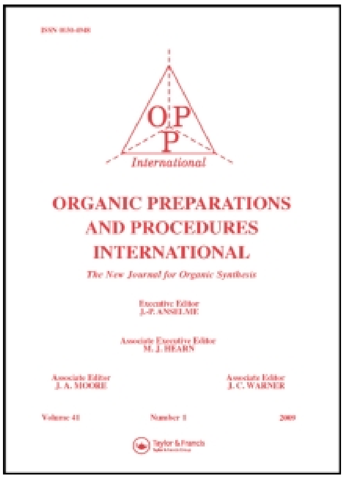

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2,10-DICHLORO-6-(SUBSTITUTED ARYLOXY)DIBENZO[*d,g*][1,3,6,2]DIOXATHIA-PHOSPHOCIN 6-OXIDES. SYNTHESIS AND SPECTRAL CHARACTERISTICS

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2,10-DICHLORO-6-(SUBSTITUTED ARYLOXY)DIBENZO[*d*,*g*][1,3,6,2]DIOXATHIA-PHOSPHOCIN 6-OXIDES. SYNTHESIS AND SPECTRAL CHARACTERISTICS

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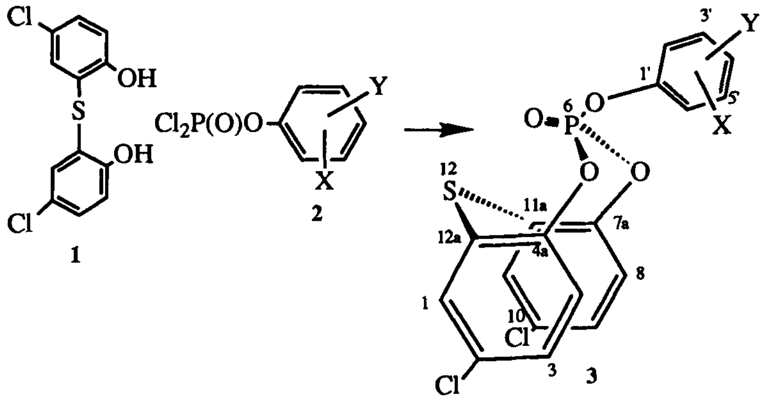
In conjunction with other studies involving the chemistry of phosphorus insecticides and herbicides and the fact that non-cyclic phosphorus esters often possess anticholinesterase activity,[1] we have developed a synthesis for 2,10-dichloro-6-(aryloxy)dibenzo[*d*,*g*][1,3,6,2]-dioxathiaphosphocin 6-oxides. Treatment of 5,5'-dichloro-2,2'-dihydroxydiphenylsulfide (**1**) with arylphosphorodichloridates **2** in toluene at 40-50° with triethylamine afforded the title compounds **3** in isolated yields of 25-38%. A variety of aryl substitutents on **2** did not effect the rate of reaction or yields of products. The easy workup consisted of (1) filtration of triethylamine hydrochloride, (2) evaporation of the solvent, and (3) washing of the residue



with water to remove traces of the amine hydrochloride, and (4) recrystallization of the solid with methanol-benzene to afford the pure esters **3**.

Spectral analysis showed IR bands for P=O, P-O-Ar, and Ar-S-Ar groups in the expected regions (Table 1).[2] As anticipated, the ^1H NMR analysis revealed signals at δ 6.90-7.69 for the Ar*H*. Assignments for these signals were made on the basis of comparison with related signals in **1** and by examination of the $J_{H\text{-}H}$ of the aryl protons.[3] Signals for H(1,11), H(3,9), and H(4,8) were visible at δ 7.68 ± 0.01, 7.32 ± 0.02, and 7.05 ± 0.05, respectively. The aryloxy group had proton signals at δ 6.90-7.62 while the methyl signals were at δ 2.32-2.46. Only a few signals were observed in the ^{13}C NMR spectra of members of **3** because of the

TABLE I
Analytical Data for Members of **3**

					Calcd (%)		Found (%)		
Compd	X	Y	mp (°C)^a	Yield^b(%)	C	H	C	H	$^{31}P^c$ (ppm)
3a	H	H	120-121	36	50.84	2.61	51.20	2.72	-18.02
3b	H	2-CH_3	138-139	32	51.95	2.98	51.90	2.90	-18.00
3c	H	3-CH_3	112-113	32	51.95	2.98	51.90	2.90	-18.00
3d	H	4-CH_3	141-142	38	51.95	2.98	51.90	2.90	-17.98
3e	2-CH_3	3-CH_3	119-120	30	53.00	3.34	53.30	3.10	-18.50
3f	2-CH_3	6-CH_3	176-177	32	53.00	3.34	53.30	3.10	-17.80
3g	3-CH_3	4-CH_3	156-157	30	53.00	3.34	53.30	3.10	-18.01
3h	3-CH_3	5-CH_3	104-105	28	53.00	3.34	53.30	3.10	-17.80
3i	H	2-Cl	124-125	25	47.03	2.19	47.10	2.18	-17.95
3j	H	4-Cl	154-155	32	47.03	2.19	47.10	2.15	-18.02
3k	2-CH_3	4-Cl	153-154	28	48.17	2.55	48.10	2.34	-17.71
3l	3-CH_3	4-Cl	137-138	36	48.17	2.55	48.10	2.34	-17.70

a Purified by washing the residue with cold methanol and recrystallized from methanol-benzene mixture (3:1).

b After one recrystallization.

c Referenced to 85% H_3PO_4. In the IR spectra, the P=O appeared at 1280-1310 cm^{-1}, the O-C at 1180-1220 cm^{-1}, and the P-O at 960-1000 cm^{-1}. The ArC-S-CAr system had a C-S stretching frequency at 650 cm^{-1} in all examples, except for **3e** (660 cm^{-1}) and **3g** (640 cm^{-1}).

symmetry in many of the systems. Confirmation of the ^{13}C assignments in **3** was achieved via diagnosis of the off-resonance spectra and by a comparison with ^{13} C signals in **1**. Coupling with phosphorus was evident for C(4a) and C(7a) as the doublet at 150.5-150.7 ppm had a $^2J_{POC}$ of 8.5-9.4 Hz.[4] Bridged carbons C(11a) and C(12a) have shifts of 126.4-126.9 ppm with $^3J_{POCC}$ of 3.5-4.2 Hz.[5] The ^{13}C resonances for C(4) and C(8) occur as doublets at 123.4-123.5 ppm with $^3J_{POCC}$ of 4.8-5.5 Hz. The chlorine-bearing C(2) and C(10) appear at 131.7-131.9 ppm, quite distinguishable from the other signals. Shifts at 135.5-135.9 ppm and at 131.5-131.6 ppm were assigned to C(1) and C(11) and to C(3) and C(9), respectively. It was noted that ^{13}C shifts of carbons [C(4a, 7a, 11a, and 12a)] in the heterocyclic ring appeared *downfield* by 3-6 ppm compared to those counterparts in **1**. This might arise from a deshielding by the P=O group in the heterocyclic ring. In the aryloxy ring attached to phosphorus in **3**, the carbon shifts occur for C(1'), C(2'), C(3'), C(4'), C(5'), and C(6') at 146.5-150.2, 117.6-131.1, 128.1-140.4, 125.8-135.8, 125.8-140.0, and 117.1-126.8 ppm, respectively.[5] In the presence of Cl at an *ortho* or *para* position, as in **3i**, **3j**, **3k** and **3l**, C(1') experiences a small shielding effect, apparently a result of some electronic influence which is not intuitively obvious. Of course, C(1') is a doublet with $^2J_{POC}$ in the range of 6.9-8.9 Hz. Similarly, C(2',6') have doublets with a smaller $^3J_{POCC}$ range of 3.8-6.6 Hz. Notably, C(2',6') are more shielded by 20-30 ppm compared to the signals for C(1') in **3**. No carbon-phosphorus coupling is observed for C(3',4' and 5'). The methyl resonances appear at 16.3-20.8 ppm but are most shielded when *ortho* to the aryl-O-P unit. Interestingly, in **3e** crowding apparently results and, what we assumed to be the signal for the *ortho* methyl group, is highly shielded, possibly a situation caused by the *ortho* methyl group being forced out of the plane of the aryl system and into the shielding cone of the latter.[6]

The ^{31}P NMR signals of **3** encompassed a range of -17.7 to -18.50 ppm, all upfield from the reference of 85% H_3PO_4, which is a common shift for esters.[7,8] Electron impact mass spectra of members of **3** show M^{+4} and M^{+2} ions with intensities expected for the presence of two chlorine atoms and with M^+ ions at 17-36% abundance, supporting the proposed structures. Analysis of the mass spectra revealed the presence of a benzodioxathiaphosphocin

6-oxide ion, m/z 330, as the base peak. Other principal ions occur at m/z 268, 221, 205, and 189 and are analogous to those found in somewhat related organophosphorus compounds.[9] A list of principal ions and abundances can be obtained upon request. The appearance of the intense ion at m/z 189 is somewhat novel since it implies the expulsion of the C_6H_3ClS fragment. Measurements of daughter ions in these systems confirmed the structures and were diagnostic of the benzodioxathiaphosphocin 6-oxides. In summary, we have prepared a rare class of phosphorus heterocycles the spectral data of which support the structures.

EXPERIMENTAL SECTION

All melting points were determined in open capillary tubes on a Mel-Temp apparatus, Tempo Instruments India, and were uncorrected. IR spectra (ν_{max} in cm^{-1}) were recorded as KBr pellets on a Perkin-Elmer models 683 and 137 as well as on a Beckman IR 18A spectrometer. The ^1H NMR spectra were taken on a Varian XL-300, Bruker WH 90, or a JEOL 90 unit. All ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer on saturated solutions of $DCCl_3$ containing tetramethylsilane (TMS). All chemical shifts are reported in δ values (^1H) or in ppm (^{13}C and ^{31}P) relative to TMS or to 85% H_3PO_4 (^{31}P). Mass spectra were obtained from a JMS-D300 unit using an ionization potential of 70 ev and a direct inlet system. Starting materials **1** and **2** were prepared by known methods.[10,11] The ^{13}C NMR signals for **1** (in $DCCl_3$) occurred at: 117.0 [$\underline{C}$-C-OH], 123.0 [$\underline{C}$-S], 125.6 [$\underline{C}$-C-Cl], 130.0 [$\underline{C}$-Cl], 132.7 [$\underline{C}$-C-S], and 156.4 [$\underline{C}$-OH] ppm.

2,10-Dichloro-6-(phenoxy)dibenzo[*d,g*][1,3,6,2]dioxathiaphosphocin 6-Oxide (**3a**).-A General Procedure. A solution of 2.11 g (0.01 mol) of phenylphosphorodichloridate (**2**) in 30 mL of dry toluene was added dropwise over 30 min to a stirred solution of 2.87 g (0.01 mol) of 5,5'-dichloro-2,2'-dihydroxydiphenylsulfide (**1**) and 2.02 g (0.02 mol) of triethylamine in 80 mL of dry toluene at room temperature (RT). The temperature of the reaction mixture was raised slowly to 40-50° and was continued with stirring for 6 h. Progress of the reaction was followed by via thin layer chromatography with silica gel and eluting with $HCCl_3$. Triethylamine hydrochloride was filtered off, and then the solvent was evaporated. The residue was washed (water) and recrystallized [methanol-benzene (3:1)] to give ester **3a** (3.06 g, 36%) as a white solid. An analytical sample (mp 120-121°), white crystals) was obtained by additional crystallizations. All other members of **3** were prepared in similar fashion.

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8. We have discovered that 2,10-dichloro-6-alkoxy-12*H*-dibenzo[*d,g*][1,3,2]dioxaphosphocin 6-oxides exhibit ^{31}P NMR signals in the same range as found in **3** (see: R. S. N. Reddy, Ph.D. Thesis, 1988, Sri Venkateswara University, Tirupati, India). This shows that neither the bridging sulfur atom in **3** nor the CH_2 group in the compounds cited in the above thesis causes little effect on the ^{31}P shift.

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