The Chemistry of Tetraalkyl Bi(phosphine Sulfides). I. A Novel Synthesis of Phosphinic Chlorides[1a]

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Tetraalkyl bi(phosphine sulfides) react vigorously with thionyl chloride to form dialkylphosphinic chlorides in excellent yields. Dialkylphosphinothioic chlorides are also efficiently converted to dialkylphosphinic chlorides by thionyl chloride. The scope of sulfur–oxygen exchange reactions between thionyl chloride and other thiophosphoryl derivatives was investigated.

Since 1950, a number of convenient and efficient procedures have been developed for the synthesis of organophosphorus compounds which contain several carbon-phosphorus bonds. Many recent developments in this area are a result of the discovery of Kabachnik and Shepeleva,[2] in 1949, that thiophosphoryl chloride reacts with excess methylmagnesium bromide to yield tetramethyl bi(phosphine sulfide). This novel reaction was deemed anomalous until three groups[3–6] simultaneously reported other bi(phosphine sulfide) derivatives prepared by the Kabachnik-Shepeleva procedure. Subsequently, Maier[7] described the preparation of *meso* and racemic forms of mixed tetrasubstituted bi(phosphine sulfides), by treating methylphosphonothioic dibromide with Grignard reagents. These workers and others[8–10] have shown that bi(phosphine sulfides) are remarkably versatile intermediates for the preparation of dialkyl substituted organophosphorus compounds in high yield.

The present communication describes the preparation of phosphinic chlorides by the reaction of tetrasubstituted bi(phosphine sulfides) with thionyl chloride.[12] It was found that tetramethyl bi(phosphine sulfide), tetraethyl bi(phosphine sulfide), and tetrabutyl bi(phosphine sulfide) react at 10–30° with thionyl chloride to yield dimethylphosphinic chloride, diethylphosphinic chloride, and dibutylphosphinic chloride in 83, 78, and 70% yields, respectively. Approximately two moles of sulfur are formed in the reaction per mole of bi(phosphine sulfide) used. Sulfur monochloride was also shown to be a product of the reaction but the relative amount formed was not determined. Although Maier[7] originally reported that sulfur dichloride and larger quantities of sulfur are products of the reaction, his later paper formulates the reaction as we previously described it.

The reaction may, therefore, be formulated according to the following general equation.

$$R_2\overset{\overset{S}{\|}}{P}-\overset{\overset{S}{\|}}{P}R_2 + 2SOCl_2 \longrightarrow 2R_2\overset{\overset{O}{\|}}{P}-Cl + 2S + S_2Cl_2$$

The reaction of tetrasubstituted bi(phosphine sulfides) with thionyl chloride provides a route to the lower disubstituted phosphinic chlorides which compares favorably with previous methods.[5,8,13–16] Since tetramethyl bi(phosphine sulfide) and tetraethyl bi(phosphine sulfide) are prepared in about 90% yield, the over-all yields of the corresponding phosphinic chlorides, starting from thiophosphoryl chloride and Grignard reagent, are above 70%. Although a high yield of dibutylphosphinic chloride was obtained from the reaction of tetrabutyl bi(phosphine sulfide) with thionyl chloride, the over-all yield of the phosphinic chloride, based on thiophosphoryl chloride, was quite low—a result of the low yields encountered in the preparation of tetrabutyl bi(phosphine sulfide). However, when a crude thiophosphoryl chloride—butylmagnesium chloride reaction mixture was treated directly with thionyl chloride, the over-all yield of dibutylphosphinic chloride obtained, based on thiophosphoryl chloride, was 63%. The by-products[17] formed during the preparation of bi(phosphine sulfide) derivatives must therefore also be con-

(1) (a) Presented in part before the Division of Organic Chemistry at the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959; (b) present address: University of Akron, Akron, Ohio.

(2) M. I. Kabachnik and E. S. Shepeleva, *Izv. Akad. Nauk SSSR., Otd. Khim. Nauk*, 56 (1949).

(3) W. Kuchen and H. Buchwald, *Angew. Chem.*, **71**, 162 (1959).

(4) W. Kuchen, H. Buchwald, K. Strolenberg, and J. Metten, *Ann.*, **652**, 28 (1962).

(5) P. J. Christen, L. M. Van der Linde, and F. N. Hooge, *Rec. trav. chim.*, **78**, 161, 543 (1959).

(6) K. Issleib and A. Tzschach, *Chem. Ber.*, **92**, 704 (1959).

(7) L. Maier, *Angew. Chem.*, **71**, 575 (1959); *Chem. Ber.*, **94**, 3043, 3051, 3056 (1961).

(8) H. Niebergall, *Angew. Chem.*, **72**, 210 (1960).

(9) H. Niebergall and B. Lagenfeld, *Chem. Ber.*, **95**, 64 (1962).

(10) We have observed that careful chlorination of tetramethyl bi(phosphine sulfide) gave results similar to those reported for bromination (see Experimental). This is in contrast to the findings of Reinhardt and co-workers,[11] who reported that chlorination of tetramethyl bi(phosphine sulfide) gave a mixture of the highly chlorinated products, methylphosphorus tetrachloride and bis(trichloromethyl)-phosphorus trichloride.

(11) H. Reinhardt, D. Bianchi, and D. Molle, *Chem. Ber.*, **90**, 1656 (1957).

(12) After a private communication from us, Maier[7] examined the reaction of thionyl chloride with his unsymmetrical bi(phosphine sulfides). Several other examples of the conversion of bi(phosphine sulfides) to phosphinic chlorides are therefore to be found in his publications.

(13) G. M. Kosolapoff and R. M. Watson, *J. Am. Chem. Soc.*, **73**, 5466 (1951).

(14) G. M. Kosolapoff, "Organophosphorus Compounds," J. Wiley & Sons, Inc., New York, N. Y., 1950, p. 73.

(15) T. P. Dawson and K. C. Kennard, *J. Org. Chem.*, **22**, 1671 (1957).

(16) P. C. Crofts and I. S. Fox, *J. Chem. Soc.*, 2995 (1958).

vertible to phosphinic chlorides by treatment with thionyl chloride.

It was subsequently found that dimethylphosphinothioic chloride readily reacts with thionyl chloride to form dimethylphosphinic chloride in a yield comparable to that obtained from the tetramethyl bi(phosphine sulfide)–thionyl chloride reaction. This finding, as will be discussed later, suggested that the phosphinothioic chloride might be an intermediate in the bi(phosphine sulfide)–thionyl chloride reactions. The observation of a smooth sulfur–oxygen exchange between dimethylphosphinothioic chloride and thionyl chloride led to an investigation of the scope of such reactions. It was found, see Table I, that thiophosphorus

TABLE I

INFLUENCE OF STRUCTURE ON THE REACTION

$$RR'R''PS + SOCl_2 \longrightarrow RR'R''PO + \ldots\ldots$$

Reactant[a]	Time, hr.	Temp., °C.	Products	Yield, %
$(C_6H_5)_3PS$	1	25	$(C_6H_5)_3PO$[b]	69
			$(C_6H_5)_3PCl_2$	25[c]
$(CH_3)_2C_6H_5PS$	1	80	$(CH_3)_2C_6H_5PCl_2$[b]	85[c]
$(CH_3)_2\overset{S}{\overset{\|}{P}}Cl$	1.5	80	$(CH_3)_2\overset{O}{\overset{\|}{P}}Cl$	87
$(C_2H_5)C_6H_5\overset{S}{\overset{\|}{P}}Cl$	3	23	No reaction	
$(C_2H_5)C_6H_5\overset{S}{\overset{\|}{P}}Cl$	1.5	80	$(C_2H_5)C_6H_5\overset{O}{\overset{\|}{P}}Cl$	16[d]
$(C_2H_5)C_6H_5\overset{S}{\overset{\|}{P}}SH$	4	80	$(C_2H_5)C_6H_5\overset{O}{\overset{\|}{P}}Cl$	61
			$(C_2H_5)C_6H_5\overset{S}{\overset{\|}{P}}Cl$	22
$(C_6H_5)_2\overset{S}{\overset{\|}{P}}SH$	4	80	$(C_6H_5)_2\overset{O}{\overset{\|}{P}}Cl$	54
			$(C_6H_5)_2\overset{S}{\overset{\|}{P}}Cl$	34
$C_6H_5\overset{S}{\overset{\|}{P}}Cl_2$	2	80	No reaction	
$C_6H_5\overset{S}{\overset{\|}{P}}Cl_2$	8	80	$C_6H_5\overset{O}{\overset{\|}{P}}Cl_2$	24[e]
$PSCl_3$	10	80	No reaction	

[a] Excess thionyl chloride was used in all cases except triphenylphosphine sulfide. [b] See ref. 18. [c] Shown to result from a secondary reaction of the P=O + $SOCl_2$ or S_2Cl_2. [d] Conversion, 71% of the starting material was recovered. [e] Conversion, 70% of the starting material was recovered.

compounds containing electron releasing or weakly electronegative groups readily react with thionyl chloride to exchange sulfur for oxygen, whereas compounds containing strongly electron attracting groups exchange very slowly or not at all. The influence of structure on the course of the exchange reaction is dramatically illustrated by the three thiophosphinic derivatives ($RR'P\overset{S}{\overset{\|}{X}}$, where X = Cl or SH) appearing in Table I. While dimethylphosphinothioic chloride reacts readily with thionyl chloride, the ethylphenyl derivative does not react at all at 23° and undergoes only 16% conversion after 1.5 hr. at 80°. Similarly, ethylphenylphosphinodithioic acid undergoes 61% exchange after four hours at 80° while the diphenyl derivative is only 54% converted under identical conditions.[19] The influence of structure is further illustrated in that phenylphosphonothioic dichloride undergoes only 24% of the exchange reaction after eight hours at 80° and thiophosphoryl chloride does not react at all. Thus, the replacement of an alkyl group by an electronegative substituent, such as a phenyl group or a halogen, markedly decreases the reactivity of the phosphorus derivative toward the sulfur-oxygen exchange reaction. Similar results were obtained by Groenweghe and Payne[21] in their studies on equilibria involving phosphoryl and thiophosphoryl compounds.

The reaction of tertiary phosphine sulfides with excess thionyl chloride yields trisubstituted phosphine dichlorides instead of (or in addition to) the corresponding phosphine oxides, as is indicated in Table I. Presumably, phosphine oxide derivatives are formed initially in the reaction and are subsequently converted to the dichloride by excess thionyl chloride.[22] This was further shown by treating triphenylphosphine oxide with thionyl chloride to obtain a quantitative yield of the dichloride in less than one-half hour at 80°. The ability of thionyl chloride to convert trisubstituted phosphine sulfides to phosphine oxide derivatives has been used in a general scheme for preparing unsymmetrical phosphine oxides, as will be discussed in a subsequent paper.[18]

The stoichiometry of the reaction of tetrasubstituted bi(phosphine sulfides) with thionyl chloride could be satisfied by either of the following sequences:

(17) It is interesting at this point to note that Christen, *et al.*,[5] were able to obtain dibutylphosphinic chloride in 55% yield (based on thiophosphoryl chloride) by oxidizing the crude thiophosphoryl chloride–butylmagnesium bromide reaction residue with nitric acid and then treating the crude phosphinic acid with phosphorus pentachloride.

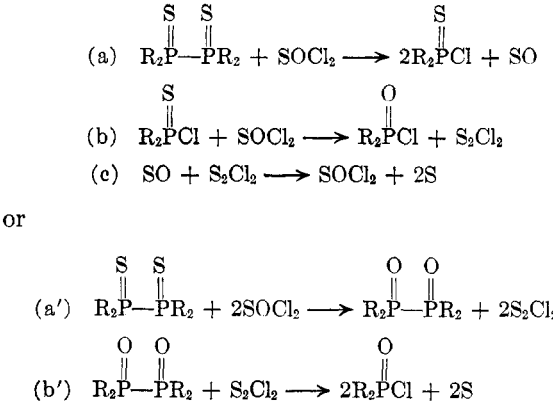
(18) H. J. Harwood and K. A. Pollart, to be published.

(19) A reviewer has suggested that the small difference between the conversions obtained in these two experiments may not be experimentally significant. In these experiments, the phosphinic chloride and the phosphinothioic chloride were collectively distilled from the reaction mixture. The relative quantities of the two materials in the distillate were then determined by n.m.r. This latter determination was probably reliable to ±1%. The distillates accounted for 83 and 88% of the starting phosphorus compounds in the ethylphenyl and the diphenyl reactions, respectively. These yields and the relative volatilities[20] of the products $(C_6H_5(Et)P\overset{S}{\overset{\|}{Cl}} > C_6H_5(Et)P\overset{O}{\overset{\|}{Cl}}$; $(C_6H_5)_2P\overset{S}{\overset{\|}{Cl}} > (C_6H_5)_2P\overset{O}{\overset{\|}{Cl}})$ are such that incomplete recovery of products would have reduced the difference between the observed extents of exchange, rather than magnify it.

(20) Ref. 14, pp. 74–75.

(21) L. C. D. Groenweghe and J. H. Payne, *J. Am. Chem. Soc.*, 83 1811 (1961).

(22) Ref. 14, pp. 59, 60.

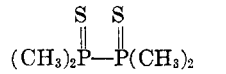
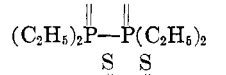
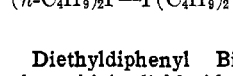


or

However, it is believed that the a,b,c route is the correct one since treatment of the asymmetrical diethyldiphenyl bi(phosphine sulfide) with thionyl chloride under controlled conditions (3 hr. at 23°) gave a 93% yield of ethylphenylphosphinothioic chloride. Under somewhat more vigorous conditions (80°) this latter material underwent sulfur–oxygen interchange to form the phosphinic chloride. Thus, this clearly demonstrates that the initial step is cleavage of the phosphorous-to-phosphorus bond rather than the sulfur–oxygen interchange.

Experimental

Synthesis of Bi(phosphine Sulfides).—The following tetraalkyl bi(phosphine sulfides), the preparations of which are now in the literature,[5] were prepared by the addition of $PSCl_3$ (in ether) to slightly more than three equivalents of the appropriate Grignard reagent at 2–8°. The products were recrystallized from alcohol or hydrocarbon solvents.

Product	Yield	M.p., °C.	M.p. (lit.,[5]) °C.
	87%	221–223	215–221
	91%	78–78.5	76
	40%	74.5–75	73–73.5

Diethyldiphenyl Bi(phosphine Sulfide).—Phenylphosphonothioic dichloride (0.5 mole) in 500 ml. of ether was added dropwise during 3.5 hr. to 1.5 moles of 3 *M* ethylmagnesium bromide in ether while the reaction temperature was maintained below 10°. After the addition was complete the reaction mixture was allowed to warm to room temperature and finally refluxed 4 hr. The reaction mixture was hydrolyzed by pouring into an ice–dilute sulfuric acid mixture. After sufficient ether had been added to dissolve all of the precipitate, the ether layer was separated, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The resulting crude product was triturated with cold hexane and solid A was collected. After the hexane was removed from the filtrate under reduced pressure, the resulting oil was triturated with two volumes of cold methanol and solid B was collected. After removal of the methanol from the filtrate, 33 g. of oil remained, but no further attempt was made to isolate more pure product from this oil.

Recrystallization of solid A from ethanol gave 10 g. of a product, m.p. 156–157°. Recrystallization of solid B from methanol gave 24.5 g. of a product, m.p. 85–87°. Treatment of either product A or B with chlorine (see later Experimental) gave ethylphenylphosphinothioic chloride and a mixture of A and B gave the following analysis.

Anal. Calcd. for $C_{16}H_{20}P_2S_2$: C, 56.80; H, 5.96; S, 18.95. Found: C, 57.04; H, 5.96; S, 18.89.

Thus, based upon the worked of L. Maier,[7] product A is considered to be *meso*-diethyldiphenyl bi(phosphine sulfide) and product B is considered to be racemic diethyldiphenyl bi(phosphine sulfide).

Dimethylphosphinothioic Chloride.—A solution of chlorine (0.1 mole) in 100 ml. of carbon tetrachloride was added dropwise to a stirred mixture of tetramethyl bi(phosphine sulfide) (0.1 mole) in 150 ml. of carbon tetrachloride at room temperature. After stirring for 6 hr., the mixture was distilled to yield 0.167 mole (84% yield) of the desired product, b.p. 76–78°/15 mm., m.p. approximately 25°. Reported b.p. 82–83°/16 mm.[23]

Ethylphenylphosphinothioic Chloride.—A solution of chlorine (0.044 mole) in 50 ml. of carbon tetrachloride was added dropwise to a stirred solution of racemic diethyldiphenyl bi(phosphine sulfide) (0.04 mole) and 25 ml. of carbon tetrachloride while the temperature was maintained below 10°. After the addition was complete, the mixture was stirred for 2 hr. at room temperature and then distilled under reduced pressure to yield 15 g. (90% yield) of the desired phosphinothioic chloride b.p. 100–103°/0.1 mm. Reported b.p. 175–190°/15 mm.[24]

The reaction was repeated with *meso*-diethyldiphenyl bi(phosphine sulfide) and the same product was obtained in 85% yield.

Dimethylphosphinic Chloride.—A suspension of tetramethyl bi(phosphine sulfide), 8.0 g. (0.043 mole) in 35 ml. benzene was chilled in an ice bath. Thionyl chloride, 15 ml. (0.208 mole) was slowly added to the suspension with shaking during 5 min. A reddish yellow color developed as the solid began to go into solution. After about one-third of the solid had dissolved, the ice bath was removed. Gas evolution became vigorous, and a clear solution was obtained. On cooling, a yellow emulsion formed. The mixture was refluxed for 45 min. Benzene and excess thionyl chloride were removed *in vacuo*, leaving a light yellow solid. When the bath was raised to 66°, the solid melted and an immiscible mixture was obtained. Further distillation yielded a small forerun of sulfur monochloride, b.p. 53–55°/35 mm., $n^{25}D$ 1.649, followed by dimethylphosphinic chloride, 8.3 g. (83.4%) b.p. 110–113°/35 mm., m.p. 66.5–68.4° [lit. b.p. 204°,[25] m.p. 66.8–68.4°[2]]. The distillation residue was extracted with 5% sodium hydroxide and washed with water, ethanol, and ether to yield 2.86 g. (0.089 mole) of sulfur, m.p. 118.5–120.0°.

Diethylphosphinic Chloride.—A solution of tetraethyl bi(phosphine sulfide), 10 g. (0.041 mole) in 50 ml. benzene was chilled in an ice bath, while thionyl chloride, 12 ml. (0.166 mole) was slowly added dropwise. A reddish orange color developed as thionyl chloride contacted the solution. After a few seconds, the solution became light yellow, and a gas began to escape. Addition of fresh thionyl chloride caused the reappearance of the red color which quickly disappeared. After the addition was completed, the mixture was stirred 6 hr. at room temperature. Benzene and excess thionyl chloride were then removed under reduced pressure, leaving a mixture of immiscible liquids. Continued distillation yielded sulfur monochloride, 0.9 g., b.p. 65–80°/35 mm., $n^{25}D$ 1.6183.

The undistilled mixture then was cooled, and the lower phase solidified. This was shown to be sulfur, 1.8 g. (0.056 mole), m.p. 107–113.° The liquid phase was separated and distilled to yield diethylphosphinic chloride, 9.0 g. (78%),

(23) S. Z. Ivin and K. V. Karavanov, *J. Gen. Chem. USSR* (Eng. Trans.), **28**, 2988 (1958).

(24) V. Plets, Dissertation, Kazan, 1938; see ref. 14, p. 75.

(25) A. W. Hofmann, *Ber.*, **6**, 303 (1873).

b.p. 62.5–64.5°/0.7 mm., $n^{25}D$ 1.4650 [lit. b.p. 108–109.5°/16 mm., $n^{20}D$ 1.4647[26]]. The product gave a negative sodium fusion test for sulfur.

Dibutylphosphinic Chloride.—A solution of thionyl chloride (9.5 g., 0.08 mole) in 20 ml. of hexane was added dropwise to a stirred solution of tetrabutyl bi(phosphine sulfide) (7.1 g., 0.02 mole) in 40 ml. of hexane while the temperature was maintained below 15°. The reaction mixture changed from colorless to dark yellow as the reaction proceeded and sulfur precipitated from solution. After the addition was complete, the mixture was refluxed for 1 hr. and distilled under reduced pressure to give 5.5 g. (70% yield) of the desired product, b.p. 95–100°/0.5 mm. Reported b.p. 85°/0.2 mm.[5]

Hydrolysis of a portion of this product with hot water gave dibutylphosphinic acid, m.p. 70° (from hexane). Reported m.p. 71°[27].

The above reaction was repeated using 2.5 moles of thionyl chloride in 400 ml. of benzene and the crude reaction product obtained from 0.7 mole of thiophosphoryl chloride and 2.4 moles of butylmagnesium chloride in 300 ml. of benzene. Distillation of the reaction mixture gave 0.44 mole of dibutylphosphinic chloride, b.p. 124–128°/4.5 mm. This is a 63% yield based upon the thiophosphoryl chloride used. Hydrolysis of a portion of this product also gave dibutylphosphinic acid, m.p. 69–70°.

Reaction of 1,2-Diethyl-1,2-diphenyl Bi(phosphine Sulfide) with Thionyl Chloride.—Thionyl chloride (0.10 mole) in 20 ml. of benzene was added dropwise to a stirred solution of 1,2-diethyl-1,2-diphenyl bi(phosphine sulfide) (0.02 mole) in 32 ml. of benzene. The mildly exothermic reaction was maintained at 23° for 3 hr. The solvent and other low boiling materials were removed at or below 23° using a rotary vacuum evaporator. The residue was distilled to yield 7.5 g. of product, b.p. 102–108°/0.2 mm. This was shown to be pure ethylphenylphosphinothioic chloride (93% yield) by n.m.r. and elemental analysis. The chemical shift observed for this material, relative to phosphoric acid, was −93.7 p.p.m.

Anal. Calcd. for $C_8H_{10}ClPS$: Cl, 17.32; S, 15.67. Found: Cl, 17.27; S, 15.64.

Reaction of Dimethylphosphinothioic Chloride with Thionyl Chloride.—Thionyl chloride 15 ml. (0.208 mole) was added with shaking to a chilled solution of dimethylphosphinothioic chloride, 12.1 g. (0.094 mole) in 15 ml. benzene. In contrast to the behavior of bi(phosphine sulfide) derivatives with thionyl chloride, the addition was mild and took place without color formation or gas evolution. The mixture became light yellow after refluxing for 1.5 hr. It was concentrated on the water bath *in vacuo* to a two-phase mixture. Further distillation yielded sulfur monochloride, 3.4 g. (26.5%), b.p. 60–70°/42 mm., $n^{25}D$ 1.584, and dimethylphosphinic chloride, 9.2 g. (86.7%), b.p. 107–111°/35 mm., m.p. 70–72°. Reported b.p. 204–205°, m.p. 64–66°.[11]

The dark distillation residue on treatment with 5% sodium hydroxide followed by washing with water, ethanol, and ether yielded 1.61 g. (0.050 mole) sulfur, m.p. 107–110°.

Reaction of Ethylphenylphosphinothioic Chloride with Thionyl Chloride.—Thionyl chloride (0.05 mole) in 10 ml. of benzene was added dropwise to a stirred solution of ethylphenylphosphinothioic chloride (0.025 mole) in 20 ml. of benzene. The resulting mixture was stirred at 23° for 3 hr. The solvent and other low boiling materials were removed at or below 23° using a rotary vacuum evaporator. The residue was distilled, b.p. 100–107°/0.15 mm., and shown by n.m.r. to be pure recovered starting material (90% recovery). The chemical shift observed, relative to phosphoric acid, was −93.5 p.p.m.

The above reaction was repeated except that the reaction mixture was heated at 80° for 1.5 hr. Distillation gave 4.38 g. of material, b.p. 104–108°/0.5 mm., which was shown by n.m.r. to the ethylphenylphosphinic chloride (chemical shift −58.5 p.p.m.) (16% conversion) and recovered starting material (71% recovered).

Reaction of Ethylphenylphosphinodithioic Acid with Thionyl Chloride.—Thionyl chloride (0.045 mole) in 10 ml. of benzene was added dropwise to a stirred solution of the dithioic acid (0.015 mole) in 15 ml. of benzene. The reaction was mildly exothermic, and after the addition was complete the mixture was heated to 80° and maintained there for 4 hr. Distillation gave 2.42 g. of product, b.p. 112–120°/1 mm., which was shown by n.m.r. to be a mixture of ethylphenylphosphinic chloride (61% yield, chemical shift −58.7 p.p.m., H_3PO_4 reference) and ethylphenylphosphinothioic chloride (22% yield, chemical shift −94.1 p.p.m., H_3PO_4 reference.)

Reaction of Diphenylphosphinodithioic Acid with Thionyl Chloride.—The dithioic acid[28] (0.04 mole) in 20 ml. of benzene was treated with thionyl chloride (0.12 mole) in 10 ml. of benzene under conditions identical to those described above. Distillation gave 8.5 g. of product, b.p. 151–155°/0.1 mm., which was shown by n.m.r. to be 40% diphenylphosphinothioic chloride (34% yield, chemical shift −78.8 p.p.m., H_3PO_4 reference) and 60% diphenylphosphinic chloride (54% yield, chemical shift −42.6 p.p.m., H_3PO_4 reference).

Reaction of Phenylphosphonothioic Dichloride with Thionyl Chloride.—A mixture of phenylphosphonothioic dichloride (21 g., 0.1 mole) and thionyl chloride (0.12 mole) was heated at 80° for 2 hr. Distillation gave 20.5 g. of material, b.p. 73–75°/0.1 mm. N.m.r. indicated this material was unchanged starting material (chemical shift −74.8 p.p.m., H_3PO_4 reference).

The above reaction was repeated using the same molar quantities with the exception that the mixture was heated at 80° for 8 hr. Distillation gave 19.5 g. of material, b.p. 70–76°/0.1 mm. N.m.r. indicated that this material was 24% phenylphosphonic dichloride (24% yield, chemical shift −34.5 p.p.m., H_3PO_4 reference) and the remainder unreacted starting material (70% recovered).

Reaction of Thiophosphoryl Chloride with Thionyl Chloride.—A mixture of thionyl chloride (0.15 mole) and thiophosphoryl chloride (0.1 mole) was heated at 80° for 10 hr. and without distillation a sample was examined by n.m.r. It was found that no reaction had occurred (observed chemical shift of −31.0 p.p.m., but none at −1.9 p.p.m., H_3PO_4 reference).

Acknowledgment.—The authors are grateful to Messrs. W. S. Coakley and J. V. Pustinger for infrared and n.m.r. data and to Mrs. W. Harden and Mr. J. W. Johnson for elemental analyses.

(26) A. I. Razumov, O. A. Mukhacheva, and Sun Do-Khen, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 894–901 (1952); *Chem. Abstr.*, **47**, 10466.

(27) G. M. Kosolapoff and R. M. Watson, *J. Am. Chem. Soc.*, **73**, 4101 (1951).

(28) We would like to thank the Lubrizol Corp. for generously providing us with a sample of diphenylphosphinodithioic acid.