TABLE I

S-*p*-CHLOROBENZYLTHIURONIUM SALTS

	Phosphorus compound	Derivative[a]	M.p., °C.	Cryst. solvent	C Calcd.	C Found	H Calcd.	H Found	Cl Calcd.	Cl Found	S Calcd.	S Found
I.	$C_8H_{17}PO(OH)_2$	$C_8H_{17}P(OH)O_2Q$	192–193	Ethanol	48.67	48.57	7.15	7.08	8.95	8.86	8.12	7.88
II.	$PhPO(OH)_2$	$PhP(OH)O_2Q$	200–202	Pyridine	46.73	46.76	4.49	4.70	9.85	9.57	8.93	9.44
III.	PhPHO(OH)	$PhPHO_2Q$	180–182	Ethanol	49.05	49.04	4.70	4.74	10.35	10.36	9.35	9.33
IV.	$(EtO)_2POSNa$	$(EtO)_2POSQ$	81–82	Ether	38.86	39.41	5.44	5.40	9.56	9.38	17.30	17.16
V.	$(EtO)_3PO$	$(EtO)_2PO_2Q$	160–161	Acetone	40.62	40.71	5.68	5.79	9.88	9.48	9.04	9.17
VI.	$EtPO(OEt)_2$	$EtP(OEt)O_2Q$	166–167	Acetone	42.54	42.41	5.95	6.11	10.47	9.94	9.46	9.65
VII.	$EtSPO(OEt)_2$	$EtSP(OEt)O_2Q$	151–152	Water	38.86	39.34	5.44	5.38	...	...	...	...
VIII.	$PhSPO(OEt)_2$	$PhSP(OEt)O_2Q$	174–176	Water	45.87	46.13	4.81	4.87	...	...	15.31	15.02

[a] $Q = p\text{-}ClC_6H_4CH_2\overset{+}{S}{=}C(NH_2)_2$.

slowly as the reaction mixture stood at room temperature. Recrystallization from the appropriate solvent, indicated in Table I, furnished the analytically pure derivative.

The derivative of sodium O,O-diethylphosphorothioate (IV) was prepared in similar fashion, except that the neutralization step was not necessary.

Derivatives from Organophosphorus Esters.—For the preparation of S-*p*-chlorobenzylthiuronium salts from phosphate (V), phosphonate (VI), or phosphorothioate (VII, VIII) esters, the following procedure is recommended: Sodium ethyl mercaptide is prepared by dissolving sodium (220 mg., 10 mmoles) in a mixture of 10 ml. of ethyl mercaptan and 3 ml. of ethanol. The ester (10 mmoles) is added and the resulting solution heated under reflux for 24 hr. A saturated alcoholic solution of S-*p*-chlorobenzylthiuronium chloride (2.38 g., 10 mmoles) is added and the resulting precipitate of sodium chloride removed by filtration. The solvent is evaporated from the filtrate and the residue crystallized from the appropriate solvent, indicated in Table I.

Recovery of the Free Acid from the Thiuronium Salt.—One gram of the S-*p*-chlorobenzylthiuronium derivative of phenylphosphinic acid (III) was dissolved in 30 ml. of 50% aqueous ethanol and passed through a column of 16 g. of Dowex 50W-X8 resin which previously had been well washed with 50% alcohol. The aqueous alcohol eluate was concentrated to about 10 ml. and extracted with ether. Evaporation of the ether gave phenylphosphinic acid, 264 mg., 64% recovery, m.p. 81–83°.

Reactions of Elemental Phosphorus with Organometallic Compounds

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The direct synthesis of phenylphosphine from phosphorus was achieved in 25% and 40% yields, respectively, by reaction of white phosphorus with phenylmagnesium bromide and with phenyllithium. *n*-Butylphosphine was prepared in 7 to 9% yields by reactions of phosphorus with *n*-butylmagnesium bromide and with *n*-butyllithium. In these reactions much of the phosphorus was converted to nonmelting, insoluble yellow solids, believed to be organopolyphosphines. Reactions of phenylsodium and tri-*n*-butylaluminum with phosphorus gave organopolyphosphines, exclusive of monomeric phosphines.

The susceptibility of white phosphorus to nucleophilic attack is suggested by its well known reaction with hydroxide ion. Hypophosphite, phosphite, phosphine, and hydrogen are obtained as products, and while the mechanism is complex,[1] the first step would appear to involve a nucleophilic attack by hydroxide on the P_4 tetrahedron.

To test the possibility of obtaining organophosphorus compounds by reaction of phosphorus with organic nucleophiles, we have treated a variety of organometallic compounds with white phosphorus. The results are summarized in Table I. The reactions were carried out by adding the organometallic solution dropwise to a slurry of finely divided white phosphorus (method A), or by adding the phosphorus as 0.1-g. pieces in one portion to the organometallic solution (method B). In all of the experiments the phosphorus reacted completely in one to three hours giving deep red solutions. Hydrolysis of reaction mixtures from experiments with organolithium and organomagnesium compounds gave mixtures of corresponding organophosphines with the primary phosphine generally predominating. Liberation of phosphine or hydrogen during hydrolysis could not be detected by mass spectroscopy.

The highest organophosphine yields were obtained from phenyllithium in ether solution and from phenylmagnesium bromide in refluxing tetrahydrofuran (THF). Butyllithium and butylmagnesium bromide gave butylphosphines in low yields under the conditions studied. In the phenyllithium reactions the order of addition had little effect on yields but with butyllithium and butylmagnesium bromide better yields were obtained using addition method B. The choice of solvent was critical for reactions of phenyllithium and phenylmagnesium bromide. For phenyllithium, ether was far superior to tetrahydrofuran, but for phenylmagnesium bromide refluxing tetrahydrofuran gave substantially better yields. Phenylmagnesium bromide in di-*n*-butyl ether at 100° gave predominately diphenylphosphine but the over-all yield of phosphine was relatively poor.

In the experiments with phenyllithium, ratios of starting materials were varied from one mole of phenyllithium per gram-atom of phosphorus to four moles of phenyllithium per gram-atom of phosphorus. Varying reactant ratios in the range of 1.6:1 to 4:1 had little effect on over-all yields based on phosphorus but some-

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(1) J. R. VanWazer, "Phosphorus and Its Compounds," Interscience Publishers, Inc., New York, N. Y., 1958, p. 356.

TABLE I

REACTIONS OF ORGANOMETALLICS WITH WHITE PHOSPHORUS[a]

Organometallic	Moles	Solvent	Ml.	Addition method[b]	Temp.	Phosphine yields[c] RPH$_2$	R$_2$PH	R$_3$P
C_6H_5Li	0.77	Tetrahydrofuran	500	A	35–40	5	0	0
C_6H_5Li	0.50	Et_2O	600	B	35–40	6[d]	small	0
C_6H_5Li	0.80	Et_2O Tetrahydrofuran	1000 100	A	35–40	36	trace	0
C_6H_5Li	0.77	Et_2O C_6H_6	600 150	A	0–5	19[f]	trace	0
C_6H_5Li	1.0	Et_2O	750	B	35–40	27[e]	6	5
C_6H_5Li[g]	1.0	Et_2O	750	B	35–40	40	trace	0
C_6H_5Li	2.0	Et_2O	1600	B	25–30	27[f]	15	0
n-C_4H_9Li	0.75	Heptane	4000	A	25–30	0	0	0
n-C_4H_9Li	1.1	Et_2O	600	B	0–25	9	1	0
C_6H_5MgBr	0.5	Et_2O	300	B	35–40	9[f]	0	0
C_6H_5MgBr	0.5	Tetrahydrofuran	350	A	71	25	trace	0
C_6H_5MgBr	1.0	$(C_4H_9)_2O$	700	B	100	trace[f]	13	0
n-C_4H_9MgBr[h]	1.0	Et_2O	500	B	25–30	7	1	0
C_6H_5Na	1.0	$C_6H_5CH_3$	400	B	45–50	0	0	0
$(i$-$C_4H_9)_3Al$[i]	1.25	$C_6H_5CH_3$	1000	B	100–105	0	0	0

[a] Reactions are based on 0.5 g.-atom of phosphorus. [b] See Experimental. [c] Yields are per cent conversions based on phosphorus. [d] In this experiment a black solid separated during hydrolysis. The solid gradually decomposed liberating hydrogen. In other experiments neither hydrogen or phosphine were observed. [e] Reaction of the phenyllithium was substantially complete after 3 hr. as indicated by carbonation of an aliquot. [f] About 10% unchanged organometallic was found by carbonation of an aliquot after 3 hr. [g] After complete reaction of the phenyllithium with phosphorus, the mixture was refluxed for 1 hr. with excess lithium aluminum hydride. [h] In a similar experiment after the phosphorus had reacted, 5.0 g. of anhydrous cobalt(II) chloride was added and reflux was continued for 3 hr. Similar results were obtained. [i] One-tenth gram of iodine was added as a catalyst. The reaction time was 6 hr.

what higher yields of diphenylphosphine were obtained at the higher ratios. A reactant ratio of 1:1 gave only a 6% yield of phenylphosphine and much of the phosphorus was recovered as a black polymeric solid, which evolved hydrogen on standing. When a 4:1 ratio of phenyllithium to phosphorus was used, disappearance of the phenyllithium was about 90% complete after three hours, but with butylmagnesium bromide, only about one mole of the magnesium compound reacted per gram-atom of phosphorus, even after extended reaction periods.

In all of the reactions substantial amounts of nonmelting, insoluble, amorphous, yellow solids were obtained. In reactions with phenylsodium and with triisobutylaluminum such solids were the only products isolated. These solids contained from 40% to 60% combined phosphorus by analysis and appeared to be cross-linked organopolyphosphines. Several attempts were made to break phosphorus–phosphorus bonds in these polymers and their phosphide precursors in an effort to increase yields of monomeric phosphine products. In one such experiment, phosphorus and phenyllithium were allowed to react completely, and the reaction mixture was then refluxed with lithium aluminum hydride. The yield of phenylphosphine was increased from 27% to 40%, but yields of diphenylphosphine and triphenylphosphine were reduced. In a similar experiment the phenyllithium–phosphorus reaction mixture was refluxed several hours with metallic lithium. The lithium, however, was not attacked. Also unsuccessful was an attempt to effect a free radical phosphorus–phosphorus bond cleavage by adding anhydrous cobalt(II) chloride to a reaction mixture of excess butylmagnesium bromide and phosphorus.

Pyrolysis of the yellow amorphous solid obtained from the phenyllithium–phosphorus reaction gave small amounts of water and white phosphorus which codistilled. The nonvolatile residue was a white powdery solid which inflamed on exposure to the air.

In its simplest terms the reaction of phenyllithium with phosphorus might be expected to conform to the following equation.

$$C_6H_5Li + P_4 \longrightarrow Li_3P + Li_2PC_6H_5 + LiP(C_6H_5)_2 + P(C_6H_5)_3$$

Hydrolysis of such a reaction mixture would give substantial amounts of phosphine, diphenylphosphine, and triphenylphosphine in addition to phenylphosphine. In the actual experiments, however, phosphine was not found and only minor amounts of diphenylphosphine and triphenylphosphine were obtained. This result casts doubt on the existence of simple lithium phenylphosphides as reaction intermediates. While dilithium phenylphosphide has not been ruled out as the precursor of the phenylphosphine obtained, the absence of substantial amounts of the complimentary lithium diphenylphosphide suggests that the actual products present before hydrolysis may be complex lithium phenylpolyphosphides.[2] This hypothesis is reinforced by our observation that solutions of these phosphide intermediates which are free of unchanged phenyllithium, will nevertheless react further with additional phosphorus. The result after hydrolysis is a decreased yield of phenylphosphine and an increased yield of polymeric products. The situation seems analogous to the well known reaction of ammonium sulfide with sulfur to give ammonium polysulfides.

$$2\ Li_2{}^+[(C_6H_5)_2P_4]^{-2} + P_4 \longrightarrow 2\ Li_2{}^+[(C_6H_5)_2P_8]^{-2}$$

$$2\ (NH_4)_2{}^+S^{-2} + S_8 \longrightarrow 2\ (NH_4)_2{}^+S_5{}^{-2}$$

Experimental[3]

Reactions of Organometallic Compounds with White Phosphorus.—Individual experiments are described in Table I. The general procedures are described below.

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(2) Additional support for this view is found in the following paper, M. M. Rauhut and A. M. Semsel, *J. Org. Chem.*, **28**, 473 (1963).

(3) White or "yellow" phosphorus must be treated with *substantial caution*. It is highly toxic, can cause cumulative poisoning, and ignites spontaneously when warmed in air.

Method A.—White phosphorus (15.5 g., 0.5 g.-atom) was combined with 100–150 ml. of tetrahydrofuran, benzene, or toluene under nitrogen in a three-necked, creased flask, and the mixture was heated to 50° to melt the phosphorus. The mixture was stirred vigorously and cooled so that the phosphorus solidified in a finely divided state. The organometallic solution was then added dropwise during a 1-hr. period. The reactions were exothermic and the phosphorus gradually dissolved leaving deep red solutions. The mixtures were stirred for an additional 2 hr. at the indicated temperature and then hydrolyzed either with water for the organolithium experiments or 10% hydrochloric acid for the organomagnesium experiments. Yellow amorphous solids generally separated at this point and were collected by filtration. These solids were nonmelting and insoluble in a variety of solvents. A typical solid obtained from phenylmagnesium bromide was refluxed first with carbon disulfide, then with ether, dried, and analyzed.

Anal. Found: C, 39.68; H, 4.01; P, 42.99; Mg, <0.1.

A yellow, amorphous solid obtained from *n*-butylmagnesium bromide was purified in an analogous manner and analyzed.

Anal. Found: C, 17.48; H, 4.76; P, 59.89.

In several of the experiments gas samples were collected during hydrolysis and analyzed mass spectroscopically. Only solvent vapors and nitrogen were detected; hydrogen and phosphine were absent. However, in one experiment where a 1:1 ratio of phenyllithium to phosphorus was used, a black solid separated during hydrolysis. This solid gradually decomposed giving off hydrogen.

After hydrolysis and filtration, the liquid phases were separated, and the aqueous layer was extracted with three 50-ml. portions of ether. Aqueous layers from organomagnesium experiments were neutralized before extracting. The combined ether phases were dried over anhydrous sodium sulfate and distilled to obtain the products, which were characterized by comparison of boiling points, infrared spectra and v.p.c. retention times with authentic samples.

Method B.—The method used was that described under method A except that the phosphorus was cut into approximately 0.1-g. pieces under water, washed first with acetone, then with ether, and then added in one portion to the organometallic solutions. The reactions, except where noted, were run at reflux during 3 hr. Reaction mixtures from experiments with phenylsodium and triisobutylaluminum were hydrolyzed with substantial caution at 0°.

Pyrolysis of the Yellow Amorphous Solid Obtained from the Reaction of Phenyllithium with Phosphorus.—A 50-ml. distillation flask containing 8.0 g. of yellow solid from the reaction of phenyllithium with phosphorus was strongly heated under nitrogen. A mixture of water and white phosphorus was collected in a cold receiver connected to the arm of the distillation flask. Approximately 1 g. of water and 1.6 g. of phosphorus were obtained. The residue was a white powdery solid. This solid was pyrophoric, burning vigorously when exposed to air.

Reactions of Elemental Phosphorus with Organometallic Compounds and Alkyl Halides. The Direct Synthesis of Tertiary Phosphines and Cyclotetraphosphines

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Unsymmetrical tertiary phosphines were obtained by treating alkyl halides with organophosphides prepared from white phosphorus and organolithium compounds or phenylsodium. Tetrabutylcyclotetraphosphine was prepared in 42% yield by the one-step reaction of phosphorus with butylmagnesium bromide and butyl bromide. Other reactions are described and the constitution of the organophosphides is discussed.

Introduction

Organophosphides can be prepared by reaction of a primary or secondary phosphine with an alkali metal,[1,2] an organoalkali, or an organomagnesium compound[2,3]; reaction of a halophosphine with an alkali metal[4,5]; or by cleavage of a tertiary phosphine,[6] a tetraaryldiphosphine,[7] or a tetraarylcyclotetraphosphine[4,8] with an alkali metal.

Reactions of such phosphides with hydrolytic agents give corresponding primary or secondary phosphines, while reactions with alkyl halides give tertiary phosphines.

$$(C_6H_5)_2PLi + H_2O \longrightarrow (C_6H_5)_2PH + LiOH$$

$$(C_6H_5)_2PLi + C_4H_9Br \longrightarrow (C_6H_5)_2PC_4H_9 + LiBr$$

In the preceding paper a method was described for the direct preparation of organophosphides from elemental phosphorus and organolithium or organomagnesium compounds.[9] Thus, reaction of white phosphorus with phenyllithium in ether gave a deep red organophosphide solution, which on hydrolysis provided a 36% yield of phenylphosphine along with a substantial amount of a yellow solid, which from its analysis and properties was evidently an organopolyphosphine. In simplest terms this reaction might have been expected to conform to the following equation.

$$C_6H_5Li + P_4 \longrightarrow Li_3P + C_6H_5PLi_2 + (C_6H_5)_2PLi + (C_6H_5)_3P$$

However, failure to obtain substantial amounts of phosphine, diphenylphosphine, and triphenylphosphine on hydrolysis indicated that this simple picture was not valid and suggested that the actual organophosphide products were more complex. The formation of amorphous polyphosphines on hydrolysis also supported this view.

To provide a sharper insight into the nature of these organophosphides and to investigate their preparative

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(2) F. G. Mann and I. T. Millar, F. H. Stewart, *J. Chem. Soc.*, 2832 (1954).

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(9) M. M. Rauhut and A. M. Semsel, *J. Org. Chem.*, **28**, 471 (1963).