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Hydroxyalkylphosphines and Hydroxyalkylphosphine Oxides

K.A.Petrov and V.A.Parshina

The paper discusses the condensation of phosphine and of primary and secondary phosphines with aliphatic and aromatic aldehydes and ketones, the reaction mechanisms, and the influence of the structure of the starting materials on the final products.
A detailed account is given of the chemical properties of the hydroxymethylphosphonium halides and of hydroxymethylphosphines and -phosphine oxides. Particular attention is paid to the reactions of tervalent phosphorus—oxidation, addition of sulphur, formation of quaternary phosphonium compounds with alkyl halides, alkene oxides, aldehydes, unsaturated acids, and other compounds—and also reactions at the labile hydrogen atom of the hydroxymethyl groups in hydroxymethylphosphines.
Information is given on methods for preparing organophosphorus polymers from tetrakishydroxymethylphosphonium chloride and its derivatives by the processes of polytransesterification, alcoholysis, phenolysis, and polycondensation with nitrogen-containing compounds. Problems of the practical application of the products are examined. The bibliography contains 162 references.

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I. INTRODUCTION

An important place in the chemistry of organophosphorus compounds is occupied by compounds containing a coordinatively unsaturated phosphorus atom. Among them are phosphites and phosphines, by means of which it is possible to synthesise diverse derivatives containing tervalent and quinquevalent phosphorus. The Michaelis and Arbuzov reactions, which have served as foundation for numerous researches on the chemistry of organic phosphorus compounds, are based on the use of acid and normal phosphites.

The present paper gives information, widely scattered in the literature, on the condensation of phosphine and of primary and secondary phosphines with aldehydes and ketones, the chemical properties of the condensation products, and the use of hydroxymethylphosphonium halides and of hydroxymethyl-phosphines and -phosphine oxides for the synthesis of organophosphorus polymers possessing flame-resistant and ion-exchange properties, and of alkylenediphosphine oxides suitable for use as extractants in the recovery and preparation of valuable elements.

II. CONDENSATION OF PHOSPHINE AND OF PRIMARY AND SECONDARY PHOSPHINES WITH ALDEHYDES AND KETONES

Hoffmann was the first to show that phosphine reacts with formaldehyde in the presence of hydrochloric acid at 80°C in the absence of stirring with the slow formation of tetrakishydroxymethylphosphonium chloride[1,2]:

$$PH_3 + 4CH_2O + HCl \rightarrow [P(CH_2OH)_4]^+\bar{Cl}.$$

It has since been established that the reaction is best conducted with a molar ratio of formaldehyde to hydrochloric acid of 4.2 : 1 at 20°C with vigorous stirring. These conditions ensure good absorption of phosphine and its reaction with formaldehyde. The yield of tetrakishydroxymethylphosphonium chloride reaches 85–90%.[3-7]

Condensation between phosphine and formaldehyde takes place not only under the influence of acids but also in the presence of many metals of Groups II–VII or their salts, as well as in the absence of catalysts. Good results are given by the use of mercury, silver, platinum, or palladium deposited on kieselguhr or pumice[7-9]. The reaction

is usually conducted in aqueous–alcoholic and aqueous dioxan solutions at temperatures between −10° and +40°C. When phosphine is passed into aqueous formaldehyde (pH 4–8), tetrakishydroxymethylphosphonium hydroxide $(HOCH_2)_4POH$ (pH 8.5) is formed initially[8–10], and is then further treated with phosphine, without being isolated, to be converted into trishydroxymethylphosphine (pH 6.5).[9,11] This last compound is obtained also from paraformaldehyde, suspended in water or acetonitrile, and phosphine in the presence of platinum(IV) chloride at 20–35°C:[9]

$$PH_3 + CH_2O \xrightarrow{PtCl_4\ etc.} \begin{matrix} P(CH_2OH)_3 \\ [P(CH_2OH)_4]^+\,\bar{O}H \end{matrix}.$$

Interaction between phosphine and aqueous formaldehyde under a pressure of 150–300 mmHg at 40–80°C gives a good yield of tetrakishydroxymethylphosphonium hydroxide[12,13]. When paraformaldehyde is used, the reaction is conducted at 40 atm and 80–100°C in the absence of solvent or catalyst, when a high yield of trishydroxymethylphosphine is obtained[14–16].

The hydroxymethylation of phosphine can be accomplished also in the absence of pressure, by passing phosphine into heated paraformaldehyde. Under these conditions, however, the yield of trishydroxymethylphosphine is considerably diminished[17].

Tetrakishydroxymethylphosphonium chloride consists of colourless crystals of m.p. 151°C,[17] soluble in water and the lower aliphatic alcohols but insoluble in most of the usual organic solvents. Aqueous solutions of tetrakishydroxymethylphosphonium chloride have a strongly acid reaction: at 20°C a 10% solution has pH 1.92. On neutralisation to pH not exceeding 6.5 the solutions are stable on storage for a long time[18].

Tetrakishydroxymethylphosphonium hydroxide is a colourless viscous oil, sparingly soluble in water, the pH of the solution being 8.5. With an alcoholic solution of mercuric chloride it forms the complex $(HOCH_2)_4POH.HgCl_2$ melting at 140°C, which is insoluble in water and alcohol[8,10].

Trishydroxymethylphosphine is a colourless substance of m.p. 58°C, which boils with decomposition at 115°C (2.5 mmHg [13]), and possesses the characteristic odour of phosphines. It is readily soluble in water and alcohol, but does not dissolve in non-polar organic solvents. It forms yellow adducts with quinol $(HOCH_2)_3P.C_6H_4O_2$ (m.p. 160°C) and a complex with mercuric chloride $(HOCH_2)_3P.HgCl_2$ (m.p. 135°C). Unlike the simple phosphines, which possess weakly basic properties, trishydroxymethylphosphine has a slightly acid reaction in water (pH 6.5).[9,15] Trishydroxymethylphosphine can be used as intermediate in the synthesis of various organophosphorus compounds and also of insecticides, as a component of flame-resistant treatments for textiles and wood, and as an additive to lubricating oils.

In some cases phosphines reacts with other aldehydes, depending on their structure, in the same way as with formaldehyde, to form tetrakishydroxyalkylphosphonium salts, whereas in other cases more complicated compounds are formed. The peculiarity of these reactions is mostly due to transformations of unstable intermediate products of the condensation of one or two aldehyde molecules with the phosphine.

Aldehydes without branching at the α-carbon atom react similarly to formaldehyde with phosphine. It was initially supposed that, in the presence of hydrogen chloride and bromide in ether, adducts are formed containing four moles of the aldehyde together with one mole each of phosphine and the hydrogen halide, which were not isolated in pure form[19]:

$$4\,RC\begin{matrix}O\\H\end{matrix} + PH_3 \xrightarrow{HCl} \left(R{-}C\begin{matrix}O\\H\end{matrix}\right)_4 \cdot PH_3 \cdot HCl.$$

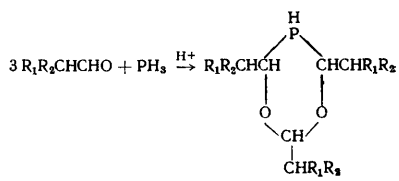
When the reaction was conducted in the presence of aqueous mineral acids (hydrochloric, hydrobromic, hydriodic, sulphuric, orthophosphoric, nitric), substances were isolated in pure form which proved to be tetrakis-1-hydroxylalkylphosphonium salts[20–23]:

$$4\,RC\begin{matrix}O\\H\end{matrix} + PH_3 \xrightarrow{HCl} \left[P\left(\begin{matrix}CH{-}R\\|\\OH\end{matrix}\right)_4\right]^+\bar{C}l$$

where R = C_{1-18} alkyl.

Good results are obtained if the aldehyde is slowly added to the reaction mixture, and organic solvents (tetrahydrofuran, butanol, dioxan) are used to increase the solubility of the phosphine and the higher aldehydes. Negative results are obtained when the reaction is conducted in the gas phase in the presence of a catalyst (aluminium silicate) at 375°C; at higher temperatures the phosphine decomposes to white phosphorus and hydrogen[20].

Aldehydes which are branched at the α-position react readily with phosphine in the presence of hydrochloric acid at room temperature, but unlike the unbranched aldehydes they form cyclic secondary phosphines having a six-membered ring. This reaction has been studied with isobutyraldehyde and 2-ethylhexanal as examples. The former gave a 75% yield of 2,4,6-tri-isopropyl-1,3-dioxa-5-phosphacyclohexane (I), and the latter a 90% yield of 2,4,6-tris-1′-ethylpentyl-1,3-dioxa-5-phosphacyclohexane (II):[20,24]



where (I) $R_1 = R_2 = CH_3$ and (II) $R_1 = C_2H_5$, $R_2 = n\text{-}C_4H_9$.

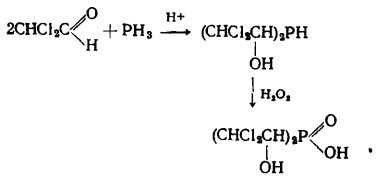
The compound (I) reacts with sulphur in benzene to form the corresponding sulphide, which possesses herbicidal activity[25]. It is assumed that the reaction involves the intermediate formation of secondary phosphines $[R_1R_2CHCH(OH)]_2PH$, which are unable to form quaternary phosphonium salts because of steric hindrance, but react with the aldehyde to give six-membered cyclic phosphines. The products have been subjected to detailed study.

Chlorinated aldehydes also react with phosphine. Chloroacetaldehyde and phosphine in the presence of hydrochloric acid (ratio 3 : 1) form an amorphous solid, which could not be isolated in pure form[20]. In the presence of a catalyst (platinum tetrachloride) it is assumed that tris-2-chloro-1-hydroxyethylphosphine is produced[26]:

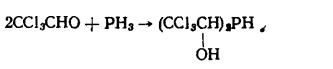
$$ClCH_2CHO + PH_3 \xrightarrow{PtCl_4} P\left(\begin{matrix}CH{-}CH_2Cl\\|\\OH\end{matrix}\right)_3.$$

Phosphine reacts with dichloroacetaldehyde in the presence of concentrated hydrochloric acid in tetrahydrofuran with the assumed formation of bis-2,2-dichloro-1-hydroxyethylphosphine, which also could not be isolated as an

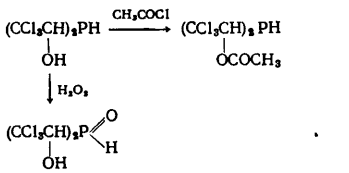
individual compound. On oxidation this product is converted into bis-2,2-dichloro-1-hydroxyethylphosphinic acid[20]:



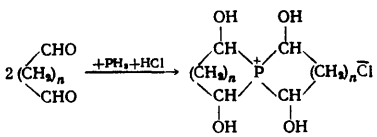
In contrast to the mono- and di-halogenated aldehydes, chloral and chloral hydrate react very vigorously with phosphine to give a 95% yield of bis-2,2,2-trichloro-1-hydroxyethylphosphine[20,27-29]:



Tris-2,2,2-trichloro-1-hydroxyethylphosphine was also obtained in this reaction[30]. On oxidation with hydrogen peroxide it yields the corresponding phosphine oxide, and on acetylation a diacetyl derivative[20]:

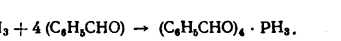


Dialdehydes, among which glutaraldehyde and succinaldehyde have been studied as examples, react readily with phosphine in the presence of concentrated hydrochloric acid in tetrahydrofuran at 20°C.[20] The products of this reaction are relatively stable five- and six-membered spirocyclic phosphonium salts. Glutaraldehyde gives a 65% yield of 2,2',6,6'-tetrahydroxy-1,1'-spirobiphosphanium chloride (I), and succinaldehyde a 34% yield of 2,2',5,5'-tetrahydroxy-1,1'-spirobiphospholanium chloride (II):

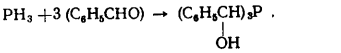


where (I) $n = 3$ and (II) $n = 2$. These spirans and their nitrogen analogues are difficultly accessible compounds.

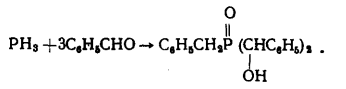
It was originally considered that phosphine reacts with aromatic aldehydes in roughly the same way as with aliphatic aldehydes. It was supposed that the interaction of benzaldehyde and phosphine in the presence of hydrogen chloride in ethereal solution gave a crystalline adduct[19]:



This has since been assigned the structure of tris-α-hydroxybenzylphosphine[31]:

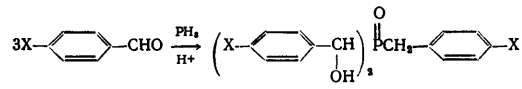


However, the compound was then found to be benzylbis-1-hydroxybenzylphosphine oxide†, whose formation involves the transfer of oxygen from carbon to phosphorus[33,35]:



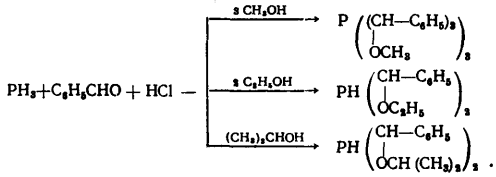
The structure of the product as an oxide is supported by many data[32,33].

Substituted aromatic aldehydes react similarly to benzaldehyde with phosphine in dioxan or tetrahydrofuran[33,35]:



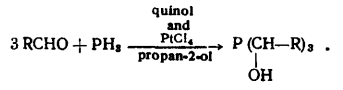
where X = Cl, Br, CH_3, C_3H_7. *p*-Nitrobenzaldehyde, *p*-hydroxybenzaldehyde, and naphthaldehyde also react with phosphine, but it has not proved possible to isolate the reaction products in pure form and establish their structure.

Benzaldehyde reacts differently with phosphine in alcoholic solution, different products being formed according to the alcohol taken[31]—tris-α-methoxybenzylphosphine in methanol, bis-α-ethoxybenzylphosphine in ethanol, and bis-α-isopropoxybenzylphosphine in propan-2-ol:



It is assumed that hemiacetals are formed in the first stage of this reaction, and these react with phosphine by a bimolecular or a termolecular mechanism[36].

Various aldehydes are able to react with phosphine in the presence of catalysts other than mineral acids to form tertiary α-hydroxy-phosphines[26], e.g.

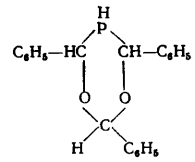


The compounds obtained, like trishydroxymethylphosphine, can be used as intermediates for organic synthesis, as insecticides, and as additives for lubricating oils.

The first attempts to promote reaction between phosphine and ketones in the presence of catalytic quantities of an acid were unsuccessful[37]. However, it has since been found that this reaction goes readily in strongly acid media.

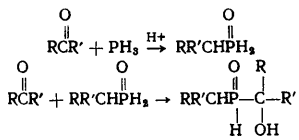
A mixture of two products—a primary phosphine oxide and a secondary 1-hydroxyalkylphosphine oxide—is obtained by the interaction of phosphine and a ketone (mixed with concentrated hydrochloric acid) in the molar proportions 1:3. Formation of the first of these products involves the transfer of oxygen from the carbonyl carbon to

† The cyclic acetal



is formed in 10–40% yield as a by-product[31,34].

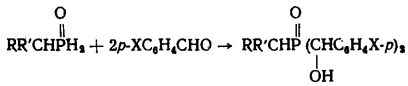
phosphorus, while the second involves the normal carbonyl addition of the ketone to the primary phosphine oxide[38,39]:



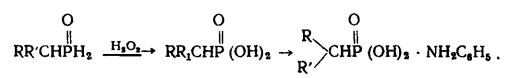
where R and R′ = alkyl, aryl.

The reaction was accomplished by passing phosphine into a solution of the ketone in concentrated hydrochloric acid at room temperature. The proportions of the products formed depends on the nature of the ketones, which can be arranged in the sequence—cyclohexanone < cyclopentanone < acetone < pentan-2-one < heptan-2-one < < pentan-3-one < acetophenone < heptan-4-one—according to increasing quantity of the primary phosphine oxide formed. The ratio of this primary product to the secondary phosphine oxide varies correspondingly from 9 : 1 with heptan-4-one to 1 : 9 with cyclohexanone, and the duration of the reaction from 30 min with cyclohexanone to 11 h with heptan-4-one; acetophenone reacts at the same rate as acetone[37].

Primary phosphine oxides, which are stable in acid solution at −80°C, have not been isolated in individual form. The presence of such compounds in the reaction mixture was proved by converting them into various derivatives. Thus treatment with aromatic aldehydes gave the corresponding tertiary bishydroxyalkylphosphine oxides:

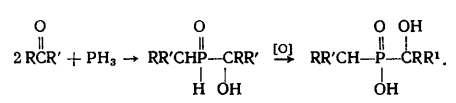


where X = H, Cl; and on oxidation the phosphonic acids were isolated (as their aniline salts):

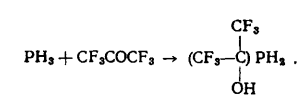


Thus the condensation of phosphines with ketones provides a convenient method for obtaining alkylphosphonic acids in which the phosphorus is bound to a secondary carbon atom.

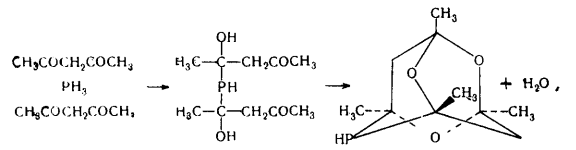
Secondary hydroxyalkylphosphine oxides have been isolated as crystalline substances from the reactions of cyclohexanone, cyclopentanone, acetone, and acetophenone with phosphine. On oxidation with nitric acid or hydrogen peroxide they gave the corresponding phosphinic acids:



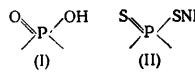
Hexafluoroacetone reacts with phosphine when heated in an autoclave to form as the sole product 2,2,2-trifluoro-1-hydroxy-1-trifluoromethylethylphosphine[40,41]:



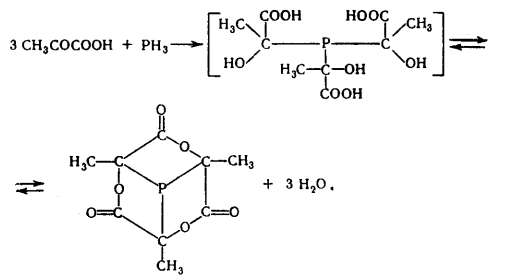
Diketones also react readily with phosphine, but heterocyclic systems are formed[42]. For example, the reaction with pentane-2,4-dione in hydrochloric acid solution has been studied, and crystalline 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphadamantane isolated, obviously formed via an intermediate secondary phosphine:



The chemical properties of the product were typical of secondary phosphines. Oxidation with hydrogen peroxide gave the phosphinic acid (I), and treatment with sulphur and ammonium hydroxide yielded the ammonium phosphinodithioate (II)



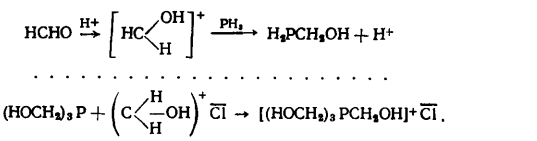
In the presence of ethereal hydrogen chloride phosphine reacts also with pyruvic acid (in the molar proportions 1 : 3) to give an almost quantitative yield of a compound $C_9H_9O_6P$, presumably with intramolecular esterification of carboxyl and hydroxyl groups present in an intermediate unstable tertiary phosphine[33]:



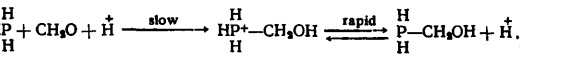
Thus the structure of the product represents a tricyclic system, in which three five-membered rings have fused at the phosphorus atom. The most intense absorption bands in the infrared spectrum of this compound are located near 1784 cm^{-1}, which corresponds to stretching vibrations of an ester carbonyl group, while no absorption bands are present corresponding to stretching vibrations of COOH and OH groups. The above reaction is general in character, and has been studied in a series of other acids of formula RCOCOOH, where R = C_{1-6} alkyl[43].

The reactions of phosphine with aldehydes and ketones yield various products depending on the starting materials, the catalysts, and the solvents. However, it is generally accepted that, whatever the final products, these reactions are very similar in their mechanism in the early stages of condensation with phosphine. Several opinions, sometimes differing only in details, are held concerning the mechanism of this reaction. According to one of them the interaction of phosphine with formaldehyde catalysed by a proton involves the initial formation of a "formaldehyde cation", which then reacts with more phosphine to give hydroxymethylphosphine and a proton. The latter again enters into reaction with formaldehyde to form the formaldehyde cation, which reacts with the hydroxymethylphosphine to give bis- and tris-hydroxymethylphosphines, and

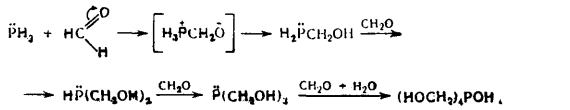
ultimately tetrakishydroxymethylphosphonium salts or bases[44]:



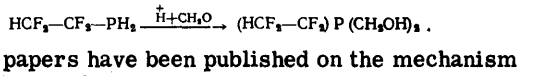
Besides this bimolecular mechanism, a termolecular reaction mechanism has been suggested, involving the initial formation of a monohydroxyalkylphosphonium salt, which is converted into a monohydroxyalkylphosphine with loss of a proton, and then into di- and tri-substituted phosphines and phosphonium salts or bases:



When condensation takes place in the absence of a catalyst, it is assumed that an intermediate phosphine—formaldehyde complex is formed, which is converted into hydroxymethylphosphine and then, by an analogous scheme, reacts with formaldehyde to form bis- and tris-hydroxymethylphosphines and tetrakishydroxymethylphosphonium hydroxide[13,15]:

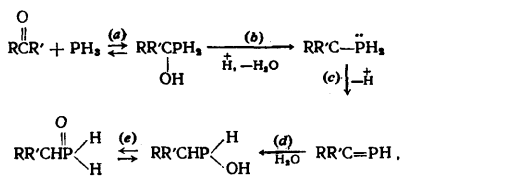


The ability of phosphine and of methyl- and dimethylphosphines to add formaldehyde is governed by the nucleophilic character of the former and the polarity of the C=O bond in the latter. The reactivity of the phosphines varies in conformity with their nucleophilic character[15] in the sequence $PH_3 < CH_3PH_2 < (CH_3)_2PH$, and when it is very low[45-49] phosphines do not react with formaldehyde in the absence of a catalyst. For example, 1,1,2,2-tetrafluoroethylphosphine, which possesses weak electron-donor power, yields with formaldehyde bishydroxymethyltetrafluoroethylphosphine only in the presence of hydrochloric acid[13]:



Several papers have been published on the mechanism of the reactions undergone by phosphine and alkylphosphines with formaldehyde; studies have been made of the kinetics, and the activation energies have been calculated[50].

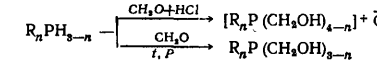
For phosphine the mechanism of the reaction, accompanied by the transfer of oxygen from carbon to phosphorus, is expressed by the scheme[37]



Phosphine first adds to the ketone as to aliphatic aldehydes (*a*). In strongly acid medium a carbonium ion is formed [*b*], which is stabilised as an intermediate compound containing a carbon–phosphorus double bond (*c*), hydration of which (*d*) yields a primary phosphine oxide (*e*).

Data have been published indicating that reactions involving the migration of oxygen from phosphorus to carbon are analogous to allyl rearrangements, and represent a general phenomenon for the series of α-substituted derivatives of tervalent phosphorus[51].

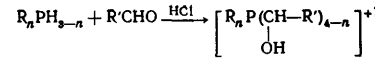
Like phosphine itself, primary and secondary phosphines react with aqueous formaldehyde in the presence of an equimolecular quantity of hydrochloric acid to form quaternary phosphonium salts[37,52-56], but when heated (to 65–100°C) with paraformaldehyde under pressure hydroxymethylphosphines are formed[13,52,57-61]:



where $n = 1, 2$ and R = alkyl, aryl.

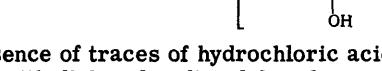
Hydroxymethylphosphonium salts are more stable towards hydrolysis[52] than are quaternary alkylhydroxymethylammonium salts, which are decomposed by water to amine hydrochlorides and formaldehyde.

The condensation of primary and secondary phosphines with aldehydes and ketones is greatly influenced by the structure of both components. Study of the reactions of aliphatic aldehydes with phosphines (propyl-, phenyl-, and diphenyl-phosphines) has shown that, in the presence of an equimolecular quantity of hydrochloric acid, phosphonium chlorides are formed[33,37,55,62,63]:

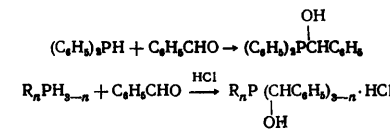


where $n = 1, 2$, R = alkyl, aryl, and R′ = alkyl.

A quaternary phosphonium salt is formed also by dibutylphosphine with benzaldehyde[33]:

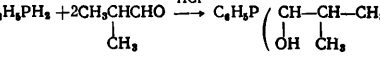


In the presence of traces of hydrochloric acid benzaldehyde condenses with diphenyl-, dicyclohexyl-, and isobutylphosphines to give tertiary phosphines[37,55,64,65] or their hydrochlorides[37]:

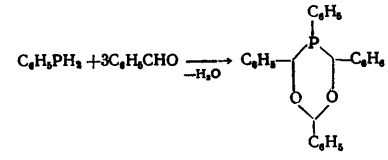


where $n = 1, 2$ and R = iso-C_4H_9, cyclo-C_6H_{11}.

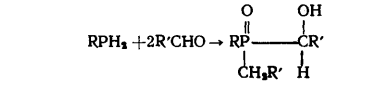
Phenylphosphine forms with isobutyraldehyde the hydrochloride of a tertiary phosphine even in excess of hydrochloric acid at 20°C:[37]



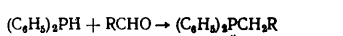
With benzaldehyde in the presence of a small amount of hydrogen chloride in acetonitrile or methanol phenylphosphine gives a 59% yield of a cyclic product[37]:



In boiling strongly acid medium primary phosphines react with aromatic aldehydes, and secondary phosphines (diphenylphosphine) react with aliphatic and aromatic aldehydes, to form phosphine oxides[37]:

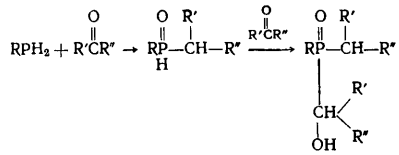


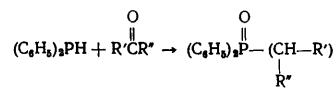
where R = alkyl, cycloalkyl, aryl and R′ = aryl, naphthyl;



where R = alkyl, aryl, naphthyl.

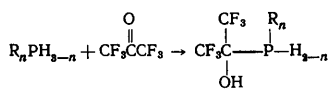
Primary and secondary aromatic phosphines react with ketones in strongly acid medium on heating to form the corresponding tertiary phosphine oxides‡ [37]:





where R = alkyl, aryl, cycloalkyl, and R′, R″ = alkyl, aryl or R′ + R″ = cycloalkyl, indol-1-yl.

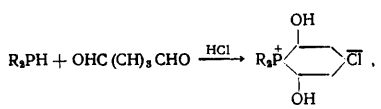
Fluorinated ketones form with primary and secondary phosphines the corresponding 1-hydroxyalkylphosphines [40,41]:



where n = 1, 2 and R = CH_3.

Several primary phosphines (isobutyl-, octyl-, phenylphosphines), on treatment with pentane-2,4-dione, give crystalline polycyclic tertiary phosphines [42].

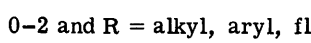
A cyclic phosphonium salt is obtained from a dialdehyde and a secondary phosphine [66]:



Thus the reactions undergone by phosphine and phosphines with aldehydes and ketones can be divided into two groups—reactions involving normal carbonyl addition with formation of phosphines, their salts, and quaternary phosphonium bases, and reactions accompanied by migration of oxygen from carbon to phosphorus in the hydroxymethylphosphines produced initially, and leading to the synthesis of tertiary phosphine oxides.

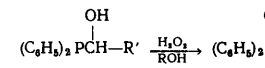
III. CHEMICAL PROPERTIES OF HYDROXYMETHYLPHOSPHONIUM HALIDES AND OF HYDROXYMETHYLPHOSPHINES AND -PHOSPHINE OXIDES

Trishydroxymethylphosphine and substituted hydroxymethylphosphines, like other compounds containing a tervalent phosphorus atom, are readily oxidised, and sulphur, and form quaternary phosphonium compounds: i.e. the chemical properties of hydroxymethylphosphines, like those of other phosphines, are determined by the presence of a coordinatively unsaturated phosphorus atom. Thus on oxidation with oxygen [52,64,67], hydrogen peroxide [13,15,37,68-71], nitric acid [67], peracetic acid [52], potassium permanganate [67], and oxides of nitrogen they are converted into phosphine oxides§.



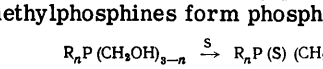
where n = 0–2 and R = alkyl, aryl, fluorinated alkyl, cycloalkyl.

Oxidation in alcohol yields α-alkoxyalkylphosphine oxides [37]:



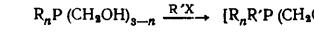
where R = alkyl, aryl and R′ = naphthyl.

With sulphur trishydroxymethylphosphine and substituted hydroxymethylphosphines form phosphine sulphides [52,72,73]:



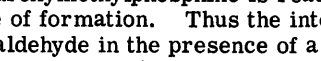
where n = 0–2 and R = alkyl, aryl.

Trishydroxymethylphosphine and substituted hydroxymethylphosphines react with alkyl halides and with toluene-*p*-sulphonic and alkyl- and aryl-phosphonic esters to form quaternary phosphonium salts [16,17,56,63,74-78]:

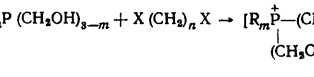


where n = 0–2, R = alkyl, aryl, and X = halogen, anion of corresponding acid.

Trishydroxymethylphosphine is readily alkylated even in the course of formation. Thus the interaction of phosphine with formaldehyde in the presence of a catalyst (a salt of a metal in Groups II–VII) and an alkylating agent yields an alkyl(aryl)trishydroxymethylphosphonium halide [79-81]:

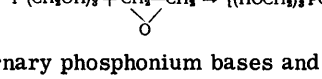


Trishydroxymethylphosphine and dialkyl(aryl)hydroxymethylphosphines react with dihalogenoalkanes, both in solution and in the absence of a solvent, to give a quantitative yield of the quaternary phosphonium salts [75,82]:

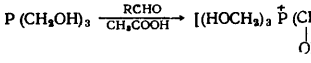


where n = 1–4, m = 0–2, R = alkyl, aryl, and X = Br, I.

Quaternary phosphonium compounds are obtained also by the interaction of trishydroxymethylphosphine with alkylene oxides [83-85] at 50–100°C in water or in an organic solvent which is miscible with water (dimethylformamide, acetonitrile, lower alcohols, ketones). Quaternary phosphonium salts are obtained in the presence of mineral or organic acids, and quaternary phosphonium hydroxides in their absence:



Quaternary phosphonium bases and salts are formed by the action of aldehydes on trishydroxymethylphosphine in the presence of water, a mineral acid, or an organic acid. Saturated and unsaturated aliphatic and aromatic aldehydes and various derivatives thereof have been studied in this reaction [10]:



Trishydroxymethylphosphine reacts with hydroxymethylated derivatives of urea to form quaternary phosphonium

‡ In the case of primary phosphines the reaction involves the addition of one or two molecules of the ketone depending on the structure of the initial phosphine and the ketone.

§ Trishydroxymethylphosphine oxide can be used as starting material for various syntheses and in flame-resistant treatments for textiles and wood.

compounds, which are recommended as intermediates in the production of flame-resistant fibre-forming plastics[86]:

$$P(CH_2OH)_3 \xrightarrow{NH_2CONH(CH_2OH)} [P(CH_2OH)_3CH_2NHCONH_2]^+\overline{OH}.$$

The action on trishydroxymethylphosphine of $\alpha\beta$-unsaturated aliphatic acids, their esters, and their amides in the presence of water and acids in a water-soluble organic solvent yields phosphorus analogues of betaines[87]:

$$P(CH_2OH)_3 \xrightarrow{CH_2=CHCOOH} \begin{matrix} \overset{+}{P}(CH_2OH)_3 \\ | \\ CH_2CH_2COO \end{matrix}.$$

Treatment of trishydroxymethylphosphine with $\alpha\beta$-unsaturated nitriles produces unstable phosphonium salts, which are able to split off hydroxymethyl groups. Thus with three moles of acrylonitrile trishydroxymethylphosphine forms tris-2-cyanoethylphosphine[88]:

$$P(CH_2OH)_3 \xrightarrow[H_2O]{CH_2=CH-CN} [(HOCH_2)_3\overset{+}{P}CH_2CH_2CN]\,\overline{OH} \xrightarrow[-(CH_2O+H_2O)]{} (HOCH_2)_3PCH_2CH_2CN$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$(HOCH_2)P(CH_2CH_2CN)_2 \xrightarrow[-(CH_2O+H_2O)]{CH_2=CHCN} [HOCH_2\overset{+}{P}(CH_2CH_2CN)_2]\,\overline{OH} \rightarrow P(CH_2CH_2CN)_3.$$

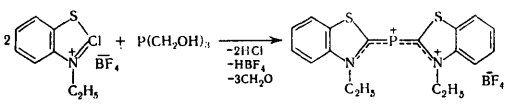
Trishydroxymethylphosphine reacts with butylsulphenyl chloride and with diethylchloramine to form quaternary phosphonium salts[89]:

$$P(CH_2OH)_3 \xrightarrow{C_4H_9SCl} \left[\begin{matrix} P(CH_2OH)_3 \\ | \\ SC_4H_9 \end{matrix}\right]^+\overline{Cl}$$

$$P(CH_2OH)_3 \xrightarrow{(C_2H_5)_2NCl} \left[\begin{matrix} P(CH_2OH)_3 \\ | \\ N(C_2H_5)_2 \end{matrix}\right]^+\overline{Cl}.$$

Quaternary phosphonium salts are recommended for use as additives in lubricating oils and as flame-resistant finishes for textiles[75], and also as pesticides and fungicides[21,23].

Trishydroxymethylphosphine has been used to prepare new coloured compounds, phosphamethincyanines, containing tervalent phosphorus having a coordination number of 2. Thus, in the presence of ethyldi-isopropylamine, 2-chloro-*N*-ethylbenzothiazole fluoroborate and trishydroxymethylphosphine gave a 45% yield of phosphamethincyanine[90]:



Other symmetrical and unsymmetrical phosphamethincyanines have been obtained in a similar manner.

Like alcohols, hydroxymethylphosphines are able to form alkoxides on treatment with metallic sodium[17]:

$$RP(CH_2OH)_2 + Na \rightarrow RP(CH_2ONa)_2 + H_2$$

where R = alkyl.

With diethylamine, hydroxymethylphosphines form aminomethylphosphines[89]:

$$R_nP(CH_2OH)_{3-n} \xrightarrow{HN(C_2H_5)_2} R_nP[CH_2N(C_2H_5)_2]_{3-n}$$

where n = 0–2 and R = alkyl. The products are able to react with compounds containing labile hydrogen[90]. Compounds of a similar type are obtained also by the action of secondary amines on tetrakishydroxymethylphosphonium chloride[91]:

$$[P(CH_2OH)_4]^+\overline{Cl} + 4HNR_2 \rightarrow (R_2NCH_2)_3P + CH_2O + R_2NH\cdot HCl$$

where R = alkyl, allyl or R_2N = morpholino; by the action of formaldehyde on phosphine and phosphines in the presence of secondary amines[92] or amides[93]:

$$R_{3-n}PH_n + nCH_2O + nHNR'_2 \rightarrow (R'_2NCH_2)_nPR_{3-n} + nH_2O$$

where n = 0–2 and R,R′ = alkyl; and also from the reaction between primary phosphines and tetraethylmethylenediamine[89]:

$$C_6H_5PH_2 + 2(C_2H_5)_2NCH_2N(C_2H_5)_2 \rightarrow C_6H_5P[CH_2N(C_2H_5)_2]_2 + 2(C_2H_5)_2NH.$$

Esters of hydroxymethylphosphines are formed by the action of acylating agents on hydroxymethylphosphines or their sodium salts[17,68]:

$$\left.\begin{matrix} R_2PCH_2OH \\ R_2PCH_2ONa \end{matrix}\right\} \xrightarrow{R'COCl} R_2P(CH_2OCOR').$$

These compounds are obtained also by the alkaline decomposition of the corresponding acylated quaternary phosphonium salts[94,95]:

$$[R_nP(CH_2OCOCH_3)_{4-n}]^+\overline{X} \xrightarrow{NaOH} R_nP(CH_2OCOCH_3)_{3-n}$$

where n = 0–2 and R = alkyl.

Cases are unknown in which ethers have been obtained directly from hydroxymethylphosphines. The alcoholysis of trischloromethylphosphine results in formation of the methylbisalkoxymethylphosphine oxide[51,96]:

$$(ClCH_2)_3P \xrightarrow[ROH]{RONa} \begin{matrix} O \\ \| \\ CH_3P(CH_2OR)_2 \end{matrix}.$$

Hydroxymethylphosphines isomerise when heated. Thus methyldicyclohexylphosphine oxide has been obtained from dicyclohexylhydroxymethylphosphine[52]:

$$(\text{cyclo-}C_6H_{11})_2PCH_2OH \xrightarrow[3\ h]{240-250^\circ} \begin{matrix} O \\ \| \\ (\text{cyclo-}C_6H_{11})_2PCH_3 \\ 40.5\% \end{matrix} + \begin{matrix} (\text{cyclo-}C_6H_{11})_2PH \\ 49.5\% \end{matrix} + CH_2O$$

and alkylphosphine oxides from 1-hydroxyalkyldiphenylphosphines on boiling in acetic acid in the presence of toluene-*p*-sulphonic acid[62]:

$$(C_6H_5)_2\underset{\underset{OH}{|}}{PCH}-R \xrightarrow[CH_3-C_6H_4-SO_3OH]{CH_3COOH} \begin{matrix} O \\ \| \\ (C_6H_5)_2PCH_2R \end{matrix}$$

where R = H, alkyl, phenyl.

The chemical properties of hydroxymethylphosphonium salts and bases, unlike those of hydroxymethylphosphines, are determined solely by the hydroxymethyl groups. These groups in the quaternary salts can be acylated by acid chlorides[94,95] or acid anhydrides[52]:

$$[R_nP(CH_2OH)_{4-n}]^+\overline{X} \rightarrow [R_nR(CH_2O\overset{O}{\overset{\|}{C}}R')_{4-n}]^+\overline{X}$$

where n = 0–3 and R, R′ = alkyl, aryl. They can be converted into chloromethyl groups by the action of phosphorus pentachloride[2,97] or thionyl chloride[52,54,63,97]:

$$[R_nP(CH_2OH)_{4-n}]^+\overline{Cl} \xrightarrow{SOCl_2(PCl_5)} [R_nP(CH_2Cl)_{4-n}]^+\overline{Cl}$$

where n = 0–2 and R = alkyl, aryl; or

$$[P(CH_2OH)_4]^+\overline{OH} \xrightarrow[CCl_4]{PCl_5} (ClCH_2)_4PCl^{12,13}.$$

With phenyl isocyanate hydroxymethyltriphenylphosphonium fluoroborate forms the corresponding phenylurethane[52]:

$$[(C_6H_5)_3PCH_2OH]^+\overline{BF_4} + C_6H_5NC{=}O \rightarrow [(C_6H_5)_3PCH_2O\overset{O}{\overset{\|}{C}}NHC_6H_5]^+\overline{BF_4}$$

and with diazomethane it gives methyltriphenylphosphonium fluoroborate[52]:

$$[(C_6H_5)_3PCH_2OH]^+\overline{BF_4} \xrightarrow[-CH_2O]{CH_2N_2} (C_6H_5)_3P + \{|CH_3^+\} \rightarrow [(C_6H_5)_3PCH_3]^+\overline{BF_4}\,.$$

An interesting property of hydroxymethylphosphonium halides is their tendency to split into tertiary phosphine and phosphine oxides. For example, treatment of tetrakishydroxymethylphosphonium chloride with excess of aqueous alkali yields the tertiary phosphine oxide, hydrogen, and an aldehyde:

$$P(CH_2OH)_4Cl + NaOH \rightarrow (HOCH_2)_3P{=}O + CH_2O + H_2 + NaCl\,.$$

Trishydroxymethylphosphine oxide was first isolated by Hoffmann as the tribenzoate. It has since been found that an 80% yield of the pure oxide can be obtained from tetrakishydroxymethylphosphonium chloride by the action of barium carbonate[98,99]. However, the isolation of trishydroxymethylphosphine oxide from an aqueous solution containing a metal chloride is extremely difficult, owing to its solubility in water and its sparing solubility in organic solvents. Good results have been obtained by prolonged extraction from concentrated solutions with alcohol. Trishydroxymethylphosphine oxide is obtained also by the action of lead carbonate in propan-1-ol on tetrakishydroxymethylphosphonium chloride[100].

When trishydroxymethylphosphine oxide is treated with alkalis under more severe conditions, a molecule of hydrogen is split off, and salts of phosphinic acids are formed:

$$P(O)(CH_2OH)_3 \xrightarrow{NaOH} \underset{\underset{ONa}{|}}{P(O)(CH_2OH)_2}\,.$$

Bishydroxymethylphosphinic acid can be obtained from tetrakishydroxymethylphosphonium chloride by boiling the latter with alkali or with sodium carbonate[98]:

$$(HOCH_2)_4PCl + Na_2CO_3 + 3H_2O \rightarrow 3\,(HOCH_2)_2P\overset{\overset{O}{\|}}{<}_{OH} + 4CH_2O + 4H_2 + 2NaCl + CO_2$$

or by heating sodium hypophosphite with paraform and then acidifying the product with an acid[101]:

$$NaH_2PO_2 + nCH_2O \rightarrow \underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}(CH_2OH)_2}\,.$$

Alkyltrishydroxymethylphosphonium halides are decomposed by excess of aqueous alkali with the formation of tertiary phosphine oxides. Thus treatment of propyltrishydroxymethylphosphonium chloride with barium hydroxide octahydrate at 60°C gives propylbishydroxymethylphosphine oxide[63]:

$$[C_3H_7P(CH_2OH)_3]^+\overline{Cl} \xrightarrow{Ba(OH)_2\cdot 8H_2O} \underset{\underset{O}{\|}}{C_3H_7P(CH_2OH)_2}\,.$$

Hydroxymethylphosphine oxides can be acylated by the ethyl esters[68] and by the chlorides[2,63,68,102-104] of carboxylic acids, when one, two, or three hydroxymethyl groups may react:

$$\underset{\underset{O}{\|}}{R_nP(CH_2OH)_{3-n}} \xrightarrow{RCOCl} \underset{\underset{O}{\|}}{R_nP(CH_2OCOR)_{3-n}}$$

where n = 0–2 and R = alkyl, aryl. The reaction of hydroxymethylphosphine oxides with thionyl chloride[52,63] and with phosphorus pentachloride[70] yields chloromethylphosphine oxides:

$$\underset{\underset{O}{\|}}{R_nP(CH_2OH)_{3-n}} \xrightarrow{PCl_5(SOCl_2)} \underset{\underset{O}{\|}}{R_nP(CH_2Cl)_{3-n}}$$

where n = 0–2 and R = alkyl, aryl.

Tetrakishydroxymethylphosphonium chloride and alkyl(aryl)hydroxymethylphosphonium halides are decomposed by the calculated quantities of alkali[53,62,68], alcoholic alkali[53,68], or sodium ethoxide[53] to tertiary hydroxymethylphosphines¶:

$$[R_nP(CH_2OH)_{4-n}]^+\overline{X} \xrightarrow{NaOH} R_nP(CH_2OH)_{3-n} + CH_2O + NaCl$$

where n = 0–2 and R = alkyl, aryl. The decomposition of bis-1-hydroxyalkyldiphenylphosphonium chlorides by aqueous alkalis is accompanied by side-reactions, which lower the yields of 1-hydroxyalkyldiphenylphosphines[61].

The action of tertiary amines on hydroxymethylphosphonium halides also splits off formaldehyde, to give good yields of tertiary phosphines[73,76]:

$$[R_nP(CH_2OH)_{4-n}]^+\overline{Cl} \xrightarrow[-(C_2H_5)_3N\cdot HCl]{(C_2H_5)_3N} R_nP(CH_2OH)_{3-n}$$

where n = 0–2 and R = alkyl, aryl.

The alkylation of hydroxymethylphosphines and the dealkylation of hydroxymethylphosphonium halides yield tertiary hydroxymethylphosphines and phosphines containing no hydroxymethyl groups[52,62,73,76], dialkylamides of bishydroxymethylphosphinous acid[89]:

$$[RP(CH_2OH)_3]^+\overline{X} \xrightarrow{\overline{B}} RP(CH_2OH)_2 \xrightarrow{R'X} [RR'P(CH_2OH)_2]^+\overline{X} \xrightarrow{\overline{B}}$$

$$\rightarrow RR'P(CH_2OH) \xrightarrow{R''X} [RR'R''P(CH_2OH)]^+\overline{X} \xrightarrow{\overline{B}} RR'R''P$$

where R = alkyl, aralkyl, dialkylamino and $\overline{B}$ = NaOH, $(C_2H_5)_3N$, and also diphosphines[82,107]:

$$\left[\begin{array}{cc} R_2\overset{+}{P}-(CH_2)_n & -\overset{+}{P}R_2 \\ | & | \\ CH_2OH & CH_2OH \end{array}\right] 2\overline{X} \xrightarrow[-(2CH_2O+2NaCl)]{\text{conc. NaOH}} R_2P(CH_2)_nPR_2.$$

Tertiary amines proved to be unsuitable for the decomposition of diphosphonium salts.

Alkylenediphosphine oxides can be obtained by the oxidation of alkylenediphosphines†.

IV. PREPARATION OF PHOSPHORUS-CONTAINING POLYMERS BASED ON TETRAKISHYDROXYMETHYLPHOSPHONIUM CHLORIDE AND ITS DERIVATIVES

In contrast to phosphorus-containing insecticides, plasticisers, lubricating-oil additives, etc., organophosphorus polymers have not hitherto found wide application.

¶ The action of alkalis on chloromethylphosphonium halides similarly yields chloromethylphosphines[2,52,54,70,105]:

$$[R_nP(CH_2Cl)_{4-n}]^+\overline{X} \xrightarrow{NaOH} R_nP(CH_2Cl)_{3-n} + nCH_2O + NaCl + H_2O$$

where n = 0–2, R = alkyl, aryl, and X = Cl, BF_4. However, side-reactions are also possible, which considerably diminish the yield of tertiary phosphines. When, for example, tetrakischloromethylphosphonium chloride is boiled, methylbischloromethylphosphine oxide is formed[106]:

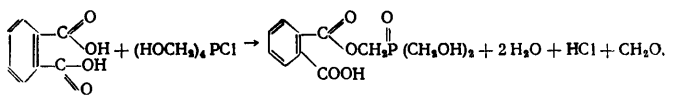
$$[P(CH_2Cl)_4]^+\overline{Cl} \xrightarrow{NaOH} \underset{\underset{O}{\|}}{CH_3P(CH_2Cl)_2}\,.$$

† Alkylenediphosphine oxides are known to be effective extractants for the recovery and separation of rare-earth metals[108-110]. Until now, however, they have been relatively difficultly accessible compounds[107,111-126].

However, available data indicate that several of them, possessing specific properties, may be of practical interest. Thus great attention is being paid to the search for phosphorus-containing polymers suitable for surface coatings on metals and for impregnating various materials in order to confer on them in some cases corrosion-resistance and in others non-flammability.

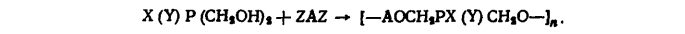
Such polymers can be obtained from tetrakishydroxymethylphosphonium chloride‡, trishydroxymethylphosphine oxide, bishydroxymethylphosphinic acid, alkyl(aryl)bishydroxymethylphosphines, and the corresponding phosphine oxides. The hydroxymethyl groups confer on these substances the properties of alcohols and aldehydes (in particular formaldehyde). Therefore they can be employed on the one hand as glycols for the preparation of polyesters (by polyesterification with dibasic acids, by the transesterification of esters, or by the alcoholysis of amides of phosphorus acids) and on the other as the phosphorus component for the production of high polymers by condensation with nitrogen-containing compounds and with phenols.

Tetrakishydroxymethylphosphonium chloride and bishydroxymethylphosphinic acid react with numerous carboxylic acids and their anhydrides to form phosphorus-containing polymers resembling alkyd resins[99,128-131]. The reaction involves the intermediate formation of monomeric substances of the following structure:



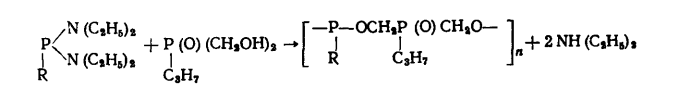
With dibasic acids the final products are fusible, transparent resins, probably of linear structure, and possessing self-extinguishability. With sebacic acid, for example, a rubberlike elastic polymer is obtained, showing good compatibility with polyethylene and conferring self-extinguishing properties on the latter; citric, succinic, phthalic, and adipic acids yield viscous liquids or brittle solids. These resins can be used for the production of corrosion-resistant films on metal surfaces.

Phosphorus-containing esters are obtained by the polycondensation of alkylbishydroxymethylphosphines and the corresponding oxides and sulphides with dicarboxylic acids or their esters, anhydrides, or chlorides[132,133]:



Phosphorus-containing carboxylic acids have also been subjected to this reaction[134].

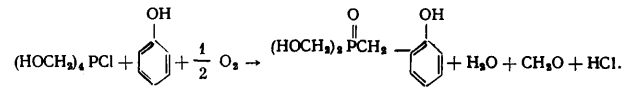
Alcoholysis of the tetraethyldiamides of methylphosphonous and phenylphosphonous acids with propylbishydroxymethylphosphine oxide gives polymers of the following type[134]:



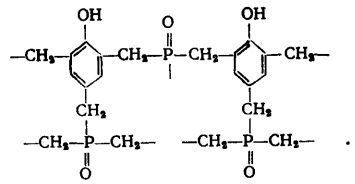
where R = alkyl, aryl. The polymers are semi-solid resinlike substances (especially those from phenylphosphonous tetraethyldiamide) having molecular weights up to 18 000. The low softening points (30–50°C) are probably due to the high phosphorus contents of the polymer molecules.

‡ When tetrakishydroxymethylphosphonium chloride is heated at 150–200°C, liquid polymers are formed which can be used for the impregnation of cellulosic materials to make them non-flammable[127].

Tetrakishydroxymethylphosphonium chloride, trishydroxymethylphosphine oxide[135], and alkylbishydroxymethylphosphines react through their hydroxy-groups with phenols, water being eliminated and phosphorus-containing polymers of linear and network structure being formed (hydroxymethyl- and bishydroxymethyl-phosphinic acids, in contrast, form not phosphorus-containing polymers but phenol–formaldehyde resins when heated with phenol[136]). Phenols containing a hydrogen atom in position 2, 4, or 6 undergo this reaction. Substituents in the phenols exert a similar influence on the condensation as in the case of the interaction of phenols with formaldehyde. Whereas the interaction of formaldehyde and phenols involves the intermediate formation of a hemiacetal[137], the condensation of tetrakishydroxymethylphosphonium chloride, trishydroxymethylphosphine oxide, and alkylbishydroxymethylphosphines with phenols obviously occurs directly at the *ortho*- and *para*-positions in the phenols, and thus bypasses the stage of semiacetal formation[131,138-143]:



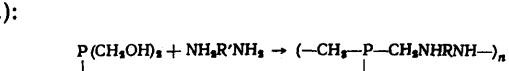
The linear polycondensation products formed initially are converted into resins of complicated three-dimensional structure only when three active centres are present in the phenols employed (phenol, resorcinol, phloroglucinol)[18,140]:



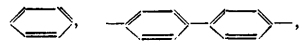
If, however, the *para*-position or one of the *ortho*-positions of the phenol is occupied by a substituent, soluble, fusible resins of linear structure are formed (with *o*-bromophenol, quinol, pyrogallol, catechol)[140,144].

A more detailed study has been made of the properties of polymers based on alkylbishydroxymethylphosphines. These polymers possess ion-exchange properties in alkaline solution. For example, the polymer prepared from propylbishydroxymethylphosphine and phenol in equimolecular proportions has an ion-exchange capacity of 0.7 mg-equiv. g^{-1}.

Tetrakishydroxymethylphosphonium chloride, trishydroxymethylphosphine oxide, and alkylbishydroxymethylphosphines also condense readily, with the liberation of water, with various nitrogen-containing compounds[3,131,134,138,142-158]. Linear polyaminomethylenephosphines are formed from alkylbishydroxymethylphosphines and diamines (hexamethylenediamine, *p*-phenylenediamine, benzidine, urea):



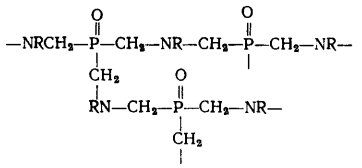
where R = alkyl and R′ = $[CH_2]_6$,



The resulting polymers (M = 42 900–54 000) are solids, mostly amorphous powders, soluble neither in acids nor in alkalis.

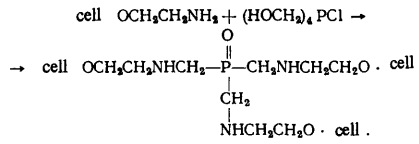
With amines (hydrazine, hydroxylamine, hexadecylamine, etc.) tetrakishydroxymethylphosphonium chloride and trishydroxymethylphosphine oxide initially form water-soluble linear products $(HOCH_2)_2POCH_2NHR$, which set on

standing in the cold for a few hours or on being heated to 100–150°C for a few minutes, to give strongly branched polymers having the structure



With ammonia and melamine tetrakishydroxymethylphosphonium chloride, trishydroxymethylphosphine oxide, and alkylbishydroxymethylphosphines form branched polymers in the form of incombustible powders, insoluble in the usual solvents.

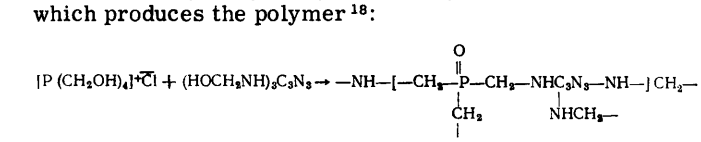
The flameproofing action of polymers obtained from tetrakishydroxymethylphosphonium chloride and amines was first discovered in a study of the properties of aminated cotton[18]. The quaternary chloride reacts with the amino-group in the aminated cotton to form a non-flammable modification of cellulose:



The phosphorus introduced into the cellulose in this way is firmly bound, and is not removed by boiling in water.

In order to confer flame-resistance on cotton without aminating it, tetrakishydroxymethylphosphonium chloride is made to react with amines, e.g. melamine, urea, thiourea, hydroxymethylmelamine. The phosphonium chloride condenses with these compounds, to form an insoluble resin on the fibre. Dicyandiamide, guanidine, melamine, and their hydroxymethyl derivatives form with tetrakishydroxymethylphosphonium chloride three-dimensional polymers, which in the cold do not dissolve in water, acids, or alkalis. The best results are obtained by condensing the quaternary chloride on the cellulosic materials with hydroxymethyl derivatives of melamine.

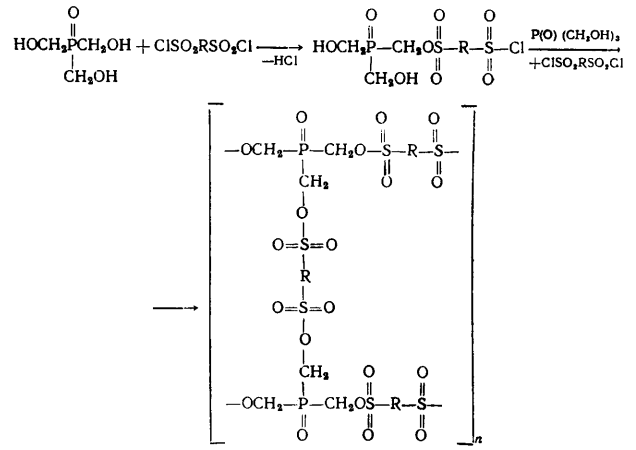
The following recipes—(1) 1868 g of tetrakishydroxymethylphosphonium chloride + 1338 g of trishydroxyethylamine + 1800 g of water; (2) 1060 g of trishydroxymethylmelamine + 1114 g of urea + 5062 g of water—have been proposed for giving cotton fabrics a non-flammable finish. Before use the two solutions are thoroughly mixed, and then applied to the fabric. The principal components of these recipes are tetrakishydroxymethylphosphonium chloride and trishydroxymethylmelamine, interaction between which produces the polymer[18]:



As a result of impregnation and a special treatment the fabric increases in weight by ~ 17%, and withstands the standard test for flame-resistance. The impregnated fabric retains its flame-resistance after 15 washes, and becomes crease-resistant and rotproof.

Copolymers obtained by the polycondensation of tetrakishydroxymethylphosphonium chloride with phenols and nitrogen compounds have also been proposed[145,159] for coating and impregnating fabrics and wood in order to confer on them non-flammable properties.

Phosphorus-containing polysulphonates are obtained by the interaction of aromatic disulphonyl chlorides with tetrakishydroxymethylphosphonium chloride, trishydroxymethylphosphine oxide, and trishydroxymethylphosphine[160]:



Tetrakishydroxymethylphosphonium chloride and trishydroxymethylphosphine oxide also find application for addition to other polymers with the aim of conferring on the latter various valuable properties, e.g. for the production of epoxide resins having improved heat-resistance[161], as modifiers in epoxide resins[156], as inhibitors of discoloration in film-forming compositions[162], etc.

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Nitrosochlorination of Alkenes

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The reaction of nitrosochlorination has recently been attracting the attention of organic chemists, since it provides a ready means of obtaining classes of compounds which are extremely interesting from both theoretical and practical points of view. The laws governing this reaction, including the fine details of the stereochemistry and mechanism of this reaction, have not hitherto been systematised. The present review gives a detailed and systematic survey of the processes involved in nitrosochlorination and of the empirical laws of this reaction. Special attention is paid to published data on the mechanism and the stereochemistry of the reaction; nitrosochlorination is shown to possess features common to other reactions of electrophilic addition. The paper is addressed to a wide circle of organic chemists and undergraduate and postgraduate students. The list of references contains 119 items.

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