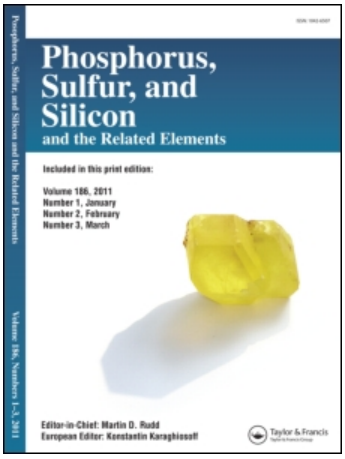

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SYNTHESIS OF 6-ARYLOXY- AND 6 *p*-TOLYLTHIOXY 2,10-DICHLORO-12-TRICHLOROMETHYL-12*H*-DIBENZO[*d,g*]-[1,3,2]DIOXAPHOSPHOCIN 6-OXIDES

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SYNTHESIS OF 6-ARYLOXY- AND 6-*p*-TOLYLTHIOXY-2,10-DICHLORO-12-TRICHLOROMETHYL-12*H*-DIBENZO[*d,g*]-[1,3,2]DIOXAPHOSPHOCIN 6-OXIDES—X-RAY DIFFRACTION ANALYSES OF 6-(4′-CHLOROPHENOXY)-2,10-DICHLORO-12-TRICHLOROMETHYL-12*H*-DIBENZO[*d,g*]-[1,3,2]DIOXAPHOSPHOCIN 6-OXIDE AND TRIETHYLAMMONIUM 2-METHYLPHENYL 2-[{2′,2′,2′-TRICHLORO-1′-(2″-HYDROXYL-5″-CHLOROPHENYL)}ETHYL]-4-CHLOROPHENYL PHOSPHATE

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Dedicated to Professor John G. Verkade on the occasion of his 60th birthday

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6-Aryloxy- and 6-*p*-tolylthioxy-2,10-dichloro-12-trichloromethyl-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-oxides were synthesized and characterized by IR, ^{1}H, ^{13}C, ^{31}P, and mass spectral analyses for the first time. The ^{1}H chemical shifts for H(12) at the carbon bridge occurred between δ 6.15 and 6.40 which suggested a common environment and one conformer, but the presence of more than one conformer in each example cannot be entirely eliminated. Obviously the trichloromethyl groups attached to C(12) induces a significant downfield shift of H(12). An X-ray diffraction analysis of solid 6-(4′-chlorophenoxy)-2,10-dichloro-12-trichloromethyl-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-oxide (**3j**) shows it is a boat-chair with the trichloromethyl group in a pseudo equatorial arrangement and with the phosphoryl group in a "down arrangement" of a boat-chair conformer. An interesting by-product, namely triethylammonium 2-methylphenyl 2-[{2′,2′,2′-trichloro-1′-(2″-hydroxyl-5″-chlorophenyl)}ethyl]-4-chlorophenyl phosphate (**5**), was isolated when attempts were made to purify a crude sample of **3b**. Thus, it appears that either the initial ring closure did not occur between **1** and **2b** or, in the purification process for **3b**, the ring was opened in the presence of residual triethylamine. System **5** was also confirmed by X-ray analysis.

Key words: 6-Aryloxy- and 6-*p*-tolylthioxy-2,10-dichloro-12-trichloromethyl-12*H*-dibenzo[*d,g*][1,3,2]-dioxaphosphocin 6-oxides, triethylammonium 2-methylphenyl 2-[{2′,2′2′-trichloro-1′-(2″-hydroxyl-5″-chlorophenyl}ethyl]-4-chlorophenyl phosphate, boat-chair conformer, NMR analysis, mass spectral analysis, conformational analysis, X-ray diffraction analysis.

INTRODUCTION

Dibenzodioxaphosphocin esters have considerable importance in the polymer and oil industries as stabilizers and antioxidants.[1-3] A facile synthesis was reported previously for the 6-alkoxy-, 6-alkylamino-, 6-alkyl-, and 6-aryloxy-derivatives of some 12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-oxides[4-6] and for a few 8-substituted-16*H*-dinaphtho[2,1-*d*: 1′,2′-*g*][1,3,2]-dioxaphosphocin 8-oxides.[7] A variable temperature study and X-ray diffraction analysis on one system suggested a tub-like conformer for the dibenzodioxaphosphocins[5] and a distorted and extended boat-like conformer for a dinaphthodioxaphosphocin system.[7] Herein we report the synthesis of dibenzodioxaphosphocin 6-oxides with the large, powerful electronegative trichloromethyl group at C(12) which we initially reasoned might well reduce the isomer population to one major conformer.

RESULTS AND DISCUSSION

Cyclization of 2,2-bis(2-hydroxy-5-chlorophenyl)-1,1,1-trichloroethane[8] (**1**) with aryl phosphorodichloridates[9] **2a–2k** was effective in dry toluene with triethylamine after 5 hours at 55–65°C to give **3**⇌**3′**, etc. We hasten to point out that for an equilibrium like **3**⇌**3′** to exist initially, it is likely that some catalytic impurities would have to be present. On the basis of spectral data to be discussed, we favor the presence of **3** as the major isomer and perhaps the only isomer in solution, although we cannot absolutely eliminate the presence of **3′** or other isomers. An alternative method involved treatment of **1** with phosphorus oxychloride/triethylamine in dry toluene at 40–50°C and led to 6-chloro-2,10-dichloro-12-trichloromethyl-12*H*-dibenzo[*d,g*]-[1,3,2]dioxaphosphocin 6-oxide (**4**). The latter was not purified but was used directly in a second condensation with a series of substituted phenols/thiophenols to yield members of **3**. This second method was advantageous in that it did not require the use of the corresponding and rather uncommon phosphorodichloridates which are often difficult to purify because of thermal decomposition during vacuum distillation. Isolation of members of **3** was simple and required filtration of the triethylamine hydrochloride followed by evaporation of the solvent to yield crude ester. Purification of these products was achieved by washing the solids with water followed by recrystallization from isopropyl alcohol. Certain physical data, along with IR and ^{31}P NMR data, are found in Table I. Tables II–V contain ^{1}H, ^{13}C, and mass spectral data for **3**. It was noted that **3j** was obtained by both routes which supports our hypothesis that **4** really has the P=O down in the major conformer and *not* as illustrated. We cannot rule out the presence of some **4** in the original reaction mixture, however. Ester **3j** was confirmed by X-ray analysis.

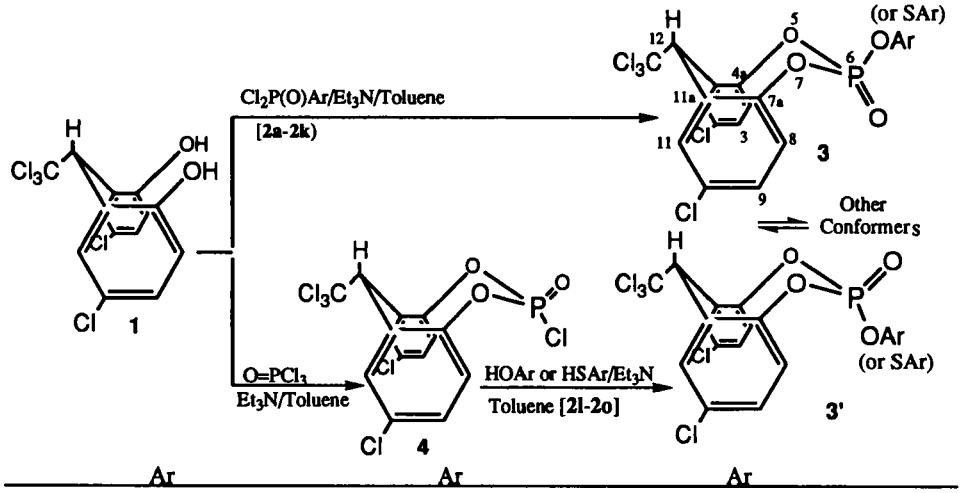
TABLE I

Physical data for **3a–3m**

Compd	Yield (%)	mp (°C)	MF	Found (Calcd %) C	H	IR (cm^{-1}) P=O	P-O-C(Ar) O-C	P-O	^{31}P NMR (ppm)
3a	65	204-05[a]	$C_{20}H_{12}Cl_5O_4P$	45.63 (45.80)	2.47 (2.31)	1290	1240	970	-17.55
3b	61	173-74[a]	$C_{21}H_{14}Cl_5O_4P$	46.68 (46.83)	2.74 (2.62)	1285	1235	960	-17.93
3c	59	188-89[a]	$C_{21}H_{14}Cl_5O_4P$	46.95 (46.83)	2.58 (2.62)	1280	1230	970	-18.26
3d	63	185-86[a]	$C_{21}H_{14}Cl_5O_4P$	46.73 (46.83)	2.48 (2.62)	1290	1230	980	-18.14
3e	57	181-82[a]	$C_{22}H_{16}Cl_5O_4P$	47.95 (47.82)	3.13 (2.92)	1270	1240	960	-18.57
3f	58	167-68[a]	$C_{22}H_{16}Cl_5O_4P$	47.76 (47.82)	2.84 (2.92)	1290	1230	980	-18.83
3g	55	202-03[a]	$C_{22}H_{16}Cl_5O_4P$	47.68 (47.82)	2.71 (2.92)	1300	1240	970	-18.76
3h	60	197-98[a]	$C_{22}H_{16}Cl_5O_4P$	47.93 (47.82)	2.97 (2.92)	1290	1230	970	-18.80
3i	53	180-81[a]	$C_{20}H_{11}Cl_6O_4P$	42.81 (42.97)	1.96 (1.98)	1290	1235	970	-16.85
3j	57	231-32[a]	$C_{20}H_{11}Cl_6O_4P$	42.76 (42.97)	1.83 (1.98)	1290	1240	980	-17.02
3k	45	230-31[b]	$C_{20}H_{11}Cl_5NO_6P$	42.04 (42.18)	1.72 (1.95)	1300	1240	980	-19.15
3l	59	233-34[b]	$C_{24}H_{20}Cl_5O_4P$	49.61 (49.64)	3.44 (3.47)	1290	1240	975	-18.34
3m	65	203-04[b]	$C_{21}H_{14}Cl_5O_3PS$	45.20 (45.48)	2.73 (2.54)	1270	1230	960	-20.15

[a]Recrystallized from 2-propanol.

[b]Recrystallized from chloroform-hexane.



a. PhO
b. 2'-H_3C-C_6H_4O
c. 3'-H_3C-C_6H_4O
d. 4'-H_3C-C_6H_4O
e. 2',3'-$(H_3C)_2C_6H_3O$
f. 2',4'-$(H_3C)_2C_6H_3O$
g. 2',6'-$(H_3C)_2C_6H_3O$
h. 3',5'-$(H_3C)_2C_6H_3O$
i. 2'-Cl-C_6H_4O
j. 4'-Cl-C_6H_4O
k. 4'-O_2N-C_6H_4O
l. 4'-$(H_3C)_3C$-C_6H_4O
m. 4'-H_3C-C_6H_4S

TABLE II

^{1}H NMR data for **3a–3m** (δ values; J in Hz)

Compd	H(12)	Ar-H	O-Ar-CH_3
3a[a]	6.36 (2.7)	7.20-8.38 (m, 11 H)	-
3b[a]	6.40 (3.5)	7.17-8.29 (m, 10 H)	2.15 (s, 3 H)
3c[a]	6.39 (3.0)	7.17-8.33 (m, 10 H)	2.37 (s, 3 H)
3d[b]	6.19 (1.6)	7.13-8.22 (m, 10 H)	2.37 (s, 3 H)
3e[b]	6.35 (1.8)	7.13-8.27 (m, 9 H)	2.08 (s, 3 H)
			2.18 (s, 3 H)
3f[a]	6.35 (2.5)	7.14-8.24 (m, 9 H)	2.16 (s, 3 H)
			2.18 (s, 3 H)
3g[b]	6.40 (2.3)	7.17-8.18 (m, 9 H)	2.17 (s, 6 H)
3h[b]	6.39	7.05-8.16 (m, 9 H)	2.11 (s, 6 H)
3i[a]	6.40 (3.6)	7.13-8.23 (m, 10 H)	-
3j[a]	6.22	7.19-8.24 (m, 10 H)	-
3k[b]	6.15	7.17-8.38 (m, 10 H)	-
3l[b]	6.20	7.15-8.24 (m, 10 H)	1.34 (s, 9 H)
3m[a]	6.27	7.10-8.24 (m, 10 H)	2.37 (s, 3 H)

[a]Recorded in DMSO-d_6. [b]Recorded in $DCCl_3$.

TABLE III

^{13}C NMR data[a] of dioxaphosphocin 6-oxide moiety of **3a–3m** (ppm values: J_{PC} in Hz)

Compd.	C(1/11)	C(2/10)	C(3/9)	C(4/8)	C(4a/7a)	C(11a/12a)	C(12)	C(13)
3a[b]	129.7	131.6	129.0	124.9(4.6)	146.0(7.2)	132.1(3.8)	53.6	97.4
3b[b]	129.8	131.3	128.6	125.2	147.1(6.0)	132.4	53.3	97.8
3c[b]	129.6	131.7	128.0	125.2	146.8(6.1)	132.8	51.8	98.6
3d[c]	130.1	130.8	129.3	124.2(4.1)	146.2(7.3)	132.6(4.0)	51.7	98.7
3e[c]	130.2	131.2	128.7	125.3	147.2(6.0)	132.1	51.9	98.5
3f[c]	130.0	131.7	129.1	125.4	147.5	133.1	52.3	99.1
3g[c]	129.2	131.8	128.6	124.6(4.1)	145.6(7.3)	131.9(4.0)	53.8	97.5
3h[b]	130.2	131.7	128.8	124.5(4.3)	146.2(7.1)	132.1	53.4	97.8
3i[b]	129.8	131.2	128.0	125.1(4.7)	147.2	132.7	52.7	98.3
3j[b]	130.3	131.5	128.7	125.2(4.3)	147.5(6.8)	132.4	54.7	98.6
3k[c]	130.8	132.2	129.4	124.1(4.2)	145.9(7.3)	133.1(3.3)	54.4	98.2
3l[c]	131.0	132.3	130.2	124.2(4.2)	146.3(7.3)	132.6	54.3	98.3
3m[c]	130.5	132.0	129.2	124.4(4.6)	145.9(7.5)	133.6(4.2)	54.2	98.3

[a]Data is parentheses are coupling constants J(PC)Hz.
[b]Recorded in DMSO-d_6.
[c]Recorded in DCCl3.

TABLE IV

^{13}C NMR Data[a] (ppm) of 6-aryloxy/thioaryloxy moieties in **3a–3m**

Compd	C(1')	C(2')	C(3')	C(4')	C(5')	C(6')	Methyl carbons
3a[b]	149.7 (6.5)	120.0 (4.9)	130.0	126.5	130.3	120.0 (4.9)	-
3b[b]	149.9 (7.6)	129.6 (4.6)	130.2	126.3	127.5	122.8 (4.1)	16.3
3c[b]	150.5	120.5 (5.2)	140.9	126.4	128.9	117.0 (4.8)	20.9
3d[c]	148.2 (7.5)	119.6 (4.7)	130.4	136.0	130.4	119.0 (4.7)	20.1
3e[c]	149.3	128.6 (4.7)	139.0	126.5	128.2	117.6	12.2, 19.8
3f[c]	147.4 (7.6)	129.2 (4.2)	132.0	135.8	127.4	119.8 (3.9)	16.1, 20.6
3g[c]	148.2 (7.9)	131.7 (3.9)	129.4	125.6	129.4	131.7 (3.9)	16.3
3h[b]	147.9 (7.2)	121.2 (4.1)	138.5	134.6	130.6	117.3 (4.6)	19.2, 19.9
3i[b]	146.9 (6.9)	130.0 (4.7)	128.1	127.2	123.5	118.3	-
3j[b]	148.5 (7.3)	121.7 (4.7)	130.2	131.9	130.2	121.7 (4.7)	-
3k[c]	152.1	130.4 (4.2)	126.1	145.6	126.1	130.5 (4.2)	-
3l[c]	149.3	119.4 (4.0)	127.0	143.4	127.0	119.4 (4.8)	31.4, 35.4
3m[c]	147.6 (6.8)	130.0 (4.9)	128.0	135.6	128.0	130.0 (4.9)	20.1

[a]Data in parentheses are coupling constants J_{PC} in Hz.

[b]Recorded in DMSO-d_6. [c] Recorded in $DCCl_3$.

TABLE V

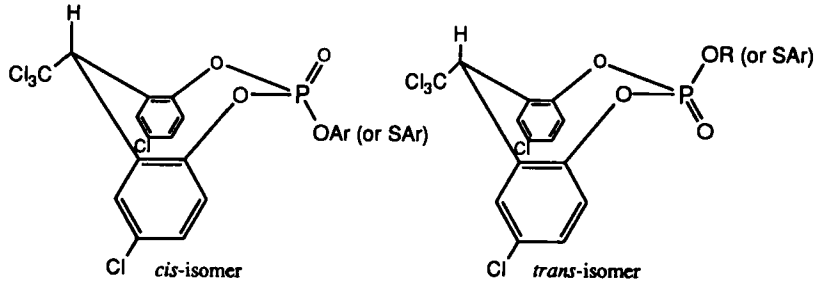
Mass spectral data (% of ions) for certain members of **3**

Compd	$[M]^+$	$(M - HCl)^+$	$[(M-HCl) - Cl]^+$	$[M- Cl_3C]^+$	$[M- C_{14}H_7Cl_5PO_3]^+$
3a	522 (5.7)	486. (1.3)	451 (24.6)	405 (100)	93 (46.8)
3b	536 (3.9)	500 (20.0)	465 (37.5)	419 (100)	107 (5.6)
3d	536 (4.1)	500 (9.7)	465 (1.0)	419 (100)	107 (17.6)
3e	550 (3.4)	514 (10.1)	479 (31.1)	433 (1.3)	121 (32.0)
3f	550 (7.7)	514 (1.3)	479 (6.7)	433 (38.4)	121 (6.8)
3h	550 (9.4)	514 (2.9)	479 (3.3)	433 (37.7)	121 (5.7)
3i	-	520 (9.3)	485 (2.7)	439 (43.7)	127 (38.7)
3k	567 (7.5)	531 (7.3)	-	450 (18.1)	-
3l	578 (10.0)	542 (5.1)	-	461 (46.3)	149 (32.5)

[a]Data not recorded for **3c**, **3g**, **3j**, and **3m**.

All ^1H NMR spectra (Table II) for **3** showed complex multiplets[5] in the range of δ 7.05–8.38 which certainly arose from $^3J_{HH}$ and $^4J_{HH}$ couplings in the aryl systems and possibly from some long range J_{PH} couplings. Interestingly, H(12) appeared as a relatively clean doublet at δ 6.15–6.40 with long range coupling $^5J_{PH}$ = 1.6–3.6 Hz with phosphorus in **3a–g** and **3i**.[5,10] Several reports have suggested that relatives of **3** may exhibit such a diagnostic coupling for the specific stereochemistry involved in terms of the relative orientation of the P=O bond to the C—CCl_3 bond in a trans isomer.[11a]

Conformations of a boat-chair, boat-boat, twist-boat, and boat-boat systems with distorted or distended features or a tub-like topology have been considered[5,7,11] for the dibenzodioxaphosphocin system. 4,8-Di-*tert*-butyl-2,10-bis(methoxycarbonyl)-6-oxo-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin reportedly had a high population of a boat-chair isomer.[11b] Certain X-ray diffraction analyses of single crystals of the cis and trans isomers of this system clearly established a boat-chair form in the solid state. Other structures with large groups present at the 4- and 8-positions exhibited other forms.[11c] It is tempting to speculate that **3a–3m** are trans isomers, and especially so since an X-ray analysis of **3j** confirmed that it was a trans-isomer with a boat-chair conformer present for the 8-membered ring in the solid state. However, small structural deformations could result in unfavorable internal dihedral angles in any of the other systems and virtually prevent any $^5J_{PH}$ coupling in these latter examples. Consequently, the $^5J_{PH}$ coupling values may not be wholly reliable to ascertain a specific configuration around the P atoms. Such a possibility cannot be eliminated from consideration, and thus, except for **3j**, we cannot define categorically the configuration in those systems which appear to be void of an observable $^5J_{PH}$.



The ^{13}C chemical shifts for all members of **3** are given in Table III. Oxygen-bearing carbons C(4a) and C(7a) have signals in the range of 145.6–147.5 ppm as doublets ($^2J_{POC}$ = 7 Hz).[12] A doublet in the region of 124.1–125.4 ppm ($^3J_{POCC}$ = 4.2 Hz) was assigned to C(4) and C(8).[13] Bridgehead carbons C(11a) and C(12a) exhibited low intensity signals as expected at 132.1–133.6 ppm ($^3J_{POCC}$ = 4.0 Hz).[13] Low intensity singlets were observed for the chlorine-bearing carbons C(2) and C(10) at 131.1–132.3 ppm. Signals near 129 ppm were assigned to C(3) and C(9) while those at about 130 ppm have been specified for C(1) and C(11). Identification of the bridging carbon C(12) was facile at 51.7–54.4 ppm[14] while the trichloromethyl carbon appeared at 97.4–99.1 ppm.[15] *The relatively narrow range of the carbon signals for C(4a/7a), C(11a/12a), and C(12) strongly implies the structures have similar arrangements for the attached groups which supports structures* **3**. The sulfur derivative **3m** gave both ^1H and ^{13}C NMR results which paralleled those of the oxygen counterparts.

The ^{13}C shifts for the 6-aryloxy or 6-*p*-tolylthiooxy group are illustrated in Table IV, and the ^{31}P shifts are in Table I. Both sets of shifts are unremarkable. A low intensity ^{13}C doublet in the range of 148.2–152.1 ppm [$^2J_{POC(1')}$ = 6.5–7.9 Hz] was assigned to C(1').[16] Both C(2') and C(6') displayed doublets [$^3J_{POCC(2',6')}$ = 3.9–5.2 Hz] with varying intensities, depending upon the substitution, in a wide range of shifts [117.0–131.7 ppm].[13] An upfield shift of approximately 5 ppm was noted for the C(2') methyl carbon in **3b**, **3f**, and **3g**, possibly due to a γ-interaction with nonbonded electrons of the exocyclic oxygen atom.[5,12] Interestingly, the corresponding

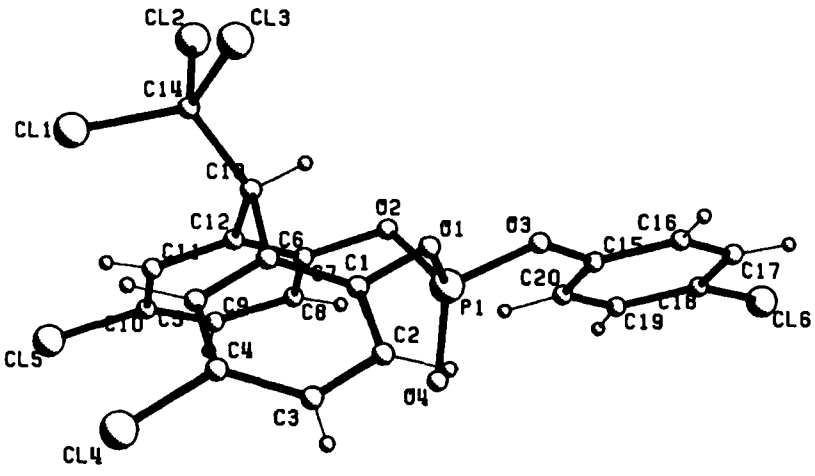
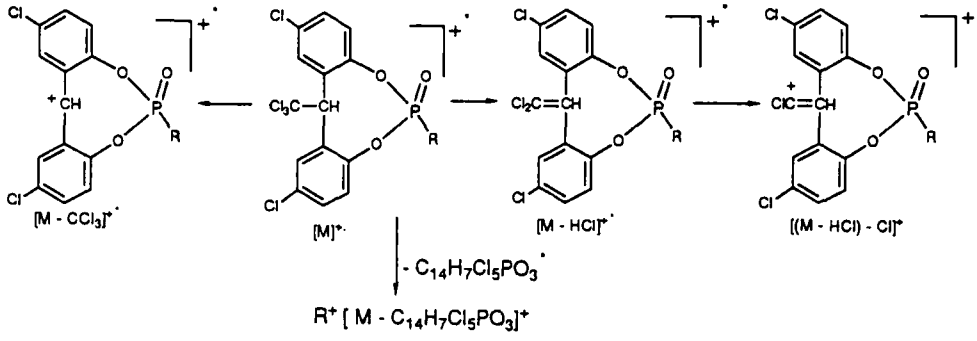


FIGURE 1 Perspective view of **3j**.

carbon C(2′) in **3e** is flanked by a methyl group [C(3′)—CH_3] and an oxygen atom which translated into a double γ-interaction producing increased shielding for C(2′) by more than 8 ppm.[7] The ^{31}P signals appeared within the region from −17.55 to −20.15 ppm from 85% phosphoric acid.[5] Unfortunately, to date no stereochemical interpretation has been assigned from these ^{31}P chemical shifts.

The EI mass spectra of members **3** exhibited m/z for $[M]^+$, $[M - HCl]^+$, $[M - CCl_3]^+$, and $[M - C_{14}H_7Cl_5PO_3]^+$. Such fragmentation is reasonable although there are essentially no model systems in the literature with which to make comparisons. The structures of the fragments shown are tentative but are also plausible.



We were able to grow crystals of **3j** and subjected them to an X-ray diffraction analysis. It is clear from Figure 1 that the structure is a boat-chair with a trichloromethyl group at C(12) in a pseudo equatorial position and the P=O group in a "down position" with respect to the bridging 8-membered ring. The molecule has a pseudo-mirror plane. This symmetry is broken by the *para*-chlorophenoxy group which is coplanar with the P—O1 bond. The P—O1 and P—O4 bond as [1.581(2) and 1.588(2) Å] are longer than the P1—O3 bond [1.564(2) Å]. The P1—O4 bond is 1.449(2) Å. The P1—O3—C15 angle is very large [126.2°(2)] due to steric crowd-

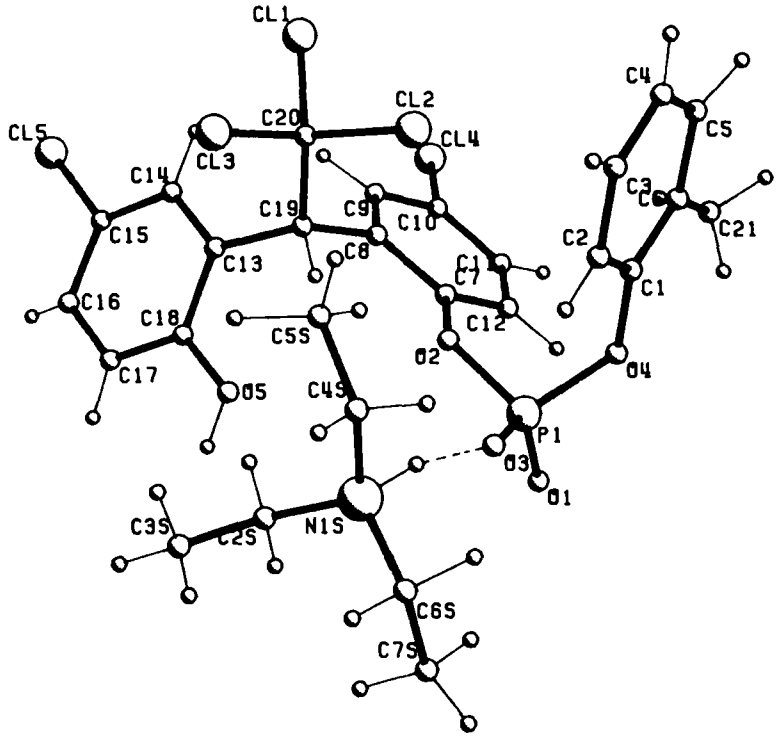


FIGURE 2 Perspective view of **5**.

ing. Similarly, the bulky $-CCl_3$ group forces the axial H(13) [this is H(12); numbering differs from that of the name for **3**] over the 8-membered ring.

An interesting observation was made when purification of ester **3b** was attempted in hot isopropyl alcohol. A crystalline material **5** was obtained with a melting point of 177–179°C. Since this value was considerably higher than had previously been obtained for **3b**, an X-ray diffraction analysis of **5** was initiated. The latter revealed an "open structure" for **5** which was the triethylammonium salt of the corresponding phosphorus acid as illustrated (Figure 2, above, note the numbering of the positions differs from what is employed in the name). Triethylammonium 2-methylphenyl 2-[{2′,2′,2′-trichloromethyl-1′-(2″-hydroxyl-5″-chlorophenyl)}ethyl]-4-chlorophenyl phosphate (**5**) represents a relatively rare class of salts of this type. In the X-ray diffraction analysis of **5**, a hydrogen atom was clearly located on the oxygen atom of the broken P—O bond, and all negative charge is thus located on the phosphate group. The P1—O2 and P1—O4 bonds are quite long [1.620(4) and 1.590(4) Å] while the P1—O1 and P1—O3 bonds are equal in length [1.476(3) and 1.475(4) Å] even though O3 makes a very strong, almost symmetrical, H-bond [O3-N1S: 2.627 Å; O3 . . . H1S: 1.43 Å; N1S-H1S: 1.22 Å] while O1 forms no H-bonds. Moreover, in this compound steric strain gives large P—O—C angles: P1—O2—O7: 127.4°(3) and P1—O4—C1: 126.1°(3).

Presumably some triethylamine was present in the crude **3b** and may have instigated the ring opening process. It is conceivable that esters **3** and traces of catalysts

can lead to an equilibrium shown in the original synthesis although we are inclined to favor the formation of **3** in preference to **3'**. Studies of this type of catalyzed equilibrium with ring-opening and ring-closing have not been common to date in this family of phosphorus heterocycles.[11]

In summary, we have developed a simple method to obtain the title compounds from available starting materials. In addition, spectral and X-ray diffraction analysis support the presence of a boat-chair conformer for the 8-membered ring. An unusual "open structure" **5** was isolated as an ammonium salt of the rare corresponding phosphate and was substantiated via X-ray diffraction analysis. The data provide a framework to which future investigations in this family of phosphorus heterocycles can make comparison.

EXPERIMENTAL

Melting points were taken on a Mel-Temp apparatus and were not corrected. Microanalyses and EI mass spectral data (70 eV) were performed by the Central Drug Research Institute, Lucknow, India. IR spectra were recorded in KBr pellets on a Perkin-Elmer 137 spectrometer. All ^{1}H, ^{13}C, and ^{31}P NMR spectra were collected from a Varian XL-400 NMR spectrometer on solutions in $DDCl_3$ or DMSO-d_6 and were referenced from TMS in δ values (^{1}H) or in ppm (^{13}C from TMS and ^{31}P from 85% H_3PO_4).

6-Phenoxy-2,10-dichloro-12-trichloromethyl-12H-dibenzo[d,g][1,3,2]dioxaphosphocin 6-Oxide (**3a**): The following procedure is typical for the syntheses of **3a–3k**. A solution of phenyl phosphorodichloridate (**2a**, 2.1 g, 0.01 mol) in dry toluene (25 mL) was added dropwise over a period of 20 min to a stirred solution of 2,2-bis(2-hydroxyl-5-chlorophenyl)-1,1,1-trichloroethane (**1**, 3.86 g, 0.01 mol) and triethylamine (2.02 g, 0.02 mol) in dry toluene (60 mL). After completion of the addition, the temperature was slowly elevated to 55–65°C and was maintained for 6 h. Progress of the reaction was monitored by TLC analysis. Triethylamine hydrochloride was then filtered from the mixture, and solvent was evaporated under reduced pressure. The residue was washed with water and then recrystallized from 2-propanol to yield 3.5 g (65%) of **3a** as white crystals, mp 204–205°C. Spectral and physical data for **3a–3m** are in Tables I–V. Analytical data are in Table I.

It was discovered that when crude **3b** (125 mg) in 15 mL of 2-propanol was heated slowly to reflux on a water bath for 15–20 min a mixture resulted. The addition of 10 ml of isopropyl alcohol and continued heating for another 10 min generated a clear solution. Filtering this hot solution and allowing the filtrate to stand at room temperature for 3 days produced crystals. The crystals were filtered, washed with cold isopropyl alcohol, and recrystallized twice again from isopropyl alcohol in the manner described above; mp 177–179°C. The sample was subjected to X-ray diffraction analysis which was discussed in the text as the "open structure" **5**.

6-(4-tert-Butylphenoxy)-2,10-dichloro-12-trichloromethyl-12H-dibenzo[d,g][1,3,2]dioxaphosphocin 6-Oxide (**3l**): The typical procedure using $Cl_3P{=}O$ is illustrated in the preparation of **3l**. To a stirred solution of **1** (3.86 g, 0.01 mol) and triethylamine (2.02 g, 0.02 mol) in dry toluene (50 mL) at 0–5°C was added dropwise phosphorus oxychloride (1.53 g, 0.01 mol) in dry toluene (15 mL) over a period of 15 min. After raising the temperature to 40–50°C, the reaction mixture was stirred for 3 h, TLC analysis (silica gel) being used to monitor the formation of the monochloride **4**. To the same reaction vessel was added dropwise a solution of 4-*tert*-butylphenol (**2l**, 1.50 g, 0.01 mol) and triethylamine (1.01 g, 0.01 mol) in dry toluene (10 mL). The temperature of this new mixture was raised to 55–65°C, and the mixture was stirred for another 3 h. Filtration of triethylamine hydrochloride left a solution which was evaporated to a solid residue. After being washed with water, the residue was recrystallized from $HCCl_3$-hexane to yield 3.1 g (53%) of **3l** as a white solid, mp 233–234°C (Table I–V). Analytical data are in Table I.

Crystallographic Data: Compounds **3j** and **5** were crystallized from isopropyl alcohol. The intensity data of both compounds were taken at room temperature. The crystal data, data collection parameters, and refinement results are summarized in Table VI. Both structures were determined by direct methods using the program SHELXS-86.[17] The refinements were carried out by a full-matrix least squares routine

TABLE VI

Crystal data, data collection, and refinement parameters

Compound	3j	5
Formula	$C_{20}H_{11}O_4Cl_6P$	$C_{21}H_{15}O_5Cl_5P{\cdot}C_6H_{16}N$
F.W.	559.0	657.8
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a	8.980(2)Å	10.425(7)Å
b	9.534(3)	17.822(8)
c	26.203(7)	16.326(9)
β	97.29(2)°	96.81(9)°
v	2225.2(6)Å^3	3011.9(10)Å^3
z	4	4
Dx	1.668 g/cm^3	1.450 g/cm^3
temperature	293K	293K
wavelength	0.71073Å	0.71073Å
radiation	MoKα	MoKα
crystal size	0.57 x 0.38 x 0.25 mm	0.40 x 0.20 x 0.15 mm
F(000)	1120	1360
μ(MoKa)	0.87 mm^{-1}	0.57 mm^{-1}
$2\theta_{max}$	53°	46°
diffractometer	CAD-4	CAD-4
total unique reflections	4550	4154
no. of observed [I≥2σ(I)]	3291	2698
absorption correction	integration	integration
max./min transmission	0.9531/0.8625	0.9042/0.8212
standard reflections	3, every 2 hr	3, every 2 hr
max. variation	1.5%	4.5%
refinement	F	F
R	0.039	0.051
R_w	0.044	0.048
no. of variables	324	349
S	1.4	1.3
$(\Delta/\sigma)_{max}$	0.05	0.07
$(\Delta\rho)_{max}$ in diff. map	0.32e/Å^3	0.34e/Å^3

using the program SHELX76.[18] The hydrogen atoms of both compounds were located from the difference Fourier maps, and the hydrogen parameters were refined isotopically.

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