$OPCl_2$ plus 69 g. of phosphorus trichloride plus 318 g. of 2-Cl-4-*t*-C_4H_9·$C_6H_3OPSCl_2$ 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 $C_{10}H_{12}Cl_3OPS$: S, 10.09. Found: S, 10.2.

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[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[1] and phosphorodichloridothioates[2] 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.[3,4] Since then the *atomic refractions* determined by Kabachnik[4] 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).

TABLE I

MOLECULAR REFRACTIONS

Type of Compound	Aryl	MR Found	MR Calculated from Atomic refr.	MR Calculated from Bond refr.
Aryl$OPCl_2$	C_6H_5	46.49	46.57	46.67
	m-C_2H_5—C_6H_2	56.22	55.81	55.97
	2-Cl—C_6H_4	51.52	51.54	51.59
	4-Cl—C_6H_4	51.52	51.54	51.59
	2-Cl-4-*t*-C_4H_9—C_6H_3	70.78	70.01	70.19
	2-Br-4-*t*-C_4H_9—C_6H_3	73.55	72.81	72.98
	2,4-Cl_2—C_6H_3	56.59	56.51	56.52
	2,5-Cl_2—C_6H_3	56.58	56.51	56.52
	3,4-Cl_2—C_6H_3	56.55	56.51	56.52
	2,4,5-Cl_3—C_6H_2	61.70	61.47	61.44
	2,4,6-Cl_3—C_6H_2	61.72	61.47	61.44
$\overset{S}{\overset{\Vert}{\text{Aryl}OPCl_2}}$	C_6H_5	53.14	53.51	53.12
	m-C_2H_5—C_6H_4	62.65	62.75	62.42
	2-Cl—C_6H_4	58.33	58.48	58.04
	4-Cl—C_6H_4	58.32	58.48	58.04
	2,4-Cl_2—C_6H_4	63.28	63.45	62.97
	2,5-Cl_2—C_6H_3	63.18	63.45	62.97
	3,4-Cl_2—C_6H_3	63.27	63.45	62.97
	2,4,5-Cl_2—C_6H_2	68.24	68.41	67.89
	2-Cl—4-NO_2—C_6H_3	65.84		65.94

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[5,6] 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 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.[7-9] They show considerable deviation in the values assigned to several P-bonds. An independent computation,

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(5) M. I. Kabachnik, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk,* 163 (1953).

(6) P. W. Vogel, Abstracts of the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 16, 1952, page 42m.

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(9) F. Feher and A. Blumcke, *Chem. Ber.*, **90,** 1934 (1957)

carried out in connection with investigations described in this paper, gave the following tentative values for refraction of phosphorus bonds: P—O (ester bond) 3.15, P-Cl 8.75 and P=S 6.45. These data in combination with the values for carbon bond refractions found by A. I. Vogel,[10] permitted calculation of theoretical molecular refractions of phosphorodichloridites and phosphorodichloridothioates on the basis of bond refractions. It was found (*cf.* Table I) that the data for experimental and theoretical molecular refractions of both groups of compounds showed an average deviation of 0.22 cc./mole.

Vapor pressure. The literature was found to contain very little on relationships of vapor pressure with structure of organic phosphorus compounds. Stull[11] had reported on the vapor pressure of some aryl phosphates and Kosolapoff[12] had investigated aliphatic phosphonates. For the purpose of the present investigation, the boiling points of five phenyl phosphorodichloridites and five phenyl phosphorodichloridothioates were measured under reduced pressure (*cf.* Table II).

TABLE II

BOILING POINTS OF PHOSPHORODICHLORIDITES AND PHOSPHORODICHLORIDOTHIOATES

[Pressure (p) in Mm. Hg; Temperature (t) in °C.]

	C_6H_5		2-Cl—C_6H_4—		4-Cl—C_6H_4—		2,4-$Cl_2C_6H_3$—		2,4,5-$Cl_3C_6H_2$—	
Aryl	*p*	*t*	*p*	*t*	*p*	*t*	*p*	*t*	*p*	*t*
$ArOPCl_2$	29.4	117.1	29.6	137.5	29.6	139.6	29.3	160.3	27.2	178.8
	33.1	122.3	32.9	142.0	33.0	144.2	33.2	164.0	32.2	184.1
	51.6	134.9	51.5	154.7	51.8	157.2	51.6	177.9	50.8	198.6
	92.3	151.9	92.1	172.3	92.3	174.6	91.9	195.7	90.2	216.2
	189.5	176.6	189.6	196.9	189.4	198.6	190.0	220.0	189.3	239.3
$ArOPSCl_2$	25.6	136.4	29.6	161.8	29.3	169.1	28.2	178.3	32.6	201.1
	33.9	144.3	32.9	166.0	33.0	174.2	33.6	184.9	33.4	205.0
	51.6	157.4	50.7	179.3	50.9	187.8	51.9	201.6	51.8	219.5
	90.2	174.6	91.7	196.8	91.9	205.9	91.9	218.7	92.1	239.0
	189.9	199.5	189.4	222.5	189.6	230.8	190.0	244.2	190.1	265.7

Thomson[13] had found that the Antoine equation, $\log_{10} p = A - B/(t + C)$, gives sufficiently accurate data for vapor pressure–temperature relationships and is less complicated in its application than the Henglein equation. Moreover, Antoine's equation was found to be useful over a wider pressure-temperature range than the commonly used equation, $\log p = A - B/T$. Antoine's equation requires a determination of three constants, A, B, and C, for each of the ten compounds investigated by us. Calculation of C was done on the basis of Thomson's relation by using the data of three experimentally determined boiling points of each compound.

$$\frac{t_3 - t_1}{t_3 + C} = 1 - \frac{\log p_3 - \log p_2}{\log p_2 - \log p_1} \cdot \frac{t_2 - t_1}{t_3 - t_2} \quad \begin{matrix}(t \text{ in } ^\circ\text{Cels.})\\(p \text{ in mm. Hg})\end{matrix}$$

The C-values thus obtained (*cf.* Table III) permitted calculation of the B-constants according to[13]

$$B = \frac{\log p_3 - \log p_1}{t_3 - t_1} \cdot (t_1 + C)(t_3 + C)$$

Finally, the A-values were calculated on the basis of the Antoine equation itself. It was found that the B-values of all compounds investigated actually were a constant; its value was 2336.25. All of the A-values also were found to be a constant whose figure was 7.5622.

To check the reliability of the values determined for A, B, and C, a series of boiling pionts at reduced pressure were calculated on the basis of the Antoine equation and compared with the experimental boiling point data published previously for some of the compounds investigated. The results of this comparison were those given in the Tables IV and V.

For interpretation of the data in the Tables IV and V, all data with a difference of not more than 2° between experimental theoretical boiling points were considered to be in agreement.

TABLE III

INDIVIDUAL C-VALUES

Aryl	Aryl-$OPCl_2$	Aryl-$OPSCl_2$
C_6H_5—	266	241
2-Cl—C_6H_4—	246	222
4-Cl—C_6H_4	244	214
2,4-Cl_2—C_6H_3	222	197
2,4,5-Cl_3—C_6H_2—	202	180

In a total of thirty-two comparisons a satisfactory agreement was found in twenty-five cases and a moderate agreement in four cases. A clear discrepancy between calculated boiling points and experimental data reported in the literature was found in only three cases. These cases concerned the boiling point reported by Strecker[17] for *p*-

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(12) G. M. Kosolapoff, *J. Chem. Soc.*, 2964 (1955).

(13) G. W. Thomson, *Chem. Revs.*, **38**, 1 (1946).

TABLE IV

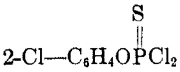
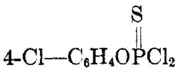
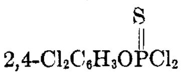
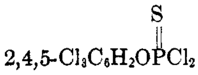
BOILING POINTS OF PHOSPHORODICHLORIDITES

Pressure		10 Mm., °C.	11 Mm., °C.	12 Mm., °C.	13 Mm., °C.	190 Mm., °C.
$C_6H_5OPCl_2$	Calcd.	90	92.3			176.2
	Obsd.	90[1]	90–92[14,15]			177[a]
2-Cl—$C_6H_4OPCl_2$	Calcd.	110			116.3	196.2
	Obsd.	111–112[1]			116–120[16]	197[a]
4-Cl—$C_6H_4OPCl_2$	Calcd.	112		116.4		198.2
	Obsd.	113–113.5[1]		118–120[15] 128–130[17]		199[a]
2,4-Cl_2—$C_6H_3OPCl_2$	Calcd.	134				220.2
	Obsd.	134[1]				220[a]
2,4,5-Cl_3—$C_6H_2OPCl_2$	Calcd.	154				240.2
	Obsd.	154–155[1]				240[a]

[a] Cf. Table II.

TABLE V

BOILING POINTS OF PHOSPHORODICHLORIDOTHIOATES

Pressure		2 Mm., °C.	4 Mm., °C.	10 Mm., °C.	11 Mm., °C.	15 Mm., °C.	16 Mm., °C.	22 Mm., °C.	190 Mm., °C.
 $C_6H_5O\overset{S}{\overset{\|}{P}}Cl_2$	Calcd.			115	117.3	124.8	126.5	134.6	201.2
	Obsd.			116[2]	119–120[18]	133–135[19]	132[19]	133[20,21]	199.8
 2-Cl—$C_6H_4O\overset{S}{\overset{\|}{P}}Cl_2$	Calcd.			134					220.2
	Obsd.			134[2]					223.1[a]
 4-Cl—$C_6H_4O\overset{S}{\overset{\|}{P}}Cl_2$	Calcd.		121.7	142	144.3				228.2
	Obsd.		125[22]	141[2]	143–145[17]				231.1[a]
 2,4-$Cl_2C_6H_3O\overset{S}{\overset{\|}{P}}Cl_2$	Calcd.	124.7		159					245.2
	Obsd.	126–128[22]		158[2]					244.2[a]
 2,4,5-$Cl_3C_6H_2O\overset{S}{\overset{\|}{P}}Cl_2$	Calcd.			176					263.2
	Obsd.			175[2]					265.4[a]

[a] *Cf.* Table II.

TABLE VI

C-VALUES OF PHOSPHORODICHLORIDATES

2-Cl—$C_6H_4OPOCl_2$	4-Cl—$C_6H_4OPOCl_2$	2,4-Cl_2—$C_6H_3OPOCl_2$	2,4,5-Cl_3—$C_6H_2OPOCl_2$
225	221	208	188

chlorophenyl phosphorodichloridite (Table IV) and the boiling points reported by Autenrieth[19] for phenyl phosphorodichloridothioate (Table V). In view of the agreement found in the high majority of comparisons, it appeared possible that these three boiling points were actually inaccurate.

It was concluded that boiling points at pressures of 5 to 200 mm. of chlorinated phenyl phosphorodichloridites and phosphorodichloridothioates could be calculated with practically acceptable accuracy from the following simplified Antoine equation (by using the C-values given in Table III):

$$t(°C.) = \frac{2336.25}{7.5622 - \log_{10} P} - C$$

An application of this finding to a series of aryl phosphorodichloridates showed that it was not possible to calculate the correct boiling points of *p-tert*-butylphenyl phosphorodichloridate and biphenylyl phosphorodichloridate from the same equation. It was found, however, that fairly correct boiling points of some chlorinated phenyl phosphorodichloridates could be calculated if the following individual C-values were used (*cf.* Table VI).

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