IOWA STATE UNIVERSITY
Digital Repository

1951

Reactions of phosphine and phosphonium iodide

Glenn Halstead Brown

Iowa State College

Recommended Citation

www.manaraa.com

REACTIONS OF PHOSPHINE AND

PHOSPHONIUM IODIDE

by

Glenn H. Brown

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

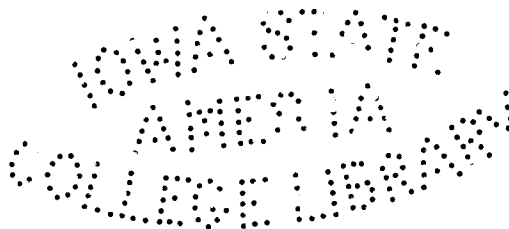Major Subject: Inorganic Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State College

1951

TABLE OF CONTENTS

I. INTRODUCTION

A survey of the chemical literature showed that the chemistry of phosphine and phosphonium iodide has been studied rather generally. Much of the work was done to determine if the chemical properties of phosphine and phosphonium iodide could be correlated with those of ammonia and ammonium iodide, respectively. Thus in many of the investigations recorded in the literature the investigator set out to study the behavior of a given chemical compound with a series of other chemical compounds of which two were phosphine and phosphonium iodide.

Much of the literature on the chemistry of these two compounds is rather old and often times contradictory. A great portion of the research on phosphine and phosphonium iodide was done before the beginning of the present century and during the early part of this century; recent studies are few.

The absence of recent studies of the chemistry of phosphine and phosphonium iodide, contradictions which are encountered in the literature about the behavior of these two compounds, and the possibilities of extending the usefulness of these two compounds as preparatory reagents made a study of them seem promising.

The phosphorus bromides and iodides have been prepared almost exclusively by the direct union of the elements in an inert solvent. A part of this investigation was to prepare these compounds by the action of phosphine and/or phosphonium iodide on the halogen. The most significant contribution in this portion of this work is the preparation of diphosphorus tetraiodide.

A reinvestigation of the action of phosphine on antimony (III) chloride and disulfur dichloride was undertaken. Also, the preparation of thiophosphoryl bromide from phosphine and a stoichiometric mixture of sulfur in bromine was studied briefly.

The preparation of the primary metallic phosphides of the more active metals in a pure form, or nearly pure form, has apparently been carried out for only one metal-- namely, sodium[1]. The present investigation showed that through the use of organometallic compounds primary phosphides of active metals and of reasonable purity can be prepared. The procedure was extended to the preparation of two amides.

The preparation of the phosphorus analogues of the amides has intrigued some chemists for over a century. Cloez[2] as early as 1846 attempted to prepare the phosphorus

[1]Albers and Schuler, Ber., 76B, 23 (1943).

[2]Cloez, Ann. chim., (3) 17, 311 (1846).

analogue of acetamide by the action of phosphine on acetyl
chloride. In the present investigation several different
techniques were studied to prepare these compounds and
a product was obtained from acetyl chloride and
phosphonium iodide which appears to be an analogue of
acetamidine hydroiodide, or more probably a polymeric
form of the analogue.

It has been known for a long time that phosphine
does not coordinate nearly as easily to metal ions as does
ammonia. This study showed that the coordination of
phosphine to aluminum bromide will take place at room
temperature if a solvent medium is used. This technique
was extended to the preparation of an ammine of aluminum
bromide.

A previous study of the action of phosphine on sodium
hydride does not appear to have been made. In the present
study an attempt was made to determine if the primary
phosphide of reasonable purity could be obtained by this
method.

Every effort has been made to use the best modern
practices of nomenclature of inorganic compounds. Inorganic
nomenclature needs an extensive systemization and fortunately

important steps are being taken in this direction[3,4,5,6,7].

[3]Jorissen, Bassett, Damiens, Fichter and Rémy, J. Am. Chem. Soc., 63, 889 (1941).

[4]Chemical Abstracts, "The Naming and Indexing of Chemical Compounds by Chemical Abstracts", 39, 5867 (1945).

[5]Fernelius, Chem. Eng. News, 26, 161 (1948).

[6]Fernelius, Larsen, Marchi and Rollinson, ibid., 26, 520 (1948).

[7]Scott, "Inorganic Syntheses", Vol. 2, McGraw-Hill Book Company, Inc., New York, N. Y., 1946, p. 257.

II. HISTORICAL

The chemistry of phosphine and phosphonium iodide prior to 1925 is summarized in Mellor[8]. Recent studies of these compounds deal primarily with their physical properties[9]. The literature survey considered in this section is rather general and further background material that is pertinent to a given subject is to be found in the experimental section. Also, this survey is directed toward the topics studied in this investigation and does not cover the chemistry of phosphine and phosphonium iodide exhaustively.

It was recognized early that one of the properties exhibited by these two compounds is that they are both strong reducing agents with phosphonium iodide being a very strong reducing agent. Baeyer[10] found that certain aromatic hydrocarbons such as toluene and m-xylene could be reduced to $C_7 H_{10}$ and $C_8 H_{14}$, respectively, when refluxed

---

[8] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 8, Longmans, Green and Company, New York, N. Y., 1940 impression, pp. 810, 822.

[9] See Yost and Russell, "Systematic Inorganic Chemistry", Prentice-Hall, Inc., New York, N. Y., 1944, p. 245 ff.

[10] Baeyer, Ann., 155, 266 (1870).

with phosphonium iodide. Likewise, there are many references to the reducing action of phosphine. For example, Moser and Brukl[11] reported that phosphine reduces iodic acid to iodine and Cavazzi[12] reported that phosphine plus an aqueous solution of sulfur dioxide resulted in the reduction of the sulfur to the elemental form.

The early investigators of the reactions of bromine and iodine with phosphine reported that the products obtained were phosphorus and the hydrogen halide. Balard[13] reported that bromine decomposes phosphine forming phosphorus and hydrogen bromide while Hofmann[14] observed that phosphine inflames on making contact with bromine water. Thomson[15] reported that iodine and phosphine react to form phosphorus and hydrogen iodide.

---

[11]Moser and Brukl, Z. anorg. u. allgem. Chem., 121, 73 (1921).

[12]Cavazzi, Gazz. chim. ital., 16, 169 (1886). Original not examined; cited by Mellor (10) p. 813.

[13]Balard, Ann. chim., (3) 17, 311 (1846).

[14]Hofmann, Ber., 4, 200 (1871).

[15]Thomson, Ann. Phil., 8, 93 (1816). Original not available for examination; cited in Mellor (10) p. 813.

Hanslian[16] reported that phosphonium iodide is de-
composed by iodine to form phosphorus and hydrogen iodide.
A study of the action of bromine on phosphonium iodide
does not appear to have been carried out.

Rose[17] reported that phosphine reacted with disulfur
dichloride to yield a product to which he assigned the
composition, $PS_5 Cl_2$. He described his product as a yellow,
syrupy liquid decomposed by water with the separation of
sulfur and the evolution of hydrogen sulfide. He claimed
that nitric acid oxidized the product to yield sulfuric
and phosphoric acids.

Ragg[18] reported that he could not prepare antimony
(III) phosphide by the action of phosphine on antimony (III)
chloride at room temperature. His procedure was to pass
phosphine through an acidic solution of antimony (III)
chloride. Ramsay and McIvor[19] obtained antimony (III)
phosphide by the action of phosphorus on a solution of
antimony (III) bromide in carbon disulfide. They described

---

[16]Hanslian, "Molekulargewichtsbestimmungen in
gefrierendem und siedendem Jod", Weida 1 Th., 1910, p. 85.
Original not available for examination; cited in Mellor
(10) p. 827.

[17]Rose, Pogg. Ann., 24, 304 (1832), [Chem. Centr., 3,
397 (1832)].

[18]Ragg, Oesterr. Chem. Ztg., 1, 94 (1898).

[19]Ramsay and McIvor, Ber., 6, 1362 (1873).

the compound as red in color and insoluble in benzene,
diethyl ether and carbon disulfide. Their analysis of
the red solid showed 79.48% antimony and 20.21% phosphorus
(calculated for Sb P: antimony = 79.72% and P = 20.28%).
Ragg[18] claimed that he could not reproduce their results.

A literature survey showed that very little work has
been done on the use of organometallic compounds in inorganic
syntheses. The preparation of inorganic compounds from
organometallic compounds has been done for the most part
by organic chemists who were studying either the properties
of the organometallic compounds or were attempting to
prepare an inorganic compound for use in organic syntheses.
An example of the former is the study by Gilman, Jacoby
and Ludeman[20] of the action of hydrogen on the organoalkali
metal compounds to establish the relative reactivity of
these compounds. An example of the latter is the preparation
of primary sodium phosphide, Na PH_2, by the action of
phosphine on triphenylmethylsodium[1]. These investigators
were seeking a source of primary sodium phosphide for use
in the preparation of organic phosphines.

Probably the first use of an organometallic compound
in the synthesis of an inorganic compound was the preparation

---

[20]Gilman, Jacoby and Ludeman, J. Am. Chem. Soc., 60,
2336 (1938).

of zinc amide by Frankland[21]. He passed ammonia into an ether solution of diethylzinc to obtain the amide. Schlenk and Ochs[22] passed ammonia into a solution of triphenyl-methylsodium and obtained sodium amide. They did not report an analysis of the product to establish its purity. Schlenk, W., Jr.[23] prepared magnesium amide by bubbling ammonia through a solution of diethylmagnesium. The analysis of the magnesium amide gave 46.2% and 46.05% nitrogen and 39.85% and 39.54% magnesium (calculated for $Mg(NH_2)_2$: N = 49.71% and Mg = 43.14%). Bergstrom and Fernelius[24] have summarized those reactions in liquid ammonia in which an alkali metal amide is formed as one of the products in the preparation of certain organo-metallic compounds (especially organotin and organogermanium).

Very recently Wiberg and Bauer[25] prepared magnesium hydride by the action of diborane on dialkylmagnesium

---

[21]Frankland, J. prakt. Chem., (1) 73, 35 (1858). Original not examined; cited in Franklin, "Nitrogen System of Compounds", Reinhold Publishing Corporation, New York, N. Y., 1935, p. 59.

[22]Schlenk and Ochs, Ber., 49, 608 (1916).

[23]Schlenk, W., Jr., Ber., 64, 736 (1931).

[24]Bergstrom and Fernelius, Chem. Revs., 20, 413 (1937).

[25]Wiberg and Bauer, Z. Naturforsch., 5b, 396 (1950).

compounds. These authors formulated the reaction as follows:

$$3R_2Mg + B_2H_6 \longrightarrow 3MgH_2 + 2R_3B$$
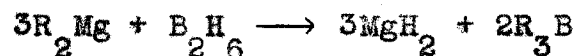
The organometallic compound must be in excess in order to obtain the hydride. The magnesium hydride decomposes into its elements at 280 - 300°. They also found that dialkyl-magnesium compounds and diborane in the ratio of 1:1.5 reacted to give magnesium borohydride[26], $Mg(BH_4)_2$. They described the reaction as quantitative at room temperature and that it is as follows:

$$3R_2Mg + 4B_2H_6 \longrightarrow 3Mg(BH_4)_2 + 2R_3B$$
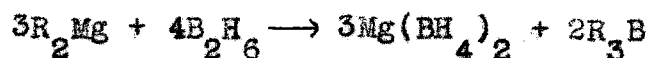
Different investigators have attempted to prepare the phosphorus analogues of the organic amides. Cloez[2] found that phosphine would not react with acetyl chloride. Later Steiner[27] and Evans and Vanderkleed[28] attempted to prepare acetyl phosphine[29] by the action of phosphine on acetyl chloride. However, chloroacetyl chloride[27], dichloroacetyl

---

[26] Wiberg and Bauer, ibid., 5b, 397 (1950).

[27] Steiner, Ber., 8, 1179 (1875).

[28] Evans and Vanderkleed, Am. Chem. J., 27, 142 (1902).

[29] Nomenclature after Kosolapoff, "Organo-Phosphorus Compounds", John Wiley and Sons, Inc., New York, N. Y., 1950, p. 14.

chloride[28] and trichlorocecetyl chloride[2] have been converted to their respective acylphosphines by the action of phosphine. Hofmann, in a footnote to Steiner's article[27], stated that he attempted to prepare acetyl phosphine by the action of phosphonium iodide on silver acetate but was unsuccessful. He also made reference to his study of the action of phosphine on acetyl chloride and likewise benzoyl chloride and pointed out that he did not obtain the acetyl or benzoyl phosphine.

Cuneo[30] prepared a compound which he reported to be carbophosphide, $CO(PH_2)_2$, by the action of phosphine on a 20% solution of phosgene in toluene. He described the reaction as taking place most readily in the presence of zinc carbonate. The yellow powder, carbophosphide, was found to be insoluble in the usual solvents, to decompose at 250°, and in moist air to undergo slow decomposition with the formation of carbon dioxide, phosphine and oxygenated phosphorus compounds.

A study of the reaction between acyl halides and phosphonium iodide does not appear to have been carried out.

Several attempts to prepare a compound from the action of phosphine on aluminum chloride were carried out before

---

[30] Cuneo, Atti. acad. Lincei, (V) 32, ii, 230 (1923) [C. A., 18, 1528 (1924)].

the successful work of Höltje and Meyer[31]. Rose[17] reported
that aluminum chloride absorbs about 3.67% phosphine in
five hours at room temperature and that the product could
be sublimed in the presence of phosphine gas to yield
crystals to which he assigned the composition, $3AlCl_3 \cdot PH_3$.
Peters[32] reported that aluminum chloride exposed to phos-
phine gas for four hours at room temperature gave a yellow
solid which he described as $P_{12}H_6$ and after a day this yellow
solid was, in turn, converted to a red solid which he
claimed to be P_9H_2. His conclusions were that aluminum
chloride and phosphine do not form a compound. It remained
for Höltje and Meyer[31] to prepare not only $AlCl_3 \cdot PH_3$ but
also $AlBr_3 \cdot PH_3$ and $AlI_3 \cdot PH_3$.

A previous study of the action of phosphine on sodium
hydride does not appear to have been made. However, the
action of ammonia on alkali metal hydrides to form the
amides has been known for a long time. Moissan[33] prepared
the alkali metal amides by the action of ammonia on the
alkali metal hydrides at room temperature.

Also, the action of phosphine on heated sodium was

---

[31]Höltje and Meyer, *Z. anorg. u. allgem. Chem.*, *197*,
93 (1925).

[32]Peters, *Z. anorg. Chem.*, *89*, 207 (1914).

[33]Moissan, *Compt. rend.*, *136*, 587 (1903).

studied by Schober and Spanatius[34]. They described their product as a mixture of primary, secondary and tertiary phosphides. They reported that primary sodium phosphide reacted with carbon monoxide to form NaCP which is very unstable and reacts with water to form phosphine and sodium formate. Evidence to support the formation of NaCP is not very convincing.

[34]Schober and Spanatius, Am. Chem. J., 16, 229 (1894).

III. PHOSPHINE: POISONOUS EFFECTS,
DETECTION AND DETERMINATION

The literature of toxicology contains reference to only a few fatal cases of poisoning by phosphine. Webster[35] cites the case of a man who inhaled a considerable quantity of phosphine generated by the action of water upon calcium phosphide placed in a saucer outside the door of his room by a prankster. The same author cites the case of a young chemist who died of the effects of phosphine with which he was experimenting. Most fatal cases have arisen among crew members of freight boats that were carrying ferrosilicon as cargo[35]. Phosphine is generated by the action of water on phosphides in the ferrosilicon.

Some studies have been made on the effects of phosphine on animals. Müller[36] found that rabbits were injured or killed by prolonged exposure to phosphine in a concentration of one part phosphine to 400,000 parts air. He described poisoning as cumulative and prognosis as unfavorable and that the respiratory tract, liver and kidneys

---

[35] Webster, "Legal Medicine and Toxicology", W. B. Saunders Company, Philadelphia, Pa., 1930, p. 586.

[36] Müller, Arch. exptl. Path. Pharmakol., 195, 184 (1940) [C. A., 35, 1865 (1941)].

suffer the worst damage. According to Flury[37] one cubic centimeter of phosphine in one liter of air is fatal to animals within one hour.

The first symptoms of slight cases of poisoning from phosphine are headache, loss of appetite, thirst and dizziness[38]. The physiological action on man in fatal cases has been confused with food poisoning. Fatal cases produce dyspnea, fainting, lowered blood pressure, slowed heart; nausea and vomiting; convulsions and paralyses; coma and asphyxia[39]. Postmortem examination shows pulmonary congestion and exudation. The blood is not changed. Prolonged exposure to small amounts of phosphine may produce the ordinary phenomena of chronic phosphorus poisoning[39].

Jacobs[40] has compiled data on the toxic effects of phosphine to man. A concentration of 2.8 mg. per liter, equivalent to approximately 2000 parts per million (ml. PH_3 per million ml. air) is fatal in a few minutes; a

[37]Flury, Anz. Schädlingskunde, 13, 26 (1937) [C. A., 31, 5874 (1937)].

[38]Brookes and Alyea, "Poisons, Their Chemical Identification and Emergency Treatments". D. Van Nostrand Company, Inc., New York, N. Y., 1946, p. 156.

[39]Sollmann, "A Manual of Pharmacology", 6th Ed., W. B. Saunders Company, Philadelphia, Pa., 1942, p. 884.

[40]Jacobs, "The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents", 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1949, pp. 348, 756.

concentration of 0.56 - 0.84 mg. per liter, equivalent to
approximately 400 to 600 parts per million, is dangerous
for exposures of 30 to 60 minutes; a concentration of 0.14 -
0.26 mg. per liter, equivalent to approximately 100 to
190 parts per million is the maximum tolerated for exposures
of 60 minutes. The maximum concentration that can be
tolerated for several hours without symptoms is 0.01 mg.
per liter, equivalent to 7 parts per million. The
maximum allowable concentration for safety over a period
of time is considered to be 0.05 parts per million[41].

Jacobs[40] has compiled a table principally from reports
submitted by the Committee on Threshold Limits, American
Conference of Governmental Industrial Hygienists in
"Industrial Hygiene, Newsletter" listing different poisonous
compounds along with maximum allowable concentrations for
an eight hour period of exposure. Phohphine is rated as
one of the most poisonous gases. The recommended maximum
allowable concentration of phosphine for an eight hour
exposure is 0.05 parts per million, equivalent to approx-
imately 0.00007 mg. per liter of air. For comparative
purposes this same report gives the concentration for
phosgene under the same conditions as one part per million;
hydrogen cyanide as ten parts per million; and methyl

---

[41] Report of Committee on Threshold Limits, American
Conference of Governmental Industrial Hygienists, Ind. Hyg.
Newsletter, 7, No. 8, 15 (1947).

alcohol as 200 parts per million. In addition to being more toxic than hydrogen cyanide, Flury[37] says that resuscitation is less likely than with hydrogen cyanide.

In order to insure safety to an experimenter who is working with phosphine, methods for its detection must be available. Phosphine may be detected by odor or better still by the use of silver nitrate paper. According to Wilmet[42] the minimum warning concentration detected by the sense of smell is in the range 20 to 50 parts per million. Silver nitrate paper will show the presence of phosphine at a concentration of one part per million[42]. The silver nitrate paper is prepared by impregnating filter paper with a 0.1 N solution of silver nitrate. The silver nitrate paper will be colored brown to black depending on (1) the time of exposure and/or (2) the concentration of the phosphine.

If it is desired to determine phosphine in air quantitatively this can be done rapidly by allowing it to react with mercury (II) chloride[43]. The reaction is described as follows:

$$PH_3 + 3HgCl_2 \longrightarrow P(HgCl)_3 + 3HCl$$

---
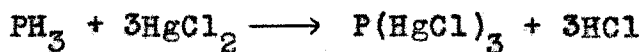
[42] Wilmet, Compt. rend., 184, 1456 (1927).

[43] Ibid., 185, 206, (1927).

The liberated acid is titrated with standard base. Also, phosphine may be sampled by drawing the air through washing towers, filled with standard potassium permanganate which has been acidified with five per cent sulfuric acid. The contents of the towers are combined, the excess permanganate is decolorized with oxalic acid and the phosphate determined colorimetrically by the procedure of Mellon and Kitson[44].

The discussion above on the toxicity of phosphine makes it very evident that special care must be exercised in working with this compound. All operations in which this gas was involved were carried out under a hood with an adequate fan system. Periodic checks with silver nitrate paper were made in the vicinity of the experimenter. After a few experiences with phosphine an experimenter can detect the gas quickly once the concentration is within the range of the sense of smell.

A. Handling of Phosphonium Iodide

Special care must be exercised in handling phosphonium iodide. Phosphonium iodide reacts slowly with dry air to give iodine and oxides of phosphorus[45]. With moist air

---

[44]Mellon and Kitson, Anal. Chem., 16, 466 (1944).

[45]Yost and Russell, op, cit., p. 249.

phosphine and hydrogen iodide will be formed in addition
to iodine and the oxides of phosphorus. Therefore, the
same precautions should be taken in handling phosphonium
iodide as phosphine.

IV. EXPERIMENTAL

A. Preparation of Phosphonium Iodide

The phosphonium iodide was prepared, with several modifications in apparatus, according to the procedure of Work[46].

1. Apparatus.

The apparatus for the preparation of the phosphonium iodide from the phosphorus-diphosphorus tetraiodide mixture was assembled as shown in Figure 1.

A is a dropping funnel; B is a pressure regulator to allow liquid to flow smoothly from A into flask D; C is a T tube; D is a 1000 ml. round-bottomed flask; E is a Gooch filter tube with the stem bent at a right angle and serves as an expansion valve for the water when it is heated in the condenser; F is a thermometer; G is a tube 20 mm. in diameter (inner) and about 60 cm. in length, surrounded by the jacket H, 45 mm. in diameter (inner) and 50 cm. in length; I is a receiver for the phosphonium iodide and can be quickly removed and stoppered; J and K are safety flasks,

---

[46]Work, "Inorganic Syntheses", Vol. 2, McGraw-Hill Book Company, Inc., New York, N. Y., 1946, p. 141.
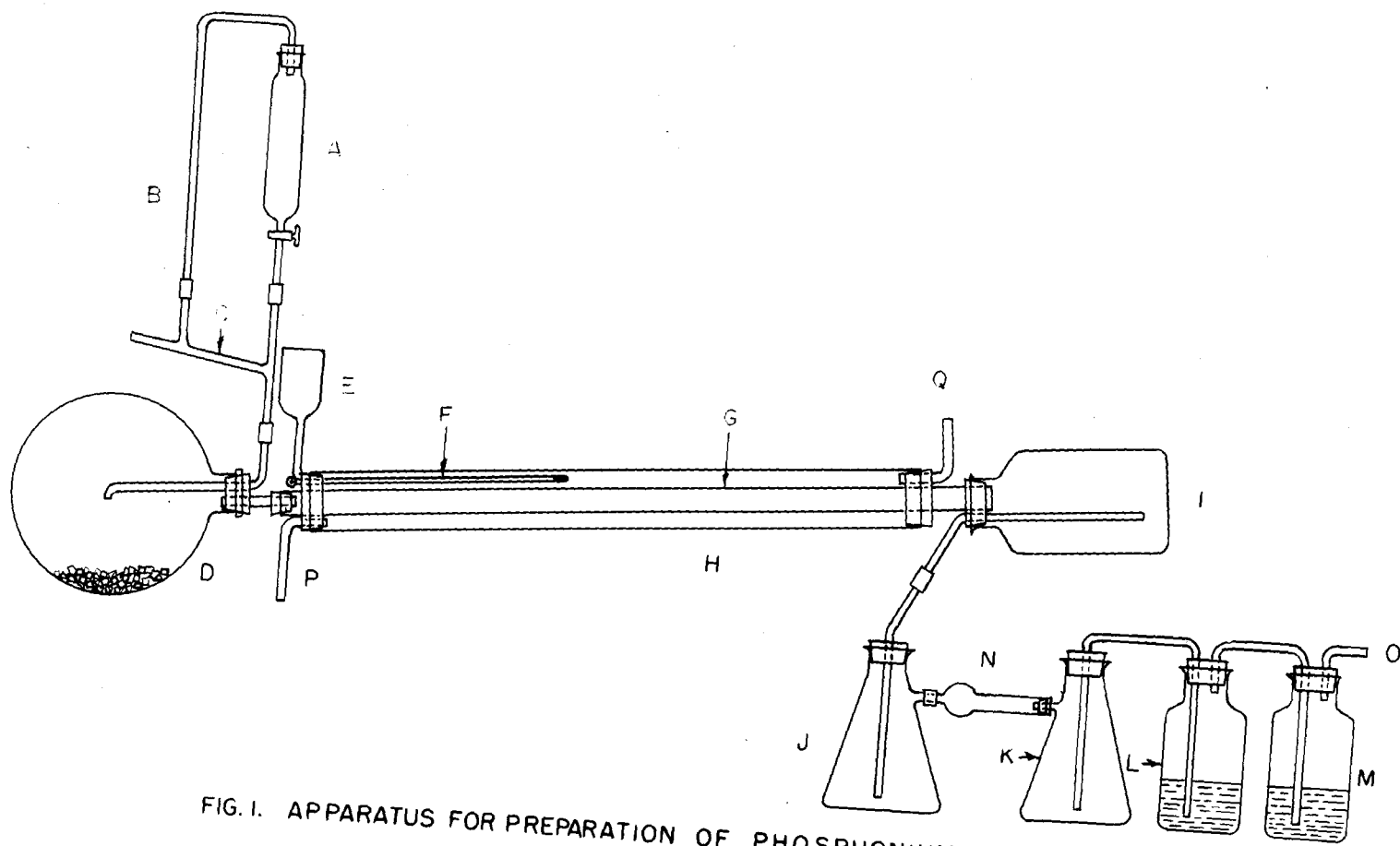
FIG. I. APPARATUS FOR PREPARATION OF PHOSPHONIUM IODIDE

the former to collect any phosphonium iodide which might
get through I and the latter serves as a trap for any
water that may be drawn back from L; L and M contain
water to absorb excess hydriodic acid and to serve as
a guide to the rate of flow of gases through the system.
N is a calcium chloride drying tube. Rubber stoppers are
used throughout the system. The whole operation is best
carried out in an efficient hood. If such is not possible
the outlet, O, must lead to an efficient hood for disposal
of the excess phosphine. The condenser is inclined up-
ward at a slight angle with D at the lower end in order
to prevent mechanical transfer of solids from D to I.

2. Preparation of phosphonium iodide.

The mixture of phosphorus-diphosphorus tetraiodide
prepared according to Work[46] was placed in flask D from
which all air had been swept with carbon dioxide. Flask
D was then connected to G and the air was swept out of the
system with a stream of dry carbon dioxide. The carbon
dioxide used throughout this investigation was "bone dry"
grade purchased from the Matheson Company, Inc. and was
bubbled through concentrated sulfuric acid and then passed
over calcium chloride. With cold water circulating through
the condenser, water was allowed to drip slowly from A
onto the mixture in D. The rate of addition of the water

was such that bubbles of gases flowed continually through L and M.

When all of the water had been added, D was heated in a "Glas-Col" spherical heating mantle at 80 - 85° until the phosphonium iodide had sublimed into G. This operation was speeded by passing a slow stream of carbon dioxide through the system occasionally. After all of the phosphonium iodide had sublimed from D, as indicated when cooling D did not result in the deposition of phosphonium iodide on the inner wall, the flask was cooled and removed. G was connected to a carbon dioxide supply and a very slow stream of this gas was passed through the system.

The condenser was inclined at a 30° angle with the table top with I at the lower end and surrounded by an ice-water bath. Tube P was closed by means of a pinch clamp and water was run into the condenser until it entered E. Then tube Q was pinched off. Two 250-watt infra-red lamps (preferably amber colored glass) were directed on the condenser and the water was heated to 80 - 85°. This technique for sublimation of the phosphonium iodide from G into I was much more convenient than trying to circulate hot water through the condenser as recommended by Work. Wrapping the outside of the condenser with a heating coil is not practical either since it is necessary to observe what is

happening in tube G throughout the operation of preparation and sublimation of the phosphonium iodide. The temperature of the water in the condenser can be controlled easily by moving the lamps closer or farther away from the condenser. With the aid of the slow stream of carbon dioxide the phosphonium iodide was sublimed into I. This required about two hours for yields of approximately 30 grams. The phosphonium iodide prepared in this manner can be used immediately for the study of its properties or used for the preparation of phosphine as described below. If the phosphonium iodide is to be used within a short period of time it may be stored in a bottle fitted with a ground-glass stopper, but if it must be kept for a long period of time the bottle should be sealed with paraffin or the iodide may be sealed in a large glass tube.

B. Preparation of Phosphine

The phosphine was prepared from the phosphonium iodide by the action of 25% potassium hydroxide solution on the iodide. The phosphine was collected over water in a gasometer.

1. Apparatus for generation and collection.

A diagram of the apparatus used to generate and collect the phosphine is given in Figure 2. A is a dropping funnel;
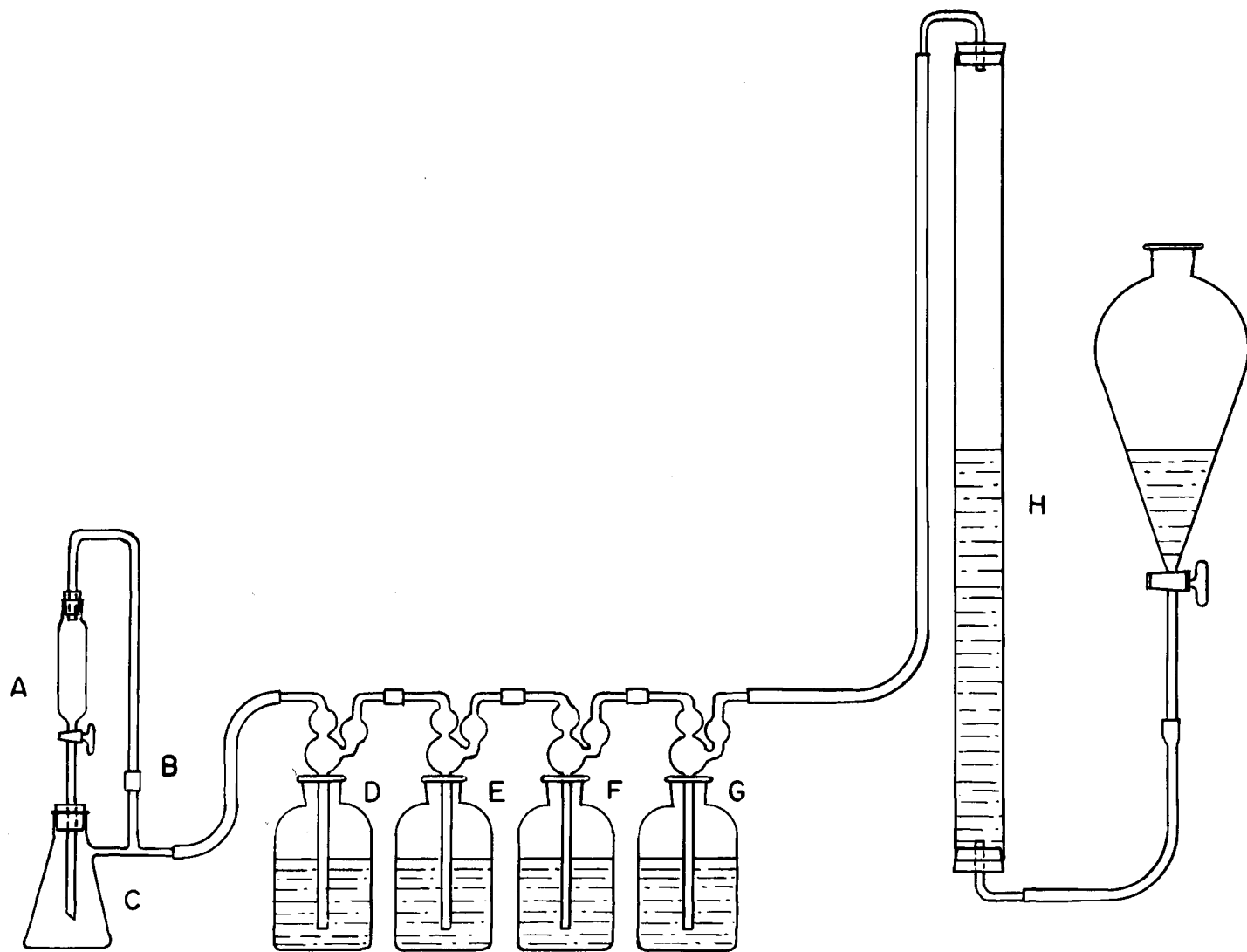
FIG. 2. APPARATUS FOR PREPARATION OF PHOSPHINE

B is a pressure regulator to allow liquid to flow smoothly
from A into flask C thus controlling the rate of evolution
of the phosphine; C is a 250 ml. pyrex filter flask to
which a T tube has been sealed; D and E are 500 ml. gas
washing bottles containing concentrated hydrochloric acid
to remove any tetrahydrogen diphosphide, P_2H_4; F and G are
500 ml. gas washing bottles containing 25% potassium
hydroxide to remove hydrogen chloride and hydrogen iodide;
H is a gasometer made of large pyrex tubing with an inner
diameter of 44 mm. and approximately 70 cm. long and with
a capacity of approximately 1000 ml.; I is a large
separatory funnel. The stopcock on the separatory funnel
serves as a means of regulating the flow of phosphine
from the gasometer.

For those experiments which required rather large
quantities of phosphine the gas was collected in large
aspirator bottles of approximately four liter capacity.

The collection of phosphine over water is possible
because phosphine is only moderately soluble in water,
0.26 ml. per ml. of water at 17° (compare ammonia which
has a solubility of 700 ml. per ml. of water at 20°)[47].
Also, the rate of diffusion of the gas into water at the

[47]Yost and Russell, op. cit., pp. 135, 245.

gas-liquid interface is slow. This was observed qualitatively by collecting a sample of the gas over water in a gas buret and observing the change in volume of gas with time. These properties make it practical to collect the gas over water. The phosphine was always used immediately after collection.

2. Purification.

According to Stephenson and Giauque[48] phosphine prepared by the action of potassium hydroxide on phosphonium iodide and washed with hydrochloric acid and potassium hydroxide is free of tetrahydrogen diphosphide, P_2H_4, and hydrogen iodide. The procedure for drying the phosphine was that of Stephenson and Giauque in which the phosphine was passed through drying towers containing potassium hydroxide pellets and then through absorption bulbs containing phosphorus (V) oxide. It is necessary to sweep out the train with dry nitrogen before starting phosphine through it. The nitrogen used throughout this study was "oil pumped" grade purchased from The Matheson Company, Inc. and was purified further by passing it through alkaline pyragallol, concentrated sulfuric acid and then over calcium chloride.

---

[48] Stephenson and Giauque, J. Chem. Phys., 5, 149 (1937).

The dry phosphine was found to be spontaneously inflammable in air at room temperature. If the dry gas was passed through water it no longer ignited spontaneously on contact with air. These observations are in harmony with those of Ritchie[49] and Stephenson and Giauque[48] but are in contradiction with the observations of Durrant, Pearson and Robinson[50] who claimed that they had pure phosphine and that their product did not inflame spontaneously in air. Since Stephenson and Giauque established that the impurities in the phosphine which they prepared were less than four moles per one hundred thousand moles, it may be concluded that the pure gas is spontaneously inflammable on contact with air at room temperature.

C. Preparation of Diphosphorus Tetraiodide

Of the different reactions which have been studied for the preparation of diphosphorus tetraiodide[51], the procedure of Corenwinder[52], refined by Germann and Traxler[53],

---

[49]Ritchie, Proc. Roy. Soc. (London), A128, 551 (1930).

[50]Durrant, Pearson and Robinson, J. Chem. Soc., 1934, 730.

[51]Mellor, op. cit., p. 1038.

[52]Corenwinder, Ann., 78, 76 (1851).

[53]Germann and Traxler, J. Am. Chem. Soc., 49, 307 (1927).

in which stoichiometric quantities of the two elements
are allowed to react in a carbon disulfide medium has been
used almost exclusively. The procedure has the advantage
of being easily carried out because of the ready avail-
ability of the reactants and solvent. Germann and Traxler
found that special purification of the carbon disulfide
had to be carried out if the resulting diphosphorus tetra-
iodide is to be of a high grade of purity. They claimed
that the free sulfur in redistilled carbon disulfide formed
compounds which lowered the melting point of the diphos-
phorus tetraiodide. The composition of these interfering
compounds was not established. It seems probable that in
addition to these compounds some phosphorus (III) iodide
might be present. The procedure using phosphonium iodide
and a carbon disulfide solution of iodine eliminates the
difficulties encountered in the procedure of Germann and
Traxler. Phosphine and sulfur do not react at room
temperature[54], carbon disulfide is not attacked by hydrogen

---

[54]Jones, J. Chem. Soc., 29, 641 (1876) made a rather
extensive study of the behavior of the hydrogen compounds
of the elements of Group V-B on sulfur and found that the
reaction between phosphine and sulfur is very slight at
room temperature in diffused light.

iodide at room temperature[55], hydrogen iodide and sulfur react very slowly in the cold[56], and dry hydrogen sulfide and diphosphorus tetraiodide do not react at room temperature[57]. Since these side reactions do not result in interferences this procedure furnishes a ready means for preparing pure diphosphorus tetraiodide. Another important factor to consider is that there will not be any phosphorus (III) iodide present.

It might be noted in passing that phosphonium iodide and iodine will react to form diphosphorus tetraiodide without the use of a solvent medium (for best results the reaction should be carried out in a nitrogen atmosphere). The two finely powdered solids can be intimately mixed under a nitrogen atmosphere and the container warmed in an electrical hot pad at 60 - 70°. The phosphonium iodide must be in excess of that needed for the following reaction:

---

[55]According to Berthelot the reaction takes place only at high temperatures. Berthelot, Ann. chim., (3) 53, 121 (1855). Original not examined; cited in Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 6, Longmans, Green and Company, New York, N. Y., 1940 impression, p. 110.

[56]Berthelot, Bull. soc. chim. France, (5) 15, 185 (1878).

[57]Ouvrard, Compt. rend., 115, 1301 (1892).

$$2PH_4I + 5I_2 \longrightarrow P_2I_4 + 8HI \qquad (1)$$

or, $\qquad PH_4I \longrightarrow PH_3 + HI$

$$2PH_3 + 5I_2 \longrightarrow P_2I_4 + 6HI$$
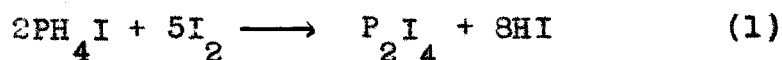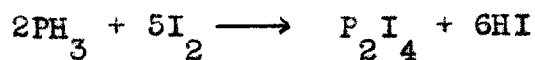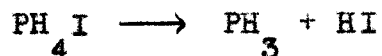
The orange-colored solid, P_2I_4, resulting from the reaction melted at 124.5° (corrected). The procedure in which the iodine solution of carbon disulfide was used worked more efficiently.

1. Procedure.

A 5% solution of iodine[53] in carbon disulfide[58] (by weight) was treated with an amount of phosphonium iodide in excess of that required in equation (1) (stoichiometric amounts: 1 g. PH_4I to 3.92 g. I_2). At first the carbon disulfide was brown and then a beautiful, transparent red. The reaction took place smoothly at room temperature. To obtain a product of highest purity the reactants were placed in a flask and protected with a nitrogen atmosphere. For the preparation of large quantities the reaction can be carried out under normal conditions as discussed by

---

[53] The iodine used throughout the study was the "reagent" grade manufactured by Merck and Company, Inc. The carbon disulfide used was the "C. P." grade manufactured by Merck and Company, Inc. and further purified by distillation.

Germann and Traxler. The solution of the diphosphorus tetraiodide was concentrated by evaporation of the carbon disulfide at a temperature of 45 - 50°. During the evaporation process the excess phosphonium iodide was left in contact with the carbon disulfide solution of the diphosphorus tetraiodide. The warm solution, when quite concentrated, but before any solid separated out, was removed from the heating pad (semi-spherical, Glas-Col) and decanted (freed of the excess PH_4I) into a flask previously filled with nitrogen. On cooling the flask containing the concentrated solution in a salt-ice bath, beautiful, needle-like orange-colored crystals separated out. The excess mother liquor was decanted off, the crystals recrystallized from carbon disulfide, and then dried at 45 - 50° under a nitrogen atmosphere to free them of excess solvent. The product was kept in a glass-stoppered weighing bottle in a desiccator over calcium chloride. The orange-colored solid melted at 124.5^{o} (corrected). The melting point was taken by the capillary tube method. This value checks with that obtained by Germann and Traxler for diphosphorus tetraiodide. Results of a quantitative analysis of the product are given in Table 1.

Table I

Analysis of Diphosphorus Tetraiodide

Analysis Number	Wt. of Sample	Wt. AgI	% I	Calc. % I in P_2I_4
1	0.2597	0.4276	89.01	89.12
2	0.3064	0.5039	88.90	

The iodide analysis was carried out by dissolving the diphosphorus tetraiodide in water, acidifying the solution with nitric acid, adding a small amount of solid sodium hydrogen sulfite to insure that all of the iodine is in the form of the iodide, sweeping the excess sulfur dioxide from the solution with carbon dioxide and then precipitating the iodide as silver iodide.

D. Preparation of Phosphorus (III) Iodide

Of the different reactions which have been developed for the preparation of phosphorus (III) iodide[59], the procedure of Corenwinder[52], refined by Germann and Traxler[53],

---

[59] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. 8, Longmans, Green and Company, New York, N. Y., 1940 impression, p. 1039.

in which stoichiometric quantities of the two elements are allowed to react in a carbon disulfide medium, has been used almost exclusively. The procedure suffers the same difficulties of interference from impurities as encountered in the preparation of the diphosphorus tetraiodide.

1. Procedure.

A 5% solution of iodine in carbon disulfide (by weight) was treated with an amount of phosphonium iodide (stoichiometric amounts: 1 g. PH_4I to 4.70 g. I_2) slightly less than that required by the following equation:

$$PH_4I + 3I_2 \longrightarrow PI_3 + 4HI \qquad (2)$$

or,
$$PH_4I \longrightarrow PH_3 + HI$$

$$PH_3 + 3I_2 \longrightarrow PI_3 + 3HI$$
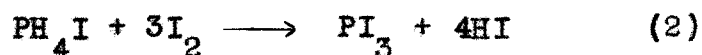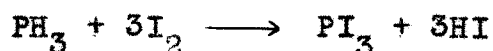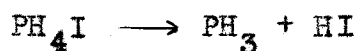
The reaction goes smoothly at room temperature with the rate of the reaction decreasing as the iodine concentration decreases. After standing at room temperature for approximately fifteen minutes (for samples of about 3 g. of PI_3), the reaction can be completed quickly by warming the reaction flask to 40 - 50°. After all of the phosphonium iodide had reacted the solution of phosphorus (III) iodide was concentrated by evaporation of the carbon

disulfide at a temperature of 45 - 50°. This evaporation
must be carried out until crystals form in the warm
solution. The mixture was then cooled in a salt-ice
bath and the excess mother liquor was decanted off. The
dark red crystals which were left were recrystallized
from carbon disulfide and dried at room temperature under
a vacuum. The vacuum was broken with nitrogen and the
product was kept in a glass-stoppered weighing bottle in
a desiccator over calcium chloride. The resulting product
melted at 61° (capillary tube method) and checked with the
value obtained by Germann and Traxler[53] for phosphorus
(III) iodide. An iodide analysis of the dark red solid
gave the results shown in Table II.

Table II

Analysis of Phosphorus (III) Iodide

Analysis Number	Wt. of Sample	Wt. AgI	% I	Calc. % I in PI_3
1	0.1647	0.2806	92.10	92.48
2	0.1724	0.2946	92.38	

E. Preparation of Phosphorus (V) Bromide
from Phosphonium Iodide

If an excess of a solution of bromine in carbon
tetrachloride is added dropwise to phosphonium iodide at
room temperature, phosphorus (V) bromide is formed. Carbon
tetrachloride was chosen as the solvent because phosphorus
(V) bromide is less soluble in it than in carbon disulfide
which is mostly commonly used as a solvent medium for the
preparation of phosphorus (V) bromide. If the concen-
tration of the bromine is greater than 10% (by volume),
or if it is added too rapidly, the reaction becomes quite
rapid and in addition to the other products reported below
a yellow solid which is apparently $P_{12}H_6$ is deposited on
the sides of the reaction flask. A detailed study of the
yellow solid was not made, but it was found to be insoluble
in water which eliminates phosphorus (V) bromide.

The reaction takes place readily and smoothly at room
temperature using 10% solutions of bromine. The products
of the reaction between phosphonium iodide and excess
bromine are phosphorus (V) bromide, hydrogen bromide,
iodine and undoubtly some iodine bromide. The last named
compound can be prepared by the direct union of the
elements at room temperature[60] and is therefore undoubtedly
present although its identity was not established.

---

[60]Yost, Anderson and Skogg, J. Am. Chem. Soc., 55,
552 (1933).

The procedure does not appear to have practical usefulness as a means of preparing phosphorus (V) bromide because the product as it first forms is contaminated with iodine. It takes several recrystallizations to free the bromide of the iodine. This alone eliminates the reaction as a competitor with the conventional procedures of direct union of the elements or the action of bromine on phosphorus (III) bromide. The quantity of bromine to be added can be determined by use of the following equation:

$$2PH_4I + 9Br_2 \longrightarrow 2PBr_5 + I_2 + 8HBr$$
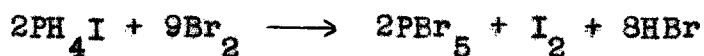
In brief, the procedure involved the addition of an excess (stoichiometric quantities: 1 g. PH_4I to 4.44 g. Br_2) of the 10% bromine solution dropwise to the phosphonium iodide crystals. Since the carbon tetrachloride was not present in very large volume much of the phosphorus (V) bromide and iodine crystallized out. Stirring or shaking hasten the reaction as it nears completion. The carbon tetrachloride was decanted off and the phosphorus (V) bromide was recrystallized several times from carbon disulfide. The phosphorus (V) bromide was freed of carbon disulfide by warming it at $40 - 50^\circ$ under a carbon dioxide atmosphere. The bromide was further purified by sublimation

in a sealed tube to obtain yellow-colored crystals of phosphorus (V) bromide. Analysis of the phosphorus (V) bromide is given in Table III.

Table III

Analysis of Phosphorus (V) Bromide

	Bromide				Phosphorus		
Sample number	Wt. of sample	Wt. of AgBr	% Br*	Sample number	Wt. of sample	Wt. of $Mg_2P_2O_7$	% P*
1	0.3883	0.8502	93.19	1	0.4250	0.1046	6.85
2	0.2237	0.4899	93.22	2	0.4421	0.1104	6.95

*Calculated for PBr_5: P = 7.19%; Br = 92.81%.

The product melts with apparent decomposition at approximately 104°. Handbooks do not give an exact value for the melting point of phosphorus (V) bromide but report a value greater than 100°.

F. Preparation of Phosphorus (III) Bromide

Balard[13] and Hofmann[14] did not obtain phosphorus (III) bromide when they reacted phosphine with bromine. Evidently they did not control the conditions of the reaction properly. It was found in this investigation that several factors have to be controlled or an explosion will result when dry phosphine comes in contact with solutions of bromine in organic solvents or with bromine vapors. These factors are (1) too rapid addition of phosphine to the bromine solution results in an explosion even in an inert atmosphere, (2) too concentrated solutions of bromine (in excess of approximately 10% bromine by volume) result in an explosive reaction mixture even in an inert atmosphere and (3) that an explosive mixture results at low concentrations of bromine and with slow addition of dry phosphine unless the union is brought about in an inert atmosphere. The explosive action observed under (3) when the reaction is carried out in air may be due to the reaction of phosphine and air as well as the reaction between the bromine and phosphine. The reaction between phosphine and bromine will go smoothly at room temperature if dry phosphine is passed slowly through a solution of bromine in carbon tetrachloride (5 to 10% bromine by volume) and an inert atmosphere is maintained.

The various published methods for the preparation of phosphorus (III) bromide are modifications of the reaction of phosphorus with bromine[61]. The preparation from phosphine and bromine probably will not compete with this procedure but the procedure has some advantages over the conventional method of preparation--namely, (1) there is no danger of contamination of the product with phosphorus (V) bromide, (2) contamination of the product with bromine is avoided and (3) the reaction can be carried out at room temperature.

1. Procedure.

A 5% solution of bromine in carbon tetrachloride (by volume) was placed in a three-necked flask, with ground-glass joints, which was previously swept out with nitrogen. Into the main neck was placed a reducing adapter, ground-glass joint with a glass tube sealed to the smaller end through which a slow stream of nitrogen entered. Into one of the side necks was placed a reducing adapter, ground-glass joint, with a glass tube running through the adapter and into the bromine solution. The glass tube was sealed to the adapter by means of cloth tape. Into the other side neck was placed a reducing adapter, ground-glass joint,

---

[61] Gay and Maxson, "Inorganic Syntheses", Vol. 2, McGraw-Hill Book Company, Inc., New York, N. Y., 1946, p. 147.

which served as an outlet for the gases. Pure phosphine
was passed slowly through the solution (approximately two
bubbles per second) until the solution became colorless
and then for a short period longer to insure an excess.
The carbon tetrachloride was removed by the procedure of
Noller and Dinsmore[62] and the phosphorus (III) bromide was
distilled according to the procedure of Gay and Maxson[61].
The middle fraction of the compound boiled at $172.9°$
(corrected to 760 mm. Hg pressure) which corresponds to
the value recorded in the literature for the boiling point
of phosphorus (III) bromide.

If it is desired, the phosphorus (III) bromide in
the carbon tetrachloride can be very conveniently converted
to the phosphorus (V) bromide by the dropwise addition of
bromine to the solution. The phosphorus (V) bromide
crystallizes out in beautiful yellow crystals with very
little of the red variety if the quantity of bromine added
is just slightly in excess of the stoichiometric amount.
Phosphorus (V) bromide prepared in this manner was freed
of the mother liquor by decantation, dried at $60°$ in a stream
of carbon dioxide and sublimed under vacuum at $40°$. The
product decomposed with melting at approximately $106°$ and
gave the bromide analysis recorded in Table IV.

_____

[62]Noller and Dinsmore, "Organic Syntheses", Vol. 13,
John Wiley and Sons, Inc., New York, N. Y., 1933, p. 21.

Table IV

Analysis of Phosphorus (V) Bromide

Analysis Number	Wt. of Sample	Wt. of AgBr	% Br	Calc. % Br in PBr$_5$
1	0.3072	0.6724	93.19	92.81
2	0.2840	0.6206	93.00	

G. Preparation of Antimony (III) Phosphide

Antimony (III) phosphide has been prepared by several different procedures. Pelletier[63] reported the preparation of antimony (III) phosphide by the action of molten antimony on metaphosphoric acid. Ramsay and McIvor[19] prepared antimony (III) phosphide by the action of phosphorus on a solution of antimony (III) bromide in carbon disulfide. Ruff[64] obtained the phosphide by the action of phosphorus on antimony (III) chloride in the presence of aluminum chloride. These investigators found that the antimony (III) phosphide prepared by the fusion

---

[63] Pelletier, Ann. chim., 13, 132 (1792). Original not examined; cited in Mellor (10) p. 851.

[64] Ruff, Ber., 34, 1749 (1901).

processes is a brittle, white mass while that prepared
by precipitation reactions is a red powder insoluble in
carbon disulfide, diethyl ether, and benzene.

Of the different techniques tried in this investigation
for the preparation of antimony (III) phosphide from
phosphine and antimony (III) chloride, one was found to
procede successfully at room temperature and the other
in molten antimony (III) chloride. For the preparation
at room temperature the antimony (III) chloride was
dissolved in toluene, the solution placed in a Cheronis[65]
semimicro hydrogenator and the phosphine was introduced
through the microporous dispenser as very fine bubbles.
A reddish-brown precipitate formed quickly but the pores
of the dispenser soon became clogged with the reddish-
brown solid. This technique is useful for preparing only
small quantities of the phosphide.

Evidently for the reaction to proceed with any degree
of efficiency at room temperature it is necessary to intro-
duce the phosphine into the toluene solution of the
antimony (III) chloride in very fine bubbles; a surface
area on which the reaction can take place is evidently
beneficial. Attempts to reproduce these results using
6 mm. glass tubing instead of the microporous dispenser

---

[65] Cheronis and Koeck, J. Chem. Education, 20, 488 (1943).

gave only traces of the phosphide. Another procedure
which was tried involved placing the toluene solution of
antimony (III) chloride into a container along with glass
beads to furnish a surface area on which the reaction might
take place. The phosphine was introduced through a 6 mm.
glass tube extending to the bottom of the container. The
amount of reddish-browm solid formed was greater than in
the case in which the phosphine was introduced through
the 6 mm. tube in the absence of the beads. However, the
yield was small and the recovery of the solid was difficult.

The second technique involved the passage of phosphine
through molten antimony (III) chloride. This procedure
was utilized for the preparation of the antimony (III)
phosphide prepared for study.

1. Procedure.

The antimony (III) chloride was Baker's "analyzed"
and purified by distillation with the middle fraction
distilling at 220° collected for study. The distillation
was carried out in all-glass apparatus with standard-taper,
conical-joint connections and the joints were lubricated
with the viscous liquid made by grinding together
phosphorus (V) oxide and a little orthophosphoric acid.

The reaction flask was a three-necked flask with ground-glass joints assembled similarily to that used for the reaction between phosphine and bromine in carbon tetrachloride. The antimony (III) chloride was melted (m. p. 73.4°) and the temperature of the reaction flask kept at approximately 100°. The dry phosphine was passed through the molten chloride and a reddish-brown precipitate formed quickly. No effort was made to carry the reaction to completion but after a quantity of the reddish-brown solid had accumulated it was isolated and analyzed. The equation for the reaction is as follows:

$$Sb\ Cl_3 + PH_3 \longrightarrow SbP + 3HCl$$
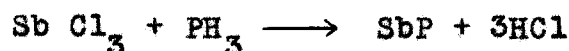
The antimony (III) phosphide was freed of the unreacted antimony (III) chloride by the use of warm benzene (approximately 40°). The solubility of antimony (III) chloride in benzene at 40° is reported as 44.1 g. of the chloride per 100 g. of benzene[66]. The washing with benzene was continued until the reddish-brown solid gave a negative chloride test. The spot test recommended by Feigl[67] was used to establish the absence of chloride.

---

[66]Siedell, "Solubilities of Inorganic and Metal Organic Compounds", 3rd Ed., D. Van Nostrand Company, New York, N. Y., 1940, p. 1476.

[67]Feigl, "Spot Tests", 3rd Ed., Elsevier Publishing Company, Inc., New York, N. Y., 1946, p. 283.

The reddish-brown solid was dried at 105° and analyzed following the procedure in "Scott's Standard Methods of Chemical Analysis"[68] for the solution of the sample, the separation and analysis of the antimony and for the determination of phosphate gravimetrically as ammonium dodecamolybdophosphate. The results of the analyses are recorded in Table V.

Antimony (III) phosphide is insoluble in water at room temperature. It shows only very slight solubility in benzene at 40° and slight solubility in carbon disulfide at room temperature. Concentrated hydrochloric acid reacts slowly with it with the evolution of some phosphine. Concentrated hydrochloric acid plus an oxidizing agent dissolves the antimony (III) phosphide.

An attempted melting point by the capillary tube method showed that the compound had no sharp melting point. The solid darkened at a temperature of approximately 300° and there was a deposit of a red solid on the capillary tube above the sample under investigation. Although no tests were run to verify this conclusion, it is probable that the antimony (III) phosphide decomposes into its elements at around 300°.

---

[68] Furman, "Scott's Standard Methods of Chemical Analysis", 5th Ed., D. Van Nostrand Company, New York, N. Y., pp. 74, 694.

Table V

Analysis of Antimony (III) Phosphide

Antimony				Phosphide			
Sample number	Wt. of sample	Ml. of 0.1238N $KBrO_3$	% Sb[**]	Sample number	Wt. of Sample[*]	Wt. of $(NH_4)_3$ $P(Mo_3O_{10})_4$	% P[**]
1	0.1130	11.90	79.37	1	0.1165	0.1417	19.95
2	0.1252	13.21	79.52	2	0.1252	0.1527	20.00

[*]The sample was placed in a total volume of 500 ml. and then 50 ml. portions used for analysis.

[**]Calculated for SbP: Sb = 79.72%; P = 20.28%.

H.   Action of Phosphine on Disulfur Dichloride

The only reference encountered in the literature
dealing with the reaction between these two compounds was
that of Rose[17]. Rose described his product as a yellow,
syrupy liquid with a composition of PS_5Cl_2. The product
was undoubtedly a mixture of a disulfur dichloride, sulfur
dissolved in the disulfur dichloride, and some phosphorus
(V) sulfide dissolved in the disulfur dichloride. In the
present investigation it was found that a small amount of
dry phosphine passed into disulfur dichloride[69] at room
temperature was absorbed almost quantitatively and, in
harmony with Rose, a yellow liquid was obtained which
contained phosphorus. It was thought that at least one
of the products might be thiophosphoryl chloride so efforts
were made to isolate this compound. The different pro-
cedures used were: (1) fractional distillation of the
reaction mixture at atmospheric pressure (b. p. of $PSCl_3$
is reported as 125°), (2) freezing out the thiophosphoryl
chloride at the temperature of a Dry-Ice-acetone bath,
(3) seeding the liquid with phosphoryl chloride at a
temperature of a Dry-Ice-acetone bath and (4) fractional

---

[69]Prepared by distilling the technical grade and
collecting the fraction boiling at 136° (uncorrected).

distillation under a vacuum. All procedures failed to isolate any compound of definite composition. In the fractionation procedures phosphorus was found in varying amounts in all fractions separated. For example, in the fractionation at atmospheric pressure three samples were collected; the fraction collected at 134 - 136° gave a good phosphorus test, the fraction collected at 136 - 140° gave a good phosphorus test, while the residue appeared to be mostly sulfur. In the freezing and seeding studies no solid separated out.

When the addition of dry phosphine to the disulfur dichloride was continued a yellow solid separated out. This solid was studied as described below. If desired the disulfur dichloride can be dissolved in an organic solvent such as carbon tetrachloride and the phosphine added to this solution. In this study a 10% solution of disulfur dichloride in carbon tetrachloride was used.

This reaction was not studied exhaustively but three different products were identified. Hydrogen chloride, sulfur and phosphorus (V) sulfide (tetraphosphorus deca-sulfide) were identified in those reactions which were carried to the point of precipitate formation. The sulfur and phosphorus (V) sulfide which were in the yellow precipitate described above were separated by extracting the yellow solid in a Soxhlet extractor using carbon disulfide as the

extracting solvent. The phosphorus (V) sulfide was crystallized from this solvent and a melting point run on the crystals. The solid melted at 287 - 288° to a reddish-brown liquid. The value recorded in the literature for the melting point of phosphorus (V) sulfide is 286 - 290° [70a]. The solid reacted with water to give off hydrogen sulfide. Qualitative evidences which indicate the absence of the tetraphosphorus trisulfide and tetraphosphorus heptasulfide are (1) moderate solubility of the phosphorus sulfide in carbon disulfide [70b] and (2) that the carbon disulfide solution of the sulfide was not oxidized by iodine; this would eliminate tetraphosphorus trisulfide [71]. The presence of sulfur was qualitatively verified by treating the original yellow solid with dilute nitric acid. Such a treatment always left a residue of yellow solid. Qualitative tests on the residue indicated sulfur as the only element present.

The reaction was not studied further since phosphorus (V) sulfide is more conveniently prepared by the union of

---

[70] (a) Treadwell and Beeli, *Helv. Chim. Acta*, 18, 1161 (1935); (b) these authors report that tetraphosphorus trisulfide has a solubility of 100 g. P_4S_3 per 100 g. CS_2 at 17°; phosphorus (V) sulfide a solubility of 0.222 g. P_4S_{10} per 100 g. CS_2 at 17°; tetraphosphorus heptasulfide 0.029 g. P_4S_7 per 100 g. CS_2 at 17°.

[71] Yost and Russell, "Systematic Inorganic Chemistry", Prentice-Hall, Inc., New York, N. Y., 1944, p. 185.

the elements using the procedure of Stock and Herscovici[72].

I. Preparation of Thiophosphoryl Bromide

A mixture of sulfur and bromine in stoichiometric quantities (S_2Br_2) was placed in a small reaction flask which was cooled in a salt-ice bath. This mixture is not pure disulfur dibromide as has been shown by Ruff and Wenzel[73]. To obtain the pure compound they heated stoichiometric quantities of the two reagents in a tube at 100° and purified the product by fractional distillation in a vacuum.

Dry phosphine was passed slowly through the sulfur-bromine mixture and the reaction appeared to be complete as evidenced by the absence of phosphine in the escaping gases. The quantity of phosphine added was small in comparison to the total amount of the sulfur-bromine mixture taken. This was done with the idea of keeping the sulfur-bromine mixture in excess and thus maintain an oxidizing medium. The addition of this limited amount of phosphine did not cause a change in the color of the garnet-red mixture.

To establish the presence of the thiophosphoryl bromide

---

[72] Stock and Herscovici, Ber., 42, 1223 (1910).

[73] Ruff and Wenzel, Ber., 36, 2438 (1903).

the mixture was treated according to the procedure of Booth and Seabright[74]. Using an all-glass apparatus with standard-taper, conical-joint connections, the red liquid was fractionally distilled under a pressure of 25 mm. Hg. The fraction boiling between 120 - 130° and supposedly containing the crude thiophosphoryl bromide was collected. The crude product at this point was a red liquid which qualitative analysis revealed to contain sulfur, phosphorus and bromine. To this crude product was added a volume of distilled water about double its volume and a few drops of a 10% solution of potassium bromide. This mixture was warmed until solution was complete and then a gentle stream of air was allowed to bubble through the liquid for a few minutes. Next, most of the water was decanted and any sulfur appearing as a coagulated mass was removed.

The yellow layer was then allowed to crystallize and the remainder of the water removed. This product was given a second water treatment as described above and then allowed to dry in a desiccator over phosphorus (V) oxide. The purified product containing phosphorus, sulfur and bromine was yellow in color and melted between 37 - 38°. The value recorded in the literature for the melting point of thiophosphoryl bromide is 37.4°.

---

[74]Booth and Seabright, J. Am. Chem. Soc., 65, 1834 (1943).

The reaction was not studied further since thiophos-
phoryl bromide is much more conveniently prepared by
the action of phosphorus (V) bromide on phosphorus (V)
sulfide[74].

J.   Preparation of Lithium and Magnesium Phosphides

Legoux[75] prepared primary lithium phosphide by
passing phosphine through a solution of lithium in liquid
ammonia at -80°. The product was described as a white
powder with a composition of $LiPH_2 \cdot 4NH_3$ and could not be
freed of the ammonia without the simultaneous evolution
of phosphine. Legoux[76] found that the thermal decomposition
resulted in the formation of the diammoniate and then the
monoammoniate. The last molecule of ammonia could not
be removed without decomposition of the primary phosphide
with the formation of a product which he described as
secondary lithium phosphide, Li_2PH.

Apparently the only attempt to prepare a primary
phosphide of magnesium was that of Albers and Schuler[1].
They passed phosphine into an ether solution of ethyl-
magnesium bromide and obtained a grayish-white solid which

---

[75]Legoux, _Compt. rend._, _207_, 634 (1938).

[76]_Ibid._, _Bull. soc. chim. France_, _7_, 545 (1940).
Original not available for examination; cited in _C. A._,
_36_, 3448 (1942).

reacted readily with water to liberate phosphine. They
did not report an analysis of their product but assumed
it to be principally $Mg(PH_2)Br$.

1. Preliminary discussion.

Some introductory studies which in themselves did
not yield results of quantitative nature but did aid in
helping to develop a procedure for the preparation of the
phosphides will be discussed first. Even though it was
known that lithium bromide is rather soluble in diethyl
ether and would thus be a contaminant in the phosphide,
it was decided to study the action of phosphine on
phenyllithium prepared from phenyl bromide and lithium
since the phenyllithium is easily prepared from these re-
agents. In such a study it could be determined if phos-
phine will react with phenyllithium and the development
and manipulation of satisfactory apparatus could be studied.
The phenyllithium prepared from the bromide and metal
served these purposes.

The phenyllithium can be readily prepared by the pro-
cedure of Gilman, Zoellner and Selby[77]. A portion of the
clear ether solution was placed in a reaction flask and
dry phosphine at room temperature was bubbled through it.

---

[77]Gilman, Zoellner and Selby, J. Am. Chem. Soc., 54,
1957 (1932).

A precipitate which was a mixture of white and red colored solids started to form as soon as the first phosphine was added. This solid, after being freed of the mother liquor, was washed with anhydrous ether. It reacted with water to evolve phosphine and leave an aqueous solution which was basic to litmus and contained lithium.

Another observation of interest concerns the addition of phosphine to an ether solution of phenyllithium prepared from diphenylmercury. Again the white solid contaminated with red was obtained as was the case with the phenyllithium prepared from phenyl bromide and lithium. In this preparation the sample was not contaminated with the bromide. An analysis for lithium was run on the sample and found to be 20.8%. The calculated value for lithium in primary lithium phosphide is 17.38%. A phosphorus analysis was not run on this sample. The high results for lithium can be attributed to the presence of secondary and tertiary phosphides of lithium. The red colored solid is probably tertiary lithium phosphide. Brauer and Zintl[78] found that lithium and phosphorus unite to form a reddish-brown solid which is primarily tertiary lithium phosphide. The high value for lithium confirms observations made by Albers and Schuler[1] in their study of primary sodium phosphide.

---

[78] Brauer and Zintl, Z. physik. Chem., B37, 323 (1937).

As discussed later, the procedure for bringing the
phosphine and organometallic compound together was re-
versed from the procedure above, i. e., the organometallic
compound was added dropwise to ether through which a rapid
stream of phosphine was passing. This same procedure was
applied to the preparation of primary magnesium phosphide
and the amides of magnesium and lithium.

Another observation which was carried out dealt with
di-n-butylmercury and phosphine. The di-n-butylmercury
was prepared according to the procedure of Gilman and
Brown[79]. Dry phosphine was bubbled through an ether
solution of the di-n-butylmercury at room temperature.
No solid separated out and only a small phosphorus test
was obtained on the liquid. This phosphorus probably
came from the dissolved phosphine.

If the presence of the bromide does not interfere
with the proposed use of the phosphide the use of the
organolithium compound prepared from the alkyl or aryl
bromide and lithium should furnish a practical method for
the preparation of the phosphide.

2. Apparatus for preparation.

The reaction flask used for the preparation of these
compounds is given in Figure 3. A is a 500 ml., four-necked

---

[79] (a) Gilman and Brown, J. Am. Chem. Soc., 51, 928
(1929); (b) Gilman and Brown, ibid., 52, 3314 (1930).
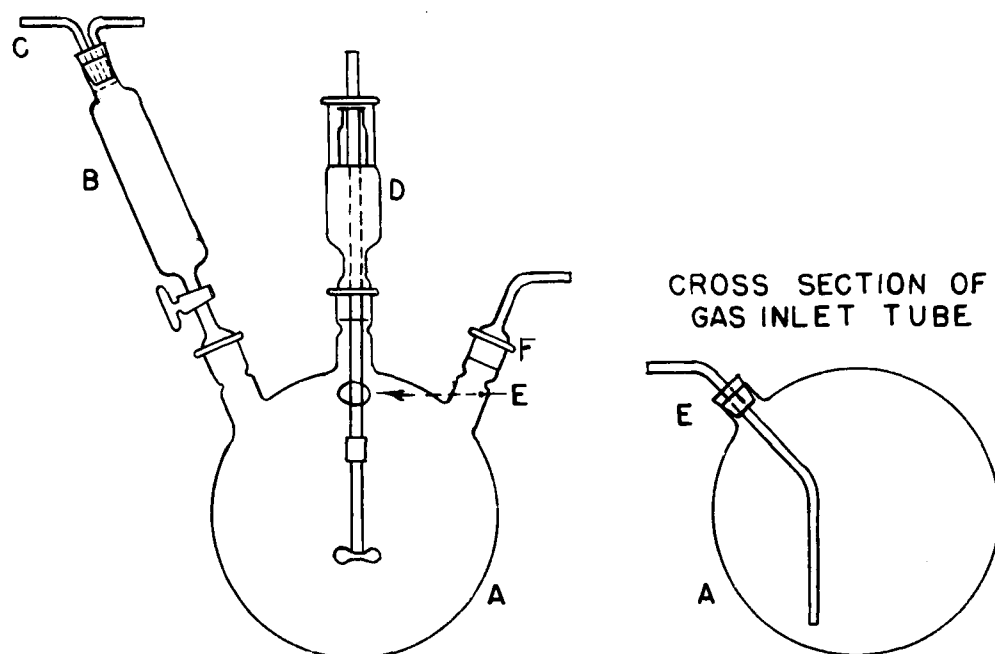
FIG. 3. REACTION FLASK FOR PREPARATION OF METALLIC PHOSPHIDES

CROSS SECTION OF GAS INLET TUBE
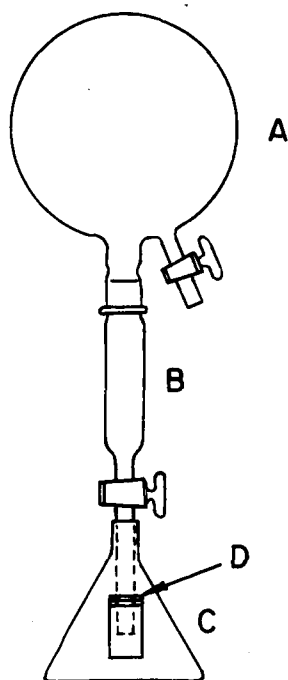
FIG. 4. APPARATUS FOR DRYING AND SAMPLING METALLIC PHOSPHIDES

flask with three of the necks having standard-taper, ground-glass joints and the fourth sealed to the flask for this study; B is a dropping funnel with a ground-glass fitting and has a capacity of approximately 300 ml.; C is a two-hole rubber stopper containing an inlet and outlet tube for nitrogen which was kept over the organometallic compound to protect it from the air. D is a mercury-sealed stirrer; E is the inlet tube attached to the gas supply. The outlet tube, F, is connected to an absorption bulb containing phosphorus (V) oxide. The remainder of the train included a bubble counter containing mineral oil and finally an outlet tube which went into water.

3. Procedure for preparation of primary lithium phosphide.

The phenyllithium was prepared from diphenylmercury using the procedure of Schlenk and Holtz[80]. The diphenylmercury, in turn, was prepared by the procedure of Bachmann[81]. An ether solution of phenyllithium was used in this study.

One hundred milliliters of anhydrous ether[82] was placed in the reaction flask which had been previously dried at 110° and swept out with dry nitrogen. Next, the gas inlet

---

[80] Schlenk and Holtz, _Ber._, _50_, 273 (1917).

[81] Bachmann, _J. Am. Chem. Soc._, _55_, 2827 (1933).

[82] Prepared by the procedure of Gilman, Wilkinson, Fishel and Meyers, _ibid._, _45_, 150 (1923).

tube was connected to the phosphine supply and a rapid
stream of phosphine was passed through the ether and this
phosphine supply was continued throughout the addition
of the phenyllithium. With the properllor just under
the surface of the ether and the stirrer running at low
speed, the phenyllithium was added dropwise to the ether.
The reaction was carried out at room temperature. A white
precipitate formed when the phenyllithium dropped into
the ether. There was no evidence of the red solid which
was observed when the phosphine was passed directly into
the ether solution of the phenyllithium. All of the
phenyllithium solution was added dropwise and the stream
of phosphine gas was continued for about five minutes
after all of the solution had been added. The equation
for the reaction is as follows:

$$C_6H_5Li + PH_3 \longrightarrow LiPH_2 + C_6H_6$$
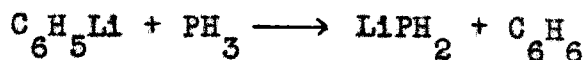
The stirrer was shut off and the gas inlet tube, E, was
replaced by a one-hole rubber stopper which contained
a short glass tube; this tube was sealed with a screw
clamp over a rubber connection. Once the precipitate
settled, a major portion of the mother liquor was removed
by decantation; the remainder was removed by the use of
an immersion filter assemblage which replaced outlet tube F.

This assemblage consisted of a two-hole rubber stopper through which were placed two glass tubes bent at right angles. A stopcock was sealed to each glass tube. An immersion filter tube with fritted disc of coarse porosity was sealed to one of the glass tubes. Care must be exercised to keep the fritted disc from coming in contact with the solid or it will become clogged. A slight nitrogen pressure applied through one tube of the immersion filter assemblage forced the liquid out through the fritted filter.

The precipitate was washed five times with anhydrous ether (25 ml. portions for approximately 2 g. samples) by introducing the ether through the dropping funnel, stirring the mixture, allowing the precipitate to settle and then removing the wash solution each time by the use of the immersion filter. During the ether additions the solid was protected from the atmosphere by means of a slow stream of nitrogen entering through the tube on the filter assemblage and leaving through E. After the washings were completed, the immersion filter, stirrer and funnel were removed and the gas inlet tube, E, was clamped tightly. The solid was protected with nitrogen throughout this operation. Into the main neck was placed a ground-glass stopper and into one of the side necks was placed a reducing adapter, ground-glass joint, with a glass tube

running through the adapter and nearly touching the surface of the solid. The glass tube was sealed to the adapter by means of a rubber connection. Into the other side neck was placed the connection, F, diagrammed in Figure 3; F was connected to a tube containing calcium chloride. A stream of nitrogen was directed over the solid to remove the adhering ether. The solid was then powdered with a glass rod and transferred into a flask for drying under reduced pressure and for sampling later for analysis. A diagram of the flask and its connections is given in Figure 4. The transfer of the solid from the reaction flask to the flask diagrammed in Figure 4 was carried out in the absence of air by connecting the two flasks through a coupling made of ground-glass joints.

The sample was dried at room temperature for two hours under a vacuum of approximately 0.5 mm. Hg. The joints, both rubber to glass and ground-glass, were sealed with Dow's Silicone Lubricant. The vacuum was broken with nitrogen and the flask kept tightly closed.

4. **Apparatus for drying and sampling the primary lithium phosphide.**

The phosphide was sampled as diagrammed in Figure 4. A is a 200 ml. flask, with a ground-glass, standard-taper joint, to which was sealed a glass tube with a stopcock;

B is a tube with a ground-glass, standard-taper connection
to which a large stopcock was sealed; C is a powder funnel;
D is a weighing bottle. The hole in the stopcock on B
was bored until its diameter was the same as the inner
diameter of the glass tubing to which it is connected
(approximately 4 mm.). The small weighing bottle, D,
had a ground-glass stopper (empty bottle weighed approx-
imately 8 g.). The weighing bottle must be small enough
to go inside the apparatus used for the analysis (see
Figure 5).

In the sampling process the apparatus was inverted
as diagrammed and a stream of nitrogen was directed into
the funnel, C, to protect the sample from air. The stop-
cock in B was opened and the powdered solid transferred
into the previously weighed weighing bottle. The weighing
bottle was kept in a desiccator over phosphorus (V) oxide
for transfer to the balance.

5. Analysis of the primary lithium phosphide.

The phosphorus content of the phosphide was determined
by measuring the volume of the phosphine evolved when water
reacted with a weighed amount of the phosphide. The
lithium was determined by titration against standard acid.

A diagram of the apparatus used for the analysis of
the phosphorus is given in Figure 5. A is a 25 mm. by
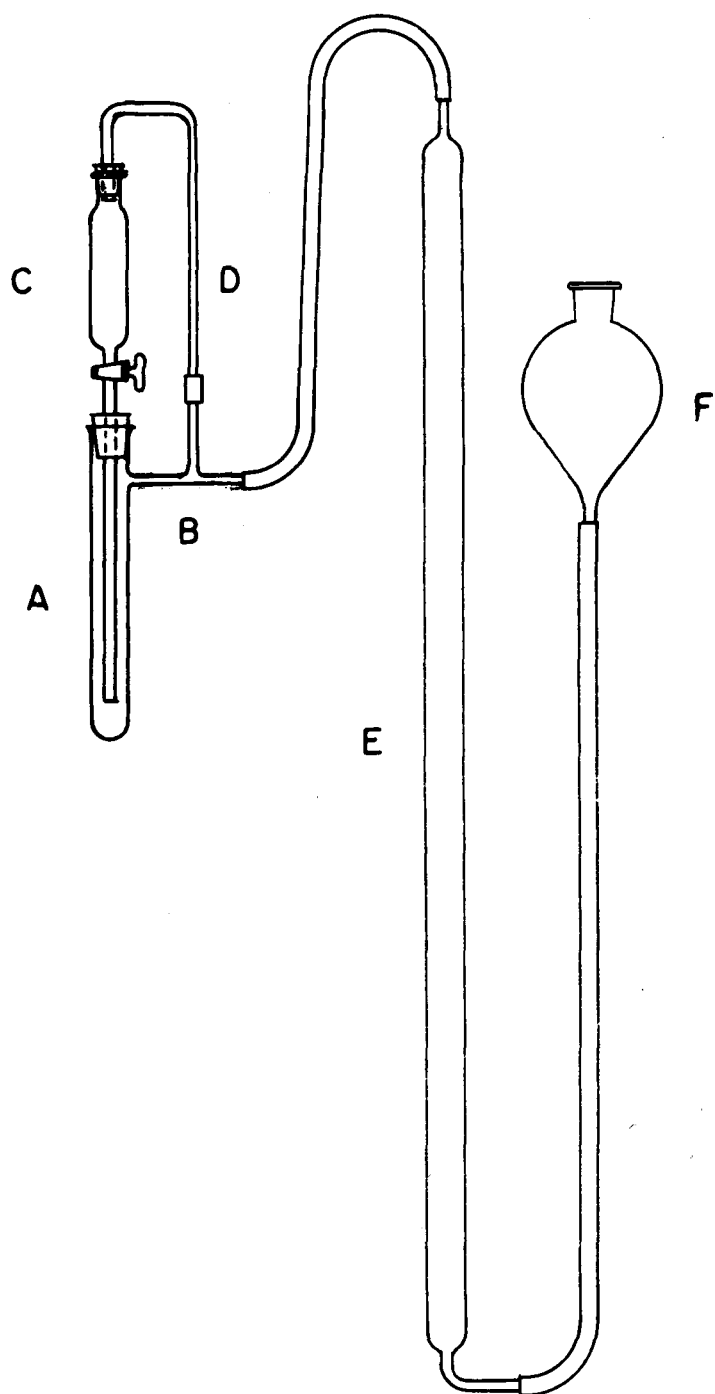
FIG.5 APPARATUS FOR ANALYSIS OF PHOSPHORUS
IN LITHIUM PHOSPHIDE

20 cm. pyrex test tube with a side arm; B is a T tube
which was sealed to the side arm of the test tube; C is
a dropping funnel; D is a pressure regulator; E is a
100 ml. gas buret; F is a leveling bulb.

The apparatus, exclusive of the gas buret and the
leveling bulb, was dried in an oven at $110°$, cooled and
swept out with a stream of nitrogen passing through the
funnel while B was clamped. The weighing bottle with
weighed sample, cover removed, was placed in A while
protected from air with a stream of nitrogen. B was
connected to C. Water was added dropwise from C onto the
sample and the phosphine which was liberated was collected
over mercury and its volume measured. The total volume
of water added to the phosphide was approximately two
milliliters.

For the lithium determination the solution was washed
from the reaction tube, A, into an evaporating dish,
carefully evaporated to dryness and redissolved in dis-
tilled water. The lithium hydroxide was determined by
titration with standard acid. Results of the analyses
of the primary lithium phosphide are recorded in Table VI.

Primary lithium phosphide is a white solid which
does not have a definite melting point but decomposes
with the evolution of phosphine when heated in a vacuum.
It is stable in a nitrogen atmosphere but is hydrolyzed

Table VI

Analysis of Primary Lithium Phosphide

Lithium analyses

Sample number	Wt. of sample	Ml. of 0.1045 N HCl	% Li*
1	0.1062	24.50	16.73
2	0.1085	25.15	16.81
3	0.1144	26.71	16.93

Phosphorus analyses

Sample number	Wt. of sample	Ml. PH_3	Temp.	Bar. pressure (mm. Hg.)	V.P. H_2O (mm. Hg.)	Wt. of PH_3	% P*
1	0.1062	67.4	25°	748.7	23.7	0.0894	76.8
2	0.1085	68.0	24°	747.8	22.4	0.0905	76.1
3	0.1144	72.4	24°	747.8	22.4	0.0963	76.8

*Calculated for $LiPH_2$: Li = 17.38%; P = 77.57%.

in moist air. A sample finely powdered and tossed into
the air will burn. The phosphide reacts very rapidly
with water to liberate phosphine.

6. Procedure for the preparation of the primary
   magnesium phosphide.

The technique for the preparation of primary magnesium
phosphide from a dialkylmagnesium compound was essentially
the same as that described for the lithium phosphide.
The di-n-butylmagnesium was prepared by the procedure
of Noller[83]. Di-n-butylmagnesium was chosen for study
because it had been found by Johnson and Adkins[84] that
approximately 82% of the active Grignard reagent prepared
from butyl bromide and magnesium was present in the form
of the di-n-butylmagnesium[85]. This was one of the highest
values found in their study.

The analyses of the phosphide are recorded in Table VII.
The phosphine was analyzed as described under the primary
lithium phosphide preparation and the magnesium was de-

---

[83] Noller, J. Am. Chem. Soc., 53, 635 (1931).

[84] Johnson and Adkins, ibid., 54, 1943 (1932).

[85] The dioxane used for the precipitation of the
RMgBr and $MgBr_2$ was Eastman white label, dried, distilled
and stored over sodium.

Table VII

Analysis of Primary Magnesium Phosphide*

Magnesium analyses

Sample number	Wt. of sample	Wt. of $Mg_2 P_2 O_7$	% Mg**
1	0.1381	0.1613	25.52
2	0.1152	0.1323	25.09

Phosphorus analyses

Sample number	Wt. of sample	Vol. of PH_3	Temp.	Bar. pressure (mm. Hg.)	V.P. H_2O (mm. Hg.)	Wt. of PH_3	% P**
1	0.1381	75.4	24°	752.0	22.4	0.101	66.7
2	0.1021	55.7	24°	752.0	22.4	0.0746	66.5

*See text for comment on impurities.

**Calculated for $Mg(PH_2)_2$: Mg = 26.93%; P = 68.61%.

termined as magnesium pyrophosphate. The di-n-butyl-
magnesium was found to contain a small amount of bromide
(compare Noller). Also on solution of each of the
samples for analysis there was always a small amount of
acid-insoluble residue. The insoluble residue was not
characterized. These two factors probably contributed
to the low results of the amide and phosphide. However,
the results obtained here are nearer to the calculated
results than were those obtained by Schlenk, W., Jr.[23].
A solution of di-n-butylmagnesium of higher quality should
give better results.

Primary magnesium phosphide is a white solid which
decomposes on warming in a vacuum with the evolution of
phosphine. It is stable in a nitrogen atmosphere but very
unstable in air. It reacts readily with water to evolve
phosphine and form magnesium hydroxide.

7. Preparation of primary potassium phosphide.

Preliminary studies of the action of phosphine on
triphenylmethylpotassium[86] showed that a white solid was
formed which reacted with water to evolve phosphine and
give a basic solution which contained potassium ions. The
slight solubility of the organopotassium compound in ether

---

[86] Prepared by the procedure of Gilman and Young,
J. Org. Chem., 1, 315 (1936).

makes the preparation of a workable sample of the phosphide rather difficult to obtain. However, it can be prepared by this method.

K. Preparation of Aluminum Bromide Monophosphinate

Studies of the action of phosphine on aluminum bromide have been reported by Rose[17], Peters[32], Höltje[87] and Höltje and Meyer[31]. Only Höltje and Meyer were successful in preparing a compound of definite composition. By heating a mixture of phosphine and solid aluminum bromide together at a temperature of 70° they obtained a white compound which melted at $114 - 118^\circ$. The compound formed was aluminum bromide monophosphinate, $AlBr_3 \cdot PH_3$.

It seemed logical that the reaction might take place at room temperature if the aluminum bromide were dissolved in an organic solvent. Such was found to be the case. Either carbon disulfide or benzene served satisfactorily as the solvent. It was found that the aluminum bromide monophosphinate was rather soluble in benzene but only slightly soluble in carbon disulfide. If the aluminum bromide was dissolved in carbon disulfide and dry phosphine bubbled through this solution, the aluminum bromide monophosphinate precipitated out very quickly. However, if

---

[87]Höltje, Z. anorg. u. allgem. Chem., 190, 241 (1930).

the aluminum bromide was dissolved in benzene and dry
phosphine bubbled through this solution, the aluminum
bromide monophosphinate would not precipitate out unless
the solution became quite concentrated. Both solvents
were used in preliminary observations and benzene was
decided upon for the study as the solvent for carrying
out the reaction and then the aluminum bromide monophos-
phinate was precipitated from the benzene by addition of
carbon disulfide to its benzene solution. By the procedure
of Höltje and Meyer it is difficult to determine when the
reaction has gone to completion because of the solid-gas
phase reaction. This difficulty is overcome by the pro-
cedure described in this study.

1. Procedure.

The aluminum bromide used in this study was "C. P."
grade from Eimer and Amend Company. It was purified
further by distillation, using all-glass apparatus, into
the reaction flask where it was protected by a nitrogen
atmosphere.

A nitrogen atmosphere was maintained throughout the
entire preparation. The apparatus was similar to that
described under the preparation of phosphorus (III) bromide.
The reaction flask was a 300 ml. three-necked flask with
ground-glass connections. Into the main neck was placed

a reducing adapter, ground-glass joint, with a glass tube
sealed to the smaller end through which a slow stream of
nitrogen entered. Into one of the side necks was placed a
reducing adapter, ground-glass joint, with a glass tube
running through the adapter into the aluminum bromide
solution in benzene. The glass tube was sealed to the
adapter by means of a rubber connection. Into the other
side neck was placed a reducing adapter, ground-glass joint,
which served as an outlet for the gases. This outlet tube
was connected to a tube filled with calcium chloride to
protect the reaction medium from moisture.

A sample of 3 - 4 g. of aluminum bromide was distilled
into the reaction flask and dissolved in 50 ml. of benzene.
An approximate weight to the nearest tenth of a gram was
taken on the sample before dissolving it in benzene. Dry
phosphine was bubbled through the solution at room temp-
erature until an amount in excess of that needed to form
the aluminum bromide monophosphinate was added. The phos-
phine was absorbed almost completely when it was added at
a moderate rate. No precipitate formed at this point
but upon addition of a volume of carbon disulfide approx-
imately equivalent to the benzene present, a white pre-
cipitate settled out. The precipitate was allowed to
settle, the benzene-carbon disulfide layer was decanted
and the solid washed with carbon disulfide. To hasten the
washing process the solid was transferred to centrifuge

tubes which had been previously filled with nitrogen and which could be tightly stoppered during the centrifuging operation. After three or four washings with carbon disulfide the white solid was freed of the adhering carbon disulfide by use of a stream of nitrogen at room temperature and then dried under a vacuum at room temperature for one hour. The sample was then sublimed at $60 - 70^{\circ}$ under a vacuum, the vacuum broken with nitrogen and the compound sampled by the same procedure as described under sampling of the lithium phosphide. The compound was analyzed for phosphine by the same procedure as described for the analysis of phosphorus under lithium phosphide. The aluminum was precipitated as the hydroxide and weighed as the oxide while the bromide was precipitated as silver bromide and weighed as such. Results of the analyses are recorded in Table VIII.

Aluminum bromide monophosphinate is a white solid which is stable in a nitrogen atmosphere but unstable in moist air. The powdered solid, in moist air, will liberate phosphine which bursts into flame spontaneously. If water is added to the solid in air there is likewise a spontaneous burning and if the quantity of phosphinate is large there is an explosion. If the addition of water is carried out in a nitrogen atmosphere the procedure can be used to determine the phosphine quantitatively. The phosphinate can be readily sublimed at $60 - 70^{\circ}$ and melts at $114 - 118^{\circ}$.

Table VIII

Analysis of Aluminum Bromide Monophosphinate

Aluminum analyses				Bromide analyses			
Sample number	Wt. of sample	Wt. of Al_2O_3	% Al	Sample number	Wt. of sample	Wt. of AgBr	% Br
1	0.6524	0.1055	8.55	1	0.2092	0.3981	80.38
2	0.7322	0.1190	8.60	2	0.5633	1.0612	80.18

Phosphine analyses

Sample number	Wt. of sample	Vol. of PH_3	Temp.	Bar. pressure (mm. Hg.)	V.P. H_2O (mm. Hg.)	Wt. of PH_3	% P
1	0.2092	18.0	25°	754	23.7	0.0240	10.5
2	0.5633	48.1	26°	754	25.2	0.0640	10.4

Calculated for $AlBr_3 \cdot PH_3$: Al = 8.97%; Br = 79.73%; PH_3 = 11.31%.

L. Action of Phosphine on Sodium Hydride

Primary sodium phosphide in varying degrees of purity has been prepared (1) by the action of phosphine on heated sodium[34], (2) by the action of phosphine on sodium in liquid ammonia[88], and (3) by the action of phosphine on triphenylmethylsodium[1]. The present study was carried out to determine if the primary phosphide could be prepared from sodium hydride[89] and phosphine with a reasonable degree of purity by passing the phosphine over the hydride.

Hansley and Carlisle[90] have published recent information on the preparation, properties and handling of sodium hydride.

Of the different conditions studied, one has been reported and two others have been mentioned. In all of the procedures studied the sodium hydride was placed in

---

[88](a) Joannis, Compt. rend., 119, 557 (1894); (b) Legoux, Bull. soc. chim. France, 7, 545 (1940).

[89]Kindly furnished by the E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware.

[90]Hansley and Carlisle, Chem. Eng. News, 23, 1332, (1945). Also see, "New Products Bulletin", No. 25, Electrochemicals Department, E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware.

a pyrex glass tube and the phosphine passed over it.
Keyes[91] reported that glass was not attacked by the
hydride at temperatures below 375°. In one experiment a
thin layer of the hydride was transferred under a nitrogen
atmosphere to the reaction tube which was surrounded by a
water jacket. The temperature of the water was controlled
at 65 - 75° and a stream of dry phosphine was passed over
the hydride. Tests on the solid in the tube showed only
a small amount of phosphorus present in the product. This
would indicate that a higher temperature was needed for
the reaction. Another experiment was carried out in
which the reaction tube was heated to 200 - 300° in a
furnace and a rapid stream of phosphine was passed over
a thin layer of the hydride. The solid in the reaction
tube changed from the grayish-white color of the hydride
to white. After the phosphine had passed over the hydride
for about 20 minutes (amount of hydride used was approx-
imately 0.5 g.) the phosphine supply was cut off and
nitrogen passed over the solid. Sodium analyses of the
product, carried out by the procedure described for the
analysis of lithium under the procedure for the analysis
of lithium phosphide, gave values of 50.54% and 50.35%
sodium. The calculated per cent of sodium in primary
sodium phosphide is 41.07%; sodium in secondary

---

[91] Keyes, J. Am. Chem. Soc., 34, 779 (1912).

phosphide is 58.98%; and sodium in tertiary sodium phosphide is 69.01%. The sample obtained above was in all probability a mixture of the primary, secondary and/or tertiary phosphides.

Having made the two observations recorded above, it was decided to try an intermediate temperature for the reaction. After several trials it was decided to use a temperature of approximately 150°. The sodium hydride (approximately 0.5 g.) was placed in a pyrex glass tube previously swept out with nitrogen. The hydride was spread out in a thin layer and a rapid stream of phosphine passed over it. The solid in the reaction tube turned from the gray color of the hydride to the white color of the phosphide. The sample was analyzed for phosphorus and sodium according to the procedure given under the analysis of lithium phosphide. Results of the analyses are reported in Table IX.

The high results for sodium may be attributed to two sources--namely, (1) the presence of secondary and tertiary phosphides and/or (2) the presence of unreacted sodium hydride. The low results for phosphorus may be attributed to the presence of secondary and tertiary phosphides, the presence of the hydride and to a loss in sampling. The high value for sodium and the low value

Table IX

Analysis of Primary Sodium Phosphide

	Sodium analyses		
Sample number	Wt. of sample	Ml. of 0.1071 N HCl	% Na[*]
1	0.066	11.8	44.0
2	0.114	20.1	43.4

	Phosphorus analyses						
Sample number	Wt. of sample	Vol. of PH_3	Temp.	Bar. pressure (mm. Hg.)	V.P. H_2O (mm. Hg.)	Wt. of PH_3	% P[*]
1	0.066	28.0	28°	750	28.3	0.0367	50.6
2	0.114	48.9	28°	750	28.3	0.0640	51.2

[*]Calculated for $NaPH_2$: Na = 41.07%; P = 55.32%.

for phosphorus are in agreement with results obtained by Dennis and Browne[92] in their studies on the preparation of sodium amide. Shober and Spanatius[34] obtained similar results when they passed phosphine over sodium.

Primary sodium phosphide is a white solid, spontaneously inflammable in moist air but stable in a nitrogen atmosphere. It reacts readily with water according to the following equation:

$$NaPH_2 + H_2O \longrightarrow NaOH + PH_3$$

The reaction with water is explosive in air unless the samples are very small, but in the presence of nitrogen the reaction goes smoothly but rapidly.

A portion of the sample was warmed in a vacuum and phosphine was evolved. No attempt was made during this study to establish the decomposition temperature of the phosphide. Legoux[76] reported that the phosphide decomposed slowly through loss of phosphine and that it liberated sodium at 380°.

In the discussion, an idea is considered for improving the technique for the study of this reaction.

---

[92] Dennis and Browne, *ibid.*, 26, 587 (1904).

M. Action of Phosphonium Iodide on Acid Chlorides

The action of phosphonium iodide on different classes of organic compounds is summarized by Kosolapoff[93]. A literature survey revealed no study of the action of phosphonium iodide on acid chlorides and so it would seem that no such study had been made.

The action of phosphonium iodide on acetyl chloride at room temperature resulted in the formation of an orange-colored solid. Qualitative analysis of the solid showed that it was organic in nature and that it contained phosphorus and iodine. Qualitative analysis of the gases liberated from the reaction flask indicated that hydrogen chloride was formed in large quantities along with a small amount of hydrogen iodide. A test for hydrogen showed it to be absent. Some phosphine was liberated throughout the reaction.

This solid was found to be insoluble in any solvent tried unless the solvent reacted with it. The solvents tried were acetone, benzene, carbon disulfide, carbon tetrachloride, chloroform, 1-4 dioxane, ethyl acetate, ethyl alcohol, glacial acetic acid, ligroin, methyl alcohol, petroleum ether, toluene, dilute ammonium hydroxide (0.1N), dilute hydrochloric acid (3N), dilute

---

[93]Kosolapoff, op. cit., pp. 10, 15, 20.

nitric acid (3N), concentrated potassium hydroxide (10%), and water. Of the solvents listed, water and the alcohols reacted with the solid very slowly at room temperature to evolve some phosphine; iodine was present in the wash solution. If enough washings were carried out with water or ethyl alcohol the orange-colored solid could be freed of the iodine leaving a yellow solid. Dilute hydrochloric acid reacted very slowly in the cold and slowly when warmed with the solid to liberate phosphine. Dilute nitric acid dissolved the solid slowly while concentrated nitric acid dissolved it with explosive action at room temperature. The solid dissolved in warm 10% potassium hydroxide with the evolution of phosphine. Dilute ammonium hydroxide reacted very slowly with the solid at room temperature to remove iodine and if the ammonium hydroxide was warmed it reacted with the solid to liberate phosphine.

Different procedures were tried for the purification of the orange solid. Efforts to find a solvent for crystallization were not successful. Efforts to sublime the product at atmospheric pressure and also under reduced pressure were not successful. It was found that washing the solid with anhydrous ether until the ether wash was free of iodine gave a product which gave reproducable analysis.

1. <u>Procedure</u>.

The acetyl chloride used in this study was Merck
"reagent" grade. Samples of the orange-colored solid
prepared in this study were approximately 2 g. in size.
Although the conditions were not studied in detail, it
was found that the reaction yielded the orange-colored
solid as long as the acetyl chloride was present in
excess. If the phosphonium iodide was present in excess
a pasty, red-colored solid resulted. In a typical pre-
paration approximately 3 g. of phosphonium iodide was placed
in a flask and then a small amount (approximately 5 ml.)
of acetyl chloride was added. The reaction started
immediately with the formation of the orange-colored solid.
After the reaction had started, more acetyl chloride in
an amount of about 30 ml. was added. If the entire amount
of acetyl chloride was added at one time, the reaction was
slow in starting. Once the reaction has been started by
the procedure given, it will continue smoothly at room
temperature with the evolution of hydrogen chloride and
some phosphine. The reaction was then allowed to proceed
at room temperature until all of the phosphonium iodide
had reacted. This will take about four hours for a 3 g.
sample of phosphonium iodide. The reaction flask was a
200 ml. flask with ground-glass joint and the reaction

mixture was protected from outside contamination by a
tube filled with calcium chloride.

After the reaction was complete the orange-colored
solid was separated from the mother liquor by centrifug-
ing and then washed in the centrifuge tubes with anhydrous
ether until the ether wash no longer showed the presence
of iodine. This took about five washings for a sample of
approximately 0.5 gram. After washing, the solid was
freed of ether by means of a stream of nitrogen and then
transferred from the centrifuge tube into a flask similar
to the one described for the drying of lithium phosphide
under vacuum; it was dried under a vacuum for two hours
at room temperature. The vacuum was broken with nitrogen,
the sample transferred to a weighing bottle and kept in
a desiccator over calcium chloride. This solid gave a
negative test for chloride using the spot test of Feigl[67].

The results of phosphorus and iodine analyses are
reported in Table X. Samples 1 and 2 are from two
different preparations carried out by the procedure
described above.

For the phosphorus analysis the sample was treated
with 3N nitric acid and then (1:1) nitric acid to complete
the solution. The (1:1) nitric acid was not added directly
to the sample as this acid reacted very rapidly with it.
The procedure of adding the 3N nitric acid and then the (1:1)

Table X

Analysis of $CH_3C(=PH)PH_2 \cdot HI$

Phosphorus					Iodine			
Sample number	Wt. of sample	Wt. of $(NH_4)_3P(Mo_3O_{10})_4$	% P[*]		Sample number	Wt. of sample	Wt. of AgI	% I[*]
1	0.1041	1.7848	28.12		1	0.1376	0.1480	58.14
2	0.0550	0.9268	27.64		2	0.1035	0.1092	57.03

[*]Calculated for $CH_3C(=PH)PH_2 \cdot HI$: P = 28.18%; I = 57.73%.

acid gave smooth solubility of the sample at room temperature. To insure complete solution 5 ml. of concentrated nitric acid was always added. The nitric acid solution was heated to boiling and a 2% solution of potassium permanganate was added dropwise to the boiling solution until a permanent brown precipitate formed. This precipitate was dissolved by the dropwise addition of sodium sulfite solution. The phosphorus was determined gravimetrically as the ammonium dodecamolybdophosphate by the procedure described in "Scott's Standard Methods of Chemical Analysis"[94].

For the iodine analysis the weighed sample was treated with 25% potassium hydroxide at room temperature. The solid reacted with the 25% potassium hydroxide at room temperature to give a copious evolution of phosphine. After allowing the reaction to go at room temperature for about fifteen minutes, the sample was warmed under reflux conditions to complete the solution. The solution was allowed to cool, neutralized with nitric acid (first dilute and then concentrated) and then made slightly acid with concentrated nitric acid. Solid sodium hydrogen sulfite was added to the solution to insure complete reduction of any elemental iodine to iodide and then a rapid stream of carbon dioxide was bubbled through the

---

[94]Furman, op. cit., p. 694.

solution to remove the excess sulfur dioxide. The iodide was precipitated as silver iodide and weighed.

An attempt to determine the molecular weight of the orange-colored solid by the Rast method was unsuccessful because the compound is insoluble in camphor. The solid did not melt but decomposed to a red solid at approximately 125° with the evolution of phosphine and hydrogen iodide. The orange-colored solid was insoluble in any solvent studied unless that solvent reacted with it. If the solid was exposed to the atmosphere for some time it absorbed water to give an acid solution.

An attempt to assign a structure to this compound on the basis of the information available is quite speculative. The evidences collected to date which would indicate that the compound might be the phosphorus analogue of acetamidine hydroiodide are three in number. First, the fact that the compound reacts with water and more readily with strong bases to liberate phosphine would indicate that the compound has a phosphine linkage[95]. Second, the fact that the iodide can be removed with water or more readily with a base would indicate that the iodine is in the form

---

[95](a) Kosolapoff, op. cit., p. 24; (b) Patterson, Private communication. A copy of Dr. Patterson's letter is appended.

of a salt. Third, the quantitative analysis of the compound would indicate the relationship suggested.

If it is assumed that the compound is the phosphorus analogue of acetamidine hydroiodide a structure which might be assigned to it is as follows:

$$CH_3 - C \overset{\displaystyle /\!/ PH}{\underset{\displaystyle \diagdown PH_2}{}} \cdot HI$$
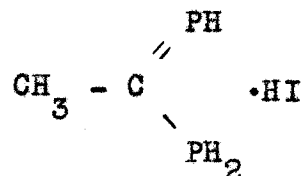
Again, if this simple compound is assumed it might be named ethylidynediphosphine hydroiodide[95]. As Dr. Patterson pointed out in his letter, such a name would be out of order if the structure is polymeric.

The reaction between phosphonium iodide and propionyl chloride (Eastman white label) was studied. The two reacted at room temperature to give a yellow-orange solid which did not give phosphorus analyses to check with the structure $CH_3CH_2C(=PH)PH_2 \cdot HI$ which would correspond to the compound made from the acetyl chloride and phosphonium iodide. The reaction was carried out under conditions identical with those described for the acetyl chloride. Typical results of the phosphorus analyses on three different samples prepared at different times but by the same procedure are recorded in Table XI.

Table XI

Analysis of Product Formed by the Action of
Phosphonium Iodide on Propionyl Chloride

Sample number	Wt. of sample	Wt. of $(NH_4)_3 P(Mo_3O_{10})_4$	% P[***]
1	0.0855	2.0615	39.54
2	0.0708[*]	0.3496	40.37
3	0.2790[**]	0.6688	39.67

[*]Sample placed in 250 ml. and a 50 ml. portion used for analysis.

[**]Sample placed in 500 ml. and a 50 ml. portion used for analysis.

[***]Calculated for $CH_3CH_2C(=PH)PH_2 \cdot HI$: P = 26.49%.

These phosphorus analyses were carried out by the same procedure as described for the analysis of the so-called, ethylidynediphosphine hydroiodide. An iodine analysis was not run on this product. In all proabability there was a mixture of a series of products with some of the compounds richer in phosphorus than the $CH_3CH_2C(=PH)PH_2 \cdot HI$. Reproducibility of results from different preparations would indicate that if there was a mixture

formed, the different products were always present in the same ratio.

Phosphonium iodide and n-butyryl chloride (Eastman white label) reacted under the same conditions as discussed above to yield a yellow solid which gave a phosphorus analysis totally out of line with that expected for a compound analogous to the one obtained from acetyl chloride and phosphonium iodide. A 0.2118 g. sample of the yellow solid was dissolved in nitric acid oxidized with permanganate and diluted to 500 ml. Fifty milliliter aliquots were taken for analysis and the weights of ammonium dodecamolybdophosphate obtained were 0.3583 g. and 0.3550 g. equivalent to 55.51% and 54.93% phosphorus, respectively. An iodine analysis on a portion of this sample gave 25.98% iodine.

N. Action of Phosphine on Acetyl Chloride

The work of Cuneo[30] on the action of phosphine on phosgene made it seem probable that phosphine and acetyl chloride might react in the presence of a catalytic agent. Cuneo reported that he could prepare carbophosphide, $CO(PH_2)_2$, from phosphine and phosgene by the use of zinc carbonate as a catalyst.

In the study of the action of phosphine on acetyl chloride several different inorganic compounds were used but none promoted the reaction. Those tried were dry zinc carbonate, zinc oxide, cadmium carbonate and zinc acetate. Dry phosphine was bubbled through a capillary tube into the suspension of the inorganic compound in the acetyl chloride at room temperature. The procedure was repeated at the temperature of a salt-ice bath and at a temperature of 50°. The solid material left in the flask on all occasions was the inorganic compound along with a small amount of a phosphorus-containing material. From the information reported below it would seem that the use of such inorganic compounds as mentioned here would not be practical because of the difficulties encountered in the separation of the phosphorus-containing compound from the inorganic compound.

In addition to the catalytic agents studied above the use of a Cheronis[65] semimicro hydrogenator as a means of bringing the phosphine and acetyl chloride together was studied. The acetyl chloride was placed in the reaction flask and phosphine was bubbled through the microporous dispenser into it. The reaction tube was surrounded by a water bath which was kept at a temperature of 50°. A white solid, in very small yield, formed in the acetyl chloride. The solid was allowed to settle, the acetyl

chloride was decanted and the solid studied qualitatively.
The white solid was found to contain phosphorus and to be
very unstable once the mother liquor was removed. The
solid reacted readily with water to give off phosphine.
A sample of the solid was not captured for analysis. The
procedure was repeated at room temperature and at the
temperature of a salt-ice bath. In both cases a very small
yield of the sample was obtained. The yield was greater
at 50°.

If the acetyl chloride was dissolved in ether and then
phosphine bubbled through this solution using the Cheronis
hydrogenator a very small amount of a white solid was
formed and again a sample was not captured for analysis.
If the excess ether was decanted from the small sample
of white solid and then ethyl alcohol added there was a
rapid reaction with the evolution of phosphine. Part of
the reaction was evidently between acetyl chloride, which
had not been removed, and alcohol.

Certainly nothing definite can be said about the
white solid mentioned above. Improved techniques of hand-
ling the solid which were later developed in the study of
the metallic phosphides might possibly result in its
capture for quantitative analysis. Possibly the yield of
the solid might be increased if the microporous dispenser
used were of fine porosity instead of the medium one used

in this study.

Of the possibilities concerning the composition of the white solid, it seems probable that the hydrogen compounds of phosphorus which form with some reactions of phosphine could be eliminated. These hydrogen compounds are either a colorless gas (PH_3), a colorless liquid (P_2H_4), a yellow solid ($P_{12}H_6$) or a red solid (P_9H_2).

O. Studies in the Preparation of Lithium Amide and Magnesium Amide

1. **Preparation of lithium amide.**

It seemed of interest to study the action of ammonia on an organolithium compound to determine its usefulness as a means for preparing lithium amide. If the presence of bromide does not interfere with the proposed use of the amide, the amide may be prepared from the organolithium compound which, in turn, had been prepared from the alkyl or aryl halide and the metal. Also the amide might be prepared from an organolithium compound whose preparation had been carried out in petroleum ether[96]. In this case the lithium halide is insoluble in the petroleum ether and would therefore not be a contaminant of the amide.

---

[96] Gilman, Langham and Moore, *J. Am. Chem. Soc.*, 62, 2327 (1940).

Lithium amide was prepared by the action of ammonia on phenyllithium. The procedure was identical with that used for the preparation of the phosphide. It was found best to introduce the ammonia under the surface of the liquid in the reaction flask. Otherwise, some amide would form on the stem of the funnel. The ammonia used was the "anhydrous" grade purchased from the Matheson Company, Inc. and was passed over "ascarite" and soda-lime according to the procedure of Dennis and Browne[92].

The amide was analyzed according to the procedure of Dennis and Browne. A weighed portion of the sample was placed in a Kjeldahl flask provided with a Kjeldahl trap and a dropping funnel. Water was introduced through the dropping funnel and the liberated ammonia was distilled off into standard hydrochloric acid. Excess acid was back titrated using methyl red as the indicator. For the determination of the lithium it was necessary that the ammonia be completely removed from the solution which remains in the Kjeldahl flask. This solution was transferred to an evaporating dish and carefully evaporated to dryness, redissolved in water and again evaporated to dryness. The lithium was determined by titrating the hydroxide with standard acid. The results of the analyses of the amide are recorded in Table XII.

Table XII

Analysis of Lithium Amide

Lithium analysis			
Sample number	Wt. of sample	M. of 0.1045 N HCl	% Li*
1	0.1142	46.63	29.61
2	0.1024	41.55	29.43

Nitrogen analysis				
Sample number	Wt. of sample	Ml. of 0.1045 N HCl	Ml. of 0.1214 N NaOH	% N*
1	0.1142	50.00	2.45	60.44
2	0.1024	50.00	6.80	60.15

*Calculated for $LiNH_2$: Li = 30.22%; N = 60.99%.

2. <u>Preparation of magnesium amide.</u>

Similarly, the action of ammonia on di-n-butylmagnesium produced magnesium amide. Analyses of the amide are recorded in Table XIII.

Table XIII

Analysis of Magnesium Amide*

Magnesium analyses			
Sample number	Wt. of sample	Wt. of $Mg_2P_2O_7$	% Mg**
1	0.1767	0.3328	41.28
2	0.0852	0.1621	41.57

Ammonia analyses			
Sample number	Wt. of sample	Vol. of 0.1045 N HCl	Vol. of 0.1214 N HCl	% N**
1	0.1767	75.00	14.70	47.93
2	0.0852	50.00	19.04	47.98

*See text for comment on impurities.

**Calculated for $Mg(NH_2)_2$: Mg = 43.14%; N = 49.71%.

P. A Study of the Preparation of
Pentammine Aluminum Bromide

Success with the preparation of the phosphinate from phosphine and aluminum bromide in benzene led to a study of the action of ammonia on the benzene solution of aluminum bromide. Pentammine aluminum bromide can be prepared by the action of ammonia on a solution of aluminum bromide in benzene or carbon disulfide. In this study the aluminum bromide solution in benzene was prepared and treated with ammonia in the same manner as described for the preparation of the aluminum bromide monophosphinate. The ammonia was the anhydrous commercial grade dried over "ascarite" and soda-lime. The pentammine aluminum bromide precipitated out as a white solid. This precipitate was allowed to settle, the mother liquor was decanted and the ammine was washed two or three times with benzene. The washings were carried out in centrifuge tubes as described under the preparation of aluminum bromide monophosphinate. After washing, the pentammine aluminum bromide was dried under vacuum at 75° for two hours. The results of the analyses of the ammine are given in Table XIV.

The pentammine aluminum bromide is a white solid which reacts with water to liberate ammonia. It is unstable in moist air but stable in a nitrogen atmosphere.

Table XIV

Analysis of Pentammine Aluminum Bromide

Aluminum analyses

Sample number	Wt. of sample	Wt. of Al_2O_3	% Al[*]
1	0.3202	0.0490	8.09
2	0.4281	0.0639	7.90

Bromide analyses

Sample number	Wt. of sample	Wt. of AgBr	% Br[*]
1	0.1270	0.2048	68.63
2	0.4575	0.7333	68.21

Ammonia analyses

Sample number	Wt. of sample	Ml. of 0.1045 N HCl	Ml. of 0.1214 N NaOH	% NH_3[*]
1	0.1270	50.00	28.40	23.82
2	0.4575	75.00	11.60	23.89

[*]Calculated for $AlBr_3 \cdot 5NH_3$: Al = 7.66%; Br = 68.14%; NH_3 = 24.20%.

V. DISCUSSION

The improvements recorded in this study for the preparation of phosphonium iodide from phosphorus and iodine reduced the time of its preparation considerably over those previously described. Also many of the operations can be carried out, once they have been started, with only an occasional check. The older procedures required considerable attention from the operator.

A reinvestigation of the action of phosphine or phosphonium iodide on bromine and iodine showed that the respective phosphorus halide could be prepared if the conditions and amounts of reagents were controlled properly. The results obtained in this study are in contradiction with some reported earlier. The reports of the earlier investigators are probably correct for the conditions which they studied but they did not attempt to control the reactions for useful purposes.

The ease with which pure diphosphorus tetraiodide can be prepared from phosphonium iodide and iodine should make a study of the properties of this compound more attractive. The properties of this compound have not been studied very extensively. In all probability diphosphorus tetraiodide might find more extensive use in organic syntheses. One

example of its use in this field is the work of Auger and Billy[97] who found that ethylmagnesium bromide and diphosphorus tetraiodide react to form tetramethylphosphonium iodide. Likewise the field of inorganic chemistry should afford some interesting studies for diphosphorus tetraiodide. Mellor[59] records some reactions of diphosphorus tetraiodide such as that reported by Tarible[98] on its reaction with boron (III) bromide to form $P_2I_4 \cdot 2BBr_3$.

A solution of pure phosphorus (III) bromide in an inert organic solvent can be prepared conveniently by the action of phosphine on a solution of bromine in the solvent. The total time and equipment involved in the preparation would not appear to be greater than encountered when the bromide is prepared from the elements.

The preparation and isolation of antimony (III) phosphide in relatively pure form seems to have been done only once before and that was by Ramsy and McIvor[19]. However, their method of preparation was different from that reported in this study. This compound might have interesting catalytic properties.

The few references that are scattered throughout the literature, the recent work of Wiberg and Bauer[25,26] and the

---

[97] Auger and Billy, Compt. rend., 139, 597 (1904).

[98] Tarible, ibid., 132, 204 (1901).

present study would indicate that the organometallic compounds can be a useful tool to the inorganic chemist. They may never play as important a role in synthetic inorganic chemistry as they have in synthetic organic chemistry but they certainly can have application. It seems reasonable to say that many of the hydrogen compounds of the inorganic elements would react with organometallic compounds to form inorganic compounds which have not been prepared previously or to prepare some of those that have been prepared of a higher degree of purity than heretofore attained. Certainly phosphine and ammonia can be extended to the preparation of metallic phosphides and amides other than those considered in this study. Some additional hydrogen compounds which might be studied are hydrogen sulfide, arsine, stibine, hydrogen selenide, hydrogen telluride and silane. Of course, this list is not exhaustive.

In addition to the fundamental research involved, some of these preparations could have practical use. The primary inorganic phosphines can be used in the synthesis of organic phosphines. Often times small amounts of an inorganic amide are needed around the laboratory. The preparation of amides by other procedures requires special apparatus. The use of organometallic compounds

would afford a useful method for the preparation of small amounts of these amides.

It would be of interest to study the therapeutic properties of the ethylidynediphosphine hydroiodide. Cuneo[30] studied the therapeutic effects of carbophosphide and reported that it had advantages over other sources in all cases in which administration of phosphorus is indicated. Further study on the conditions of the reaction of phosphonium iodide on the acid chlorides is needed. It might be that a higher or lower temperature is needed in the cases of the propionyl and butyryl chlorides. It may be necessary to add dry hydrogen iodide to the system in order to increase its content to compensate for the loss in formation of propionyl and butyryl iodides.

Further use of an inert reaction medium to accomplish the preparation of coordination compounds which involve reaction between a solid and a gas should prove interesting. Practically all of the studies to date deal with the formation of coordination compounds in aqueous medium, with the reaction of a gas-solid mixture or with the treatment of the salt with a sample of the liquefied coordinating agent. The use of an aqueous system eliminates the formation of some coordination compounds even though they might form under appropriate conditions, because the water is preferentially coordinated. The gas-solid mixture suffers

difficulties of carrying the reaction to completion. In
the third case liquefaction of the gas always requires
special apparatus.

The literature contains many references to the
formation of different coordination compounds of aluminum
bromide. The preparation in many cases was difficult to
accomplish by the procedure used. A reinvestigation of
some of these by the use of the procedure described in
this study should be of interest. Other coordinating
agents than those already studied could be investigated.
The procedure could be extended to other aluminum halides
and to other salts that are soluble in a solvent that is
inert to the reactants.

A study of the reaction of sodium hydride and phos-
phine by a procedure similar to the one used in the pre-
paration of lithium phosphide from an organometallic com-
pound would be of interest. At the time that this pro-
cedure was developed the supply of sodium hydride had been
exhausted. A possible procedure would be to pass the
phosphine through a liquid inert to the reactants and which
boils at a temperature of over 100° and then add the sodium
hydride in small amounts either as a powder from a powder
adapter or from an agitated suspension of the hydride in an
inert liquid. This might also furnish a practical means of
preparing the phosphides of other alkali metals and a

means of preparing laboratory quantities of the amides of certain metals. Certain of the hydrides are now available commercially which makes their use practical.

VI. SUMMARY

1. Improvements in the procedure for the preparation of phosphonium iodide have been reported which reduce the total time needed for its preparation considerably. These improvements have reduced the actual time of attention required from the operator.

2. A study of the action of phosphonium iodide and/or phosphine on bromine and iodine was conducted. A useful preparation of diphosphorus tetraiodide was obtained and a means for preparing pure phosphorus (III) bromide was described.

3. Antimony (III) phosphide was prepared.

4. The action of phosphine on disulfur dichloride was found to yield phosphorus (V) sulfide. With a stoichiometric mixture of sulfur and bromine (S_2Br_2) thiophosphoryl bromide was obtained.

5. The preparation of primary lithium phosphide and primary magnesium phosphide from organometallic compounds was carried out. The procedure was extended to the respective amides.

6. The action of phosphine on sodium hydride was studied.

7. The preparation of aluminum bromide monophosphinate
   was accomplished at room temperature. Pentammine
   aluminum bromide was prepared by the same procedure.

8. The action of phosphonium iodide on acid chlorides
   was studied and a new compound prepared from acetyl
   chloride and phosphonium iodide was obtained. It is
   possible that the compound is ethylidynediphosphine
   hydroiodide.

VII. ACKNOWLEDGMENTS

VIII. APPENDIX

COPY

Austin M. Patterson
221 North King St.
Xenia, Ohio

August 8, 1951

Mr. Glenn H. Brown
Department of Chemistry
Iowa State College
Ames, Iowa

Dear Mr. Brown:

I have delayed answering your letter of August 2 until I could consult with Dr. L. T. Capell and the other organic members of the C. A. staff.

By present methods the best names we can suggest for the compound $CH_3C(:PH)PH_2$ is ethylidynediphosphine or, as a second choice, (1-phosphinoethylidene) phosphine. C. A. has used such trivalent radicals as ethylidyne in di-names similar to the present case. An advantage of either phosphine name is that it puts the compound under Phosph- (and therefore with other phosphorus compounds) on the C. A. index.

There is no accepted name for the radical :PH; it might be named phosphylene by analogy with arsylene, :AsH; the latter name is in the C. A. list of radicals but has not been recognized by the International Union.

It is a temptation to coin the name "acetophosphidine" by analogy with acetamidine, but I would not suggest this without committee consultation. I do not think "phosphidine" has been used for any compound; it was proposed in a committee as a name for PH_5 but the name "phosphorane" was chosen instead (not yet officially adopted). Unless there is likelihood that a class of compounds of phosphorus analogous to the amidines of nitrogen can exist, I would not advise such a name.

Mr. Glenn H. Brown (continued)

The possibility of polymerization is something of
a deterrent to any name for the simple compound, for
the simple name would be a misnomer for the polymer.
The name "siliconic acid" for compounds of the formula
$RSi(:O)OH$ was not adopted by the organosilicon group
because such compounds are believed to be always poly-
meric.

Sincerely yours,

/s/ Austin M. Patterson