 0.60
10	$C_{16}H_{13}N_2O_2P$	113	21	(64.87) 64.75	(4.42) 4.36	(9.46) 9.51	1213	-	-	1202,730	-	-	-
11	$C_{24}H_{18}N_3OP$	105	17	-	-	-	1224	1213	1612	1185,706	-	-	-
12	$C_8H_7BrNO_3P$	122	32	-	-	-	1215	1260	1616	1145,760	-	698	-
13	$C_{16}H_{11}Br_2N_2O_2P$	125	18	(42.32) 42.19	(2.44) 2.53	(6.17) 6.21	1242	-	-	1210,715	-	710	-6.94
14	$C_{24}H_{15}Br_3N_3OP$	140	12	-	-	-	1245	-	-	1212,712	-	729	-

Table 2: ^{1} H NMR spectral data of Diazaphospholes, Phosphonic acids

Comp. No.	O-H	N-H (Endocyclic)	C-4	C-5	Ar-H
1	9.14 (1H,s)	8.72 (2H,s)	3.38 (2H,m)	3.07 (2H,m)	-
2	8.65 (3H,s)	8.25 (2H,s)	2.37 (2H,m)	2.05 (2H,m)	-
3	-	7.52 (2H,s)	4.68 (2H,m)	3.29 (2H,m)	6.9-7.21 (6H,m)
4	-	7.31 (2H,s)	4.12 (2H,m)	3.66 (2H,m)	7.09-7.25 (H,s,4H,m)
5	7.75 (2H,s)	7.46 (2H,s)	3.08 (2H,m)	2.53 (2H,m)	6.98-7.29 (6H,m)
6	7.78 (2H,s)	7.5 (2H,s)	3.21 (2H,m)	2.89 (2H,m)	6.93-7.05 (6H,m)
7	8.02 (2H,s)	8.7 (2H,s)	4.13 (2H,m)	2.50 (2H,m)	6.8-7.8 (5H,m)
8	8.55 (2H,s)	10.7 (2H,s)	4.94 (2H,m)	3.49 (2H,m)	6.9-7.55 (4H,m)
9	10.6 (2H,s)	-	-	-	7.1-7.45 (6H,m)
10	10.62 (H,s)	-	-	-	7.3-7.9 (12H,m)
11	-	-	-	-	7.27-7.82 (24H,m)
12	10.91 (2H,s)	-	-	-	7.08-7.56 (H,s,4H,m)
13	10.85 (H,s)	-	-	-	7.1-7.47 (2H,s,8H,m)
14	-	-	-	-	6.9-7.8 (3H,s,12H,m)

‡ *$CDCl_3$ was used as solvent for compounds 1- 6.*
CD_3OD was used as solvent for compounds 7- 9 and 11.
DMSO-d_6 + CDOD were used as solvent for compounds 10, 12, and 13.

Table-3: ^{13}C NMR spectral data of diazaphospholes, phosphonic acids

Compound No	Chemical shift in ppm
1	30.52 (C-4), 31.71 (C-5).
2	31.75 (C-4), 31.1 (C-5).
3	32.03 (C-4), 31.62 (C-5), 117.8 (C^1-2), 114.5 (C^1-3), 113.25 (C^1-4), 114.2 (C^1-5), 119.35 (C^1-6), 122.8 (C^1-7), 113.54 (C^1-8), 117.59 (C^1-9).
4	34.03 (C-4), 32.2 (C-5), 123.5 (C^1-2) 129.68(C^1-3), 123.5(C^1-4), 129.8 (C^1-5), 134.4 (C^1-6), 129.2 (C^1-7) 127.95 (C^1-8), 125.4 (C^1-9).
5	31.3 (C-4), 32.6 (C-5), 123.2 (C^1-2) 121.15 (C^1-3), 120.4 (C^1-4), 119.5 (C^1-5), 122.3 (C^1-6), 121.8 (C^1-7), 126.54 (C^1-8), 123.9 (C^1-9).
6	31.1 (C-4), 30.4 (C-5), 118.25 (C^1-2) 121.0 (C^1-3), 121.4 (C^1-4), 118.0 (C^1-5), 122.3 (C^1-6), 121.8 (C^1-7), 126.54 (C^1-8), 123.9 (C^1-9).
7	32. 3 (C-3), 31.62 (C-4), 116.41 (C^1-2), 115.8 (C^1-3), 119.5 (C^1-4), 134.5 (C^1-5), 129.8 (C^1-6), 129.2 (C^1-7) 127.5 (C^1-8), 126.24 (C^1-9).
8	34.03 (C-4), 33.12 (C-5), 122.5 (C^1-2) 129.68 (C^1-3), 123.5 (C^1-4), 134.4 (C^1-5), 129.8 (C^1-6), 129.2 (C^1-7) 127.95 (C^1-8), 129.8 (C^1-9).
9	117.83 (C-2), 121.9 (C-3), 121.2 (C-4), 120.5 (C-5) 119.4 (C-6), 121.95 (C-7), 122.8 (C-8), 113.9 (C-9).
10	115.59 (C-2), 119.7 (C-3), 114.5 (C-4), 123.5 (C-5), 125.4 (C-6), 122.9 (C-7), 123.2 (C-8), 117.95 (C-9). 123.59 (C^1-2), 123.1 (C^1-3), 123.1 (C^1-4), 123 (C^1-5), 123.25 (C^1-6), 122.3 (C^1-7), 116.2 (C^1-8), 113.9 (C^1-9).
11	115.88 (C-2), 123.9 (C-3), 123.2 (C-4), 123.5 (C-5), 123.4 (C-6),122.3 (C-7), 122.8 (C-8), 123.18 (C-9), 123.59 (C^1-2), 123.25 (C^1-3), 123.35 (C^1-4), 123.4 (C^1-5), 124 (C^1-6), 122.8 (C^1-7), 126.54 (C^1-8), 123.59 (C^1-9), 123.9 (C^{11}-2), 123.2 (C^{11}-3), 123.5 (C^{11}-4), 123.4 (C^{11}-5), 123.2 (C^{11}-6), 122.8 (C^{11}-7), 125.4 (C^{11}-8), 123.9 (C^{11}-9).
12	117.59 (C-2), 122.8 (C-3), 123.25 (C-4), 134.32 (C-5), 129.8(C-6), 122.2(C-7), 121.5 (C-8), 117.6 (C-9).
13	119.6 (C-2), 121.2 (C-3), 123.5 (C-4), 134.99(C-5),129.8 (C-6), 129.7 (C-7), 117.5(C-8), 118.2(C-9),123.1(C^1-2),123.2 (C^1-3),119.8 (C^1-4), 134.21 (C^1-5), 129.4 (C^1-6), 124.25 (C^1-7), 115.4 (C^1-8), 113.12 (C^{11}-9).
14	120.52 (C-2), 128.0 (C-3), 123 (C-4),134.0(C-5), 129.8 (C-6), 129.2 (C-7), 127.5 (C-8), 120.01 (C-9), 119.3(C^1-2),123 (C^1-3), 129.8 (C^1-4), 134.32, (C^1-5),129.2 (C^1-6) 127.5 (C^1-7), 125.4(C^1-8), 129.8 (C^1-9), 120 (C^{11}-2), 123 (C^{11}-3), 129.8 (C^{11}-4), 134.19 (C^{11}-5), 129.2 (C^{11}-6)127.5 (C^{11}-7), 125.4 (C^{11}-8), 129.8 (C^{11}-9).

Table: 4 Mass spectral data of diazaphospholes, Phosphonic acids

Compound NO	m/z(% relative abundance)
1	121 (15, M-1)$^+$, 102(8).
2	139 (10, M-1)$^+$.
3	220.7 (51, M+1) $^+$.
4	296 (75, M-2)$^+$.
5	239 (20, M^+).
6	276 (24), (M+2)$^+$.
7	316 (35),(M-2)$^+$
8	350 (100, M-2), 235(10),137(10).
9	197 (38, M^+).
10	296 (78, M^+), 278 (100).
11	395 (20, M^+).
12	278 (100, M^+).
13	451 (25, M-2)$^+$.
14	629.8 (15, M^+).

The proton NMR chemical shifts (δ) of the compounds were presented in Table -2. The aromatic protons of daiazaphosphole derivatives appeared in the region δ 6.8-7.9 as multiplet. The N-H proton (Endocyclic) was in the range of δ 7.31 - 8.72 ppm. The aliphatic – CH_2 - CH_2 - protons appeared in the range of 2.05 – 4.94 ppm as multiplet. O-H proton was shown as a singlet in the region of δ 7.75 - 10.91 ppm [8]. ^{13}C NMR spectral data were recorded in Table - 3. Aliphatic C_4 and C_5 carbon atoms are in the region of δ 30-35 ppm, aromatic carbons were in the range of δ 113-129.8 ppm. [8,23]. Carbon atom of aromatic ring that was attached to bromine appeared in the range of 134 – 135 ppm [24]. ^{31}P NMR spectral data for some of the title compounds were given in Table-1.^{31}P NMR chemical shifts of these compounds appeared in the region -6.94 to 1.699 [8] as reported earlier.

Mass spectra of these compounds were recorded and presented in Table-4. Many of these compounds showed molecular ions indicating the stability of these molecules.

CONCLUSION

Title compounds were synthesised by condensing of 1,2 -ethylenediamine phosphorus oxychloride and water or indole or 5-bromoindole in good yields. All these compounds are colour less to light brown solid with moderate mp. These compounds structure were elucidated with – IR, ^{1}H NMR,^{13}C NMR and ^{31}P NMR, MASS spectral data and elemental analysis.

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