Facile Syntheses and Antimicrobial Studies of 6-(aryloxy/arylthio/chloroethoxy)-2,10-Dichloro-4,8-Dinitro-12-Trichloromethyl-12*H*-Dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-Oxides

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Synthesis of several novel 6-aryloxy/arylthio/chloroethoxy-2,10-dichloro-4,8-dinitro-12-trichloromethyl-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-oxides (**4a-k**) was accomplished by reacting 2,2-bis (2-hydroxy-5-chloro-3-nitrophenyl)-1,1,1-trichloroethane **2** with different aryl phosphorodichloridates (**3a-g**) and *O*-2-chloroethyl phosphoryldichloride (**3h**) in the presence of triethylamine in dry toluene at 60-65 °C. Actually some of these compounds were prepared by reacting monochloride **5** resulting from the condensation of phosphorus oxychloride with **2** *in situ*, with different phenols and thiophenols. The chemical structures were confirmed by elemental, ir and ^{1}H, ^{13}C, ^{31}P nmr and mass spectral data analyses. These compounds were screened for antifungal activity against *Aspergillus flavus, Alternaria alternata, Fusarium solani, Curvularia lunata* and *Pyricularia oryzae* and antibacterial activity on *Bacillus subtilis, Staphylococcus aureus, Escherichia coli, Pseudomonas syringae* and *Klebsiella pneumoniae*. Some of them possessed significant activity.

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Introduction.

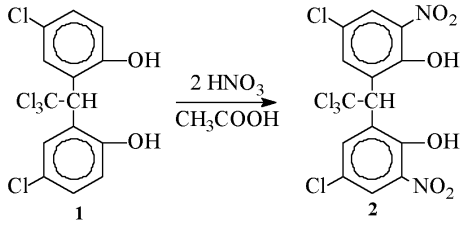
The synthesis of organophosphorus compounds containing the dioxaphosphocin eight membered ring have acquired much importance recently as these compounds have been investigated for their insecticidal, bactericidal, antiviral and anticarcinogenic properties [1-4]. In view of their possible applications, synthesis of the title compounds (**4a-h**) was accomplished using two methods. In the first one various aryl phosphorodichloridates (**3a-g**) and *O*-2-chloroethylphosphoryldichloride (**3h**) were reacted with **2** in the presence of triethylamine in dry toluene. However, introduction of substituted phenols or thiophenols as bulky substituents in **4** was not always successful by this method due to the difficulties in preparation of the corresponding phosphorodichloridates that are moisture sensitive, thermally unstable and explosive in nature. Therefore an alternative method, starting from phosphorus oxychloride, was used: the monochloride, **5** was first prepared by the standard procedure from **2** and then various substituted phenols or thiophenols were added to it *in situ* in the presence of base.

Results and Discussion.

Reaction of 4-chlorophenol with chloral in the presence of concentrated sulphuric acid gave 2,2-bis(2-hydroxy-5-chlorophenyl)-1,1,1-trichloroethane **1** [5]. Nitration of **1** using nitric acid in acetic acid afforded 2,2-bis(2-hydroxy-5-chloro-3-nitrophenyl)-1,1,1-trichloroethane **2** (Scheme I).

Cyclocondensation of this nitro compound **2** with various aryl phosphorodichloridates (**3a-g**) and *O*-2-chloroethylphosphoryldichloride **3h** in the presence of triethylamine at 60-65 °C yielded the eight membered

Scheme I



1 2

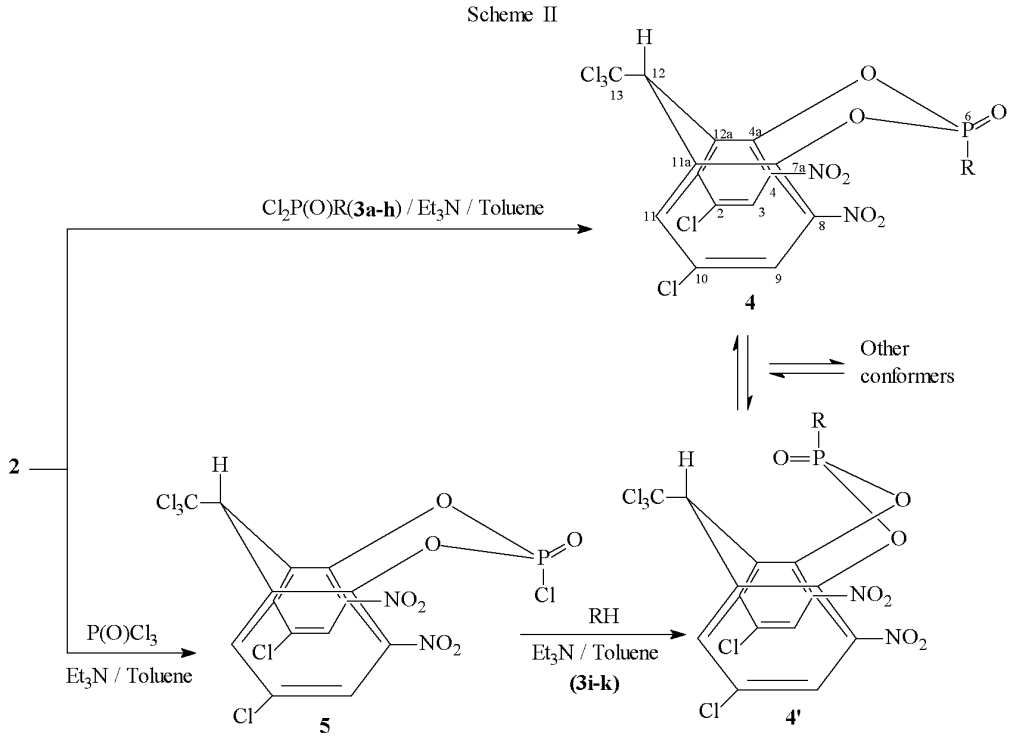
ring dioxaphosphocin 6-oxides **4a-h**. Compounds **4i-k** were prepared through the monochloride, dioxaphosphocin 6-oxide **5** obtained by the reaction of **2** with phosphorus oxychloride/triethylamine in dry toluene at 55-60 °C followed by its reaction with corresponding phenols or thiophenols to give **4** (Scheme II).

The advantages of the second method over the first one are that it does not require the preparation of sometimes highly toxic, moisture sensitive or thermally unstable phosphorodichloridates of corresponding substituted phenol and thiophenols. The isolation and purification of the intermediate monochloride **5** is not required. The condensation products **4** were easily isolated and purified by recrystallization.

The reaction yields, elemental analyses, ir and ^{31}P nmr data of **4** are given in Table 1. Tables 2, 3 and 4 contain ^{1}H and ^{13}C nmr spectral data. The infrared absorption bands for **4a-k** were present in the regions 1241-1320 cm^{-1} and 1533-1542 & 1319-1356 cm^{-1} for P=O and Ar-NO_2 [6-8] respectively.

^{1}H nmr spectra of **4a-k** showed complex multiplets for the aromatic protons of the dibenzodioxaphosphocin moieties at δ 7.50-8.38 [9,10]. The resonance signal for the

Scheme II



Compd.	R	Compd	R	Compd	R
4a	OC_6H_5	**4e**	OC_6H_3-$(CH_3)_2$(2',5')	**4i**	OC_6H_4-$C(CH_3)_3$(4')
4b	OC_6H_4-CH_3(2')	**4f**	OC_6H_4-Cl(2')	**4j**	SC_6H_4-Cl(4')
4c	OC_6H_4-CH_3(3')	**4g**	OC_6H_4-Cl(4')	**4k**	SC_6H_4-CH_3(4')
4d	OC_6H_4-CH_3(4')	**4h**	OCH_2CH_2Cl		

bridged methine proton in all the compounds appeared as singlets in the region δ 6.30-6.68. Similarly, the protons of aryloxy or arylthio moieties showed signals in the region δ 6.70-7.69. The methyl and *tert*-butyl protons of the 6-aryloxy/arylthio moieties in **4b-e, 4k** and **4i** appeared as singlets in the range of δ 2.15-2.49 and δ 0.96 respectively.

A rigid boat-boat (BB), boat-chair (BC) and twist-boat may be more likely conformations considered for the eight-membered dibenzodioxaphosphocin ring as illustrated in Scheme II [9a,b,11]. The structure of the two aromatic rings may assist the cyclization reaction.

The ^{13}C nmr chemical shifts of dibenzodioxaphosphocin moieties of **4** are given in Table 3 and were interpreted based on additivity rules and computed chemical shifts of **2**, carbon couplings with phosphorus and intensity of signals. The oxygen-bearing C(4a) and C(7a) signal appeared in the downfield region at δ 149.4-152.6 [12]. The chemical shift of the bridged C(11a) and C(12a) appeared at δ 122.8-124.7 [12b]. The nitro-substituted C(4) and C(8) gave signals at δ 137.2-138.6. The chlorine bearing C(2) and C(10) resonated in the region δ 129.4-132.5. The unsubstituted C(1) & C(11) and C(3) & C(9) showed signals with high intensity in the region δ 133.8-137.2 and 124.6-129.7 respectively. The bridged C(12) and C(13) resonated at δ 51.5-53.1 and δ 98.0 - 99.9 respectively.

Similarly, ^{13}C nmr chemical shifts of the 6-aryloxy (**4a-g**) and arylthio (**4k**) groups are presented in Table 4. The low intensity signals observed at δ 143.7-152.3 is for C(1'). C(2') and C(6') resonated in the region δ 119.3-130.7. Chemical shifts for the C(3'), C(4') and C(5') were located at δ 130.2-142.9, 123.7-135.2 and 128.5-137.1 respectively on the basis of the nature of substituents at various positions. The observed upfield shift of about 4 ppm for the methyl carbon attached to C(2') (**4b** and **4e)** is attributed to its γ-interaction with the exocyclic oxygen [11b,12c]. In **4h**, the signals observed at δ 63.2 and 44.2 are due to C(1') and C(2') respectively.

The ^{31}P nmr signals of all dibenzodioxaphosphocin 6-oxides (**4a-k**) are given in the range of -21.0 to -1.62 ppm. Only one ^{31}P nmr signal is observed in the spectra of **4a**, **4f** and **4h-k** (Table 1). In other compounds of **4**, two distinct signals were observed with varying intensities [13] and this may be attributable to the presence of two conformers in solution.

The Gas-Chromatography Mass Spectrum of **4b** is rationalized in the Scheme III. It did not show the molecular ion peak. However, the peak at m/z 592 (5.5) represents [$M^{+\cdot}$-HCl] fragment. The base peak ion was observed at m/z 86(100). The ion at m/z 476(4) might be the result of

the ejection of CCl_3 and Cl as radicals from $M^{+\cdot}$ [14,11c]. Expulsion of CCl_2 and C_7H_6O radicals from the parent $M^{+\cdot}$ led to the appearance of the ion at m/z 440(3). This ion on subsequent loss of HCl and H radical gave the ion at m/z 403(25). The daughter ion at m/z 357(48) might have formed by the successive loss of NO_2, two moles of HCl and subsequent abstraction [15] of two hydrogen radicals from the dibenzodioxaphosphocin system. The other important major fragment ions are observed at m/z 339 (50), 293 (17), 207 (13), 184 (25), 149 (14), 137 (18), 107 (43), 86 (100), 53 (48).

Antimicrobial Activity.

The dioxaphosphocin 6-oxides (**4a-k**) were screened for antibacterial activity [16] against the growth of *Bacillus subtilis*, *Staphylococcus aureus* (gram +ve) and *Escherichia coli, Klebsiella pneumoniae, Pseudomonas syringae* (gram -ve) at concentrations 250, 500 and 1000 ppm. The results are given in Table 5. Most of these compounds showed good antibacterial activity at all concentrations against the *Bacillus subtilis, Staphylococcus aureus* and *Escherichia coli* when compared to *Pseudomonas syringae* and *Klebsiella pneumoniae*.

Scheme III

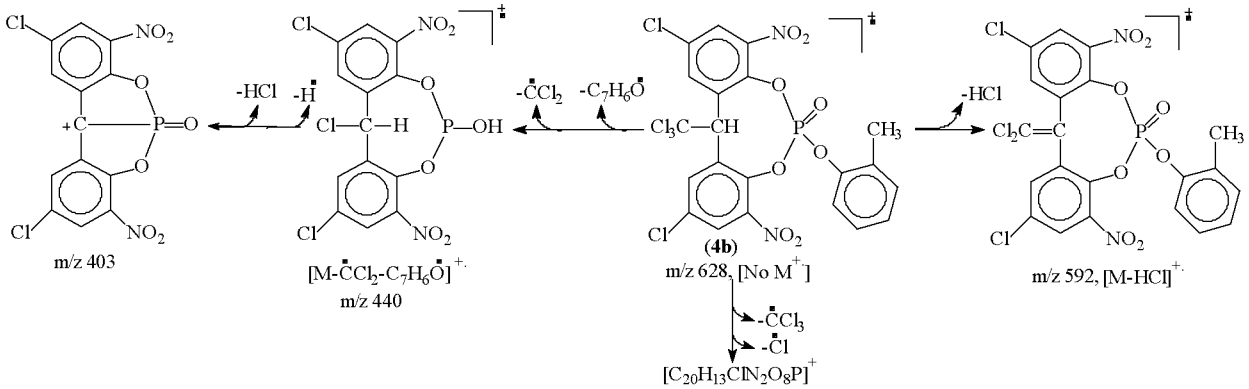


Table 1

Physical, IR and ^{31}P NMR Spectral Data of 6-Aryloxy/arylthio/chloroethoxy-2,10-dichloro-4,8-dinitro-12-trichloromethyl-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-Oxides (**4a-k**)

Compd.	Yield (%)	Mp (°C)	Molecular Formula	Elemental Analysis Found (Calcd) (%)			IR (cm^{-1})			^{31}P NMR Data
				C	H	N	P=O	Ar-NO_2		Ppm
4a	64 [a]	178-180	$C_{20}H_{10}Cl_5N_2O_8P\bullet Et_3N$	43.41 (43.63)	3.40 (3.52)	5.72 (5.87)	1244	1540	1326	-14.48
4b	59 [a]	103-105	$C_{21}H_{12}Cl_5N_2O_8P\bullet Et_3N$	44.28 (44.44)	3.62 (3.73)	5.60 (5.76)	1243	1542	1354	-15.55, -1.62
4c	55 [a]	112-115	$C_{21}H_{12}Cl_5N_2O_8P\bullet Et_3N$	44.24 (44.44)	3.60 (3.73)	5.58 (5.76)	1244	1541	1356	-9.86, -9.68
4d	60 [a]	190-192	$C_{21}H_{12}Cl_5N_2O_8P\bullet Et_3N$	44.64 (44.44)	3.82 (3.73)	5.62 (5.76)	1247	1540	1321	-15.46, -1.62
4e	55 [b]	191-192	$C_{22}H_{14}Cl_5N_2O_8P\bullet Et_3N$	45.01 (45.22)	3.84 (3.93)	5.51 (5.65)	1248	1539	1319	-14.13, -9.16
4f	58 [b]	222-224	$C_{20}H_9Cl_6N_2O_8P\bullet Et_3N$	41.40 (41.63)	3.15 (3.23)	5.42 (5.60)	1248	1539	1320	-5.98
4g	60 [b]	98-100	$C_{20}H_9Cl_6N_2O_8P\bullet Et_3N$	41.41 (41.63)	3.03 (3.23)	5.48 (5.60)	1241	1542	1354	-15.97, -9.02
4h	55 [b]	263-265	$C_{16}H_9Cl_6N_2O_8P\bullet Et_3N$	37.45 (37.64)	3.33 (3.45)	5.84 (5.98)	1312	1533	1351	-4.98
4i	65 [b]	253-255	$C_{24}H_{18}Cl_5N_2O_8P\bullet Et_3N$	46.43 (46.68)	4.20 (4.31)	5.28 (5.44)	1315	1539	1348	-19.3
4j	62 [a]	280 (Dec)	$C_{20}H_9Cl_6N_2O_7PS\bullet Et_3N$	40.51 (40.76)	3.03 (3.16)	5.28 (5.48)	1312	1542	1352	-21.0
4k	58 [a]	234-236	$C_{21}H_{12}Cl_5N_2O_7PS\bullet Et_3N$	43.28 (43.48)	3.56 (3.65)	5.48 (5.63)	1320	1534	1326	-19.1

[a] Recrystallized from methanol; [b] Recrystallized from ethylacetate-hexane; Et_3N = Triethylamine.

Table 2

^{1}H NMR Chemical Shifts [a] of 6-Aryloxy/arylthio/chloroethoxy-2,10-dichloro-4,8-dinitro-12-trichloromethyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-Oxides (**4a-k**)

Compd.	H(3,9) & H(1,11)	H(12)	Ar-H	OAr-CH_3
4a [b]	7.72-8.20 (m, 4H)	6.44 (s, 1H)	6.80-7.59 (m, 5H)	-
4b [c]	7.82-8.31 (m, 4H)	6.39 (s, 1H)	6.75-7.65 (m, 4H)	2.15 (s, 3H, 2 -CH_3)
4c [b]	7.84-8.20 (m, 4H)	6.50 (s, 1H)	6.85-7.17 (m, 4H)	2.26 (s, 3H, 3 -CH_3)
4d [b]	7.68-8.12 (m, 4H)	6.40 (s, 1H)	6.84-7.08 (m, 4H)	2.24 (s, 3H, 4 -CH_3)
4e [c]	7.98-8.21 (m, 4H)	6.51 (s, 1H)	6.97-7.69 (m, 3H)	2.49 (s, 3H, 2 -CH_3)
				2.19 (s, 3H, 5 -CH_3)
4f [c]	7.99-8.11 (m, 4H)	6.49 (s, 1H)	6.82-7.67 (m, 4H)	-
4g [c]	7.83-8.29 (m, 4H)	6.39 (s, 1H)	6.70-7.68 (m, 4H)	-
4h [c]	7.69-8.15 (m, 4H)	6.53 (s, 1H)	-	4.01-4.09 (m, 2H, OCH_2)
				3.68-3.79 (m, 2H, CH_2Cl)
4i [b]	7.50-8.12 (m, 4H)	6.30 (s, 1H)	6.92-7.25 (m, 4H)	0.96 (s, 9H, 4 -$C(CH_3)_3$)
4j [b]	7.98-8.27 (m, 4H)	6.47 (s, 1H)	6.98-7.47 (m, 4H)	-
4k [c]	7.92-8.38 (m, 4H)	6.68 (s, 1H)	6.88-7.30 (m, 4H)	2.24 (s, 3H, 4 -CH_3)

[a] Chemical shifts relative to TMS; [b] Recorded in Deuteriochloroform; [c] Recorded in Dimethylsulphoxide-d_6.

Table 3

^{13}C NMR Chemical Shifts [a,d] of 2,10-Dichloro-4,8-dinitro-12-trichloromethyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-Oxides **4**

Compd.	C(1/11)	C(2/10)	C(3/9)	C(4/8)	C(4a/7a)	C(11a/12a)	C(12)	C(13)
4a [b]	134.7	130.7	126.5	137.5	149.9	123.5	51.9	98.7
4b [c]	137.2	132.5	129.7	138.6	152.6	124.7	53.1	99.2
4c [b]	134.3	131.2	127.2	137.2	149.4	123.0	52.1	99.2
4d [b]	133.8	129.7	124.7	137.3	152.3	124.6	52.4	98.9
4e [c]	135.0	130.2	124.6	136.7	150.0	122.8	51.6	99.6
4f [c]	135.1	130.5	125.0	137.4	150.0	123.0	51.7	99.9
4g [c]	137.2	129.4	125.1	138.5	152.5	124.0	53.1	99.4
4h [c]	134.9	130.3	124.8	137.3	149.7	122.8	51.5	99.7
4k [c]	135.3	129.6	125.1	137.9	-	123.3	52.8	98.0

[a] Chemical shifts in ppm from TMS; [b] Recorded in Deuteriochloroform; [c] Recorded in Dimethylsulphoxide-d_6; [d] **4i & 4j** not recorded.

Table 4

^{13}C NMR Chemical Shifts of 6-Aryloxy/arylthio/chloroethoxy Moieties in **4**

Compd.	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	Methyl carbons
4a [b]	148.6	119.3	133.6	125.9	133.6	119.3	-
4b [c]	152.3	129.9	134.1	123.7	128.7	119.7	20.6
4c [b]	148.9	121.4	142.9	126.7	128.5	118.8	20.1
4d [b]	146.2	121.7	130.4	135.2	130.4	121.7	21.4
4e [c]	148.7	130.4	135.9	124.9	137.1	122.7	19.4 (C-2)
							20.8 (C-5)
4f [c]	148.8	130.7	137.8	125.2	135.9	122.8	-
4g [c]	143.7	12.13	132.6	130.2	132.6	121.3	-
		(4.6)				(4.6)	
4h [c]	-	-	-	-	-	-	63.2 (C-1)
							44.2 (C-2)
4k [c]	143.7	121.4	130.2	129.5	130.2	121.4	20.8 (C-4)

[a] Chemical shifts in ppm and J (Hz) given in parenthesis; [b] Recorded in Deuteriochloroform; [c] Recorded in Dimethylsulphoxide-d_6; [d] **4i & 4j** not recorded.

Similarly, the antifungal activity was evaluated against the growth of *Aspergillus flavus*, *Alternaria alternata*, *Fusarium solani*, *Curvularia lunata* and *Pyricularia oryzae* at different concentrations (250, 500 and 1000 ppm) [17] (Table 6). Compounds **4b**, **4c** and **4g** showed significant activity against all the fungi at different concentrations. However, compounds **4a-k** exhibited moderate antifungal activity against *Fusarium solani* when compared to their activity on other organisms.

EXPERIMENTAL

Melting points were determined in open capillary tubes 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 Perkin-Elmer 1000 unit. All ^{1}H and ^{13}C nmr spectra were recorded on a varian XL-300 spectrometer operating at 300 MHz for ^{1}H and 75.46 MHz for ^{13}C. ^{31}P nmr spectra were recorded on a Varian XL-400 spectrometer operating at 161.89 MHz. All nmr data were taken in deuteriochloroform or dimethyl-d_6 sulfoxide solutions and were referenced to tetramethylsilane (^{1}H and ^{13}C) or 85% phosphoric acid (^{31}P). The Gas-Chromatography Mass Spectra (GCMS) were recorded on a Shimadzu QP 5000 instrument using ionization potential at 70 eV.

Table 5
Antibacterial Activity of Compounds **4a-k**

Compd.	Concentration (ppm)	Zone of inhibition (mm)				
		Bacillus subtilis	*Staphylococcus aureus*	*Escherichia coli*	*Pseudomonas syringae*	*Klebsiella pneumoniae*
4a	250	11	13	8	9	7
	500	15	16	10	11	8
	1000	23	20	15	14	10
4b	250	10	13	7	-	-
	500	18	18	8	-	7
	1000	24	24	14	7	8
4c	250	13	17	8	9	7
	500	19	20	12	11	9
	1000	27	25	18	13	13
4d	250	10	8	7	8	-
	500	13	9	8	10	-
	1000	16	14	9	11	7
4e	250	9	7	-	-	-
	500	13	8	7	-	-
	1000	18	11	10	-	7
4f	250	8	12	-	-	-
	500	11	16	-	-	7
	1000	15	19	8	-	10
4g	250	13	12	7	-	-
	500	18	18	8	-	-
	1000	23	25	13	-	9
4h	250	11	10	-	-	-
	500	14	13	-	-	-
	1000	17	15	9	-	7
4i	250	9	9	8	-	-
	500	11	11	9	-	-
	1000	14	15	12	-	9
4j	250	7	7	-	-	-
	500	9	9	7	-	-
	1000	11	12	9	-	9
4k	250	7	10	-	-	-
	500	8	13	-	-	-
	1000	10	17	8	-	8

'-' indicates no activity.

Preparation of 2,2-Bis(2-hydroxy-5-chloro-3-nitrophenyl)-1,1,1-trichloroethane (**2**).

Nitric acid (7 ml, 0.1 mole) was added over a period of twenty minutes to a stirred solution of 2,2-bis(2-hydroxy-5-chlorophenyl)-1,1,1-trichloroethane **1** (19.3 g, 0.05 mole) in acetic acid (120 ml) at 14-15 °C. After the addition, the reaction was continued with stirring at room temperature for 3-4 hours. The crude nitro product was collected by filtration. It was washed with water, dried and recrystallized from ethylacetate-hexane (3:1) to yield 17.4 g (73%) of 2,2-bis(2-hydroxy-5-chloro-3-nitrophenyl)-1,1,1-trichloroethane (**2**), mp 212-214 °C; ir (potassium bromide): 1539, 1320 (Ar-NO_2), 3259 (Ar-OH) cm^{-1}; ^1H nmr (deuteriochloroform): δ 11.22 (s, 2H, 2 & 2 -OH), 8.15(d, J = 2.6 Hz, 2H, 4 & 4 -H), 8.01 (d, J = 2.6 Hz, 2H, 6 & 6 -H), 6.33 (s, 1H, 2-CH) ; ^{13}C nmr (deuteriochloroform): δ 125.0 (s, 2C, C-1 & 1), 152.8 (s, 2C, C-2 & 2), 137.7 (s, 2C, C-3 & 3), 125.1 (s, 2C, C-4 & 4), 130.1 (s, 2C, C-5 & 5), 134.3 (s, 2C, C-6 & 6), 99.4 (s, 1C, CCl_3), 52.9 (s, 1C, CH) ; gcms: m/z (%) 476 [2, ($M^{+\cdot}$+2), 474 (1.5, $M^{+\cdot}$), 439 (2), 403 (9), 357 (18.5), 339 (43.5), 295 (14), 220 (18), 207 (26), 186 (18), 173 (25), 150 (21), 137 (27), 121 (57), 117 (94), 63 (100).

Anal.Calcd.for $C_{14}H_7Cl_5N_2O_6$: C 35.27, H 1.48, N 5.88; Found: C 34.99, H 1.34, N 5.67.

6-(4-Methylphenoxy)-2,10-dichloro-4,8-dinitro-12-trichloromethyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-Oxide (**4d**).

A solution of 4-methylphenylphosphorodichloridate (**3d**, 2.25 g. 0.01 mole) in 25 ml of dry toluene was added dropwise over a period of twenty minutes to a stirred solution of 2,2,-bis(2-hydroxy-5-chloro-3-nitrophenyl)-1,1,1-trichloroethane (**2**, 4.76 g, 0.01 mole) and triethylamine (2.02 g, 0.02 mole) in 60 ml of dry toluene. After completion of the addition, the temperature was slowly raised to 60-65 °C and stirring was continued for an additional six hours. Progress of the reaction was monitored by tlc analysis. Triethylamine hydrochloride was then removed from the reaction mixture by filtration and the solvent was evaporated under reduced pressure. The residue was washed with water, dried and then recrystallized from ethylacetate-hexane (8:2) to yield pure compound **4d**, 3.8 g (60%), mp 190-192 °C. Physical and spectral data of **4d** are given in Tables 1-4.

Other members of the compounds were prepared by this procedure.

Table 6

Antifungal Activity of Compounds **4a-k**

Compd.	Concentration n (ppm)	Zone of inhibition (mm)				
		Aspergillus flavus	*Alternaria alternata*	*Fusarium solani*	*Curvularia lunata*	*Pyricularia oryzae*
4a	250	8	-	-	8	-
	500	9	-	-	9	7
	1000	13	8	-	11	9
4b	250	7	8	8	7	7
	500	8	9	9	10	9
	1000	10	12	13	12	13
4c	250	7	7	7	13	8
	500	9	8	8	18	9
	1000	12	11	12	22	13
4d	250	7	-	-	7	-
	500	8	-	-	8	-
	1000	9	-	-	11	-
4e	250	-	-	-	7	-
	500	-	-	-	9	-
	1000	7	-	-	13	-
4f	250	-	-	-	7	-
	500	7	-	-	8	-
	1000	10	-	-	11	-
4g	250	7	8	11	8	7
	500	8	11	15	10	8
	1000	11	14	24	14	12
4h	250	-	-	-	7	-
	500	-	-	-	9	-
	1000	7	-	-	10	-
4i	250	-	-	-	7	-
	500	-	-	-	8	-
	1000	-	-	-	10	-
4j	250	-	-	-	7	-
	500	-	-	-	8	-
	1000	-	-	-	12	-
4k	250	-	-	-	7	-
	500	-	-	-	8	-
	1000	8	-	-	10	-

'-' indicates no activity

6-(4-*tert*-Butylphenoxy)-2,10-dichloro-4,8-dinitro-12-trichloromethyl-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-Oxide (**4i**).

The typical procedure using phosphorus oxychloride is illustrated in the preparation of **4i**. To a cooled (0 °C) and stirred solution of 2,2-bis(2-hydroxy-5-chloro-3-nitrophenyl)-1,1,1-trichloroethane (**2**, 4.76 g, 0.01 mole) and triethylamine (2.02 g, 0.02 mole) in 60 ml of dry toluene, was added dropwise phosphorus oxychloride (1.53 g, 0.01 mole) in 25 ml of dry toluene over a period of twenty minutes. After raising the temperature to 55-60 °C, the reaction mixture was stirred for five hours at this temperature, tlc analysis (silica gel; ethylacetate-hexane, 3:7) was used to monitor the formation of monochloride **5**. To this reaction mixture, in the same vessel, at 0-5 °C, was added dropwise a solution of 4-*tert*-butylphenol(1.5 g, 0.01 mole) and triethylamine (1.01 g, 0.01 mole) in 25 ml dry toluene. The temperature of the reaction was brought to 60-65 °C and the mixture was stirred for another four hours. Triethylamine hydrochloride was removed by filtration and evaporation of the solvent under reduced pressure afforded a solid residue, which after washing with water, was dried and recrystallized from methanol to give 4.4 g (65%) of **4i**, mp 253-255 °C. The physical and spectral data for **4i-k** are given in Tables 1-4.

4j-k are prepared by this procedure.

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