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Phosphine in the synthesis of organophosphorus compounds

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Abstract. Published data on the synthesis of organophosphorus compounds based on phosphine are fully surveyed, described systematically and analysed for the first time. The bibliography includes 211 references.

I. Introduction

Phosphine is used in the chemistry of organic compounds of phosphorus for the formation of C – P bonds and for the synthesis of organic and heteroorganic phosphines including functionally substituted ones, which are important auxiliary reagents, building blocks, intermediate products, ligands for metal-complex catalysts, extractants and fire-proofing agents.[1 – 11]

Phosphine, possessing versatile reactivity, reacts with various classes of organic compounds (oxidants, organyl halides, alkenes, alkynes, aldehydes, ketones, oxiranes, thiiranes, amines, alcohols, esters, organyl isocyanates, *etc*.) both with transition into the tetracoordinated state and according to the substitution – addition patterns under conditions of base and acid catalysis and radical initiation.

The interest in the chemistry of phosphine does not attenuate; in our opinion, phosphine deserves even more attention. Known methods for the synthesis of organic compounds of phosphorus based on phosphine are being developed and improved; simultaneously, new phosphine-based methods for the synthesis of organophosphorus compounds appear (for example, the method based on the use of superbasic suspensions such as 'alkali metal hydroxide – high-polarity non-hydroxylic solvent' systems[6, 7, 12] or phase transfer catalysis[6, 7, 12]).

In recent years, considerable attention has been paid to nucleophilic reactions of phosphine with organyl halides[12, 13] and reactions with electrophilic aryl(hetaryl)alkenes[14 – 20] and -alkynes[21 – 23] in superbasic systems, which permit selective and efficient syntheses of primary, secondary and tertiary phosphines. Most of these reactions occur under mild conditions at an atmospheric pressure of phosphine. The use of these methods was greatly facilitated by the development of a convenient procedure for the generation of phosphine from red phosphorus and an alkali metal hydroxide in a water-organic medium.[14]

Although the chemistry of organic phosphines has been the subject of numerous reviews[10, 11, 24, 25] and even monographs,[1, 9, 25] the reactions of phosphine with organic compounds have not been considered systematically and are represented by few examples. Several reactions of phosphine are described in monographs[1, 2, 9] and handbooks (see, for example, Ref. 25). The data on the use of phosphine in the synthesis of organophosphorus compounds published before 1961 were discussed most fully (but not exhaustively) in a short (13 pages) review,[3] the bibliography of which includes 70 references. In another review,[11] which is devoted to α-hydroxyalkylphosphines and -phosphine oxides, reactions of PH_3 and organic phosphines with carbonyl compounds have been considered in detail.

The purpose of the present review, in which data on the phosphine-based methods of the synthesis of organophosphorus compounds are described fully and systematically for the first time, is to provide the reader with not only general information but also data concerning particular reactions of phosphine and its organic derivatives.

II. Phosphine in substitution reactions

1. Alkylation of phosphine

a. Alkylation with organic halides

According to patents,[26 – 29] the vapour-phase (210 – 280 °C) catalytic alkylation of phosphine with alkyl halides yields alkylphosphonium halides, their structures being dependent on the ratio of the reactants. Activated carbon or Pt, Pd and Au supported on Al_2O_3 or SiO_2 are used as catalysts. When excess alkyl halide with respect to phosphine is used, the reaction (210 – 280 °C, 11 atm, 85 h, activated carbon) gives tetraalkylphosphonium halides (in up to 83% yields).[26, 27]

$$PH_3 + RX \longrightarrow [R_4P^+]X^-$$

R = Alk(C_1 – C_4); X = Cl, Br.

The reactions of phosphine with alkyl chlorides (equimolar ratio, 280 °C, 5 days, activated carbon) afford mixtures of mono-, di- and trialkylphosphonium chlorides, monoalkylphosphonium chloride being the major product, which are converted into the corresponding phosphines on treatment with aqueous NaOH.[28]

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$$PH_3 + RCl \longrightarrow RPH_2 \cdot HCl + R_2PH \cdot HCl + R_3P \cdot HCl \xrightarrow{NaOH} \longrightarrow RPH_2 + R_2PH + R_3P$$

R = Alk, cyclo-Alk, $PhCH_2$.

Having been bound in a complex on heating (70–80 °C) with an equimolar amount of $AlCl_3$, phosphine reacts with alkyl halides,[30–31] cycloalkyl halides[30] and adamantyl bromide[32] to give, after the subsequent treatment of the reaction mixture with ice water and HCl, primary phosphines in 15%–83% yields. When alkyl iodides are used, phosphorylation is complicated by side processes. Aryl halides do not enter into this reaction.[30]

$$PH_3 + AlCl_3 \longrightarrow PH_3 \cdot AlCl_3 \xrightarrow[3.\ HCl]{1.\ RX;\ 2.\ H_2O} RPH_2$$

R = Alk(C_4–C_6) (37%–64%), Alk(C_8–C_{18}) (62%–83%), cyclo-Alk (15%–28%); X = Cl, Br.

It should be noted that even when the complex $PH_3 \cdot AlCl_3$ reacts with excess alkyl halide, the reaction occurs as monoalkylation; the formation of minor amounts of secondary phosphines was detected only for lower alkyl halides.[30]

The reactions of phosphine with alkyl halides under the Friedel–Crafts conditions occur most likely by a carbocationic mechanism. This is indicated, in particular, by the fact that the reaction of dodecyl bromide with the complex $PH_3 \cdot AlCl_3$ yields a mixture of primary phosphines, presumably,[31] structural isomers of dodecylphosphine.

The reaction of phosphine with chlorides of aromatic carboxylic acids in dry pyridine gives rise to tris(aroyl)phosph-ines.[33–35]

$$PH_3 + ArCOCl \longrightarrow (ArCO)_3P$$

Ar = Ph,[33] 3-MeC_6H_4, 4-MeC_6H_4, α-$C_{10}H_7$, β-$C_{10}H_7$.[33–35]

b. Alkylation with alcohols, ethers and amines

The synthesis of akylphosphines by high-temperature catalytic alkylation of phosphine with alcohols,[36] ethers[36] and amines[37,38] has been described in patents.[36–38]

Thus aliphatic and cycloaliphatic primary and secondary phosphines are formed in good yields when phosphine reacts (200–300 °C, atmospheric pressure) with alcohols and ethers in the presence of dehydrated natural and synthetic metal aluminosilicates or zeolites of various brands, the pores of which are permeable for mono- and diorganylphosphines but impermeable for triorganylphosphines.[36]

$$PH_3 + ROR' \longrightarrow RPH_2 + R_2PH + R'OH$$

R = Alk, cyclo-Alk; R′ = H, Alk.

A method for the preparation of primary, secondary and tertiary alkylphosphines by heating phosphine (150–400 °C, pressure up to 2 atm) with amines in the presence of a catalyst (activated carbon, copper chromite, Group IB and VIIIB metals) has been proposed.[37]

$$PH_3 + R_nNH_{3-n} \longrightarrow RPH_2 + R_2PH + R_3P$$

R = Me, Et, Pr; n = 1–3.

Under the same conditions, phosphine can also be alkylated by mixtures of amines with hydrogen halides and/or alkyl halides, *i.e.* by the corresponding ammonium salts.[38]

2. Reactions of phosphide ions with organic halides

In the presence of strong bases, phosphine is converted into phosphide ions, which react with organyl halides by nucleophilic substitution to give primary and secondary phosphines. The role of bases in these reactions is played by the systems 'alkali (or alkaline earth) metal–organic solvent (or liquid ammonia),' organometallic compounds (triphenylmethylsodium, phenyllithium, butyllithium) or strong bases generated from alkali metal hydroxides in polar non-hydroxylic solvents or under conditions of phase transfer catalysis.

a. Reactions of metal phosphides

Phosphorylation of organyl halides by the 'phosphine–alkali (or alkaline earth) metal' systems yields predominantly primary phosphines.[1,2,39–45] This reaction can be carried out for alkyl halides,[39–41] aryl halides,[1,42] aminoalkyl halides,[43] sodium halocarboxylates[44,45] and dihaloalkanes.[41,46–49] The process is carried out in an organic solvent or in liquid ammonia using stoichiometric amounts of reactants.

Thus alkylphosphines and allylphosphines have been obtained in good yields (55%–78%) by a one-pot procedure which includes the reaction of sodium, dispersed preliminarily in hexamethylphosphotriamide (HMPA), with phosphine and the addition of alkyl halides to the resulting solution of sodium dihydrophosphide.[40]

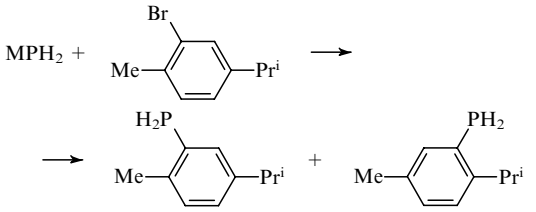
$$PH_3 + Na \xrightarrow[-H_2]{HMPT} NaPH_2 \xrightarrow[HMPT]{RX} RPH_2$$

R = Me, Et, $CH_2{=}CHCH_2$; X = Cl, Br.

When calcium metal is used in this process instead of sodium and liquid ammonia is used instead of HMPA, phosphorylation becomes more efficient; for example, the reaction between chloromethane and phosphine gives methylphosphine in 87% yield.[41]

$$PH_3 + Ca \xrightarrow[-H_2]{NH_3} Ca(PH_2)_2 \xrightarrow[NH_3]{MeCl} MePH_2$$

It has been reported that aryl halides can be involved in the reaction with alkali metal phosphides.[1,42] Thus potassium phosphide prepared from phosphine and potassium in liquid ammonia slowly reacts with bromo- and iodobenzene to give phenylphosphine.[1] A mixture of (5-isopropyl-2-methylphenyl)phosphine and 2-isopropyl-5-methylphenyl)phosphine is formed when 2-bromo-4-isopropyl-1-methylbenzene reacts with sodium phosphide or lithium phosphide in boiling ether.[42]



M = Li, Na.

The 'phosphine–sodium–liquid ammonia' system has been used successfully in phosphorylation of aminoalkyl halides[43] and halocarboxylic acids[44,45] aimed at synthesising the corresponding functionalised primary phosphines. Thus (2-R,R′-aminoethyl)phosphines have been obtained in 54%–70% yields from 2-R,R′-aminoethyl chloride and phosphine.[43]

$$PH_3 + Na \xrightarrow[-H_2]{NH_3} NaPH_2 \xrightarrow[NH_3]{ClCH_2CH_2NRR'} \longrightarrow H_2PCH_2CH_2NRR'$$

R, R′ = H, Et.

When sodium halocarboxylates are treated with phosphine in the 'sodium–liquid ammonia' system and then the reaction mixture is treated with dilute sulfuric acid, 1- and 2-carboxyalkylphosphines are formed in 70%–85% yields.[44,45]

$$PH_3 + Na \xrightarrow[-H_2]{NH_3} NaPH_2 \xrightarrow[NH_3]{XRCO_2Na} \longrightarrow H_2PRCO_2Na \xrightarrow{H_2SO_4} H_2PRCO_2H$$

R = CH_2, CHMe, CHEt, CMe_2, CH_2CH_2; X = Cl, Br.

Under the same conditions, sodium 2,5-dibromoadipate was converted into 2,5-diphosphinoadipic acid formed as a mixture of racemic and meso forms in 45 : 55 ratio.[44]

$$NaPH_2 + NaO_2CCH(CH_2)_2CHCO_2Na \xrightarrow{H_2SO_4} \longrightarrow HO_2CCH(CH_2)_2CHCO_2H$$

(Br, Br; PH_2, PH_2)

The synthesis of 3-carboxypropylphosphine from 4-chlorobutyric acid demonstrated that not only salts but also acids themselves can efficiently react with phosphine and excess sodium in liquid ammonia.[44]

$$PH_3 + Na \xrightarrow[-H_2]{NH_3} NaPH_2 \xrightarrow[-PH_3]{ClCH_2(CH_2)_2CO_2H} \longrightarrow H_2PCH_2(CH_2)_2CO_2Na \xrightarrow{H_2SO_4} H_2PCH_2(CH_2)_2CO_2H$$

Thus, metallation of phosphine with an alkali or alkaline earth metal followed by treatment of the phosphide with an organyl halide results in the formation of primary phosphines of various structures in high yields.[40,41,43–45] However, this approach has scarcely been used for the synthesis of diorganylphosphines, apparently, due to the difficulty of formation of disubstituted metal derivatives upon metallation of phosphine.[1] Only preparation of dimethylphosphine in a relatively low yield (33%) by treatment of calcium hydrophosphide with chloromethane in liquid ammonia has been reported.[41]

$$PH_3 + Ca \xrightarrow{NH_3} Ca(PH_2)_2 \cdot 6NH_3 \xrightarrow[\text{vacuum}]{50\ ^\circ C} \longrightarrow CaPH + PH_3 + 6NH_3 \xrightarrow{MeCl,\ NH_3} Me_2PH$$

Dihaloalkanes can be phosphorylated by the 'PH_3–alkali metal–liquid ammonia' system to give, depending on the length of the alkylene chain, either cyclic phosphines or their mixtures with primary alkylenediphosphines. The reaction of 1,2-dichloroethane with sodium dihydrophosphide in liquid ammonia yields phosphirane **1** as the main product (yield 74%).[47–49]

$$PH_3 + Na \xrightarrow[-H_2]{NH_3} NaPH_2 \xrightarrow[NH_3]{ClCH_2CH_2Cl} \triangleright PH$$

1

The cyclisation was suggested [47] to occur as follows:

$$ClCH_2CH_2Cl + {}^-PH_2 \xrightarrow[-Cl^-]{} ClCH_2CH_2PH_2 \overset{-PH_2}{\rightleftharpoons} \rightleftharpoons ClCH_2CH_2PH^- \xrightarrow[-Cl^-]{} \mathbf{1}.$$

Methyl- and ethylphosphiranes have been prepared from the corresponding 1,2-dichloroalkanes under the same conditions (yields 30% and 25%, respectively).[40]

$$PH_3 + Na \xrightarrow[-H_2]{NH_3} NaPH_2 \xrightarrow[NH_3]{RCHClCH_2Cl} R\triangleright PH$$

R = Me, Et.

α,ω-Dihaloalkanes with a number of methylene units $n \geqslant 3$ are phosphorylated by phosphine in the 'sodium–liquid ammonia' system yielding simultaneously cyclic secondary phosphines and alkylenediphosphines.[48,49]

$$PH_3 + Na \xrightarrow[-H_2]{NH_3} NaPH_2 \xrightarrow[NH_3]{X(CH_2)_nX} \longrightarrow \ulcorner CH_2(CH_2)_{n-1}PH\urcorner + H_2P(CH_2)_nPH_2$$

X = Cl, Br; n = 3–7.

The transformation of 1,4-dichlorobutane under these conditions gave a mixture of phospholane and 1,4-diphosphinobutane (each in 47% yield).[48]

Phosphine can be metallated with equal success by some organometallic compounds, for example, triphenylmethylsodium,[1] phenyllithium [1,50,51] and butyllithium.[52]

For example, when a fast stream of phosphine is passed through diethyl ether to which phenyllithium is being simultaneously added, lithium dihydrophosphide is formed; its subsequent treatment with organyl halide affords primary phosphines in 65%–75% yields.[50]

$$PH_3 + PhLi \longrightarrow LiPH_2 \xrightarrow{RX} RPH_2$$

R = Et, Pr^n, Bu^t, $PhCH_2$; X = Cl, Br.

Depending on the reactant ratio, the reaction of butyllithium with phosphine gives rise to lithium phosphide, trilithium phosphide or its mixture with dilithium phosphide. The reactions of these phosphides with chlorotrimethylsilane at 0–10 °C resulted in the formation of trimethylsilylphosphine (yield 30%), a mixture of bis- and tris(trimethylsilyl)phosphines (yields 35% and 24%, respectively) or tris(trimethylsilyl)phosphine (yield 45%).[52]

$$PH_3 \xrightarrow{BuLi} \begin{cases} LiPH_2 \xrightarrow{Me_3SiCl} Me_3SiPH_2 \\ Li_2PH + Li_3P \xrightarrow{Me_3SiCl} (Me_3Si)_2PH + (Me_3Si)_3P \\ Li_3P \xrightarrow{Me_3SiCl} (Me_3Si)_3P \end{cases}$$

b. Reactions of phosphine in the presence of a strong base

Methylation was the first example of alkylation of phosphine with an organyl halide in the presence of a strong base.[53,54] When methyl iodide is added to a DMSO suspension of KOH preliminarily saturated with phosphine, methylphosphine or dimethylphosphine is formed, depending on the initial ratio of reactants (yields 75% [53] and 65%,[54] respectively).

$$PH_3 \xrightarrow{KOH,\ DMSO} \begin{cases} \xrightarrow{2MeI} Me_2PH \\ \xrightarrow{MeI} MePH_2 \end{cases}$$

Later, other organyl halides have also been involved in this reaction; this gave monoorganylphosphines in 70%–94% yields.[12] The reaction was carried out in a mixture of a 56%–64% aqueous solution of KOH with DMSO (depending on the nature of the halide used, the temperature and pressure varied in the ranges 0–60 °C and 4–7.5 atm).

$$PH_3 + RX \xrightarrow{KOH,\ DMSO\ (H_2O)} RPH_2$$

R = Me, Et, $CH_2{=}CHCH_2$, Bu^n, Bu^t, $PhCH_2$; X = Br, Cl.

Diallyl- and dibutylphosphines were obtained in this reaction (yields 53% and 23%, respectively) by using a two- or four-fold excess of potassium hydroxide with respect to the corresponding organyl bromide.[12]

$$PH_3 + RBr \xrightarrow{KOH,\ DMSO\,(H_2O)} R_2PH$$

R = Bu, $CH_2=CHCH_2$.

No products of the possible prototropic rearrangement — propen-1-yl- or di(propen-1-yl)phosphines — have been obtained under these conditions, although this rearrangement does occur during phosphorylation of allyl halides with red phosphorus in a highly basic aqueous-organic emulsion.[5,55,56]

Recently dibenzylphosphine has been prepared in 50% yield from phosphine and benzyl chloride.[13,57] The reaction occurs under mild conditions (atmospheric pressure, 40 °C). Benzyl chloride is slowly added to a suspension of KOH in DMSO in the presence of a slight amount of water and simultaneously, a phosphine–hydrogen mixture, generated from red phosphorus and an alkali metal hydroxide, is vigorously passed through the suspension.

$$PH_3–H_2 + PhCH_2Cl \xrightarrow{KOH,\ DMSO\,(H_2O)} (PhCH_2)_2PH$$

This reaction gives as well a noticeable amount of dibenzyl ether (up to 20%) resulting from solvolytic transformations of benzyl chloride.[13]

Unlike reactions of metal phosphides with dihalopropane, which afford phosphorus-containing heterocycles[48,49] (Section II.2.a), the reactions of phosphine with 1,3-dihalopropane or -butane in the KOH–DMSO (H_2O) system give only acyclic products, 1,3-diphosphinopropane or -butane (yields 59% and 75%, respectively).[12]

$$PH_3 + BrCH_2CH_2\underset{\displaystyle R}{\underset{|}{C}}HBr \xrightarrow{KOH,\ DMSO\,(H_2O)} H_2PCH_2CH_2\underset{\displaystyle R}{\underset{|}{C}}HPH_2$$

R = H, Me.

Phosphorylation of 1,4-dibromopentane under similar conditions gives rise to 2-methylphospholane (yield 80%), only minor amounts of the corresponding acyclic product, 1,4-diphosphinopentane, being formed.[12]

$$PH_3 + BrCH_2(CH_2)_2\underset{\displaystyle Me}{\underset{|}{C}}HBr \xrightarrow{KOH,\ DMSO\,(H_2O)}$$

$$\longrightarrow \underset{H}{\overset{Me}{P}} + H_2PCH_2(CH_2)_2\underset{\displaystyle Me}{\underset{|}{C}}HPH_2$$

Alkylation of phosphine with organyl halides has also been carried out in the presence of bases generated under conditions of phase transfer catalysis, *i.e.* in the systems 'aqueous potassium hydroxide–organic solvent (toluene, pentane)–tetraalkylammonium or tetraalkylphosphonium salt.'[12,58,59] Depending on the reactant ratio and the reaction conditions (temperature, pressure), primary or secondary phosphines are formed in the 55%–92% yields.

$$PH_3 \xrightarrow{KOH,\ H_2O} \begin{cases} \xrightarrow{RX} RPH_2 \\ \xrightarrow{R'X} R'_2PH \end{cases}$$

R = Alk(C_1–C_{24}), $CH_2=CHCH_2$,[12,58] $PhCH_2$,[58]


CH_2CH_2,[12] Ph_2PCH_2;[59] R′ = Me,[12] Ph_2PCH_2;[59] X = Cl, Br.

1,3-Dihaloalkanes react with phosphine under the conditions of phase transfer catalysis to give, as in the KOH–DMSO system,[12] 1,3-diphosphinoalkanes in yields of up to 89%.[12,58]

$$PH_3 + X\underset{\displaystyle R}{\underset{|}{C}}H_2CH_2CHX \xrightarrow{KOH,\ H_2O} H_2P\underset{\displaystyle R}{\underset{|}{C}}H_2CH_2CHPH_2$$

R = H, Alk; X = Cl, Br.

III. Phosphine in addition reactions

1. Addition to C=C bonds

The reaction of phosphine with alkenes is a convenient method for the synthesis of organic phosphines. Phosphine can add to C=C bonds by both ionic and radical mechanisms. The reaction pathway is determined by its conditions and the nature of the alkene used.

a. Nucleophilic addition

Nucleophilic addition of phosphine to the C=C bond was first described by Rauhut *et al.*[60,61] for alkenes containing strong electron-withdrawing substituents at the sp^2 carbon atom. In the presence of bases (a 10 M aqueous solution of KOH, heptamethylbiguanide, a concentrated solution of ammonia, solid sodium hydroxide), phosphine reacts with acrylonitrile,[60,62] acrylamide, nitroethylene, mesityl oxide and lauryl acrylate[61] to give a mixture of primary, secondary and tertiary phosphines.

$$PH_3 + RCH{=}CH_2 \longrightarrow$$

$$\longrightarrow RCH_2CH_2PH_2 + (RCH_2CH_2)_2PH + (RCH_2CH_2)_3P$$

R = CN, $CONH_2$, NO_2, *etc.*

The process selectivity can be increased by varying its conditions (the molar ratio and the rate of mixing of the reactants, temperature, heating duration or pressure).[60,61] For example, when a flow of phosphine is passed through the system 'aqueous KOH–acetonitrile' heated to 30–35 °C and acrylonitrile is simultaneously added to it, the addition rate being adjusted in such a way as to maintain a slight excess of acrylonitrile relative to phosphine, tris(2-cyanoethyl)phosphine is obtained in 80% yield. A decrease in the concentration and the rate of addition of acrylonitrile under the same conditions results in bis(2-cyanoethyl)phosphine being formed predominantly (yield 63%). The primary phosphine is formed in 52% yield in the phosphorylation of acrylonitrile in an autoclave under an elevated pressure of phosphine (28–32 atm).[60]

In the 1970s, a series of studies was published on the nucleophilic addition of phosphine to dialkyl vinylphosphonates,[63,64] vinyldialkylphosphine sulfides,[65,66] and even to relatively weak electrophiles — vinyldiphenylphosphine[67–70] and vinylphosphonous diamides.[71] The reactions occur in boiling THF in the presence of Bu^tOK,[63–66,70] or in benzene in the presence of PhLi at 100 °C (autoclave),[67–69] or in the 'metallic potassium–liquid ammonia' system[71] and result in the formation of functionalised tertiary phosphines **2a–e**, their yields ranging from 24% (**2a**) to 95% (**2e**).

$$PH_3 + R_2P(X)CH{=}CH_2 \xrightarrow[\text{or PhLi}]{Bu^tOK} \underset{\textbf{2a–e}}{[R_2P(X)CH_2CH_2]_3P}$$

R = Ph (**a**), Me_2N (**b**), X is absent; R = Me_2CHO (**c**), X = O;
R = Me (**d**), Me_3CCH_2 (**e**), X = S.

Recently[14–21] it has been found that phosphine is capable of adding to weakly electrophilic C = C bonds in aryl and hetarylethenes in the KOH–DMSO system, and preparative methods for the synthesis of bis- and tris(2-arylethyl)- and -(2-hetarylethyl)phosphines have been developed. In the absence of KOH, all other factors being the same, phosphorylation does not occur, which confirms the nucleophilic mechanism of the reaction. Phosphine is generated as a mixture with hydrogen by the addition of an aqueous solution of KOH (or NaOH) to a suspension of red phosphorus in dioxane.[14]

Bis(2-arylethyl)- and bis(2-hetarylethyl)phosphines have been selectively synthesised in 60% – 80% yields by slow addition of an alkene to a suspension of KOH in DMSO heated to 45 – 60 °C with simultaneous vigorous passing of a phosphine stream through the suspension.[14 – 20]

$$PH_3 + RR'C{=}CH_2 \xrightarrow[45-60\ ^\circ C]{KOH,\ DMSO\ (H_2O)} (RR'CHCH_2)_2PH$$

R = H, R′ = Ph, 4-FC_6H_4, , , , ;

R = Me, R′ = Ph.

1-Methyl-2-vinylpyrrole could not be involved in the reaction with phosphine, apparently, because of the low electrophilicity of the double bond in this alkene (due to the electron-donating mesomeric effect of the 1-methyl-2-pyrrolyl group).[14]

Exhaustive and selective aryl(hetaryl)ethylation of phosphine by styrene and vinylpyridines occurs at 95 – 98 °C and 65 – 67 °C, respectively, in the KOH – DMSO system, giving rise to tris(2-phenylethyl)-, tris[2-(4-pyridyl)ethyl]- and tris[2-(2-methyl-5-pyridyl)ethyl]phosphines (yields 65% – 76%).[18, 19]

$$PH_3 + RCH{=}CH_2 \xrightarrow[67-98\ ^\circ C]{KOH,\ DMSO\ (H_2O)} (RCH_2CH_2)_3P$$

R = Ph, , .

When this reaction is conducted at a lower temperature (30 – 40 °C), the corresponding primary phosphines can also be obtained in 20 % – 24% yields. However, bis(2-phenylethyl)- and bis(2-pyridylethyl)phosphines are the main reaction products under these conditions.[19, 20]

It has been noted that a base generated under the conditions of phase transfer catalysis (a 60% aqueous solution of KOH – dioxane – benzyltrimethylammonium chloride) is not sufficiently strong to enable phosphorylation of arylalkenes and vinylpyridines with phosphine.[19]

An unsuccessful attempt to carry out the reaction of phosphine with diphenylethene and fumaronitrile in the presence of a base has been reported.[72]

b. Electrophilic addition

The acid-catalysed addition of phosphine to unsaturated compounds is relatively little studied. It has been reported[73, 74] that alkenes of various structures (linear and branched alkenes, cycloalkenes, polypropenes, polybutenes, styrene, limonene, *etc.*) react with phosphine under relatively rigorous conditions (60 – 90 °C, 30 – 47 atm, acid catalysis) according to the Markovnikov rule to give mostly primary phosphines.

$$PH_3 + RR'C{=}CH_2 \xrightarrow{H^+} MeCR(R')PH_2$$

R, R′ = H, Alk(C_1 – C_{63}), Ph, *etc.*

Best results in this reaction are obtained when 1,1-disubstituted alkenes are used, because they form the most stable intermediate tertiary carbocations and in addition, they are the least susceptible to cationic polymerisation.

$$R_2C{=}CH_2 \overset{H^+}{\rightleftharpoons} R_2\overset{+}{C}{-}Me \overset{PH_3}{\rightleftharpoons} H_3\overset{+}{P}CR_2Me \underset{-H^+}{\rightleftharpoons} H_2PCR_2Me$$

Thus the highest yield (90%) of the primary phosphine was observed when phosphine was made to react with C_{12}-polypropene.[73] The reaction of phosphine with 2-methylprop-1-ene, 2-ethylhex-1-ene and 1-methylcyclopentene is less efficient (the yield of the corresponding primary phosphines is 41% – 75%), which is apparently due to the fact that these alkenes are more prone to undergo polymerisation than C_{12}-polypropene. Phosphorylation of linear alkenes, ethene, propene and dodec-1-ene, results in even lower yields (14% – 20%) of primary phosphines.

Among the catalysts tested in the reaction of phosphine with alkenes (mineral and organic acids, sulfonic acids, Lewis acids), methanesulfonic acid is the most active.[73] It should be noted that for this reaction to go to completion, almost stoichiometric amounts of acid catalysts are needed, because the monoalkylphosphines, which are formed in the process, are stronger bases than phosphine; therefore, they react reversibly with the acid to give phosphonium ions.

$$RPH_2 + H^+ \rightleftharpoons RP^+H_3$$

The reactions of phosphine with some alkenes (styrene, limonene) in an acid medium are accompanied by polymerisation giving rise to telomeric phosphines.[74]

Since the electrophilic addition of phosphine to alkenes is a carbocationic process, the reactions of linear alkenes with phosphine under these conditions may be accompanied by isomerisation of the hydrocarbon chain (as has been shown in relation to the interaction of phosphine with alkyl halides in the presence of $AlCl_3$).[31] However, in the study cited,[73] this aspect is not considered.

c. Radical addition

The addition of phosphine to alkenes under conditions of radical initiation [organic peroxides, azobisisobutyronitrile (AIBN), UV irradiation] has been studied fairly comprehensively. This method is used to prepare organic phosphines of various structures, because this reaction has been performed for a broad range of unsaturated organic compounds including functionally substituted ones: linear unsubstituted alkenes with a terminal[74 – 88] or (more rarely) internal[80, 81, 93, 94] double bond, cycloalkenes,[75, 76, 78, 80, 81, 85, 90] arylalkenes,[75, 78, 80, 81, 90] dienes,[78, 79, 90, 113 – 118] trienes,[119] fluorinated alkenes,[103 – 109] vinyl[75, 80, 81] and divinyl[111, 112] ethers and thioethers,[80, 81] alcohols,[76, 80, 81, 85, 95] amines,[76, 80, 81] ketones,[80, 81] acrylic acid derivatives,[75, 80, 81, 96 – 98] and allyl[80, 81] and vinyl[99, 100] carboxylates and phosphonates.[80, 81, 85]

Radical addition of phosphine to alkenes normally results in the formation of mixtures of primary, secondary and tertiary phosphines, their ratio being dependent most of all on the ratio of the initial reactants.[75, 77]

$$PH_3 + RCH{=}CH_2 \longrightarrow$$

$$\longrightarrow RCH_2CH_2PH_2 + (RCH_2CH_2)_2PH + (RCH_2CH_2)_3P$$

R = Alk, Ph, H_2NCH_2, $HOCH_2$, MeO, BuO, MeS, MeO_2C, EtO_2C, $Me(CH_2)_3CH(Et)CH_2O_2C$, *etc.*

Primary phosphines are formed as the major products when a substantial excess of phosphine in relation to alkene is used.[75, 78, 79] Octylphosphine is formed in 65% yield when a mixture of phosphine with oct-1-ene (molar ratio 3.6 : 1) is heated (78 – 89 °C, AIBN) at a pressure of ~33 atm. The yields of dioctyl- and trioctylphosphines under these conditions are 18% and 4%, respectively.[75] An even higher yield (80%) of octylphosphine was attained when the reaction was carried out at a phosphine pressure of 120 – 180 atm,[78] because at higher phosphine pressures, its solubility in the liquid phase increases and, hence, the yield of primary phosphine also increases.[75]

A similar influence of high pressures of phosphine on the yield of the reaction product was observed[75] for 2-methylprop-1-ene.

Tertiary phosphines are prepared in high yields (70% – 96%) by using excess alkene with respect to phosphine.[75, 76, 80 – 85] For instance, phosphorylation of oct-1-ene by phosphine at a molar ratio of 3 : 1 (80 – 100 °C, pressure 3.3 atm, AIBN) afforded trioctylphosphine in 83% yield.[75] The synthesis of tributylphosphine in a nearly quantitative yield (96%) from phosphine and but-1-ene under conditions of radical initiation is described in a patent.[83]

However, the yield of secondary phosphines in the radical addition of phosphine to alkenes is, as a rule, relatively low (20%–30%).[75]

Naturally, the structure of the alkene used also has an influence on the ratio of primary, secondary and tertriary phosphines formed in the alkylation of phosphine with alkenes. Sterically hindered alkenes (2-methylpropene, but-2-ene,[80,81,93,94] cyclohexene[75,76,78,80,81,85,90]) react less vigorously than, for example, oct-1-ene to give mostly primary and secondary phosphines even when an excess of alkene with respect to PH_3 is used.

UV irradiation of an equimolar mixture of phosphine and styrene gives rise to phenethylphosphine.[81] The same product is formed, together with bis(phenethyl)phosphine (yields 36% and 29%, respectively), when styrene is phosphorylated with a 1.5-fold molar excess of phosphine in the presence of AIBN (80 °C, ~28 atm).[75]

Phosphorylation of fluorine-substituted alkenes with phosphine is activated by heating (150–160 °C)[103–105] or UV radiation.[106–109] This reaction gives mostly primary phosphines, the yields of which are higher (up to 74%–91%) in the case of UV activation.

The reactions of phosphine with alkyl vinyl ethers,[75,80,81] alkyl vinyl sulfides,[80,81] allylamines[76,80,81] and allyl alcohol[76,80,81] (a two-fold molar excess of the corresponding alkene was normally used) occurring on exposure to UV radiation[76,80,81] or in the presence of AIBN (80 °C, 31 atm)[75] afford mostly primary and secondary phosphines (total yield 50%–75%); the yields of tertiary phosphines do not exceed 10%.

On exposure of an equimolar mixture of phosphine and vinyl methyl ketone to UV radiation, (2-acetylethyl)phosphine was formed as the major product.[80,81]

A complex mixture of phosphines is formed when ethyl acrylate is made to react with phosphine (70–100 °C, AIBN, 28 atm).[75] The reaction products contain not only the expected primary, secondary and tertiary phosphines **3a–c** (yields 21%, 20% and 23%, respectively) but also bis(2-ethoxycarbonylethyl)-2,4-diethoxycarbonylbutylphosphine **4** (yield 19%).

$$PH_3 + EtOOCCH{=}CH_2 \longrightarrow \underset{\mathbf{3a}}{EtOOCCH_2CH_2PH_2} + \underset{\mathbf{3b}}{(EtOOCCH_2CH_2)_2PH} + \underset{\mathbf{3c}}{(EtOOCCH_2CH_2)_3P} + \underset{\mathbf{4}}{(EtOOCCH_2CH_2)_2PCH_2CH(COOEt)CH_2CH_2COOEt}$$

The phosphine **4** is formed apparently upon the addition of bisphosphine **3b** to diethyl α-methyleneglutarate resulting from dimerisation of the initial ethyl acrylate.

$$EtOOCCH{=}CH_2 \longrightarrow EtOOCCH_2CH_2(EtOOC)C{=}CH_2 \xrightarrow{\mathbf{3b}} \mathbf{4}$$

The radical addition of phosphine (AIBN, 90–120 °C, 15 atm) to acrylonitrile at a molar ratio of the reactants of 2.9–3.2 : 1 occurs selectively to give tris(2-cyanoethyl)phosphine in 93% yield.[97,98] Nevertheless, the synthesis of this tertiary phosphine from acrylonitrile and phosphine under the conditions of base catalysis (Section III.1.a) is undoubtedly more convenient and practically feasible, because it readily occurs on moderate heating (25–30 °C) under atmospheric pressure.[60]

A mixture of primary, secondary and tertiary phosphines **5a–c** is produced upon photochemical addition of phosphine to allyl[80,81] and vinyl[99,100] carboxylates (most often, to vinyl acetate).

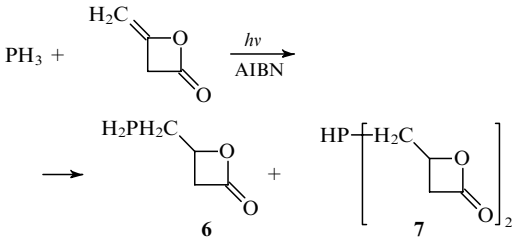
$$PH_3 + RCH{=}CH_2 \xrightarrow{h\nu} \underset{\mathbf{5a}}{RCH_2CH_2PH_2} + \underset{\mathbf{5b}}{(RCH_2CH_2)_2PH} + \underset{\mathbf{5c}}{(RCH_2CH_2)_3P}$$

R = $MeCO_2$, $MeCO_2CH_2$.

Photoinitiated addition of phosphine to vinyl-[80,85] and allylphosphonates[81] has been described. Thus UV irradiation of an equimolar mixture of phosphine and dibutyl allylphosphonate gave 3-(dibutoxyphosphoryl)propylphosphine.[81]

$$PH_3 + (BuO)_2P(O)CH_2CH{=}CH_2 \xrightarrow{h\nu} (BuO)_2P(O)CH_2CH_2CH_2PH_2$$

NMR analysis of the reaction mixture obtained upon UV irradiation of phosphine and diketene in the presence of AIBN showed the presence of 2-oxo-4-oxetanylmethyl- (**6**) and bis(2-oxo-4-oxetanylmethyl)phosphines **7**; these products were not isolated because of their low stability.[101]

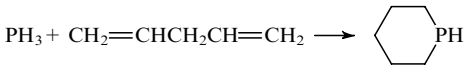


The addition of phosphine to terpenes and their derivatives in the presence of AIBN has been patented.[102]

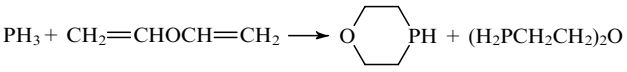
On exposure of a mixture of allene and phosphine to UV radiation, the first representative of primary vinylphosphines, propen-2-ylphosphine, was obtained in 3% yield.[110]

$$PH_3 + CH_2{=}C{=}CH_2 \xrightarrow{h\nu} CH_2{=}C(Me)PH_2$$

Under conditions of radical initiation (AIBN, 50–70 °C, 10–20 atm), phosphine reacts with penta-1,4-diene to give phosphorinane.[79]

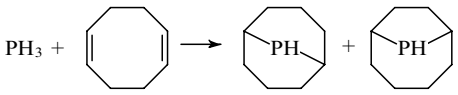


The radical addition of phosphine to divinyl ether (AIBN or UV irradiation, 75–80 °C, 10 atm) results in the formation of both a cyclic phosphine (4-oxaphosphorinane) and a linear primary diphosphine (the yield of each product is 7%–10%).[111,112]

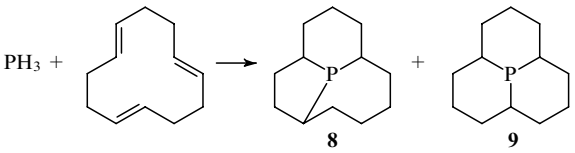


According to patent data,[113] the reaction between phosphine and dicyclopentadiene under conditions of radical initiation (AIBN or organic peroxides, 90 °C, 3–20 atm) gives rise to a mixture of isomeric secondary phosphines with the composition $C_{20}H_{27}P$. It was proposed to use this mixture as a ligand for the preparation of metal-complex catalysts and also as a flotation reagent.[113]

Bicyclic secondary phosphines are formed upon homolytic addition of phosphine to 4-vinylcyclohex-1-ene[114] and to cyclic dienes.[78,90,115–118] Thus heating (70–180 °C) cycloocta-1,5-diene with phosphine under a pressure of 30–40 atm in the presence of AIBN or organic peroxides affords a mixture of 9-phosphabicyclo[3.3.1]nonane and 9-phosphabicyclo[4.2.1]nonane (in a total yield of up to 96%, ratio 1 : 0.8).[115]



Prolonged (79 h) γ-irradiation (^{60}Co) of a mixture of phosphine and cyclododeca-1,5,9-triene has given rise to isomeric tricyclic phosphines **8** and **9** (overall yield 20%).[119]



8 **9**

d. Addition in the presence of heterogeneous and metal-complex catalysts

Data on the interaction of phosphine with branched and cyclic alkenes and with dienes in the presence of heterogeneous solid catalysts (zeolites, phosphates and metal oxides) at an elevated pressure (8–190 atm) and at temperatures of 100–200 °C have been reported.[120] Thus heating of phosphine and 2-methylpropene in an autoclave (200 °C, 190 atm) in the presence of a borosilicate zeolite gave *tert*-butylphosphine in 70% yield.[120]

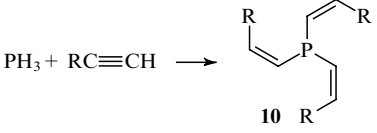
$$PH_3 + Me_2C{=}CH_2 \longrightarrow Me_3CPH_2$$

As noted above (Section III.1.b), this reaction can be carried out under milder conditions (60 °C, 33 atm) in the presence of methanesulfonic acid, *tert*-butylphosphine being formed in a comparable yield (61%).[73]

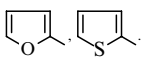
The addition of phosphine to acrylonitrile has been accomplished in the presence of metal-complex catalysts [a mixture of $P(CHR(OH))_3$, where R = H [121, 122] or Alk (C_1–C_6),[122] with reduced iron[121] or chloroplatinic acid [122]]. The reaction occurs in the medium of a lower aliphatic alcohol at room temperature to give tris(2-cyanoethyl)phosphine.[121, 122] However, this compound can be easily prepared without expensive metal-complex catalysts by cyanoethylation of phosphine with excess acrylonitrile in the presence of an aqueous solution of KOH[60] (Section III.1.a).

2. Addition to C≡C bonds

Known examples of the addition of phosphine to triple carbon–carbon bonds are limited to phosphorylation of aryl- and hetarylalkynes.[21–23] The reaction proceeds under mild conditions (55–60 °C, atmospheric pressure) upon passing a phosphine–hydrogen mixture, generated from red phosphorus and potassium hydroxide in aqueous dioxane, through an alkyne–KOH–HMPA (H_2O) suspension. The reaction occurs stereoselectively to give tris(*Z*-2-organylvinyl)phosphines **10** in 60%–80% yields.



10

R = Ph, 4-FC_6H_4, .

The kinetic control of this reaction was confirmed by the thermal transformation (160–165 °C, 7 h) of tris[(*Z*)-styryl]-phosphine into the complete *E*-isomer *via* the intermediate formation of the corresponding mixed *E,Z,Z*- and *E,E,Z*-isomers.[123] In the absence of KOH, all other factors being the same, phosphine does not react with alkynes, pointing to a nucleophilic mechanism of this process.

Unlike the reactions of phosphine with aryl- and hetarylalkenes (Section III.1.a), the addition of phosphine to alkynes in highly basic suspensions (KOH–HMPA) cannot be terminated at the stage of formation of mono- or diadducts;[22] this has been explained [7] by the fact that vinylphosphines are more acidic than alkylphosphines.

3. Addition to C=O bonds

a. Reactions of phosphine with aldehydes

Although the first data concerning the reactions of phosphine with aliphatic aldehydes in the presence of hydrogen halides to give tetrakis(1-hydroxyalkyl)phosphonium halides were reported back in 1888 [124] and in 1921,[125] this reaction has not attracted attention of researchers for a long period.

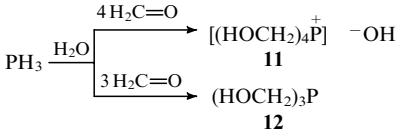
Only 35 years later, did a series of studies appear[126–134] in which tetrakis(hydroxymethyl)phosphonium salts were prepared in quantitative yields by passing a flow of phosphine through an aqueous or aqueous-organic solution of formaldehyde (−10 to 40 °C, atmospheric pressure) in the presence of acids.

$$PH_3 + H_2C{=}O \xrightarrow[H_2O]{H_nX^{n-}} [(HOCH_2)_4\overset{+}{P}]_n\ X^{n-}$$

X = Cl^-, F^-, SO_4^{2-}, $MeCOO^-$, $^-OOC-COO^-$; *n* = 1, 2.

This reaction, which occurs presumably [2] *via* the intermediate formation of the H_2C^+OH cation, has also been carried out for non-branched aliphatic aldehydes.[128, 135, 136]

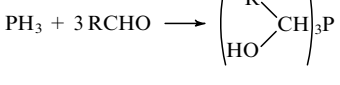
In the presence of heavy metals (Fe, Pt, Pd, Hg, Ag) or their salts ($PtCl_4$, $HgCl_2$, *etc.*), phosphine reacts with an aqueous solution of formaldehyde to give, depending on the ratio of the reactants [137–139] and the nature [140] and the amount [130] of the catalyst, either tetrakis(hydroxymethyl)phosphonium hydroxide **11** [128, 130, 134, 137, 138, 140] or tris(hydroxymethyl)phosphine **12**.[130, 139–142] In the acid-catalysed reaction the latter product was not detected.[126–134]



11 **12**

Since the phosphine **12** has also been obtained by treatment of the phosphonium hydroxide **11** with PH_3 in the presence of heavy metals or heavy metal salts,[11, 139] it can be suggested that the compound **12** is formed *via* the compound **11**.

Hydroxyalkylation of phosphine is a general reaction, which has been described for a broad range of aliphatic, unsaturated, aromatic and heteroaromatic aldehydes including acrolein, glyoxal, cinnamaldehyde and furfural. Tris(1-hydroxyalkyl)phosphines can be readily prepared by this reaction in high yields (up to 92%).[143]

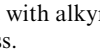


R = Me, Et, CH=CH_2, Ph, 2-FC_6H_4, Cl_3C, *etc.*

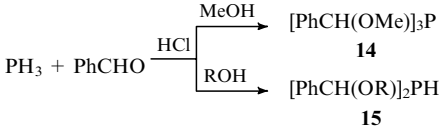
If phosphorylation of aldehydes with phosphine is carried out in the presence of a co-reagent, for example, an organyl halide or an alcohol, and a heavy metal or a heavy metal salt, non-symmetrical phosphonium compounds **13** can be obtained.[144–146]

$$PH_3 + 3\,RCHO + R'X \longrightarrow \{R'\overset{+}{P}[CH(OH)R]_3\}\ X^-$$

13

R = H, Alk, Ar; R′ = Alk, $CH_2{=}CHCH_2$, $PhCH_2$, $HOCH_2CH_2$, CH_2I, , ; X = Hal, OH.

Benzaldehyde reacts with phosphine in methanol saturated with HCl [131, 147] to give tris[methoxy(phenyl)methyl]phosphine **14** in 85% yield. Phosphorylation of benzaldehyde with phosphine in the medium of C_2–C_4 alcohols gives the corresponding secondary phosphines **15** as the main products (yield 80%–90%).[147]

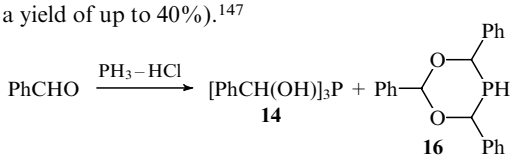


14 **15**

R = Et, Pr^n, Pr^i, Bu^n.

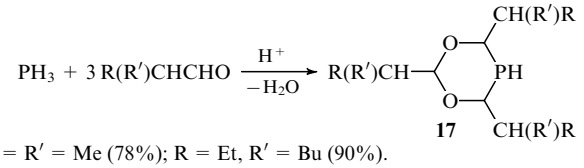
In the absence of alcohol, benzaldehyde reacts with the PH_3–HCl system to give, in addition to the tris[hydroxy(phenyl)-

methyl]phosphine, 2,4,6-triphenyl-1,3,5-dioxaphosphorinane **16** (in a yield of up to 40%).[147]



14 **16**

1,3,5-Dioxaphosphorinanes **17** are the main products of the reaction of phosphine with aliphatic aldehydes substituted at the α-carbon atom carried out in an acid medium.[135, 148–151]

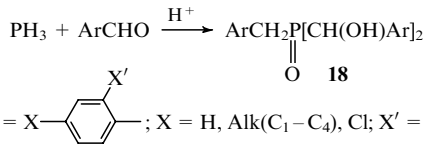


17

R = R′ = Me (78%); R = Et, R′ = Bu (90%).

Apparently, the addition of the secondary phosphines $[R(R')CHCH(OH)]_2PH$, formed initially in this reaction, to a third aldehyde molecule involves the hydroxy group rather than the PH group and thus gives an acetal fragment.[151]

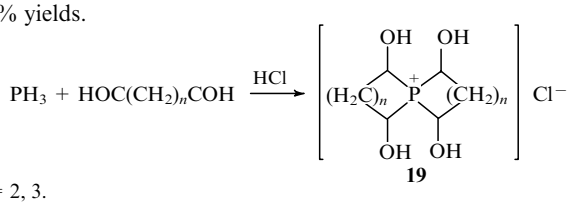
Unlike the hydroxyalkylation of phosphine with aldehydes in dilute acids, which gives phosphines,[3, 131, 147] the reaction of PH_3 with aromatic aldehydes in concentrated aqueous solutions of HCl, HBr and H_2SO_4 affords tertiary phosphine oxides **18** (yield 35%–65%),[152, 153] apparently as a result of transfer of the aldehyde oxygen atom to phosphorus (the mechanism of this process is described in Section III.3.b).



18

Ar = X–C$_6$H$_3$(X′)–; X = H, Alk(C$_1$–C$_4$), Cl; X′ = H, Cl.

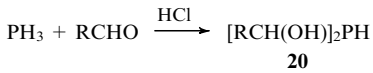
Dialdehydes (glutaric, succinic,[135, 151, 154] phthalic,[154] *etc.*) are usually phosphorylated with phosphine in the presence of concentrated aqueous HCl to give spirophosphonium salts **19** in up to 65% yields.



19

n = 2, 3.

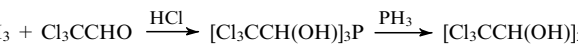
α-Halo-containing aldehydes, for example, chloral,[135, 155, 156] dichloroacetic,[135, 156] trifluoroacetic, 2,2-dichlorobutyric and 2,2,3-trichlorobutyric [156] aldehydes react with phosphine in the presence of acids [135, 155, 156] or without acids in an organic solvent (ether) [155] to give secondary phosphines **20** in high yields (80%–90%).



20

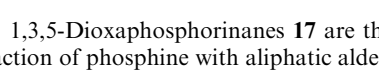
R = CCl_3, $CHCl_2$, CF_3, $EtCCl_2$, $MeCHClCCl_2$.

It has been reported [157] that tris(2,2,2-trichloro-1-hydroxyethyl)phosphine is formed in 75% yield from chloral and PH_3 in the presence of aqueous HCl. However, later it has been shown [158] that passing phosphine through the chloral hydrate–HCl–H_2O system yields initially tris(2,2,2-trichloro-1-hydroxyethyl)phosphine, which then undergoes disproportionation with PH_3 to give a secondary phosphine, bis(2,2,2-trichloro-1-hydroxyethyl)phosphine.



The reaction of phosphine with chloral in the presence of concentrated HCl gave only tris(2,2,2-trichloro-1-hydroxyethyl)phosphine in 92% yield.[158]

Phosphorylation of fluorinated aldehydes with phosphine occurs under mild conditions (for example, in the case of trifluoroacetic aldehyde, on cooling to −70 °C), requires no catalyst and affords tertiary phosphines **21** in 50%–94% yields.[159]

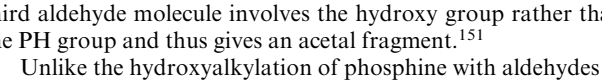


21

R = F_3C, CF_2CHF_2, $(CF_2)_4H$.

It should be noted that in the absence of a catalyst, phosphine reacts with formaldehyde only at elevated temperatures (80–150 °C) and pressures (4–40 atm) [160–168] to give, depending on the ratio of the reactants, tris(hydroxymethyl)phosphine [160–164] or tetrakis(hydroxymethyl)phosphonium hydroxide.[165, 166]

Phosphorylation of formaldehyde with phosphine in the presence of secondary amines follows the Mannich reaction pattern giving rise to tertiary aminomethylphosphines **22**.[169–171]

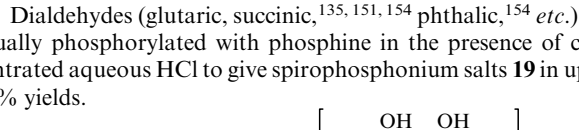


22

R = Alk, cyclo-Alk, Ar; R′ = H, Alk.

b. Reactions with ketones

Being weaker electrophiles than aldehydes, unsubstituted aliphatic ketones do not react with phosphine in the absence of acids or catalysts even under relatively rigorous conditions (100 °C, elevated pressure);[172] in the presence of hydrogen halides in anhydrous solvents [2, 11, 124] or in dilute aqueous solutions of acids [173–175] the reaction does not occur either. However, in the presence of concentrated mineral acids, phosphine adds to ketones at 60 °C and 2–3 atm to give a mixture of primary alkylphosphine oxides **23** and secondary alkyl(1-hydroxyalkyl)-phosphine oxides **24**.[173–175]



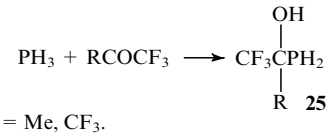
23 **24**

R = R′ = Me, Et; R = Me: R′ = Pr, Ph; R–R′ = $(CH_2)_4$, $(CH_2)_5$.

The primary phosphine oxides **23**, which were first synthesised by this method, are formed, in the opinion of the researchers cited,[173] upon the transfer of the oxygen atom from carbon to phosphorus according to the following scheme:

The second stage of the process, which gives rise to the phosphine oxides **24**, occurs as the normal addition of the P–H bond to the carbonyl group.[173] The **23** : **24** ratio depends on the structure of the initial ketone and increases in the sequence cyclohexanones < cyclopentanone < acetone < pentan-2-one < heptan-2-one < pentan-3-one < acetophenone < heptan-4-one from 1 : 9 (for cyclohexanone) to 9 : 1 (for heptan-4-one).[173, 174]

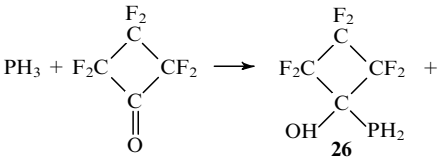
Trifluoro- [176, 177] and hexafluoroacetone [172, 177] react with phosphine without a catalyst at an elevated temperature (60–100 °C) and pressure (10–30 atm) to give primary phosphines **25** in 85% and 62% yields, respectively.

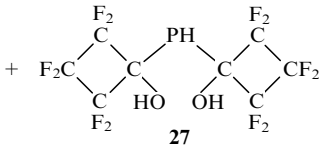


R = Me, CF_3.

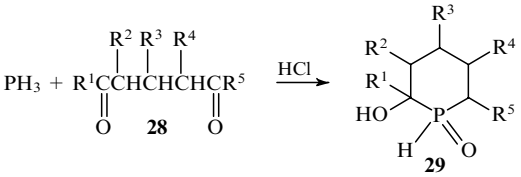
It is believed [172, 176, 177] that the reaction stops at the stage of formation of the primary phosphines **25** because these products are less nucleophilic than PH_3. However, recently the synthesis of a secondary phosphine, bis[(1-hydroxy-1-trifluoromethyl)-ethyl]-phosphine, from phosphine and trifluoroacetone has been reported.[178]

Phosphine and hexafluorocyclobutanone readily react at room temperature to give primary (**26**) and secondary (**27**) phosphines. When excess ketone is used, the yield of the phosphine **27** amounts to 91%.[179]



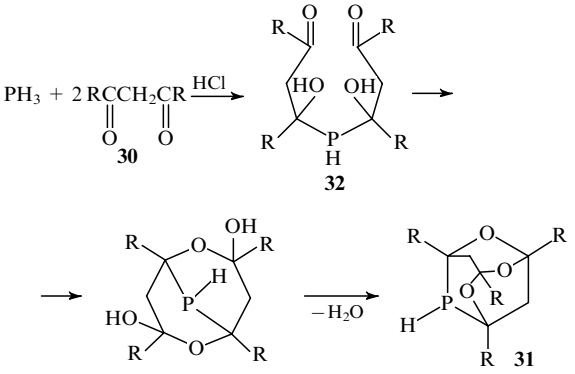


The reaction of 1,5-diketones **28** with phosphine occurs in the presence of HCl as addition–cyclisation with simultaneous transfer of oxygen on the phosphorus atom and results in the formation of 2-hydroxyphosphorinane 1-oxides **29** (yield 30%–80%).[180–182]



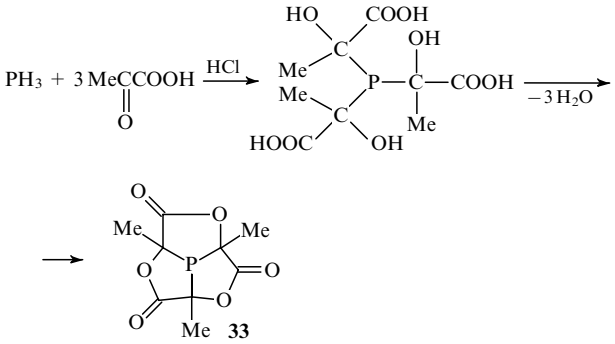
$R^1 = R^5 = Ph$, $R^2 = R^3 = R^4 = H$; $R^1 - R^2 = (CH_2)_4$, $R^3 = R^4 = H$, $R^5 = Ph$; $R^1 - R^2 = R^4 - R^5 = (CH_2)_4$, $R^3 = Ph$; $R^1 - R^2 = (CH_2)_4$, $R^3 = R^5 = Ph$, $R^4 = H$; $R^1 - R^2 = CH_2CMe_2OCH_2$, $R^3 = R^5 = Ph$, $R^4 = H$.

Unlike 1,5-diketones, 1,3-diketones **30** react with phosphine in the presence of concentrated HCl to give tricyclic phosphines **31**.[183–185] The reaction occurs apparently *via* the intermediate secondary phosphine **32**, which forms from two 1,3-diketone molecules; this intermediate undergoes intramolecular cyclisation involving the cross attack on the carbonyl carbon atoms by the hydroxy groups and elimination of water.



R = Me, CF_3.

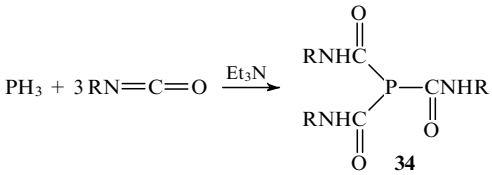
Tricyclic phosphine **33** with three lactone rings has been obtained from phosphine and pyruvic acid.[153, 186]



The general character of this reaction was confirmed by involvement of some other oxo acids into the interaction with phosphine.[186]

4. Addition to C = N bonds

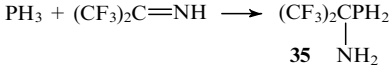
The addition of phosphine to organyl isocyanates occurs in the presence of triethylamine (room temperature, 2–3 atm, anhydrous benzene), involves the C = N bond and gives rise to tricarbamoylphosphine derivatives **34**, their yields being dependent on the nature of the substituent in the isocyanate and ranging from 13% (phosphorylation of phenyl isocyanate) to 100% (the reaction with nitrophenyl isocyanate).[187–189]



R = Et, C_8H_{17}, Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-$NO_2C_6H_4$.

The fact that mono- or diadducts have not been detected during this reaction (even when the reactants were taken in equimolar amounts) suggests that the intermediate organic carbamoylphosphines are more active nucleophilic addends in this process than PH_3.[187]

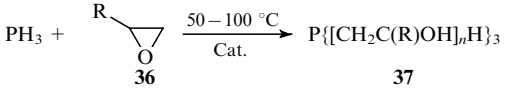
The addition of equimolar amounts of phosphine to the C = N bond in hexafluoroisopropylideneimine stops when primary phosphine **35** has been produced (yield 96%).[190]



5. Reactions of phosphine with oxiranes and thiiranes

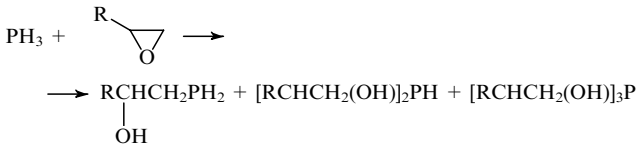
Cleavage of an oxirane or thiirane ring by phosphine occurs in the presence of various catalysts.

Heating (50–100 °C) phosphine with oxiranes **36** in the presence of inorganic or organic bases or acids has resulted in the synthesis of tertiary phosphines **37** with oligooxyalkylene oxide radicals.[191] Complexes of tris(hydroxymethyl)phosphine with nickel(II) chloride [192] or with chloroplatinic acid [193] can also be used successfully as the catalysts in this reaction.



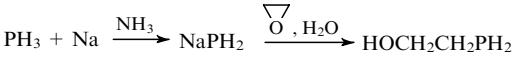
R = H, Me, CH_2Cl, Ph; $n = 3-10$.

In the absence of a catalyst (heating a mixture of phosphine with an oxirane in an autoclave), the total yield of mono-, bis- and tris(2-hydroxyalkyl)phosphines does not exceed 17%.[194]

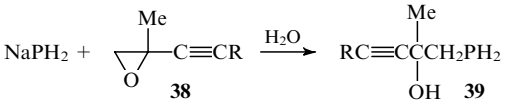


R = H, Me.

A convenient and efficient method for the synthesis of 2-hydroxyethylphosphine (yield 70%) based on phosphorylation of oxirane by the 'phosphine–sodium metal–liquid ammonia' system has been reported.[194]



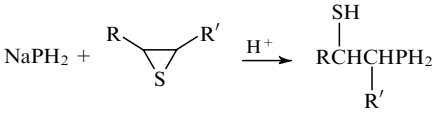
Later, organylethynyloxiranes **38** have also been involved in this reaction to give the corresponding primary hydroxyorganylphosphines **39** in yields of up to 73%.[195]



R = Me, Bu, $CH_2=CH$.

The attempt to carry out phosphorylation of 1-methyl-1-propyloxirane by the 'phosphine–sodium–liquid ammonia' system failed.[195]

Thiirane and its alkyl- and dialkyl-substituted derivatives react with alkali metal dihydrophosphides to give primary 2-sulfanylalkylphosphines.[196–198]



R = R′ = H, Me; R = Me, R′ = H.

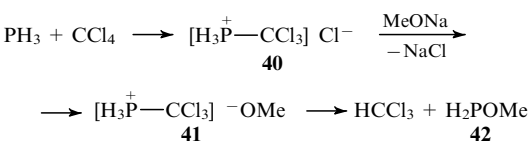
IV. Other reactions of phosphine with organic compounds

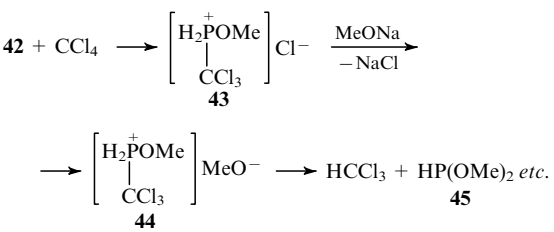
1. Synthesis of esters and amides of phosphorous and phosphoric acids

According to patents,[199–201] phosphine reacts with sodium alkoxides[199,200] or with the alcohol–alkali metal hydroxide systems[201] in a halogenated hydrocarbon solvent to give triorganyl phosphites. Thus trimethyl phosphite was prepared in a quantitative yield from phosphine and sodium methoxide in CCl_4 at 0–20 °C.[199]

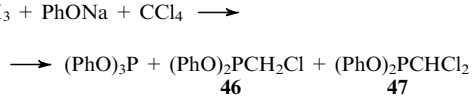
$$PH_3 + 3\,MeONa + 3\,CCl_4 \longrightarrow (MeO)_3P + 3\,CHCl_3 + 3\,NaCl$$

Apparently, the reaction starts with the formation of phosphonium salt **40**; the chloride ion in this salt is replaced by the methoxy ion to give the phosphonium salt **41**. This is followed by elimination of chloroform, and the resulting methoxyphosphine **42** reacts again with CCl_4 to give phosphonium salt **43**. The latter is converted into salt **44** upon exchange with sodium methoxide and then into dimethoxyphosphine **45** upon elimination of a $CHCl_3$ molecule. The last hydrogen atom in the compound **45** is substituted in a similar way.





Heating (80 °C) a mixture of phosphine, sodium phenoxide and CCl_4 in a propylene carbonate medium gives not only triphenyl phosphite but also chloromethylphosphonite **46** and dichloromethylphosphonite **47**, the total yield of the products being 90% (30% of each compound).[200]



Phosphine reacts with trifluoromethanesulfenyl chloride at −95 °C to give, depending on the ratio of the reactants, *S*,*S*,*S*-tris(trifluoromethyl) trithiophosphite or *S*,*S*-bis(trifluoromethyl) phosphonodithioite in 96% and 72% yields, respectively.[3,202]

In recent years, studies have been published dealing with oxidative dehydrocondensation of phosphine with alcohols,[140,203,204] primary[205] and secondary[140] amines and pyridine;[206] these reactions occur in the presence of copper and platinum compounds and give trialkyl phosphites,[140] trialkyl phosphates,[140,203,204] phosphorous triamides,[205] alkylimidophosphoric triamides[140] and tris(2-pyridyl)phosphine,[206] respectively. Unfortunately, these publications[140,203–206] barely give any experimental details and, what is more important, they present no data confirming the structures of the compounds synthesised.

2. Synthesis of organophosphorus compounds with a mono- or dicoordinated phosphorus atom

Synthesis of organophosphorus compounds with mono- or dicoordinated phosphorus atoms based on phosphine is a topical line of research in modern organic chemistry. However, to the best of our knowledge, the data on these reactions are limited to a few publications.[207–210]

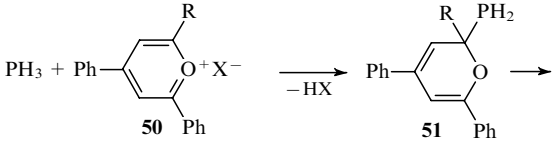
Thus the reaction of phosphine with *O*-nitrosobis(trifluoromethyl)hydroxylamine at room temperature gave *N*-bis(trifluoromethyl)nitroxyiminophosphine (yield 60%).[207]

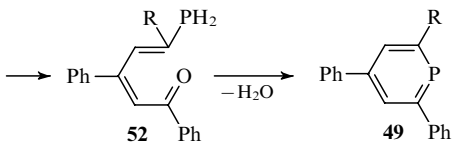
$$PH_3 + (CF_3)_2NON{=}O \longrightarrow (CF_3)_2NON{=}PH$$

The reaction of phosphine with cyanogen bromide affords aminocarbophosphyl hydrobromide **48**.[208] The reaction occurs *via* the initial formation of cyanophosphine hydrobromide, which rearranges into the hydrobromide **48**.

$$PH_3 + BrC{\equiv}N \longrightarrow H_2PC{\equiv}N\cdot HBr \longrightarrow \underset{\mathbf{48}}{H_2NC{\equiv}P\cdot HBr}$$

Phosphorus analogues of pyridine, phosphorines **49**, have been prepared by treatment of the pyrylium salts **50** with phosphine in butanol in the presence of mineral acids at 120–130 °C (yields up to 61%).[209,210] Apparently, the reaction passes through the intermediate formation of primary phosphines **51** and **52**.





R = Me, Ph; X = BF_4.

V. Conclusion

The data considered in this review demonstrate that phosphine, which is the simplest available phosphorus compound, is a convenient reagent for the formation of a C–P bond in the synthesis of various organic, organoelement and functionally substituted phosphines, which are finding ever increasing use as ligands for the preparation of metal-complex catalysts.

The ease and practical feasibility of the preparation of phosphine by direct hydrolysis of elemental phosphorus, which had been noted long ago by D I Mendeleev and V N Ipat'ev,[211] and its high, although not adequately studied, reactivity are the objective prerequisites for more extensive involvement of phosphine in organophosphorus synthesis.

However, it should be noted that unlike its nitrogen analogue — ammonia — which has became the synthetic base for the whole chemistry of the organic compounds of nitrogen, phosphine has not found equally wide use in organophosphorus chemistry despite the numerous obvious advantages of phosphine over, for example, phosphorus chlorides.

The authors hope that this review would be favourable for further development of the chemistry of phosphine and, first of all, development of new convenient methods for the synthesis of various organophosphorus compounds based on phosphine. The exceptionally simple method for the generation of a phosphine–hydrogen mixture by alkaline hydrolysis of red phosphorus that we developed previously may stimulate further studies along this line.[6, 7, 14, 22]

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