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.

$$(C_6H_5)_2PLi + H_2O \longrightarrow (C_6H_5)_2PH + Li\,OH$$

$$(C_6H_5)_2PLi + C_4H_9Br \longrightarrow (C_6H_5)_2PC_4H_9 + Li\,Br$$

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.

$$C_6H_5Li + P_4 \longrightarrow Li_3P + C_6H_5PLi_2 + (C_6H_5)_2P\,Li + (C_6H_5)_3P$$

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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(1) C. Walling, U. S. Patents, 2,437,795; 2,437,797 (March 16, 1948); C. H. Hitchcock and F. G. Mann, *J. Chem. Soc.*, 2081 (1958); F. G. Mann, I. T. Millar, and H. R. Watson, *ibid.*, 2516 (1958). For corresponding reactions with phosphine, itself, see: W. B. Shober and F. W. Spanutius, *Am. Chem. J.*, **16**, 229 (1894); M. A. Joannis, *Compt. rend.*, **119**, 557 (1894); C. Legroux, *ibid.*, **207**, 634 (1938).

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

(3) A Job and G. Dusollier, *Compt. rend.*, **184**, 1454 (1927); K. Issleib, A. Tzschach, *Chem. Ber.*, **92**, 1118 (1959). For corresponding reactions with phosphine see: H. Albers and W. Schuler, *ibid.*, **76**, 23 (1943); N. Kreutzkamp, *ibid.*, **87**, 919 (1954); G. W. Parshall and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **81**, 6273 (1959).

(4) P. R. Bloomfield and K. Parvin, *Chem. Ind.* (London), 541 (1959).

(5) K. Issleib and D. Müller, *Chem. Ber.*, **92**, 3175 (1959).

(6) D. Wittenberg and H. Gilman, *J. Org. Chem.*, **23**, 1063 (1958); K. Issleib and H. O. Frohlich, *Z. Naturforsch.*, **14B**, 349 (1959).

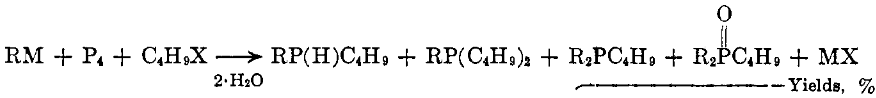
(7) W. Kuchen and H. Buchwald, *Angew. Chem.*, **69**, 307 (1957).

(8) J. W. Resor and G. F. Wright, *J. Org. Chem.* **22**, 385 (1957); W. Kuchen and H. Buchwald, *Chem. Ber.*, **91**, 2296 (1958).

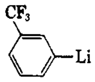
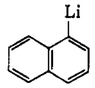
(9) M. M. Rauhut and A. M. Semsel, *J. Org. Chem.*, **28**, 471 (1963).

TABLE I

REACTIONS OF ORGANOALKALI COMPOUNDS WITH WHITE PHOSPHORUS AND BUTYL HALIDES[a]



$$RM + P_4 + C_4H_9X \xrightarrow[2\cdot H_2O]{} RP(H)C_4H_9 + RP(C_4H_9)_2 + R_2PC_4H_9 + R_2\overset{O}{\overset{\|}{P}}C_4H_9 + MX$$

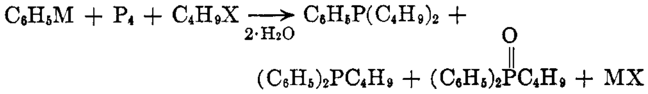
Organometallic reagent	Moles	Butyl halide	Moles	Solvent	Ml.	Addition method[b]	Temp.	Yields, %[c]				
								$RP(H)C_4H_9$	$RP(C_4H_9)_2$	$R_2PC_4H_9$	$R_2\overset{O}{P}C_4H_9$	Total
C_6H_5Li	1.0	C_4H_9Br	1.0	$(C_2H_5)_2O$	500	A	40–42	0	24	39	8	81[d]
C_6H_5Li	1.0	C_4H_9Br	1.0	$(C_2H_5)_2O$	500	B	40–42	0	20	38	11	69[e]
C_6H_5Li	1.0	C_4H_9Cl	1.0	$(C_2H_5)_2O$	800	A	40–42	0	37	44	[f]	81
C_6H_5Li	1.5	C_4H_9Cl	1.0	$(C_2H_5)_2O$	1200	A	40–42	0	30	37	[f]	67
	1.0	C_4H_9Br	1.0	$(C_2H_5)_2O$	700	A	35–40	0	15	20	0	35
	1.0	C_4H_9Br	1.0	$(C_2H_5)_2O$	700	A	35–40	0	36	37	0	73
	1.0	C_4H_9Br	1.0	$(C_2H_5)_2O$	900	A	20–25	35	0	18	0	53
C_4H_9Li	1.0	C_4H_9Br	0.75	$(C_2H_5)_2O$	600	B	0–38[g]	10	39	..	0	49
C_6H_5Na	1.0	C_4H_9Cl	1.2	$C_6H_5CH_3$	400	B	45–50	0	34	28	10	72
C_4H_9Na	1.0	C_4H_9Cl	1.0	n-C_8H_{18}	400	B	35–40	13	1	..	0	14

[a] Reactions are based on 0.5 g.-atom of phosphorus. [b] Method A: The phosphorus was added in one portion to a stirred mixture of the other reactants. Method B: The phosphorus was added in one portion to the stirred organometallic solution, and the reaction was allowed to go to completion during 3 hr. The butyl halide was then added dropwise during 30 min., and the mixture was stirred at the indicated temperature for an additional 3 hr. [c] Yields are per cent conversions based on phosphorus. [d] Phenylphosphine (10%) was also obtained; 32% of the butyl bromide remained unchanged at the end of the reaction. [e] Phenylphosphine was not found; 36% of the butyl bromide remained unchanged at the end of the reaction. [f] Not determined. [g] The phosphorus was added to the butyllithium solution at 5°. The mixture was stirred at 5° for 1 hr., and at 26° for 2 hr. The butyl bromide was then added dropwise during 75 min. at 0°. The temperature was allowed to rise to 38° during 30 min., and the solution was stirred at 38° for 2 hr.

value in chemical synthesis, we have studied their reactions with butyl halides and, to a lesser extent, their reactions with propylene oxide and with benzaldehyde. Experiments were carried out with organophosphides prepared from reactions of phosphorus with organolithium, organosodium, and organomagnesium compounds.

Results

Reactions of phenyllithium or phenylsodium with phosphorus and butyl halides followed by hydrolysis gave dibutylphenylphosphine and butyldiphenylphosphine as major products along with smaller yields of butyldiphenylphosphine oxide.

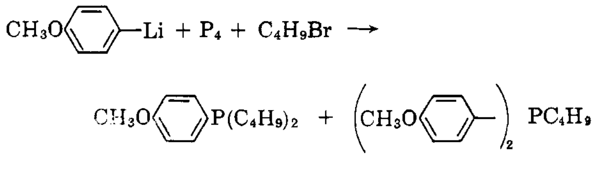


$$C_6H_5M + P_4 + C_4H_9X \xrightarrow[2\cdot H_2O]{} C_6H_5P(C_4H_9)_2 + (C_6H_5)_2PC_4H_9 + (C_6H_5)_2\overset{O}{\overset{\|}{P}}C_4H_9 + MX$$

Reactions run under a variety of conditions are summarized in Table I. Two methods of addition were used in the experiments. In method A, the phosphorus was added in one portion to a solution of the organolithium compound and butyl halide. Under these conditions the butyl halide was immediately available for reaction with the organophosphide as it was formed. In method B, the organometallic was allowed to react completely with the phosphorus, and the resulting organophosphide was allowed to react with the butyl halide in a separate step. Under these conditions reaction of the organophosphide with the butyl halide occurred in the absence of excess organometallic. Indeed, in the phenyllithium experiments carbonation of an aliquot before addition of the butyl halide indicated that the phenyllithium had been virtually consumed. Method B was necessarily used for experiments with butyllithium and organosodium compounds to avoid a direct reaction between the organometallic and butyl halide. Significantly, in experiments with phenyllithium and butyl bromide, the order of addition had almost no effect on yields of major products. However, method A provided phenylphosphine in 10% yield as an additional product.

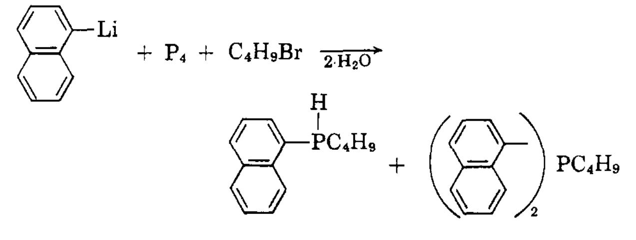
In experiments with phenyllithium, butyl chloride gave somewhat higher yields than butyl bromide. Although the butyl halide was in excess in all of the phenyllithium reactions, quaternary phosphonium compounds were not formed under the mild conditions employed. The use of a substantial excess of phenyllithium in the reaction with phosphorus and butyl chloride gave somewhat reduced yields.

Reaction of 4-methoxyphenyllithium with phosphorus and butyl bromide followed the pattern of the phenyllithium reaction, providing dibutyl(4-methoxyphenyl)phosphine and butylbis(4-methoxyphenyl)phosphine.



Similarly 3-trifluoromethylphenyllithium gave dibutyl(3-trifluoromethylphenyl)phosphine and butylbis(3-trifluoromethylphenyl)phosphine. Reaction of 1-naphthyllithium with phosphorus and butyl bromide followed a somewhat different pattern, giving butyl(1-naphthyl)phosphine and butylbis(1-naphthyl)phosphine. Dibutyl(1-naphthyl)phosphine was not found.

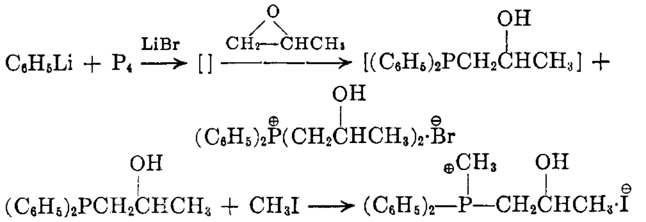
Butyllithium reacted with phosphorus and butyl bromide to give dibutylphosphine and tributylphosphine in 10% and 39% yields, respectively. Reaction of butyl-



sodium with phosphorus and butyl chloride gave dibutylphosphine in 13% yield along with a 1% yield of tributylphosphine.

$$C_4H_9M + P_4 + C_4H_9X \longrightarrow (C_4H_9)_2PH + (C_4H_9)_3P + MX$$
(in the presence of by-product lithium bromide)

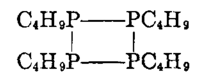
Reaction of phosphorus with phenyllithium (in the presence of bi-product lithium bromide) followed by reaction *in situ* of the resulting organophosphide with propylene oxide gave a complex reaction mixture from which only bis(2-hydroxypropyl)diphenylphosphonium bromide (19% yield) could be isolated directly. Additional reaction with methyl iodide, however, provided a 19% yield of (2-hydroxypropyl)methyldiphenylphosphonium iodide, probably derived from (2-hydroxypropyl)diphenylphosphine.



$$C_6H_5Li + P_4 \xrightarrow{LiBr} [\,] \xrightarrow{CH_2\text{—}CHCH_3} [(C_6H_5)_2PCH_2\overset{OH}{C}HCH_3] +$$
$$(C_6H_5)_2\overset{\oplus}{P}(CH_2\overset{OH}{C}HCH_3)_2\cdot\overset{\ominus}{Br}$$
$$(C_6H_5)_2PCH_2\overset{OH}{C}HCH_3 + CH_3I \longrightarrow (C_6H_5)_2\text{—}\overset{\oplus CH_3}{P}\text{—}CH_2\overset{OH}{C}HCH_3\cdot\overset{\ominus}{I}$$

Reaction of phosphorus with phenyllithium, followed by reaction of the resulting organophosphide with benzaldehyde, also gave a complex reaction mixture. Bis(α-hydroxybenzyl)phenylphosphine oxide was obtained in 12% yield, but other products were not isolated.

In contrast to the reactions with phenyllithium and phenylsodium, the reaction of butylmagnesium bromide with phosphorus and butyl bromide gave tetrabutylcyclotetraphosphine as the major product. A molar reactant ratio of 2:1:2 ($C_4H_9MgBr:P_4:C_4H_9Br$) in refluxing tetrahydrofuran provided the cyclotetraphosphine in 42% yield along with a 6% yield of dibutylphosphine and a trace of tributylphosphine.



$$2\ C_4H_9MgBr + P_4 + 2\ C_4H_9Br \longrightarrow$$

With a molar reactant ratio of 6:1:10 the yield of cyclotetraphosphine dropped to 17%; dibutylphosphine (15%), tributylphosphine (1%), and tetrabutylphosphonium bromide (10%) were also obtained.

Thus, reaction of an alkylmagnesium compound with phosphorus and an alkyl halide provides an efficient, one-step synthesis for tetraalkylcyclotetraphosphines which unlike older methods[4,8,10] does not require initial preparation of a difficulty accessible dihalophosphine.

Discussion

An understanding of the chemical nature of the organophosphides formed by reaction of phosphorus with organometallic compounds must be consistent with the observations summarized below.

(a) Both phenyllithium and phenylsodium react with phosphorus to give stable organophosphides which react with butyl halides to give substantial amounts of both dibutylphenylphosphine and butyldiphenylphosphine.

(b) Hydrolysis of the organophosphide from phenyllithium and phosphorus gives phenylphosphine in 36% yield. Phosphine is not obtained and diphenylphosphine and triphenylphosphine are obtained in only minor amounts even under forcing conditions.[9]

(c) Hydrolysis of the phenylsodium–phosphorus reaction product gives neither phenylphosphine nor diphenylphosphine in appreciable amounts.[9]

(d) The high over-all yields obtained in reactions with alkyl halides demonstrate that conversion of phosphorus to phenylphosphides is virtually complete, with each phosphorus atom in the P_4 molecule undergoing attack by the organometallic reactant.

(e) The organophosphide from phenyllithium and phosphorus reacts with butyl bromide to give butyldiphenylphosphine (38%) in the essential absence of free phenyllithium.

(f) Hydrolysis of all the organophosphides give substantial amounts of amorphous organopolyphosphines.[9]

(g) Organophosphide solutions prepared from phenyllithium and phosphorus, but which are free of unchanged phenyllithium, will react further with at least a 100% excess of additional phosphorus. Hydrolysis of the resulting solutions gives a drastically reduced yield of phenylphosphine but an increased yield of amorphous organopolyphosphines.[9]

It is evident from (a) that the organophosphide products from phenyllithium and phenylsodium include structural units having two phenyl groups attached to a single phosphorus atom. However, this unit cannot be the simple diphenylphosphide ion because of (b), since lithium diphenylphosphide is hydrolyzed cleanly to diphenylphosphine.[6] Similarly, the organophosphides must include units having only one phenyl group bonded to phosphorus, but in the case of the phenylsodium product, at least, this unit cannot be the simple phenylphosphide ion because of (c).

The formation of polyphosphines during hydrolysis through the interaction of free phosphorus with organophosphines must be rejected because of (d). Similarly, the formation of phenylalkylphosphines through a process of alternating attack by the organometallic and the alkyl halide on phosphorus must be rejected because of (e).

With these relatively straight-forward possibilities eliminated and in view of (f) and (g), it seems indicated that organoalkali compounds react with phosphorus to give complex organopolyphosphides, which [because of (g)] have variable compositions depending on the reactant ratios. Since these complex phosphides must contain phosphorus–phosphorus bonds as well as carbon–phosphorus bonds, and, since one or two negative charges must be accommodated on the phosphorus atoms, bonding participation by phosphorus *d* orbitals seems required. Moreover, the evident stability of the complex phosphides suggests resonance stabilization,

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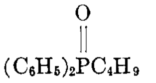
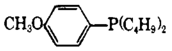
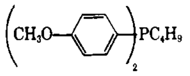
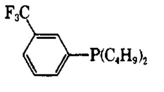
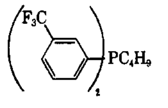
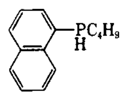
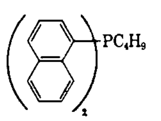
(10) H. Kohler and A. Michaelis, *Chem. Ber.*, **10**, 807 (1877); T. Weil, B. Prijs, and H. Erlenmeyer, *Helv. Chim. Acta.*, **35**, 616 (1952); W. Mahler, A. B. Burg, *J. Am. Chem. Soc.*, **79**, 251 (1957); V. N. Kulakova, Y. V. Zinovev, and L. Z. Soborovskii, *Zh. Obsch. Khim.* **29**, 3957 (1959); K. Issleib and B. Mitcheiling, *Z. Naturforsch.*, **15B**, 267 (1960); K. Issleib and W. Seidel, *Z. Anorg. Allgem. Chem.*, **303**, 155 (1960).

TABLE II

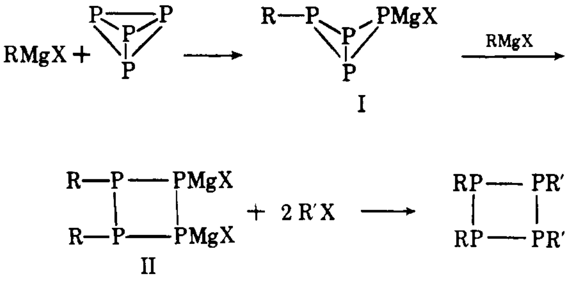
PRODUCTS FROM REACTIONS OF ORGANOALKALI COMPOUNDS WITH PHOSPHORUS AND BUTYL HALIDES

		Analytical data					
		Carbon, %		Hydrogen, %		Phosphorus, %	
Compound	B.p., °C. (mm.)	Calcd.	Found	Calcd.	Found	Calcd.	Found
$C_6H_5P(C_4H_9)_2$	83 (0.2)[a]	75.64	75.98	10.43	10.70	13.93	14.13
$(C_6H_5)_2PC_4H_9$	114–115 (0.15)[b]	79.31	79.27	7.90	7.98	12.78	12.81
 $(C_6H_5)_2\overset{O}{\overset{\|}{P}}C_4H_9$	161–163 (0.3)[c]	74.40	74.66	7.41	7.56	11.99	11.84
	116–118 (0.1) $n^{25}\text{D}$ 1.5277[d]	...	...	...	...	...	...
	175–178 (0.3)	71.50	71.38	7.67	7.61	10.25	10.24
	147 (18)	62.05	61.76	7.64	8.13	10.67	10.34
	174–175 (18)	57.14	57.37	4.53	4.87	8.18	8.30
	111–113 (0.1)	77.75	77.55	7.93	7.96	14.32	13.63
	210 (0.2)	84.18	83.33	6.77	6.83	9.05	8.99
$(C_4H_9)_2PH$	72 (12)[e]	...	...	...	...	...	...
$(C_4H_9)_3P$	118–122 (17)[f]	...	...	...	...	...	...

[a] Lit. b.p. 184.5–185.5 (50). [W. C. Davies and W. J. Jones, *J. Chem. Soc.*, 33 (1929).] [b] Lit.[7] b.p. 180–182° (11). [c] Lit. m.p. 89.5°. [D. C. Morrison, *J. Am. Chem. Soc.*, **72,** 4820 (1950)]. [d] Lit. b.p. 190 (16); $n^{25}\text{D}$ 1.5274. [I. K. Jackson, W. C. Davies, and W. J. Jones, *J. Chem. Soc.*, 2298 (1930).]. Characterized further as the methiodide, m.p. 87°. (Lit.[c] m.p. 87°.). [e] Lit. b.p. 181–185°. Characterized by infrared and v.p.c. comparisons with an authentic sample. [A. R. Stiles, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **74,** 3282 (1952).]. [f] Lit. b.p. 121–122° (16). Characterized further by infrared and v.p.c. comparison with an authentic sample. [G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, 2342 (1929).]

which would benefit from cyclic structures in perhaps much the same way that the P_4 molecule itself is stabilized.

The reaction of organomagnesium compounds with phosphorus and alkyl halides is more easily pictured.



It is likely, however, that the process is complicated by reaction of intermediates I and II with unchanged P_4 to give more complex phosphides, which in turn are broken down.

It seems reasonable that reactions of organoalkali compounds with phosphorus also proceed through intermediates such as I and II, but that the greater reactivity of the organoalkali compounds permits further attack leading to more complex ions.

Experimental[11,12]

Materials.—Phenyllithium, butyllithium, phenylmagnesium bromide, and butylmagnesium bromide were prepared from the corresponding bromides and metals by conventional procedures. Phenylsodium[13] and butylsodium[14] were prepared from the corresponding chlorides and dispersed sodium. 1-Naphthyllithium,[15] 4-methoxyphenyllithium,[16] and 3-trifluoromethylphenyllithium[17] were obtained by reaction of the corresponding aryl bromide with butyllithium. Other materials were obtained from commercial sources.

Reactions of Organoalkali Compounds with White Phosphorus and Butyl Halides.—Individual experiments are described in Table I, and the products are described in Table II. The general procedures are given below.

Method A.—White phosphorus (15.5 g., 0.5 g.-atom) was cut into approximately 0.3-g. pieces under water and washed with acetone and with benzene. The phosphorus was added in one portion to an ether solution of the aryllithium compound and butyl halide[18] under nitrogen, and stirring was begun. The re-

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[11] 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.

[12] Boiling points and melting points are uncorrected.

[13] J. F. Nobis and L. F. Moormeier, *Ind. Eng. Chem.*, **46,** 539 (1954).

[14] See: A. A. Morton, *et. al.*, *J. Am. Chem. Soc.*, **72,** 3785 (1950).

[15] H. Gilman, C. G. Brannen, and R. K. Ingham, *J. Org. Chem.*, **22,** 685 (1957).

[16] R. J. Pratt and E. V. Jensen, *J. Am. Chem. Soc.*, **78,** 4430 (1956).

[17] H. Gilman and L. A. Woods, *ibid.*, **66,** 1981 (1944).

[18] In experiments with substituted aryllithium compounds, the required butyl bromide was provided automatically by the exchange reaction: $ArBr + C_4H_9Li \longrightarrow ArLi + C_4H_9Br$.

actions were moderately exothermic, requiring about 30 min. to reach the reflux temperature and then were refluxed gently for 30 to 45 min. The mixtures were then allowed to cool and were stirred an additional 2 hr. at room temperature. By the end of the reactions, a white solid had separated, the original dark color had lightened, and unchanged phosphorus was no longer observed. The mixtures were treated dropwise with 500 ml. of water, and the phases were separated. The aqueous phases were extracted with three 50-ml. portions of ether, and the combined extracts were dried over anhydrous sodium sulfate. Treatment of the aqueous phases with sodium tetraphenylboride failed to give a precipitate, indicating the essential absence of quaternary phosphonium compounds. The organic phases were freed of solvent under reduced pressure and the residues fractionally distilled to obtain the products. In some experiments with phenyllithium, yield data was obtained chromatographically. An Aerograph Model A-100-C gas chromatograph was used with a 5-ft.-long, $^1/_4$-in.-diameter Apiezon L column operated at 244° with a helium flow rate of 60 ml./min. Quantitative results were obtained using dibutyl phthalate as an internal standard. Under the conditions used the retention times were: $C_6H_5P(C_4H_9)_2$, 6.0 min.; dibutyl phthalate, 14.1 min.; $(C_6H_5)_2PC_4H_9$, 16.8 min.

Method B.—White phosphorus (15.5 g., 0.5 g.-atom), prepared as described under method A above, was added in one portion to a mixture of the organoalkali compound and solvent under nitrogen, and stirring was begun. The reactions were initially exothermic and maintained at the indicated temperature (Table I) by cooling. At the end of the exothermic reaction, heat was applied and the indicated temperature was maintained for an additional 2 hr. The alkyl halide was then added dropwise during 60 min. at 35–40°. The reactions were exothermic and required cooling to maintain the desired temperature. The reaction mixtures were stirred an additional 2 hr. at 35–40°, and then hydrolyzed (very cautiously in the case of organosodium reactions) with 500 ml. of water at 10–20°. The organic phase was separated and dried over anhydrous sodium sulfate. Vapor phase chromatography of the organic phases on a polyglycol column at 66° or on an apiezon column at 128° demonstrated the essential absence of primary phosphine products. Products were obtained by fractional distillation under reduced pressure. Addition of sodium tetraphenylboride to the aqueous phases failed to give a precipitate indicating the essential absence of quaternary phosphonium products.

Reaction of Butylmagnesium Bromide with White Phosphorus and Butyl Bromide.—White phosphorus (31.0 g., 1.0 g.-atom) was cut into 0.3-g. pieces under water and washed with acetone and with benzene. The phosphorus was added in one portion to a solution of 0.55 mole of butylmagnesium bromide and 75.4 g. (0.55 mole) of butyl bromide in 300 ml. of tetrahydrofuran under nitrogen. The mixture was stirred at reflux (82°) for 1 hr. A white solid separated and the mixture became very viscous. The reaction mixture was cooled to 25°, diluted with 400 ml. of ether, and treated dropwise with 200 ml. of water. The mixture was filtered from a small amount of magnesium hydroxide, and the phases were separated. The aqueous phase was extracted with three 50-ml. portions of ether, and the combined organic phases were dried over anhydrous sodium sulfate. Distillation of the organic phase gave 9.0 g. (6%) of dibutylphosphine, b.p. 71–78° (18 mm.), a trace of tributylphosphine, and 37.2 g. (42%) of tetrabutylcyclotetraphosphine, b.p. 149–156° (0.01 mm.). Redistillation of the latter gave an analytical sample, b.p. 136–140° (0.007 mm.).

Anal. Calcd. for $C_{16}H_{36}P_4$: C, 54.53; H, 10.29; P, 35.16; mol. wt., 352. Found: C, 54.59; H, 10.11; P, 35.07; mol. wt. (vapor pressure thermister method[19] in benzene), 379.

The infrared spectrum closely resembled the spectrum of tributylphosphine. The ultraviolet spectrum, taken in the vapor phase at 186.2° showed maxima at 275, 281 and 290 mμ. The n.m.r. phosphorus spectrum showed a singlet at −10 p.p.m. referred to 85% phosphoric acid.

A similar reaction carried out with 12.4 g. (0.4 g.-atom) of phosphorus, 0.6 mole of butylmagnesium bromide, and 137.0 g. (1.0 mole) of butyl bromide in 500 ml. of tetrahydrofuran at reflux for 6 hr. gave 8.5 g. (15%) of dibutylphosphine, 1.0 g. (1%) of tributylphosphine, 6.1 g. (17%) of tetrabutylcyclotetraphosphine, and 13.8 g. (10%) of tetrabutylphosphonium bromide, m.p. 94–97° (lit.,[20] m.p. 101°), which did not depress the melting point of an authentic sample.

Reaction of Propylene Oxide with the Organophosphide from Phenyllithium and Phosphorus.—White phosphorus (15.5 g., 0.5 g.-atom) was combined with a solution of 1 mole of phenyllithium (and 1 mole of bi-product lithium bromide) in 700 ml. of ether under nitrogen. The mixture was stirred at reflux for 3 hr. and allowed to cool to room temperature. A solution of 58.1 g. (1.0 mole) of propylene oxide in 50 ml. of ether was added dropwise during 45 min. at 25–30°. The reaction was strongly exothermic and required cooling. The color changed sharply from dark red to pale yellow at the end of the addition. The reaction mixture was stirred an additional 30 min. and then treated dropwise with 66.0 g. (1.1 moles) of glacial acetic acid, followed by the addition of 400 ml. of water. The mixture was filtered to obtain 28.2 g. (15%) of diphenylbis(2-hydroxypropyl)-phosphonium bromide, m.p. 183–187°. The solid was washed with hot chloroform and recrystallized twice from isopropyl alcohol to obtain an analytical sample, m.p. 197–200°.

Anal. Calcd. for $C_{18}H_{24}BrO_2P$: C, 56.41; H, 6.31; Br, 20.85; P, 8.08. Found: C, 56.45; H, 6.46; Br, 20.81; P, 8.24.

The two liquid phases present in the filtered reaction mixture were separated, and the organic phase was dried over anhydrous sodium sulfate. Concentration of the aqueous phase gave an additional 6.9 g. (4%) of diphenylbis(2-hydroxypropyl)phosphonium bromide, m.p. 191–194: An attempt to obtain additional products from the aqueous phase was unsuccessful.

The dried organic phase was combined with 85.2 g. (0.6 mole) of methyl iodide, and the solution was refluxed for 90 min. An insoluble oil separated. The ether phase was decanted, and the oil was stirred with 100 ml. of isopropyl alcohol. The oil crystallized, and the resulting solid was collected to obtain 35.9 g. (19%) of methyldiphenyl-2-hydroxypropylphosphonium iodide, m.p. 159–162°. Two recrystallizations from isopropyl alcohol gave an analytical sample, m.p. 163–164°.

Anal. Calcd. for $C_{16}H_{20}IOP$: C, 49.75; H, 5.21; I, 32.86; P, 8.02. Found: C, 49.53; H, 5.16; I, 32.74; P, 8.14.

In a second identical experiment an unsuccessful attempt was made to distil the organic phase from the reaction. Decomposition occurred leaving a substantial amount of a nonvolatile yellow glass as the distillation residue. Only traces of organophosphorus compounds were found in the distillate.

Reaction of Benzaldehyde with the Organophosphide from Phenyllithium and Phosphorus.—White phosphorus (7.8 g., 0.25 g.-atom) was combined with a solution of 0.5 mole of phenyllithium in 750 ml. of ether under nitrogen. The mixture was stirred at reflux for 3 hr. and allowed to cool to room temperature. A solution of 53.1 g. (0.5 mole) of benzaldehyde in 50 ml. of ether was added dropwise with stirring during 30 min. The reaction was moderately exothermic, and the mixture refluxed gently. Near the end of the addition the color changed from dark red to yellow. The mixture was stirred one additional hour and then treated dropwise with 30.0 g. (0.5 mole) of glacial acetic acid. The mixture was treated with 100 ml. of water, and the phases were separated. The aqueous phase was extracted with three 25-ml. portions of chloroform; evaporation of the extract did not give a residue. Treatment of the aqueous phase with sodium tetraphenylboride did not give a precipitate, indicating the absence of quaternary phosphonium compounds. Other attempts to obtain products from the aqueous phase were unsuccessful.

The organic phase was diluted to 1 l. with ether and allowed to stand at 0° overnight. The solution deposited a crystalline solid, which was collected to obtain 10.2 g. (12%) of bis(α-hydroxybenzyl)phenylphosphine oxide, m.p. 186–187°. (Lit.,[21] m.p. 187–188°). A mixed melting point with an authentic sample was not depressed. An attempt to obtain other products from the organic phase by distillation was unsuccessful. Also unsuccessful were attempts to prepare derivatives by reaction with methyl iodide or sulfur.

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(19) A. Wilson, L. Bini, and R. Hofstader, *Anal. Chem.*, **33**, 135 (1961).

(20) Wm. A. Henderson Jr. unpublished work.

(21) S. A. Buckler and M. Epstein *Tetrahedron*, **18**, 1221 (1962).