

NRL REPORT 3633

FR-3633

**ORGANOPHOSPHORUS COMPOUNDS
THE PREPARATION OF ALKYLDICHLOROPHOSPHINES**

Robert B. Fox

February 20, 1950

Approved by:

Dr. P. King, Head, High Polymers Branch
Dr. P. Borgstrom, Superintendent, Chemistry Division



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ABSTRACT

The synthesis of alkyldichlorophosphines by the reaction of dialkylcadmium compounds with phosphorus trichloride is described. A homologous series of n-alkyldichlorophosphines from ethyl- to n-octyldichlorophosphine has been prepared, and some physical properties of each compound have been determined.

PROBLEM STATUS

This is an interim report on the problem; work is continuing.

AUTHORIZATION

NRL Problem CO6-09R.
NR 406-090

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ORGANOPHOSPHORUS COMPOUNDS

THE PREPARATION OF ALKYLDICHLOROPHOSPHINES

INTRODUCTION

Although a considerable amount of synthetic and development work in the field of organophosphorus chemistry has been reported in the literature,¹ most of these papers have been concerned with aromatic derivatives. With a study of the simpler aliphatic organophosphorus molecules, the chemistry of the field should be established on a firmer basis; at the same time, a development of synthetic methods for these compounds will open up for exploitation a large class of hitherto little-known derivatives of phosphorus.

Aliphatic organophosphorus compounds have been neglected not through a lack of interest in this part of the field but through the lack of a suitable synthetic procedure for the preparation of the alkyldichlorophosphines. It is through these compounds as intermediates in various reactions that nearly all aliphatic organophosphorus derivatives must be obtained, particularly where trivalent phosphorus is involved.

The basic approach to the synthesis of alkyldichlorophosphines is, as in the case of the aromatic analogues, through a metathetical reaction in which a chlorine atom of phosphorus trichloride is replaced with an aliphatic radical:



Aromatic dichlorophosphines are usually prepared by the Michaelis modification of the Friedel-Crafts reaction,² but the reaction of phosphorus trichloride and aliphatic hydrocarbons of less than six-carbon chain length in the presence of aluminum chloride yields decomposition products, primarily red phosphorus.³

The synthesis of alkyldichlorophosphines has, however, been accomplished through the use of organometallic compounds. These methods involve dialkylmercury^{4,5,6} or tetraalkyllead⁷ derivatives. Several disadvantages attending these methods preclude their use as general procedures for obtaining alkyldichlorophosphines. Work with mercury and lead derivatives, particularly the latter, is extremely hazardous because of the high toxicity of these compounds and ease of absorption through the skin. Pure products are difficult to obtain using dialkylmercury

¹Cf. for example the literature survey on this subject matter by R. B. Fox and L. B. Lockhart, "The Chemistry of Organophosphorus Compounds," NRL Report C-3323, July 1948.

(Unclassified)

²NRL Report C-3645, "An Improved Method of Synthesis of Aryldichlorophosphines," by B. Buchner, 1950.

³Woodstock, U. S. Patent 2,137,792 (1938).

⁴Michaelis, Ber. 13, 2174 (1880).

⁵Guichard, Ber. 32, 1572 (1899).

⁶Drake and Marvel, J. Org. Chem. 2, 389 (1937).

⁷Kharasch, Jensen, and Weinhouse, J. Org. Chem. 14, 429 (1949).

derivatives because of contamination with the alkylmercuric chloride which forms in the reaction



In addition, it is necessary to run the reaction under pressure at relatively high temperatures; yields are only moderate. Tetraethyllead has been reported to give excellent yields of ethyl-dichlorophosphine;⁸ however, the hazards of the laboratory preparation of other tetraalkyllead intermediates which are not commercially available make this method an undesirable procedure.

Other more reactive organometallic compounds, such as Grignard reagents and lithium alkyls, are usually used in the synthesis of trialkylphosphines from phosphorus trichloride; no mono- or di-substituted products have been reported.

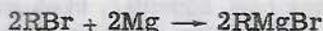
It would appear that the solution to this problem of synthesis would lie in the use of some other organometallic reagent. This reagent would necessarily be less reactive than a Grignard reagent, would have to involve a minimum of toxicity hazard, and should not yield volatile by-products in its reaction with phosphorus trichloride. An obvious suggestion presents itself through the recent work on the synthesis of ketones from acid chlorides by reaction with cadmiumdialkyls.⁹ These reagents are generally considered to have a reactivity between that of the organomercury and organomagnesium compounds, as shown by their reactions with Michler's ketone.¹⁰ Organocadmium compounds are easily prepared in the laboratory and the primary by-product from their reaction with phosphorus trichloride would be the non-volatile cadmium chloride. The expectation that these reagents would react according to



has been borne out with the preparation of all the n-alkyldichlorophosphines from two- to eight-carbon chain length. The reaction is probably a general one, yielding any alkyldichlorophosphine for which the corresponding dialkylcadmium derivative can be prepared.

GENERAL DESCRIPTION OF THE REACTION

Essentially, the reaction consists of three steps: preparation of the appropriate Grignard reagent, conversion to the corresponding organocadmium compound, and reaction of the cadmium derivative with phosphorus trichloride according to the following scheme:



The first two steps are achieved by conventional means¹¹ using diethyl ether as a solvent. In the third step, if the phosphorus trichloride is added to the cadmium derivative (which would then always be in excess), there results a mixture of mono-, di-, and tri-substituted products. However, reverse addition, i.e., addition of the cadmium compound to an excess of phosphorus trichloride, gave little evidence of reaction with more than one halogen atom; after removal of the alkyldichlorophosphine, only a very small residue of higher boiling material remained. While no systematic study to determine the optimum conditions for the reaction were carried out, it was found that the best yields of alkyldichlorophosphines were obtained by the addition of the

⁸Kharrasch, et al., *op. cit.*

⁹Cason, *Chem. Rev.* **40**, 15 (1947).

¹⁰Gilman, "Advanced Organic Chemistry," 2nd Ed., Vol. I, p. 548. Wiley and Sons, New York, 1943.

¹¹Cason, *J. Amer. Chem. Soc.* **68**, 2079 (1946), and preceding papers.

dialkylcadmium to the phosphorus trichloride at a rate consistent with maintenance of the reaction temperature in the vicinity of -20°C . After the addition, the reactions were essentially complete on refluxing the mixtures for two to three hours.

EXPERIMENTAL

Materials and Apparatus

In all phases of the synthesis, diethyl ether dried over sodium was used as a solvent. The cadmium chloride was a powdered anhydrous c.p. grade, dried an additional hour at 110°C and stored in a desiccator over calcium chloride. The alkyl bromides were redistilled commercial products. A c.p. grade of phosphorus trichloride was used without further purification.

All cadmium reactions were carried out in an atmosphere of dry nitrogen in an all-glass apparatus consisting of a three-necked round-bottom flask fitted with a Nichrome wire Hershberg stirrer, reflux condenser through which nitrogen was admitted, and a dropping funnel. By means of nitrogen pressure, the dialkylcadmium reaction mixture was added to the phosphorus trichloride through a delivery tube which replaced the dropping funnel and led to a second three-necked flask fitted in the same manner as the first but with a drying tube at the opening of the reflux condenser. Filtration of the final precipitate was carried out with sintered-glass filters of fine porosity. All distillations were performed under nitrogen in conventional equipment.

Preparation of Dialkylcadmium Compounds

The preparation of the dialkylcadmium reagents was generally carried out according to the methods of Cason,¹² except that a Gilman test was not used before adding the mixture to the phosphorus trichloride. For each compound, the only variation in procedure was in the time and temperature of the reaction between the Grignard reagent and the cadmium chloride: after the addition of the cadmium chloride to the Grignard reagent, the reaction mixture was stirred at room temperature for one hour and refluxed for one hour for the ethyl and n-propyl compounds, and stirred in an ice-bath for two hours in the case of the n-butyl and higher compounds.

Grignard reagents were prepared in the usual way from 0.5 mole of magnesium and 0.55 mole of the alkyl bromide in 550 ml. of diethyl ether. The reaction mixture was usually refluxed until most of the magnesium had been reacted, an excess of alkyl bromide being used to prevent any unreacted magnesium from clogging the delivery tube in later phases of the procedure. Conversion of the Grignard reagent to the dialkylcadmium derivative was accomplished by rapidly adding 0.275 mole of cadmium chloride to the cold (ice-bath) Grignard reagent followed by a reaction period as indicated in the preceding paragraph. This method has been used successfully in runs up to 1.0 mole; the only practical limitation is the volume of solvent necessary to give a slurry thin enough to be forced through the delivery tube in the subsequent reaction with phosphorus trichloride.

Preparation of Alkyldichlorophosphines

Since the procedure subsequent to the preparation of the dialkylcadmium was the same for all the alkyldichlorophosphines, the synthesis of n-butylidichlorophosphine will serve as an illustration of the method.

Di-n-butylcadmium was prepared by the rapid addition of 50.4 g. (0.275 mole) of cadmium chloride to the cooled solution of n-butylmagnesium bromide formed from 12.15 g. (0.5 mole) of magnesium and 75.4 g. (0.55 mole) n-butyl bromide in 550 ml. of diethyl ether. Following the addition, the mixture was stirred in an ice-bath for two hours. The di-n-butylcadmium reaction mixture, including the precipitate, was then added to a stirred solution of 85.9 g. (0.625 mole) of phosphorus trichloride in 100 ml. of ether. The phosphorus trichloride reaction mixture was

¹²J. Amer. Chem. Soc., op. cit.

dialkylcadmium to the phosphorus trichloride at a rate consistent with maintenance of the reaction temperature in the vicinity of -20°C . After the addition, the reactions were essentially complete on refluxing the mixtures for two to three hours.

EXPERIMENTAL

Materials and Apparatus

In all phases of the synthesis, diethyl ether dried over sodium was used as a solvent. The cadmium chloride was a powdered anhydrous c.p. grade, dried an additional hour at 110°C and stored in a desiccator over calcium chloride. The alkyl bromides were redistilled commercial products. A c.p. grade of phosphorus trichloride was used without further purification.

All cadmium reactions were carried out in an atmosphere of dry nitrogen in an all-glass apparatus consisting of a three-necked round-bottom flask fitted with a Nichrome wire Hershberg stirrer, reflux condenser through which nitrogen was admitted, and a dropping funnel. By means of nitrogen pressure, the dialkylcadmium reaction mixture was added to the phosphorus trichloride through a delivery tube which replaced the dropping funnel and led to a second three-necked flask fitted in the same manner as the first but with a drying tube at the opening of the reflux condenser. Filtration of the final precipitate was carried out with sintered-glass filters of fine porosity. All distillations were performed under nitrogen in conventional equipment.

Preparation of Dialkylcadmium Compounds

The preparation of the dialkylcadmium reagents was generally carried out according to the methods of Cason,¹² except that a Gilman test was not used before adding the mixture to the phosphorus trichloride. For each compound, the only variation in procedure was in the time and temperature of the reaction between the Grignard reagent and the cadmium chloride: after the addition of the cadmium chloride to the Grignard reagent, the reaction mixture was stirred at room temperature for one hour and refluxed for one hour for the ethyl and n-propyl compounds, and stirred in an ice-bath for two hours in the case of the n-butyl and higher compounds.

Grignard reagents were prepared in the usual way from 0.5 mole of magnesium and 0.55 mole of the alkyl bromide in 550 ml. of diethyl ether. The reaction mixture was usually refluxed until most of the magnesium had been reacted, an excess of alkyl bromide being used to prevent any unreacted magnesium from clogging the delivery tube in later phases of the procedure. Conversion of the Grignard reagent to the dialkylcadmium derivative was accomplished by rapidly adding 0.275 mole of cadmium chloride to the cold (ice-bath) Grignard reagent followed by a reaction period as indicated in the preceding paragraph. This method has been used successfully in runs up to 1.0 mole; the only practical limitation is the volume of solvent necessary to give a slurry thin enough to be forced through the delivery tube in the subsequent reaction with phosphorus trichloride.

Preparation of Alkylchlorophosphines

Since the procedure subsequent to the preparation of the dialkylcadmium was the same for all the alkylchlorophosphines, the synthesis of n-butyldichlorophosphine will serve as an illustration of the method.

Di-n-butyldcadmium was prepared by the rapid addition of 50.4 g. (0.275 mole) of cadmium chloride to the cooled solution of n-butyilmagnesium bromide formed from 12.15 g. (0.5 mole) of magnesium and 75.4 g. (0.55 mole) n-butyl bromide in 550 ml. of diethyl ether. Following the addition, the mixture was stirred in an ice-bath for two hours. The di-n-butyldcadmium reaction mixture, including the precipitate, was then added to a stirred solution of 85.9 g. (0.625 mole) of phosphorus trichloride in 100 ml. of ether. The phosphorus trichloride reaction mixture was

¹²J. Amer. Chem. Soc., op. cit.

maintained at -20°C throughout the addition by means of a dry-ice-acetone bath. After the addition, 100 ml. of ether was flushed through the cadmium reaction vessel into the main reaction mixture from which the delivery tube was then withdrawn. The cooling bath was removed, the stirred reaction mixture allowed to warm to room temperature (1/2 hour), and refluxed for 2-1/2 hours.

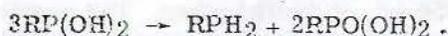
The reaction was worked up by allowing the mixture to stand overnight at room temperature followed by decantation of the main portion of the supernatant liquid. The residual precipitate was diluted with 100 ml. of ether, filtered by gravity on a sintered-glass filter of fine porosity, and washed with ether. The solvent was removed from the combined decantate, filtrate, and washings by distillation at atmospheric pressure, and the residue was distilled under reduced pressure to yield the crude n-butyldichlorophosphine. Fractionation of the crude product through an 18-inch glass-helices-packed column gave 37.4 g. (47% based on magnesium) of n-butyldichlorophosphine, b.p. $58-60^{\circ}$ at 22 mm.

During the distillation of the crude residue, some decomposition to an unidentified yellow material (not white phosphorus) takes place. This phenomenon is more pronounced in the lower members of the series, but it does not interfere with the distillation.

Care must be taken in the disposal of the final precipitate, since hydrolysis of traces of residual alkyldichlorophosphine occluded in the precipitate yields some alkylphosphine. (A dry distillation of this precipitate failed to give a significant amount of the alkyldichlorophosphine, however.) Careful addition of this precipitate to a large volume of cold water in an efficient fume hood is necessary.

Properties of Alkyldichlorophosphines

The alkyldichlorophosphines are water-white liquids with obnoxious odors, probably due to the disproportionation of the alkanephosphonous acid to the alkylphosphine. The acid is formed by hydrolysis of the dichlorophosphine with atmospheric moisture:



On standing, particularly in contact with atmospheric moisture, the alkyldichlorophosphines slowly deposit an unidentified yellow amorphous solid similar to that found in the distillation of the crude residue. Both the odor and the tendency to deposit the yellow solid decrease as the length of the carbon chain increases. A sample of n-amyl-dichlorophosphine under nitrogen in a sealed bottle was kept at room temperature for seven months without appreciable change in purity. These compounds are fairly stable to pyrolysis, as shown by the fact that n-amyl-dichlorophosphine and its lower homologues can be distilled at atmospheric pressure without apparent decomposition in the still-pot residue.

Physical Measurements

The physical properties of the n-alkyldichlorophosphines are shown in Table I. Refractive indices were measured on an Abbe-type refractometer, and densities were determined in a Weld pycnometer of approximately 10 ml. capacity. Boiling points at various pressures were found by distilling a fractionated sample of constant boiling range through an 18-inch glass-helices-packed column and observing the vapor temperature in the still head; a high reflux ratio was maintained at all times to minimize superheating of the vapor. A closed-tube manometer was used for pressure observations. Boiling points at atmospheric pressure were determined by sand-bath distillation of a constant-boiling sample in a Claisen flask with all-glass joints. These data, shown on the Cox chart (Figure 1), indicate that the vapor pressure curve of $\log p$ vs. $1/T$ is not quite a straight-line function.

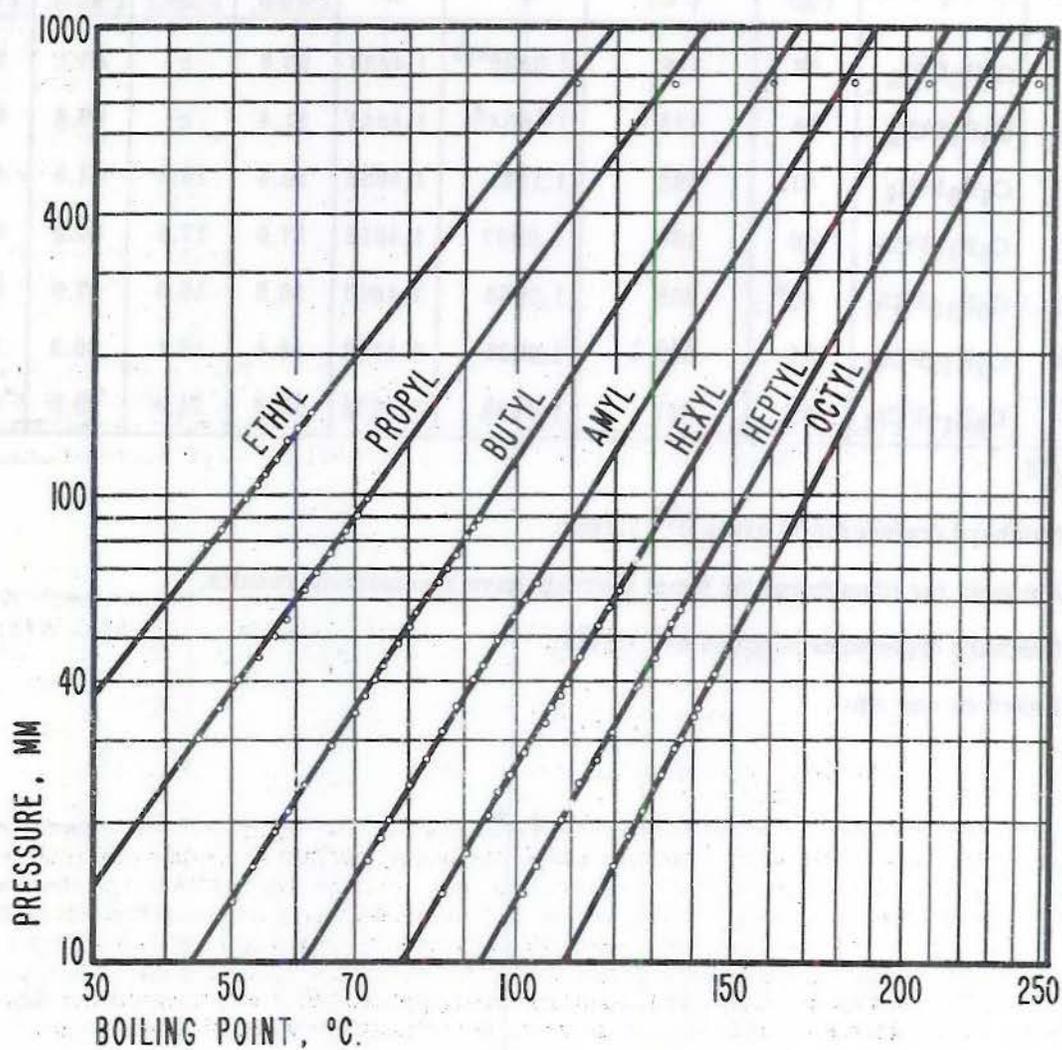


Figure 1. Boiling points of some n-alkyldichlorophosphines at various pressures.

TABLE 1

Some Alkyldichlorophosphines

Compound	Formula	Yield (%)	Normal b.p. (°C)	d_4^{27}	n_D^{25}	Analysis, (%)			
						Phosphorus		Chlorine	
						Calcd.	Found	Calcd.	Found
Ethyl	$C_2H_5PCl_2$	26	112	1.2485 ^{a,b}	1.4930	23.6	c	54.1	54.3
n-Propyl	$C_3H_7PCl_2$	44	134.5	1.1664 ^d	1.4842	21.4	c	48.8	48.7
n-Butyl	$C_4H_9PCl_2$	47	160	1.1341	1.4838	19.4	19.2	44.5	43.7
n-Amyl	$C_5H_{11}PCl_2$	40	184	1.0997	1.4815	17.9	17.9	40.9	40.6
n-Hexyl	$C_6H_{13}PCl_2$	41 ^e	208	1.0653	1.4800	16.5	16.0	37.9	37.6
n-Heptyl	$C_7H_{15}PCl_2$	42	228.5	1.0636	1.4788	15.4	15.1	35.3	35.5
n-Octyl	$C_8H_{17}PCl_2$	33	247	1.0433	1.4778	14.4	14.4	33.0	32.6

(a) d_4^{23} .(b) Guichard (reference 5) gives d_4^{19} 1.2952.

(c) Analysis for phosphorus by usual methods gave inconsistent results.

(d) Guichard (reference 5) gives d_4^{19} 1.1771.

(e) Based on one run.