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Synthesis and Antimicrobial Activity of 2,10-Dichloro-6-Substituted-4,8-Dinitro-12*H*-Dibenzo[*d,g*][1,3,2]Dioxaphosphocin 6-Oxides/Sulfides

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ABSTRACT: *Novel 2,10-dichloro-6-substituted-4,8-dinitro-12H-dibenzo[d,g][1,3,2]dioxaphosphocin 6-oxides (***4a–h***) were synthesized by reacting 5,5′-dichloro-3,3′-dinitro-2,2′-dihydroxydiphenylmethane (***2***) with different aryl phosphorodichloridates (***3a–g***) or bis(2-chloroethyl)phosphoramidic dichloride (***3h***) in the presence of triethylamine at 55–60°C, and the compounds* **4i–l** *were prepared by reacting the 2,6,10-trichloro-4,8-dinitro-12H-dibenzo[d,g][1,3,2]dioxaphosphocin 6-sulfide (***5***) in situ with substituted phenols and thiophenol* **5** *was prepared by condensing* **2** *with thiophosphoryl chloride. IR, ^1H, ^{13}C, ^{31}P NMR, and mass spectra supported all the proposed structures. Several title compounds exhibited significant activity in the assays against the bacteria Bacillus subtilis and Escherichia coli and fungi Curvularia lunata and Aspergillus niger.* © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:10–15, 2001

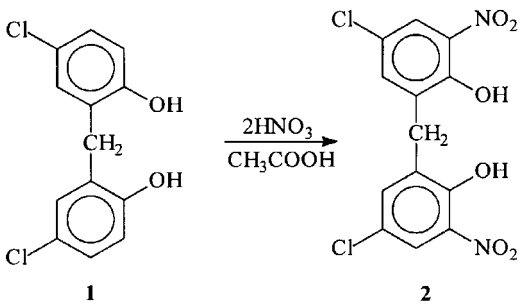
INTRODUCTION

Dibenzodioxaphosphocin esters have considerable importance as stabilizers and antioxidants [1–3] in the polymer and oil industries and also proved to be superior ligands in transition-metal-mediated hydroformylation reactions [4]. Some phosphorus heterocyclic esters are known to be insecticides and bactericides [5–7]. This background prompted us to synthesize and characterize the title compounds (**4a–l**) by elemental, IR, NMR (^1H, ^{13}C, and ^{31}P) and mass spectral analyses and to evaluate their antimicrobial activity.

RESULTS AND DISCUSSION

Reaction of 4-chlorophenol with formaldehyde afforded 5,5′-dichloro-2,2′-dihydroxydiphenylmethane (**1**) [8]. Nitration of **1** using HNO_3 gave 5,5′-dichloro-3,3′-dinitro-2,2′-dihydroxydiphenylmethane (**2**) (Scheme 1).

Cyclocondensation of **2** with aryl phosphorodichloridates (**3a–g**) or bis(2-chloroethyl)phosphoramidic dichloride (**3h**) in the presence of triethylamine, yielded 2,10-dichloro-6-aryloxy/bis(2-chloroethyl)amino-4,8-dinitro-12*H*-dibenzo[*d,g*][1,3,2]di-



1 **2**

SCHEME 1

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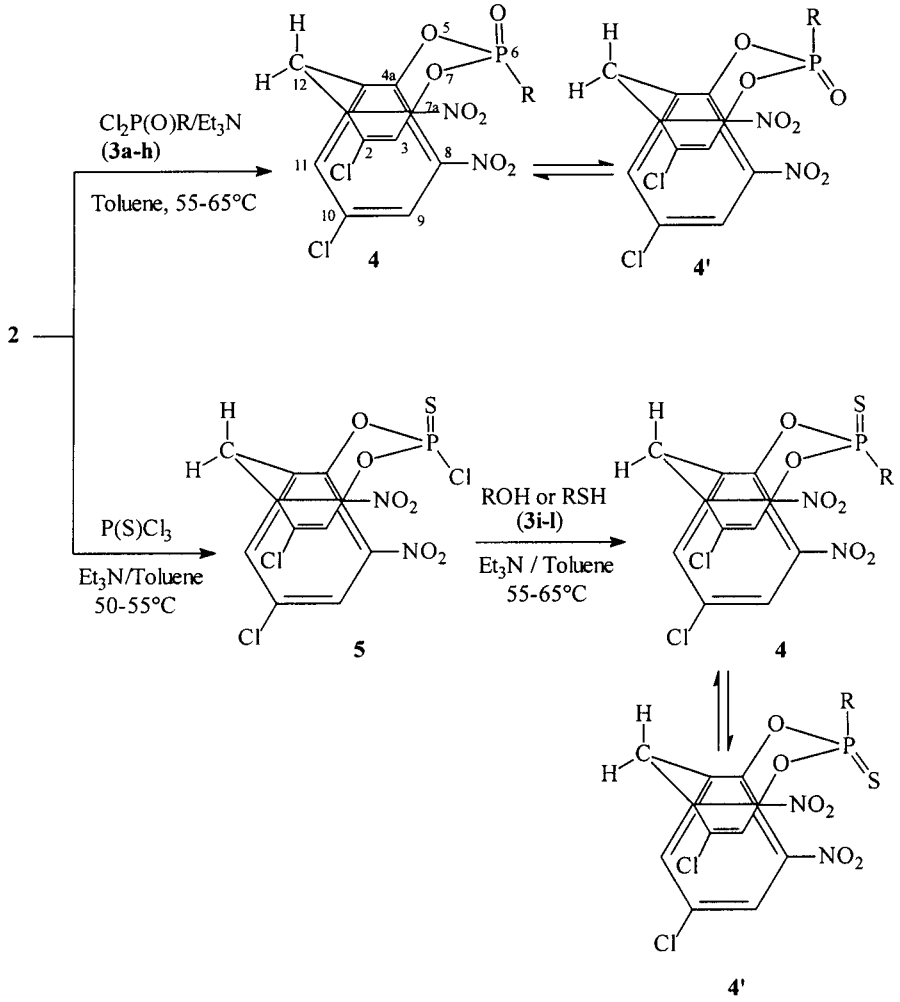
oxaphosphocin 6-oxides (4⇌4′). In an alternative approach, **2** when treated with thiophosphoryl chloride/triethylamine in dry toluene at 50–55°C gave 2,6,10-trichoro-4,8-dinitro-12*H*-dibenzo[*d*,*g*][1,3,2] dioxaphosphocin 6-sulfide (**5**). Compound **5**, which, on subsequent reaction with phenols/thiophenol, yielded **4** (Scheme 2). The second method is advantageous in that it does not require the preparation of highly toxic, moisture-sensitive, and thermally unstable arylphosphorothioic dichlorides of the corresponding phenols and thiophenol and isolation and purification of the intermediate monochloride, **5.** The condensation products (**4**) were isolated by filtering off the triethylamine hydrochloride, followed by evaporation of the solvent from the filtrate under reduced pressure. Further purification was carried out by washing the residue with water followed by flash chromatography using hexane-ethyl acetate mixture as eluent.

Reaction yields, elemental analyses, and IR data



	R		R
4 a)	OC_6H_5	**4 g)**	OC_6H_4-Cl (4′)
b)	OC_6H_4-CH_3 (2′)	**h)**	$N(CH_2CH_2Cl)_2$
c)	OC_6H_4-CH_3 (3′)	**i)**	OC_6H_5
d)	OC_6H_4-CH_3 (4′)	**j)**	OC_6H_4-CH_3 (4′)
e)	OC_6H_3-$(CH_3)_2$ (2′,5′)	**k)**	OC_6H_4-Cl (4′)
f)	OC_6H_4-Cl (2′)	**l)**	SC_6H_5

SCHEME 2

[9–11] are given in Table 1. Tables 2–4 contain ^{1}H, ^{13}C, ^{31}P NMR and mass spectral data for **4**. ^{1}H NMR spectra (Table 2) exhibited two meta-coupled ($J \approx$ 2.4 Hz) doublets at δ 7.62–8.20 for H(1 and 11) and δ 8.02–8.35 for H(3 and 9). The bridged methylene protons (H-12) resonated as a doublet in the region δ 3.90–4.15 ($^{2}J_{H\text{-}H}$ = 13.4–13.6 Hz) and a doublet of doublets in the region δ 4.18–4.60 ($^{2}J_{H\text{-}H}$ = 13.4–13.6 Hz and $^{5}J_{H\text{-}P}$ = 2.4–2.6 Hz) [12]. Space filling models imply that a rigid, twist-boat (TB) conformation is possible, but a boat-chair (BC) conformation **4** may be more likely for the eight-membered dibenzodioxaphosphocin ring [13,14]. Unfortunately, it was not possible to grow a suitable crystal of **4** for X-ray analysis to determine its configuration in the solid state. Most of the proton signals in the phenoxy moiety were quite distinguishable.

The ^{13}C NMR chemical shifts were recorded for some of the title compounds. The oxygen-bearing carbons C(4a) and C(7a) appeared in the downfield region δ 149.9–150.2 [15]. The bridged carbons C(11a) and C(12a) resonated at δ 135.4–135.8 [16]. The nitro-substituted carbons C(4) and C(8) gave signals at δ 135.8–136.8. The chlorine-bearing carbons C(2) and C(10) gave signals in the region δ 130.2–132.3. The signals of unsubstituted carbons C(1 and 11) and C(3 and 9) appeared with high intensity in the regions δ 129.4–130.0 and 123.8–123.9, respectively. The signals of bridged carbon C-12 occurred at δ 29.8–32.3.

^{31}P NMR signals appeared in the region of −17.20 to 1.79 ppm. In **4i** and **4j**, ^{31}P chemical shifts appeared at 54.39 and 52.32 ppm, respectively. Only one ^{31}P signal is observed in the spectrum of **4e, 4f, 4g, 4i,** and **4j.** In the spectra of other compounds of **4,** two distinct signals are observed with varying intensities, which may be due to the existence of two epimeric forms in solution (**4**,**4′**) [17,18].

Electron impact mass spectra of **4** showed M^+, (M^+ + 2) and (M^+ + 4) along with their characteristic daughter ions further agree with the proposed structures.

ANTIMICROBIAL ACTIVITY

All the compounds were tested at two different concentrations (250 and 500 ppm) (Table 5) for antifungal activity, following the Benson [19] technique, against *Aspergillus niger* and *Curvularia lunata*. Their antibacterial activity was evaluated on *Bacillus subtilis* and *Escherichia coli* by the method of Vincent and Vincent [20]. Few of them exhibited significant toxicity against either the fungi or the bacteria.

TABLE 1 Physical and IR Data of Compounds **4**

				Analysis Found (Required) (%)			*IR (cm^{-1})*			
Compound	*m.p. (°C)*	*Yield (%)*	*Mol. Formula*	*C*	*H*	*N*	*P=O*	*P=S*	*Ar-NO_2*	
4a	252–254	50	$C_{19}H_{11}Cl_2N_2O_8P$	45.78 (45.90)	2.22 (2.23)	5.70 (5.63)	1177	—	1541	1347
4b	210–212	40	$C_{20}H_{13}Cl_2N_2O_8P$	47.06 (46.99)	2.60 (2.56)	5.40 (5.48)	1190	—	1540	1351
4c	220–222	45	$C_{20}H_{13}Cl_2N_2O_8P$	46.70 (46.99)	2.62 (2.56)	5.50 (5.48)	1192	—	1542	1351
4d	228–230	43	$C_{20}H_{13}Cl_2N_2O_8P$	47.10 (46.99)	2.59 (2.56)	5.45 (5.48)	1182	—	1545	1349
4e	262–264	38	$C_{21}H_{15}Cl_2N_2O_8P$	47.98 (48.02)	2.90 (2.88)	5.38 (5.33)	1200	—	1535	1351
4f	252–253	42	$C_{19}H_{10}Cl_3N_2O_8P$	42.66 (42.93)	1.94 (1.90)	5.25 (5.27)	1203	—	1538	1348
4g	260–262	40	$C_{19}H_{10}Cl_3N_2O_8P$	42.98 (42.93)	1.92 (1.90)	5.31 (5.27)	1216	—	1534	1361
4h	268–270	32	$C_{17}H_{14}Cl_4N_3O_7P$	37.30 (37.46)	2.80 (2.59)	7.69 (7.71)	1294	—	1541	1356
4i	270–272	42	$C_{19}H_{11}Cl_2N_2O_7PS$	44.70 (44.46)	2.08 (2.16)	5.42 (5.46)	—	757	1537	1351
4j	258–260	32	$C_{20}H_{13}Cl_2N_2O_7PS$	45.51 (45.56)	2.47 (2.48)	5.32 (5.31)	—	762	1538	1354
4k	268–270	34	$C_{19}H_{10}Cl_3N_2O_7PS$	41.62 (41.67)	1.88 (1.84)	5.10 (5.11)	—	783	1545	1351
4l	240–242	32	$C_{19}H_{11}Cl_2N_2O_6PS_2$	43.19 (43.11)	2.01 (2.09)	5.30 (5.29)	—	782	1541	1356

TABLE 2 ^{1}H and ^{31}P NMR Spectral Data of **4** (δ from TMS)

Compound	*H-1, H-11*	*H-3, H-9*	*H-12*	*Ar-H*	*OAr-CH_3*	*^{31}P NMR*
4a[b]	8.02 (d, 2.5, 2H)	8.12 (d, 2.4, 2H)	4.04 (d, 13.5, 1H) 4.45 (dd, 13.5, 2.4, 1H)	7.35–7.56 (m, 5H)	—	−9.47, −16.91
4b[b]	7.63 (d, 2.5, 2H)	8.39 (2, 2.5, 2H)	4.10 (d, 13.4, 1H) 4.50 (dd, 13.5, 2.5, 1H)	7.10–7.51 (m, 4H)	2.37 (s, 3H)	−7.96, −15.27
4c[b]	7.62 (d, 2.4, 2H)	8.10 (d, 2.4, 2H)	4.01 (d, 13.5, 1H) 4.46 (dd, 13.4, 2.5, 1H)	7.25–7.38 (m, 4H)	2.32 (s, 3H)	−9.01, −16.20
4d[b]	7.65 (d, 2.4, 2H)	8.02 (d, 2.3, 2H)	3.90 (d, 13.4, 1H) 4.52 (dd, 13.4, 2.6, 1H)	7.20–7.35 (m, 4H)	2.40 (s, 3H)	−8.86, −17.20
4e[b]	7.72 (d, 2.5, 2H)	8.08 (d, 2.4, 2H)	3.98 (d, 13.5, 1H) 4.48 (dd, 13.5, 2.5, 1H)	7.22–7.40 (m, 3H)	1.90 (s, 3H, 2′-CH_3) 2.20 (s, 3H, 5′-CH_3)	−9.08
4f[c]	7.68 (d, 2.3, 2H)	8.18 (d, 2.5, 2H)	3.96 (d, 13.5, 1H) 4.40 (dd, 13.4, 2.4, 2H)	7.12–7.40 (m, 4H)		−11.22
4g[c]	7.70 (d, 2.4, 2H)	8.05 (d, 2.4, 2H)	4.02 (d, 13.4, 1H) 4.18 (dd, 13.6, 2.5, 1H)	7.10–7.45 (m, 4H)		−9.71
4h[b]	7.94 (d, 2.4, 2H)	8.05 (d, 2.5, 2H)	4.05 (d, 13.6, 1H) 4.45 (dd, 13.6, 2.4, 1H)	3.98–4.02 (m, 4H, $N(CH_2)_2$) 4.08–4.10 (m, 4H, $(CH_2Cl)_2$)		1.79, −13.44
4i[b]	8.20 (d, 2.4, 2H)	8.35 (d, 2.4, 2H)	4.15 (d, 13.5, 1H) 4.42 (dd, 13.4, 2.6, 1H)	7.30–7.60 (m, 5H)		54.39
4j[c]	7.94 (d, 2.4, 2H)	8.23 (d, 2.5, 2H)	4.05 (d, 13.4, 1H) 4.41 (dd, 13.4, 2.6, 1H)	7.49–7.87 (m, 4H)	2.52 (s, 3H)	52.32
4k[c]	7.91 (d, 2.4, 2H)	8.06 (d, 2.4, 2H)	4.06 (d, 13.4, 1H) 4.60 (dd, 13.5, 2.4, 1H)	7.24–7.51 (m, 4H)		—
4l[c]	8.05 (d, 2.4, 2H)	8.25 (d, 2.5, 2H)	4.10 (d, 13.5, 1H) 4.40 (dd, 13.5, 2.4, 1H)	7.28–7.52 (m, 5H)		—

[a]Data in parentheses are coupling constants: *J* in Hz.
[b]Recorded in DMSO-d_6.
[c]Recorded in Pyridine-d_5.
[d]^{31}P Chemical shifts were expressed in δ, from 85% H_3PO_4 as external standard.

TABLE 3 ^{13}C NMR Spectral Data of **4**[a,b]

Carbons	*4a*	*4b*	*4d*	*4e*	*4h*	*4i*
C-1, C-11	129.5	129.5	130.0	130.0	129.4	—
C-2, C-10	130.6	130.4	130.2	131.2	131.9	132.3
C-3, C-9	123.8	123.8	123.9	123.9	123.8	123.8
C-4, C-8	135.8	136.1	136.8	136.2	136.7	136.2
C-4a, C-7a	149.9	150.0	150.2	150.2	150.2	149.9
C-11a, C-12a	135.3	135.5	135.8	135.8	135.8	135.9
C-12	32.0	32.0	31.9	31.4	32.3	29.8
C-1′	150.1	149.0	150.1	150.1	50.1 (4.4)	—
C-2′	120.6	129.5	121.4	129.0	42.2	122.6
C-3′	129.0	131.4	130.2	128.7		—
C-4′	125.9	125.9	133.9	126.2		125.8
C-5′	129.2	127.4	130.2	124.8		—
C-6′	120.6	119.8	121.4	122.2		122.6
C-CH_3		16.4 (2″-CH_3)	20.5 (4″-CH_3)	15.3 (2″-CH_3) 20.4 (5″-CH_3		

[a]Data in parentheses are coupling constants: $J_{P\text{-}C}$ in Hz.
[b]**4c**, **4f**, **4g**, **4j**, and **4k** gave unresolved spectra due to poor solubility.

EXPERIMENTAL

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. IR spectra were recorded as KBr pellets on a Perkin-Elmer 283 double beam spectrophotometer. The ^{1}H and ^{13}C NMR spectra were taken on a Varian Gemini 600 MHz spectrometer, and ^{31}P NMR spectra were recorded on a Brucker 400 MHz spectrometer. All spectra were recorded using DMSO-d_6 or pyridine-d_5 with TMS as the reference for ^{1}H and ^{13}C and 85% H_3PO_4 for ^{31}P NMR. Mass spectra (EI) were recorded on a Auto Spec Q instrument using solid probe at 70 eV.

Aryl phosphorodichloridates (**3a–g**) were prepared by following the reported procedure [21,22].

Bis(2-chloroethyl)phosphoramidic dichloride (**3h**) was prepared according to the literature procedure [23].

5,5′-Dichloro-3,3′-dinitro-2,2′-dihydroxydiphenylmethane (**2**)

7 mL (0.1 mole) of 70% nitric acid was added over a period of 15–20 minutes to a stirred solution of 5,5′-dichloro-2,2′-dihydroxydiphenylmethane (**1**, 13.45 g, 0.05 mol) in acetic acid (125 mL) at 14–15°C. After the addition, the reaction was allowed to continue at room temperature for 2–3 hours. After completion of the reaction, the solid obtained was filtered off, washed with water, dried, and recrystallized from ethyl acetate to yield 13.2 g (73.5%) of **2**, m.p. 202–

TABLE 4 Mass Spectral Data (% of important ions) of **4**

Compound[a]	*m*/z (Relative Abundance)
4a	500 [11.1, ($M^{+\cdot}$ + 4)], 498 [62.0, ($M^{+\cdot}$ + 2)], 496 [83.6, ($M^{+\cdot}$)], 479 [100, ($M^{+\cdot}$ − OH)], 432 [7.2, ($M^{+\cdot}$ − OH)-HNO_2], 402 [14.8, ($M^{+\cdot}$ − C_6H_5OH)], 367 [15.4, ($M^{+\cdot}$ − C_6H_5OH)-Cl], 339 (14.8), 323 (15.7), 305 (35.2), 295 (40.7), 279 (8.1), 264 (11.1), 249 (11.8), 236 (16.7), 207 (21.3), 189 (11.0), 173 (53.4), 139 (37.2), 126 (11.5), 111 (14.4), 94 (53.5), 77 (84.6)
4b	514 [13.1, ($M^{+\cdot}$ + 4)], 512 [70.5, ($M^{+\cdot}$ + 2)], 510 [100, (M^{+})], 493 (60.0), 446 (6.2). 416 (11.1), 381 (9.8), 340 (8.9), 323 (19.0), 305 (19.3), 295 (35.0), 279 (8.5), 264 (10.5), 236 (14.4), 207 (16.7), 199 (32.1), 186 (13.4), 173 (42.3), 139 (27.9), 108 (47.5), 91 (62.6), 77 (57.3).
4d	514 [15.7, ($M^{+\cdot}$ + 4)], 512 [76.0, ($M^{+\cdot}$ + 2)], 510 [100, ($M^{+\cdot}$)], 493 (52.5), 448 (9.5), 416 (10.8), 381 (9.8), 340 (8.5), 323 (26.2), 305 (30.0), 295 (43.2), 279 (11.1), 264 (9.8), 236 (13.8), 207 (16.4), 186 (11.4), 173 (43.6), 139 (29.1), 108 (72.1), 91 (57.3), 77 (59.0).
4e	524 [2.6, ($M^{+\cdot}$)], 493 (1.0), 368 (2.6), 314 (3.9), 236 (5.2), 207 (4.9), 122 (100), 107 (80.2), 91 (28.9), 77 (31.9)
4g	536 [0.7, ($M^{+\cdot}$ +6)], 534 [6.6, ($M^{+\cdot}$ + 4)], 532 [20.0, ($M^{+\cdot}$ + 2)], 530 [20.4, ($M^{+\cdot}$)], 513 (13.1), 448 (5.9), 358 (100), 340 (54.2), 323 (50.7), 305 (75.0), 295 (96.3), 279 (17.7), 264 (17.4), 249 (23.0), 221 (11.1), 207 (32.9), 186 (30.9), 173 (98.0), 139 (82.2), 126 (44.0), 111 (35.5), 99 (37.5), 75 (65.1).
4h	543 [6.0, ($M^{+\cdot}$), 494 (100), 432 (46.8), 402 (6.0), 372 (7.5), 322 (15.0), 295 (25.0), 249 (15.6), 186 (15.6), 173 (31.2), 139 (25.0), 111 (9.3).
4i	516 [3.6, ($M^{+\cdot}$ + 4)], 514 [17.0, ($M^{+\cdot}$ + 2)], 512 [23.6, ($M^{+\cdot}$)], 495 (100), 467 (7.2), 403 (5.2), 340 (7.2), 325 (27.5), 295 (18.7), 279 (20.7), 264 (12.4), 236 (14.4), 207 (35.0), 187 (31.3), 173 (65.7), 139 (50.0), 99 (23.9), 75 (36.6).
4l	528 [3.3, ($M^{+\cdot}$)], 511 (22.0), 419 (5.6), 340 (9.5), 323 (9.2), 305 (8.6), 295 (10.5), 264 (6.9), 249 (5.6), 236 (6.9), 207 (10.5), 187 (16.4), 173 (24.0), 141 (100), 125 (30.2), 109 (80.9), 77 (21.7).

[a]**4c**, **4f**, **4j**, and **4k** were not recorded.

204°C. Anal. Calcd. for $C_{13}H_8C_{12}N_2O_6$ (359.122): C, 43.48, H, 2.24; N, 7.80. Found: C, 43.25; H, 2.20; N, 7.85. IR (KBr): 1532, 1341 (Ar-NO_2), 3437 (Ar-OH) cm^{-1}. ^1H NMR ($CDCl_3$): δ 11.00 (s, 2H, 2-OH, 2′-OH), 8.06 (d, J = 2.3 Hz, 2H, 4-H, 4′-H), 7.58 (d, J = 2.4 Hz, 2H, 6-H, 6′-H), 4.15 (s, 2H, 12-H). ^{13}C NMR (Pyridine-d_5): δ 122.9 (s, 2C, C-1, C-1′), 152.7 (s, 2C, C-2, C-2′), 137.1 (s, 2C, C-3, C-3′), 123.8 (s, 2C, C-4, C-4′), 133.6 (s, 2C, C-5, C-5′), 135.8 (s, 2C, C-6, C-6′) 31.6 (s, 1C, C-12). MS (70 eV) *m/z* (%): 362 [10.1, ($M^{+\cdot}$ + 4)], 360 [62.0, ($M^{+\cdot}$ + 2)], 358 [100, ($M^{+\cdot}$)], 340 [5.2, ($M^{+\cdot}$-H_2O)], 323 [40.5, ($M^{+\cdot}$-Cl)], 305 [62.7, ($M^{+\cdot}$-Cl)-H_2O], 295 [77.1, ($M^{+\cdot}$-NO_2&OH)], 279 [15.0, ($M^{+\cdot}$-NO_2&OH)-O], 249 (15.7), 236 (16.9), 207 (23.5), 186 (23.5), 173 (60.1), 139 (61.4), 126 (16.0), 111 (20.2).

2,10-Dichloro-6-phenoxy-4,8-dinitro-12H-dibenzo[d,g][1,3,2]dioxaphosphocin 6-oxide **(4a)**

A solution of phenyl phosphorodichloridate (**3a,** 2.11 g, 0.01 mol) in 25 mL of dry toluene was added dropwise over a period of 15 minutes to a stirred solution of **2** (3.59 g, 0.01 mol) and triethylamine (2.02 g, 0.02 mol) in 60 mL of dry toluene. After the addition, the temperature of the reaction mixture was allowed to rise slowly to 55–60°C, and stirring was continued for an additional 6 hours. Progress of the reaction was monitored by TLC analysis. The reaction mixture was filtered to remove triethylamine hydrochloride, and the solvent was evaporated from the filtrate under reduced pressure. The residue, after washing with water, was purified by flash chromatography on silica gel using hexane-ethyl acetate (9:1) as eluent to yield 2.49 g (50%) of **4a**, m.p. 252–254°C. Physical and spectral data of **4a–h** are provided in Tables 1–4. Compounds **4b–h** were synthesized by adopting the same procedure.

2,10-Dichloro-6-phenoxy-4,8-dinitro-12H-dibenzo[d,g][1,3,2]dioxaphosphocin 6-sulfide **(4i)**

To a stirred solution of **2** (3.59 g, 0.01 mol) and triethylamine (2.02 g, 0.02 mol) in dry toluene (60 mL) at 0–5°C was added dropwise thiophosphoryl chloride (1.70 g, 0.01 mol) in dry toluene (25 mL) over a period of 15 minutes. After the temperature rose to 50–55°C, the reaction mixture was stirred for 3 hours. TLC analysis was used to monitor the formation of **5**. To the same reaction mixture in the same vessel was added dropwise a solution of phenol (0.94 g, 0.01 mol) and triethylamine (1.01 g, 0.01 mol) in dry toluene (25 mL). The temperature of this mixture was brought to 55–65°C, and the mixture was stirred for another 4 hours. Separation of triethylamine hydrochloride by filtration left a solution, which upon evaporation afforded a solid residue. After it had been washed with water, it was purified by flash chromatography on silica gel, using hexane-ethyl acetate (8:2) as eluent to give 2.17 g (42%) of

TABLE 5 Antimicrobial Activity of **4**

	Zone of Inhibition (mm)							
	Fungi				*Bacteria*			
	Curvularia lunata		*Aspergillus niger*		*Bacillus subtilis*		*Escherichia coli*	
Compound	*250 ppm*	*500 ppm*	*250 ppm*	*500 ppm*	*250 ppm*	*500 ppm*	*250 ppm*	*500 ppm*
4a	12	20	10	17	11	19	14	22
4b	11	18	11	20	10	18	11	21
4c	10	18	9	16	13	26	9	16
4d	7	12	11	19	9	17	11	19
4e	8	14	14	22	7	12	11	18
4f	11	19	16	30	10	18	13	22
4g	12	19	14	26	12	19	12	20
4h	16	30	12	19	14	25	16	27
4i	15	28	17	31	15	27	17	30
4j	17	31	19	34	16	28	18	28
4k	16	30	16	30	14	26	15	26
4l	15	27	16	26	12	22	13	22
Penicillin					24		20	
Tetracycline					32		28	
Griseofulvin	34		34					

4i, m.p. 270–272°C. Compounds **4i–l** were synthesized by adopting the same procedure.

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