

[CONTRIBUTION FROM THE EDGAR C. BRITTON RESEARCH LABORATORY OF THE DOW CHEMICAL CO.]

## Aromatic Phosphorodichloridites and Phosphorodichloridothioates.

### II. *O*-Aryl Phosphorodichloridothioates

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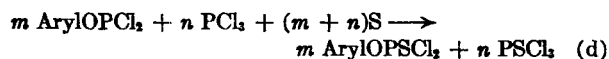
*O*-Aryl phosphorodichloridothioates are formed from phenols and  $\text{PSCl}_2$  in the presence of catalysts or HCl-acceptors in yields of less than 75%. Sulfuration of *O*-aryl phosphorodichloridites with  $\text{PSCl}_2$  produces *O*-aryl phosphorodichloridothioates in yields of 75–92%. Noncatalytic sulfuration with elemental sulfur gives yields of 86–90% but does not produce pure compounds. Reaction with sulfur in the presence of catalytic amounts of activated carbon and molar amounts of  $\text{PSCl}_2$  give yields of 70–95% of pure compound. The composite reaction of *O*-aryl phosphorodichloridites and  $\text{PCl}_3$  with sulfur gives pure compounds in about 85% yield. The same reaction in the presence of molar amounts of an aryl phosphorodichloridothioate of the same structure as the one to be prepared gives pure compounds in yields of 93–98%.

In the past *O*-aryl phosphorodichloridothioates have been prepared in two ways:



Reaction (a), in the absence of catalysts or HCl-acceptors, was reported to produce no *O*-phenyl phosphorodichloridothioate.<sup>1</sup> In the presence of aqueous sodium hydroxide, or with sodium phenate in place of phenol, the yields were found to be low, owing to unavoidable side reactions involving hydrolysis and overesterification.<sup>2</sup> Reaction (b) was reported to give *O*-aryl phosphorodichloridothioates at temperatures of about 200° but no yields were given.<sup>1,3</sup> Both reactions were studied in various modifications to find methods which would produce high yields of phosphorodichloridothioate.

The following reactions also were investigated:



**A. Synthesis from phenols and  $\text{PSCl}_2$ .** Reaction (a) was investigated in the presence of pyridine, metal chloride catalysts, and phosphorus trichloride, respectively, which were expected to act as reaction promoters. The results obtained showed that the formation of *O*-aryl phosphorodichloridothioates from phenols and  $\text{PSCl}_2$  in the presence of reaction promoters occurred in yields of less than 75% (cf. Table I).

**B. Reactions of phosphorodichloridites with  $\text{PSCl}_2$ .** Formation of phosphorothioates from certain phosphites and stoichiometric amounts of  $\text{PSCl}_2$  has been reported.<sup>4</sup> The availability of a series of aromatic phosphorodichloridites<sup>5</sup> permitted investigation of their reaction with  $\text{PSCl}_2$  according to reaction (c).

(1) R. Anschutz and W. O. Emery, *Ann.*, **253**, 105 (1889).

(2) W. Authenrieth and W. Meyer, *Ber.*, **58**, 840 (1925).

(3) W. Strecker and Ch. Grossmann, *Ber.*, **49**, 63 (1916).

(4) H. B. Gottlieb, *J. Am. Chem. Soc.*, **54**, 748 (1932).

(5) H. Tolkmith, *J. Org. Chem.*, **23**, 1682 (1958).

TABLE I

ArylOPSCl<sub>2</sub> FROM PHENOL AND PSCl<sub>2</sub> DIRECTLY

Reaction Promoter	ArylOPSCl <sub>2</sub> Obtained	Yield (% Theory)
Pyridine	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> OPSCl <sub>2</sub>	55
	2-Cl-4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> OPSCl <sub>2</sub>	38.2
	3-Cl-4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> OPSCl <sub>2</sub>	38.1
	2,4,6-Cl <sub>3</sub> -C <sub>6</sub> H <sub>2</sub> OPSCl <sub>2</sub>	55.6
MgCl <sub>2</sub>	2,4,5-Cl <sub>3</sub> -C <sub>6</sub> H <sub>3</sub> OPSCl <sub>2</sub>	51
CuCl	2,4,5-Cl <sub>3</sub> -C <sub>6</sub> H <sub>3</sub> OPSCl <sub>2</sub>	65
MgCl <sub>2</sub> + CuCl	2,4,5-Cl <sub>3</sub> -C <sub>6</sub> H <sub>3</sub> OPSCl <sub>2</sub>	66.5
	2-Cl-4- <i>t</i> -C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>3</sub> OPSCl <sub>2</sub>	73.1
	C <sub>6</sub> H <sub>5</sub> OPSCl <sub>2</sub>	62.1
MgCl <sub>2</sub> + PCl <sub>3</sub>	2,4,5-Cl <sub>3</sub> -C <sub>6</sub> H <sub>3</sub> OPSCl <sub>2</sub>	67

It was found that phosphorodichloridothioates were formed with maximum yield when 100% excess of  $\text{PSCl}_2$  was used and the phosphorus trichloride formed was removed by fractional distillation under atmospheric pressure during the reaction. On the basis of these findings a series of aryl phosphorodichloridothioates was prepared by sulfurating crude aryl phosphorodichloridites with excess  $\text{PSCl}_2$  in the absence of metal chloride catalysts (cf. Table II). This method was found to be very convenient for laboratory preparation of various aromatic phosphorodichloridothioates in yields of 75–92% and purities of higher than 97%.

TABLE II

ArylOPSCl<sub>2</sub> FROM ArylOPCl<sub>2</sub> + PSCl<sub>2</sub>

ArylOPSCl <sub>2</sub>	Boiling Range (°C. at 10 mm.)	Yield (% Theory)
C <sub>6</sub> H <sub>5</sub> OPSCl <sub>2</sub>	108–117	75.5
3-C <sub>2</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>4</sub> OPSCl <sub>2</sub>	130–138	92
2-Cl-C <sub>6</sub> H <sub>4</sub> OPSCl <sub>2</sub>	127–136	76
2-Cl-4- <i>t</i> -C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>3</sub> OPSCl <sub>2</sub>	167–176	90.5
2-Br-4- <i>t</i> -C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>3</sub> OPSCl <sub>2</sub>	175–186	80
2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> OPSCl <sub>2</sub>	151–158	81.5
2,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> OPSCl <sub>2</sub>	155–164	76.5
3,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> OPSCl <sub>2</sub>	152–162	84.5
2,4,5-Cl <sub>3</sub> C <sub>6</sub> H <sub>3</sub> OPSCl <sub>2</sub>	167–177	79.5

#### C. Noncatalytic reactions of phosphorodichloridites

with sulfur. A reinvestigation of the known reaction (b) with several aryl phosphorodichloridites showed that this reaction did not take place below 150° if catalysts were absent. At around 170° undiluted equimolar mixtures of reactants produced exothermic reactions causing a rapid rise of the reaction temperature to 230–250°. At such reaction end-temperatures partial decomposition took place causing unsatisfactory yields.

It was found that reaction temperatures of 160–180° were critical for obtaining high yields and that reaction times of 1.5–2 hours were sufficient to complete the reaction. The necessary range of reaction temperature was maintained by slow addition of one reactant to the other or by heating the mixture of the reactants under the same conditions in the presence of small amounts of a diluent which boiled at 125–160° under atmospheric pressure. Under these precautions stoichiometric mixtures of reactants gave consistently high yields of *O*-aryl phosphorodichloridothioates. It was found, however, that the reaction main products were regularly contaminated by unreacted starting products (*cf.* Table III). Removal of these impurities by repeated vacuum fractionation was not entirely successful. Therefore, this method was not suitable without modification for preparation of aromatic phosphorodichloridothioates in high purity.

dite caused a noticeable reduction of yield. Reactions in the presence of activated carbon and silica gave reaction temperatures which went through a characteristic minimum (*cf.* Experimental, Table VIII). This indicated that  $\text{PSCl}_2$  was not merely a diluent but participated in the sulfuration reaction although it was finally recovered in high yields. Sulfur monochloride in place of  $\text{PSCl}_2$  gave reduced yields.

Reaction (b), when carried out in the presence of  $\text{PSCl}_2$  and catalytic amounts of activated carbon, gave phosphorodichloridothioate which contained less than 0.5% of elemental sulfur as the only impurity. However, the yields obtained were not better than those obtained from the nonmodified reaction (b).

*E. Composite reaction of sulfur with phosphorodichloridite and  $\text{PCl}_3$ .* The results described in Section D led to the conclusion that pure aryl phosphorodichloridothioates could be obtained by the reaction of phosphorodichloridites with an excess of sulfur, if coupled with removal of unreacted sulfur by a scavenger which would form a volatile sulfur derivative that could easily be separated from the main product by fractional distillation. Most suitable for this purpose appeared to be the use of phosphorus trichloride. Accordingly, the sulfuration was based upon the following composite reaction:

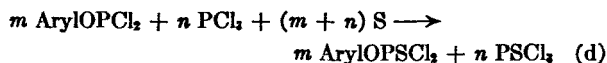
TABLE III  
NONCATALYTIC ArylOPCl<sub>2</sub>-SULFUR REACTIONS

Moles of Diluent/Mole ArylOPCl <sub>2</sub>	ArylOPSCl <sub>2</sub> Obtained		
	Structure	Yield (% Theory)	Purity (%)
None	2,4,5-Cl <sub>3</sub> -C <sub>6</sub> H <sub>2</sub> OPSCl <sub>2</sub>	86	96.5
0.2	s-C <sub>2</sub> H <sub>5</sub> Cl <sub>4</sub>	86	96.0
0.37	C <sub>6</sub> H <sub>5</sub> Br	90.5	96.0
0.2	PSCl <sub>2</sub>	90.0	98.8

*D. Catalytic phosphorodichloridite-sulfur reactions.*

The observation that the reaction of phosphorodichloridites with sulfur gave phosphorodichloridothioates in high yield and fair purity, if carried out in the presence of  $\text{PSCl}_2$  (*cf.* Table III), was apparently new though not entirely unexpected in view of the findings reported in the Sections B and C. This reaction was investigated more in detail in the presence of catalytic amounts of anhydrous aluminum chloride,<sup>6</sup> silica-powder and activated carbon.

It was found (*cf.* Table IV) that the reaction was most effectively catalyzed by highly activated carbon (Darco G60). The other catalysts investigated proved to be inferior. Presence of increasing quantities of  $\text{PSCl}_2$  up to 2.5 moles per mole of phosphorodichloridite gave increasing yields. Chlorination of the aryl group of the phosphorodichlori-



In practice, reaction (d) was carried with an excess of  $\text{PCl}_3$  and studied with 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OPCl<sub>2</sub>, because chlorinated aryl phosphorodichloridites were found to sulfurate less readily than nonhalogenated aryl phosphorodichloridites. It was found that reactions in the presence of an excess of sulfur and  $\text{PCl}_3$  gave 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub> with 99.3% purity and in a yield of about 85% (*cf.* Table V). From previous experiences it was known that sulfur would react somewhat better if dissolved prior to reaction. This suggested that reaction (d) could advantageously be carried out by employing as the sulfur solvent an aryl phosphorodichloridothioate of the same structure as the one to be prepared. Thus, it was possible to obtain the pure main product in yields of 93–98% by employing as the sulfur solvent 1.0–1.5 moles of 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>-

(6) *Cf.* F. F. Knotz, U. S. Patent 2,715,561 (1955).

TABLE IV  
 ArylOPCl<sub>2</sub>-SULFUR REACTIONS IN THE PRESENCE OF PSCl<sub>2</sub> AND VARIOUS CATALYSTS

Catalyst	Moles of PSCl <sub>2</sub> per Mole of ArylOPCl <sub>2</sub>	Structure	Yield (% Theory)	Impurities (% S)
AlCl <sub>3</sub>	3.0	2,4,6-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub> OPSCl <sub>2</sub>	41.5	0.4
SiO <sub>2</sub>	2.0	3-C <sub>2</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>4</sub> OPSCl <sub>2</sub>	62.5	0.23
	2.0	3-C <sub>2</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>4</sub> OPSCl <sub>2</sub>	95.0	0.23
	2.0	2-Cl-C <sub>6</sub> H <sub>4</sub> OPSCl <sub>2</sub>	94.5	0.34
Act. Carbon	2.0	4-Cl-C <sub>6</sub> H <sub>4</sub> OPSCl <sub>2</sub>	88.0	0.35
	2.5		88.0	0.3
	0.74	2,4,5-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub> OPSCl <sub>2</sub>	68.5	0.4
	None		59.5	0.5

 TABLE V  
 COMPOSITE REACTION (d) IN THE ABSENCE AND IN THE PRESENCE OF ArylOPSCl<sub>2</sub>

PCl <sub>5</sub> <sup>a</sup>	S <sup>a</sup>	ArylOPSCl <sub>2</sub> <sup>a</sup>	Structure	Yield (%) Theory)	Impurities
0.4	1.0	—		78.7	10% 2,4,5-Cl <sub>3</sub> - C <sub>6</sub> H <sub>2</sub> OPCl <sub>2</sub>
0.5	1.16	—	2,4,5-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub> OPSCl <sub>2</sub>	84.5	0.6% S
0.5	1.16	0.1		86.6	
0.5	1.16	0.5		88.0	
0.5	1.16	1.0		92.6	
0.5	1.16	1.5		97.5	
0.5	1.10	1.0	2-Cl-4- <i>t</i> -C <sub>4</sub> H <sub>9</sub> C <sub>6</sub> H <sub>3</sub> OPSCl <sub>2</sub>	95.8	Less than 0.2% S

<sup>a</sup> In moles per mole of phosphorodichloridite.

 TABLE VI  
 ARYL PHOSPHORODICHLORIDOTHIOATES

Aryl	Sulfur Analysis		d <sub>4</sub> <sup>20</sup>	n <sub>D</sub> <sup>20</sup>	B.P., °C/10 mm.
	(Calcd.)	(Found)			
C <sub>6</sub> H <sub>5</sub> -	14.12	14.16	1.4091	1.5766	116
3-C <sub>2</sub> H <sub>5</sub> -C <sub>6</sub> H <sub>4</sub> -	12.57	12.70	1.3327	1.5683	136
2-Cl-C <sub>6</sub> H <sub>4</sub> -	12.26	12.31	1.5048	1.5861	134
4-Cl-C <sub>6</sub> H <sub>4</sub> -	12.26	12.10	1.5068	1.5869	141
2-Cl-4- <i>t</i> -C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>3</sub> -	10.09	10.04	<sup>a</sup>		175
2-Br-4- <i>t</i> -C <sub>4</sub> H <sub>9</sub> -C <sub>6</sub> H <sub>3</sub> -	8.86	9.02	<sup>b</sup>		185
2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -	10.83	10.72	1.5913	1.5960	158
2,5-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -		10.80	1.5943	1.5962	162
3,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> -		10.66	1.5998	1.5985	160
2,4,5-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub> -	9.70	9.78	1.6728 <sup>c</sup>	1.6072 <sup>c</sup>	175
2,4,6-Cl <sub>3</sub> C <sub>6</sub> H <sub>2</sub> -	9.70	9.72	<sup>d</sup>		178
4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -	11.85	12.06	<sup>e</sup>		—
2-Cl-4-NO <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> -	10.46	10.32	1.6127 <sup>f</sup>	1.6094 <sup>f</sup>	—
3-Cl-4-NO <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> -	10.46	10.90	1.6219 <sup>f</sup>	1.6063 <sup>f</sup>	—

<sup>a</sup> M.p. 37–38°. <sup>b</sup> M.p. 41–42°. <sup>c</sup> M.p. +14°. <sup>d</sup> M.p. 47–48°. <sup>e</sup> M.p. 53–54°. <sup>f</sup> Data on crude product.

OPSCl<sub>2</sub> per mole of 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OPCl<sub>2</sub> (cf. Table V).

This method was found to produce pure aryl phosphorodichloridothioates in almost quantitative yields and to be the most economical of all methods investigated. It was not suitable for thermo-unstable compounds, like nitrophenyl phosphorodichloridites.

*E. Physical properties.* For the purpose of purification the *O*-aryl phosphorodichloridothioates prepared were vacuum fractionated twice through a 15 cm. Vigreux column. The highest thermal

stability was shown by 2-halo-4-*tert*-butylphenyl phosphorodichloridothioates which did not decompose when heated at 190–200° for 10 hours. Polyhalophenyl compounds showed some decomposition under these conditions. Nitrophenyl phosphorodichloridothioates are much less stable and tend to decompose violently at such temperatures.

The pure phosphorodichloridothioates were isolated as viscous, almost colorless liquids. Some of them solidified after a few hours and were recrystallized from petrol ether (30–60°). All compounds prepared (cf. Table VI) were found to be soluble

without decomposition in those organic solvents which did not contain reactive hydrogen or carbonyl groups.

#### EXPERIMENTAL

*Starting products.* The phenols and aryl phosphorodichloridites used were of a purity as described in the preceding paper.<sup>6</sup> Thiophosphoryl chloride, pyridine, and phosphorus trichloride were employed as freshly redistilled commercial grade products.

*Reaction (a) in the presence of pyridine.* Pyridine, 565 g., was added to an agitated solution of 1385 g. of 2,4,6-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OH and 5940 g. of PSCl<sub>2</sub> in 3.5 l. of benzene at 25–28°. The reaction mixture was agitated for 24 hr. at room temperature, filtered, the pyridine hydrochloride washed with ether, and the combined filtrates concentrated under atmospheric pressures up to a pot temperature of 130°. After cooling, the residue was filtered again and the filtrate concentrated up to a pot temperature of 110° at 13 mm. The residue was dissolved in 1 l. of petroleum ether (b.p. 30–60°) and set aside for crystallization. A total of 785 g. of white crystals of 2,4,6-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub> was obtained, m.p. 47–48°. Chemical analysis gave 53.7% Cl, 9.73% S, and 9.5% P. The mother liquor was evaporated and the residue vacuum fractionated. This gave 498 g. of 2,4,6-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub> which boiled sharply at 166° at 6 mm. Total yield of 2,4,6-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub>, 1283 g. (55.6% yield).

*Anal.* Calcd. for C<sub>6</sub>H<sub>2</sub>Cl<sub>3</sub>OPS: Cl, 53.7; P, 9.4; S, 9.7. Found: Cl, 53.5; P, 9.3; S, 9.8.

Chloronitrophenol, 347 g., and *p*-nitrophenol, 278 g., respectively, were dissolved in 1 l. of ether. These solutions were added to agitated mixtures of 1700 g. of PSCl<sub>2</sub> plus 0.2 l. of methylene dichloride plus 165 g. of pyridine at +4 to +8° during 5 hr. (water cooling). The reaction mixtures were kept agitated for 6 hr. at 10–20°. After having stood overnight at room temperature, the mixtures were filtered and the filtrates evaporated to a pot temperature of 65°/12 mm. Methylcyclohexane (700 cc.) was added and again evaporated in the same manner. Each residue was extracted twice with a mixture of 500 cc. of cyclohexane and 500 cc. of petroleum ether (30/60°) and then with 500 cc. of cyclohexane alone. The hydrocarbon solution was evaporated to a pot temperature of 76° under 12 mm. and left the crude main products.

Recrystallization of crude 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>OPSCl<sub>2</sub> from petroleum ether (30/60°) gave 299 g. (55% yield) of almost colorless crystals melting at 53–54°.

*Anal.* Calcd. for C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>NO<sub>2</sub>PS: S, 11.85. Found: S, 12.06.

The crude *O*-chloronitrophenyl phosphorodichloridothioates could not be brought to crystallization and were analyzed without further purification. The data obtained are shown in Table VII.

hydrous CuCl, and 5.0 g. of a 1:1 mixture of anhydrous MgCl plus CuCl, respectively. After a reaction time of 15 hr. the mixtures were filtered and fractionated through a 15 cm. Vigreux column at 10 mm. pressure. While the first fraction consisted of excess PSCl<sub>2</sub>, the second fraction of all three runs consisted of unreacted phenol, identified by freezing point and IR-analysis as described in the preceding paper. The runs were repeated with a total reflux time of 40 hr. and vacuum fractionated. The runs in the presence of MgCl<sub>2</sub> and CuCl again gave unreacted 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OH, in amounts of 68 g. and 25 g. respectively. Their third fraction consisted of 385 g. and 490 g. of 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub>, boiling at 172–177° under 10 mm. pressure. The run in the presence of a MgCl<sub>2</sub>-CuCl catalyst mixture gave no unreacted 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OH and 501 g. (66.5% yield) of 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub>, boiling at 170–177° at 10 mm. Redistillation of main product gave 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub>, boiling at 175° at 10 mm. and showing a freezing point of +14°.

*Anal.* Calcd. for C<sub>6</sub>H<sub>2</sub>Cl<sub>3</sub>OPS: S, 9.7. Found: S, 9.78.

Solutions of C<sub>6</sub>H<sub>2</sub>OH, 94g., and 2-Cl-4-*t*-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>3</sub>OH, 185 g., respectively, in 850 g. of PSCl<sub>2</sub> were refluxed at atmospheric pressure with agitation in the presence of 1 g. of anhydrous MgCl<sub>2</sub> plus 1 g. of anhydrous CuCl. After a reaction time of 36 hr. the excess of PSCl<sub>2</sub> was removed by distillation under a pressure of 50 mm. The residues obtained were filtered and fractionated through a 15 cm. Vigreux column at a pressure of 10 mm. In either run, no unreacted phenol was recovered. The main cuts of these runs represented the desired phosphorodichloridothioates, *i.e.*, C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub> [141 g. (62.1% yield) of a boiling range of 112–117° at 10 mm.] and 2-Cl-4-*t*-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>3</sub>OPSCl<sub>2</sub> [232 g. (73.1% yield) of a boiling range of 171–178° at 10 mm.]. Redistillation of them under the same pressure gave boiling points of 116° and 175°, respectively. The 2-chloro-4-*t*-butylphenyl derivative solidified upon standing and was recrystallized from petroleum ether (30/60°) to give white crystals melting at 37–38°.

*Anal.* Calcd. for C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>OPS: S, 14.12; Found: S, 14.16. Calcd. for C<sub>10</sub>H<sub>12</sub>Cl<sub>2</sub>OPS: S, 10.09. Found: S, 10.04.

*Reaction (a) in the presence of PCl<sub>5</sub> plus MgCl<sub>2</sub>.* A solution of 594 g. of 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OH in a mixture of 3000 g. of PSCl<sub>2</sub> plus 1650 g. of phosphorus trichloride was refluxed with agitation under atmospheric pressure in the presence of 3 g. of anhydrous magnesium chloride. After 24 hr. of reaction time at 100–102° the reaction mixture was vacuum fractionated as described and gave 666 g. (67% yield) of 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub>, boiling at 166–176° at 10 mm. and identified by infrared analysis.

*Reaction (c).* A mixture of one mole of an *O*-aryl phosphorodichloridite and two moles of PSCl<sub>2</sub> was heated with agitation under atmospheric pressure. At a pot temperature of 125°, phosphorus trichloride started to evolve and was immediately removed through a saddle-packed column of 50 cm. length. During a reaction time of 4 hr. the pot temperature rose steadily to 155° while the temperature at the

TABLE VII  
O-CHLORONITROPHENYL PHOSPHORODICHLORIDOTHIOATES

Structure	2-Cl-4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> OPSCl <sub>2</sub>	3-Cl-4-NO <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> OPSCl <sub>2</sub>
Exterior appearance	Reddish-brown oil	Olive-colored oil
Crude yield	234 g. (38.2%)	233 g. (38.1%)
(Cl)	34.3	34.6
Found (P)	10.1	10.6
(S)	10.32	10.9

*Anal.* Calcd. for C<sub>6</sub>H<sub>3</sub>Cl<sub>2</sub>NO<sub>2</sub>PS: Cl, 34.8; P, 10.22; S, 10.46.

*Reaction (a) in the presence of metal chlorides.* In three parallel runs a mixture of 453 g. of 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OH and 1700 g. of PSCl<sub>2</sub> was refluxed with agitation under atmospheric pressure in the presence of 2.5 g. anhydrous MgCl<sub>2</sub>, 2.5 g. of an-

head of the column remained at the boiling point of PCl<sub>5</sub> (78–80°). Then the temperature at the head of the column rose rather rapidly to 124° and remained there (boiling temperature of PSCl<sub>2</sub>). This indicated that the reaction was complete. The reaction mixture was fractionated first under a pressure of 50 mm. to remove all unreacted PSCl<sub>2</sub> and then

under a pressure of 10 mm. to obtain the phosphorodichloridothioate formed. The results obtained were as given in Table II. The compounds isolated were twice vacuum fractionated through a 15 cm. Vigreux column and the distillates analyzed for sulfur. The data obtained were those given in Table VI.

*Reaction (b), noncatalytic.* Sulfur, 21.5 g., was added in portions over a period of 1 hr. to an agitated quantity of 200 g. of 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OPCl<sub>2</sub>, heated at 160° under atmospheric pressure. Agitation was continued for 2 hr. at 160–166°. Vacuum distillation of the reaction product gave 197 g. (86% yield) of 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub> of 96.5 purity according to IR analysis employing pure standards of 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub> and 2,4,5-Cl<sub>3</sub>C<sub>6</sub>H<sub>2</sub>OPCl<sub>2</sub>.

A mixture of 3-C<sub>2</sub>H<sub>5</sub>-C<sub>6</sub>H<sub>4</sub>OPCl<sub>2</sub>, 112 g., with sulfur, 16 g., and *s*-C<sub>2</sub>H<sub>5</sub>Cl, 17 g., was heated to 160° over a period of 1 hr. with agitation under atmospheric pressure. The reaction mixture was kept agitated under the same conditions for 2 hr. and then fractionated through a 15 cm. Vigreux column under reduced pressure. After removal of diluent a main cut of 110 g. (86% yield) of 3-C<sub>2</sub>H<sub>5</sub>-C<sub>6</sub>H<sub>4</sub>OPSCl<sub>2</sub>, b.p. 129–138° at 10 mm., was obtained. Infrared analysis employing pure standards indicated a purity of 96.0%.

Sulfur, 39 g., was added in portions over a period of 1.5 hr. to an agitated solution of 3,4-Cl<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>OPCl<sub>2</sub>, 320 g., in C<sub>6</sub>H<sub>5</sub>Br, 70 g., heated at 170–177° under atmospheric pressure. The reaction mixture was kept agitated under these conditions for another 0.5 hr. Workup of reaction mixture and analysis of main cut was as described in the preceding run. Obtained was 325 g. (90.5% yield) of 3,4-Cl<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>OPSCl<sub>2</sub>; boiling range, 157–162° at 10 mm.; purity, 96% by infrared analysis.

Sulfur, 48 g., was added in small portions over a period of 1½ hr. to an agitated solution of 2-Cl-C<sub>6</sub>H<sub>4</sub>OPSCl<sub>2</sub>, 345 g., in PSCl<sub>3</sub>, 51 g., and heated at 175–180° under atmospheric pressure. Agitation was continued for another 0.5 hr. under the same conditions. Workup of reaction mixture, isolation, and analysis of main cut was as described in the preceding experiment. Obtained was 353 g. (90% yield) of 2-Cl-C<sub>6</sub>H<sub>4</sub>OPSCl<sub>2</sub>, boiling at 128–138° at 10 mm. and showing 98.8% infrared purity.

*Catalytic reaction (b) in the presence of PSCl<sub>3</sub>.* An agitated mixture of 10.5 g. of sulfur with 158 g. of PSCl<sub>3</sub> was warmed to 75° and then 2 g. of anhydrous aluminum chloride added. Over a period of 1 hr. 93 g. of 2,4,6-Cl<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OPCl<sub>2</sub> was added at 55–80°. The reaction mixture was refluxed for 1 hr. under atmospheric pressure, filtered, and vacuum fractionated through a 15 cm. Vigreux column. The first cut, boiling at 58–65° at 100 mm. weighed 135 g. and was found to consist of unreacted PSCl<sub>3</sub>, by infrared analysis. The main cut, boiling at 177–181° at 11 mm., weighed 43 g. (41.5% yield) and represented 2,4,6-Cl<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub> of 99% infrared purity.

*Anal.* Calcd. for C<sub>6</sub>H<sub>2</sub>Cl<sub>3</sub>OPS: S, 9.7. Found: S, 10.1.

An agitated mixture of 67 g. of 3-C<sub>2</sub>H<sub>5</sub>-C<sub>6</sub>H<sub>4</sub>OPCl<sub>2</sub> with 102 g. of PSCl<sub>3</sub> and 10.0 g. of sulfur was heated at reflux under atmospheric pressure in the presence of 1.5 g. of anhydrous, powdered silica, and 1.5 g. of activated carbon (Darco G60), respectively. In the presence of silica the reaction temperature of the refluxing mixture changed from 137–114–132° over a period of 26 hr. In the presence of Darco G60 the reaction temperature changed from 132–115–140° within 19 hr. After these reaction times the mixtures were filtered and vacuum fractionated as described in the foregoing run. The run in the presence of silica gave 48 g. (62.5% yield) and the run in the presence of activated carbon gave 72.5 g. (95% yield) of main cut, boiling at 130–137° at 10 mm. and identified by infrared analysis.

*Anal.* Calcd. for C<sub>8</sub>H<sub>9</sub>Cl<sub>2</sub>OPS: S, 12.57. Found: S, 12.8.

Mixtures of 115 g. of monochlorophenyl phosphorodichloridite with 170 g. of PSCl<sub>3</sub>, 16.5 g. of sulfur and 3 g. of Darco G60 were refluxed with agitation under atmospheric pressure. The reaction temperature of the mixtures

changed from 132–115–140° C. during 19 hr. The runs were filtered and vacuum fractionated as described above. Obtained 124 g. (94.5% yield) of 2-Cl-C<sub>6</sub>H<sub>4</sub>OPSCl<sub>2</sub>, boiling at 130–136° under 10 mm., identified by infrared analysis. The other run gave 115 g. (88% yield) of a compound boiling at 135–142° under 10 mm.

*Anal.* Calcd. for C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>OPS: Cl, 40.68; P, 11.85; S, 12.26. Found: Cl, 40.8; P, 11.5; S, 12.6.

An agitated mixture of 149 g. of 2,4,5-Cl<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OPCl<sub>2</sub> with 16.5 g. of sulfur, 20 g. of S<sub>2</sub>Cl<sub>2</sub>, and 2.5 g. of activated carbon was refluxed under atmospheric pressure for 85 min. The reaction temperature rose from 135° to 148°. The run was filtered and vacuum fractionated. The main cut consisted of 86 g. (52% yield) of 2,4,5-Cl<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub>, boiling at 155–179° at 11 mm. It showed 90 ± 2% purity by infrared analysis.

*Anal.* Calcd. for C<sub>6</sub>H<sub>2</sub>Cl<sub>3</sub>OPS: S, 9.7. Found: S, 10.87.

Mixtures of 298 g. of 2,4,5-Cl<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OPCl<sub>2</sub> with 33 g. of sulfur and 5 g. of Darco G60 were heated with agitation under atmospheric pressure in the presence of varying quantities of PSCl<sub>3</sub>. The runs were worked up as described in the previous experiments. The results obtained were as given in Table VIII.

TABLE VIII  
REACTION OF 2,4,5-Cl<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OPCl<sub>2</sub> WITH SULFUR IN THE PRESENCE OF PSCl<sub>3</sub> AND ACTIVATED CARBON

PSCl <sub>3</sub> (g.)	Reaction		Main Product	
	Temp., °C.	Time (hrs.)	Yield (g.)	Sulfur found (%)
None	135–138	2	195	10.2
125	136–122–160	16	226	10.1
420	130–122–137	20	290	10.0

*Composite Reaction (d).* Sulfur, 32 g., was added in small portions over a period of 3.5 hr. to an agitated mixture of 298 g. of 2,4,5-Cl<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OPCl<sub>2</sub> and 55 g. of phosphorus trichloride at a temperature of 155–175° at atmospheric pressure. Vacuum fractionation of the reaction mixture gave 44 g. of a PCl<sub>3</sub>-PSCl<sub>3</sub> mixture and 288 g. of an impure 2,4,5-Cl<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub>. This product had a boiling range of 155–176° at 11 mm. and contained 10% of 2,4,5-Cl<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OPCl<sub>2</sub>, by infrared analysis.

A mixture of 298 g. of 2,4,5-Cl<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OPCl<sub>2</sub> with 69 g. of phosphorus trichloride was added to 37 g. of sulfur over a period of 2 hr. at 160–175° with agitation under atmospheric pressure. The reaction mixture was kept agitated for an additional 2 hr. under the same reaction conditions and then vacuum fractionated. This gave 281 g. (84.5% yield) of a 2,4,5-Cl<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub> boiling at 171–176° at 10 mm.

*Anal.* Calcd. for C<sub>6</sub>H<sub>2</sub>Cl<sub>3</sub>OPS: S, 9.7. Found: S, 10.3.

In order to carry out the composite reaction (d) in the presence of aryl phosphorodichloridothioate, mixtures of 298 g. of 2,4,5-Cl<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OPCl<sub>2</sub> with 69 g. of phosphorus trichloride were added dropwise over a period of 2 hr. at 160–175° to agitated mixtures of 37 g. of sulfur and 2,4,5-Cl<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub> in amounts of 33, 165, 330, and 495 g. respectively. After completed addition the mixtures were kept agitated under the same reaction conditions for another 2 hr. Vacuum fractionation of the runs gave 2,4,5-Cl<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub> in amounts of 319, 455, 636, and 816 g. respectively. The main cuts showed a boiling range of 171–178° at 10 mm. The amounts of 2,4,5-Cl<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OPSCl<sub>2</sub> actually produced were 286, 290, 306, and 321 g., respectively. The products, isolated by vacuum fractionation, showed absence of unreacted 2,4,5-Cl<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>OPCl<sub>2</sub> by infrared analysis. Sulfur analysis gave 9.7 to 9.72% of total sulfur in the products.

Sulfur, 32 g., was added portionwise over a period of 2 hr. to an agitated mixture of 286 g. of 2-Cl-4-*t*-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>3</sub>-

$\text{OPCl}_2$  plus 69 g. of phosphorus trichloride plus 318 g. of 2-Cl-4-*t*- $\text{C}_6\text{H}_3$ - $\text{C}_6\text{H}_5$ OPSCl<sub>2</sub> at 160–175° under atmospheric pressure. The reaction mixture was kept under the same conditions for an additional 2 hr. and then vacuum-fractionated. A total of 622 g. of desired product was obtained,

boiling at 173–177°/10 mm. Actual yield, 304 g. = 95.8% theory.

Anal. Calcd. for  $\text{C}_{18}\text{H}_{12}\text{Cl}_2\text{OPS}$ : S, 10.09. Found: S, 10.2.

MIDLAND, MICH.

[CONTRIBUTION FROM THE E. C. BRITTON RESEARCH LABORATORY OF THE DOW CHEMICAL COMPANY]

## Aromatic Phosphorodichloridites and Phosphorodichloridothioates. III. Structure and Physical Properties

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The refractive and vapor pressure data of *O*-aryl phosphorodichloridites and *O*-aryl phosphorodichloridothioates were investigated.

The availability of a series of aryl phosphorodichloridites<sup>1</sup> and phosphorodichloridothioates<sup>2</sup> of sufficient purity made it possible to study some relationships between their structure and certain physical properties. The investigation described in the following concerned refractive and vapor pressure data.

**Molecular refraction.** Some extensive studies on refractivities of organic phosphorus compounds have been carried out.<sup>3,4</sup> Since then the *atomic refractions* determined by Kabachnik<sup>4</sup> were found to be the most accurate ones, they were employed in the calculation of the molecular refraction of phosphorodichloridites and phosphorodichloridothioates (*cf.* Table I).

Aryl phosphorodichloridites were found to show an average deviation of 0.25 cc./mole of the theoretical values from the experimental molecular refractions. The calculation of the theoretical refractions of aryl phosphorodichloridothioates was made on the basis of two different values<sup>5,6</sup> for the atomic refraction of sulfur in the P=S group. It was found that the experimental values of the molecular refraction were about 0.2 cc./mole lower than the theoretical values, based upon Vogel's sulfur value of 10.23 (*cf.* Table I) and about 0.33 cc./mole higher than those theoretical values as calculated from Kabachnik's value of 9.7.

It is well known that the atomic refraction of phosphorus is not constant but varies with the structure of its organic compounds. Even for a given type of compound, containing direct C—P

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TABLE I  
MOLECULAR REFRACTIONS

Type of Compound	Aryl	MR Found	MR Calculated from		
			Atomic refr.	Bond refr.	
ArylOPCl <sub>2</sub>	$\text{C}_6\text{H}_5$	46.49	46.57	46.67	
	<i>m</i> - $\text{C}_2\text{H}_5$ - $\text{C}_6\text{H}_4$	56.22	55.81	55.97	
	2-Cl- $\text{C}_6\text{H}_4$	51.52	51.54	51.59	
	4-Cl- $\text{C}_6\text{H}_4$	51.52	51.54	51.59	
	2-Cl-4- <i>t</i> - $\text{C}_6\text{H}_3$ - $\text{C}_6\text{H}_5$	70.78	70.01	70.19	
	2-Br-4- <i>t</i> - $\text{C}_6\text{H}_3$ - $\text{C}_6\text{H}_5$	73.55	72.81	72.98	
	2,4-Cl <sub>2</sub> - $\text{C}_6\text{H}_3$	56.59	56.51	56.52	
	2,5-Cl <sub>2</sub> - $\text{C}_6\text{H}_3$	56.58	56.51	56.52	
	3,4-Cl <sub>2</sub> - $\text{C}_6\text{H}_3$	56.55	56.51	56.52	
	2,4,5-Cl <sub>3</sub> - $\text{C}_6\text{H}_2$	61.70	61.47	61.44	
	2,4,6-Cl <sub>3</sub> - $\text{C}_6\text{H}_2$	61.72	61.47	61.44	
S    ArylOPCl <sub>2</sub>	$\text{C}_6\text{H}_5$	53.14	53.51	53.12	
	<i>m</i> - $\text{C}_2\text{H}_5$ - $\text{C}_6\text{H}_4$	62.65	62.75	62.42	
	2-Cl- $\text{C}_6\text{H}_4$	58.33	58.48	58.04	
	4-Cl- $\text{C}_6\text{H}_4$	58.32	58.48	58.04	
	2,4-Cl <sub>2</sub> - $\text{C}_6\text{H}_3$	63.28	63.45	62.97	
	2,5-Cl <sub>2</sub> - $\text{C}_6\text{H}_3$	63.18	63.45	62.97	
	3,4-Cl <sub>2</sub> - $\text{C}_6\text{H}_3$	63.27	63.45	62.97	
	2,4,5-Cl <sub>3</sub> - $\text{C}_6\text{H}_2$	68.24	68.41	67.89	
		2-Cl-4-NO <sub>2</sub> - $\text{C}_6\text{H}_3$	65.84		65.94

bonds, the value for the atomic refraction of phosphorus is known to depend on the nature of the carbon atom (aliphatic or aromatic). Moreover, refraction is a property not of atoms but of bonds, fundamentally. It is desirable, therefore, to compute molecular refractions of phosphorus compounds from *P-bond refractions*. So far, three attempts at establishing systems of refractive values for phosphorus bonds have been reported.<sup>7–9</sup> They show considerable deviation in the values assigned to several P-bonds. An independent computation,

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