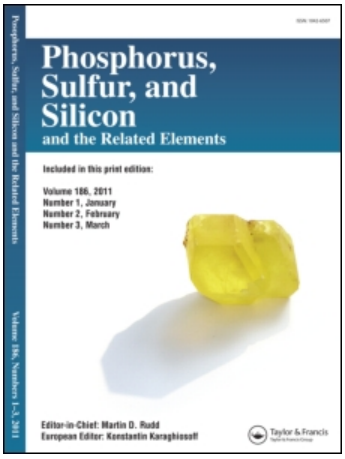

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SYNTHESIS AND SPECTRAL STUDIES OF NOVEL 2-CHLOROETHYL DIOXA/DIOXATHIAPHOSPHOCINS AND BENZODIAZAPHOSPHOLE 2/6/8-OXIDES

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SYNTHESIS AND SPECTRAL STUDIES OF NOVEL 2-CHLOROETHYL DIOXA / DIOXATHIAPHOSPHOCINS AND BENZODIAZAPHOSPHOLE 2/6/8-OXIDES

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Anew class of phosphonates, 2,10-dichloro-12-trichloromethyl-6-(2- chloroethyl)- 12*H*-dibenzo [*d,g*] [1,3,2]dioxaphosphocin 6-oxide **3a**, 2,10-dichloro-6-(2-chloroethyl) dibenzo [*d,g*] [1,3,6,2] dioxathiaphosphocin 6-oxide **3b**, 8-(2-chloroethyl)-16*H*-dinaphtho[2,1-*d*:1,2′-*g*] 1,3,2-dioxaphosphocin 8-oxide **5**, 2,10-dichloro-6-(2-chloroethyl)-4,8-dinitrodibenzo[*d,g*] [1,3,6,2] dioxathiaphosphocin 6-oxide **9** and 2-(2-chloroethyl)2,3-dihydro-5-thiophenoxy-1*H*-1,3,2-benzodiazaphosphole 2-oxide **13** have been synthesized from reactions of equimolar quantities of diols (**2a,2b,4,7**)/diamine (**12**) with 2-chloroethyl phosphonyl dichloride **1** at various temperatures in dry toluene in the presence of triethylamine. Oxidation studies with H_2O_2 (30%) in acetic acid showed interesting results. Compound **9** on oxidation yielded only the corresponding 12-sulphoxide (**10**) and not its sulphone (**11**). But similar oxidation of **13** afforded sulphone (**14**), thus showing that steric and electronic factors control the oxidation process. Alternative approach for the preparation of **11** by oxidation of **7** to sulphone **8** and its cyclocondensation with **1** were unsuccessful due to the existence of strong intramolecular H-bonding. Their IR, ^{1}H, ^{13}C, ^{31}P NMR and mass spectral data were analyzed.

Keywords: : 2-chloroethyl dioxaphosphocins / dioxathiaphosphocins / benzodiazaphospholes; ^{1}H, ^{13}C and ^{31}P NMR analysis; mass spectral analysis

INTRODUCTION

Organophosphorus pesticides comprise one of the major groups among the synthetic pesticides. These are well known for their insecticidal activities[1a] owing to the phosphorus ester which are easily degraded

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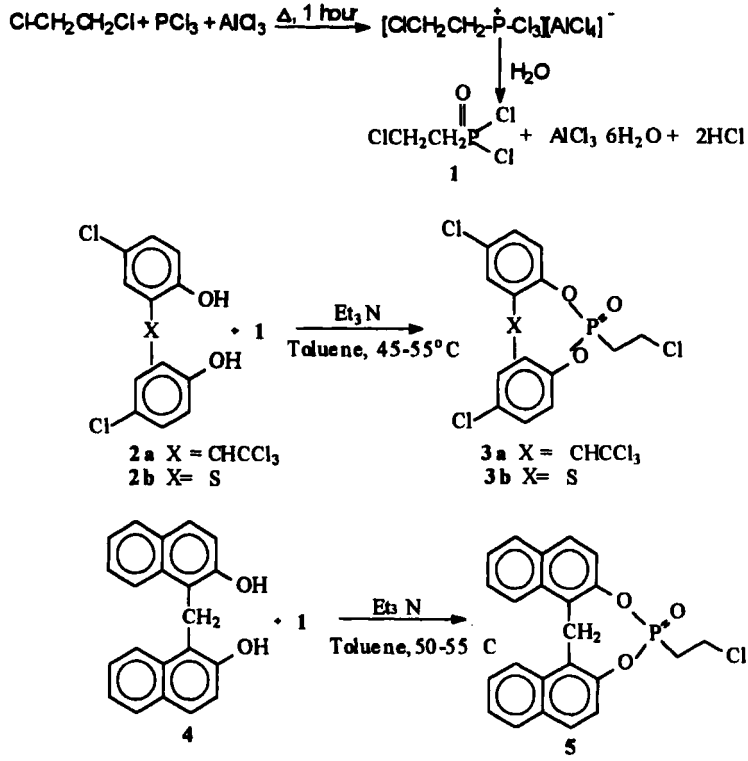
hydrolytically and enzymatically to non-toxice residues. The fungicidal properties of these group of compounds constitute a recent developments[1b]. From a chemist's view point the most valuable aspect of organophosphorus compounds is the sheer diversity of combination of substituents at the phosphorus atom which precisely govern variation of their bio and chemical activity[2]. In view of their potential biological importance, the title compounds were synthesized and characterized by elemental and spectral analyses.

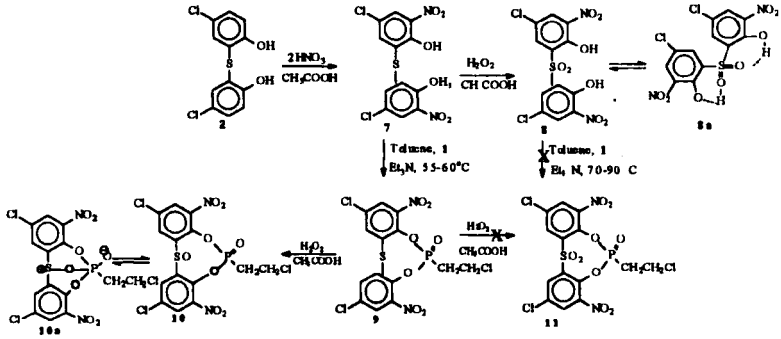
RESULTS AND DISCUSSION

When equimolar quantities of 2,2′-bis (2-hydroxy –5-chlorophenyl) –1,1,1- trichloroethane (**2a**), 5,5′-dichloro-2,2′-dihydroxydiphenyl sulphide (**2b**), bis (2-hydroxy-1-naphthyl)methane (**4**) and 4-thiophenoxy-1,2-phenylenediamine (**12**) were condensed with 2-chloroethyl phosphonyl dichloride (**1**) in presence of triethylamine, **3a, 3b, 5** and **13** were obtained as illustrated (Schemes 1&3). Two equivalents of triethylamine base dry toluene solvent and temperature between 45–55°C are found to be ideal conditions for obtaining **3a, 3b, 5** and **13**. Isolation and purfication of these products was achieved by filtering off the triethylamine hydrochloride, evaporating the filtrate, washing the residue with water, and recrystallization of the solid residues from suitable solvents. Physical and spectral data for all the products are found in Tables I-IV.

Reaction of 4-chlorophenol with sulphur dichloride afforded 5,5′-dichloro-2,2′-dihydroxydiphenyl sulphide (**6**). Nitration of **6** using HNO_3 gave 5,5′-dichloro-3,3′-dinitro-2,2′-dihydroxydiphenyl sulphide (**7**). Cyclocondensation of **7** with 2-chloroethyl phosphonyl dichloride (**1**) in the presence of triethylamine yielded 2,10-dichloro-6-(2-chloroethyl)-4,8-dinitrodibenzo[*d,g*][1,3,6,2]dioxathiaphosphocin 6-oxide (**9**) (Scheme 2). Oxidation of **13** with H_2O_2 (30%) in acetic acid afforded the sulphone derivative **14**. Similar attempts to prepare sulphone (**11**) by oxidising 9 with hydrogenperoxide (30%) in aceticacid resulted in the formation of the corresponding sulphoxide (**10**) but not the expected sulphone (**11**) (Scheme 2). The presence of the sulphoxide function between the two bulky chloronitrophenyl moieties in the rigid heterocyclic system may perhaps prevent further oxidation to the sulphone due to the electronic and



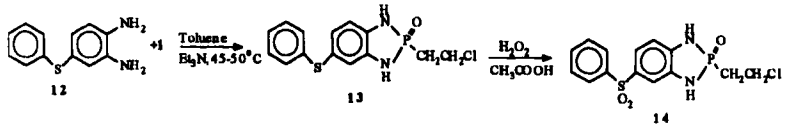
SCHEME 1



SCHEME 2

steric factors. Another view could be that 10 may be in equilibrium with its ring-closed isomer(**10a**) which may electronically prevent further oxidation.

In an alternative approach, oxidation of **7** with hydrogen peroxide (30%) in acetic acid formed the sulphone (**8**). Cyclization of **8** with **1** at 70–90°C in the presence of triethylamine, did not yield the cyclized product (**11**). The reason may be due to the electronic and steric factors and the presence of strong intramolecular hydrogen bonding between the oxygen atoms of the SO_2 and hydrogens of OH groups (**8a**).



SCHEME 3

The IR absorption bands (Table -I) for P=O stretching frequencies in 3–14 were observed at 1206 –1264 cm^{-1}. The P-C stretching absorptions[5] resonated between 730–760 cm^{-1}. In the ^1H NMR spectra (Table II) of 3(a) the doublet at δ 6.02 may be attributed to the long range coupling of the methine proton with phosphorus atom of dioxaphosphocin ring[6] (or) They may be viewed as to different chemical shifts arising from two different diastereomers of **3a**. The bridged methylene protons of dioxaphosphocin 8-oxide (**5**) resonated as two distinct doublets in the regions δ 5.14 and 4.80, $^2J_{H,H}$ = 15.8 and 16.1 Hz indicating their non-equivalence. A study of the signal pattern in comparison with the related dioxaphosphocins[7] revealed that there is long-range coupling ($^5J_{H,P}$= 2.9 Hz) between one of the methylene protons and phosphorus in **5**. The dibenzodioxasulfinyl phosphocin moiety in **10** showed four meta coupled (J = 2.5 Hz) doublets, in the range of 7.85 – 8.22 ppm, which suggest the possibility of at least two isomers exists in the solution for the dibenzodioxasulfinylphosphocin moiety[6b,8]. Out of these four signals, two more intense signals compared to the other two signals. Due to the presence of sulphoxide group, the aromatic protons (1,11 & 3,9 – H) are deshielded compared to the aromatic protons (1,11 & 3,9 – H) in 9. In 8, the two singlets at δ 8.15, 7.94 are attributed for H (4,4′) and H (6,6′) respectively, thus showing the deshielding effect of the sulphone group. The methylene protons of the 2-chloroethyl moieties in **3a, b, 5, 9, 10** and **13** exhibited signals as two multiplets in the regions 2.68 – 3.27 and 3.80 – 4.07 ppm respectively.

TABLE I Physical and Spectral Data for **3a, b, 5, 7–10, 13** and **14**

MF	*MP (°C)*	*Yield (%)*	*Analysis Found (Calcd %)*		*IR (cm^{-1})*
			C	*H*	
$C_{16}H_{11}Cl_6O_3P$	270–271	62[a]	39.02 (38.83)	2.13 (2.24)	1223(P=O), 758 (P-$C_{(aliphatic)}$)cm^{-1}
$C_{14}H_{10}Cl_3O_3PS$	262(dec)	58[a]	– (42.50)	– (2.55)	1225 (P=O), 755 (P-$C_{(aliphatic)}$)cm^{-1}
$C_{23}H_{18}ClO_3P$	148–149	65[a]	67.81 (67.57)	4.62 (4.44)	1217 (P=O), 742, (P-$C_{(aliphatic)}$)cm^{-1}
$C_{12}H_6Cl_2N_2O_6S$	188–189	75[b]	37.89 (38.21)	1.94 (1.60)	1520, 1315 (Ar-NO_2), 3210 (Ar-OH)cm^{-1}
$C_{12}H_6Cl_2N_2O_8S$	278–280	86[b]	35.14 (35.23)	1.64 (1.48)	1532, 1316 (Ar-NO_2), 1120, 1348(SO_2), 3192 (Ar-OH)c
$C_{14}H_8Cl_3N_2O_7PS$	202–204	52[b]	– (34.63)	– (1.66)	1535, 1335 (Ar-NO_2),1230 (P-O), 735 (P-$C_{(aliphatic)}$) cr
$C_{14}H_8Cl_3N_2O_8PS$	183–184	78[b]	33.45 (33.52)	1.54 (1.61)	1528, 1329 (Ar-NO_2), 1243 (P-O), 1083 (S=O), 760 (P-$C_{(aliph}$
$C_{14}H_{14}ClN_2OPS$	175–177	55[a]	51.62 (51.78)	4.45 (4.34)	1206 (P=O), 740 (P-$C_{(aliphatic)}$) cm^{-1}
$C_{14}H_{14}ClN_2O_3PS$	188–190	85[a]	47.24 (47.13)	4.08 (3.96)	1262 (P=O), 1313, 1153 (SO_2), 730 (P-$C_{(aliphatic)}$) cm

thanol.
thyl acetate.

TABLE II H-1 and P-31 NMR Chemical Shift Data and *J* values for members **3a, b, 5, 7–10, 13** and **14** (from TMS)

Chemical Shifts in δ ^1H *NMR*	^{31}P *NMR (85%*
3.16 (s, 2H, 1,11-H), 7.18 (d, *J*=7.6 Hz, 2H, 3,9-H), 7.13 (d, *J*=7.4 Hz, 2H, 4,8-H), 6.02 (d, 1H, 12-H), 3.88–3.98 (m, 2H, $C\underline{H}_2Cl$), 2.68–2.84 (m, 2H, $PC\underline{H}_2$).	13.26, 17
7.1–7.45 (m, 6H, Ar-H), 3.72 –3.89 (m, 2H, CH_2Cl), 2.98–3.06 (m, 2H, PCH_2)	–
8.15 – 8.24 (m, 12H, naphthyl-H), [5.14 (d, *J*=15.8 Hz, 1H, H_a), 4.80 (d, *J* = 16.1Hz, 1H, H_b); bridged CH_2], 3.91–4.02 (m, 2H CH_2Cl), 2.70–2.82 (m, 2H, PCH_2)	14.36, 19
8.01 (d, *J*=2.7 Hz, 2H, 4,4′-H), 7.48 (d, *J*=2.6 Hz, 2H, 6,6′-H).	
8.15 (s, 2H, 4,4′-H), 7.94 (s, 2H, 6,6′-H)	
7.58–7.96 (m, 4H, 1,11&3,9-H), 3.80 – 3.84 (m, 2H, CH_2Cl), 3.03–3.14 (m, 2H, PCH_2).	32.23, 37
8.05–8.22 (m, 4H, 1,11&3,9-H), 3.85 – 3.88 (m, 2H, CH_2Cl), 3.06–3.15 (m, 2H, PCH_2).	12.99, 17
6.72 (s, 1H, 4-H), 7.08 (d, *J*=7.8 Hz, 1H, 6-H), 7.12 (d, *J*=7.6 Hz, 1H, 7-H), 7.15–7.43 (m, 5H, S-C_6H_5), 5.94 (brs, 2H, NH), 3.98–4.07(m, 2H, $C\underline{H}_2Cl$), 3.05–3.27 (m, 2H, $PC\underline{H}_2$)	17.75, 24
7.60–7.81 (m, 3H, 4,6,7-H), 7.79–8.48 (m, 5H, S-C_6H_5), 6.98 (d, *J*=8.9 Hz, 1H, N$\underline{H}$), 7.13(d, *J*=8.8Hz, 1H, N$\underline{H}$), 3.85–4.32 (m, 4H, PC_2H_4Cl).	15.76, 22

MR spectra not recorded.

TABLE III C-13 NMR Chemical Shifts for **3a,5,7,9** and **10** (ppm Values from TMS)[a]

	Chemical Shifts (Coupling Constants)
3a	129.1 (d, J=3.4 Hz, 2C, C-1,11), 131.9 (d, J=3.5 Hz, 2C, C-2,10), 125.4 (d, J=5.7 Hz, 2C,C-3,9), 123.5 (d, 2C, C-4,8), 144.7 (d, J=10. C-4a,7a), 137.8 (s, 2C, C-11a, 12a), 53.5 (s, 1C, C-12), 97.4 (d, J=9.2 Hz, 1C, C-13), 28.4 (d, J=142 Hz, 1C, C-1′; P<u>C</u>H_2), 35.4 (s, 1 <u>C</u>H_2Cl).
5	127.5 (s, 2C, C-1,15), 125.4 (s, 2C, C-2,14), 123.5 (s, 2C, C-3,13), 129.3 (s, 2C, C-4, 12), 129.0 (s, 2C, C-5,11), 119.9 (d, J=5.7 Hz, 6,10), 148.3 (d, J=11.4 Hz, 2C, C-6a,9a), 124.0 (d, J=4.6 Hz, 2C, C-15b,16a), 132.7 (s, 2C, C-4a,11a), 131.8 (s, 2C, C- 15a,16b), 24 16; bridged CH_2), 30.7 (d, J=139.7 Hz, 1C, C-1′; P<u>C</u>H_2), 36.9 (s, 1C, C-2′; <u>C</u>H_2Cl).
7	3.1 (s, 2C, C-1,1′), 150.2 (s, 2C, C-2,2′), 137.6 (s, 2C, C-3,3′), 124.5 (s, 2C, C-4,4′), 126.6 (s, 2C, C-5,5′), 136.6 (s, 2C, C-6,6′).
9	37.4 (s, 2C, C-1,11), 126.9 (s, 2C, C-2,10), 124.8 (s, 2C, C-3,9), 138.0 (s, 2C, C-4,8), 152.3 (s, 2C, C-4a,7a), 121.0 (s, 2C, C-11a,12a) = 141.2 Hz, 1C, C-1′; PCH_2), 35.8 (s, 1C, C-2′;<u>C</u>H_2Cl).
10	40.6 (s, 2C, C-1,11), 130.2 (s, 2C, C-2,10), 127.5 (s, 2C, C-3,9), 142.4 (s, 2C, C-4,8), 154.5 (s, 2C, C-4a,7a), 126.8 (s, 2C, C-11a,12a) = 140.5 Hz, 1C, C-1′; P<u>C</u>H_2), 36.5 (s, 1C, C-2′;<u>C</u>H_2Cl).

[a] constants (J_{PC}) are in parentheses in Hz.

TABLE IV Mass Spectral m/z Values (% of Important Ions) for **5**and **7**

	m/z Values
5	10 [35, (M^+. +2)], 408 (65, M^+.), 372 (40), 345 (16), 327 (20), 281 (100), 265 (45), 252 (44), 239 (24), 226 (13), 213 (9), 189 (11), 26 (20), 115 (15).
7	80 [30, (M^+. +4)], 378 [85, (M^+. +2)], 376 (100, M^+.), 358 (20), 328 (14), 314 (22), 293 (13), 284 (17), 282 (19), 279 (17), 254 (21), 92 (23), 173 (26), 157 (37), 141(17).

The ^{13}C NMR chemical shifts were recorded, for most examples of the title compounds, namely for **3a, 5, 7, 9** and **10** (Table III). In 3a the bridged methine carbon[6c,6d], C-12, attached to trichloromethyl group resonated as a singlet in the down field region at δ 53.5 compared to the bridged methylene carbon in the compound **5**. The carbon of the trichloromethyl, C-13, appeared as a doublet at δ 97.4 (d, J = 9.2 Hz). The C-1′ carbon ($P\underline{C}H_2$) in compounds **3a, 5, 9** and **10** resonated as a doublet at δ 28.4 – 30.7 ($^1J_{(P,C)}$ = 139.7 – 142.0)[9]. The C-2′ carbon ($\underline{C}H_2Cl$) signal appeared as a singlet in the region 35.4–36.9 ppm.

Phosphorus – 31 NMR signals were observed in the ranges of 13.26 – 37.11 ppm for **3a, 5, 9, 10, 13** and **14**. Electron impact mass spectral analysis was confirmatory for the proposed structures[10] due to the presence of its molecular ions in **5** and **7**.

CONCLUSIONS

Simple methodology has been developed to obtain several members of the title compounds whose structures are supported by elemental and a variety of spectral analyses. The advantages of the technology is that the reactions can be performed smoothly, and the products are relatively easy to isolate and purify.

EXPERIMENTAL

General

All melting points were determined on a Mel-Temp apparatus and were uncorrected. Elemental analyses were performed by the Central Drug Research Institute, Lucknow, India. The IR spectra were recorded as KBr pellets on a Perkin-Elmer 683 unit. The ^1H, ^{13}C, and ^{31}P NMR spectra were taken on a Varian Gemini 300 MHz NMR spectrometer operating at 299.9 MHz (^1H), 75.5 MHz (^{13}C), and 121.7 MHz (^{31}P). Some of the ^1H NMR spectra were recorded on a Varian AMX 400 MHz spectrometer with data acquisition at 400 MHz. Compounds were dissolved in $CDCl_3$/DMSO-d_6 and chemical shifts were referenced to TMS (^1H and

^{13}C) and 85% H_3PO_4 (^{31}P). The electron impact mass spectral data were collected on a JEOL JMSD-300 instrument at 70 eV with a direct inlet system.

Preparation of 2,10-dichloro-12-trichloromethyl-6-(2-chloroethyl)-12*H*-dibenzo[*d*,*g*][1,3,2] dioxaphosphocin 6-oxide (3a)

The general procedure to obtain members of **3b, 5** is illustrated for the preparation of **3a**. 2-Chloroethyl phosphonyl dichloride (**1**, 0.91 g, 0.005 mol) in dry toluene (20 mL) was added dropwise over a period of 15 min to a stirred solution of **2a** (1.93 g, 0.005 mol) and triethylamine (1.01 g, 0.01 mol) in dry toluene (50 mL) at 0°C. After completion of the addition, the temperature was slowly raised to 50–55°C and stirring was continued for an additional 5 h. The progress of the reaction was monitored by TLC analysis. After cooling to room temperature, the triethylamine hydrochloride was filtered off, and the solvent was evaporated under reduced pressure. The residue was washed with water and then recrystallized from ethanol to give 1.54g of pure **3a** in 62% yield mp 270–271°C. Physical and spectral data for **3a,b,5** are in Tables I-III.

Preparation of 5,5′-dichloro-3,3′-dinitro-2,2′-dihydroxydiphenyl sulphide (7)

Nitric acid 7 mL (0.1 mol) was added over a period of 15–20 min to a stirred solution of 5,5′-dichloro-2,2′-dihydroxydiphenyl sulphide (**6**, 14.35 g, 0.05 mol) in acetic acid (125 mL) at 14–15°C. The reaction was continued at room temperature for 2–3 hours. After completion of the reaction, the solid 5,5′-dichloro-3,3′-dinitro-2,2′-dihydroxydiphenyl sulphide was collected; washed with water, dried and recrystallized from ethyl acetate to yield 14.5 g (75%) of **7**, mp 188–189°C. Physical and spectral data for **7** is in Tables I-IV.

Preparation of 2,10-dichloro-6-bis (2-chloroethyl) amino-4,8-dinitrodibenzo [*d*,*g*] [1,3,6,2] dioxathiaphosphocin 6-oxide (9)

2-Chloroethyl phosphonyl dichloride (**1**, 0.91 g, 0.005 mol) in dry toluene (25 mL) was added dropwise over a period of 20 min to a stirred solution of **7** (1.89 g, 0.005 mol) and triethylamine (1.01 g, 0.01 mol) in dry tolu-

ene (40 mL) at 0°C. After completion of the addition, the temperature was slowly raised to 55–60°C and stirring was continued for an additional 6 h. Progress of the reaction was monitored by TLC analysis. After cooling to room temperature, the triethylamine hydrochloride was filtered off, and the solvent was evaporated under reduced pressure. The residue was washed with water and then recrystallized from ethyl acetate to give 1.26 g of pure **9** in 52% yield mp 202–204°C.

Oxidation of 2,10-dichloro-6-(2-chloroethyl)-4,8-dinitrodibenzo[*d*,*g*] [1,3,6,2]dioxathiaphosphocin 6-oxide (9 → 10)

Compound **9** (1.21 g, 0.0025 mol) was dissolved in 30- 40 mL of acetic acid. To this, 1 mL of hydrogen peroxide (30%) was added dropwise over a period of 5 min at 15°C. After the addition, the temperature of the reaction mixture was allowed to rise slowly to room temperature and stirring was continued for 3 h. Purification of this product was achieved by removing acetic acid under reduced pressure followed by washing the crude solid with water. The crude product was recrystallized from ethyl acetate to give pure 0.98 g of sulphoxide (**10**) in 78% yield, mp C. Physical and spectral data given in Tables I-III.

Oxidation of 5,5′-dichloro-3,3′-dinitro-2,2′-dihydroxydiphenyl sulphide (7→8)

Compound **7** (3.77 g, 0.01 mol) was dissolved in 50 mL of acetic acid. To this, 2 mL of hydrogen peroxide (30%) was added dropwise over a period of 10 min at 15°C. After the addition, the temperature of the reaction mixture was raised to room temperature and stirring was continued for 2–3 h. Purification of this product was achieved by removing the acetic acid under reduced pressure followed by washing the crude solid with water. The crude product was recrystallized from ethyl acetate to give pure 3.64 g of sulphone (**8**) in 86% yield, mp 197–198°C. Physical and spectral data given in Tables I-II.

Preparation of 2-(2-chloroethyl)-2,3-dihydro-5-thiophenoxy-1*H*-1,3,2-benzodiazaphosphole 2-oxide (13)

2-Chloroethyl phosphonyl dichloride (**1**, 0.91 g, 0.005 mol) in dry toluene (20 mL) was added dropwise (15 min) to a stirred solution of 4-thiophe-

noxy-1,2-phenylenediamine (**12**, 1.08 g, 0.005 mol) and triethylamine (1.01g, 0.01 mol) in dry toluene (50 mL) at 0°C. After the addition, the temperature was brought to 45–50°C and was maintained for 5 h with stirring. After cooling to room temperature, the triethylamine hydrochloride was filtered off, and the filtrate was evaporated under reduced pressure. The gummy residue was washed with water, dried, and treated with 2-propanol. A crude amorphous compound was separated from the solution and this was recrystallized from ethanol to yield 0.89 g (55 %) of **13**, mp. Physical and spectral data are in Tables I-II.

Oxidation of 2-(2-chloroethyl)-2,3-dihydro-5-thiophenoxy-1*H*-1,3,2-benzodiazaphosphole 2-oxide (13→14)

To a solution of sulfide **13** (0.81 g, 0.0025 mol) in acetic acid (30 mL) was added dropwise 1 mL hydrogen peroxide (30%) over a period of 5 min at 15°C. When the addition was complete, the mixture was allowed warm to room temperature slowly, and the resulting mixture was stirred for 2h. Acetic acid was removed (reduced pressure), and the residual solid was washed with water and recrystallized (ethanol) to give pure **14** (0.76 g, 85%) mp. Physical and spectral properties of **14** are in Tables I-II.

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