A Facile Synthesis and Spectral (IR, ^1H, ^{13}C, ^{31}P NMR) Studies of 2,10-Dichloro-6-aryloxy-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-Sulfides

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Received September 15, 1994
Revised April 25, 1995

The synthesis of new 2,10-dichloro-6-aryloxy-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-sulfides **4** was achieved in two steps with high yields from the simple materials 5,5'-dichloro-2,2'-dihydroxydiphenylmethane (**1**) and thiophosphoryl chloride (**2**) which produced the key intermediate 2,6,10-trichloro-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-sulfide (**3**). Treatment of **3** with substituted phenols under phase transfer catalytic (PTC) conditions led to members of **4**. Long range coupling [$^5J_{(P,H)}$ = 3.6 Hz] was observed between phosphorus and one of the bridged methylene protons in **4**. A ^{13}C nmr analysis revealed $^2J_{(P,O,C)}$, $^3J_{(P,O,C)}$, $^4J_{(P,O,C)}$ and $^5J_{(P,O,C)}$ couplings. All ^{31}P nmr chemical shifts for thirteen members of these new heterocycles are reported for the first time. The nmr data are not totally definitive to confirm a boat-chair as the major conformer for the central eight-membered dioxaphosphocin ring, but such a conformer is tentatively suggested as favored.

J. Heterocyclic Chem., **32**, 1483 (1995).

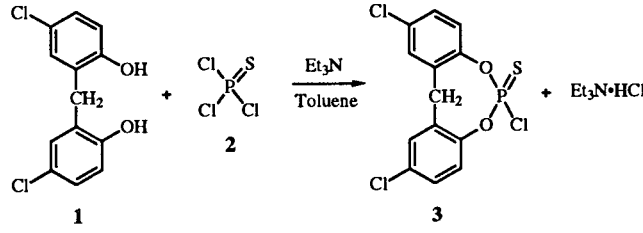
Introduction.

Our previous experience in the synthesis of 6-substituted-dibenzodioxaphosphocin 6-oxides/sulfides by conventional methods [1] revealed that the overall yield of the final products was often modest. Furthermore, the introduction of substituted phenol moieties with bulky substituents was not successful since the preparation and purification of the corresponding phosphorodichloridates [2] was found to be difficult since the compounds were moisture and thermal sensitive and sometimes explosive in nature. An alternative approach involving a two-step process has now been developed to overcome these difficulties. First, the precursor 2,6,10-trichloro-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-sulfide (**3**) was prepared in standard fashion from 5,5'-dichloro-2,2'-dihydroxydiphenylmethane (**1**) and thiophosphoryl chloride (**2**). In the second step, **3** was reacted with various substituted phenols under phase transfer catalytic (PTC) condition. We report herein the preparation of thirteen members of the title compounds **4**. The interest in the synthesis of these compounds arises from the possibility of their application as pesticides and additives to certain polymers and oils [3-5].

Results and Discussion.

2,6,10-Trichloro-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-sulfide (**3**) was prepared by reacting 5,5'-dichloro-2,2'-dihydroxydiphenylmethane (**1**) with thiophosphoryl chloride (**2**) in the presence of triethylamine in

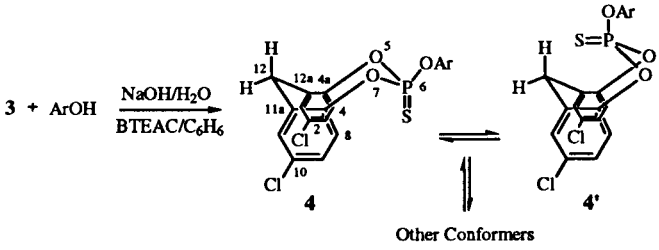
Scheme I



dry toluene at 60° (Scheme I). The intermediate monochloride **3** was isolated, purified and characterized by elemental analysis, ir, ^1H, ^{13}C and ^{31}P nmr spectral data. In the second step, **3** was treated with various substituted phenols under phase transfer catalytic condition in benzene. Benzyltriethylammonium chloride (BTEAC) in 40% sodium hydroxide solution was used as the phase transfer catalytic system (Scheme II).

This method was found to offer advantages over the previously reported technology [1,2] in that (a) the yields (55-88%) of the final products were high, (b) the reactions occurred at room temperature, (c) the process required only a simple experimental set up, (d) dry conditions are not required and (e) the handling of corrosive starting reagents like phosphorodichloridates and the liberated hydrogen chloride during the reaction was avoided. Members of **4** are soluble in chloroform, carbon tetrachloride and benzene and insoluble in alcohols. The physical, ir and ^{31}P nmr spectral data of **4a-4m** are given in Table 1. All members of **4** exhibited characteristic ir absorptions

Scheme II



Compound	Ar	Compound	Ar
4a	2-Cl-C_6H_4	**4h**	2,4,6-$(NO_2)_3$-C_6H_2
4b	2,4-Cl_2-C_6H_3	**4i**	4-Br-C_6H_4
4c	2,4,6-Cl_3-C_6H_2	**4j**	2,4,6-$(Br)_3$-C_6H_2
4d	2,3,4,6-Cl_4-C_6H	**4k**	3-CH_3-C_6H_4
4e	4-NO_2-C_6H_4	**4l**	2,4-$(CH_3)_2$-C_6H_3
4f	2-NO_2-C_6H_4	**4m**	4-$(CH_3)_3C$-C_6H_4
4g	2,4-$(NO_2)_2$-C_6H_3		

for ν P = S and ν P-O-$C_{(Ar)}$ groups [6,7] as shown in Table 1.

Table 2 contains the ^1H nmr chemical shifts for **4**. The six aromatic protons of the dibenzodioxaphosphocin group showed only three separate signals (2H each) because of the symmetrical nature of the substituted benzene rings [8]. The signals due to the aromatic protons of dibenzodioxaphosphocin moiety are distinguished from that of the phenoxy moieties based on the chemical shift values of the intermediate **3**. A doublet at δ 7.24-7.38 (J = 2.0-2.5 Hz) was assigned to H-1 and H-11. The doublet of doublet at δ 7.10-7.25 (J = 7.6-8.7 and 1.9-2.6 Hz) was attributed to H-3 and H-9. Another doublet at δ 6.94-7.10 (J = 7.6-8.8 Hz) was ascribed to H-4 and H-8. The bridged methylene protons (H-12) in **4a-4m** resonated as a doublet in the region δ 3.44-3.79 (J = 12.4-13.7 Hz) and doublet of doublet in the region δ 4.05-4.42 (J = 12.8-14.0 and 3.3-4.0 Hz). The coupling constant J = 12.8-14.0 Hz can be rationalized as geminal coupling ($^2J_{H-H}$) between the bridged methylene protons. The smaller coupling constant (J = 3.3-4.0 Hz) can be attributed to the long range coupling of one of the methylene protons ($^5J_{H-P}$) with phosphorus, based on the signal patterns of dioxaphosphocins [9]. Data were confirmed by decoupling experiments.

Space-filling models imply that a rigid, boat-boat (BB) conformation **4'** is possible but a boat-chair (BC) **4** may be more likely for the eight-membered dibenzodioxaphos-

Table 1

Physical IR and ^{31}P NMR Spectral Data of 2,10-Dichloro-6-aryloxy-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-Sulfides **4**

Compound	Yield [a] (%)	Mp (°C)	C & H Analysis Found, (Calcd.) C	H	Molecular formula	IR data (cm^{-1}) ν P=S	ν P-O-$C_{(ar)}$	^{31}P NMR Data [b] ppm
4a	73	125-126	50.00 (49.86)	2.60 (2.64)	$C_{19}H_{12}Cl_3O_3PS$	735	1210, 930	+53.4
4b	85	133-134	45.42 (45.54)	2.36 (2.41)	$C_{19}H_{11}Cl_4O_3PS{\cdot}0.5H_2O$	740	1215, 935	+53.3
4c	88	119-120	42.36 (42.61)	2.12 (2.07)	$C_{19}H_{10}Cl_5O_3PS{\cdot}0.5H_2O$	750	1215, 935	+54.4
4d	69	84-85	39.24 (40.03)	1.94 (1.77)	$C_{19}H_9Cl_6O_3PS{\cdot}0.5H_2O$	740	1215, 940	+55.1
4e	77	206-207	47.67 (47.82)	2.97 (2.75)	$C_{19}H_{12}Cl_2NO_5PS{\cdot}0.5H_2O$	740	1215, 940	+52.6
4f	68	183-184	47.60 (47.82)	2.52 (2.75)	$C_{19}H_{12}Cl_2NO_5PS{\cdot}0.5H_2O$	745	1210, 930	+52.6
4g	58	161-163	43.50 (43.70)	2.01 (2.32)	$C_{19}H_{11}Cl_2N_2O_7PS{\cdot}0.5H_2O$	750	1210, 935	+52.3
4h	55	165-167	40.30 (40.23)	1.56 (1.95)	$C_{19}H_{10}Cl_2N_3O_9PS{\cdot}0.5H_2O$	735	1205, 940	[c]
4i	70	180-181	45.95 (45.45)	2.15 (2.41)	$C_{19}H_{12}BrCl_2O_3PS$	740	1210, 930	+53.7
4j	68	215-216	35.06 (34.58)	1.40 (1.53)	$C_{19}H_{10}Br_3Cl_2O_3PS$	750	1210, 935	+53.5
4k	70	136-138	54.60 (54.94)	3.15 (3.46)	$C_{20}H_{15}Cl_2O_3PS$	745	1205, 935	+54.2
4l	69	144-145	55.50 (55.89)	3.80 (3.80)	$C_{21}H_{17}Cl_2O_3PS$	750	1210, 930	+53.9
4m	72	167-169	57.98 (57.63)	4.28 (4.42)	$C_{23}H_{21}Cl_2O_3PS$	740	1215, 935	+52.3

[a] Recrystallized from benzene-hexane (2:1), reported yields are after one recrystallization. [b] Chemical shifts in ppm from 85% phosphoric acid, positive values indicate downfield from phosphoric acid. [c] ^{31}P nmr spectrum not recorded for **4h**.

Table 2

^{1}H NMR Chemical Shift (Multiplicity, J in Hz) Data [a] of 2,10-Dichloro-6-aryloxy-12*H*-dibenzo[*d*,*g*][1,3,2]dioxaphosphocin 6-Sulfides **4**

Compound	-CH_2-	H (1,11)	H (3,9)	H (4,8)	H (Ar)
4a	4.33 (dd, 13.6, 3.7) 3.66 (d, 13.5)	7.31 (d, 2.0)	7.23	7.03 (d, 8.6)	7.05-7.19 (m, 6'H) 7.49-7.60 (m, 3', 4', 5'H)
4b	4.30 (dd, 13.5, 3.5) 3.60 (d, 13.7)	7.32 (d, 2.3)	7.25 (d, 8.0)	6.99	7.03-7.18 (m, 5', 6'H) 7.36 (s, 3'H)
4c	4.35 (dd, 13.5, 3.7) 3.68 (d, 13.6)	7.32 (d, 2.3)	7.25	7.06 (d, 8.8)	7.36-7.52 (m, 3', 5'H)
4d	4.35 (dd, 13.6, 3.7) 3.69 (d, 13.4)	7.30 (d, 2.3)	7.23 (dd, 8.7, 2.5)	7.06 (d, 8.4)	7.60 (s, 5'H)
4e	4.35 (dd, 13.3, 3.8) 3.64 (d, 13.5)	7.31 (d, 2.4)	7.23 (dd, 7.8, 2.0)	7.00 (d, 7.6)	7.56 (d, 8.7, 2', 6'H) 7.35 (d, 9.1, 3', 5'H)
4f	4.33 (dd, 13.6, 3.8) 3.65 (d, 13.6)	7.38 (d, 2.4)	7.21 (dd, 8.6, 1.9)	7.03 (d, 8.5)	7.26 (s, 6'H), 7.36 (s, 4'H) 7.69 (d, 7.7, 5'H), 8.07 (d, 8.2, 3'H)
4g	4.32 (dd, 13.6, 4.0) 3.67 (d, 13.6)	7.34 (d, 2.2)	7.22 (dd, 7.9, 2.2)	6.97 (d, 8.3)	7.90 (d, 8.6, 6'H), 8.55 (dd, 2.2, 8.4, 5'H), 8.94 (d, 2.6, 3'H)
4h	4.05 (dd, 14.0, 3.4) 3.79 (d, 12.4)	7.31 (d, 2.2)	7.20 (dd, 8.3, 2.2)	7.02 (d, 8.4)	8.98 (s, 3', 5'H)
4i	4.34 (dd, 13.6, 4.0) 3.67 (d, 13.6)	7.31 (d, 2.2)	7.19 (dd, 7.9, 2.2)	6.94 (d, 8.3)	7.47 (dd, 8.0, 2.2, 2', 6'H) 7.56 (dd, 7.8, 2.0, 3', 5'H)
4j	4.37 (dd, 13.6, 3.8) 3.68 (d, 13.6)	7.33 (d, 2.5)	7.21 (dd, 8.5, 2.5)	7.10 (d, 8.3)	7.99 (s, 3', 5'H)
4k	4.34 (dd, 13.4, 3.7) 3.60 (d, 13.2)	7.31 (d, 2.2)	7.19 (dd, 7.9, 2.6)	6.96 (d, 8.3)	7.16-7.32 (m, 2', 4', 5', 6'H) 2.39 (s, 3H, 3'-CH_3)
4l	4.40 (dd, 13.4, 3.7) 3.64 (d, 12.7)	7.34 (d, 2.2)	7.25 (dd, 7.6, 2.2)	7.04 (d, 8.8)	7.12-7.32 (m, 3', 5', 6'H) 2.10 (s, 3H, 2'-CH_3), 2.38 (s, 3H, 4'-CH_3)
4m	4.42 (dd, 12.8, 3.3) 3.44 (d, 12.7)	7.24 (d, 2.3)	7.10 (dd, 8.3, 2.1)	6.94 (d, 7.9)	7.26 (s, 2', 6'H) 6.94 (s, 3', 5'H) 1.30 (s, 9H, 4'-$C(CH_3)_3$)

[a] Chemical shifts in δ and J (Hz) given in parentheses.

phocin ring as illustrated in Scheme II [10]. Undoubtedly, an equilibrium exists between several forms in solution [10]. Through space shielding, long range $^5J_{P-H}$ coupling of phosphorus and H-12 over five bonds is rare although not unknown [8,9]. Most of the proton signals in the phenoxy moiety of **4a-4m** are quite distinguishable (Table 2).

The ^{13}C chemical shifts are given in Tables 3 and 4. The interpretation of the data was based on additivity rules, C-P couplings, intensity of signals, SFORD spectra and chemical shifts of **3**. A low intensity doublet at 146.1-146.7 ppm [$^2J_{(P,O,C-4a,7a)}$ = 6.3-7.2 Hz] was assigned to C-4a and C-7a respectively [11], which bear oxygen atoms. A doublet at 124.3-124.7 ppm [$^3J_{(P,O,C,C-4,8)}$ = 4.9-5.2 Hz] was attributed to C-4 and C-8, respectively [12]. Both carbons C-11a and C-12a gave signals at 133.4-133.8 ppm [$^3J_{(P,O,C,C-11a,12a)}$ = 4.3-4.5 Hz] [12]. Chlorine bearing carbons C-2 and C-10 resonated as a doublet [13] at 131.7-132.4 ppm (^5J = ~3 Hz). Carbons C-3 and C-9 gave signals at 128.7-129.1 ppm. These carbons also coupled [13] to phosphorus [$^4J_{(P,O,C-3,9)}$ = ~2 Hz] in a few members of **4**. A doublet [$^4J_{(P,O,C-1,11)}$ = ~2 Hz] in the region 130.1-130.4 ppm was attributed to C-1 and C-11. The bridged methylene carbon C-12 showed a resonace in the range of 33.0-33.2 ppm. It is worthy of mention that C-12 in **4f** resonated as a doublet [$^4J_{(P,O,C-12)}$ = 1.7 Hz]. It was also interesting that a C-12 resonance was observed at 35.8 ppm in a somewhat related pentavalent phosphorus containing system [14]. No long range $^4J_{(P,C)}$ coupling was reported in that system [14], however, although a $^5J_{(P,H)}$ coupling was noted. The increased shielding of C-12 in our systems may well be the result of through space interaction with the P=S group [10].

The ^{13}C nmr chemical shifts of the phenoxy carbons are presented in Table 4. A low intensity doublet [$^2J_{(P,O,C-1')}$ = 6.2-7.6 Hz] in the region 143.4-149.4 ppm was assigned to C-1' which was attached to an oxygen atom [11]. However, in **4e**, the C-1' resonated at 154.7 ppm due to the presence of a nitro group at the *para* position. Interestingly, C-2' coupled to phosphorus [$^3J_{(P,O,C)}$ = 2.8-5.0 Hz] and resonated in the region of 118.5-131.0 ppm due to the presence of substituents on this carbon. In **4j**, the resonance signal (118.5 ppm) for C-2' was shielded considerably and the C-4' resonance signal for **4i** and **4j** was upfield at 119.3 and 119.7 ppm respectively. The rea-

Table 3

^{13}C NMR Chemical Shift (Multiplicity, J in Hz) Data [a] of 2,10-Dichloro-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-Sulfides **4**

Compound	C (1,11)	C (2,10)	C (3,9)	C (4,8)	C (4a,7a)	C (11a,12a)	C (12)
4a	130.2	131.8 (d, 3.1)	128.8	124.6 (d, 5.1)	146.6 (d, 7.2)	133.7 (d, 4.4)	33.1
4b	130.2	131.9 (d, 3.1)	128.8	124.5 (d, 4.9)	146.3 (d, 6.9)	133.7 (d, 4.3)	33.1
4c	130.2	131.9	128.9	124.4 (d, 5.1)	146.7 (d, 6.9)	133.5 (d, 4.4)	33.2
4d	130.3 (d, 2.1)	132.0 (d, 3.1)	128.9 (d, 2.2)	124.3 (d, 5.2)	146.6 (d, 7.0)	133.5 (d, 4.5)	33.2
4e	130.3	132.0 (d, 3.0)	128.9	124.4 (d, 4.9)	146.3 (d, 7.0)	133.6	33.0
4f	130.3 (d, 2.2)	132.2 (d, 3.2)	129.0 (d, 2.1)	124.4 (d, 5.2)	146.3 (d, 7.0)	133.7 (d, 4.5)	33.1 (d, 1.7)
4g	130.4	132.4 (d, 3.1)	129.1	124.3 (d, 5.2)	146.1 (d, 7.2)	133.4 (d, 4.4)	33.1
4i	130.2	131.9 (d, 3.0)	128.8	124.5 (d, 5.2)	146.4 (d, 6.9)	133.7 (d, 4.4)	33.1
4j	130.3 (d, 1.7)	131.9 (d, 3.2)	128.9 (d, 2.0)	124.4 (d, 5.1)	146.7 (d, 7.0)	133.6 (d, 4.4)	33.2
4k	130.3 (d, 1.5)	131.7 (d, 3.0)	128.7 (d, 2.1)	124.6 (d, 5.1)	146.7 (d, 7.0)	133.8 (d, 4.4)	33.1
4l	130.1 (d, 1.9)	131.7 (d, 3.0)	128.7 (d, 2.1)	124.7 (d, 5.0)	146.7 (d, 6.3)	133.8 (d, 4.3)	33.1

[a] Chemical shifts in ppm and J (Hz) given in parentheses. ^{13}C nmr spectra not recorded for compounds **4h** and **4m**.

son for the shielding is due to the substituent effect of bromine atom. A signal for C-4' was far downfield in **4e** and **4g** in the region of 144.8-145.6 ppm due to the presence of a nitro group on this carbon. A downfield signal at 133.7 ppm was ascribed to C-5' in **4f**, and this was likely due to the presence of a nitro group *para* to it. In **4j**, C-3' and C-5' resonated downfield at 135.4 ppm due to the presence of bromine on either side of these carbons. The C-6' resonated as a doublet [$^3J_{(P,O,C)}$ = 3.0-5.0 Hz] in the region of 118.50-128.30 ppm depending on the particular substituent effect. In **4k**, the 3'-CH_3 resonated at 20.8 ppm while in **4l** the methyls gave signals for 2'-CH_3 at 16.7 ppm and for 4'-CH_3 at 20.8 ppm. The upfield shift of about 4 ppm by 2'-CH_3 is attributed to γ-interaction with the exocyclic oxygen atom [11]. All dibenzodioxaphosphocin 6-sulfides **4a-4m** exhibited ^{31}P chemical shifts in the region +52.3 to +55.1 ppm (Table 1).

Table 4

^{13}C NMR Chemical Shift (Multiplicity, J in Hz), Data [a] of the 6-Aryloxy Groups in **4**

Compound	C (1')	C (2')	C (3')	C (4')	C (5')	C (6')
4a	146.6 (d, 7.2)	131.0	128.8	126.9	127.9	122.4 (d, 3.3)
4b	147.5 (d, 6.2)	124.4	128.3	129.9	128.2	122.2
4c	143.4	124.5 (d, 4.6)	129.0	129.7	129.0	124.5 (d, 4.6)
4d	144.2	128.8 (d, 2.8)	132.3	129.5	129.0	128.3
4e	154.7 (d, 7.2)	121.9 (d, 4.6)	125.7	145.6	125.7	121.9 (d, 4.6)
4f	154.5	128.3	128.8	125.8	133.7	122.0 (d, 5.0)
4g	147.3	128.9	122.0	144.8	128.9	124.9 (d, 3.7)
4i	149.4	123.0 (d, 4.6)	132.9	119.3	132.9	123.0 (d, 4.6)
4j	146.7	118.5 (d, 5.0)	135.4	119.7	135.4	118.5 (d, 5.0)
4k [b]	148.1 (d, 6.5)	123.4	135.8	125.2	130.1	120.8
4l [c]	147.1 (d, 7.6)	124.7 (d, 5.0)	129.9	129.8	127.5	120.4 (d, 3.0)

[a] Chemical shifts in ppm and J (Hz) given in parentheses. [b] C(3')-CH_3 = 20.8 ppm. [c] C(2')-CH_3 = 16.7 ppm, C(4')-CH_3 = 20.8 ppm. ^{13}C nmr spectra not recorded for compounds **4h** and **4m**.

Unfortunately, it was not possible to grow a suitable crystal of any member of **4** for X-ray diffraction analysis to determine the conformer in the solid state. Spectral data alone are not adequate to conclusively confirm or deny the existence of a major conformer. Large groups at the 4- and 8-positions of related systems are reported to favor a **BB** conformer [10,15]. Such substituents are not present in **4**, and thus we tentatively conclude a **BC** form exists as the major conformer.

In conclusion, a facile synthesis of new 2,10-dichloro-6-aryloxy-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-sulfides was accomplished with high yields by adopting phase transfer catalytic conditions in the final step. These new phosphorus heterocycles have potential value as insecticides and additives to lubricants.

EXPERIMENTAL

Melting points were determined in open capillary tubes on a Mel-temp apparatus and were uncorrected. Microanalyses were performed by the Central Drug Research Institute, Lucknow, India. The ir spectra were recorded as potassium bromide pellets on a Perkin-Elmer 137 spectrophotometer. All ^1H nmr spectra were recorded on a Jeol FX 90 MHz instrument. Certain nmr spectra were obtained in the Fourier Transform mode on samples contained in 10 mm tubes (^{13}C) or 5 mm tubes (^{31}P, and ^1H) on a Varian XL-300 nmr spectrometer with data acquisition at 75.43 MHz (^{13}C) and 121.48 MHz (^{31}P). All the spectra were recorded for solutions [30% (w/v) for ^{31}P and ^1H and 60-70 mg in 1 ml for ^{13}C] at 25° using deuteriochloroform with tetramethyl silane as the reference for ^1H and ^{13}C spectra and 85% phosphoric acid for the ^{31}P spectra. All downfield shifts are on the δ or ppm scale from the standard and are labelled as positive. For ^{13}C nmr spectra, typical parameters were SW = 15085.9 Hz, PW = 17.7 μs (90°), acquisition time = 1 second, and spectral window = 20,000 Hz.

2,6,10-Trichloro-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-Sulfide (**3**).

A solution of 1.69 g (0.01 mole) of thiophosphoryl chloride (**2**) in 20 ml of dry toluene was added dropwise to a cold (0°) and stirred solution of 2.69 g (0.01 mole) of 5,5'-dichloro-2,2'-dihydroxydiphenylmethane (**1**) and 2.02 g (0.02 mole) of triethylamine in 40 ml of dry toluene. After the addition, the reaction mixture was stirred at room temperature for 2 hours, and then stirred at 50-60° for another 3 hours. Progress of the reaction was monitored by thin layer chromatography. Triethylamine hydrochloride was filtered off, and the solvent was evaporated. The residue was washed with petroleum ether (60-70°) and recrystallization from benzene-hexane mixture (2:1) afforded 1.78 g (49%) of **3**, mp 119-120°; ir (potassium bromide): ν 1220 (P-O-C_{ar}), 940 (P-O-C_{ar}), 740 (P=S) cm^{-1}; pmr (deuteriochloroform): δ 7.05 (dd, J = 8.3, 2.6 Hz, 2H, 4 & 8-H), 7.23 (dd, J = 6.1, 2.5 Hz, 2H, 3 & 9-H), 7.31 (d, J = 2.6 Hz, 2H, 1 & 11-H), 4.02 (dd, J = 11.0, 3.1 Hz, 1H, 12-H), 3.80 (d, J = 12.0 Hz, 1H, 12-H); ^{13}C nmr (deuteriochloroform): 147.2 (d, J = 7.9 Hz, 2C, C-4a & 7a), 133.2 (d, J = 4.8 Hz, 2C, C-11a & 12a), 132.3 (d, J = 3.5 Hz, 2C, C-2 & 10), 130.4 (s, 2C, C-1 & 11), 128.9 (s, 2C, C-3 & 9), 124.3 (d, J = 5.7 Hz, 2C, C-4 & 8), 33.2 (s, 1C, C-12) ppm; ^{31}P nmr (deuteriochloroform): +60.8 ppm.

Anal. Calcd. for $C_{13}H_8Cl_3O_2PS$: C, 42.71; H, 2.21. Found: C, 42.45; H, 2.16.

2,10-Dichloro-6-(4-nitrophenoxy)-12*H*-dibenzo[*d,g*][1,3,2]-dioxaphosphocin 6-Sulfide (**4e**).

A solution of 1.83 g (0.005 mole) of 2,6,10-trichloro-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-sulfide (**3**) in 20 ml of benzene was added dropwise to a stirred mixture of 4-nitrophenol (0.69 g, 0.005 mole) in 20 ml of benzene, 20 ml of 40% aqueous sodium hydroxide solution, and 1 g of benzyltriethylammonium chloride (BTEAC). The temperature of the reaction mixture was slowly raised to 50-60° and stirred for another 3 hours. Then the reaction mixture was transferred into a separatory funnel, and the benzene layer was separated and washed with water until free from alkali. The solution was dried (magnesium sulfate anhydrous) and then the solvent was removed under reduced pressure to a solid. Recrystallization from hexane-benzene mixture (1:2) gave 1.85 g (77%) of **4e**, mp 206-207°. Spectral data of **4e** are given in Tables 1-4.

Anal. Calcd. for $C_{19}H_{12}Cl_2NO_5PS \cdot 0.5H_2O$: C, 47.82; H, 2.75. Found: C, 47.67; H, 2.97.

Other members of **4** were prepared by this procedure.

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