THE PHOSPHONOUS ACIDS AND THEIR DERIVATIVES[1],

ARLEN W. FRANK

Research Center, Hooker Chemical Corporation, Niagara Falls, New York

CONTENTS

CONTENTS (Continued)

I. INTRODUCTION

A. GENERAL

The phosphonous acids (RPO_2H_2) are the organophosphorus members of the group of substances known as the lower acids of phosphorus. They contain one carbon–phosphorus bond and occupy a position intermediate between the phosphonic acids (RPO_3H_2), in which the phosphorus is fully oxidized, and the primary phosphines (RPH_2), in which it is fully reduced.

A characteristic feature of the lower acids of phosphorus is their tendency to assume whenever possible a form in which the phosphorus is tetravalent and to exhibit one less acidic function than might be expected. The phosphonous acids also show this behavior. Of the tautomeric structures that can be written, II reflects the monobasic character of the phosphonous acids and is a better representation of the free acids than I.

$$R-P\diagdown_{OH}^{OH} \qquad R-P\diagup_{H}^{O}-OH$$
$$\quad\ I \qquad\qquad\qquad II$$

The derivatives of the phosphonous acids, however, may be subdivided into two broad classes: derivatives based on the trivalent structure (I) and derivatives based on the tetravalent structure (II). Derivatives in which both hydroxyl groups have been replaced contain trivalent phosphorus, whereas derivatives in which only one hydroxyl group has been replaced exhibit the behavior of compounds in which the phosphorus is

tetravalent. Their chemistry is quite different, as will be seen in this review.

B. SCOPE AND LIMITATIONS OF PRESENT REVIEW

The literature on the phosphonous acids has not previously been explicitly reviewed. Surveys of work done prior to 1950 may be found in texts by Kosolapoff (175), Fox and Lockhart (81), Goddard (98), and Plets (272). Related topics appearing more recently in reviews are the phosphonic and secondary phosphinic acids by Kosolapoff (176), the phosphonic acids by Freedman and Doak (86), and the secondary and tertiary phosphine oxides by Berlin and Butler (36).

The present review covers the synthesis and reactions of the phosphonous acids from their discovery through 1959. Following the section dealing with the phosphonous acids themselves are separate sections on their acid chlorides, esters, thio esters, amides, and anhydrides. Looked at in another way, the review covers all of the organophosphorus compounds that contain a single phosphorus–carbon bond with the exception of the primary phosphines (RPH$_2$), the phosphonic acids (RPO$_3$H$_2$), and the newly discovered primary phosphine oxides (RPOH$_2$).

The basic plan of this review may be briefly outlined as follows: *Synthetic methods* used to prepare the phosphonous acids and their derivatives are described in detail. Syntheses in which a carbon–phosphorus bond is formed are described first, followed by syntheses from compounds which already contain a carbon–phosphorus bond. Syntheses in which a second carbon–phosphorus bond is ruptured are described last. All of the phosphorus compounds (of which the author is aware) known to have been synthesized by each method have been included in the text or listed separately in tables, depending on their number. *Reactions* of the phosphonous acids and their derivatives are described only in general terms, but an effort has been made to provide a complete list of references for each reaction. The order of presentation follows the same rule as given above for the syntheses, with the added proviso that reactions involving no valence change of phosphorus are described first.

C. NOMENCLATURE

The nomenclature of the organophosphorus compounds described in this review follows in general the system adopted by the American Chemical Society's Committee on the Nomenclature of Organic Phosphorus Compounds (7). Unfortunately, this report does not state whether compounds containing the P—OH $\rightleftharpoons$ P(O)H system should be named as compounds of trivalent or of tetravalent phosphorus, i.e., whether they should be named as derivatives of phosphonous acid, (HO)$_2$PH, or as derivatives of phosphinic acid, HOP(O)H$_2$. The author has arbitrarily selected the

former because "phosphonous" unambiguously denotes a single class of substances, whereas "phosphinic" is more often associated with secondary organophosphorus compounds than with primary compounds. However, the use of "primary phosphinic" is also considered correct.

The use of the phosphonous nomenclature should not, of course, be construed as a plea for the adoption of the trivalent form for the phosphonous acids or their derivatives. It is used simply to avoid ambiguity.

II. PHOSPHONOUS ACIDS

The phosphonous acids are monobasic acids of the formula RPH(O)OH. Most of the aromatic members are crystalline and are easily characterized by their melting points. The aliphatic members, however, are usually liquid, and since they easily undergo disproportionation on heating cannot be purified by distillation. Only one phosphonous acid, C$_3$F$_7$PH(O)OH, has a recorded boiling point (table 3). Many of the liquid phosphonous acids for which no data are given in the tables have been characterized instead by refractive index or density.

A. SYNTHESIS OF PHOSPHONOUS ACIDS

1. From elemental phosphorus

(a) With acetone

In 1864 it was reported that the distillation of acetone with iodine and elemental phosphorus gave an oily phosphonous acid believed to be 2-oxopropylphosphonous acid (263). The acid formed an amorphous barium salt, soluble in water and insoluble in ethanol. No work has been done since to verify this reaction.

(b) With olefins and oxygen

Solutions of olefins and white phosphorus in benzene or petroleum ether rapidly absorb oxygen and deposit crystalline "phosphorates," which contain phosphorus and oxygen in a 2:4 ratio (258, 289, 333, 350, 351, 352). These, on treatment with water, are hydrolyzed to β-hydroxyalkylphosphonous acids (258, 351, 352). The intermediate esters can be isolated by salting out with ammonium chloride (351).

$$RCH=CH_2 + \tfrac{1}{2}P_4 + 2O_2 \rightarrow RCH\underset{\underset{O}{|}}{\overset{\overset{}{|}}{\text{—}}}CH_2$$

$$\xrightarrow{2H_2O} \underset{\underset{OP(O)(OH)_2}{|}}{RCHCH_2PO_2H_2} \xrightarrow{H_2O} RCHOHCH_2PO_2H_2 + H_3PO_4$$
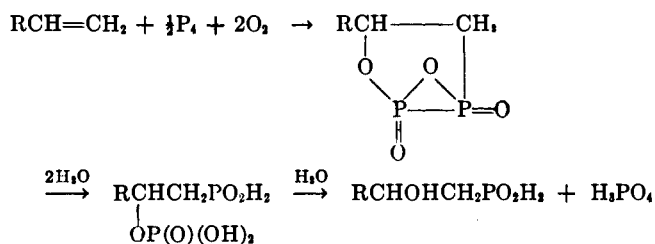
Willstätter claimed that he had prepared an intermediate "phosphorite" having one less oxygen atom than the phosphorate, but later work has not substantiated this (333). However, olefins whose phos-

phorates are not insoluble absorb one more atom of oxygen, giving compounds of the formula RP_2O_5 (333).

Few phosphonous acids have actually been prepared and characterized by this method. The phosphorates have generally been characterized by oxidation with nitric acid to the phosphonic acids.

The "phosphorates" and "phosphorites" described in this work are apparently identical to those prepared by the reaction of olefins with phosphorus trichloride and acetic anhydride (Section II,A,2), though the proposed structures are different. A new polymeric structure has recently been proposed (333).

2. From phosphorus trichloride, olefins, and acetic anhydride

Olefins react with phosphorus trichloride and acetic anhydride giving crystalline "phosphorites," which are converted to α,β-unsaturated phosphonous acids on hydrolysis (320, 321). Overall yields are in the order of 50–60 per cent.

$$RCH{=}CH_2 + 2PCl_3 + 3(CH_3CO)_2O \rightarrow RCH\underset{\underset{P-O}{O\quad O-P}}{\overline{\qquad\qquad}}CH_2$$

$$\xrightarrow{2H_2O} RCH{=}CHPO_2H_2 + H_3PO_3$$

If oxygen or air is passed into the reaction mixture the phosphorite redissolves and is oxidized to a "phosphorate," but the product of hydrolysis is the same phosphonous acid. In this case the by-product is phosphoric acid. Both intermediates react with alcohols, giving ester derivatives which still contain two phosphorus atoms (320, 321).

These "phosphorites" and "phosphorates" are apparently the same intermediates as those obtained in the reaction of elemental phosphorus with olefins (Section II,A,1), though the structures given are different.

The corresponding α,β-unsaturated phosphonous dichlorides $(RCH{=}CHPCl_2)$ can be prepared by a different method (Section III,A,9).

3. From hypophosphorous acid or its salts

(a) With olefins

Sodium hypophosphite adds to olefins in the presence of free-radical initiators, giving sodium salts of phosphonous acids (316, 325). Initiators that have been used are di-tert-butyl peroxide and 2,2-bis(tert-butylperoxy)-butane (325).

$$RCH{=}CH_2 + H_2P(O)ONa \rightarrow RCH_2CH_2PH(O)ONa$$
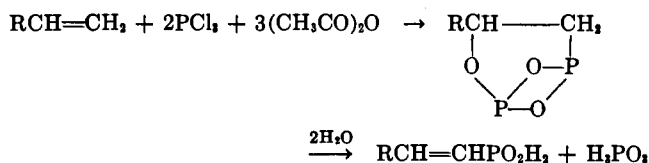
Products of this type have been prepared from 1-hexene, 1-octene, 1-tetradecene, diallyl sulfide, and divinyl sulfide (325). The yields from the first two were quantitative.

Hydroxy-substituted olefins, such as 3-buten-1-ol or methallyl alcohol, yield phosphonous acids which can be

dehydrated on heating to cyclic esters called phostones (316).

(b) With secondary or tertiary alcohols

Hypophosphorous acid reacts with certain secondary and tertiary alcohols to give phosphonous acids (78, 79, 111, 323). The mechanism of this reaction is not clear. The reaction may proceed through the isomerization of an initially formed hypophosphite ester, but the presence of triphenylmethyl chloride as a by-product in the reaction of hypophosphorous acid with triphenylcarbinol makes a carbonium-ion mechanism more likely (111). The overall reaction is written as follows:

$$(C_6H_5)_3COH + H_2P(O)OH \rightarrow (C_6H_5)_3CPH(O)OH + H_2O$$
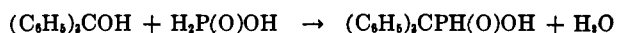
Substantial amounts of the corresponding hydrocarbons may also be formed, depending on the reaction conditions (78, 79).

The phosphonous acids that have been prepared by this method are $(C_6H_5)_3CPO_2H_2$, m.p. 245–248°C., from triphenylcarbinol (78, 111, 323), and $[p\text{-}(CH_3)_2NC_6H_4]_2\text{-}CHPO_2H_2$, m.p. 90°C., from Michler's hydrol (78). A crystalline phosphonous acid was also prepared from 1,2,7,8-dibenzoxanthol and hypophosphorous acid (79).

(c) With carbonyl compounds

Crystalline hypophosphorous acid adds to aldehydes or ketones when the reactants are heated together on the water bath for prolonged periods of time, forming α-hydroxyalkylphosphonous acids:

$$RR'CO + H_2P(O)OH \rightarrow RR'C(OH)PH(O)OH$$
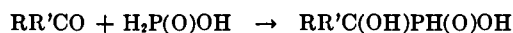
Since the products still contain a replaceable hydrogen attached to phosphorus, care must be taken to prevent further reaction with the aldehyde or ketone. This is done by keeping the hypophosphorous acid in excess (328). This precaution is not necessary with ketones higher than acetone, since they do not form disubstitution products (213, 214).

A list of the compounds that have been prepared by this method is given in table 1.

(d) With Schiff bases

Hypophosphorous acid adds to the C=N bond in Schiff bases in a manner similar to the reaction with carbonyl compounds described above. In practice it is not necessary to prepare and isolate the Schiff base; a mixture of hypophosphorous acid, an amine, and a carbonyl compound (often used in excess as the solvent) is heated for a few hours on a water bath, and the product usually separates in crystalline form. Only primary amines undergo this reaction.

$$(CH_3)_2CO + H_2P(O)OH + RNH_2 \rightarrow \underset{CH_3}{\overset{CH_3}{\underset{\diagup}{\overset{\diagdown}{C}}}}\overset{NHR}{\underset{PH(O)OH}{\diagup}}$$

TABLE 1

Phosphonous acids prepared from carbonyl compounds

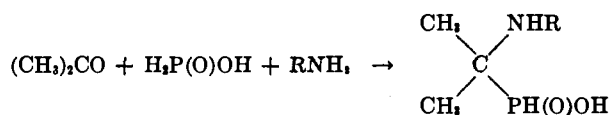| Phosphonous Acid	Carbonyl Compound	Yield	Melting Point	References
		per cent	°C.	
(HOCH₂PO₂H)₂Ca	Trioxymethylene		Crystalline*	(315)
CH₃CHOHPO₂H₂	Acetaldehyde			(212, 329)
iso-C₄H₉CHOHPO₂H₂	Isovaleraldehyde			(212, 329)
n-C₆H₁₃CHOHPO₂H₂	Enanthaldehyde		55–57	(114, 329)
⬡CHOHPO₂HNa	1,2,5,6-Tetrahydrobenzaldehyde	71	236 (d.)	(301)
C₆H₅CHOHPO₂H₂	Benzaldehyde		108	(114, 217, 328, 329, 330)
4-Iso-C₃H₇C₆H₄CHOHPO₂H₂	Cumaldehyde		105	(329)
1,3-C₆H₄(CHOHPO₂HNa)₂	Isophthalaldehyde		Crystalline*	(114)
2-HOC₆H₄CHOHPO₂H₂	Salicylaldehyde			(329)
Camphor-3-CHOHPO₂HNa	(Hydroxymethylene)camphor		Crystalline*	(114)
(CH₃)₂COHPO₂H₂	Acetone	58	52	(208, 209, 217)
C₂H₅(CH₃)COHPO₂H₂	Ethyl methyl ketone			(213, 217)
(C₂H₅)₂COHPO₂H₂	Diethyl ketone			(215, 217)
C₃H₇(CH₃)COHPO₂H₂	2-Butanone			(214, 217)
C₆H₅(CH₃)COHPO₂H₂	Acetophenone		85	(215, 217)
(C₆H₅)₂COHPO₂H₂	Benzophenone	61	150–151	(214, 217)
C₆H₅COHPO₂H₂ ⎮ C₆H₅CH₂	Deoxybenzoin		135–137	(274)
C₆H₅COHPO₂H₂ ⎮ C₆H₅CHOH	Benzoin or benzil		150 (d.)	(274)
4-BrC₆H₄COHPO₂H₂ ⎮ 4-BrC₆H₄CHOH	4,4′-Dibromobenzil		125 (d.)	(274)
2-CH₃OC₆H₄COHPO₂H₂ ⎮ 2-CH₃OC₆H₄CH₂	o-Anisoin, o-anisil, or o-deoxyanisoin		190 (d.)	(274)
3-CH₃OC₆H₄COHPO₂H₂ ⎮ 3-CH₃OC₆H₄CHOH	m-Anisil			(274)

* No melting point given.

Reactions of this type are listed in table 2. The reactants are listed instead of the products because of the complexity of many of the amines employed. Those amines noted more for their physiological activity than for their chemical behavior have been given their trivial names.

4. From phosphonous dichlorides

Phosphonous dichlorides are readily hydrolyzed to phosphonous acids. Uusually dropwise addition to water followed by refluxing for a few minutes is sufficient.

$$RPCl_2 + 2H_2O \rightarrow RPH(O)OH + 2HCl$$
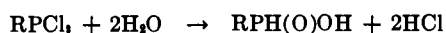
Concentrated hydrochloric acid has also been recommended (335). For compounds which suffer scission of the carbon–phosphorus bond in acid solution, such as triphenylmethylphosphonous dichloride (111) and p-dimethylaminophenylphosphonous dichloride (33, 40, 290, 307), aqueous alkali may be used. Perfluorinated alkylphosphonous dichlorides suffer scission of the carbon–phosphorus bond in alkaline solution but can be hydrolyzed with water (35, 73, 74).

While seemingly straightforward, the hydrolysis of phosphonous dichlorides with water does not proceed entirely in accordance with the equation above. The phosphonous acids, themselves odorless, are contaminated by an intense phosphine-like odor, and the yields (none given for any of the compounds in table 3) are less than quantitative.

Hydrolysis with ethanol and water, though mentioned in the early literature (169, 251), has been little used until recently (71, 180). The products obtained by this method are odorless and the yields are improved. The method is made possible by the ease of hydrolysis of the partial esters initially formed in the reaction.

$$RPCl_2 + 2C_2H_5OH \rightarrow RPH(O)OC_2H_5 + C_2H_5Cl + HCl$$

$$RPH(O)OC_2H_5 + H_2O \xrightarrow{HCl} RPH(O)OH + C_2H_5OH$$
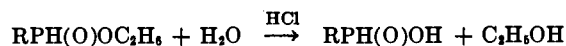
The phosphonous acids prepared from phosphonous dichlorides by hydrolysis are given in table 3.

5. From phosphonous esters

The first ester group in phosphonous diesters is cleaved by a trace of mineral acid, but the second ester group is much more resistant to hydrolysis (305). Phosphonous acids may be prepared from phosphonous diesters or phosphonous monoesters by hydrolysis with concentrated acid or base (193, 305). For a résumé of older work on the hydrolysis of phosphonous monoesters see Section VIII.

TABLE 2

Phosphonous acids prepared from Schiff bases

Phosphonous Acid Prepared from Schiff Base of		Yield	Melting Point	References
Amine	Carbonyl Compound			
		per cent	°C.	
Aniline	Paraldehyde		190 (d.)	(309, 311)
Aniline	Benzaldehyde	47	150	(309, 311)
Benzylamine	Salicylaldehyde	56	225	(309)
Aminoguanidine carbonate	Benzaldehyde		152	(311)
4-NH₂SO₂C₆H₄CH₂NH₂	Salicylaldehyde	Good	190 (d.)	(311)
4,4'-Diaminodiphenyl sulfone	Paraldehyde	100		(309)
Propylamine	Acetone	71	227 (d.)	(309, 310)
Isohexylamine	Acetone		217	(310)
Cyclohexylamine	Acetone		217 (d.)	(309, 310)
Stearylamine	Acetone	71	208	(310)
Aniline	Acetone	62	214 (d.)	(309, 310)
Benzylamine	Acetone		220 (d.)	(310)
N,N-Diethyl-p-phenylenediamine	Acetone		218	(349)
N,N-Diethyl-p-phenylenediamine	Ethyl methyl ketone		208	(349)
N,N-Diethyl-p-phenylenediamine	Diacetone alcohol		210	(349)
N-Ethyl-N-(2-hydroxyethyl)-p-phenylenediamine	Acetone		216	(349)
p-Phenetidine	Acetone		189 (d.)	(309, 310)
p-Phenetidine	Acetophenone		167 (d.)	(309, 310)
p-Diethylamino-o-phenetidine	Acetone			(349)
p-Aminophenol	Acetone		205	(349)
p-Aminoacetanilide	Acetone	64	216 (d.)	(309, 310)
p-Aminoacetanilide	Ethyl methyl ketone	Good	142 (d.)	(309, 310)
4-Amino-2-chloroacetanilide	Acetone		200 (d.)	(309, 310)
p-Aminophenyl-1-pyrrolidine	Acetone		198	(349)
Aminoguanidine carbonate	Acetone	Good	186	(309, 310)
Phenylhydrazine	Acetone		165	(309, 310)
Aminoantipyrine	Acetone	Good	185 (d.)	(310)
p-Aminobenzenesulfonamide	Acetone	62	200 (d.)	(309, 310)
4-NH₂SO₂C₆H₄CH₂NH₂	Acetone		232 (d.)	(309, 310)
4,4'-Diaminodiphenyl sulfone	Acetone	87	204 (d.)	(310)
4,4'-CH₂CONHC₆H₄SO₂C₆H₄NH₂	Acetone	Good	192 (d.)	(310)
Sulfapyridine	Acetone	85	180 (d.)	(310)
Sulfathiazole	Acetone		184 (d.)	(309, 310)

6. From primary phosphines

Phosphonous acids may be prepared from primary organophosphines by carefully controlled oxidation. More vigorous oxidants, such as nitric acid, yield only phosphonic acids (104, 119). In most cases air, oxygen, or hydrogen peroxide is sufficient. Phosphonous acids prepared from alkylphosphines are partially oxidized to the phosphonic acids during the oxidation, more so with nitrogen dioxide than with oxygen or 30 per cent hydrogen peroxide (44). Hydrogen peroxide at 80–100°C. does not readily effect the oxidation. The use of acetic acid as a solvent and molybdenum oxide as a promoter is beneficial (44). The oxidation of alkylphosphines with air or oxygen yields phosphoric acid, the phosphonous acid, and the phosphonic acid in 3:6:1 ratio regardless of the temperature or the concentration of oxygen (44).

$$RPH_2 \xrightarrow{O_2} H_3PO_4 + RPH(O)OH + RP(O)(OH)_2$$

An attempted carbylamine reaction with phenylphosphine, chloroform, and alcoholic potassium hydroxide gave instead phenylphosphonous acid (242). An alternative route to the direct oxidation of primary phosphines is halogenation to the phosphonous dihalide, followed by hydrolysis (Section III,A,8).

A list of the phosphonous acids prepared by the oxi-

dation of phosphines is given in table 4.

7. From higher organophosphorus compounds

Reactions of this type are known only in the trifluoromethyl series, and are due to the ease with which compounds containing the CF₃—P system liberate fluoroform on aqueous or alkaline hydrolysis. Trifluoromethylphosphonous acid is obtained by the following reactions (35, 73):

$$(CF_3)_3P + NaOH + H_2O \rightarrow CF_3PH(O)ONa + 2CHF_3$$

$$(CF_3)_2P(O)H + H_2O \rightarrow CF_3PH(O)OH + CHF_3$$
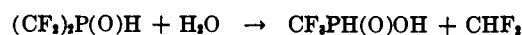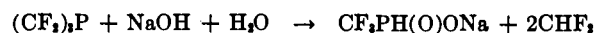
B. REACTIONS OF PHOSPHONOUS ACIDS

The reactions of phosphonous acids which yield derivatives described in detail in other sections of this review are not considered here. These include the reaction with phosphorus trichloride to form phosphonous dichlorides (Section III,A,5) and the reaction with alcohols or with phosphonous diesters to form phosphonous monoesters (Section VIII,A,4).

1. Disproportionation

The phosphonous acids, in common with other lower acids of phosphorus containing the tautomeric P—OH ⇌ P(O)H system, undergo a characteristic disproportionation reaction when heated by themselves to

TABLE 3

Phosphonous acids prepared from phosphonous dichlorides

Phosphonous Acid	Phosphonous Dichloride	Yield	Melting Point	References
		per cent	*°C.*	
CF₃PO₂H₂	CF₃PCl₂			(35)
C₂H₅PO₂H₂	C₂H₅PCl₂			(104)
C₃H₇PO₂H₂	C₃H₇PCl₂			(104)
C₃F₇PO₂H₂	C₃F₇PCl₂ or C₃F₇PI₂	72	71/0.7 mm. (b.p.)	(74)
iso-C₃H₇PO₂H₂	iso-C₃H₇PCl₂			(104)
iso-C₄H₉PO₂H₂	iso-C₄H₉PCl₂			(104)
iso-C₅H₁₁PO₂H₂	iso-C₅H₁₁PCl₂			(104)
C₅H₁₁PO₂H₂	C₅H₁₁PCl₂			(342)
iso-C₅H₁₁PO₂H₂	iso-C₅H₁₁PCl₂			(335)
C₆H₅CH₂PO₂H₂	C₆H₅CH₂PCl₂			(342)
(C₆H₅)₃CPO₂H₂	(C₆H₅)₃CPCl₂		245–248	(111)
C₆H₅CH=CHPO₂H₂	C₆H₅CH=CHPCl₂		74–75	(335)
C₆H₅PO₂H₂	C₆H₅PCl₂		70, 86	(169, 180, 230, 240, 340, 341, 342)
4-ClC₆H₄PO₂H₂	4-ClC₆H₄PCl₂		131	(28, 234)
4-BrC₆H₄PO₂H₂	4-BrC₆H₄PCl₂		143	(163, 234, 342, 361, 362)
2-CH₃C₆H₄PO₂H₂	2-CH₃C₆H₄PCl₂			(235, 251, 342)
3-CH₃C₆H₄PO₂H₂	3-CH₃C₆H₄PCl₂			(235)
4-CH₃C₆H₄PO₂H₂	4-CH₃C₆H₄PCl₂		104–105	(232, 250, 251, 323, 342)
3-Cl-4-CH₃C₆H₃PO₂H₂	3-Cl-4-CH₃C₆H₃PCl₂		70	(225)
4-C₂H₅C₆H₄PO₂H₂	4-C₂H₅C₆H₄PCl₂		63–64	(235, 342)
2,3-(CH₃)₂C₆H₃PO₂H₂	2,3-(CH₃)₂C₆H₃PCl₂		43	(235)
2,4-(CH₃)₂C₆H₃PO₂H₂	2,4-(CH₃)₂C₆H₃PCl₂		100	(235)
2,5-(CH₃)₂C₆H₃PO₂H₂	2,5-(CH₃)₂C₆H₃PCl₂		Crystalline*	(235, 344)
4-(iso-C₃H₇)C₆H₄PO₂H₂	4-(iso-C₃H₇)C₆H₄PCl₂			(236)
2,4,5-(CH₃)₃C₆H₂PO₂H₂	2,4,5-(CH₃)₃C₆H₂PCl₂		128	(236)
2,4,6-(CH₃)₃C₆H₂PO₂H₂	2,4,6-(CH₃)₃C₆H₂PCl₂		147	(236)
2,5(or 5,2)-CH₃(iso-C₃H₇)C₆H₃PO₂H₂	CH₃(iso-C₃H₇)C₆H₃PCl₂			(236)
4-C₆H₅C₆H₄PO₂H₂	4-C₆H₅C₆H₄PCl₂		Crystalline*	(238)
4-C₆H₅CH₂C₆H₄PO₂H₂	4-C₆H₅CH₂C₆H₄PCl₂		84	(238)
4-C₆H₅CH₂CH₂C₆H₄PO₂H₂	4-C₆H₅CH₂CH₂C₆H₄PCl₂		156–157	(238)
1-C₁₀H₇PO₂H₂	1-C₁₀H₇PCl₂		125–126	(153, 342)
2-C₁₀H₇PO₂H₂	2-C₁₀H₇PCl₂		138	(191, 342)
4-CH₃OC₆H₄PO₂H₂	4-CH₃OC₆H₄PCl₂		114–114.5	(128, 142, 234)
4-C₂H₅OC₆H₄PO₂H₂	4-C₂H₅OC₆H₄PCl₂		115	(234)
Dibenzofuran-3-PO₂H₂	Dibenzofuran-3-PCl₂		125	(66)
Thiophene-2-PO₂H₂	C₄H₃SPCl₂		70	(304)
4-(CH₃)₂NC₆H₄PO₂H₂	4-(CH₃)₂NC₆H₄PCl₂		162	(33, 40, 252, 290, 307)
4-(C₂H₅)₂NC₆H₄PO₂H₂	4-(C₂H₅)₂NC₆H₄PCl₂			(40)
4-C₆H₅(CH₃)NC₆H₄PO₂H₂	4-C₆H₅(CH₃)NC₆H₃PCl₂		150.5	(252)
4-C₆H₅CH₂(CH₃)NC₆H₄PO₂H₂	4-C₆H₅CH₂(CH₃)NC₆H₄PCl₂		96	(252)
2-CH₃-4-(CH₃)₂NC₆H₃PO₂H₂	2-CH₃-4-(CH₃)₂NC₆H₃PCl₂			(33)
2-CH₃-4-(C₂H₅)₂NC₆H₃PO₂H₂	2-CH₃-4-(C₂H₅)₂NC₆H₃PCl₂			(33)

* No melting point given.

about 150°C. (35, 73, 104, 169, 188, 189, 202, 228, 230, 234, 235, 236, 238, 240, 251, 305). One mole of a primary phosphine is produced for every two moles of phosphonic acid:

$$3RPH(O)OH \xrightarrow{heat} RPH_2 + 2RP(O)(OH)_2$$

Until recently it was believed that aliphatic phosphonous acids began to undergo disproportionation at a lower temperature than aromatic phosphonous acids, possibly as low as 60°C. (104), but this is not the case (305).

TABLE 4

Phosphonous acids prepared from primary phosphines

| Phosphonous Acid	Primary Phosphine	Yield	Melting Point	References
		per cent	*°C.*	
n-C₇H₁₅PO₂H₂	n-C₇H₁₅PH₂			(336)
n-C₉H₁₉PO₂H₂	n-C₉H₁₉PH₂			(262)
tert-C₁₂H₂₅PO₂H₂	tert-C₁₂H₂₅PH₂	77		(44)
C₆H₅CH₂PO₂H₂	C₆H₅CH₂PH₂			(189)
C₆H₅PO₂H₂	C₆H₅PH₂		70	(84, 169, 242)
4-CH₃C₆H₄PO₂H₂	4-CH₃C₆H₄PH₂		104–105	(251)
2,4,5-(CH₃)₃C₆H₂PO₂H₂	2,4,5-(CH₃)₃C₆H₂PH₂			(236)
2,4,6-(CH₃)₃C₆H₂PO₂H₂	2,4,6-(CH₃)₃C₆H₂PH₂			(236)
2-ClC₆H₄OCH₂PO₂H₂	2-ClC₆H₄OCH₂PH₂			(194)
4-ClC₆H₄OCH₂PO₂H₂	4-ClC₆H₄OCH₂PH₂		122–124	(194)
2,4-Cl₂C₆H₃OCH₂PO₂H₂	2,4-Cl₂C₆H₃OCH₂PH₂		100–101	(194)
2,4,5-Cl₃C₆H₂OCH₂PO₂H₂	2,4,5-Cl₃C₆H₂OCH₂PH₂		129–130	(194)

When used for the synthesis of an organophosphine, the phosphonous acid is usually heated rapidly to 250°C., at which temperature the organophosphine distils. The phosphonous acid may be generated *in situ* by treatment of a phosphonous dihalide with ethanol, and converted directly to the phosphine by distilling to dryness (169, 188, 202, 228, 230, 246, 251). It is advantageous to add sodium carbonate to trap the phosphonic acid, which might otherwise break down to metaphosphoric acid and the hydrocarbon (202).

Kosolapoff and Powell (180) suggested, on the basis of molecular-weight determinations on phosphonous acids which showed that they were in a state of trimeric aggregation, that disproportionation may be the result of a rearrangement of the protons and oxygen atoms within the cyclic trimer in such a way as to produce the maximum concentration of oxygen at two of the three phosphorus atoms.

The only known exceptions to this disproportionation are acids which break down in other ways at temperatures below the disproportionation temperature, such as the *p*-dialkylaminophenylphosphonous acids (307) or the α-hydroxyalkylphosphonous acids (209, 328), which suffer scission of the carbon–phosphorus bond.

2. Scission of the carbon–phosphorus bond

Some phosphonous acids undergo scission of the carbon–phosphorus bond at temperatures below the disproportionation temperature. *p*-Dialkylaminophenylphosphonous acids, alone among the aromatic members, break down when heated in neutral or acid solution as follows (207, 307):

$$p\text{-}(CH_3)_2NC_6H_4PO_2H_2 + H_2O \xrightarrow{\text{heat}} (CH_3)_2NC_6H_5 + H_3PO_3$$
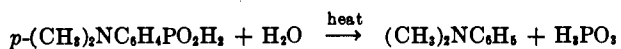
The acids, however, are stable to alkaline or alcoholic solution (307). When heated by itself *p*-dimethylaminophenylphosphonous acid yields a variety of decomposition products including dimethylaniline, metaphosphoric acid, phosphine, and elemental phosphorus (307). The α-hydroxyalkylphosphonous acids as a class undergo scission of the carbon–phosphorus bond under relatively mild conditions (209, 328). On stronger heating, phosphine is evolved and metaphosphoric acid is left (328). Triphenylmethylphosphonous acid suffers scission of the carbon–phosphorus bond in acid solution giving triphenylcarbinol, and in alcoholic sodium ethoxide giving triphenylmethane (111). The acid is stable, however, to aqueous alkali. Phosphonous acids containing fluoroalkyl substituents are unstable to hot water or aqueous alkali (34, 35, 73, 74, 195).

3. Oxidation

The reducing power of phosphonous acids is characteristic of compounds containing the P—H group. Phosphonous acids reduce ammoniacal silver nitrate to metallic silver (209, 230, 240, 328), cupric salts to metal-

lic copper (209), ferric salts to ferrous (209), mercuric chloride to calomel (73, 74, 209, 210, 230, 240, 251, 252, 307, 328), and sulfur dioxide to elemental sulfur (230, 240); they react with metallic zinc and iron, evolving hydrogen (230, 240, 328). The phosphonous acids are oxidized in the process to phosphonic acids.

Oxidant systems which have been found useful in preparative work are iodine/acetic acid (111), iodine/sodium bicarbonate (74), mercuric chloride (210, 213, 214, 215, 217), alkaline permanganate (111), 50 per cent hydrogen peroxide (74), bromine water (211, 212, 213, 214, 215, 217), and nitric acid. The use of more dilute hydrogen peroxide for the synthesis of phosphonous acids from organophosphines was noted in Section II,A,6. Nitric acid has been found useful with aliphatic phosphonous acids because of the high stability of the products toward oxidation (44, 104, 233), but aromatic phosphonous acids may suffer nitration of the ring in the process (28, 251). Electrolytic oxidation has been attempted unsuccessfully (210).

4. Reduction

Phosphonous acids are not readily reduced to the primary phosphines. The classical reducing agents, such as sodium/alcohol, zinc dust/alkali, amalgamated zinc/hydrochloric acid, red phosphorus/iodine, etc., are ineffective (84). The reduction has, however, recently been accomplished with lithium aluminum hydride, phenylphosphine being obtained from phenylphosphonous acid in 13 per cent yield (341).

5. Reaction with halogens

Phosphonous acids do not react with chlorine in the cold, but on warming a violent reaction takes place with evolution of clouds of hydrogen chloride and bursts of flame (230, 240, 251). The residue is a mixture of charcoal and phosphonic anhydride. These phenomena are probably the result of reaction of the chlorine with primary organophosphines produced from the phosphonous acids by disproportionation (230, 240).

The use of bromine water for the oxidation of a phosphonous acid has already been described (Section II,B,3).

6. Condensation reactions

The phosphonous acids contain a reactive hydrogen attached to phosphorus which can be replaced by alkyl groups in reactions similar to those used to prepare the acids themselves. One such reaction is the free-radical-initiated reaction of sodium *n*-hexylphosphonite with 1-hexene (325):

$$C_6H_{13}PH(O)ONa + C_4H_9CH{=}CH_2 \rightarrow (C_6H_{13})_2P(O)ONa$$
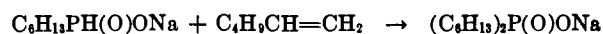
Secondary phosphinic acids are also formed in the reaction of α-hydroxyalkylphosphonous acids with aldehydes or acetone (209, 216), but not with ketones

higher than acetone (213, 214, 216):

$$(CH_3)_2C(OH)PH(O)OH + C_6H_5CHO \rightarrow \begin{matrix} (CH_3)_2COH \\ \diagdown \\ P(O)OH \\ \diagup \\ C_6H_5COH \end{matrix}$$
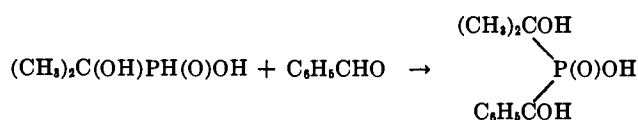
7. Reactions not involving the phosphorus atom

Few reactions of phosphonous acids are known which do not involve the phosphorus atom. p-Bromophenyl-phosphonous acid when heated with ammonium hydroxide and cuprous oxide in a sealed tube at 150°C. gives p-aminophenylphosphonous acid, m.p. 169°C., in 54 per cent yield (163, 164). The yield drops to 40 per cent if p-chlorophenylphosphonous acid is used (164). The hydroxyl groups in α-hydroxyalkylphosphonous acids (328) or β-hydroxyalkylphosphonous acids (258) can be acetylated without affecting the acid groups.

III. PHOSPHONOUS DIHALIDES

The lower alkyl phosphonous dihalides are water-white liquids with obnoxious odors; they rapidly deposit amorphous yellow solids on exposure to air (80, 158), but can be stored indefinitely in an inert atmosphere (80). The tendency to form a yellow solid decreases with increasing chain length.

Phosphonous dibromides are unstable to sunlight (246).

A. SYNTHESIS OF PHOSPHONOUS DIHALIDES

1. From aromatic hydrocarbons

(a) With Friedel–Crafts catalysts

The Friedel–Crafts reaction has been used extensively for the synthesis of organophosphorus compounds for over eighty years and is still one of the best methods for preparing the aromatic compounds. The catalyst usually employed is anhydrous aluminum chloride, though ferric chloride has been found to be effective with phenolic ethers (330, 331).

$$RH + PCl_3 \xrightarrow{AlCl_3} RPCl_2 + HCl$$
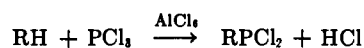
For best results the aluminum chloride should be present in slight molar excess over the aromatic hydrocarbon (45). The yield falls sharply if the amount of aluminum chloride present is less than one-third of the molar amount of the aromatic hydrocarbon (175, p. 44). This, together with the stability of the complex formed between the aluminum chloride and the product, made the reaction a very inefficient one until recently; yields reported in all of the earlier work are low because most of the product was tied up as the complex.

This problem has been solved by the addition of phosphorus oxychloride to the reaction mixture at the end of the reaction (45, 71, 72). The phosphorus oxychloride forms a granular complex, $AlCl_3 \cdot POCl_3$, with the catalyst which can easily be removed by filtration. With this technique 64–78 per cent yields of phosphonous dihalides are common (45, 46). The only known failure has been with naphthalene, which forms too stable a complex. The complexes may also be decomposed with water (in sufficient amount to break the complex but not to hydrolyze the phosphonous dihalide) (71, 72) or with pyridine (71, 91, 92). If the phosphonous dihalide is to be used for the synthesis of phosphonous or phosphonic esters, the complex may be decomposed with an alcohol or phenol (353) or with chlorine followed by an alcohol or phenol (178, 179).

If the reaction is carried out in the presence of an aliphatic hydrocarbon containing a tertiary carbon atom, such as methylcyclohexane or isopentane, the phosphonous dihalide is found to be reduced to the primary phosphine (308). The reaction of benzene with phosphorus trichloride and aluminum chloride, for example, yields phenylphosphine when the reaction is carried out in the presence of methylcyclohexane.

The use of prolonged refluxing periods as described in the early literature is not necessary except in the case of sluggishly reacting compounds, such as the halogenated aromatic hydrocarbons, and may lead to the production of substantial amounts of phosphinous halides as by-products. With aromatic hydrocarbons containing several alkyl substituents the diaryl compounds constitute the major (235, 236) or only (82) reaction products. In one case a triarylphosphine was found (252).

A serious disadvantage of the Friedel–Crafts method is that mixtures of isomers are often obtained. For example, in toluene the o:m:p orientation of substitution was found to be 10:27:63 (177). Another disadvantage is the well-known tendency of aluminum chloride to isomerize aromatic hydrocarbons. The reaction of n-amylbenzene with phosphorus trichloride and aluminum chloride gave 5 per cent of tert-butylphenylphosphonous dichloride in addition to the normal product (45). In other reactions the alkyl substituent has been split off (45).

Other variations of the Friedel–Crafts reaction involve the use of aliphatic hydrocarbons containing six carbon atoms or more (353) (those with less than six carbon atoms tend to deposit large amounts of free phosphorus) and the use of phosphorus tribromide instead of phosphorus trichloride (190, 191).

Phenolic ethers such as anisole or phenetole are cleaved by strictly anhydrous aluminum chloride, but not by ordinary anhydrous aluminum chloride (184). The cleavage products are arylphosphorodichloridites, $ArOPCl_2$.

Failure to take part in the Friedel–Crafts reaction has been reported with stilbene (238), anthracene (257), ethyl α-naphthyl ether (184), acetophenone (234), benzophenone (234), ethyl benzoate (234), dibenzylaniline (330), phthalanil (330), benzonitrile (234),

iodobenzene (234), and trichlorobenzene (179). A list of the successful reactions is given in table 5.

(b) With no catalysts

Certain aromatic hydrocarbons can be made to react with phosphorus trichloride in the absence of a catalyst. Dimethylaniline, for example, is sufficiently reactive to condense with phosphorus trichloride at the reflux temperature (33, 40, 290, 330), giving p-dimethylamino-phenylphosphonous dichloride in 60–65 per cent yield. The dimethylaniline is used in sufficient excess to trap the hydrogen chloride produced.

$$2(CH_3)_2NC_6H_5 + PCl_3 \rightarrow$$
$$p\text{-}(CH_3)_2NC_6H_4PCl_2 + (CH_3)_2NC_6H_5 \cdot HCl$$
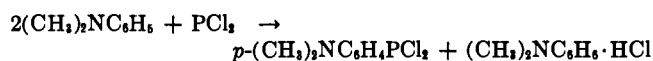
Other dialkylanilines have been used, including two N-alkylcarbazoles (33, 50).

Benzene reacts with phosphorus trichloride when a mixture of the two substances is passed through a hot tube at 600°C. (226, 230). The mixture is recycled for several hours and the heavier phenylphosphonous dichloride is drawn off from time to time. Small amounts of phosphorus and biphenyl are obtained as by-products (166). Numerous improvements on the original procedure of Michaelis have been described (8, 41, 71, 188, 192, 224, 274), dealing principally with the design of the apparatus. Yields are of the order of 50 per cent (230).

Other than benzene, the only aromatic hydrocarbon

TABLE 5

Phosphonous dihalides prepared from aromatic hydrocarbons with Friedel–Crafts catalysts

| Phosphonous Dihalide	Preparation from		Yield	Melting Point	Boiling Point	References
	Aromatic hydrocarbon	PX₃				
			per cent	°C.	°C.	
$C_6H_5PCl_2$	Benzene	PCl₃	80		90–92/10 mm.	(45, 46, 71, 72, 92, 103, 134, 141, 174,179,201,232, 234,330,353,365)
$4\text{-}ClC_6H_4PCl_2$	Chlorobenzene	PCl₃	72		253–255	(28, 30, 173, 179, 234, 236, 265)
$4\text{-}BrC_6H_4PCl_2$	Bromobenzene	PCl₃	25		271–272	(63, 134, 234, 236, 330)
$2\text{-}CH_3C_6H_4PCl_2$	Toluene	PCl₃			244	(177, 234)
$3\text{-}CH_3C_6H_4PCl_2$	Toluene	PCl₃	20		235	(177, 234)
$4\text{-}CH_3C_6H_4PCl_2$	Toluene	PCl₃	66	25	245	(45, 46, 103, 134, 161, 177, 179, 190, 201, 204, 232, 234, 247, 250,251,287,337)
$4\text{-}CH_3C_6H_4PBr_2$	Toluene	PBr₃		160–161		(190)
$3\text{-}Cl\text{-}4\text{-}CH_3C_6H_3PCl_2$	o-Chlorotoluene	PCl₃	15		265–266	(225)
$4\text{-}C_2H_5C_6H_4PCl_2$	Ethylbenzene	PCl₃	70		250–252	(45, 46, 128, 134, 235, 348)
$2,3\text{-}(CH_3)_2C_6H_3PCl_2$	o-Xylene	PCl₃			278	(235, 343)
$2,4\text{-}(CH_3)_2C_6H_3PCl_2$	m-Xylene	PCl₃	30		257	(234, 250, 343)
$2,5\text{-}(CH_3)_2C_6H_3PCl_2$	p-Xylene	PCl₃	30	−30	253–254	(130, 134, 234, 344)
$3,5\text{-}(CH_3)_2C_6H_3PCl_2$	m-Xylene	PCl₃				(343, 344)
$4\text{-}C_3H_7C_6H_4PCl_2$	n-Propylbenzene	PCl₃	47		127–131/5 mm.	(45)
$4\text{-}(iso\text{-}C_3H_7)C_6H_4PCl_2$	Cumene	PCl₃	64		268–270	(45, 46, 134, 175, 234, 236)
$2,4,5\text{-}(CH_3)_3C_6H_2PCl_2$	Pseudocumene	PCl₃	30		279–280	(234, 236)
$2,4,6\text{-}(CH_3)_3C_6H_2PCl_2$	Mesitylene	PCl₃	8	35–37	273–275	(60, 234, 236)
$4\text{-}C_4H_9C_6H_4PCl_2$	n-Butylbenzene	PCl₃	39		116–119/1.0 mm.	(45)
$4\text{-}(sec\text{-}C_4H_9)C_6H_4PCl_2$	sec-Butylbenzene	PCl₃	33		116–120/1.5 mm.	(45)
$2\text{-}CH_3\text{-}5\text{-}(iso\text{-}C_3H_7)C_6H_3PCl_2$	p-Cymene	PCl₃	7		275–278	(234, 236, 251)
$4\text{-}C_5H_{11}C_6H_4PCl_2$	n-Amylbenzene	PCl₃			130–210/20 mm.	(133)
$4\text{-}(sec\text{-}C_5H_{11})C_6H_4PCl_2$	sec-Amylbenzene	PCl₃	22		118–121/1.0 mm.	(45)
$(C_5H_{11})_2C_6H_3PCl_2$	Diamylbenzene	PCl₃			160–250/20 mm.	(133)
$4\text{-}(n\text{-}C_6H_{13})C_6H_4PCl_2$	n-Hexylbenzene	PCl₃	50		146–149/1.5 mm.	(45)
$2\text{-}C_{10}H_7PCl_2$	Naphthalene	PCl₃	15	58–59	180/10 mm.	(191, 342)
$2\text{-}C_{10}H_7PBr_2$	Naphthalene	PBr₃		65–68		(191)
$4\text{-}C_6H_5C_6H_4PCl_2$	Biphenyl	PCl₃	6	5	200–220	(192, 238)
$4\text{-}C_6H_5CH_2C_6H_4PCl_2$	Diphenylmethane	PCl₃	15		221/20 mm.	(234, 238)
$4\text{-}C_6H_5CH_2CH_2C_6H_4PCl_2$	Bibenzyl	PCl₃	20	2	250/60 mm.	(234, 238)
$4\text{-}CH_3OC_6H_4PCl_2$	Anisole	PCl₃	35		140–140.5/11 mm.	(63, 128, 134, 142, 184, 234, 330)
$4\text{-}C_2H_5OC_6H_4PCl_2$	Phenetole	PCl₃			266 (d.)	(234)
$2,4\text{-}(CH_3O)_2C_6H_3PCl_2$	1,3-Dimethoxybenzene	PCl₃	27	147	175–180/12–15 mm.	(331)
$4\text{-}C_6H_5OC_6H_4PCl_2$	Phenyl ether	PCl₃	14		200/12 mm.	(64, 134)
Dibenzofuran-3-PCl₂	Diphenylene oxide	PCl₃	7		245–250/25 mm.	(66)
$4\text{-}(CH_3)_2NC_6H_4PCl_2$	Dimethylaniline	PCl₃	25	66	158–160/0.6 mm.	(57, 101, 252, 307)
$4\text{-}(C_2H_5)_2NC_6H_4PCl_2$	Diethylaniline	PCl₃				(252)
$4\text{-}C_6H_5(CH_3)NC_6H_4PCl_2$	N-Methyldiphenylamine	PCl₃	32			(252)
$4\text{-}C_6H_5CH_2(CH_3)NC_6H_4PCl_2$	N-Benzyl-N-methylaniline	PCl₃				(252)
$4\text{-}C_6H_5CH_2(C_2H_5)NC_6H_4PCl_2$	N-Benzyl-N-ethylaniline	PCl₃				(252)
Thiophene-2-PCl₂	Thiophene	PCl₃	Low			(304)

to which this procedure has been successfully applied is thiophene (304). 2-Thienylphosphonous dichloride, b.p. 218°C., was obtained in 6 per cent yield. Toluene gave, in addition to much bibenzyl, stilbene, and phosphorus, a trace of a tolylphosphonous dichloride believed to be the meta isomer (235, 247).

2. From organometallic reagents

Grignard reagents and organolithium compounds react with phosphorus trichloride, giving exclusively tertiary phosphines (80, 340). Even under the most favorable conditions it has not been found possible to prepare phosphonous dichlorides by this method. One must therefore have recourse to milder organometallic reagents.

In recent patents, however, the use of a complex of the Grignard reagent with an oxygen or nitrogen heterocycle was said to give a phosphonous dichloride with phosphorus trichloride (288). The syntheses of C_8H_{17}-PCl_2 and p-$C_{18}H_{37}C_6H_4PCl_2$ were cited as examples.

Historically, the oldest and most important of these are the *organomercury* compounds. Michaelis used this method to synthesize aromatic phosphonous dichlorides of unambiguous structure for comparison with the products obtained from the Friedel–Crafts reaction. It was also until recently the only method available for the synthesis of aliphatic phosphonous dihalides. The reaction is usually carried out in sealed tubes at high temperatures (230–250°C.) to destroy the unreactive RHgCl by-product which might otherwise contaminate the product (104, 233).

$$R_2Hg + PCl_3 \rightarrow RPCl_2 + RHgCl$$
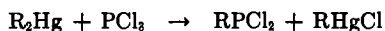
In a few cases the mercury in the organomercury compound was entirely converted to mercuric chloride (234, 251). The method does not work well with phosphorus tribromide because of the difficulties of purifying the phosphonous dibromide (104).

Grignard reagents may be used if they are first converted to *organocadmium* compounds (R_2Cd) or to *organozinc* compounds ($RZnBr$) by reaction with cadmium chloride or zinc chloride. Fox (80) prepared a series of n-alkylphosphonous dichlorides in 26–47 per cent yields by the reaction of phosphorus trichloride with dialkylcadmium compounds at $-20°C$.

$$R_2Cd + 2PCl_3 \rightarrow 2RPCl_2 + CdCl_2$$
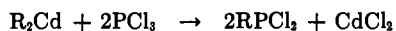
This reaction, however, gives satisfactory yields only with aliphatic compounds (340). The organozinc bromides, on the other hand, are useful for the synthesis of both aliphatic and aromatic phosphonous dichlorides (340).

$$RZnBr + PCl_3 \rightarrow RPCl_2 + ZnBrCl$$
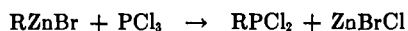
The organozinc compound is added in the form of a slurry to the phosphorus trichloride in boiling ether. The compound is used in the form of RZnBr rather than

R_2Zn, because the latter compounds are much more reactive and give exclusively tertiary phosphines (233, 340). A parallel can be drawn with the organomercury compounds, which are reactive in the form R_2Hg and unreactive in the form RHgCl.

A newer method which gives excellent yields (73–85 per cent) of aromatic phosphonous dichlorides is the reaction of an aryltrichlorosilane (or diaryldichlorosilane) with aluminum chloride at room temperature, followed by reaction of the arylaluminum halide with phosphorus trichloride (360, 361, 362).

$$RSiCl_3 + AlCl_3 \rightarrow RAlCl_2 + SiCl_4$$

$$RAlCl_2 + PCl_3 \rightarrow RPCl_2 + AlCl_3$$
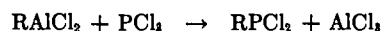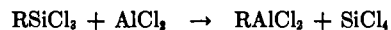
The aluminum chloride is separated from the product in the usual manner by complexing with phosphorus oxychloride, as done in the Friedel–Crafts reaction (Section III,A,1,(a)).

Another method involving organoaluminum compounds is the reaction of an *aluminum trialkyl* with phosphorus trichloride (267, 363, 364). The yield is much improved if the aluminum trialkyl is first complexed with ether or pyridine (267).

$$R_3Al + 3PCl_3 \rightarrow 3RPCl_2 + AlCl_3$$
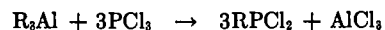
The alkyl radical is not isomerized in the reaction. The method failed with the lowest alkyl member, aluminum trimethyl, as the methylphosphonous dichloride could not be separated from the reaction products (267).

Ethylphosphonous dichloride may be conveniently prepared by the reaction of an *organolead* compound, tetraethyllead, with phosphorus trichloride (158, 159, 160). The reagents are heated under reflux for 30 hr., and the yields are quantitative.

$$(C_2H_5)_4Pb + 3PCl_3 \rightarrow 3C_2H_5PCl_2 + PbCl_2 + C_2H_5Cl$$

No reaction occurs with tetraphenyllead (51).

Syntheses of a few phosphonous dibromides have been reported in which phosphorus tribromide was substituted for the trichloride in reactions with organomercury compounds (104, 246) or organolead compounds (302). Furthermore, a reaction of phosphorus tribromide with an *organotin* compound was reported (302) which failed to take place when phosphorus trichloride was used.

$$(C_2H_5)_4Sn + PBr_3 \rightarrow C_2H_5PBr_2 + (C_2H_5)_3SnBr$$

In addition to the reactions described, displacement reactions with phosphorus trihalides also occur with the more metallic elements of the phosphorus subgroup. Phosphorus trichloride will abstract a phenyl group from triphenylbismuthine and from triphenylstibine, but not from triphenylarsine (51, 52).

The phosphonous dihalides prepared by the reaction of phosphorus trihalides with organometallic reagents are listed in table 6.

TABLE 6

Phosphonous dihalides prepared from organometallic reagents

Phosphonous Dihalide	Preparation from		Yield	Melting Point	Boiling Point	References
	Organometallic reagent	PX₃				

Organomercury method

			per cent	°C.	°C.	
C₂H₅PCl₂	(C₂H₅)₂Hg	PCl₃			114–117	(104, 233)
CH₂=CHPCl₂	(CH₂=CH)₂Hg	PCl₃	50		104/760 mm.	(31, 140)
C₃H₇PCl₂	(C₃H₇)₂Hg	PCl₃			140–143	(104)
iso-C₃H₇PCl₂	(iso-C₃H₇)₂Hg	PCl₃			135–138	(104, 233)
C₄H₉PCl₂	(C₄H₉)₂Hg	PCl₃	61		157–150/750 mm.	(70)
iso-C₄H₉PCl₂	(iso-C₄H₉)₂Hg	PCl₃			155–157	(104)
iso-C₅H₁₁PCl₂	(iso-C₅H₁₁)₂Hg	PCl₃			180–183	(104)
C₆H₅CH₂PCl₂	(C₆H₅CH₂)₂Hg	PCl₃	31		110–111/12 mm.	(132)
C₆H₅PCl₂	(C₆H₅)₂Hg	PCl₃	16		220	(230, 245)
C₆H₅PBr₂	(C₆H₅)₂Hg	PBr₃	Low		255–257	(246)
3-ClC₆H₄PCl₂	(3-ClC₆H₄)₂Hg	PCl₃			101–103/5 mm.	(355)
2-CH₃C₆H₄PCl₂	(2-CH₃C₆H₄)₂Hg	PCl₃	78		244	(235. 251)
3-CH₃C₆H₄PCl₂	(3-CH₃C₆H₄)₂Hg	PCl₃			235	(235)
4-CH₃C₆H₄PCl₂	(4-CH₃C₆H₄)₂Hg	PCl₃	66	25	245	(234, 251)
2,4-(CH₃)₂C₆H₃PCl₂	[2,4-(CH₃)₂C₆H₃]₂Hg	PCl₃	50		256–258	(56, 343)
2,4,5-(CH₃)₃C₆H₂PCl₂	[2,4,5-(CH₃)₃C₆H₂]₂Hg	PCl₃			280	(236)
1-C₁₀H₇PCl₂	(1-C₁₀H₇)₂Hg	PCl₃			250	(152)
2-C₁₀H₇PCl₂	(2-C₁₀H₇)₂Hg	PCl₃			180/10 mm.	(191)
4-CH₃OC₆H₄PCl₂	(4-CH₃OC₆H₄)₂Hg	PCl₃				(234)
4-C₂H₅OC₆H₄PCl₂	(4-C₂H₅OC₆H₄)₂Hg	PCl₃				(234)
4-(CH₃)₂NC₆H₄PCl₂	[4-(CH₃)₂NC₆H₄]₂Hg	PCl₃	66		250/125 mm,	(252, 307)
4-C₆H₅(CH₃)NC₆H₄PCl₂	[4-C₆H₅(CH₃)NC₆H₄]₂Hg	PCl₃				(234)

Organocadmium method

C₂H₅PCl₂	(C₂H₅)₂Cd	PCl₃	26		112	(80, 147)
C₃H₇PCl₂	(C₃H₇)₂Cd	PCl₃	44		134.5	(80, 147)
iso-C₃H₇PCl₂	(iso-C₃H₇)₂Cd	PCl₃			41–42/17 mm.	(298)
C₄H₉PCl₂	(C₄H₉)₂Cd	PCl₃	47		58–60/22 mm.	(80, 147, 148, 297)
iso-C₄H₉PCl₂	(iso-C₄H₉)₂Cd	PCl₃	26		48.5–49/12 mm.	(297)
C₅H₁₁PCl₂	(C₅H₁₁)₂Cd	PCl₃	40		184	(80)
n-C₆H₁₃PCl₂	(n-C₆H₁₃)₂Cd	PCl₃	41		208	(80)
n-C₇H₁₅PCl₂	(n-C₇H₁₅)₂Cd	PCl₃	42		228.5	(80)
n-C₈H₁₇PCl₂	(n-C₈H₁₇)₂Cd	PCl₃	33		247	(80)
1-C₁₀H₇PCl₂	(1-C₁₀H₇)₂Cd	PCl₃	25	54	118–120/0.5 mm.	(101)

Organozinc method

C₆H₅PCl₂	C₆H₅ZnBr	PCl₃	44		74/33 mm.	(342)
C₅H₁₁PCl₂	C₅H₁₁ZnBr	PCl₃	34		93–94.5/12 mm.	(342)
C₆H₅CH₂PCl₂	C₆H₅CH₂ZnBr	PCl₃	42		118–119/12 mm.	(342)
C₆H₅PCl₂	C₆H₅ZnBr	PCl₃	32		99–101/11 mm.	(340, 342)
4-BrC₆H₄PCl₂	4-BrC₆H₄ZnBr	PCl₃	8	55–60	65/0.8 mm.	(342)
2-CH₃C₆H₄PCl₂	2-CH₃C₆H₄ZnBr	PCl₃	38		127–129/12 mm.	(342)
4-CH₃C₆H₄PCl₂	4-CH₃C₆H₄ZnBr	PCl₃	23	24	116.5/11 mm.	(340, 342)
4-C₆H₅C₆H₄PCl₂	4-C₆H₅C₆H₄ZnBr	PCl₃	17		85/0.4 mm.	(342)
1-C₁₀H₇PCl₂	1-C₁₀H₇ZnBr	PCl₃	17	55	135–137/0.5 mm.	(342)
2-C₁₀H₇PCl₂	2-C₁₀H₇ZnBr	PCl₃	9	41–45	110/0.2 mm.	(342)

Organosilicon method

C₂H₅PCl₂	C₂H₅SiCl₃	PCl₃ (AlCl₃)	83		140–141/57 mm.	(360, 361. 362)
C₆H₅PCl₂	(C₆H₅)₂SiCl₂	PCl₃ (AlCl₃)	80		138–139/55 mm.	(361, 362)
4-ClC₆H₄PCl₂	4-ClC₆H₄SiCl₃	PCl₃ (AlCl₃)	77		252–253	(173, 360, 361, 362)
4-BrC₆H₄PCl₂	4-BrC₆H₄SiCl₃	PCl₃ (AlCl₃)	73		270	(360, 361, 362)
4-CH₃C₆H₄PCl₂	4-CH₃C₆H₄SiCl₃	PCl₃ (AlCl₃)	85	24.5	243–244	(361, 362)

Organoaluminum method

C₂H₅PCl₂	(C₂H₅)₃Al	PCl₃ [(C₂H₅)₂O]	62		112	(267)
C₃H₇PCl₂	(C₃H₇)₃Al	PCl₃ [(C₂H₅)₂O]	51		133	(267)
iso-C₃H₇PCl₂	(iso-C₃H₇)₃Al	PCl₃ [(C₂H₅)₂O]	43		130/745 mm.	(267)
C₄H₉PCl₂	(C₄H₉)₃Al	PCl₃ [(C₂H₅N)]	57		38.5–39/9 mm.	(267)
iso-C₄H₉PCl₂	(iso-C₄H₉)₃Al	PCl₃ [(C₂H₅)₂O or C₂H₅N]	36		148–149/740 mm.	(267, 363)
n-C₆H₁₃PCl₂	(n-C₆H₁₃)₃Al	PCl₃	42		83–84/9 mm.	(267)

TABLE 6 *(Continued)*

Organolead method						
C₁H₁PCl₁...................	(C₁H₁)₄Pb	PCl₁	96		113–116	(32, 84, 158, 159. 160. 264. 297)
C₁H₁¹¹PCl₁...................	(C₁H₁)₄Pb	¹¹PCl₁	99			(306)
C₁H₁PBr₁...................	(C₁H₁)₄Pb	PBr₁	78		161	(302)

Organotin method						
C₁H₁PBr₁...................	(C₇H₁)₄Sn	PBr₁	67		160–164	(302)

3. From phosphorus trihalides

(a) With olefins

Phosphorus trichloride can be made to add to olefins under free-radical conditions. The products are β-chloroalkylphosphonous dichlorides:

$$RCH=CH_2 + PCl_3 \rightarrow RCHClCH_2PCl_2$$
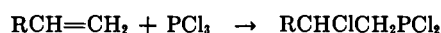
The free radicals may be generated by the thermal decomposition of acetyl peroxide (155, 156) or azobisisobutyronitrile (366), by ultraviolet irradiation (157, 186), or by subjecting high-molecular-weight linear polymers to shear stresses (266). For effective propagation of the chain reaction, the group R should be aliphatic and the carbon atom to which it is attached should carry a hydrogen atom (156).

Only two compounds have been prepared by this method. 2-Chlorooctylphosphonous dichloride, b.p. 85–88°C./0.5 mm., was obtained from 1-octene and phosphorus trichloride in 38 per cent yield (155, 156), and 2-chloro-2-(3-cyclohexen-1-yl)ethylphosphonous dichloride, b.p. 99–102°C./1 mm., was obtained from 4-vinylcyclohexene and phosphorus trichloride in 17 per cent yield (186).

For another reaction of olefins with phosphorus trichloride see Section II,A,2.

(b) With diazo compounds

At temperatures low enough to moderate the violence of the reaction (−50° to −60°C.), phosphorus trichloride reacts with diazoalkanes giving α-chloroalkylphosphonous dichlorides in 35–50 per cent yields (357, 359).

$$RCHN_2 + PCl_3 \rightarrow RCHClPCl_2 + N_2$$
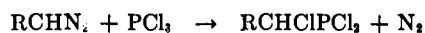
Equally satisfactory results are obtained with phosphorus tribromide (357, 359). Phosphonous dihalides prepared by this method are given in table 7.

4. From elemental phosphorus with alkyl halides

Elemental phosphorus reacts with alkyl halides at elevated temperatures to give mixtures of organophosphorus compounds. If the conditions are suitable, primary phosphonous dihalides can be made the predominant products. The perfluoroalkyl iodides may be made to give the desired products simply by adjusting the proportions of the reagents (34, 49, 74):

$$CF_3I + P \rightarrow CF_3PI_2$$
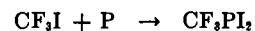
Rigorous exclusion of atmospheric contaminants is necessary if good yields are to be attained (49). When white phosphorus is used, iodine should be added as a catalyst (49).

Red phosphorus reacts with alkyl halides in the presence of copper powder at 280–440°C., giving phosphonous dihalides as the principal products (196). Small amounts of phosphinous halides and phosphorus trihalides are obtained as by-products.

The phosphonous dihalides prepared by this method are listed in table 8.

5. From phosphonous acids

Although the phosphonous dichlorides may be considered to be acid chlorides of the phosphonous acids, few attempts have been made to prepare them by the usual methods. Phosphorus pentachloride gives the phosphonic dichloride, owing to oxidation (230, 240), but phosphorus trichloride gives the phosphonous dichloride (111). Only one reaction of this type is known. Prolonged refluxing of triphenylmethylphosphonous acid with phosphorus trichloride gave an unstated yield of triphenylmethylphosphonous dichloride, m.p. 138–140°C., together with much phosphorous acid and free phosphorus (111).

TABLE 7

*Phosphonous dihalides prepared from diazo compounds*

Phosphonous Dihalide	Preparation from		Yield	Boiling Point	References
	Diazo compound	PX₃			
			per cent	*°C.*	
ClCH₁PCl₁........................	CH₁N₁	PCl₁	40	80–81/140 mm.	(357, 359)
BrCH₁PBr₁........................	CH₁N₁	PBr₁	50	70/4 mm.	(357, 359)
CH₁CHClPCl₁.......................	CH₁CHN₁	PCl₁	35	63.5–64.5/50 mm.	(357, 359)
C₁H₁CHClPCl₁.......................	C₁H₁CHN₁	PCl₁			(357)

TABLE 8

Phosphonous dihalides prepared from elemental phosphorus with alkyl halides

Phosphonous Dihalide	Preparation from		Yield	Boiling Point	References
	Alkyl halide	Catalyst			
			per cent	*°C.*	
CH₃PCl₂	CH₃Cl	Cu		78	(196)
CH₃PBr₂	CH₃Br	Cu		139–141	(196)
CH₃PI₂	CH₃I	Cu		73–75/5 mm.	(196)
CF₃PI₂	CF₃I		42	69/29 mm.	(34, 49)
C₆H₅PBr₂	C₆H₅Br	Cu		161	(196)
C₆F₅PI₂	C₆F₅I		18	190	(74)

6. From phosphonous diesters

Treatment of phosphonous diesters with phosphorus trichloride at 5°C. in ether solution gives phosphonous dichlorides in 50–60 per cent yield (305):

$$RP(OR)_2 + PCl_3 \rightarrow RPCl_2 + (RO)_2PCl$$
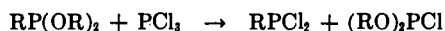
If excess phosphorus trichloride is added, the by-product is an alkylphosphorodichloridite, ROPCl₂ (305). The phosphonous dichlorides which have been prepared by this method are butylphosphonous dichloride, b.p. 60–65°C./17 mm., and phenylphosphonous dichloride, b.p. 82–85°C./5 mm., both prepared from the corresponding diethyl ester (305).

### 7. From phosphorobenzene and related compounds

Treatment of phosphorobenzene (see Section III,B,3) with bromine in carbon tetrachloride gave phenylphosphonous dibromide, b.p. 132°C./14 mm., 93°C./2 mm., in quantitative yield (182, 183).

$$(C_6H_5P)_4 + 4Br_2 \rightarrow 4C_6H_5PBr_2$$
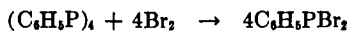
A similar reaction with chlorine gave phenylphosphonous dichloride (169). Tetrakis(trifluoromethyl)cyclo-tetraphosphine, another compound with a P₄ ring structure, reacts with iodine at room temperature giving a quantitative yield of trifluoromethylphosphonous diiodide, but chlorine gives only the tetrachlorophosphorane, CF₃PCl₄ (195).

8. From primary phosphines

Treatment with a halogen converts primary phosphines to the phosphonous dihalides (332).

$$RPH_2 + 2X_2 \rightarrow RPX_2 + 2HX$$
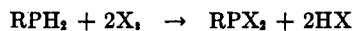
The halogen is added gradually to a dilute solution of the phosphine at 20°C. until a precipitate of the tetrahalophosphorane appears. Further addition would, of course, convert all of the dihalide to the tetrahalophosphorane. Butylphosphonous dibromide, b.p. 80–95°C./10 mm., was thus obtained in 44 per cent yield (332).

Treatment of phenylphosphine with phosgene gives phenylphosphonous dichloride according to the following equation (242):

$$C_6H_5PH_2 + 2COCl_2 \rightarrow C_6H_5PCl_2 + 2CO + 2HCl$$
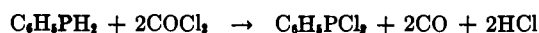
9. From tetrahalophosphoranes

Elemental phosphorus reduces alkyl- or aryltetra-halophosphoranes (RPX₄) to the phosphonous di-halides (96, 97, 335):

$$3RPCl_4 + 2P \rightarrow 3RPCl_2 + 2PCl_3$$
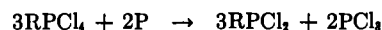
Iodine may be added as a catalyst, but its presence is not essential (96). The tetrachlorophosphoranes are prepared by the addition of chlorine to phosphonous dichlorides or by the addition of phosphorus penta-chloride to olefins. The latter reaction gives β-chloro-alkyltetrachlorophosphoranes, which when reduced lose the elements of hydrogen chloride, giving α,β-unsaturated phosphonous dichlorides (335, 354):

$$3RCHClCH_2PCl_4 + 2P \xrightarrow{I_2} 3RCH=CHPCl_2 + 2PCl_3 + 3HCl$$

A new reducing agent, useful because it yields volatile by-products, is methylphosphorodichloridite (285). The reduction of methyltetrachlorophosphorane proceeds as follows:

$$CH_3PCl_4 + CH_3OPCl_2 \rightarrow CH_3PCl_2 + POCl_3 + CH_3Cl$$
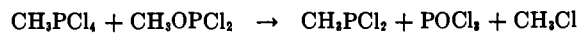
The complexes obtained in the Kinnear–Perren synthesis are complexes of aluminum chloride with tetra-chlorophosphoranes. They may be reduced to the phosphonous dichlorides by elemental phosphorus (172, 327), aluminum (118, 172), or sodium (172). Freshly calcined potassium chloride is used to bind the aluminum chloride, except when sodium is used as the reducing agent, as the sodium chloride produced serves the same purpose (172).

$$3[RPCl_3][AlCl_4] + 2P + 3KCl \rightarrow$$
$$3RPCl_2 + 2PCl_3 + 3K_2AlCl_4$$
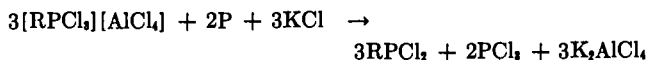
The phosphonous dihalides prepared by these methods are given in table 9.

10. From other phosphonous dihalides

Phosphonous dibromides can be prepared by treatment of phosphonous dichlorides with dry hydrogen bromide at the reflux temperature until no more is absorbed (246).
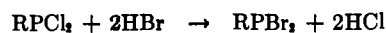
$$RPCl_2 + 2HBr \rightarrow RPBr_2 + 2HCl$$

TABLE 9

Phosphonous dihalides prepared from tetrahalophosphoranes

Phosphonous Dihalide	Preparation from		Yield	Melting Point	Boiling Point	References
	Tetrahalo-phosphorane	Reducing agent				
			per cent	°C.	°C.	
CH_3PCl_2	CH_3PCl_4	CH_3OPCl_2	77		81–82	(285)
CH_3PI_2	CH_3PI_4	P	43		68–70/2 mm.	(96)
CF_3PCl_2	CF_3PCl_4	Hg	99			(195)
CCl_3PCl_2	CCl_3PCl_4	CH_3OPCl_2		47	69–70/23 mm.	(285)
CCl_3PCl_2	CCl_3PCl_4	P, PI₃	60	50–52	82–83/7 mm.	(97)
$C_6H_5PCl_2$	$C_6H_5PCl_4$	P	96		91–93/6 mm.	(335)
Olefin–PCl₃ method						
$C_3H_7PCl_2$	2-Methylpropene, PCl₃	P	68		98–104/100 mm.	(335, 354)
$C_5H_{11}PCl_2$	1-Pentene, PCl₃	P			100–102/100 mm.	(354)
$C_8H_{17}PCl_2$	Diisobutylene, PCl₃	P	66		70–72/3 mm.	(335, 354)
$C_6H_5CH=CHPCl_2$	Styrene, PCl₃	P	54		135–138/8 mm.	(335, 354)
$C_9H_7PCl_2$	Indene, PCl₃	P	28		104–105/1 mm.	(335)
Kinnear–Perren method						
CH_3PCl_2	CH₃Cl, PCl₃, AlCl₃	Al, KCl	72		81–82	(118, 172)
CCl_3PCl_2	CCl₄, PCl₃, AlCl₃	P	61	40	67/20 mm.	(327)
$C_2H_5PCl_2$	C₂H₅Cl, PCl₃, AlCl₃	P, KCl	70		113–114/752 mm.	(172)

The reactions are far from simple however, as benzene, bromobenzene, phosphorus, phosphorus trichloride, and phosphorus tribromide have been isolated as by-products (246).

A similar treatment of phosphonous dichlorides with hydrogen iodide at elevated temperatures yields the hydriodic acid salts of the phosphonous diiodides (96, 188, 230). These are dark-colored compounds which resemble iodine in appearance and which evolve hydrogen iodide on heating.

Conversely, phosphonous dichlorides may be prepared from the diiodides (and probably also from the dibromides) by treatment with silver chloride (34, 74).

According to Anderson (6), exchange reactions with other covalent halides occur whenever a more volatile component can be distilled from the reaction medium. Thus, phenylphosphonous dichloride reacts with silicon and germanium tetrabromides to give phenylphosphonous dibromide, and with propyltriiodosilane to give phenylphosphonous diiodide (6).

$$2C_6H_5PCl_2 + GeBr_4 \rightarrow 2C_6H_5PBr_2 + GeCl_4$$

$$3C_6H_5PCl_2 + 2C_3H_7SiI_3 \rightarrow 3C_6H_5PI_2 + 2C_3H_7SiCl_3$$
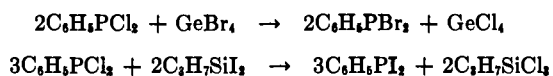
The same principle is used in exchanging chloride groups for isocyanate and isothiocyanate groups (see Section III,B,4).

The phosphonous dihalides that have been prepared by these methods are listed in table 10.

11. From higher organophosphorus compounds

No method has yet been devised for converting secondary or tertiary phosphorus compounds to primary phosphonous dichlorides. The thermal decomposition of tertiary phosphine dihalides (R_3PX_2) gives secondary phosphinous halides (R_2PX) with the elimination of alkyl halide, but attempts to extend this reaction to the synthesis of primary phosphonous dihalides have not been successful. Likewise, attempts to induce trivinylphosphine or dibutyldivinyltin to undergo redistribution reactions with phosphorus trichloride gave only black solids, despite the success of these reactions with arsenic and antimony analogs (140).

B. REACTIONS OF PHOSPHONOUS DIHALIDES

The reactions of phosphonous dihalides which yield derivatives described in detail in other sections of this

TABLE 10

Phosphonous dihalides prepared by halogen exchange

Phosphonous Dihalide	Preparation from		Yield	Melting Point	Boiling Point	References
	Phosphonous dihalide	Reagent				
			per cent	°C.	°C.	
$CH_3PI_2 \cdot HI$	CH_3PCl_2	HI	75	85–87		(96)
CF_3PCl_2	CF_3PI_2	AgCl	82		37	(34, 195)
$C_2F_5PCl_2$	$C_2F_5PI_2$	AgCl	98		86.4	(74)
$C_6H_5PBr_2$	$C_6H_5PCl_2$	HBr			255–257	(246)
$C_6H_5PI_2 \cdot HI$	$C_6H_5PCl_2$	HI				(188, 230)

review are not considered here. These include hydroly-
sis to phosphonous acids (Section II,A,4); esterification
to phosphonous monoesters (Section VIII,A,2), to
phosphonous diesters (Section IV,A,3), to phosphono-
chloridous esters (Section VII,A) or to phosphonodi-
thious esters (Section V,A); amidation to phosphonous
diamides or iminophosphines (Section VI,A) or to
phosphonamidous chlorides (Section VII,B); synthesis
of mixed anhydrides with dialkyl phosphites (Section
X,A,1) or with phosphonous monoesters (Section
X,A,2); and exchange reactions with other halides to
form different phosphonous dihalides (Section III,A,10).

1. Scission of the carbon–phosphorus bond

A few phosphonous dichlorides have been observed
to undergo scission of the carbon–phosphorus bond
under conditions where most such compounds are
stable. Phosphonous dichlorides which contain strongly
electronegative substituents on the carbon atom at-
tached to the phosphorus atom are the most suscepti-
ble. Trichloromethylphosphonous dichloride, for exam-
ple, suffers scission of the carbon–phosphorus bond on
treatment with oxygen-free boiling water (97):

$$CCl_3PCl_2 + 3H_2O \rightarrow CHCl_3 + H_3PO_3 + 2HCl$$
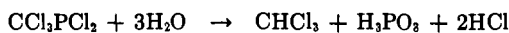
Triphenylmethylphosphonous dichloride, $(C_6H_5)_3$-
$CPCl_2$, undergoes cleavage when subjected to the
oxidizing treatments usually employed to convert
phosphonous dichlorides to phosphonic acids, such as
chlorination and hydrolysis or chlorination and treat-
ment with sulfur dioxide (111). The same result is ob-
tained on shaking with iodine and sodium bicarbonate
(111).

Another class of sensitive compounds comprises the
p-dialkylaminophenylphosphonous dichlorides (252).
The p-dimethylamino derivative in dry ether absorbs
anhydrous hydrogen chloride, giving a white precipitate
which redissolves and then deposits dimethylaniline
hydrochloride:

$$p\text{-}(CH_3)_2NC_6H_4PCl_2 + 2HCl \rightarrow (CH_3)_2NC_6H_5 \cdot HCl + PCl_3$$
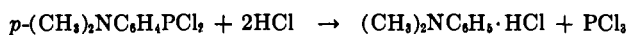
The chlorination of methylphosphonous dichloride in
concentrated solution or at temperatures above 40°C.
is accompanied by some cleavage of the carbon–phos-
phorus bond (285).

2. Reduction

Phosphonous dihalides may be reduced to primary
phosphines with lithium aluminum hydride (35, 123,
124, 182, 183, 268, 299, 339). If an excess of the dihalide
is present in the reaction mixture, as it usually is, the
yield of phosphine cannot be greater than 50 per cent
because the product reacts with the starting material
forming a compound with a phosphorus–phosphorus
bond. Phenylphosphonous dichloride, for example,
forms "phosphorobenzene" (see Section III,B,3). Sub-

sequent aqueous treatment of the reaction mixture to
decompose the hydride converts the phosphorobenzene
to equal parts of phenylphosphine and phenylphos-
phonic acid (123).

Phenylphosphonous dichloride can also be reduced to
phenylphosphine by lithium hydride (123), by sodium
hydride (123), and by a finely divided dispersion of so-
dium in toluene followed by water (122, 123, 268). Potas-
sium borohydride is said to be unreactive (123), but
lithium borohydride reduces phenylphosphonous di-
chloride to a crystalline borine adduct, $C_6H_5PH_2 \cdot BH_3$
(347). A deficiency of the reducing agent in the latter
reaction yields an unstable adduct, $C_6H_5PHCl \cdot BH_3$,
which gradually loses hydrogen chloride and hydrogen
forming a high-molecular-weight polymer, $(C_6H_5\text{-}
PBH)_x$ (347).

Other reducing agents have been tried without suc-
cess (35, 228, 230). Some yielded traces of phenylphos-
phine, detected by its odor. Two-step reduction via the
phosphonous acid is discussed in Section II,B,1.

3. Phosphorobenzene and related compounds

Phosphorobenzene, as described in the preceding sec-
tion, is obtained when phenylphosphonous dichloride is
reduced with lithium aluminum hydride (123, 268, 299).
It may also be prepared by the reaction of equal parts of
phenylphosphine and phenylphosphonous dichloride in
ether solution (169, 182, 183, 268, 339). The product is a
colorless, crystalline compound, m.p. 149–150°C. Most
texts give its structure as a dimer (I), but measurements
of the molecular weight of phosphorobenzene in numer-
ous solvents show that it is actually a tetramer, $(C_6\text{-}
H_5P)_4$. Recent investigators have suggested that it con-
tains a cyclic structure (II) and have renamed it tetra-
phenylcyclotetraphosphine (182, 183, 195, 268).

$$\begin{array}{cc} & C_6H_5P-PC_6H_5 \\ & | \quad\quad | \\ C_6H_5P=PC_6H_5 & C_6H_5P-PC_6H_5 \\ I & II \end{array}$$

In addition to this compound, which melts at 149–
150°C., higher-melting solids have been isolated, melt-
ing at 171°C. (339) and 188–192°C. (299). The struc-
tural relationship of these compounds to the cyclic
tetramer has not been definitely established, but they
appear to be oligomers of higher molecular weight
(299).

Other aromatic compounds related to phosphoro-
benzene have also been prepared. The product from p-
chlorophenylphosphine and p-chlorophenylphosphonous
dichloride was found to be resinous (234). The conden-
sation of phenylphosphonous dichloride with phenyl-
arsine gives a phosphoarsenobenzene, designated as
$C_6H_5P{=}AsC_6H_5$ (322), which easily undergoes dismuta-
tion to arsenobenzene and phosphorobenzene, even on
recrystallization from benzene.

The only other four-membered cyclic organophos-

phorus compound to have been investigated in detail is tetrakis(trifluoromethyl)cyclotetraphosphine, m.p. 66.3–66.4°C., b.p. 145° (48, 195). This compound is prepared by shaking trifluoromethylphosphonous diiodide with a large volume of mercury at room temperature.

$$4CF_3PI_2 + 4Hg \rightarrow (CF_3P)_4 + 4HgI_2$$
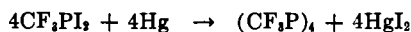
In addition to the tetramer a cyclic pentamer, m.p. −33°C., b.p. 190°C., is produced in this reaction (195).

Several reactions are recorded in the early literature on organophosphorus chemistry which gave ill-defined products apparently related to those described above.

The reaction of phenylphosphonous dichloride with phosphine gave hydrogen chloride and a yellow viscous solution which was believed to contain the following product (229):

$$C_6H_5PCl_2 + PH_3 \rightarrow C_6H_5P{=}PH + 2HCl$$
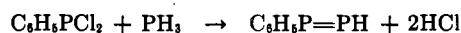
The structure of the product follows from its oxidation with nitric acid to give phenylphosphonic acid and phosphoric acid.

Similar substances are apparently formed by the action of moisture on phenylphosphonous dichloride (99, 253). The reaction of phenylphosphonous dichloride with one mole of water commences at 100°C., with the copious evolution of hydrogen chloride, and is complete at 260°C. On cooling there is obtained a bright yellow mass from which phenylphosphonous acid, phenylphosphonic acid, and diphenylphosphinic acid are extracted with water. The residue contains the yellow compounds $C_6H_5P_4H$ and $C_6H_5P_4H \cdot C_6H_5PO_2$, separated by their difference in solubility in carbon disulfide. The compound $C_6H_5P_4H$ yields the same products on chlorination or oxidation as would be expected from the compound $C_6H_5P{=}PH$ (99). The same results are obtained in the reaction of phenylphosphonous dichloride with phenylphosphonous acid (99). Larger amounts of water, of course, hydrolyze phosphonous dichlorides to the corresponding acids (see Section II,A,4).

Phenylphosphonous dichloride reacts with hydrogen sulfide when heated near its boiling point, evolving hydrogen chloride (170). The phosphonous dichloride is believed to suffer initially a dismutation, since the sulfur-containing products yield diphenylphosphinic acid and not phenylphosphonic acid on oxidation.

4. Reaction with pseudohalogen compounds

Phosphonous dihalides react with silver cyanide (234), silver cyanate (112, 113, 196), and silver thiocyanate (234), giving products with properties similar to those of the phosphonous dihalides themselves. The preparation of phenylphosphonous diisothiocyanate is given as an example:

$$C_6H_5PCl_2 + 2AgSCN \rightarrow C_2H_5P(NCS)_2 + 2AgCl$$
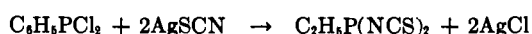
These compounds can also be prepared by exchange reactions with other covalent isocyanates or isothiocyanates, if conditions are such that the halide which is produced in the exchange can be distilled from the reaction mixture (6):

$$C_6H_5PCl_2 + (C_2H_5)_2Si(NCS)_2 \rightarrow C_6H_5P(NCS)_2 + (C_2H_5)_2SiCl_2$$
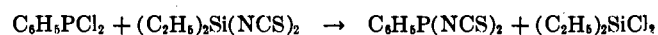
The dicyanides, $RP(CN)_2$, are stable to water but are hydrolyzed by dilute sodium hydroxide solution to sodium cyanide and the sodium salt of the phosphonous acid (234). They form adducts with chlorine, but subsequent treatment with sulfur dioxide gives no homogeneous product. The diisothiocyanates are decomposed by water and give organophosphorus tetrachlorides with chlorine (234):

$$RP(NCS)_2 + 3Cl_2 \rightarrow RPCl_4 + S_2 + 2ClCN$$
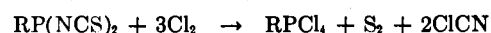
The diisocyanates form the expected urethan and urea derivatives with alcohols and amines (112, 113).

5. Addition of oxygen, sulfur, or selenium

As compounds of trivalent phosphorus, the phosphonous halides are capable of adding oxygen (97, 111), sulfur (19, 22, 80, 104, 118, 131, 168, 196, 267, 297, 335), or selenium (196) to form the corresponding phosphonic, ·phosphonothionic, or phosphonoselenonic dihalides.

The direct oxidation of phosphonous dihalides is seldom if ever used as a preparative method, but the addition of sulfur is well known. A catalyst such as aluminum chloride is required (19, 131); in its absence, sulfur is precipitated unchanged even after heating to 114°C. (19). At higher temperatures phosphonous dichlorides and sulfur react with violence (168).

$$RPCl_2 + S \xrightarrow{AlCl_3} RP(S)Cl_2$$
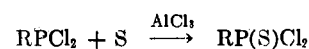
For best results, the sulfur should be added to a mixture of the phosphonous dichloride and aluminum chloride (118). Thiophosphoryl chloride (100, 131) or phosphorus pentasulfide (131) may be used in place of elemental sulfur.

6. Addition of halogens

Phosphonous dichlorides react vigorously with chlorine giving yellow crystalline adducts resembling phosphorus pentachloride in appearance (64, 92, 104, 190,

$$RPCl_2 + Cl_2 \rightarrow RPCl_4$$
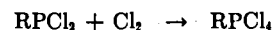
191, 192, 195, 223, 225, 227, 230, 233, 234, 235, 236, 238, 250, 251, 252, 265, 304, 343, 344, 348, 355, 357). Adducts with bromine have also been prepared (186, 190, 230, 234, 246).

Methylphosphonous dichloride, CH_3PCl_2, absorbs more than the theoretical amount of halogen, owing to halogenation of the alkyl group (285, 358, 366). The intermediates can be isolated if the calculated amount of halogen is used. Chlorination of the aromatic ring in arylphosphonous dichlorides has also been observed (331).

If phosphorus pentoxide is present in the slurry during halogenation, the product is converted to a phosphonic dichloride (326). Sulfuryl chloride also oxidizes phosphonous dichlorides to phosphonic dichlorides (264, 306). Sulfur monochloride, however, produces a mixture of phosphonothionic dichloride and tetrachlorophosphorane in 2:1 ratio (131, 165, 198):

$$3RPCl_2 + S_2Cl_2 \rightarrow 2RP(S)Cl_2 + RPCl_4$$
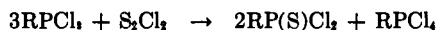
Phosphonous dichlorides undergo a redox reaction with antimony pentachloride (167). The products are complexes:

$$RPCl_2 + 2SbCl_5 \rightarrow RPCl_4 \cdot SbCl_5 + SbCl_3$$
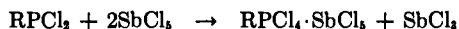
No reaction is observed with silicon tetrachloride, zinc chloride, or titanium tetrachloride (167). Antimony pentafluoride gives the tetrafluorophosphorane (318), replacement of the chlorine atoms occurring simultaneously with the redox reaction. The same results are achieved with a mixture of phosphorus pentachloride and antimony trifluoride (318).

7. Other addition reactions

Methylphosphonous dihalides react with metallic nickel under mild conditions giving complexes such as $Ni(CH_3PCl_2)_4$ in high yield (196, 284). Phenylphosphonous dichloride does not react with nickel under the same conditions, but the complex $Ni(C_6H_5PCl_2)_4$ can be made by the reaction of phenylphosphonous dichloride with nickel carbonyl (199) or by an exchange reaction with tetrakis(dichloromethylphosphine)nickel (284). Cobalt carbonyl gave a product which could not be characterized (303).

Phenylphosphonous dichloride reacts with the sodium salts of chloroamides of aromatic sulfonic acids, forming dichlorophenylphosphazosulfonaryls (314):

$$C_6H_5PCl_2 + ArSO_2NNaCl \rightarrow C_6H_5P(=NSO_2Ar)Cl_2 + NaCl$$
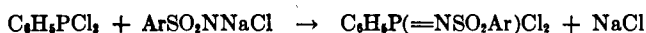
The same products can be prepared by the reaction of $C_6H_5PCl_4$ with aromatic sulfonamides (314).

Phenylphosphonous dichloride forms an equimolecular adduct, m.p. 160°C., with dimethylphenylphosphine (169), the identity of which has not been clearly established.

8. Condensations in which one new carbon–phosphorus bond is formed

Phosphonous dihalides take part in condensation reactions with replacement of one or both of the halogen atoms. The former will be discussed first.
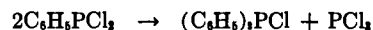
(a) Phosphinous compounds

Phosphinous halides are often by-products of the synthesis of phosphonous dihalides. With the use of more severe reaction conditions it is possible to convert phosphonous dichlorides to phosphinous chlorides in good yield, as in the reaction with organolead com-

pounds (32), organozinc compounds (338), or organomercury compounds (63, 109, 206, 224, 231, 238, 248, 274, 287, 337):

$$C_6H_5PCl_2 + R_2Hg \rightarrow C_6H_5RPCl + RHgCl$$
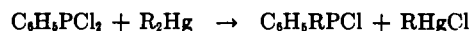
An attempt to use an organolithium reagent failed because even when the lithium compound was added slowly to a large excess of the phosphonous dichloride in ether solution, the only products were the tertiary phosphine and unreacted dichloride (109).

Phosphinous halides are also obtained, albeit in low yield, when phosphonous dihalides are heated for prolonged periods at 300°C. (17, 34, 43, 69, 74, 94). This method has been used with phenylphosphonous dichloride and two fluoroalkylphosphonous diiodides (RPI$_2$: R = CF$_3$ or C$_3$F$_7$), but does not work with the tolyl or higher aryl homologs (238).

$$2C_6H_5PCl_2 \rightarrow (C_6H_5)_2PCl + PCl_3$$

In these reactions the trivalency of the phosphorus atom is preserved.

(b) Secondary phosphinic compounds

The use of a phosphonous dihalide as the phosphorus component in several well-known reactions of phosphorus trichloride gives rise to compounds with one new carbon–phosphorus bond. In the Kinnear–Perren reaction, a crystalline ternary complex is formed from a phosphonous dichloride, aluminum chloride, and an alkyl halide, and is then decomposed by the addition of enough water to break up the complex (37, 126, 162):

$$RPCl_2 + AlCl_3 + R'Cl \rightarrow [RR'PCl_2][AlCl_4] \xrightarrow{H_2O} RR'P(O)Cl$$

If the complex is decomposed with sulfur or a sulfide (of aluminum, phosphorus, arsenic, or antimony) instead of water, the product is a phosphinothionic chloride (126).

In the oxidative phosphonation method, gaseous oxygen is passed into a solution of a phosphonous dihalide in an aliphatic hydrocarbon such as cyclohexane until no more heat is evolved (319, 367):

$$2RPCl_2 + O_2 + C_6H_{12} \rightarrow RC_6H_{11}P(O)Cl + RP(O)Cl_2 + HCl$$

If the aliphatic hydrocarbon is an unsaturated one, such as propylene, the product will contain a chloroalkyl group (367).

In the diazonium fluoborate method, a phosphonous dihalide is treated with an aromatic diazonium fluoborate in the presence of cuprous bromide (83, 85, 87, 88):

$$RPCl_2 + R'N_2BF_4 \xrightarrow{Cu_2Br_2} RR'P(O)OH$$
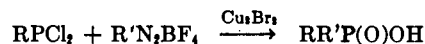
Unlike the products obtained in reactions of diazonium fluoborates with phosphorus trichloride, the secondary phosphinic acids are not contaminated with higher condensation products; no tertiary phosphine oxides

are produced (83). The yields are somewhat low, however, owing to difficulties in removing small amounts of symmetrical secondary phosphinic acids which arise from redistribution reactions (83).

Equally good results are obtained with diazonium fluosilicates (85). The fluosilicates have the advantage of being more stable and easy to isolate than the fluoborates, and react with less violence (85).
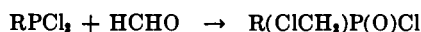
Phosphonous dihalides react with aldehydes under mild conditions, giving α-hydroxyalkylphosphinates (234).

$$RPCl_2 + CH_3CHO \rightarrow R(CH_3CHOH)P(O)OH$$
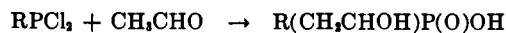
This reaction takes a different course in the presence of a tertiary nitrogen base. The product is a vinyl ester of a phosphonic acid, probably resulting from the formation and dehydrohalogenation of an intermediate α-chloroethyl ester (93, 271). No new carbon–phosphorus bond is formed.

$$RPCl_2 + CH_3CHO \xrightarrow{\text{base}} RP(O)(OCH=CH_2)_2$$
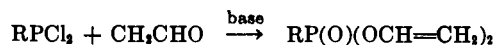
At higher temperatures phosphonous dichlorides react with aldehydes, giving α-chloroalkylphosphinates (137).

$$RPCl_2 + HCHO \rightarrow R(ClCH_2)P(O)Cl$$

Phosphonous dihalides react with α,β-unsaturated ketones giving cyclic adducts which yield γ-ketophosphinic acids on hydrolysis (55). If acetic anhydride is added to the reaction mixture, the intermediate is a cyclic anhydride (55, 70).

$$C_6H_5PCl_2 + C_6H_5CH=CHCOC_6H_5 \xrightarrow{(CH_3CO)_2O}$$
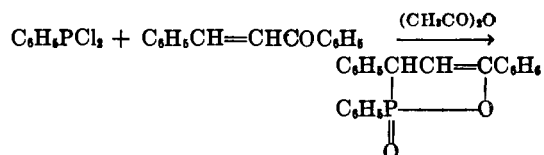
Glacial acetic acid gives the γ-ketophosphinic acid directly (54).

9. Condensations in which two new carbon–phosphorus bonds are formed

Of the reactions which proceed with replacement of both the halogen atoms in phosphonous dihalides, the best known is the reaction with Grignard reagents (29, 30, 53, 59, 60, 61, 62, 63, 64, 65, 67, 89, 94, 102, 103, 125, 128, 129, 130, 132, 134, 140, 141, 148, 196, 197, 201, 203, 205, 206, 224, 274, 288). A typical example is the following (201):

$$C_6H_5PCl_2 + 2C_2H_5MgI \rightarrow (C_2H_5)_2PC_6H_5 + 2MgClI$$
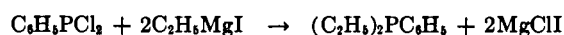
Secondary alkyl bromides do not give the expected products (67) unless the Grignard reagent is used in large excess (59).

The use of organozinc compounds is commonly found in the older literature (56, 58, 153, 230, 234, 235, 236, 238, 240, 241, 252, 304):

$$R'PCl_2 + R_2Zn \rightarrow R'R_2P + ZnCl_2$$
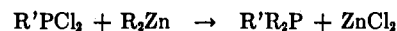
In one instance the use of metallic zinc with an alkyl halide was recorded (244). The product was actually the tertiary phosphine oxide (203) and probably arose from oxidation during the reaction or later. The organozinc compounds have been superseded by the Grignard reagents.

Tertiary phosphines may also be prepared with organolithium compounds (95, 109, 187). The novel heterocyclic compound "pentaphenylphosphole" was prepared by this method, using a dilithium compound derived from diphenylacetylene (187). The phosphole was also prepared from the iron tricarbonyl derivative of diphenylacetylene (42).

Phosphonous dihalides react with alkyl or aryl halides in the presence of sodium, forming tertiary phosphines (69, 120, 121, 200, 203, 238, 243, 252, 307, 313). This reaction has been used to synthesize several five- and six-membered heterocyclic phosphorus compounds. Ethyl acetate is added as a catalyst (120, 203). The yields are much poorer than the yields of the corresponding arsenic analogs (49, 121), probably because of formation of quaternary salt with the excess alkyl halide (122).

The reaction of chloromethylphosphonous dichloride with diazomethane does not give secondary or tertiary phosphines (97). Instead, there is obtained a homogeneous, amorphous substance with the empirical composition $C_4H_9P_2Cl_3O_2$. One possible formula for this substance is the following (97):

$$(ClCH_2)_2PCH_2P(O)(CH_2Cl)OH$$

Phosphonous dihalides react with a wide variety of Diels–Alder type dienes, giving 1-substituted 1-phospha-3-cyclopentene P,P-dihalides, which are readily converted to the phosphine oxides by hydrolysis (221). A typical example is the reaction of phenylphosphonous dichloride with isoprene (221):

$$C_6H_5PCl_2 + CH_2=CHC=CH_2 \rightarrow$$
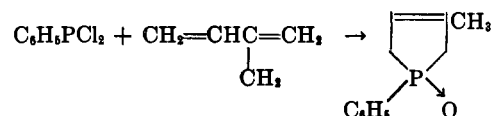
An inhibitor is added to prevent polymerization of the diene (221). The initially formed dichloride may also be converted to the phosphine sulfide by treatment with hydrogen sulfide (222), or to the phospholene by reduction with lithium aluminum hydride (29).

IV. PHOSPHONOUS DIESTERS

The phosphonous diesters are colorless liquids with characteristic unpleasant odors. They are easily oxidized and are best handled in an inert atmosphere. The lower alkyl members burst into flame when poured onto filter paper (19).

A. SYNTHESIS OF PHOSPHONOUS DIESTERS

1. From phosphorochloridites

(a) With Grignard reagents

Dialkyl (138, 305) and diaryl (146, 305) phosphorochloridites react with Grignard reagents, giving phosphonous diesters in 45–70 per cent yields. Trialkyl phosphites are unexplained by-products (305).

$$(RO)_2PCl + R'MgCl \rightarrow R'P(OR)_2 + MgCl_2$$
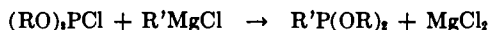
If the reaction is run at a low temperature, the chlorine atom is selectively replaced without contamination by alkoxy group substitution (138). Such contamination may account for the differences in physical properties observed (19) between esters prepared by this method and those prepared by the phosphonous dichloride/alcohol/amine method described in the following section.

Other organometallic compounds have been used in place of Grignard reagents, but they have not been as successful. Cadmium alkyls give lower yields, and lithium alkyls attack the alkoxy groups as well as the halogen (305).

A list of the phosphonous diesters prepared by this method is given in table 11.

(b) With alkyl halides and sodium

Phosphonous diesters, especially the aromatic diesters, may be prepared by the reaction of phosphorochloridites with alkyl halides in the presence of sodium (75).

$$(RO)_2PCl + R'Cl + 2Na \rightarrow R'P(OR)_2 + 2NaCl$$

The reaction is carried out in a finely divided dispersion of sodium in xylene at 260–280°C. (75). The patent in which this reaction is described does not describe the products in detail. They were produced by the reaction of diarylphosphorochloridites with chlorinated esters of abietic acid and may have contained other by-products such as the products of self-coupling of the halides.

2. From trialkyl phosphites with Grignard reagents

Under carefully controlled conditions Grignard reagents react with trialkyl phosphites to give phosphonous diesters, together with small amounts of the unreacted phosphite (305):

$$(RO)_3P + R'MgX \rightarrow R'P(OR)_2 + Mg(OR)X$$

More stringent reaction conditions yield higher substitution products (193, 305). The temperature at which reaction takes place depends on the Grignard reagent.

This method is more convenient to use than the reaction of Grignard reagents with phosphorochloridites, because the phosphorochloridites are more difficult to obtain in a pure state (305).

The reaction of tributyl phosphite with butylmagnesium chloride gave dibutyl butylphosphonite, b.p. 109–112°C./13 mm., in 69 per cent yield (305). Other phosphonous diesters have been prepared by the reaction of trimethyl phosphite with ethylmagnesium chloride, butylmagnesium bromide, benzylmagnesium chloride, and phenylmagnesium chloride in 30–54 per cent yields (193, 305).

3. From phosphonous dichlorides

Phosphonous diesters may also be prepared by the reaction of a phosphonous dihalide with (a) an alkoxide or (b) an alcohol in the presence of a tertiary amine. In the

TABLE 11

Phosphonous diesters prepared from phosphorochloridites

Phosphonous Diester	Preparation from		Yield	Boiling Point	References
	Phosphoro-chloridite	Grignard reagent			
			per cent	*°C.*	
CH₃P(OC₄H₉)₂	(C₄H₉O)₂PCl	CH₃MgCl	70	39–40/1 mm.	(138)
CH₃P(OC₆H₅)₂	(C₆H₅O)₂PCl	CH₃MgI	45	212–213/10 mm.	(146)
C₂H₅P(OC₆H₅)₂	(C₆H₅O)₂PCl	C₂H₅MgCl	57	53/30 mm.	(305)
C₂H₅P(OC₄H₉)₂	(C₄H₉O)₂PCl	C₂H₅MgCl	64	56–56.5/7 mm.	(138)
C₃H₇P(OC₄H₉)₂	(C₄H₉O)₂PCl	C₃H₇MgCl	70	47–48/1 mm.	(138)
C₃H₇P(OC₆H₅)₂	(C₆H₅O)₂PCl	C₃H₇MgBr	67	223–225/11 mm.	(146)
C₃H₇P(OC₄H₉)₂	(C₄H₉O)₂PCl	C₃H₇MgCl	70	59.8–60.3/1 mm.	(138, 210)
iso-C₃H₇P(OC₆H₅)₂	(C₆H₅O)₂PCl	iso-C₃H₇MgBr		212–214/11 mm.	(146)
C₄H₉P(OC₆H₅)₂	(C₆H₅O)₂PCl	C₄H₉MgCl	63	78/20 mm.	(305)
C₄H₉P(OC₄H₉)₂	(C₄H₉O)₂PCl	C₄H₉MgCl	68	68–69/1 mm.	(138)
C₄H₉P(OC₆H₅)₂	(C₆H₅O)₂PCl	C₄H₉MgBr		225–226/8 mm.	(146)
[cyclo]P(OC₄H₉)₂	(C₄H₉O)₂PCl	[cyclo]MgCl		81.5–83/2 mm.	(138)
C₆H₁₁P(OC₆H₅)₂	(C₆H₅O)₂PCl	C₆H₁₁MgBr	49	233–235/10 mm.	(146)
C₆H₅CH₂P(OC₆H₅)₂	(C₆H₅O)₂PCl	C₆H₅CH₂MgCl	50	88–90/3 mm.	(305)
C₆H₅CH₂P(OC₄H₉)₂	(C₄H₉O)₂PCl	C₆H₅CH₂MgCl	54	103–104/1 mm.	(138)
C₆H₅P(OC₆H₅)₂	(C₆H₅O)₂PCl	C₆H₅MgCl	63	100/5 mm.	(138, 305)
C₆H₅P(OC₄H₉)₂	(C₄H₉O)₂PCl	C₆H₅MgCl	62	73–74/1 mm.	(138)
C₆H₅P(OC₆H₅)₂	(C₆H₅O)₂PCl	C₆H₅MgCl	63	97.5–98.5/1 mm.	(138)
C₆H₅P(OC₆H₅)₂	(C₆H₅O)₂PCl	C₆H₅MgBr	75	223–224/10 mm.	(146)
1-C₁₀H₇P(OC₄H₉)₂	(C₄H₉O)₂PCl	1-C₁₀H₇MgBr		245–247/10 mm.	(146)

older alkoxide method, the phosphonous dihalide is added to a dry alkoxide under ether (9, 251):

$$RPCl_2 + 2R'ONa \rightarrow RP(OR')_2 + 2NaCl$$
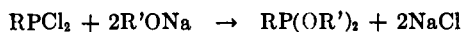
The alcohol/tertiary amine method is now preferred. The amine is added as an acid acceptor; in its absence the phosphonous diester is converted to the monoester with the loss of one mole of alkyl halide (see Section VIII,A,2). The tertiary amines most commonly used have been pyridine, dimethylaniline, diethylaniline, and triethylamine. Diethylaniline has an advantage in forming an easily filtered, nonhygroscopic hydrochloride (77). Other amines such as anhydrous ammonia may be used if they are added at a rate just sufficient to neutralize the hydrogen chloride as it is formed (108). The esterification is usually run in ether solution at room temperature or below, and in an inert atmosphere, as the products are easily oxidized.

$$RPCl_2 + 2R'OH + 2\ amine \rightarrow RP(OR')_2 + 2\ amine \cdot HCl$$
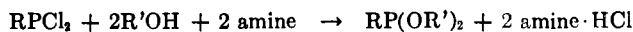
The tertiary amine can be omitted in the esterification of phosphonous dichlorides with phenols, as the aromatic esters are not attacked by acids (15, 220), and in the esterification of phosphonous dichlorides with oxiranes, as no hydrogen chloride is liberated (270).

The phosphonous diesters that have been prepared by these methods are listed in table 12.

4. From other phosphonous diesters

Treatment of a phosphonous diester with an alcohol results in a random redistribution reaction giving a mixture of esters, the proportions depending on the original ratio of diester to alcohol (117). For example, the transesterification of diethyl methylphosphonite (one mole) with n-octyl alcohol (three moles) gives on careful fractionation one mole of the diethyl ester, one mole of the ethyl n-octyl ester, and one mole of the di-n-octyl ester (117):
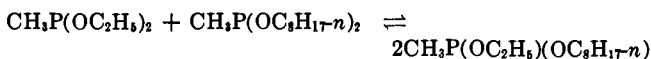
$$CH_3P(OC_2H_5)_2 + CH_3P(OC_8H_{17}-n)_2 \rightleftharpoons$$
$$2CH_3P(OC_2H_5)(OC_8H_{17}-n)$$

A list of the phosphonous diesters that have been prepared by this method is given in table 13. These phosphonous diesters, unlike the corresponding trialkyl phosphites, require no sodium catalyst for transesterification (115).

B. REACTIONS OF PHOSPHONOUS DIESTERS

The reactions of phosphonous diesters which yield derivatives of phosphonous acids described in detail in other sections of this review are not considered here. These include the hydrolysis to phosphonous acids (Section II,A,5) or to phosphonous monoesters (Section II,A,5; Section VIII,A,3); the reaction with phosphonous acids to form phosphonous monoesters (Section VIII,A,4); the reaction with phosphorus trichloride giving phosphonous dichlorides (Section III,A,6); and

the transesterification with alcohols to form other phosphonous diesters (Section IV,A,4).

The phosphonous diesters undergo most of the reactions known for the trialkyl phosphites. Moreover, the reactions usually occur more readily and under milder conditions. The order of reactivity increases as follows (297):

$$(RO)_3P < R'P(OR)_2 < R_2'POR < R_3P$$
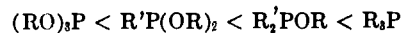
Aromatic phosphonites are, of course, less reactive than aliphatic phosphonites, for the presence of the aromatic ring decreases the availability of the unshared electrons on the phosphorus atom (297).

1. Reduction

The reduction of diethyl phenylphosphonite with lithium aluminum hydride gives phenylphosphine in 62 per cent yield (305).

2. Addition of oxygen, sulfur, or selenium

Phosphonous diesters, especially the lower alkyl members, readily add oxygen (21, 147, 295, 296, 297), sulfur (19, 21, 104, 115, 116, 138, 220, 270, 295, 297, 298), or selenium (295, 297), giving the corresponding phosphonic esters. No catalyst is required. The products of oxidation have seldom been characterized, as they are more easily synthesized by other methods. Oxidants other than atmospheric oxygen have not been described. The addition of sulfur to phosphonous diesters gives phosphonothionates in 70–80 per cent yields according to the following equation:

$$R'P(OR)_2 + S \rightarrow R'P(S)(OR)_2$$
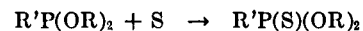
The phosphonothionic diesters are fuming liquids of characteristic unpleasant odor (19, 297). The ethyl esters, however, possess a pleasant and refreshing grassy odor (295). The selenium adducts of phosphonous diesters are refractive liquids of weak odor; they deposit selenium on standing in the air but can be stored indefinitely under carbon dioxide (295).

3. Other addition reactions

Phosphonous diesters, in common with other trivalent phosphorus compounds, react with copper monohalides to give adducts which are usually crystalline (9, 15, 19, 21, 138, 146, 147, 161, 295, 297). These adducts are often used for the characterization of the esters.

The reaction of diethyl ethylphosphonite with phenyl azide gives N-phenyl O,O-diethyl ethylphosphonimidate (135):

$$C_2H_5P(OC_2H_5)_2 + C_6H_5N_3 \rightarrow$$
$$C_2H_5P(=NC_6H_5)(OC_2H_5)_2 + N_2$$
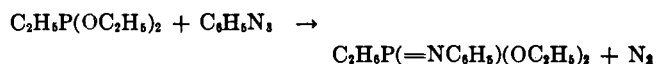
With carbon disulfide the phosphonous diesters form deep red solutions and differ therefore from the tertiary phosphines, which form crystalline adducts with car-

TABLE 12

Phosphonous diesters prepared from phosphonous dichlorides

Phosphonous Diester	Preparation from		Yield	Melting Point	Boiling Point	References
	Phosphonous dichloride	Alkoxide or alcohol				

Alkoxide method

			per cent	°C.	°C.	
$C_6H_5P(OCH_3)_2$	$C_6H_5PCl_2$	CH_3ONa			101–102/15 mm.	(9)
$C_6H_5P(OC_2H_5)_2$	$C_6H_5PCl_2$	C_2H_5ONa			235	(8, 171)
$C_6H_5P(OC_4H_9\text{-}iso)_2$	$C_6H_5PCl_2$	iso-C_4H_9ONa			134.5/7 mm.	(10)
4-$CH_3C_6H_4P(OC_2H_5)_2$	4-$CH_3C_6H_4PCl_2$	C_2H_5ONa			280	(251)
2,4,5-$(CH_3)_3C_6H_2P(OC_2H_5)_2$	2,4,5-$(CH_3)_3C_6H_2PCl_2$	C_2H_5ONa			232–233/100 mm.	(236)
2,4,5-$(CH_3)_3C_6H_2P(OC_2H_5)_2$	2,4,5-$(CH_3)_3C_6H_2PCl_2$	C_2H_5ONa		59	283 (d.)/40 mm.	(236)
4-$(CH_3)_2NC_6H_4P(OCH_3)_2$	4-$(CH_3)_2NC_6H_4PCl_2$	CH_3ONa	46		119–120/0.8 mm.	(57, 101)

Alcohol/amine method

$CH_3P(OC_2H_5)_2$	CH_3PCl_2	C_2H_5OH	82		47/50 mm.	(108, 115, 117)
$CH_3P(OC_3H_7)_2$	CH_3PCl_2	C_3H_7OH	78		76/33 mm.	(115)
$CH_3P(OC_3H_7\text{-}iso)_2$	CH_3PCl_2	iso-C_3H_7OH	80		55/36 mm.	(115)
$C_2H_5P(OCH_3)_2$	$C_2H_5PCl_2$	CH_3OH	35		73.5–74.5/225 mm.	(19, 21)
$C_2H_5P(OC_2H_5)_2$	$C_2H_5PCl_2$	C_2H_5OH	66		60/35 mm.	(19, 21, 117, 291, 297)
$C_2H_5P(OC_3H_7)_2$	$C_2H_5PCl_2$	C_3H_7OH	64		65–66.5/11 mm.	(19, 21)
$C_2H_5P(OC_3H_7\text{-}iso)_2$	$C_2H_5PCl_2$	iso-C_3H_7OH	40		73.5–74.5/35 mm.	(19, 21)
$C_2H_5P(OCH_2CH=CH_2)_2$	$C_2H_5PCl_2$	$CH_2=CHCH_2OH$			65–67/11 mm.	(300)
$C_2H_5P(OCH_2C\equiv CH)_2$	$C_2H_5PCl_2$	$CH\equiv CCH_2OH$			126–127/6 mm.	(147)
$C_2H_5P(OC_4H_9)_2$	$C_2H_5PCl_2$	C_4H_9OH	80		63–64/3 mm.	(19, 21)
$C_2H_5P(OC_5H_{11})_2$	$C_2H_5PCl_2$	$C_5H_{11}OH$			81–82/2 mm.	(300)
$C_2H_5P(OC_5H_{11})_2$	$C_2H_5PCl_2$	$n\text{-}C_5H_{11}OH$	92		100–101/2 mm.	(19, 21)
$C_2H_5P(OC_8H_{17})_2$	$C_2H_5PCl_2$	$n\text{-}C_8H_{17}OH$	90		142–144/3 mm.	(19, 21, 108)
$C_2H_5P(OCH_2C_6H_5)_2$	$C_2H_5PCl_2$	$C_6H_5CH_2OH$			140–141/1.5 mm.	(300)
$C_2H_5P(OC_6H_5)_2$	$C_2H_5PCl_2$	C_6H_5OH	72		115–115.5/1 mm.	(19)
$C_3H_7P(OC_2H_5)_2$	$C_3H_7PCl_2$	C_2H_5OH	64		52–53/12 mm.	(294)
$CH_3P(OC_3H_7)_2$	$C_3H_7PCl_2$	C_3H_7OH	74		81–82/11 mm.	(294)
$C_3H_7P(OCH_2C\equiv CH)_2$	$C_3H_7PCl_2$	$CH\equiv CCH_2OH$			136–136.5/6 mm.	(147)
iso-$C_3H_7P(OC_3H_7\text{-}iso)_2$	iso-$C_3H_7PCl_2$	iso-C_3H_7OH	60		59.5–60.5/14 mm.	(298)
$C_4H_9P(OC_2H_5)_2$	$C_4H_9PCl_2$	C_2H_5OH	64		68–70/12 mm.	(294)
$C_4H_9P(OC_3H_7)_2$	$C_4H_9PCl_2$	C_3H_7OH	70		99.5–101/14 mm.	(294)
$C_4H_9P(OCH_2CH=CH_2)_2$	$C_4H_9PCl_2$	$CH_2=CHCH_2OH$	64		98–100/11 mm.	(147)
$C_4H_9P(OCH_2C\equiv CH)_2$	$C_4H_9PCl_2$	$CH\equiv CCH_2OH$			146–147/6 mm.	(147)
$C_4H_9P(OC_4H_9)_2$	$C_4H_9PCl_2$	C_4H_9OH	64		116.5–118.5/10 mm.	(294)
iso-$C_4H_9P(OC_4H_9\text{-}iso)_2$	iso-$C_4H_9PCl_2$	iso-C_4H_9OH	85		105.5–107.5/12.5 mm.	(297)
$C_5H_{11}P(OC_2H_5)_2$	$C_5H_{11}PCl_2$	C_2H_5OH	31		58–60/0.12 mm.	(108)
$C_6H_5P(OCH_3)_2$	$C_6H_5PCl_2$	CH_3OH	70		94.5/13 mm.	(16, 57, 110, 144)
$C_6H_5P(OC_2H_5)_2$	$C_6H_5PCl_2$	C_2H_5OH	81		70/0.5 mm.	(16, 144, 181)
$C_6H_5P(OC_3H_7)_2$	$C_6H_5PCl_2$	C_3H_7OH	75		137/15 mm.	(16, 144)
$C_6H_5P(OCH_2CH=CH_2)_2$	$C_6H_5PCl_2$	$CH_2=CHCH_2OH$	43		100/0.3 mm.	(107, 149, 150, 259)
$C_6H_5P(OCH_2CHCH_2O)_2$	$C_6H_5PCl_2$	Glycidol			99/0.5 mm.	(317)
$C_6H_5P(OC_3H_7\text{-}iso)_2$	$C_6H_5PCl_2$	iso-C_3H_7OH	60		121–122/10 mm.	(14)
$C_6H_5P(OC_4H_9\text{-}iso)_2$	$C_6H_5PCl_2$	iso-C_4H_9OH	77		104/0.8 mm.	(144, 181)
$C_6H_5P(OC_5H_{11})_2$	$C_6H_5PCl_2$	$C_5H_{11}OH$	45		123–126/0.3 mm.	(108)
$C_6H_5P(OCH_2C_6H_5)_2$	$C_6H_5PCl_2$	$C_6H_5CH_2OH$	74		65–70/0.1 mm.	(5)
$C_6H_5P(OC_6H_5)_2$	$C_6H_5PCl_2$	C_6H_5OH	45		230/14 mm.	(15)
$C_6H_5P(OC_6H_4CH_3\text{-}o)_2$	$C_6H_5PCl_2$	$o\text{-}CH_3C_6H_4OH$	42		229–231/10 mm.	(15)
$C_6H_5P[OC_6H_4N(CH_3)_2\text{-}m]_2$	$C_6H_5PCl_2$	$m\text{-}(CH_3)_2NC_6H_4OH$				(76)
4-$ClC_6H_4P(OCH_2CH=CH_2)_2$	4-$ClC_6H_4PCl_2$	$CH_2=CHCH_2OH$	56		126–127/3 mm.	(149, 150)
4-$CH_3C_6H_4P(OCH_3)_2$	4-$CH_3C_6H_4PCl_2$	CH_3OH	52		107–109/14 mm.	(161)
4-$CH_3C_6H_4P(OC_2H_5)_2$	4-$CH_3C_6H_4PCl_2$	C_2H_5OH	50		123–125/9 mm.	(161)
4-$CH_3C_6H_4P(OC_3H_7)_2$	4-$CH_3C_6H_4PCl_2$	C_3H_7OH	82		129–130/6 mm.	(161)
4-$CH_3C_6H_4P(OC_4H_9)_2$	4-$CH_3C_6H_4PCl_2$	C_4H_9OH	89		170–171/13 mm.	(161)
4-$CH_3C_6H_4P(OC_4H_9\text{-}iso)_2$	4-$CH_3C_6H_4PCl_2$	iso-C_4H_9OH	77		155–156/13 mm.	(161)
4-$CH_3OC_6H_4P(OC_2H_5)_2$	4-$CH_3OC_6H_4PCl_2$	C_2H_5OH			136–138/13 mm.	(145)
1-$C_{10}H_7P(OCH_3)_2$	1-$C_{10}H_7PCl_2$	CH_3OH			101/0.15 mm.	(101)

Alcohol/no acid acceptor method

|						
$CH_3P(OCH_2CHClCH_3)_2$	CH_3PCl_2	Propylene oxide	100			(270)
$C_4H_9P(OCH_2CHClCH_3)_2$	$C_4H_9PCl_2$	Propylene oxide	100			(270)
$C_6H_5P(OC_6H_5)_2$	$C_6H_5PCl_2$	C_6H_5OH	40		222–223/12 mm.	(15)
$C_6H_5P(OC_6H_4Cl\text{-}p)_2$	$C_6H_5PCl_2$	$p\text{-}ClC_6H_4OH$			223.5–226/1 mm.	(220)
$C_6H_5P(OC_6H_4CH_3\text{-}o)_2$	$C_6H_5PCl_2$	o-Cresol	39		229–231/10 mm.	(15)
$C_6H_5P[OC_6H_4(C_5H_{11}\text{-}tert)\text{-}p]_2$	$C_6H_5PCl_2$	$p\text{-}(tert\text{-}C_5H_{11})C_6H_4OH$			225–228/3 mm.	(220)

TABLE 13

Phosphonous diesters prepared by transesterification

Phosphonous Diester	Preparation from		Yield	Boiling Point	References
	Phosphonous diester	Alcohol			
			per cent	*°C.*	
CH₃P(OCH₂CH₂SC₂H₅)₂	CH₃P(OR)₂ (R = CH₃, C₂H₅, or iso-C₃H₇)	C₂H₅SCH₂CH₂OH	30	80–84/0.025 mm.	(115)
CH₃P(OC₅H₁₁-n)₂	CH₃P(OC₂H₅)₂	n-C₅H₁₁OH		125–130/0.3 mm.	(117)
CH₃P(OC₁₀H₂₁-n)₂	CH₃P(OC₂H₅)₂	n-C₁₀H₂₁OH		138/0.075 mm.	(117)
C₂H₅P(OC₅H₁₁-n)₂	C₂H₅P(OC₂H₅)₂	n-C₅H₁₁OH		123/0.05 mm.	(117)
C₂H₅P(OC₁₀H₂₁-n)₂	C₂H₅P(OC₂H₅)₂	n-C₁₀H₂₁OH		150/0.05 mm.	(117)
C₄H₉P(OC₄H₉)₂	C₄H₉P(OC₂H₅)₂	C₄H₉OH (Na)	73	125–128/15 mm.	(305)
CH₃P(OCH₃)OCH₂CH₂SC₂H₅	CH₃P(OCH₃)₂	C₂H₅SCH₂CH₂OH	34	42–43/0.04 mm.	(115)
CH₃P(OC₂H₅)OCH₂CH₂SC₂H₅	CH₃P(OC₂H₅)₂	C₂H₅SCH₂CH₂OH	34	40/0.04 mm.	(116)
CH₃P(OC₂H₅)OCH₂CH₂SC₂H₅	CH₃P(OC₂H₅)₂	C₂H₅SCH₂CH₂OH	24	53–56/0.025 mm.	(115, 116)
CH₃P(OC₃H₇-iso)OCH₂CH₂SC₂H₅	CH₃P(OC₃H₇-iso)₂	C₂H₅SCH₂CH₂OH	45	42–46/0.1 mm.	(115, 116)
CH₃P(OC₂H₅)OC₅H₁₁-n	CH₃P(OC₂H₅)₂	n-C₅H₁₁OH		65/0.1 mm.	(117)
CH₃P(OC₂H₅)OC₁₀H₂₁-n	CH₃P(OC₂H₅)₂	n-C₁₀H₂₁OH		85/0.25 mm.	(117)
C₂H₅P(OC₂H₅)OC₅H₁₁-n	C₂H₅P(OC₂H₅)₂	n-C₅H₁₁OH		72/0.3 mm.	(117)
C₂H₅P(OC₂H₅)OC₁₀H₂₁-n	C₂H₅P(OC₂H₅)₂	n-C₁₀H₂₁OH		100/0.06 mm.	(117)
C₂H₅P(OC₂H₅)OC₆H₅	C₂H₅P(OC₂H₅)₂	C₆H₅OH		51/0.08 mm.	(117)

bon disulfide, and from the tertiary phosphites, which give no color with carbon disulfide (305).

4. Reaction with halogens

Phosphonous diesters react quantitatively with bromine (297), giving products of unspecified structure. By analogy with the phosphites, however, these products are probably phosphonobromidic esters:

$$R'P(OR)_2 + Br_2 \rightarrow R'P(O)(OR)Br + RBr$$
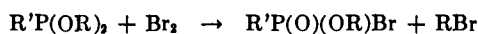
5. The Arbuzov reaction

Phosphonous diesters undergo the Arbuzov rearrangement with a wide variety of organic halides, giving esters of secondary phosphinic acids:

$$RP(OR)_2 + R'X \rightarrow RR'P(O)OR + RX$$
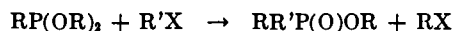
The organic halides may be simple alkyl halides (8, 11, 14, 16, 19, 21, 57, 101, 107, 110, 149, 150, 161, 219, 260, 291, 294, 295, 297, 305, 316, 324), triphenylmethyl bromide (11), carbon tetrahalides (19, 143, 144, 145, 147, 161), α-halo esters (10, 19, 38), chloromethyl methyl ether (16), 2-chloroethyl ethyl ether (16), chloromethyl ethyl sulfide (181), 2-bromoethyl acetate (110), glycol bis(chloroformates) or their thio analogs (106), α-halo malonates (13), β-bromo nitriles (38), carbamoyl chlorides (19), octachlorocyclohexa-1,4-diene (286), bis(β-bromoalkyl) phosphonates (47), C-chloro-P,P-diphenoxyisophosphazoacyls (68), or certain α-halo ketones (277). Alkyltin halides were at first believed to give products containing phosphorus–tin bonds (17), but are now known to give products with P—O—Sn bonds (18), probably owing to self-isomerization before reaction with the alkyltin halide.

The reaction with alkyl halides is usually complete in 2–3 hr. at 100–120°C., compared to the 5–6 hr. at 160°C. required for trialkyl phosphites. The use of the higher temperature is sometimes deleterious, as the product may break down to a free phosphinic acid and
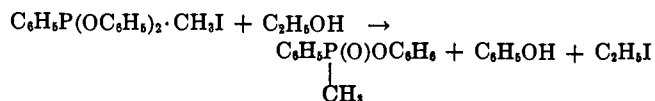
an alkene (11, 14, 295). In these cases the rearrangement may be carried out at a lower temperature, using a dialkylaniline as a catalyst (14, 181).

The increased ease of reaction of phosphonous diesters is also manifested in the partial isomerization of some esters during their preparation. Dimethyl phenylphosphonite, for example, undergoes extensive isomerization on heating, and a mixture of products is obtained whether the ester is prepared by the alkoxide method (9) or by the alcohol/tertiary amine method (14, 16, 150).
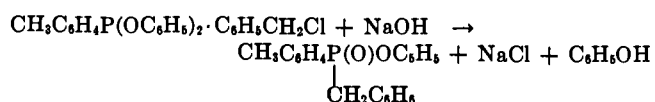
Alkylene dihalides [X(CH₂)ₙX, where $n = 3$ to 5] react with phosphonous diesters giving secondary phosphinic acid phostones (compare phosphonous acid phostones, Section VIII,A,4). Both ester groups are split out (90):

C₂H₅P(OC₂H₅)₂ + Br(CH₂)₃Br →

⌐‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾⌐
C₂H₅P(O)CH₂CH₂CH₂O + 2C₂H₅Br
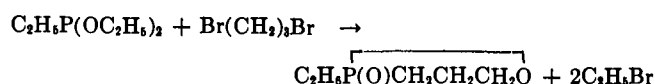
Phenolic esters of phosphonous acids, as might be expected, do not undergo the Arbuzov rearrangement except on drastic heating (15, 145, 146). The alkyl halide adducts can, however, be decomposed with alcohols (the Landauer–Rydon reaction), giving secondary phosphinic esters (15):

C₆H₅P(OC₆H₅)₂·CH₃I + C₂H₅OH →

C₆H₅P(O)OC₆H₅ + C₆H₅OH + C₂H₅I
|
CH₃

or with sodium hydroxide (238):

CH₃C₆H₄P(OC₆H₅)₂·C₆H₅CH₂Cl + NaOH →
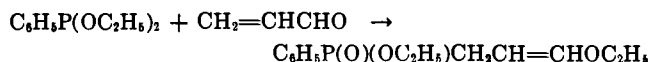
CH₃C₆H₄P(O)OC₆H₅ + NaCl + C₆H₅OH
|
CH₂C₆H₅

Phosphonous diesters react with α,β-unsaturated acids, giving saturated esters. The reaction probably proceeds through an Arbuzov-type mechanism, in which the anionic end of the molecule in the quasi-
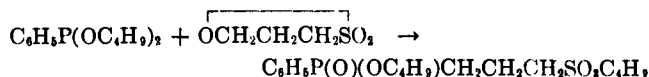
phosphonium intermediate assumes the function of the halide ion (151).

$$C_6H_5P(OR)_2 + CH_2\!\!=\!\!CHCOOH \rightarrow$$
$$C_6H_5P(O)(OR)CH_2CH_2COOR$$
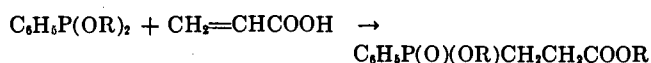
A similar reaction occurs with α,β-unsaturated aldehydes, such as acrolein (151). The products are distillable with difficulty, and only the ethyl ester given below has been isolated in pure form.

$$C_6H_5P(OC_2H_5)_2 + CH_2\!\!=\!\!CHCHO \rightarrow$$
$$C_6H_5P(O)(OC_2H_5)CH_2CH\!\!=\!\!CHOC_2H_5$$

Phosphonous diesters react with sultones in the following manner (105):

$$C_6H_5P(OC_4H_9)_2 + \overline{OCH_2CH_2CH_2SO_2} \rightarrow$$
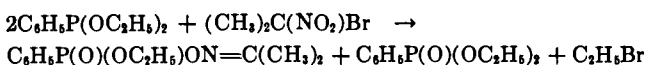$$C_6H_5P(O)(OC_4H_9)CH_2CH_2CH_2SO_2C_4H_9$$

6. Anomalous Arbuzov reactions

Phosphonous diesters undergo several so-called "anomalous" Arbuzov reactions, which are anomalous in that no new carbon–phosphorus bond is formed. Vinyl esters of phosphonic acids are formed in the reaction of phosphonous diesters with α-halo aldehydes (4, 185, 300, 312, 345, 346):

$$RP(OR')_2 + CCl_3CHO \rightarrow RP(O)(OR')OCH\!\!=\!\!CCl_2 + R'Cl$$

α-Halo ketones may give either the anomalous product as in the equation above, or the normal product of an Arbuzov rearrangement, or a mixture of both, depending on the halogen employed and the temperature of the reaction (277, 345, 346). The formation of the normal product is more favorable, however, for phosphonous diesters than for phosphites, because of the greater ease with which the phosphonites undergo the Arbuzov rearrangement.
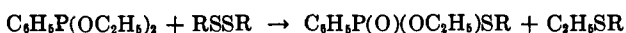
Diethyl phenylphosphonite reacts with 2-bromo-2-nitropropane giving an isopropylideneamino phosphonate (3):

$$2C_6H_5P(OC_2H_5)_2 + (CH_3)_2C(NO_2)Br \rightarrow$$
$$C_6H_5P(O)(OC_2H_5)ON\!\!=\!\!C(CH_3)_2 + C_6H_5P(O)(OC_2H_5)_2 + C_2H_5Br$$

This may be considered to be an anomalous Arbuzov reaction complicated by an additional redox reaction between the nitro group and the phosphonite.

7. Related reactions

Reactions which are closely related to the Arbuzov reaction in that they appear to proceed by a common mechanism occur when phosphonous diesters are treated with isothiocyanates (255), disulfides (256), or sulfenyl chlorides (261):

$$C_6H_5P(OC_2H_5)_2 + RNCS \rightarrow C_6H_5P(O)(OC_2H_5)SR + C_2H_5CN$$

$$C_6H_5P(OC_2H_5)_2 + RSSR \rightarrow C_6H_5P(O)(OC_2H_5)SR + C_2H_5SR$$

$$C_6H_5P(OC_2H_5)_2 + RSCl \rightarrow C_6H_5P(O)(OC_2H_5)SR + C_2H_5Cl$$

In all of these reactions a close analogy may be drawn

between the dialkyl phosphonites and the much better known trialkyl phosphites.

V. Phosphonodithious Esters

The phosphonodithious esters, $R'P(SR)_2$, are liquids with unpleasant odors, but unlike their oxygen counterparts are not appreciably oxidized in air (26).

A. SYNTHESIS

The methods used for preparing phosphonous diesters from phosphonous dihalides may also be applied to their sulfur analogs. The phosphonous dihalide can be added to an ether solution containing sodium and a mercaptan (12) or to an ether solution containing a mercaptan and a tertiary amine (26). The former method was used to prepare diethyl phenylphosphonodithioite, b.p. 143–144°C./3.5 mm., and diisobutyl phenylphosphonodithioite, b.p. 191–192°C./12.5 mm., from phenylphosphonous dichloride and the appropriate mercaptide (12); the latter method was used to prepare diethyl ethylphosphonodithioite, b.p. 98–100°C./10 mm., from ethylphosphonous dichloride, ethyl mercaptan, and pyridine in 74 per cent yield (26).

The synthesis of phosphonous diesters from trialkyl phosphites and Grignard reagents has also been applied to the dithious esters. Dipropyl butylphosphonodithioite, b.p. 110–112°C./2.5 mm., was prepared from $(C_3H_7S)_3P$ and butylmagnesium chloride in 25 per cent yield (305).

B. REACTIONS

The phosphonodithioites undergo many of the reactions characteristic of the phosphonous diesters. They combine readily with sulfur in the absence of a catalyst, and form sirupy complexes with copper monohalides (12, 26). The Arbuzov rearrangement with alkyl halides (12), α- or β-halo esters (12), or glycol chloroformates (106) proceeds normally, giving esters of phosphinothionic acids. In some cases the second thioester group is also eliminated as alkylsulfenyl halide (26). The phosphonodithious esters differ in this respect from the trithiophosphites, $(RS)_3P$, which give only the products of addition to sulfur, not to phosphorus, under the conditions of the Arbuzov reaction.
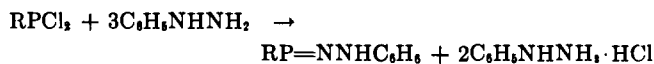
VI. Phosphonous Diamides and Iminophosphines

Phosphonous dihalides react readily with primary and secondary amines giving compounds containing phosphorus–nitrogen bonds. The literature contains few references to substances of this type despite their ease of preparation and their demonstrated usefulness as intermediates in the Arbuzov reaction (Michaelis, 1892–1903).

A. SYNTHESIS

The reaction of phosphonous dichlorides with pri-

mary or secondary amines is violent if the reagents are simply mixed together. In practice a solvent such as ether is used, and the amine is added in sufficient excess to bind the hydrogen chloride that is evolved. With phenylhydrazine the reaction is vigorous at the start but requires long standing at room temperature for completion (234):

$$RPCl_2 + 3C_6H_5NHNH_2 \rightarrow$$
$$RP=NNHC_6H_5 + 2C_6H_5NHNH_2 \cdot HCl$$

The products are iminophosphines. In one case a small amount of the dihydrazide, $C_6H_5P(NHNHC_6H_5)_2$, was also isolated (249).

Secondary amines such as piperidine or tetrahydroquinoline give phosphonous diamides:

$$RPCl_2 + 4C_5H_{10}NH \rightarrow RP(NC_5H_{10})_2 + 2C_5H_{10}NH \cdot HCl$$

Phosphonous dichlorides do not form cyclic phosphorus-nitrogen compounds with amine hydrochlorides (239).

A list of the known phosphonous diamides and iminophosphines is given in table 14.

B. REACTIONS

Little is known of the chemistry of iminophosphines and phosphonous diamides. The iminophosphines are converted to salts of the corresponding phosphonous acids by boiling water (234, 235, 236, 249).

$$RP=NNHC_6H_5 + 2H_2O \xrightarrow{\text{heat}} RPH(O)OH \cdot NH_2NHC_6H_5$$

Phosphonous diamides are stable to boiling water but are hydrolyzed by dilute acids (237). Treatment with anhydrous hydrogen chloride in benzene solution pre-

cipitates the amine hydrochloride (237). In other reactions the phosphonous diamides behave as typical compounds of trivalent phosphorus. They add sulfur at 130°C. giving phosphonothioic diamides, form adducts with carbon disulfide, and react with chlorine giving dichlorides which may be hydrolyzed to phosphonic diamides (237). They form quaternary salts with alkyl halides (237) in which the alkyl group is attached to phosphorus, not nitrogen.

A reaction peculiar to the phosphonous diamides constitutes a variant of the well-known Arbuzov reaction. The quaternary salts formed by the action of alkyl halides on the phosphonous diamides may be transformed into the quaternary hydroxides by treatment with silver oxide. These, on heating, split out the amine, giving secondary phosphinic acids (237):

$$[RP(NC_5H_{10})_2CH_3]^+OH^- + H_2O \rightarrow$$
$$R(CH_3)P(O)OH + 2C_5H_{10}NH$$
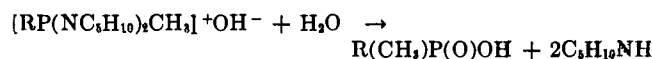
VII. PHOSPHONOUS ESTER CHLORIDES, AMIDE CHLORIDES, AND ESTER AMIDES

The presence of two replaceable hydroxyl functions in the phosphonous acids (as written in the form containing trivalent phosphorus) makes possible the existence of mixed ester chlorides, amide chlorides, and ester amides which have no counterparts in the carboxylic acids. The chemistry of this singularly interesting group of substances has not, however, been adequately studied.
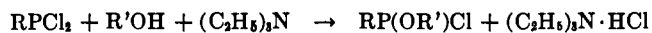
A. PHOSPHONOCHLORIDOUS ESTERS

The reaction of a phosphonous dichloride with an alcohol and a tertiary amine in equimolar proportions

TABLE 14

Phosphonous diamides and iminophosphines

Product	Preparation from		Melting Point	Boiling Point	References
	Phosphonous dichloride	Amine			
Iminophosphines (from primary amines)					
			°C.	°C.	
$C_6H_5P=NNHC_6H_5$	$C_6H_5PCl_2$	Phenylhydrazine	152		(249)
$C_6H_5P=NNHC_6H_4CH_3\text{-}p$	$C_6H_5PCl_2$	p-Tolylhydrazine	162		(249)
$C_6H_5P=NN(C_6H_5)CH_2C_6H_5$	$C_6H_5PCl_2$	$C_6H_5CH_2(C_6H_5)NNH_2$	141		(249)
$4\text{-}ClC_6H_4P=NNHC_6H_5$	$4\text{-}ClC_6H_4PCl_2$	Phenylhydrazine	161 (d.)		(234)
$4\text{-}BrC_6H_4P=NNHC_6H_5$	$4\text{-}BrC_6H_4PCl_2$	Phenylhydrazine	160		(234)
$4\text{-}C_6H_5C_6H_4P=NNHC_6H_5$	$4\text{-}C_6H_5C_6H_4PCl_2$	Phenylhydrazine	139		(235)
$2,4,6\text{-}(CH_3)_3C_6H_2P=NNHC_6H_5$	$2,4,6\text{-}(CH_3)_3C_6H_2PCl_2$	Phenylhydrazine	135		(236)
Phosphonous diamides (from secondary amines)					
$CH_3P[N(CH_3)_2]_2$	CH_3PBr_2	Dimethylamine		137–141	(196)
$C_6H_5P(NC_5H_{10})_2$	$C_6H_5PCl_2$	Piperidine	78		(71, 237, 340)
$C_6H_5P(NC_4H_8O)_2$	$C_6H_5PCl_2$	Tetrahydroquinoline	150		(237)
$4\text{-}ClC_6H_4P(NC_5H_{10})_2$	$4\text{-}ClC_6H_4PCl_2$	Piperidine	95		(237)
$4\text{-}CH_3C_6H_4P(NC_5H_{10})_2$	$4\text{-}CH_3C_6H_4PCl_2$	Piperidine	85		(237, 340)
$4\text{-}CH_3C_6H_4P(NC_4H_8O)_2$	$4\text{-}CH_3C_6H_4PCl_2$	Tetrahydroquinoline	140		(237)
$4\text{-}CH_3OC_6H_4P(NC_5H_{10})_2$	$4\text{-}CH_3OC_6H_4PCl_2$	Piperidine	69		(237)
$4\text{-}C_2H_5OC_6H_4P(NC_5H_{10})_2$	$4\text{-}C_2H_5OC_6H_4PCl_2$	Piperidine	84		(237)

at 10–20°C. leads to the replacement of one of the chlorine atoms, forming a phosphonochloridous ester (118).

$$RPCl_2 + R'OH + (C_2H_5)_3N \rightarrow RP(OR')Cl + (C_2H_5)_3N \cdot HCl$$

Treatment of this product directly in solution with sulfur flowers gives a phosphonochloridothionate in 25–28 per cent overall yield (118). The intermediate phosphonochloridous esters have not been isolated.

$$RP(OR')Cl + S \rightarrow RP(S)(OR')Cl$$
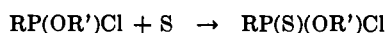
Interestingly, the addition of sulfur to the phosphonochloridite proceeds readily at 25–35°C. in the absence of a catalyst (118). Phosphonous dichlorides require a catalyst (aluminum chloride), but phosphonous diesters do not (see Sections III,B,5 and IV,B,2).

B. PHOSPHONAMIDOUS CHLORIDES

Phosphonamidous chlorides may be synthesized by the reaction of a phosphonous dichloride with two equivalents of a secondary amine (25):

$$C_2H_5PCl_2 + 2(C_2H_5)_2NH \rightarrow$$
$$C_2H_5P[N(C_2H_5)_2]Cl + (C_2H_5)_2NH \cdot HCl$$
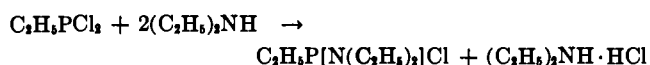
These amide chlorides react with water with bursts of flame and are rapidly decomposed in air with the separation of the amine hydrochloride (25). Treatment with an alcohol gives diethylamine hydrochloride and a phosphonous diester (25).

$$C_2H_5P[N(C_2H_5)_2]Cl + 2C_2H_5OH \rightarrow$$
$$C_2H_5P(OC_2H_5)_2 + (C_2H_5)_2NH \cdot HCl$$
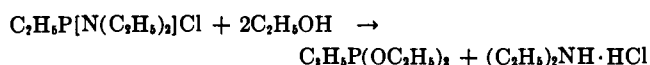
In the presence of a tertiary amine only the halogen atom is replaced (see Section VII,C).

Phosphonamidous chlorides combine with sulfur in the presence of aluminum chloride, giving phosphonamidothioic chlorides (25). No reaction occurs in the absence of the catalyst.

$$C_2H_5P[N(C_2H_5)_2]Cl + S \xrightarrow{AlCl_3} C_2H_5P(S)[N(C_2H_5)_2]Cl$$
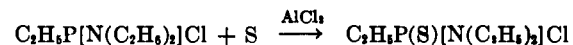
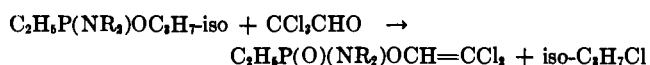The known phosphonamidous chlorides are listed in table 15.

C. PHOSPHONAMIDOUS ESTERS

Phosphonamidous esters are prepared by the action of alcohols on phosphonamidous chlorides in the presence of a tertiary amine (25). The yields for the lower alkyl members range from 60 to 70 per cent. The ester amides are colorless mobile liquids with unpleasant odors.

$$C_2H_5P[N(C_2H_5)_2]Cl + C_4H_9OH \rightarrow C_2H_5P[N(C_2H_5)_2]OC_4H_9$$

In the absence of the tertiary amine the amide group is cleaved and the product is a phosphonous diester (see preceding section).

The phosphonamidous esters combine readily with sulfur, giving esters of phosphonamidothionic acids (25), and take part in the so-called "anomalous" Arbuzov reaction in a manner similar to the phosphonous diesters (300, 312, 346). The reaction with chloral (300) proceeds as follows:

$$C_2H_5P(NR_2)OC_3H_7\text{-iso} + CCl_3CHO \rightarrow$$
$$C_2H_5P(O)(NR_2)OCH=CCl_2 + \text{iso-}C_3H_7Cl$$

The known phosphonamidous esters are listed in table 15.

VIII. PHOSPHONOUS MONOESTERS

The partial esters of phosphonous acids are relative newcomers to the family of organophosphorus compounds, owing perhaps to indications in the early litera-

TABLE 15

Phosphonous amide chlorides and ester amides

Product	Preparation from		Yield	Boiling Point	Reference
	Chloride	Amine or alcohol			
Amide chlorides (phosphonamidous chlorides)					
			per cent	*°C.*	
C₂H₅P[N(CH₃)₂]Cl	C₂H₅PCl₂	(CH₃)₂NH		51–52/16 mm.	(300)
C₂H₅P[N(C₂H₅)₂]Cl	C₂H₅PCl₂	(C₂H₅)₂NH	77	52–53/3 mm.	(25)
Ester amides (phosphonamidous esters)					
C₂H₅P[N(CH₃)₂]OC₃H₇-iso	C₂H₅P[N(CH₃)₂]Cl	iso-C₃H₇OH		71–73/27 mm.	(300)
C₂H₅P[N(C₂H₅)₂]OCH₃	C₂H₅P[N(C₂H₅)₂]Cl	CH₃OH	72	49–50/10 mm.	(25)
C₂H₅P[N(C₂H₅)₂]OC₂H₅	C₂H₅P[N(C₂H₅)₂]Cl	C₂H₅OH	63	53–54/9 mm.	(25)
C₂H₅P[N(C₂H₅)₂]OC₃H₇	C₂H₅P[N(C₂H₅)₂]Cl	C₃H₇OH	65	73–74/10 mm.	(25)
C₂H₅P[N(C₂H₅)₂]OC₃H₇-iso	C₂H₅P[N(C₂H₅)₂]Cl	iso-C₃H₇OH	61	63–65/10 mm.	(25)
C₂H₅P[N(C₂H₅)₂]OC₄H₉	C₂H₅P[N(C₂H₅)₂]Cl	C₄H₉OH	62	88–89/10 mm.	(25)
C₂H₅P[N(C₂H₅)₂]OC₄H₉-iso	C₂H₅P[N(C₂H₅)₂]Cl	iso-C₄H₉OH	71	79–80/10 mm.	(25)
C₂H₅P[N(C₂H₅)₂]OC₅H₁₁-n	C₂H₅P[N(C₂H₅)₂]Cl	n-C₅H₁₁OH	61	80–81/1 mm.	(25)
C₂H₅P[N(C₂H₅)₂]OC₇H₁₅-n	C₂H₅P[N(C₂H₅)₂]Cl	n-C₇H₁₅OH	40	101–102/1 mm.	(25)
C₂H₅P[N(C₂H₅)₂]OC₉H₁₉-n	C₂H₅P[N(C₂H₅)₂]Cl	n-C₉H₁₉OH	30	115–116/2 mm.	(25)
C₂H₅P[N(C₂H₅)₂]OC₅H₁₁-n	C₄H₉P[N(C₂H₅)₂]Cl	n-C₅H₁₁OH	27	121–122/2 mm.	(25)
C₂H₅P[N(C₂H₅)₂]OC₁₀H₂₁-n	C₂H₅P[N(C₂H₅)₂]Cl	n-C₁₀H₂₁OH	22	134–135/2 mm.	(25)

ture that they were unstable. In 1877 Köhler and Michaelis (171) observed that diethyl phenylphosphonite, though not soluble in water, was gradually decomposed by it to a partial ester which was identified by analysis as ethyl hydrogen phenylphosphonite. On further contact with water this ester formed an unstable crystalline hydrate and in time was converted to the acid, phenylphosphonous acid.

$$C_6H_5P(OC_2H_5)_2 \rightarrow C_6H_5PH(O)OC_2H_5 \rightarrow C_6H_5PH(O)OH$$
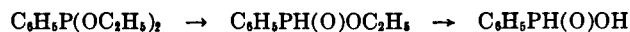
Kosolapoff (174) prepared this same ester by the method described in Section VIII,A,2 and noted that it developed an extremely foul phosphine-like odor on distillation. However, there is some question as to whether the ethyl ester differs in this respect from other members of the series (71, 281, 305).

The partial esters of alkylphosphonous acids are for the most part colorless, mobile, evil-smelling liquids (20). The higher alkyl esters (C_4 to C_{10}) do not wet glass (20).

### A. SYNTHESIS OF PHOSPHONOUS MONOESTERS

1. From phosphorochloridites with Grignard reagents

The synthesis of phosphonous diesters by the reaction of Grignard reagents with dialkyl phosphorochloridites was described in a previous section (Section IV,A,1). Direct hydrolysis of the reaction mixture with 5 per cent aqueous ammonium chloride yields the monoesters instead of the diesters (139). The products are described in table 16.

$$(RO)_2PCl + R'MgX \rightarrow R'P(OR)_2 + MgXCl$$

$$R'P(OR)_2 + H_2O \xrightarrow{NH_4Cl} R'PH(O)OR + ROH$$
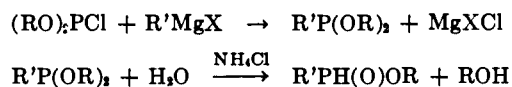
2. From phosphonous dichlorides

Partial esters of phosphonous acids are formed when a phosphonous dichloride is added to an alcohol at ice-cold temperatures (20, 174, 275, 281). In the absence of a tertiary amine, the phosphonous diester initially formed is attacked by the hydrogen chloride, generating the monoester and liberating alkyl chloride:

$$R'PCl_2 + 2ROH \rightarrow R'P(OR)_2 + 2HCl$$

$$R'P(OR)_2 + HCl \rightarrow R'PH(O)OR + RCl$$
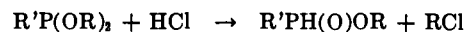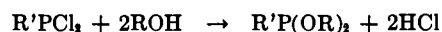
If the temperature is allowed to rise, the second ester group may also be split out; it will be remembered that alcoholysis of phosphonous dichlorides is a good method of preparing phosphonous acids (see Section II,A,4).

A better technique for preparing monoesters is to add the alcohol in a slow stream under the surface of the phosphonous dichloride while keeping the system under slightly reduced pressure to draw off the hydrogen chloride as it is formed (20, 281).

Acid-sensitive monoesters may be prepared by the reaction of phosphonous dichlorides with alcohols in the presence of one equivalent of a tertiary amine such as pyridine (107, 269).

The phosphonous monoesters prepared by this method are given in table 17.

3. From phosphonous diesters

The partial hydrolysis of phosphonous diesters takes place slowly in neutral (171) or basic medium, but with a trace of acid the partial esters are instantly produced in almost quantitative yield (305):

$$R'P(OR)_2 + H_2O \xrightarrow{H^+} R'PH(O)OR + ROH$$
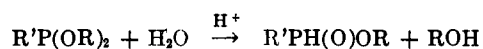
The removal of one of the benzyl groups in dibenzyl esters can be accomplished with lithium chloride in 2-ethoxyethanol (5).

Phosphonous acid esters prepared by these methods are listed in table 18. The preparation of partial esters by the reaction of a phosphonous diester with the corresponding phosphonous acid is described in Section VIII,A,4.

4. From phosphonous acids

A variety of methods have been described for preparing partial esters of phosphonous acids from the acids themselves. A classical method is the reaction of a silver salt of a phosphonous acid with an alkyl halide (111, 209, 217):

$$RPH(O)OAg + RI \rightarrow RPH(O)OR + AgI$$

TABLE 16

Phosphonous monoesters prepared from phosphorochloridites

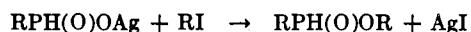| Phosphonous Monoester	Preparation from		Yield	Boiling Point	Reference
	Phosphorochloridite	Grignard reagent			
			per cent	*°C.*	
CH₃PH(O)OC₄H₉	(C₄H₉O)₂PCl	CH₃MgX	55	47–48/2 mm.	(139)
C₂H₅PH(O)OC₄H₉	(C₄H₉O)₂PCl	C₂H₅MgX	53	94–95/10 mm.	(139)
C₃H₇PH(O)OC₄H₉	(C₄H₉O)₂PCl	C₃H₇MgX	60	67–67.5/2 mm.	(139)
iso-C₃H₇PH(O)OC₄H₉	(C₄H₉O)₂PCl	iso-C₃H₇MgX	59	58.5–60.2/2.5 mm.	(139)
C₃H₇PH(O)OC₃H₇	(C₃H₇O)₂PCl	C₄H₉MgX	55	49–49.5/1.5 mm.	(139)
iso-C₃H₇PH(O)OC₃H₇	(C₃H₇O)₂PCl	iso-C₃H₇MgX	54	76–77/6 mm.	(139)
C₆H₅CH₂PH(O)OC₄H₉	(C₄H₉O)₂PCl	C₆H₅CH₂MgX	58	113–115.5/2 mm.	(139)
C₄H₉PH(O)OC₄H₉	(C₄H₉O)₂PCl	C₃H₇MgX	58	99.2–100/1 mm.	(139)

TABLE 17

Phosphonous monoesters prepared from phosphonous dichlorides

Phosphonous Monoester	Preparation from		Yield	Boiling Point	References
	Phosphonous dichloride	Alcohol			
			per cent	°*C.*	
C₂H₅PH(O)OCH₃	C₂H₅PCl₂	CH₃OH	20	65–66/11 mm.	(20)
C₂H₅PH(O)OC₂H₅	C₂H₅PCl₂	C₂H₅OH	31	68–69/9 mm.	(20)
C₂H₅PH(O)OC₃H₇	C₂H₅PCl₂	C₃H₇OH	47	81–82/10 mm.	(20)
C₂H₅PH(O)OC₃H₇-iso	C₂H₅PCl₂	iso-C₃H₇OH	42	69–70/10 mm.	(20)
C₂H₅PH(O)OC₄H₉	C₂H₅PCl₂	C₄H₉OH	57	92–93/9 mm.	(20)
C₂H₅PH(O)OC₄H₉-iso	C₂H₅PCl₂	iso-C₄H₉OH	56	86–87/9 mm.	(20)
C₂H₅PH(O)OC₆H₁₃-n	C₂H₅PCl₂	n-C₆H₁₃OH	54	87–88/1.5 mm.	(20)
C₂H₅PH(O)OC₇H₁₅-n	C₂H₅PCl₂	n-C₇H₁₅OH	42	99–100/4 mm.	(20)
C₂H₅PH(O)OC₈H₁₇-n	C₂H₅PCl₂	n-C₈H₁₇OH	52	102–103/1 mm.	(20)
C₂H₅PH(O)OC₉H₁₉-n	C₂H₅PCl₂	n-C₉H₁₉OH	59	122–123/4 mm.	(20)
C₂H₅PH(O)OC₁₀H₂₁-n	C₂H₅PCl₂	n-C₁₀H₂₁OH	49	129–130/1.5 mm.	(20)
C₂H₅PH(O)OCH₂C₆H₅	C₂H₅PCl₂	C₆H₅CH₂OH	85	90–95/0.1 mm.	(5)
C₆H₅PH(O)OCH₃	C₆H₅PCl₂	CH₃OH	66	91–93/1 mm.	(275, 281)
C₆H₅PH(O)OC₂H₅	C₆H₅PCl₂	C₂H₅OH	84	94–95/1 mm.	(71, 174, 275, 281)
C₆H₅PH(O)OC₃H₇-iso	C₆H₅PCl₂	iso-C₃H₇OH	70	106–107/1 mm.	(275, 281)
C₆H₅PH(O)OCH₂CH=CH₂	C₆H₅PCl₂	CH₂=CHCH₂OH		121–123/1.5 mm.	(107)
C₆H₅PH(O)OC₄H₉	C₆H₅PCl₂	C₄H₉OH	80	90.5–92/0.12 mm.	(127, 174)
C₆H₅PH(O)OC₄H₉-iso	C₆H₅PCl₂	iso-C₄H₉OH	88	112–113/1 mm.	(275, 281)
C₆H₅PH(O)OC₆H₁₃-n	C₆H₅PCl₂	n-C₆H₁₃OH	60	139/1 mm.	(275, 281)
C₆H₅PH(O)OC₇H₁₅-n	C₆H₅PCl₂	n-C₇H₁₅OH	80	150/1 mm.	(275, 281)
C₆H₅PH(O)OC₈H₁₇-n	C₆H₅PCl₂	n-C₈H₁₇OH	78	155/1 mm.	(275, 281)
C₆H₅PH(O)OC₉H₁₉-n	C₆H₅PCl₂	n-C₉H₁₉OH	57	158–160/1 mm.	(275, 281)
C₆H₅PH(O)OCH₂C₆H₅	C₆H₅PCl₂	C₆H₅CH₂OH	93	90–95/0.05 mm.	(5)
C₆H₅PH(O)O(CH₃)₃Si(CH₃)₃	C₆H₅PCl₂	(CH₃)₃Si(CH₃)₃OH		142–148/1 mm.	(154)

Acid- or base-catalyzed esterifications with alcohols have been described in a few instances. Allyl hydrogen octylphosphonite was prepared by esterification of octylphosphonous acid with allyl alcohol in the presence of a catalytic amount of *p*-toluenesulfonic acid, with azeotropic removal of the water (107). Esters of triphenylmethylphosphonous acid have been prepared by alkylation with dialkyl sulfates and potassium carbonate (111). Glycol esters of phosphonous acids were prepared by treatment with ethylene oxide in the presence of catalysts such as sodium hydroxide or silica gel (320, 321).

Aliphatic phosphonous acids which contain a hydroxyl group in the 3- or 4-position form cyclic esters on mild heating (316). The products are called "phostones," by analogy with the lactones of the carboxylic acid series.

Partial esters of phosphonous acids may also be prepared by heating the acids with the corresponding phosphonous diesters (334):

$$C_6H_5PH(O)OH + C_6H_5P(OR)_2 \xrightarrow{heat} 2C_6H_5PH(O)OR$$

This reaction takes place at 100–160°C. and the yield is quantitative.

Partial esters prepared by these methods are listed in table 19, together with the method of preparation.

B. REACTIONS OF PHOSPHONOUS MONOESTERS

The hydrolysis of phosphonous monoesters to phosphonous acids is described in Sections II,A,5 and II,A,4 and discussed in the introduction to Section VIII. Reactions of phosphonous monoesters with phosphonous dichlorides or phosphinous chlorides to form mixed anhydrides are described in Section X.

Phosphonous monoesters react with oxygen, sulfur, halogens, etc., giving phosphonic acids or their derivatives. These reactions are formally regarded in the following discussion as addition reactions to the esters in the tautomeric form containing trivalent phosphorus [i.e., as RP(OR′)OH], but alternative mechanisms involving direct displacement of the hydrogen attached to phosphorus should not be considered ruled out.

TABLE 18

Phosphonous monoesters prepared from phosphonous diesters

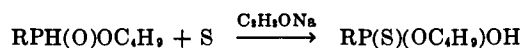| Phosphonous Monoester	Phosphonous Diester	Yield	Boiling Point	Reference
		per cent	°*C.*	
C₂H₅PH(O)OC₂H₅	C₂H₅P(OC₂H₅)₂	85	105/15 mm.	(305)
C₂H₅CH₂PH(O)OC₂H₅	C₂H₅CH₂P(OC₂H₅)₂		119/3 mm.	(305)
C₆H₅PH(O)OC₂H₅	C₆H₅P(OC₂H₅)₂	68	119–121/4 mm.	(305)
C₆H₅PH(O)OCH₂C₆H₅	C₆H₅P(OCH₂C₆H₅)₂ (LiCl)			(5)

TABLE 19

Phosphonous monoesters prepared from phosphonous acids

| Phosphonous Monoester	Reactants Used	Yield	Melting Point	Boiling Point	References
		per cent	°C.	°C.	
(CH₃)₃COHPH(O)OCH₃	(CH₃)₃COHPH(O)OAg, CH₃I				(209)
(CH₃)₃COHPH(O)OC₄H₉	(CH₃)₃COHPH(O)OAg, C₄H₉I				(209)
C₆H₅CHOHPH(O)OCH₃	C₆H₅CHOHPH(O)OAg, CH₃I		99		(217)
(C₆H₅)₃CPH(O)OC₂H₅	(C₆H₅)₃CPH(O)OAg, C₂H₅I		118–121.5		(111)
n-C₅H₁₁PH(O)OCH₂CH=CH₂	n-C₅H₁₁PO₂H₂, CH₂=CHCH₂OH			134/1 mm.	(107)
(C₆H₅)₃CPH(O)OCH₃	(C₆H₅)₃CPO₂H₂, (CH₃)₂SO₄		163–164		(111)
(C₆H₅)₃CPH(O)OC₂H₅	(C₆H₅)₃CPO₂H₂, (C₂H₅)₂SO₄		118–121.5		(111)
CH₃CH(CH₃)CH₂PH(O)O	HOCH₂CH(CH₃)CH₂PO₂H₂ (heat)			100–104/0.2 mm.	(316)
n-C₁₀H₂₁CH=CHPH(O)(OCH₂CH₂)₂OH	C₁₀H₂₁PO₂H₂, ethylene oxide	100			(320, 321)
n-C₁₁H₂₃CH=CHPH(O)(OCH₂CH₂)₂OH	C₁₁H₂₃PO₂H₂, ethylene oxide	100			(320, 321)
C₆H₅PH(O)OCH₂CH₂Cl	C₆H₅PO₂H₂, C₆H₅P(OCH₂CH₂Cl)₂				(334)
C₆H₅PH(O)OC₆H₁₁-iso	C₆H₅PO₂H₂, C₆H₅P(OC₆H₁₁-iso)₂				(334)
C₆H₅PH(O)OC₆H₅	C₆H₅PO₂H₂, C₆H₅P(OC₆H₅)₂				(334)

1. Addition of sulfur

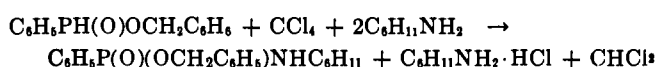The base-catalyzed addition of sulfur to phosphonous monoesters gives monoesters of phosphonothionic acids (39):

$$RPH(O)OC_4H_9 + S \xrightarrow{C_2H_5ONa} RP(S)(OC_4H_9)OH$$

2. Reaction with halogens

Phosphonous monoesters react with halogens, giving alkyl phosphonochloridates (5, 127, 292, 334):

$$C_2H_5PH(O)OR + Cl_2 \rightarrow C_2H_5P(O)(OR)Cl + HCl$$
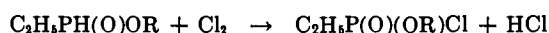
3. Reaction with amines and carbon tetrachloride

Phosphonous monoesters react with amines and carbon tetrachloride in the following manner (5):

$$C_6H_5PH(O)OCH_2C_6H_5 + CCl_4 + 2C_6H_{11}NH_2 \rightarrow$$
$$C_6H_5P(O)(OCH_2C_6H_5)NHC_6H_{11} + C_6H_{11}NH_2 \cdot HCl + CHCl_3$$

The product is a phosphonamidate.

4. Condensation reactions

Condensation reactions of phosphonous monoesters have been studied rather extensively in recent years, since reliable methods for their synthesis have been developed.

Phosphonous monoesters undergo base-catalyzed condensation reactions with a wide variety of α,β-unsaturated compounds. As an example may be given the reaction with α,β-unsaturated esters (38, 275, 281, 282):

$$C_6H_5PH(O)OR + CH_2=CHCOOCH_3 \xrightarrow{C_2H_5ONa}$$
$$C_6H_5P(O)(OR)CH_2CH_2COOCH_3$$
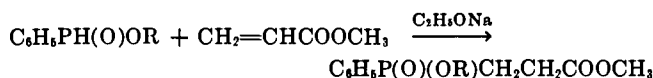
With esters of aliphatic phosphonous acids it is necessary to use the same alkyl radical in the alkoxide as in the ester (281). This is not the case with esters of aromatic phosphonous acids (281).

Phosphonous acid esters also react with α,β-unsaturated ketones (280), α,β-unsaturated nitriles (38, 279), α,β-unsaturated phosphonic esters (279, 283),

vinyl acetate (278), and 2-vinylpyridine (218). The mechanism of these reactions is presumed to be a nucleophilic attack on the polarized olefinic double bond, resembling the Michael addition (38). Proof that the addition takes place in this manner (in the opposite sense to Markownikov's rule) has been given in one instance (38).

The reaction of alkyl halides with the sodium derivatives of phosphonous acid esters provides a useful method for the synthesis of secondary phosphinic esters (24, 139, 174). A molar amount of sodium is necessary.

$$C_6H_5PH(O)OR \xrightarrow{Na} C_6H_5P(O)(OR)Na \xrightarrow{R'X} C_6H_5R'P(O)OR$$
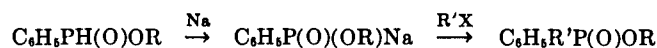
When diethylcarbamoyl chloride is used in this reaction, the product is an ester of diethylamidoformylphosphonic acid (23).

α-Hydroxy- and α-aminoalkylphosphinic acids may be prepared by the reaction of ketones (2, 136) or Schiff bases (136, 276) with phosphonous monoesters, in a manner similar to the reactions with hypophosphorous acid (Section II,A,3). A basic catalyst is used.

$$C_6H_5PH(O)OC_2H_5 + CH_3COCH_3 \rightarrow$$
$$(CH_3)_2C(OH)P(O)(OC_2H_5)C_6H_5$$

$$C_6H_5PH(O)OC_2H_5 + C_6H_5CH=NHC_6H_5 \rightarrow$$
$$C_6H_5CHNHC_6H_5$$
$$|$$
$$P(O)(OC_2H_5)C_6H_5$$
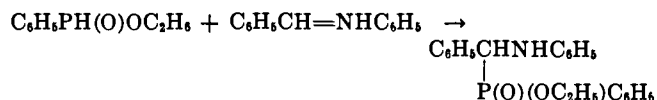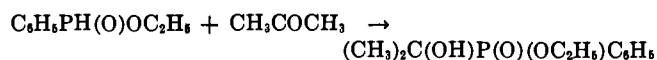
The Schiff base may be formed *in situ*, as in the reaction of ethyl hydrogen phenylphosphonite with acetone and ammonia (136). The yields are poor in this case, owing to side reactions. A reaction with ethyl isocyanate has also been described, addition taking place across the C=N bond (278).

Phosphonous monoesters add also to the C=S bond in thiourea (1).

$$C_6H_5PH(O)OR + SC(NH_2)_2 \rightarrow (NH_2)_2CP(O)(OR)C_6H_5$$
$$|$$
$$SH$$
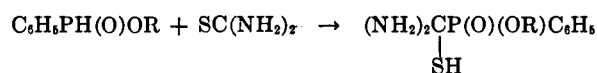
Phosphonous monoesters add to olefins in the presence of free-radical initiators such as di-*tert*-butyl per-

oxide, giving esters of secondary phosphinic acids (325). For example, ethyl hydrogen phenylphosphonite reacts with 1-octene, giving ethyl octylphenylphosphinate in 19 per cent yield:

$$C_6H_6PH(O)OC_2H_6 + C_6H_{13}CH=CH_2 \rightarrow C_8H_{17}P(O)OC_2H_6$$
$$| \atop C_6H_6$$
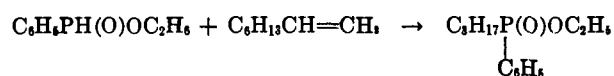
The polymerization of allyl hydrogen octylphosphonite with di-tert-butyl peroxide takes place at 120°C. to give a product which is probably a mixture of PH/olefin polymer and allyl homopolymer (107). The extent of each is not known. Copolymers with diallyl phthalate have also been described (107).

IX. PHOSPHONOTHIOUS ESTERS

Only one compound of this type is known. The reaction of butyl ethylphosphonochloridite with hydrogen sulfide gives butyl ethylphosphonothioite, b.p. 107–108°C./15 mm., in 50 per cent yield (254).

$$C_2H_6P(OC_4H_9)Cl + H_2S \rightarrow C_2H_6PH(S)OC_4H_9 + HCl$$

X. PHOSPHONOUS ANHYDRIDES

Three classes of phosphonous anhydrides are known: (1) mixed anhydrides of phosphonous and phosphorous acids, (2) true anhydrides of phosphonous acids, and (3) mixed anhydrides of phosphonous and phosphinous acids. The anhydrides of low molecular weight are distillable liquids of unpleasant odor which react with moisture and oxygen of the air, and which cause cotton to smolder.

A. SYNTHESIS OF PHOSPHONOUS ANHYDRIDES

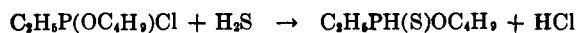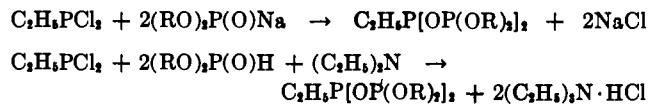##### 1. From phosphonous dichlorides with dialkyl phosphites

Mixed anhydrides of phosphonous and phosphorous acids are obtained when ethylphosphonous dichloride is treated with a dialkyl phosphite under conditions normally used for esterification, i.e., employing the sodium derivative of the phosphite or a tertiary amine as an acid acceptor (26):

$$C_2H_6PCl_2 + 2(RO)_2P(O)Na \rightarrow C_2H_6P[OP(OR)_2]_2 + 2NaCl$$

$$C_2H_6PCl_2 + 2(RO)_2P(O)H + (C_2H_6)_3N \rightarrow$$
$$C_2H_6P[OP(OR)_2]_2 + 2(C_2H_6)_3N \cdot HCl$$

Reactions of this type are listed in table 20. The first member of the series, the dimethyl ester, was apparently produced in the reaction but exploded on attempted ditsillation.

2. From phosphonous dichlorides with phosphonous monoesters

A reaction analogous to the above, using a phosphonous monoester, isopropyl hydrogen ethylphosphonite, instead of a dialkyl phosphite, gave in the presence of triethylamine an unstated yield of anhydride, b.p. 144–146°C./1 mm. (26).

$$C_2H_6PCl_2 + C_2H_6PH(O)OC_3H_7\text{-iso} \xrightarrow{(C_2H_6)_3N}$$
$$C_2H_6P[OP(C_2H_6)(OC_3H_7\text{-iso})]_2$$
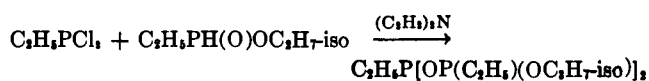
3. From phosphonous monoesters with phosphinous chlorides

Mixed anhydrides of phosphonous and phosphinous acids are prepared by the same methods as given above for other anhydrides. Only one such compound is known, obtained in 62 per cent yield, b.p. 91–93°C./1.5 mm., by the following reaction (27):

$$C_2H_6P(O)(OC_2H_6)Na + (C_2H_6)_2PCl \rightarrow$$
$$C_2H_6P(OC_2H_6)OP(C_2H_6)_2 + NaCl$$
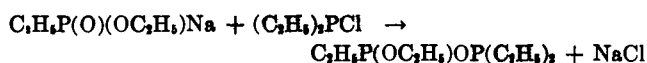
The product ignites in air.

B. REACTIONS OF PHOSPHONOUS ANHYDRIDES

The phosphonous anhydrides are sensitive to moisture and oxygen, and must be handled in a dry, inert atmosphere. They react vigorously with alkyl halides, giving quaternary phosphonium halides (26, 27):

$$C_2H_6P[OP(OC_2H_6)_2]_2 + C_2H_6Br \rightarrow (C_2H_6)_4PBr$$
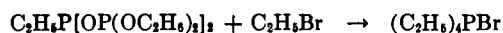
The reaction is not a simple Arbuzov rearrangement, since the product is not one which would be expected of such a rearrangement. The following mechanism for the

TABLE 20

Phosphonous anhydrides

Product	Preparation from		Yield	Boiling Point	Reference
	Phosphonous dichloride	Dialkyl phosphite or sodium phosphite			
Dialkyl phosphite/amine method					
C₂H₅P[OP(OCH₃)₂]₂.................	C₂H₅PCl₂	(CH₃O)₂PHO	*per cent*	*°C.*	(26)
C₂H₅P[OP(OC₂H₅)₂]₂.................	C₂H₅PCl₂	(C₂H₅O)₂PHO	51	128–130/1 mm.	(26)
C₂H₅P[OP(OC₃H₇-iso)₂]₂.............	C₂H₅PCl₂	(iso-C₃H₇O)₂PHO	44	165–167/2 mm.	(26)
Sodium phosphite method					
C₂H₅P[OP(OC₂H₅)₂]₂.................	C₂H₅PCl₂	(C₂H₅O)₂PONa	48	126–128/0.5 mm.	(26)
C₂H₅P[OP(OC₃H₇)₂]₂.................	C₂H₅PCl₂	(C₃H₇O)₂PONa	40	145–147/1 mm.	(26)
C₂H₅P[OP(OC₃H₇-iso)₂]₂.............	C₂H₅PCl₂	(iso-C₃H₇O)₂PONa	52	130–132/1 mm.	(26)

progressive displacement of phosphite groups has been suggested (26):

$$C_2H_5P[OP(OC_2H_5)_2]_2 + C_2H_5I \rightarrow$$
$$(C_2H_5)_2POP(OC_2H_5)_2 + (C_2H_5O)_2P(O)I$$

$$(C_2H_5)_2POP(OC_2H_5)_2 + C_2H_5I \rightarrow (C_2H_5)_3P + (C_2H_5O)_2P(O)I$$

$$(C_2H_5)_3P + C_2H_5I \rightarrow (C_2H_5)_4PI$$
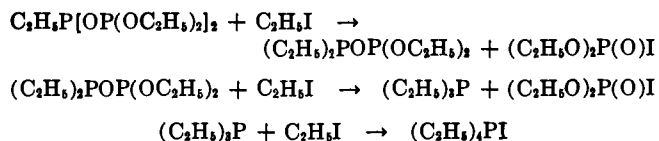
It will be noted that the first phosphorus atom, being the more easily quaternized, is the one that appears in the tetraethylphosphonium iodide. In mixed phosphinous-phosphonous anhydrides the phosphorus atom in the phosphinous portion is the more easily quaternized. The product of the reaction of $C_2H_5P(OC_2H_5)OP(C_2H_5)_2$ with butyl bromide, then, is $(C_2H_5)_2(C_4H_9)_2PBr$ and not $C_2H_5(C_4H_9)_3PBr$ (27).

XI. REFERENCES

(1) ABRAMOV, V. S.: Doklady Akad. Nauk S.S.S.R. 117, 811 (1957); Chem. Abstracts 52, 8038 (1958).
(2) ABRAMOV, V. S., AND KASHIRSKY, M. I.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 28, 3090 (1958).
(3) ALLEN, J. F.: J. Am. Chem. Soc. 79, 3071 (1957).
(4) ALLEN, J. F., AND JOHNSON, O. H.: J. Am. Chem. Soc. 77, 2871 (1955); British patents 783,697 and 784,985 (1957); Chem. Abstracts 52, 8194 and 8195 (1958).
(5) ANAND, N., AND TODD, A. R.: J. Chem. Soc. 1951, 1867.
(6) ANDERSON, H. H.: J. Am. Chem. Soc. 75, 1576 (1953).
(7) ANON.: Chem. Eng. News 30, 4515 (1952).
(8) ARBUZOV, A. E.: J. Russ. Phys.-Chem. Soc. 42, 395 (1910); Chem. Abstracts 5, 1397 (1911).
(9) ARBUZOV, A. E.: Zhur. Obshchei Khim. 4, 898 (1934); Chem. Abstracts 29, 2146 (1935).
(10) ARBUZOV, A. E., AND ARBUZOV, B. A.: J. Russ. Phys.-Chem. Soc. 61, 1599 (1929); Chem. Abstracts 24, 5289 (1930).
(11) ARBUZOV, A. E., AND ARBUZOVA, I.: J. Russ. Phys.-Chem. Soc. 61, 1905 (1929); Chem. Abstracts 24, 5289 (1930).
(12) ARBUZOV, A. E., AND KAMAI, G.: J. Russ. Phys.-Chem. Soc. 61, 2037 (1929); Chem. Abstracts 24, 5736 (1930).
(13) ARBUZOV, A. E., AND KAMAI, G.: Zhur. Obshchei Khim. 17, 2149 (1957); Chem. Abstracts 42, 4523 (1948).
(14) ARBUZOV, A. E., KAMAI, G., AND BELOROSSOVA, O. N.: Zhur. Obshchei Khim. 15, 766 (1945); Chem. Abstracts 41, 105 (1947).
(15) ARBUZOV, A. E., KAMAI, G., AND NESTEROV, L. V.: Trudy Kazan. Khim.-Tekhnol. Inst. im. S. M. Kirova 1951, No. 16, 17; Chem. Abstracts 51, 5720 (1957).
(16) ARBUZOV, A. E., AND RAZUMOV, A. I.: Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1945, 167; Chem. Abstracts 40, 3411 (1946).
(17) ARBUZOV, B. A., AND GRECHKIN, N. P.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 20, 113 (1950).
(18) ARBUZOV, B. A., AND GRECHKIN, N. P.: Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.) 1956, 429.
(19) ARBUZOV, B. A., AND RIZPOLOZHENSKY, N. I.: Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.) 1952, 765.
(20) ARBUZOV, B. A., AND RIZPOLOZHENSKY, N. I.: Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.) 1952, 843.
(21) ARBUZOV, B. A., AND RIZPOLOZHENSKY, N. I.: Doklady Akad. Nauk S.S.S.R. 83, 581 (1952); Chem. Abstracts 47, 3226 (1953).
(22) ARBUZOV, B. A., AND RIZPOLOZHENSKY, N. I.: Doklady Akad. Nauk S.S.S.R. 89, 291 (1953); Chem. Abstracts 48, 7540 (1954).
(23) ARBUZOV, B. A., AND RIZPOLOZHENSKY, N. I.: Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.) 1954, 539.
(24) ARBUZOV, B. A., AND RIZPOLOZHENSKY, N. I.: Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.) 1955, 225.
(25) ARBUZOV, B. A., RIZPOLOZHENSKY, N. I., AND ZVEREVA, M. A.: Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.) 1955, 935.
(26) ARBUZOV, B. A., RIZPOLOZHENSKY, N. I., AND ZVEREVA, M. A.: Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.) 1957, 189.
(27) ARBUZOV, B. A., RIZPOLOZHENSKY, N. I., AND ZVEREVA, M. A.: Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.) 1958, 685.
(28) ARNOLD, G. B., AND HAMILTON, C. S.: J. Am. Chem. Soc. 63, 2637 (1941).
(29) BALON, W. J.: U.S. patent 2,853,518 (1958); Chem. Abstracts 53, 5202 (1959).
(30) BARTLETT, P. D., AND MEGUERIAN, G.: J. Am. Chem. Soc. 78, 3710 (1956).
(31) BARTOCHA, B., BRINCKMAN, F. E., KAESZ, H. D., AND STONE, F. G. A.: Proc. Chem. Soc. 1958, 116.
(32) BEEBY, M. H., AND MANN, F. G.: J. Chem. Soc. 1951, 411.
(33) BENDA, L., AND SCHMIDT, W.: U.S. patent 1,607,113 (1926); Chem. Abstracts 21, 249 (1927).
(34) BENNETT, F. W., EMELÉUS, H. J., AND HASZELDINE, R. N.: J. Chem. Soc. 1953, 1565.
(35) BENNETT, F. W., EMELÉUS, H. J., AND HASZELDINE, R. N.: J. Chem. Soc. 1954, 3896.
(36) BERLIN, K. D., AND BUTLER, G. B.: Chem. Revs. 60, 243 (1960).
(37) BIDDLE, P., KENNEDY, J., AND WILLANS, J. L.: Chem. & Ind. (London) 1957, 1481.
(38) BOCHWIC, B., AND MICHALSKI, J.: Roczniki Chem. 26, 593 (1952); Chem. Abstracts 49, 2345 (1955).
(39) BORECKI, C., MICHALSKI, J., AND MUSIEROWICZ, S.: J. Chem. Soc. 1958, 4081.
(40) BOURNEUF, M.: Bull. soc. chim. France [4] 33, 1808 (1923).
(41) BOWLES, J. A. C., AND JAMES, C.: J. Am. Chem. Soc. 51, 1406 (1929).
(42) BRAYE, E. H., AND HÜBEL, W.: Chem. & Ind. (London) 1959, 1250.
(43) BROGLIE, A.: Ber. 10, 628 (1877).
(44) BROWN, H. C.: U.S. patent 2,584,112 (1952); Chem. Abstracts 46, 9580 (1952).
(45) BUCHNER, B., AND LOCKHART, L. B., JR.: J. Am. Chem. Soc. 73, 755 (1951).
(46) BUCHNER, B., AND LOCKHART, L. B., JR.: Org. Syntheses 31, 88 (1951).
(47) BULS, V. W., AND MORRIS, R. C.: U.S. patent 2,807,636 (1957); Chem. Abstracts 52, 2068 (1958).
(48) BURG, A. B., AND MAHLER, W.: U.S. patent 2,923,742 (1960); Chem. Abstracts 54, 9765 (1960).
(49) BURG, A. B., MAHLER, W., BILBO, A. J., HABER, C. P., AND HERRING, D. L.: J. Am. Chem. Soc. 79, 247 (1957).
(50) CASSELLA, L., AND Co., GES.: British patent 258,744 (1925); Chem. Abstracts 21, 3105 (1927).
(51) CHALLENGER, F., AND PRITCHARD, F.: J. Chem. Soc. 125, 864 (1924).
(52) CHALLENGER, F., AND RIDGWAY, L. R.: J. Chem. Soc. 121, 104 (1922).
(53) COLLIE, N.: J. Chem. Soc. 53, 714 (1888).
(54) CONANT, J. B., BUMP, A. H., AND HOLT, H. S.: J. Am. Chem. Soc. 43, 1677 (1921).
(55) CONANT, J. B., AND POLLACK, S. M.: J. Am. Chem. Soc. 43, 1665 (1921).

(56) CONEN, F.: Ber. 31, 2919 (1898).
(57) COYNE, D. M., McEWEN, W. E., AND VANDERWERF, C. A.: J. Am. Chem. Soc. 78, 3061 (1956).
(58) CZIMATIS, L.: Ber. 15, 2014 (1882).
(59) DAVIES, W. C.: J. Chem. Soc. 1933, 1043.
(60) DAVIES, W. C.: J. Chem. Soc. 1935, 462.
(61) DAVIES, W. C., AND JONES, W. J.: J. Chem. Soc. 1929, 33.
(62) DAVIES, W. C., AND LEWIS, W. P. G.: J. Chem. Soc. 1934, 1599.
(63) DAVIES, W. C., AND MANN, F. G.: J. Chem. Soc. 1944, 276.
(64) DAVIES, W. C., AND MORRIS, C. J. O. R.: J. Chem. Soc. 1932, 2880.
(65) DAVIES, W. C., AND MORRIS, C. J. O. R.: Bull. soc. chim. France [4] 53, 980 (1933).
(66) DAVIES, W. C., AND OTHEN, C. W.: J. Chem. Soc. 1936, 1236.
(67) DAVIES, W. C., PEARSE, P. L., AND JONES, W. J.: J. Chem. Soc. 1929, 1262.
(68) DERKACH, G. I., AND KIRSANOV, A. V.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 29, 1786 (1959).
(69) DÖRKEN, C.: Ber. 21, 1505 (1888).
(70) DRAKE, L. R., AND MARVEL, C. S.: J. Org. Chem. 2, 387 (1937).
(71) DYE, W. T., JR.: Naval Research Laboratory Report P-3044 (1946).
(72) DYE, W. T., JR.: J. Am. Chem. Soc. 70, 2595 (1948).
(73) EMELÉUS, H. J., HASZELDINE, R. N., AND PAUL, R. C.: J. Chem. Soc. 1955, 563.
(74) EMELÉUS, H. J., AND SMITH, J. D.: J. Chem. Soc. 1959, 375.
(75) ENGELKE, E. F.: U.S. patent 2,377,870 (1945); Chem. Abstracts 39, 4099 (1945).
(76) FITCH, H. M.: U.S. patent 2,759,961 (1956); Chem. Abstracts 51, 482 (1957).
(77) FORD-MOORE, A. H., AND PERRY, B. J.: Org. Syntheses 31, 111 (1951).
(78) FOSSE, R.: Bull. soc. chim. France [4] 7, 231 (1910).
(79) FOSSE, R.: Bull. soc. chim. France [4] 7, 357 (1910); Compt. rend. 150, 178 (1910).
(80) FOX, R. B.: J. Am. Chem. Soc. 72, 4147 (1950).
(81) FOX, R. B., AND LOCKHART, L. B., JR.: Naval Research Laboratory Report C-3323 (1948).
(82) FRANK, A. W.: J. Org. Chem. 24, 966 (1959).
(83) FREEDMAN, L. D., AND DOAK, G. O.: J. Am. Chem. Soc. 74, 2884 (1952).
(84) FREEDMAN, L. D., AND DOAK, G. O.: J. Am. Chem. Soc. 74, 3414 (1952).
(85) FREEDMAN, L. D., AND DOAK, G. O.: J. Am. Chem. Soc. 75, 4905 (1953).
(86) FREEDMAN, L. D., AND DOAK, G. O.: Chem. Revs. 57, 479 (1957).
(87) FREEDMAN, L. D., AND DOAK, G. O.: J. Org. Chem. 23, 769 (1958).
(88) FREEDMAN, L. D., TAUBER, H., DOAK, G. O., AND MAGNUSON, H. J.: J. Am. Chem. Soc. 75, 1379 (1953).
(89) FRUNZE, T. M., KORSHAK, V. V., KURASHEV, V. V., KOLESNIKOV, G. S., AND ZHUBANOV, B. A.: Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.) 1958, 762.
(90) GARNER, A. Y.: U.S. patent 2,916,510 (1959); Chem. Abstracts 54, 5571 (1960).
(91) GEFTER, E. L.: U.S.S.R. patent 107,266 (1957); Chem. Abstracts 52, 2065 (1958).
(92) GEFTER, E. L.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 28, 1398 (1958).
(93) GEFTER, E. L., AND KABACHNIK, M. I.: Doklady Akad. Nauk S.S.S.R. 114, 541 (1957); Chem. Abstracts 52, 295 (1958).
(94) GILMAN, H., AND BROWN, G. E.: J. Am. Chem. Soc. 67, 824 (1945).
(95) GILMAN, H., AND STUCKWISCH, C. G.: J. Am. Chem. Soc. 63, 2844 (1941).
(96) GINSBURG, V. A., AND PRIVEZENTSEVA, N. F.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 28, 716 (1958).
(97) GINSBURG, V. A., AND YAKUBOVICH, A. YA.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 28, 710 (1958).
(98) GODDARD, A. E.: In A Text-book of Inorganic Chemistry, edited by J. N. Friend, Vol. XI, Part 3. Charles Griffin and Co., Ltd., London (1936).
(99) GÖTTER, H., AND MICHAELIS, A.: Ber. 11, 885 (1878).
(100) GOTTLIEB, H. B.: J. Am. Chem. Soc. 54, 748 (1932).
(101) GREEN, M., AND HUDSON, R. F.: J. Chem. Soc. 1958, 3129.
(102) GRÜTTNER, G., AND KRAUSE, E.: Ber. 49, 437 (1916).
(103) GRÜTINER, G., AND WIERNIK, M.: Ber. 48, 1473 (1915).
(104) GUICHARD, F.: Ber. 32, 1572 (1899).
(105) HAAS, H.: German patent 938,186 (1956); Chem. Abstracts 50, 12096 (1956).
(106) HARMAN, D.: U.S. patent 2,629,731 (1953); Chem. Abstracts 48, 1418 (1954).
(107) HARMAN, D., AND STILES, A. R.: U.S. patent 2,659,714 (1953); Chem. Abstracts 48, 12168 (1954).
(108) HAROWITZ, C. L.: U.S. patent 2,903,475 (1959); Chem. Abstracts 54, 2169 (1960).
(109) HARTMANN, H., BEERMANN, C., AND CZEMPIK, H.: Z. anorg. u. allgem. Chem. 287, 261 (1956).
(110) HARWOOD, H. J., AND GRISLEY, D. W., JR.: J. Am. Chem. Soc. 82, 423 (1960).
(111) HATT, H. H.: J. Chem. Soc. 1933, 776.
(112) HAVEN, A. C., JR.: J. Am. Chem. Soc. 78, 842 (1956).
(113) HAVEN, A. C., JR.: U.S. patent 2,835,652 (1958); Chem. Abstracts 53, 221 (1959).
(114) HIRSCHMANN, H.: U.S. patent 2,370,903 (1945); Chem. Abstracts 39, 4892 (1945).
(115) HOFFMANN, F. W., AND MOORE, T. R.: J. Am. Chem. Soc. 80, 1150 (1958).
(116) HOFFMANN, F. W., AND MOORE, T. R.: U.S. patent 2,907,787 (1959); Chem. Abstracts 54, 5465 (1960).
(117) HOFFMANN, F. W., ROTH, R. G., AND SIMMONS, T. C.: J. Am. Chem. Soc. 80, 5937 (1958).
(118) HOFFMANN, F. W., WADSWORTH, D. H., AND WEISS, H. D.: J. Am. Chem. Soc. 80, 3945 (1958).
(119) HOFMANN, A. W.: Ber. 5, 104 (1872).
(120) HOLLIMAN, F. G., AND MANN, F. G.: J. Chem. Soc. 1943, 547.
(121) HOLLIMAN, F. G., AND MANN, F. G.: J. Chem. Soc. 1947, 1634.
(122) HORNER, L., BECK, P., AND HOFFMANN, H.: Chem. Ber. 92, 2088 (1959).
(123) HORNER, L., HOFFMANN, H., AND BECK, P.: Chem. Ber. 91, 1583 (1958).
(124) HORVAT, R. J., AND FURST, A.: J. Am. Chem. Soc. 74, 562 (1952).
(125) INGOLD, C. K., SHAW, F. R., AND WILSON, I. S.: J. Chem. Soc. 1928, 1280.
(126) IVIN, S. Z., AND KARAVANOV, K. V.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 28, 2988 (1958).
(127) JACKSON, H. L.: U.S. patent 2,722,538 (1955); Chem. Abstracts 50, 4218 (1956).
(128) JACKSON, I. K., DAVIES, W. C., AND JONES, W. J.: J. Chem. Soc. 1930, 2298.
(129) JACKSON, I. K., DAVIES, W. C., AND JONES, W. J.: J. Chem. Soc. 1931, 2109.
(130) JACKSON, I. K., AND JONES, W. J.: J. Chem. Soc. 1931, 575.

(131) JENSEN, W. L.: U.S. patent 2,662,917 (1953); Chem. Abstracts 48, 13711 (1954).

(132) JERCHEL, D.: Ber. 76, 600 (1943).

(133) JOLLY, S. E., AND PERRINE, J. H.: U.S. patent 2,276,492 (1942); Chem. Abstracts 36, 5008 (1942).

(134) JONES, W. J., DAVIES, W. C., BOWDEN, S. T., EDWARDS, C., DAVIS, V. E., AND THOMAS, L. H.: J. Chem. Soc. 1947, 1446.

(135) KABACHNIK, M. I., AND GILYAROV, V. A.: Doklady Akad. Nauk S.S.S.R. 96, 991 (1954); Chem. Abstracts 49, 8842 (1955).

(136) KABACHNIK, M. I., AND MEDVED, T. YA.: Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.) 1954, 893.

(137) KABACHNIK, M. I., AND SHEPELEVA, E. S.: Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.) 1953, 763.

(138) KABACHNIK, M. I., AND TSVETKOV, E. N.: Proc. Acad. Sci. U.S.S.R., Sect. Chem. (Eng. Transl.) 117, 1063 (1957).

(139) KABACHNIK, M. I., TSVETKOV, E. N., AND CHUNG-YU CHANG: Doklady Akad. Nauk S.S.S.R. 125, 1260 (1959); Chem. Abstracts 53, 21752 (1959).

(140) KAESZ, H. D., AND STONE, F. G. A.: J. Org. Chem. 24, 635 (1959).

(141) KAMAI, G.: Zhur. Obshchei Khim. 2, 524 (1932); Chem. Abstracts 27, 966 (1933).

(142) KAMAI, G.: Zhur. Obshchei Khim. 4, 192 (1934); Chem. Abstracts 29, 464 (1935).

(143) KAMAI, G.: Compt. rend. acad. sci. U.R.S.S. 55, 219 (1947); Chem. Abstracts 41, 5863 (1947).

(144) KAMAI, G.: Zhur. Obshchei Khim. 18, 443 (1948); Chem. Abstracts 42, 7723 (1948).

(145) KAMAI, G.: Doklady Akad. Nauk S.S.S.R. 66, 389 (1949); Chem. Abstracts 44, 127 (1950).

(146) KAMAI, G., AND GERASIMOVA, E. A.: Trudy Kazan. Khim.-Tekhnol. Inst. im. S. M. Kirova 1950, No. 15, 26; Chem. Abstracts 51, 11273 (1957).

(147) KAMAI, G., AND GERASIMOVA, E. A.: Trudy Kazan. Khim.-Tekhnol. Inst. im. S. M. Kirova 1957, No. 23, 138; Chem. Abstracts 52, 9946 (1958).

(148) KAMAI, G., AND KHISMATULLINA, L. A.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 26, 3815 (1956).

(149) KAMAI, G., AND KUKHTIN, V. A.: Doklady Akad. Nauk S.S.S.R. 89, 309 (1953); Chem. Abstracts 48, 7540 (1954).

(150) KAMAI, G., AND KUKHTIN, V. A.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 25, 1875 (1955).

(151) KAMAI, G., AND KUKHTIN, V. A.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 28, 913 (1958).

(152) KELBE, W.: Ber. 9, 1051 (1876).

(153) KELBE, W.: Ber. 11, 1490 (1878).

(154) KERSCHNER, P. M., AND GREENWALD, B. W.: U.S. patent 2,864,845 (1958); Chem. Abstracts 53, 12239 (1959).

(155) KHARASCH, M. S.: U.S. patent 2,489,091 (1949); Chem. Abstracts 44, 2009 (1950).

(156) KHARASCH, M. S., JENSEN, E. V., AND URRY, W. H.: J. Am. Chem. Soc. 67, 1864 (1945).

(157) KHARASCH, M. S., JENSEN, E. V., AND URRY, W. H.: J. Am. Chem. Soc. 68, 154 (1946).

(158) KHARASCH, M. S., JENSEN, E. V., AND WEINHOUSE, S.: J. Org. Chem. 14, 429 (1949).

(159) KHARASCH, M. S., AND WEINHOUSE, S.: U.S. patent 2,615,043 (1952); Chem. Abstracts 47, 9346 (1953).

(160) KHARASCH, M. S., AND WEINHOUSE, S.: U.S. patents 2,636,893 and 2,636,894 (1953); Chem. Abstracts 47, 7700 (1953).

(161) KHISAMOVA, Z. L., AND KAMAI, G.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 20, 1207 (1950).

(162) KINNEAR, A. M., AND PERREN, E. A.: J. Chem. Soc. 1952, 3437.

(163) KLOTZ, I. M., AND MORRISON, R. T.: J. Am. Chem. Soc. 69, 473 (1947).

(164) KLOTZ, I. M., AND MORRISON, R. T.: U. S. patent 2,605,280 (1952); Chem. Abstracts 47, 3875 (1953).

(165) KÖHLER, H.: Ber. 13, 463 (1880).

(166) KÖHLER, H.: Ber. 13, 1623 (1880).

(167) KÖHLER, H.: Ber. 13, 1626 (1880).

(168) KÖHLER, H., AND MICHAELIS, A.: Ber. 9, 1053 (1876).

(169) KÖHLER, H., AND MICHAELIS, A.: Ber. 10, 807 (1877).

(170) KÖHLER, H., AND MICHAELIS, A.: Ber. 10, 815 (1877).

(171) KÖHLER, H., AND MICHAELIS, A.: Ber. 10, 816 (1877).

(172) KOMKOV, I. P., KARAVANOV, K. V., AND IVIN, S. Z.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 28, 2992 (1958).

(173) KORSHAK, V. V., KOLESNIKOV, G. S., AND ZHUBANOV, B. A.: Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.) 1958, 595.

(174) KOSOLAPOFF, G. M.: J. Am. Chem. Soc. 72, 4292 (1950).

(175) KOSOLAPOFF, G. M.: Organophosphorus Compounds. John Wiley and Sons, Inc., New York (1950).

(176) KOSOLAPOFF, G. M.: Org. Reactions 6, 273 (1951).

(177) KOSOLAPOFF, G. M.: J. Am. Chem. Soc. 74, 4119 (1952).

(178) KOSOLAPOFF, G. M.: U.S. patent 2,594,454 (1952); Chem. Abstracts 47, 1179 (1953).

(179) KOSOLAPOFF, G. M., AND HUBER, W. F.: J. Am. Chem. Soc. 69, 2020 (1947).

(180) KOSOLAPOFF, G. M., AND POWELL, J. S.: J. Am. Chem. Soc. 72, 4291 (1950).

(181) KREUTZKAMP, N., AND PLUHATSCH, J.: Arch. Pharm. 292, 159 (1959); Chem. Abstracts 53, 17938 (1959).

(182) KUCHEN, W., AND BUCHWALD, H.: Angew. Chem. 68, 791 (1956).

(183) KUCHEN, W., AND BUCHWALD, H.: Chem. Ber. 91, 2296 (1958).

(184) KUNZ, P.: Ber. 27, 2559 (1894).

(185) LADD, E. C., AND HARVEY, M. P.: U.S. patent 2,631,162 (1953); Chem. Abstracts 48, 7048 (1954).

(186) LADD, E. C., AND LITTLE, J. R.: U.S. patent 2,510,699 (1950); Chem. Abstracts 44, 7348 (1950).

(187) LEAVITT, F. C., MANUEL, T. A., AND JOHNSON, F.: J. Am. Chem. Soc. 81, 3163 (1959).

(188) LECOQ, H.: Bull. soc. chim. Belges 42, 199 (1933); Chem. Zentr. 1933, II, 1189.

(189) LETTS, E. A., AND BLAKE, R. F.: Trans. Roy. Soc. Edinburgh 35, 527 (1889); J. Chem. Soc. Abstracts 58, 766 (1890).

(190) LINDNER, J., BRUGGER, O., JENKNER, A., AND TSCHEMERNIGG, L.: Monatsh. Chem. 53-54, 263 (1929).

(191) LINDNER, J., AND STRECKER, M.: Monatsh. Chem. 53-54, 274 (1929).

(192) LINDNER, J., WIRTH, W., AND ZAUNBAUER, B.: Monatsh. Chem. 70, 1 (1937).

(193) MAGUIRE, M. H., AND SHAW, G.: J. Chem. Soc. 1955, 2039.

(194) MAGUIRE, M. H., AND SHAW, G.: J. Chem. Soc. 1957, 311.

(195) MAHLER, W., AND BURG, A. B.: J. Am. Chem. Soc. 79, 251 (1957); 80, 6161 (1958).

(196) MAIER, L.: Angew. Chem. 71, 574 (1959).

(197) MAIER, L., SEYFERTH, D., STONE, F. G. A., AND ROCHOW, E. G.: J. Am. Chem. Soc. 79, 5884 (1957).

(198) MAIER-BODE, H., AND KÖTZ, G.: German (East) patent 11,241 (1956); Chem. Abstracts 53, 6156 (1959).

(199) MALATESTA, L., AND SACCO, A.: Ann. chim. (Rome) 44, 134 (1954); Chem. Abstracts 48, 13516 (1954).

(200) MANN, F. G.: The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, Bismuth, and Silicon. Interscience Publishers, Inc., New York (1950).

(201) MANN, F. G., AND CHAPLIN, E. J.: J. Chem. Soc. 1937, 527.
(202) MANN, F. G., AND MILLAR, I. T.: J. Chem. Soc. 1952, 3039.
(203) MANN, F. G., MILLAR, I. T., AND STEWART, F. H. C.: J. Chem. Soc. 1954, 2832.
(204) MANN, F. G., AND PURDIE, D.: J. Chem. Soc. 1940, 1230.
(205) MANN, F. G., AND STEWART, F. H. C.: J. Chem. Soc. 1954, 2826.
(206) MANN, F. G., AND WATSON, J.: J. Org. Chem. 13, 502 (1948).
(207) MARELLI, O.: Ann. chim. appl. 34, 149 (1944); Chem. Abstracts 40, 7515 (1946).
(208) MARIE, C.: Compt. rend. 133, 219 (1901).
(209) MARIE, C.: Compt. rend. 134, 286 (1902).
(210) MARIE, C.: Compt. rend. 134, 847 (1902).
(211) MARIE, C.: Compt. rend. 135, 1118 (1902).
(212) MARIE, C.: Compt. rend. 136, 48 (1903).
(213) MARIE, C.: Compt. rend. 136, 234 (1903).
(214) MARIE, C.: Compt. rend. 136, 508 (1903).
(215) MARIE, C.: Compt. rend. 137, 124 (1903).
(216) MARIE, C.: Compt. rend. 138, 1707 (1904).
(217) MARIE, C.: Ann. chim. et phys. [8] 3, 335 (1904).
(218) MARUSZEWSKA-WIECZORKOWSKA, E., AND MICHALSKI, J.: Bull. acad. polon. sci., Sér. sci. chim., géol. et géograph. 6, 19 (1958); Chem. Abstracts 52, 16349 (1958).
(219) MASTRYUKOVA, T. A., SHIPOV, A. E., AND KABACHNIK, M. I.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 29, 1424 (1959).
(220) MATTSON, R. W.: U.S. patent 2,769,743 (1956); Chem. Abstracts 51, 3915 (1957).
(221) MCCORMACK, W. B.: U.S. patents 2,663,736 and 2,663,737 (1953); Chem. Abstracts 49, 7601 (1955).
(222) MCCORMACK, W. B.: U.S. patent 2,663,738 (1953); Chem. Abstracts 49, 7602 (1955).
(223) MEISENHEIMER, J.: Ann. 397, 273 (1913).
(224) MEISENHEIMER, J., CASPER, J., HÖRING, M., LAUTER, W., LICHTENSTADT, L., AND SAMUEL, W.: Ann. 449, 213 (1926).
(225) MELCHIKER, P.: Ber. 31, 2915 (1898).
(226) MICHAELIS, A.: Ber. 6, 601 (1873).
(227) MICHAELIS, A.: Ber. 6, 816 (1873).
(228) MICHAELIS, A.: Ber. 7, 6 (1874).
(229) MICHAELIS, A.: Ber. 8, 499 (1875).
(230) MICHAELIS, A.: Ann. 181, 265 (1876).
(231) MICHAELIS, A.: Ber. 10, 627 (1877).
(232) MICHAELIS, A.: Ber. 12, 1009 (1879).
(233) MICHAELIS, A.: Ber. 13, 2174 (1880).
(234) MICHAELIS, A.: Ann. 293, 193 (1896).
(235) MICHAELIS, A.: Ann. 293, 261 (1896).
(236) MICHAELIS, A.: Ann. 294, 1 (1897).
(237) MICHAELIS, A.: Ber. 31, 1037 (1898).
(238) MICHAELIS, A.: Ann. 315, 43 (1901).
(239) MICHAELIS, A.: Ann. 407, 290 (1915).
(240) MICHAELIS, A. AND ANANOFF, J.: Ber. 7, 1688 (1874).
(241) MICHAELIS, A., AND ANANOFF, J.: Ber. 8, 493 (1875).
(242) MICHAELIS, A., AND DITTLER, F.: Ber. 12, 338 (1879).
(243) MICHAELIS, A., AND GLEICHMANN, L.: Ber. 15, 801 (1882).
(244) MICHAELIS, A., AND GLEICHMANN, L.: Ber. 15, 1961 (1882).
(245) MICHAELIS, A., AND GRAEFF, F.: Ber. 8, 922 (1875).
(246) MICHAELIS, A., AND KÖHLER, H.: Ber. 9, 519 (1876).
(247) MICHAELIS, A., AND LANGE, H.: Ber. 8, 1313 (1875).
(248) MICHAELIS, A., AND LINK, A.: Ann. 207, 193 (1881).
(249) MICHAELIS, A., AND OSTER, F.: Ann. 270, 123 (1892).
(250) MICHAELIS, A., AND PANEK, C.: Ber. 13, 653 (1880).
(251) MICHAELIS, A., AND PANEK, C.: Ann. 212, 203 (1882).
(252) MICHAELIS, A., AND SCHENK, A.: Ann. 260, 1 (1890).
(253) MICHAELIS, A., AND SODEN, H.: Ann. 229, 295 (1885).

(254) MICHALSKI, J.: Roczniki Chem. 29, 960 (1955); Chem. Abstracts 50, 10641 (1956).
(255) MICHALSKI, J., AND WIECZORKOWSKI, J.: Bull. acad. polon. sci. Classe III, 4, 279 (1956); Chem. Abstracts 51, 4266 (1957).
(256) MICHALSKI, J., AND WIECZORKOWSKI, J.: Bull. acad. polon. sci. Classe III, 5, 917 (1957); Chem. Abstracts 52, 6157 (1958).
(257) MIKHAILOV, B. M., AND KUCHEROVA, N. F.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 22, 855 (1952).
(258) MONTIGNIE, E.: Bull. soc. chim. France 49, 73 (1931).
(259) MORRIS, R. C., BULS, V. W., AND BALLARD, S. A.: U.S. patent 2,577,796 (1951); Chem. Abstracts 46, 9581 (1952).
(260) MORRIS, R. C., AND VAN WINKLE, J. L.: U.S. patent 2,728,806 (1955); Chem. Abstracts 50, 10760 (1956).
(261) MORRISON, D. C.: J. Org. Chem. 21, 705 (1956).
(262) MÖSLINGER, W.: Ber. 9, 1005 (1876); Ann. 185, 49 (1877).
(263) MULDER: Jahresber. 1864, 329.
(264) NEALE, E., AND WILLIAMS, L. T. D.: J. Chem. Soc. 1955, 2485.
(265) NIJK, D. R.: Rec. trav. chim. 41, 461 (1922).
(266) NOZAKI, K.: U.S. patent 2,852,565 (1958); Chem. Abstracts 53, 19838 (1959).
(267) OKHLOBYSTIN, O. YU., AND ZAKHARKIN, L. I.: Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.) 1958, 977.
(268) PASS, F., AND SCHINDLBAUER, H.: Monatsh. Chem. 90, 148 (1959).
(269) PETROV, K. A., AND BLIZNYUK, N. K.: U.S.S.R. patent 124,937 (1959); Chem. Abstracts 54, 11994 (1960).
(270) PIANFETTI, J. A., AND KOSOLAPOFF, G. M.: U.S. patent 2,881,202 (1959); Chem. Abstracts 52, 14937 (1959).
(271) PLATONOV, A. P., AND DMITRIEV, A. V.: U.S.S.R. patent 118,819 (1959); Chem. Abstracts 53, 21665 (1959).
(272) PLETS, V. M.: Organicheskiye Soedineniya Fosfora. Gosudarst. Izdatel. Oboronnoi Promyshlennosti, Moscow (1940).
(273) POLONOVSKI, M., PESSON, M., AND POLMANSS, G.: Compt. rend. 239, 1506 (1954).
(274) POPE, W. J., AND GIBSON, C. S.: J. Chem. Soc. 101, 735 (1912).
(275) PUDOVIK, A.N.: Doklady Akad. Nauk S.S.S.R. 85, 349 (1952); Chem. Abstracts 47, 5351 (1953).
(276) PUDOVIK, A, N.: Doklady Akad. Nauk S.S.S.R. 92, 773 (1953); Chem. Abstracts 49, 3050 (1955).
(277) PUDOVIK, A. N., AND AVERYANOVA, V. P.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 26, 1605 (1956).
(278) PUDOVIK, A. N., KONOVALOVA, I. V., AND KRIVONOSOVA, R. E.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 26, 3110 (1956).
(279) PUDOVIK, A. N., AND POLOZNOVA, N. G.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 25, 745 (1955).
(280) PUDOVIK, A. N., SABIROVA, R. D., AND TENER, T. A.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 24, 1025 (1954).
(281) PUDOVIK, A. N., AND YARMUKHAMETOVA, D. K.: Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.) 1952, 803.
(282) PUDOVIK, A. N., AND YARMUKHAMETOVA, D. K.: Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.) 1954, 543.
(283) PUDOVIK, A. N., AND ZAKHAROVA, M. M.: Uchenye Zapiski Kazan. Gosudarst. Univ. im. V. I. Ulyanova-Lenina 113, No. 3, 3 (1955); Chem. Abstracts 51, 5687 (1957).
(284) QUIN, L. D.: J. Am. Chem. Soc. 79, 3681 (1957).
(285) QUIN, L. D., AND ROLSTON, C. H.: J. Org. Chem. 23, 1693 (1958).

(286) RAAB, W. J., AND WHETSTONE, R. R.: U.S. patent 2,806,-049 (1957); Chem. Abstracts 52, 2063 (1958).

(287) RADCLIFFE, L. G., AND BRINDLEY, W. H.: Chem. & Ind. (London) 42, 64 (1923).

(288) RAMSDEN, H. E.: U.S. patents 2,912,465 and 2,913,498 (1959); Chem. Abstracts 54, 2170 (1960).

(289) RANKOV, G.: Ann. univ. Sofia, II, Faculté phys.-math., Livre 2, 32, 51 (1936); Chem. Abstracts 31, 2168 (1937).

(290) RAUDNITZ, H.: Ber. 60, 743 (1927).

(291) RAZUMOV, A. I.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 29, 1609 (1959).

(292) RAZUMOV, A. I., MARKOVICH, E. A., AND RESHETNIKOVA, A. D.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 27, 2455 (1957).

(293) RAZUMOV, A. I., AND MUKHACHEVA, O. A.: Doklady Akad. Nauk S.S.S.R. 91, 271 (1953); Chem. Abstracts 48, 8725 (1954); see also Chem. Abstracts 51, 5687 (1957).

(294) RAZUMOV, A. I., AND MUKHACHEVA, O. A.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 26, 1615 (1956).

(295) RAZUMOV, A. I., AND MUKHACHEVA, O. A.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 26, 2753 (1956).

(296) RAZUMOV, A. I., MUKHACHEVA, O. A., AND MARKOVICH, E. A.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 27, 2450 (1957).

(297) RAZUMOV, A. I., MUKHACHEVA, O. A., AND SIM-DO-KHEN: Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci. (Eng. Transl.) 1952, 797; see also Chem. Abstracts 50, 7050 (1956).

(298) RAZUMOV, A. I., AND SIM-DO-KHEN: Trudy Kazan. Khim.-Tekhnol. Inst. im. S. M. Kirova 1954-1955, No. 19-20, 167; Chem. Abstracts 51, 6503 (1957).

(299) REESOR, J. W. B, AND WRIGHT, G. F.: J. Org. Chem. 22, 385 (1957).

(300) RIZPOLOZHENSKY, N. I., AND ZVEREVA, M. A.: Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk 1959, 358; Chem. Abstracts 53, 17888 (1959).

(301) RUSCHIG, H., AND AUMÜLLER, W.: German patents 1,005,-063 and 1,009,623 (1957), and U.S. patent 2,904,586 (1959); Chem. Abstracts 53, 15008 and 16063 (1959) and 54, 2216 (1960).

(302) SACCO, A.: Atti accad. nazl. Lincei, Rend., Classe sci. fis., mat. e nat. 11, 101 (1951); Chem. Abstracts 49, 158 (1955).

(303) SACCO, A.: Ann. chim. (Rome) 43, 495 (1953); Chem. Abstracts 48, 5012 (1954).

(304) SACHS, H.: Ber. 25, 1514 (1892).

(305) SANDER, M.: Chem. Ber. 93, 1220 (1960).

(306) SAUNDERS, B. C., AND WORTHY, T. S.: J. Chem. Soc. 1953, 2115.

(307) SCHENK, A., AND MICHAELIS, A.: Ber. 21, 1497 (1888).

(308) SCHMERLING, L.: U.S. patent 2,902,517 (1959); Chem. Abstracts 54, 2254 (1960).

(309) SCHMIDT, H.: Chem. Ber. 81, 477 (1948).

(310) SCHMIDT, H.: German patent 870,701 (1953); Chem. Abstracts 52, 16291 (1958).

(311) SCHMIDT, H.: German patent 875,662 (1953).

(312) SCHRADER, G.: German patent 954,244 (1956); Chem. Abstracts 53, 11305 (1959).

(313) SCHREIBER, W.: U.S. patent 2,160,915 (1939); Chem. Abstracts 33, 7553 (1939).

(314) SHEVCHENKO, V. I., AND MERKULOVA, Z. V.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 29, 985 (1959).

(315) SIEGFRIED, B., A.-G.: Swiss patent 311,982 (1956); Chem. Abstracts 51, 10559 (1957).

(316) SMITH, C. W.: U.S. patent 2,648,695 (1953); Chem. Abstracts 48, 8252 (1954).

(317) SMITH, C. W., PAYNE, G. B., AND SHOKAL, E. C.: U.S. patent 2,856,369 (1958); Chem. Abstracts 53, 2686 (1959).

(318) SMITH, W. C.: U.S. patent 2,904,588 (1959); Chem. Abstracts 54, 2254 (1960).

(319) SOBOROVSKY, L. Z., AND ZINOVYEV, YU. M.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) 24, 527 (1954).

(320) STAYNER, R. D.: U.S. patent 2,686,803 (1954); Chem. Abstracts 49, 11000 (1955).

(321) STAYNER, R. D.: U.S. patent 2,693,482 (1954); Chem. Abstracts 49, 13287 (1955).

(322) STEINKOPF, W., AND DUDEK, H.: Ber. 62, 2494 (1929).

(323) STELLING, O.: Z. physik. Chem. (Leipzig) 117, 161 (1925).

(324) STILES, A. R., AND HARMAN, D.: U.S. patent 2,711,403 (1955); Chem. Abstracts 50, 5027 (1956).

(325) STILES, A. R., HARMAN, D., AND RUST, F. F.: U.S. patent 2,724,718 (1955); Chem. Abstracts 50, 10124 (1956).

(326) TOY, A. D. F.: J. Am. Chem. Soc. 70, 186 (1948).

(327) VAN WINKLE, J. L., BELL, C. S., AND MORRIS, R. C.; U..S. patent 2,875,224 (1959); Chem. Abstracts 53, 13054 (1959).

(328) VILLE, J.: Compt. rend. 110, 348 (1890).

(329) VILLE, J.: Ann. chim. et phys. [6] 23, 289 (1891).

(330) VIOUT, M. P. (NÉE LESFAURIES): J. recherches centre natl. recherche sci., Labs. Bellevue (Paris) 28, 15 (1954); Chem. Abstracts 50, 7077 (1956).

(331) VIOUT, M. P. (NÉE LESFAURIES), AND RUMPF, P.: Bull. soc. chim. France 1957, 768.

(332) WALLING, C.: U.S. patent 2,437,796 (1948); Chem. Abstracts 42, 4199 (1948).

(333) WALLING, C., STACEY, F. W., JAMISON, S. E., AND HUYSER, E. S.: J. Am. Chem. Soc. 80, 4543 (1958).

(334) WALSH, E. N.: U.S. patent 2,860,155 (1958); Chem. Abstracts 54, 1425 (1960).

(335) WALSH, E. N., BECK, T. M., AND WOODSTOCK, W. H.: J. Am. Chem. Soc. 77, 929 (1955).

(336) WATT, G. W., AND THOMSON, R. C., JR.: J. Am. Chem. Soc. 70, 2295 (1948).

(337) WEDEKIND, E.: Ber. 45, 2933 (1912).

(338) WEIL, T.: Helv. Chim. Acta 37, 654 (1954).

(339) WEIL, T., PRIJS, B., AND ERLENMEYER, H.: Helv. Chim. Acta 35, 616 (1952).

(340) WEIL, T., PRIJS, B., AND ERLENMEYER, H.: Helv. Chim. Acta 35, 1412 (1952).

(341) WEIL, T., PRIJS, B., AND ERLENMEYER, H.: Helv. Chim. Acta 36, 142 (1953).

(342) WEIL, T., PRIJS, B., AND ERLENMEYER, H.: Helv. Chim. Acta 36, 1314 (1953).

(343) WELLER, J.: Ber. 20, 1718 (1887).

(344) WELLER, J.: Ber. 21, 1492 (1888).

(345) WHETSTONE, R. R., RAAB, W. J., AND HALL, W. E.: U.S. patent 2,867,646 (1959); Chem. Abstracts 53, 12237 (1959).

(346) WHETSTONE, R. R., AND STILES, A. R.: U.S. patent 2,802,-855 (1957); Chem. Abstracts 52, 2067 (1958)

(347) WIBERG, E., AND NÖTH, H.: Z. Naturforsch. 12b, 125 (1957); Chem. Abstracts 52, 290 (1958).

(348) WILEY, R. H., AND JARBOE, C. H.: J. Am. Chem. Soc. 73, 4996 (1951).

(349) WILLEMS, J. F.: Belgian patent 557,556 (1957); Chem. Abstracts 51, 17545 (1957).

(350) WILLSTÄTTER, R.: U.S. patent 1,205,138 (1917); Chem. Abstracts 11, 187 (1917).

(351) WILLSTÄTTER, R., AND SONNENFELD, E.: Ber. 47, 2801 (1914).

(352) WILLSTÄTTER, R., AND SONNENFELD, E.: German patent 288,393 (1914); Chem. Abstracts 10, 2501 (1916).

(353) WOODSTOCK, W. H.: U.S. patent 2,137,792 (1938); Chem. Abstracts **33**, 1763 (1939).

(354) WOODSTOCK, W. H., AND WALSH, E. N.: U.S. patent 2,685,602 (1954); Chem. Abstracts **49**, 10358 (1955).

(355) YAGUPOLSKY, L. M., AND YUFA, P. A.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) **28**, 2880 (1958).

(356) YAKUBOVICH, A. YA., AND GINSBURG, V. A.: Doklady Akad. Nauk S.S.S.R. **82**, 273 (1952); Chem. Abstracts **47**, 2685 (1953).

(357) YAKUBOVICH, A. YA., AND GINSBURG, V. A.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) **22**, 1575 (1952).

(358) YAKUBOVICH, A. YA., AND GINSBURG, V. A.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) **24**, 1455 (1954).

(359) YAKUBOVICH, A. YA., GINSBURG, V. A., AND MAKAROV, S. P.: Doklady Akad. Nauk S.S.S.R. **71**, 303 (1950); Chem. Abstracts **44**, 8320 (1950).

(360) YAKUBOVICH, A. YA., AND MOTSAREV, G. V.: Doklady Akad. Nauk S.S.S.R. **88**, 87 (1953); Chem. Abstracts **48**, 143 (1954).

(361) YAKUBOVICH, A. YA., AND MOTSAREV, G. V.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) **23**, 805 (1953).

(362) YAKUBOVICH, A. YA., AND MOTSAREV, G. V.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) **23**, 1623 (1953).

(363) ZAKHARKIN, L. I., AND OKHLOBYSTIN, O. YU.: Doklady Akad. Nauk S.S.S.R. **116**, 236 (1957); Chem. Abstracts **52**, 6167 (1958).

(364) ZAKHARKIN, L. I., AND OKHLOBYSTIN, O. YU.: U.S.S.R. patent 110,920 (1958); Chem. Abstracts **52**, 14652 (1958).

(365) ZECCHINI, F.: Gazz. chim. ital. **24**, I, 34 (1894); J. Chem. Soc. Abstracts **66**, II, 221 (1894).

(366) ZIEGLER, K., DEPARADE, W., AND MEYE, W.: German patent 864,866 (1953); Chem. Abstracts **51**, 4416 (1957).

(367) ZINOVYEV, YU. M., AND SOBOROVSKY, L. Z.: J. Gen. Chem. U.S.S.R. (Eng. Transl.) **26**, 3375 (1956).