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Tertiary Phosphines with Functional-group Substituents

O.A.Erastov and G.N.Nikonov

The methods of synthesis of substituted tertiary phosphines and the characteristic features of the mutual influence of the phosphino-group and the substituent, manifested in physicochemical properties (equilibrium between the conformers or stereoisomers, geometrical parameters of the molecules) and in the reactivity (pathways leading to the decomposition of phosphonium compounds, reactions of functional groups with electrophiles, nucleophilic substitution, tautomerism, rearrangements), are examined.
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I. INTRODUCTION

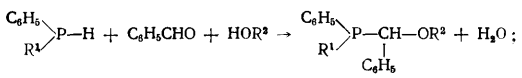
Tertiary phosphines containing electron-accepting substituents possess a high and varied reactivity. Firstly, they enter into reactions typical for tertiary phosphines and the functional groups present. The mutual influence of the active centres is manifested in the reaction rates and in the stability of the products formed. Secondly, features determined by the presence of closely linked functional groups are characteristic of such compounds. They react with electrophiles to form phosphonium compounds which are unstable and are stabilised as a result of proton transfer to the negative centre of the electrophile with formation of new tertiary phosphines or ylides. These reactions exhibit an analogy in reactivity between tertiary phosphines with functional-group substituents and primary or secondary phosphines and also esters of tervalent phosphorus acids. The presence of an electron-accepting substituent facilitates nucleophilic substitution at the carbon atom attached to the phosphorus atom and both the phosphino-group and the functional group can be eliminated. The closeness in space of the phosphino-group and the substituent creates favourable conditions for rearrangements. The accumulation of electron-accepting substituents at the carbon atom attached to the phosphorus atom leads to prototropic diad phosphorus–carbon tautomerism.

The synthesis of tertiary phosphines with functional-group substituents is based on the available starting material such as phosphine, tervalent phosphorus acid chlorides, and white phosphorus. It is therefore not surprising that during the last decade there has been a rapid development of the chemistry of compounds of this class and many investigations, which need to be surveyed, have been published. This review deals with the methods of synthesis and properties of tertiary phosphines with functional-group substituents. These problems have been partly discussed in other communications[1-5].

II. METHODS OF SYNTHESIS

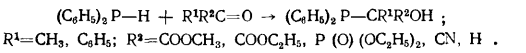
Tertiary phosphines with functional-group substituents can be obtained from phosphines, silylphosphines, phosphides, tervalent phosphorus acid chlorides, and derivatives such as phosphonium salts, phosphine oxides, and phosphine sulphides.

The most general method of synthesis involves the addition of phosphines via the P–H bond to unsaturated compounds. Phosphine[1] and primary and secondary phosphines[6-10] react with aldehydes in a neutral medium to form α-hydroxyalkylphosphines. Halogen-containing aldehydes also enter into the reaction; thus crystalline tris(α-hydroxy-β,β,β-trichloroethyl)phosphine has been obtained from PH_3 and chloral[11]. α-Alkoxyalkylphosphines are formed in the presence of alcohols[12]:



R^1=CH_3, C_6H_5; R^2=CH_3, C_2H_5, iso-C_3H_7, C_4H_9 .

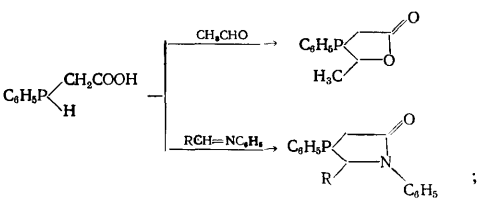
Ketones react similarly to aldehydes. Substituents do not influence the mode of reaction. α-Alkoxycarbonyl-α-hydroxyethylphosphines have been obtained by reaction with pyrubic acid esters[13,14]:



R^1=CH_3, C_6H_5; R^2=$COOCH_3$, $COOC_2H_5$, P (O) $(OC_2H_5)_2$, CN, H .

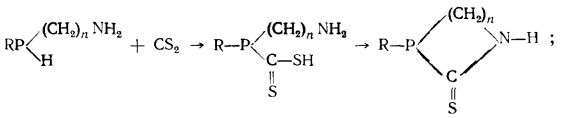
The addition of phosphines to thiobenzophenone[15], azomethines[16], isocyanates, and carbodi-imides[17,18] has been described. The interaction of phenylphosphine with azomethines and benzaldehyde leads to the formation of *N*-substituted 2,4,5,6-tetraphenyl-1,3,5-oxazaphosphorinanes[19].

The addition of primary and secondary phosphines to ethylenesulphonyl fluoride[20], vinyl sulphones[21], vinylsilanes[22,23], vinylphosphines[24], allylamines[25], and unsaturated acid esters[26] has led to the corresponding β- and γ-substituted tertiary phosphines. The reactions of primary phosphines take place stepwise and can be arrested in the first stage, which makes it possible to substitute the hydrogen atoms in succession by various functional groups. 1,3-Azaphospholan-5-ones and 1,3-oxaphospholan-5-ones[27,28], 1,3-oxaphospholans[29], 1,3-oxaphosphorinanes[30], and 1,3-azaphosphepanes[31] have been obtained in this way, for example:



$R=CH_3$, C_2H_5, C_6H_5 .

The introduction of carbon disulphide into the reaction with aminoalkylphosphines made it possible to obtain 1,3-azaphospholanes and 1,3-azaphosphorinanes with thiocarbonyl groups in the ring[32]:



n=2, 3; R=C_4H_9, C_6H_5, cyclo-C_6H_{11} .

Acylphosphines[33] and γ-hydroxypropylphosphines[34] have been obtained by the addition of phosphines to ketens and oxetan respectively.

Tertiary phosphines with functional-group substituents can be obtained from phosphines also with the aid of the substitution reaction. Aminomethylation of phosphines by alkoxymethylamines and diaminomethanes yielded aminomethylphosphines[35-37]:

$$R^1R^2PH + R_2^3NCH_2OCH_3 \rightarrow R_2^3NCH_2PR^1R^2 ;$$

R^1= iso-C_3H_7, t-C_4H_9; R^2= iso-C_3H_7, $CH_2C_6H_5$;

R_2^3=O $(CH_2CH_2)_2$;

$$[(CH_3)_2N]_2CH_2 + R_2PH \rightarrow (CH_3)_2NCH_2PR_2 ;$$

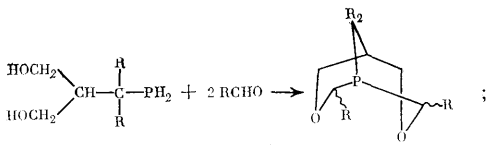
R= iso-C_3H_7 .

Secondary phosphines react with orthoformates in the presence of BF_3 at 20 °C to form phosphinoformals[38]:

$$R_2P{-}H + HC(OR)_3 \rightarrow R_2PCH(OR)_2 + ROH$$

R=C_2H_5, C_4H_9

3,7-Dioxa-1-phosphabicyclo[3.3.1]nonanes have been synthesised by the reaction of aldehydes with a primary phosphine containing two β-hydroxy-groups[39]:



R = H, CH_3, iso-C_3H_7 .

Silylphosphines are used widely to obtain tertiary phosphines with functional-group substituents. Like phosphines, which contain the P—H bond, silylphosphines react with carbonyl compounds to form siloxyalkylphosphines[40-42]:

$$R_n^1P(SiR_3^2)_{3-n} + (3-n)R^3CHO \rightarrow R_n^1P\left(\begin{matrix}CHOSiR_3^2\\ |\\ R^3\end{matrix}\right)_{3-n} ;$$

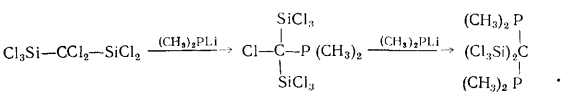
n=1, 2; R^1=C_6H_5; R^2=CH_3; R^3=H, C_6H_5, C $(CH_3)_3$, CN .

Reactions of diorganylsilylphosphines with carboxylic acid chlorides yield acylphosphines[40,43-45]. The trimethylsilylphenyl group adds to carbodi-imides[18] and substitues the chlorine atom in dichloromaleic ester[46].

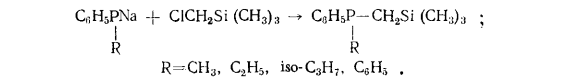
In the reactions with halogen-containing compounds, it is possible to employ metal phosphides instead of silylphosphines. Trialkoxycarbonylphosphines have been obtained from sodium phosphide and chlorocarbonic acid esters[47], while trifluorovinylphosphines are formed in small amounts from lithium phenylphosphides and trifluorovinyl halides[48]. Lithium or sodium phenyl- and methyl-phosphides react with 3-chloropropyldiphenylphosphine to form γ-diphosphines[49]. The reaction of sodium diphenylphosphide with methylene chloride results in the formation of tetraphenylmethylenediphosphine[50]:

$$2(C_6H_5)_2PNa + CH_2Cl_2 \rightarrow (C_6H_5)_2PCH_2P(C_6H_5)_2 .$$

α-Chloromethyldimethylbis(α-trichlorosilyl)phosphine, which is capable of undergoing many further transformations, has been obtained from lithium dimethylphosphide. The substitution of the mobile chlorine atom in this compound leads to new derivatives of tertiary phosphines[51]:

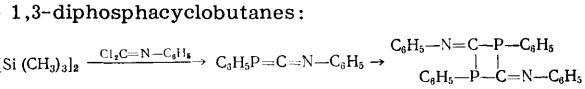


Together with the electron-accepting substituents enumerated above, the use of metal phosphides has made it possible to introduce the electron-donating trimethylsilylmethyl group in the α-position with respect to the phosphorus atom[52]:

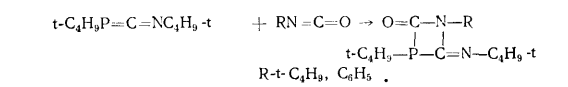


R=CH_3, C_2H_5, iso-C_3H_7, C_6H_5 .

One of the methods of synthesis of heterocyclic phosphines with functional-group substituents is the dimerisation of compounds of dicoordinate phosphorus. The interactions of disilylphosphines with carbon disulphide[53] or phenyl isocyanide dichloride[54], of lithium silylphosphide with carbonyl compounds[55], and of disilylphosphines and primary phosphines with ketones and dimethylformamide[56] lead to the formation of compounds with a dicoordinate phosphorus atom, which dimerise to 1,3-diphosphacyclobutanes:



The cycloaddition of isocyanates to "carboimidophosphene" yields 1,3-azaphosphetidines with imino- and carbonyl groups[57]:



R-t-C_4H_9, C_6H_5 .

Tervalent phosphorus acid chlorides readily react with compounds having a mobile hydrogen atom or with organometallic compounds. The abstraction of hydrogen chloride by triethylamine has been observed in the phosphorylation of methyl trifluoromethyl sulphone and malonic acid esters by chlorodialkylphosphines[58,59]:

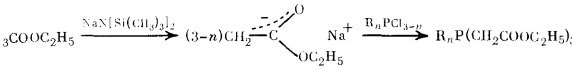
$$CH_3SO_2CF_3 + (C_2H_5)_2PCl \rightarrow (C_2H_5)_2PCH_2SO_2CF_3 + HCl ;$$
$$CH_2(COOR)_2 + (C_2H_5)_2PCl \rightarrow (C_2H_5)_2PCH(COOR)_2 + HCl ;$$

R=CH_3, C_2H_5 .

This yielded tertiary phosphines with trifluoromethanesulphonyl and alkoxycarbonyl groups. The latter are also formed in the phosphorylation of triethylstannylacetic acid esters[60] and sodio-derivatives of carboxylic acid esters having the enolate structure[61]:

$$2(C_2H_5)_3SnCH_2COOC_2H_5 + RPCl_2 \rightarrow RP(CH_2COOC_2H_5)_2 ;$$

R=CH_3, C_6H_5 ;



R= iso-C_3H_7, C_6H_5; n = 0, 1, 2 .

The interaction of tetrachloromethylenediphosphine with organomagnesium compounds leads to diphosphinomethanes[62]:

$$Cl_2PCH_2PCl_2 \xrightarrow{4RMgCl} R_2PCH_2PR_2 ;$$

R=CH_3, C_2H_5, iso-C_3H_7, s-C_4H_9, C_6H_5 .

The phosphorylation of the lithio-derivatives of these compounds makes it possible to introduce yet another phosphino-group[63,64]:

$$LiHC[P(CH_3)_2]_2 + (C_6H_5)_2PCl \rightarrow (CH_3)_2P{-}CH(P(C_6H_5)_2){-}P(CH_3)_2 .$$

Di- and tri-(*o*-hydroxyphenyl)phosphines[65] phosphorus-containing alkenes[66], and 2-vinylphosphiran[67] have also been obtained from organometallic compounds and phosphorus chlorides:

$$o\text{-}LiOC_6H_4Li + PCl_3 \rightarrow (o\text{-}HOC_6H_4)_3P;$$
$$(C_6H_5)_2PCl + BrMgCH{=}CHR \rightarrow (C_6H_5)_2PCH{=}CHR;$$
$$R{=}CH_3,\ C_6H_5;$$
$$RPCl_2 + \underset{\diagdown\!\!\diagup}{MgCH_2CH{=}CHCH_2} \rightarrow \underset{\diagdown\!\!\diagup}{RP{-}CH_2CHCH{=}CH_2};$$
$$R{=}CH_3,\ C_6H_5,\qquad t\text{-}C_4H_9.$$

The methods of synthesis of tertiary phosphines with functional-group substituents and the corresponding derivatives of quinquevalent phosphorus, namely phosphonium salts, phosphine oxides, and phosphine sulphides, are also important. The cleavage of tetra(hydroxymethyl)phosphonium salts by bases yields tri(hydroxymethyl)phosphine[1,68]. Tertiary phosphines can be used as the bases[69]:

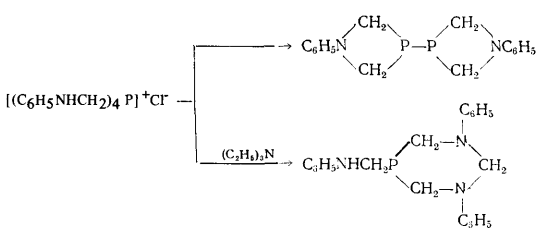
$$[(HOCH_2)_4P]^+Cl^- + (C_4H_9)_3P \rightarrow (HOCH_2)_3P + [(C_4H_9)_3PCH_2OH]^+Cl^-$$

When tetra(chloromethyl)phosphonium chloride is treated with alkali, tri(chloromethyl)phosphine is formed[70]:

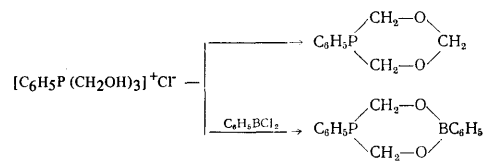
$$[(ClCH_2)_4P]^+Cl^- \xrightarrow{NaOH} (ClCH_2)_3P.$$

Methylcarbamate derivatives of tri(hydroxymethyl)phosphine have been obtained from methylcarbamate derivatives of phosphonium salts[71].

The disproportionation of phosphonium salts involves the formation of various products including tertiary phosphines with functional group substituents. Refluxing of tetra-anilinomethyl)phosphonium chloride in ethanol leads to the formation of 1,1'-diphenyl-1,1'-diaza-3,3'-diphosphetidine[72], while its treatment with triethylamine gives rise to 5-anilino-methyl-1,3-diphenyl-1,3,5-diazaphosphorinane[73]:



2,5-Diphenyl-1,3,2,5-dioxaboraphosphorinane has been obtained by heating tri(hydroxymethyl)phenylphosphonium chloride with dichlorophenylborane[74]. 5-Phenyl-1,3,5-dioxaphosphorinane is formed in the absence of dichlorophenylborane[75]:



There exist examples of the reduction of phosphine oxides containing fucntional groups. Many aromatic tertiary phosphines containing hydroxy-, cyano-, alkoxycarbonyl, and formyl groups as well as other substituents in the *ortho*-, *meta*-, and *para*-, positions in the aromatic ring have been obtained in this way[76,77]. Trichlorosilane has been used as the reducing agent. The oxides can be converted into sulphides in a preliminary step with subsequent removal of sulphur by treatment with triphenyl phosphite[78]:

$$(ClCH_2)_2\overset{O}{\overset{\|}{P}}Cl \xrightarrow{P_2S_5} (ClCH_2)_2P(S)Cl \xrightarrow{(C_6H_5O)_3P} (ClCH_2)_2PCl \xrightarrow{RMgBr} (ClCH_2)_2PR;$$
$$R{=}CH_3,\ C_2H_5.$$

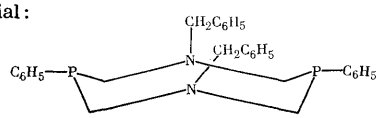
The products of the addition of hypophosphorous acid to unsaturated compounds[79,80] as well as tertiary phosphine oxides with nitro-[81], amino-[82,83], phenoxy-[84], and alkoxycarbonyl groups[5], particularly those obtained from white phosphorus[85], are of interest as compounds to be reduced.

In addition to the above discussion, attention should be drawn to the possibility of obtaining tertiary phosphines with functional-group substituents by adding aluminophosphines[86] and germylphosphines[87] to unsaturated compounds:

$$R_2AlP(C_6H_5)_2 \xrightarrow{R^1C\equiv N} R_2AlN{=}CR^1P(C_6H_5)_2;$$
$$R{=}C_6H_5,\ n\text{-}CH_3C_6H_4,\ изо\text{-}C_4H_9;\ R^1{=}C_6H_5,\ CH_3;$$
$$(CH_3)_3GeP(CH_3)_2 \xrightarrow{(CH_3)_3SiC(O)C_6H_5} (CH_3)_3GeC(C_6H_5)P(CH_3)_2.$$
$$\qquad\qquad\qquad

In the case of aryl substituents at the N atoms, conformer (VI) is absent from the equilibrium. The contents of form (IV) in the equilibrium (IV) ⇌ (V) are 24,34, and 0% for R = C_6H_5, $C_6H_4CH_3$-*p*, and C_6H_4Br-*p* respectively. 1,3-Dibenzyl-5-phenyl-1,3,5-diazaphosphorinane is a mixture of conformers (V) and (VI) (64:36). This has been confirmed by X-ray diffraction[107]; it was found that in the crystalline state the compound has the chair conformation with axial orientation of the benzyl group at one of the N atoms. In terms of the position of the conformer equilibrium, 1,3-dibenzyl-5-phenyl-1,3,5-diazaphosphorinane differs little from 1,3-dimethyl-1,3-diazane (40% of the form with the axial orientation of the methyl group[104]). Hence it follows that in 1,3,5-diazaphosphorinanes there is an interaction between the N atoms in which the P atom is not involved.

In the case of 1,5-diaza-3,7-diphosphacyclo-octanes, there are no competing interactions, which makes it possible to solve the problem of the mutual influence of the atoms in the P–C–N system. According to X-ray diffraction data[108], 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclo-octane exists in the crown conformation. The P and N atoms are involved in a trigonal-pyramidal coordination (the sums of the valence angles are 297° and 343° respectively). The positions of the phenyl groups at the P atoms are pseudo-equatorial while those of the benzyl groups of the N atoms are pseudoaxial:



The pseudoaxial orientation of the substituents at the N atoms can be regarded as a consequence of the interaction between the heteroatoms in the P–C–N system; it is analogous to that observed in the N–C–N system[103–105].

According to one concept[109], the interaction between the heteroatoms in the N–C–O and N–C–N systems, stabilising the axial orientation of the substituent at the N atom, involves the transfer of electron density from the orbital of the unshared electron pair of the nitrogen atom to the unoccupied orbital of the C–O or C–N bond. From this standpoint, the electron shifts in the P–C–O and P–C–N systems should be of different types, since they stabilise the axial orientation of the substituent at the P atom in the former case and of the substituent at the nitrogen atom in the latter case.

The influence of the interaction of the groups in tertiary phosphines with functional-group substituents can be manifested not only by the position of the conformational equilibrium or the equilibrium between the stereoisomers but also by other characteristics of the molecule: bond lengths, bond angles, dipole moments, NMR parameters, etc. 2,6,7-Trioxa-4-phosphabicyclo[2.2.2]-octanes are of interest in this connection. There exist X-ray diffraction data for the bicylcic phosphorothioate $S{=}P(OCH_2)_3P$ and its derivatives[110] as well as the complex $P(OCH_2)_3P.Fe(CO)_5.P(OCH_2)_3P$.[111] The P–C bond lengths and valence angles at the phosphorus atoms in these compounds are close to the normal values. The experimental dipole moments of $P(CH_2O)_3P$ (3.10 D) and $P(CH_2O)_3As$ (1.58 D) agree well with the calculated values (2.94 and 1.49 D respectively)[112]. The ^1H NMR spectra of the compound $P(CH_2O)_3P$ and certain analogous bicyclic compounds and their derivatives have been examined[113–116]. The spin–spin coupling constants $^2J_{PH}$ for all phosphorus(III) compounds are close to the expected values; it was not possible to observe deviations in the case of 2,6,7-trioxa-4-phosphabicyclo[2.2.2]octanes.

X-Ray diffraction data for 1,3,5-triaza-7-phospha-adamantane and its derivatives have been published[117,118]. The C–N bond length and the angles at the N atoms are close to the normal values. There are appreciable differences between the P–C bond lengths and the latter deviate from the usual value (1.841 Å). However, it is not possible to find a correlation between the observed changes and the interaction of the heteroatoms.

Such correlation has been postulated for 1,5-dibenzyl-3,7-diphosphacyclo-octane[108] and 1,3-dibenzyl-5-phenyl-1,3,5-diazaphosphorine[107]. The decrease of the C–N bond lengths (on average 1.452 Å) and the increase of the P–C bond lengths (on average 1.888 Å) in the former compound and also the decrease of the C–N bond length to 1.424 Å in the latter compound can be explained by the transfer of electron density from the unshared electron pair orbital of the N atom to the unoccupied orbitals of the P–C and C–N bonds respectively. In tetraphenyl-1,5-diaza-3,7-diphosphacyclo-octane[119] the endocyclic bond lengths agree with those found for 1,5-dibenzyl-3,7-diphenyl-1,5-diaza-3,7-diphosphacyclo-octane[108].

Apart from the results examined above, there exists also data obtained by X-ray diffraction for 2,4-di-t-butyl-2,4-bis(trimethylsiloxy)-1,3-diphosphetan[120], 4-phosphorinanones[121,122], and complexes of tri(β-cyanoethyl)phosphine[123]. The vibrational spectra of acylphosphines have been investigated[124]. In the liquid phase these compounds exist in the form of a single conformer having a plane of symmetry. The considerable decrease of the barriers to pyramidal inversion of the phosphorus atom in acylphosphines compared with tertiary phosphines have been explained by the conjugation of the unshared electron pair of the P atom with the C=O group in the planar transition state[125].

IV. CHEMICAL PROPERTIES

Tertiary phosphines with functional-group substituents undergo oxidation reactions and addition reactions involving the C atom, which are typical for tertiary phosphines. They give rise to phosphine oxides, sulphides, and selenides, phosphonium salts, and other tertiary phosphine derivatives. The influence of the functional groups is manifested by changes in the rates of reaction and in the stability of the products formed[1]. In addition there are many reactions characteristic of these compounds which are due to the presence of functional groups; these are the substitution reactions on treatment with electrophiles or nucleophiles, prototropic phosphorus–carbon diad tautomerism, and rearrangements.

1. Reactions with Electrophiles

The introduction of electron-accepting substituents leads to the appearance of new pathways to the decomposition of the phosphonium compound formed initially; they are associated with the position of the mobile hydrogen atom in the molecule. If the mobile hydrogen atom is in the α-position relative to the phosphorus atom, the phosphonium compound can be stabilised by its elimination in the form of a proton and an anion, the compound itself being converted into an ylide. When the mobile hydrogen atom is in the β-position with respect to the phosphorus atom, there is a possibility of proton transfer from this position to the anionic centre of the molecule with the dissociation of the P–C bond. As a result, the phosphonium compound can decompose into an unsaturated compound and a new tertiary phosphine. In both cases there is a possibility of a competing reaction involving the nucleophilic centre of the functional group. The anions of tertiary phosphines with functional-group substituents undergo competing reactions.

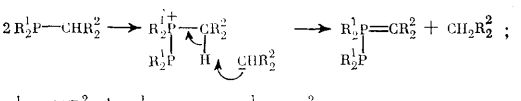
(a) Phosphines with a Mobile α-Hydrogen Atom

The stabilisation of a phosphonium compound by the elimination of a proton from the α-carbon atom with formation of phosphorus ylides has been observed in the reaction of (diethoxycarbonylmethyl)diethylphosphine with ethyl iodide in the presence of triethylamine[126]:

$$R_2PCH(COOR)_2 \xrightarrow{RI} [R_3PCH(COOR)_2]^+I^- \xrightarrow[-HI]{} R_3P{=}C(COOR)_2 ;$$

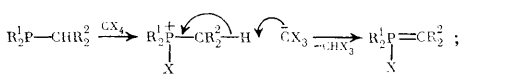
$$R{=}C_2H_5 .$$

Ylides are obtained on disproportionation of (dialkoxycarbonylmethyl)diethylphosphines and diethyl(trifluoromethanesulphonylmethyl)phosphine[127,128] and also on their interaction with chlorodiethylphosphine in the presence of triethylamine[129]:



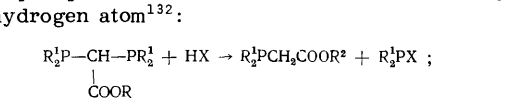
$$R^1{=}C_2H_5;\ R^2{=}COOCH_3,\ COOC_2H_5 \text{ or } CR^2_2{=}CHSO_2CF_3 .$$

The reactions of these compounds with carbon tetrahalides proceeds analogously[130,131]:



$$R^1 = \text{alkyl},\ C_6H_5;\ CR^2_2{=}CH_2,\ CHSO_2CF_3,\ C(SO_2C_6H_5)_2,\ C(CO_2CH_3)_2;\ X = Cl, Br .$$

The activation of the molecule as a result of the formation of hydrogen bonds involving the functional group can lead to the elimination of the phosphino-group on nucleophilic attack. Similar behaviour has been observed in the interaction of the esters of diphosphinoacetic acids with compounds having a mobile hydrogen atom[132]:

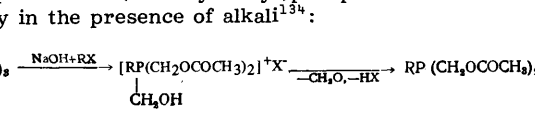


$$R^1{=}\text{iso-}C_3H_7;\ R^2{=}C_2H_5;\ X{=}OH,\ OC_2H_5,\ NR_2,\ OCOCH_3 .$$

Thus electrophilic substitution reactions leading to an increase of the coordination number of the phosphorus atom are characteristic of phosphines having a mobile α-hydrogen atom.

(b) Phosphines with a Mobile β-Hydrogen Atom

There exist numerous instances of the decomposition of phosphonium derivatives with elimination of a proton from the β-position and the liberation of an unsaturated compound, which results in the formation of a tertiary phosphine. Thus, when tri(hydroxymethyl)-phosphine was treated with alkyl halides, the hydroxymethyl groups were substituted by the alkyl groups[133]. Tri(acetoxymethyl)phosphine reacts analogously in the presence of alkali[134]:

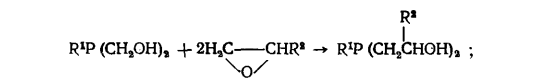


$$R{=}C_2H_5,\ C_3H_7,\ C_4H_9,\ C_6H_{11},\ C_6H_{13};\ X{=}Br,\ I .$$

Dimethyl sulphate has been used together with alkyl halides[135]. In the latter case the interaction of the phosphonium salts with hydrochloric acid leads to the formation of chloromethylphosphine oxides[136].

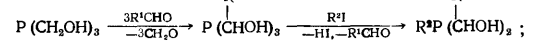
Tri(hydroxymethyl)phosphine[137] as well as di(hydroxymethyl)phosphines[138] react with acrylonitrile in a neutral medium to form the corresponding β-cyanoethylphosphines. The reaction of tri(hydroxymethyl)phosphine with acrylic acid esters proceeds analogously[139]. In an aqueous alcoholic medium β-cyanoethylphosphines are converted into β-alkoxycarbonylethylphosphines[140].

Substitution products have been obtained in the reaction of alkyldi(hydroxymethyl)phosphines with epoxides[141,142]:



$$R^1{=}CH_3,\ C_2H_5,\ C_3H_7,\ C_4H_9,\ \text{iso-}C_6H_{11};\ R^2{=}H,\ CH_3 .$$

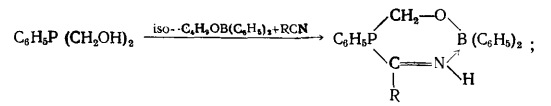
The conclusion that intermolecular exchange of hydroxymethyl groups takes place in the case of tri(hydroxymethyl)-phosphine was reached on the basis of the study of the temperature-induced changes in the NMR spectra[143-145]. The possibility of such a reaction has been confirmed by the isolation of tri(α-hydroxyalkyl)phosphines on interaction of tri(hydroxymethyl)phosphines with aliphatic aldehydes[146]:



$$R^1{=}CH_3,\ C_3H_7,\ \text{iso-}C_3H_7,\ C_6H_{13};\ R^2{=}CH_3,\ C_2H_5,\ C_3H_7 .$$

The hydroxyalkyl derivatives of the phosphines obtained in this way react with alkyl halides. After treatment of the products with triethylamine, the corresponding alkyldi-(α-hydroxyalkyl)phosphines were isolated. They were also obtained from alkyldi(hydroxymethyl)phosphines and aldehydes[146].

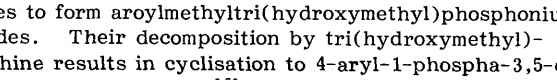
The hydroxymethyl groups are also displaced on interaction with unsaturated ketones[147,148]. Imidoylphosphines have been obtained by the reaction of di(hydroxymethyl)-phenylphosphine with isobutyl diphenylborinate in the presence of nitriles[149]:



$$R{=}CH_3,\ C_6H_5 .$$

In the absence of nitriles the product is 5-hydroxymethyl-2,2,5-triphenyl-2-borata-5-phosphonia-1,3-dioxan[150].

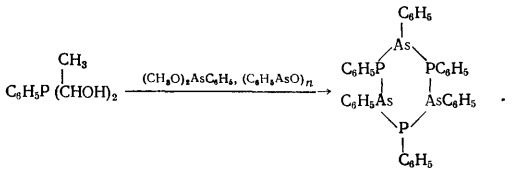
Tri(hydroxymethyl)phosphine reacts with aryl bromomethyl ketones to form aroylmethyltri(hydroxymethyl)phosphonium bromides. Their decomposition by tri(hydroxymethyl)-phosphine results in cyclisation to 4-aryl-1-phospha-3,5-dioxabicyclo[2.2.1]heptanes[151]. The reaction of tris(trimethylsiloxymethyl)phosphine with aryl bromomethyl ketones proceeds differently; when triethylamine is added, hydrogen bromide is split off with formation of ylides[152]:



$$R^1{=}Si(CH_3)_3;\ R^2{=}H,\ CH_3,\ OCH_3,\ Br,\ NO_2 .$$

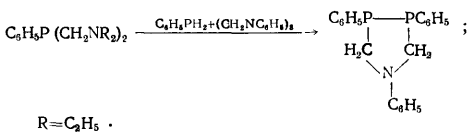
In the former case the reaction proceeds with participation of the β-hydrogen atom and in the latter case with that of the α-hydrogen atom.

There exist examples of the substitution of hydroxyalkyl groups by organoelemental groups. When di(α-hydroxyethyl)phenylphosphine was allowed to react with phenylarsine oxide or dimethyl phenylarsonite, hexaphenyl-1,3,5-triphospha-2,4,6-triarsacyclohexane was obtained[153]:



Aminomethyl groups are also capable of being substituted by organic and organoelemental groups. The reaction of 5-*p*-toluidinomethyl-1,3-di-*p*-tolyl-1,3,5-diazaphosphorinane with methyl iodide led to the isolation, instead of the addition products, of one of the symmetrisation products—5,5-dimethyl-1,3-di-*p*-tolyl-1,3,5-diazaphosphonarinane iodide having two methyl groups at the phosphorus atom[154]. A product with two aminomethyl groups at the phosphorus atom has been obtained by treating di-isopropylmorpholinomethylphosphine with methyl iodide[155]. The overall result of these two reactions is the formation of both symmetrisation products.

When bis(diethylaminomethyl)phenylphosphine is heated with phenylphosphine, diethylmethylamine and diethylamine are produced together with the formation of $(C_6H_5P)_5$ and $(C_6H_5P)_4CH_2$.[156] In the presence of 1,3,5-triphenyl-1,3,5-triazane, the product is 1,3,4-triphenyl-1,3,4-azadiphospholan[157]:



R=C_2H_5 .

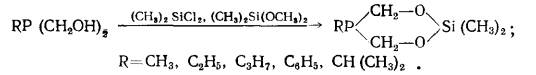
Tri(β-cyanoethyl)phosphine also reacts with methyl iodide to form substitution products[158].

An interesting instance of electrophilic substitution is provided by the reactions of tri(hydroxymethyl)phosphine leading to compounds with a dicoordinate phosphorus atom. Phosphacyanines[159] and 2,4,6-triphenylphosphabenzene[160] have been obtained in this way.

Tris(trimethylsiloxymethyl)phosphine without mobile hydrogen atoms give rise to dihalogenotris(trimethylsiloxymethyl)phosphorane on interaction with PCl_5 and HCl.[161]

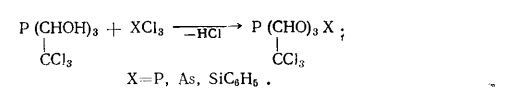
Reactions involving the functional group are extremely characteristic of phosphines having a mobile β-hydrogen atom. The interaction of alkyldi(hydroxymethyl)phosphines with phenyl and *m*-chlorophenyl isocyanates, leading to alkyldi(arylaminocarbonyloxymethyl)phosphines, takes place readily[162]. Alkyldi(hydroxymethyl)phosphines react vigorously with di-isocyanates to form polyurets[163]. Apart from isocyanates, carbonyl compounds have been used as the organic electrophiles. On heating di(hydroxymethyl)phenylphosphine or tri(hydroxymethyl)phosphine in a mixture of acetic acid and acetic anhydride, the corresponding acetates were obtained[6,134]. The reaction of di(α-hydroxyalkyl)phenylphosphines with aldehydes leads to the formation of 1,3,5-dioxaphosphorinanes[95]. When tri(hydroxymethyl)phosphine was heated with trimethyl orthoformate or trimethyl orthoacetate, trioxaphosphabicyclo[2.2.2]octane derivatives were obtained[164,165].

Organoelemental electrophiles can also react via the functional group. Tri(hydroxymethyl)phosphine[166,167] and alkyldi(hydroxyalkyl)phosphines[168] have been silylated. Chlorotriethylsilane and hexamethyldisilazane can be used instead of chlorotrimethylsilane. The employment of dichlorodimethylsilane and dimethoxydimethylsilane leads to the formation of 1,3,2,5-dioxasilaphosphorinanes. In the former case the reaction takes place in ether in the presence of triethylamine and in the latter on refluxing in toluene in the presence of sodium methoxide[169]:



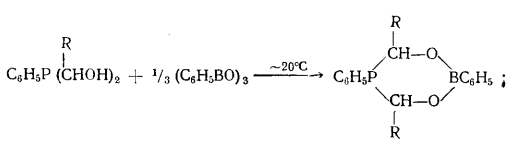
R=CH_3, C_2H_5, C_3H_7, C_6H_5, $CH(CH_3)_2$.

2,6,7-Trioxa-1,4-diphosphabicyclo[2.2.2]octane[170] and its arsenic and silicon analogues[171,172] have been obtained by the reaction of tri(hydroxymethyl)phosphine with trimethyl phosphite, trimethyl arsenite, and trichloromethylsilane. The reactions of tri(α-hydroxy-β,β,β-trichloroethyl)-phosphine with PCl_3, $AsCl_3$, and $C_6H_5SiCl_3$ in the presence of triethylamine lead to the formation of bicyclic compounds[173]:



Di(β-hydroxyethyl)phenylphosphine reacts with dichloromethylphosphine to form 1,3-dioxa-2,6-diphosphacyclooctane[174].

Organoelemental electrophiles of yet another type, which react under mild conditions with the functional group, are derivatives of boric acids. The isobutyl ester of diphenylborinic acid reacts with di(hydroxymethyl)phenylphosphine to form a *trans*-esterification product[175]. 1,3,2,5-Dioxaboraphosphorinanes have been obtained by the reaction with the diethyl ester or anhydride of phenylboronic acid[176,177]:

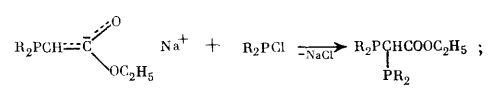


R=H, CH_3, iso-C_3H_7, C_6H_5 .

In contrast to phosphines with a mobile α-hydrogen atom, electrophilic substitution reactions without change in the coordination number of the phosphorus atom are characteristic of phosphines having a mobile β-hydrogen atom.

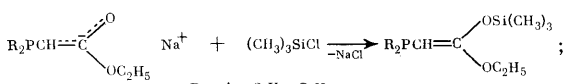
(c) Phosphine-containing Anions

Tertiary phosphines with functional-group substituents having a mobile α-hydrogen atom give rise to phosphine-containing carbanions on treatment with bases. These anions can react with chlorine-containing electrophiles both at the carbon atom and at the phosphorus atom. If the functional group contains the carbonyl moiety, the reaction can also proceed via the oxygen atom of the latter. Substitution at the carbon atom has been observed for the anions derived from phosphinoacetic esters on treatment of the latter with chlorodi-isopropylphosphine[178]:



R= iso-C_3H_7 .

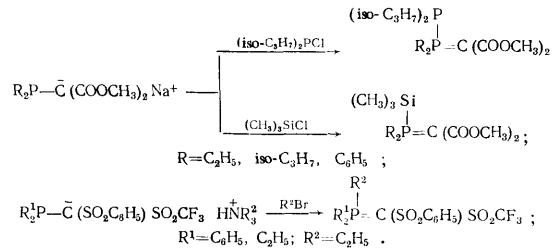
On the other hand, when the same compound was treated with chlorotrimethylsilane, the product of substitution at the oxygen atom was obtained[179]:



R= iso-C_3H_7, C_6H_5 .

Substitution at the phosphorus atom is characteristic of di(alkoxycarbonyl)methylphosphines and trifluoromethanesulphonylmethylphosphines. P–P– and P–Si– substituted ylides were obtained in the former case[180], while in the

latter case the products were alkyl-substituted phosphorus ylides[181]:



Electron-accepting substituents stabilise the $-\overset{\backslash}{P}-\overset{/}{C}R_2$ group; their accumulation increases the thermodynamic stability of the product of substitution at the phosphorus atom and drives the reaction towards its formation.

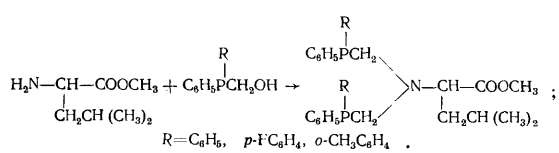
The study of the reactions with electrophiles has shown that there is an analogy in the behaviour of tertiary phosphines with a mobile hydrogen atom and the primary or secondary phosphines. Substitution at the phosphorus atom is also characteristic of the latter (examples of such reactions have been given in connection with the description of the methods of synthesis of tertiary phosphines with functional group substituents). The analogy is based on the ability of the phosphonium salts, obtained from all three types of compounds, to be stabilised by proton transfer to the negative centre of the electrophile. This method of stabilisation is related to that observed in the reactions of phosphorus(III) acids with electrophiles[182], which indicates considerable synthetic possibilities of the reactions examined. It must be emphasised that the phosphorus atom frequently does not prevent reactions with electrophiles also via the functional group.

2. Reactions with Nucleophiles

The carbon atom attached to the phosphorus atom is the electrophilic centre in the molecules of tertiary phosphines. The introduction of electron-accepting substituents should increase its reactivity. The departing groups can be both the substituent and the phosphino-group.

Nucleophilic substitution at the carbon atom has been most widely investigated for the hydroxy- and aminomethyl derivatives of phosphines. The nucleophiles employed have been primary, secondary, and tertiary amines. Various linear and cyclic products have been obtained.

The reactions of hydroxyalkylphosphines with primary and secondary amines proceed with the evolution of heat and lead to products of the substitution of the hydroxy-groups by amino-groups. Bis(diethylaminomethyl)phenylphosphine has been obtained from di(hydroxymethyl)phenylphosphine and diethylamine[183]. On treatment with hydroxymethyl derivatives of secondary phosphines, aminoacid esters have also given rise to derivatives of phosphorus-containing aminoacid[184]:



The reactions of the hydroxymethyl derivatives of secondary phosphines with ammonia and hydrazine have produced tri-(phosphinomethyl)amines, tri(phosphinomethyl)hydrazine, and tetra(phosphinomethyl)hydrazine[185]. The reactions of tri(hydroxymethyl)phosphine with secondary chiral amines and of hydroxymethyl derivatives of secondary amines with primary chiral amines proceeded analogously with formation of chiral tri(aminomethyl)phosphines and *N,N*-di(phosphinomethyl)amines respectively[186].

It has been shown that aminomethylphosphines can be obtained by heating acetoxymethylphosphines with secondary amines in methyl alcohol in the presence of alkali[187]:

$$R^1_nP(CH_2OCOCH_3)_{3-n} \xrightarrow{KOH} R^1_nP(CH_2OH)_{3\ n} \xrightarrow{R^2_2NH} R^1_nP(CH_2NR^2_2)_{3-n}\ ;$$

R^1=CH_2OH, C_2H_5, C_4H_9; R^2=CH_3, C_2H_5, C_3H_7, iso-C_4H_9; n=0—2 .

β-Hydroxyethylphosphines react with amines under the same conditions as hydroxymethylphosphines. When secondary amines are added to alkyldi(β-hydroxyalkyl)phosphines, an exothermic reaction is observed with formation of alkyldi(β-dialkylaminoalkyl)phosphines[188]:

$$R^1P(CH_2\underset{\displaystyle R^2}{\underset{|}{C}}HOH)_2 + 2R^3_2NH \rightarrow R^1P(CH_2\underset{\displaystyle R^2}{\underset{|}{C}}HNR^3_2)_2 + 2H_2O\ ;$$

R^1=CH_3, C_2H_5, C_3H_7, C_4H_9; R^2=H, CH_3; R^3=C_2H_5, C_4H_9 .

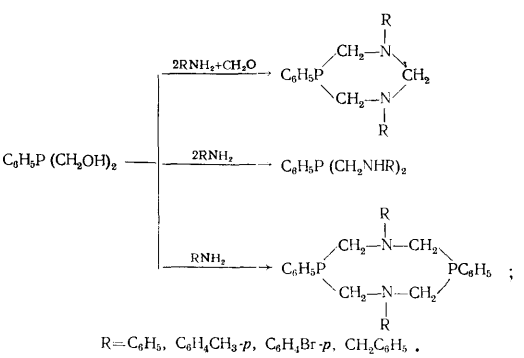
Monomeric products have been obtained by the reaction of tri(hydroxymethyl)phosphine with mono- or di-substituted ureas[189]:

$$3R^1R^2NCONH_2 + P(CH_2OH)_3 \rightarrow (R^1R^2NCONHCH_2)_3P{=}O\ ;$$

R^1=CH_3, C_2H_5, $CH_3(CH_2)_{11}$, $(CH_3)_3C$, C_6H_5; R^2=H, C_6H_5 .

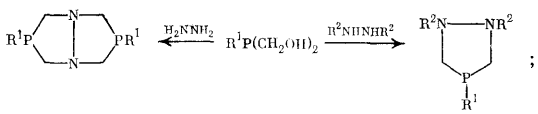
The oxidation of the product is attributed to the presence of formaldehyde in the reaction mixture.

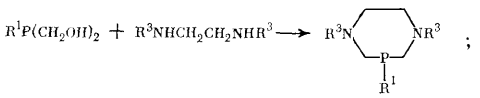
The reactions of di(hydroxymethyl)phenylphosphine with primary aromatic amines and benzylamine have attracted attention. They have been carried out in a solvent or in its absence, in the presence or absence of paraformaldehyde, and with different reactant ratios[190-192]. In all cases the reaction took place with evolution of heat. The structure of the *N,N*-disubstituted 5-phenyl-1,3,5-diazaphosphorinane was attributed to the product obtained in the presence of paraformaldehyde and two moles of the amine, while the products obtained in the absence of paraformaldehyde and in the presence of two and one moles of the amine were assumed to have the structure of *N,N*-disubstituted di(aminomethyl)phenylphosphines and 3,7-diphenyl-1,5-diaza-3,7-diphosphacyclo-octanes respectively:



The reactions of di(hydroxymethyl)phenylphosphine with boric acid esters took place analogously[193-197]. 1,5-Diaza-3,7-diphosphacyclo-octanes have also been obtained from diols containing aliphatic substituents at the phosphorus atom and a wide range of amines, including aliphatic amines[198].

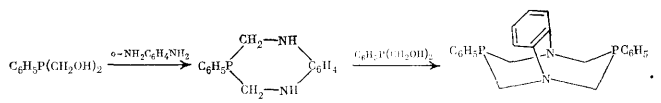
The reactions of di(hydroxymethyl)phosphines with hydrazine, substituted hydrazines, and ethylenediamine under the same conditions led to the formation of new heterocycles[199,200]:





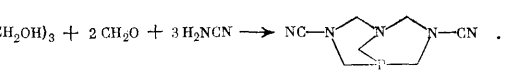
$R^1 = C_6H_5$, cyclo-C_6H_{11}, CH_3, C_2H_5; $R^2 = CH_3$, iso-C_3H_7; $R^3 = C_6H_5CHCH_3$.

o-Phenylenediamine reacts with di(hydroxymethyl)phenylphosphine only on heating and the products are 3-phenyl-6,7-benzo-1,5-diaza-3-phosphepane and 3,7-diphenyl-9,10-benzo-1,5-diaza-3,7-diphosphabicyclo[3.3.2]decane[201]:



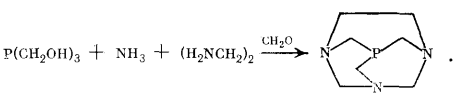
For a 1:1 reactant ratio, the product of the first stage of the reaction is obtained.

3,7-Dicyano-3,5,7-triaza-1-phosphabicyclo[3.3.1]nonane, which is capable of being oxidised and of combining with methyl iodide at the phosphorus atom, has been obtained by the reaction of tri(hydroxymethyl)phosphine with formaldehyde and cyanamide in the presence of phosphoric acid[202,203]:

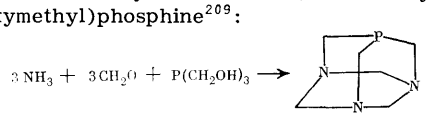


The reaction of tri(hydroxymethyl)phosphine with hexamethylenetetramine and formaldehyde (in portions of 1:1:4) has led to 1,3,5-triaza-7-phospha-adamantane[204,205]. This compound combines with methyl iodide and picric acid via one of the nitrogen atoms[206,207].

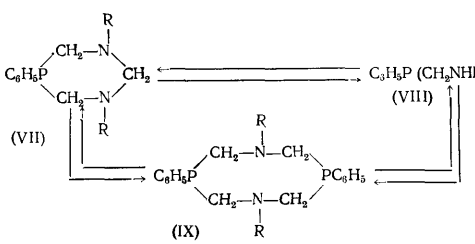
The synthesis of the next member of this series has been described[208]. Triazaphosphahomoadamantane is formed when ethylenediamine and ammonia react with tri(hydroxymethyl)phosphine in an excess of formaldehyde:



In contrast to triazaphospha-adamantane, it does not react with methyl iodide. 1,3,5-Triaza-7-phospha-adamantane is also obtained directly from ammonia, formaldehyde, and tri(hydroxymethyl)phosphine[209]:

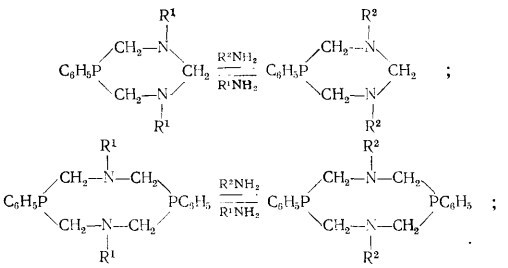


Not only the hydroxy-groups but also the amino-groups of tertiary phosphines with functional-group substituents readily undergo nucleophilic substitution. Thus the following interconversions of the aminomethyl derivatives of phenylphosphine have been demonstrated[210]:



Compounds (VII) and (IX) are converted into compound (VIII by amines. Diazadiphosphacyclo-octane (IX) can be obtained from compounds (VII) and (VIII) by the elimination of azomethines or amines respectively. The addition of azomethines to compounds (VIII) and (IX) gives rise to compound (VII). These reactions constitute nucleophilic substitution of one amino-group by another and proceed under fairly mild conditions.

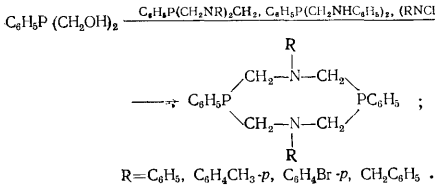
The substitution of one amino-group by another is also possible without alteration of the molecular skeleton[211]:



$R^1 = C_6H_5$; $R^2 = C_6H_4CH_3$-*p* .

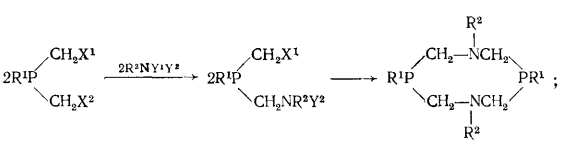
The interconversions are reversible; the direction of the reaction is determined by the conditions and the solubilities of the substances.

The hydroxy-group can be substituted by the amino-group on treatment not only with primary and secondary amines but also with triazanes or aminomethyl derivatives of phosphines. Thus di(hydroxymethyl)phenylphosphine and its borate esters give rise to 1,5-diaza-3,7-diphospha-cyclo-octanes on reaction with both primary amines and with 1,3,5-triphenyl-1,3,5-triazane, di(anilinomethyl)phenylphosphine, or 5-phenyl-1,3,5-diazaphosphorinanes[212]:



R=C_6H_5, $C_6H_4CH_3$-*p*, C_6H_4Br-*p*, $CH_2C_6H_5$.

The numerous methods of synthesis of 1,5-diaza-3,7-diphosphacyclo-octanes can be reduced to a single scheme[212]:



R^1 and R^2 — alkyls, aryls; $Y^1 = Y^2 = H$; $Y^1 = H$, $Y^2 = CH_2P$ (R) CH_2NHR; $X^1 = X^2 = OH$; $X^1 = OH$, $X^2 = OB(C_6H_5)_2$; $Y^1Y^2 = CH_2NRCH_2NRCH_2$, $X^1X^2 = OB(C_6H_5)O$, $NRCH_2NR$; $Y^1Y^2 = CH_2PRCH_2NRCH_2$, $X^1 = X^2 = NHR$.

The formation and transamination reactions and interconversions of the aminomethyl derivatives of phosphines, which constitute nucleophilic substitution at the carbon atom of the P–C–O or P–C–N fragment, proceed under milder conditions than the analogous reactions of alcohols, amines, and their derivatives. This is due to the involvement of the phosphino-group in intramolecular interactions. Examination of steric effects shows that the electron density in the P–C–O system is displaced towards the oxygen atom, while in the P–C–N system it is displaced towards the phosphorus atom. The transfer of electron density facilitates nucleophilic attack. In the former case the departing group is

the phosphino-group while in the latter it is the amino-group. The rupture of the P–C bond has been postulated in the reactions of di(hydroxyalkyl)phosphine oxides with amines[213].

The interactions of hydroxy- and amino-methylphosphines with nucleophiles have been fairly thoroughly investigated. Examples of such reactions for other tertiary phosphines with functional-group substituents are rarer. Tri(ethylchloromethyl)-phosphine is converted into tri(ethylthio)-phosphine on treatment with ethanethiol or sodium ethanethiolate[70]:

$$P(CH_2Cl)_3 \xrightarrow{2C_2H_5SH} P(CH_2SC_2H_5)_3 .$$

The addition of primary and secondary amines to diphenylvinylphosphine has been described[214]:

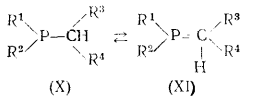
$$(C_6H_5)_2PCH_2CH_2NR_2 \xleftarrow{R_2NH} (C_6H_5)_2PCH=CH_2 \xrightarrow{+RNH_2} RN(CH_2CH_2P(C_6H_5)_2)_2 ;$$

$$R = C_6H_5,\ C_2H_5 .$$

The amine attackes the β-position relative to the phosphorus atom.

3. Tautomerism

Prototropic tautomerism is possible for tertiary phosphines with functional-group substituents having a mobile hydrogen atom in the α-position. If centres capable of stabilising the proton are absent from the functional group, diad phosphorus-carbon tautomerism takes place:

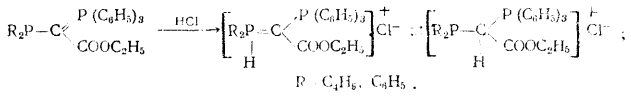


(X) (XI)

In the presence of such centres, other types of tautomerism cannot be excluded. The possibility of tautomerism depends mainly on the substituents at the carbon and phosphorus atoms.

The study of various tertiary phosphines has shown that, in the presence of alkyl and aryl substituents at the carbon atom, they exist in form (X). The stabilisation of the ylide form requires the introduction of strongly electron-accepting substituents such as the triphenylphosphonium, alkoxycarbonyl, and sulphonyl groups.

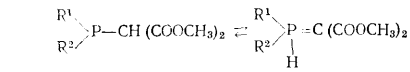
The presence of two triphenylphosphonium groups fully displaces the equilibrium towards form (XI). In the presence of butyl substituents at the phosphorus atom, the ylide has been isolated in a crystalline state[215,216]. The dependence of the equilibrium position on the substituents at the phosphorus atom has been observed for compounds containing the triphenylphosphonium and alkoxycarbonyl groups[217,218]:



$$R = C_4H_9,\ C_6H_5 .$$

The butyl substituent stabilise the ylide formed. The replacement of butyl by phenyl leads to the establishment of a mobile tautomeric equilibrium and the relative contents of the different forms in solution depend on the temperature and the polarity of the medium. Only form (X) exists in trifluoroacetic acid. The substitution of the alkoxycarbonyl group by the tosyl group displaces the equilibrium towards the ylide form[219].

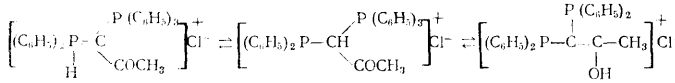
The occurrence of the diad phosphorus–carbon tautomerism has also been demonstrated for dialkyl(dimethoxycarbonylmethyl)phosphines[220–223]:



$$R^1 = t\text{-}C_4H_9,\ R^2 = iso\text{-}C_3H_7,\quad s\text{-}C_4H_9,\ (CH_3)_3SiCH_2,\ C_6H_5,$$
$$iso\text{-}C_4H_9;\ R^1 = R^2 = iso\text{-}C_4H_9,\ C_6H_5$$

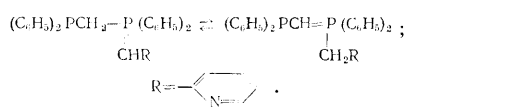
When R^1 = iso-C_4H_9 and R^3 = iso-C_3H_7, s-C_4H_9, or $(CH_3)_3SiCH_2$, the compounds are in the ylide form in the crystalline state. On fusion, a considerable proportion of the ylide is converted into a tertiary phosphine, which again crystallises in the ylide form. In solution, the compounds exist as tautomeric mixtures of forms (X) and (XI). The equilibrium position depends on the temperature, the nature of the solvent, the concentration, and the character of the substituents at the phosphorus atom. Heating shifts the equilibrium towards form (X). Bulky substituents stabilise the ylide form and in terms of their influence can be arranged in the following sequence: C_5H_9 < iso-C_4H_9 < iso-C_3H_7 < s-C_4H_9 < $(CH_3)_3SiCH_2$ < t-C_5H_9.

The substituted tertiary phosphines examined above exhibit only the diad phosphorus–carbon tautomerism despite the presence of carbonyl groups. The tetrad phosphorus–carbon tautomerism has been observed on substitution of the alkoxycarbonyl group in these compounds by the acetyl group[217,218]:



This type of tautomerism includes the diad phosphorus–carbon tautomerism and the keto-enol tautomerism.

The introduction of an ylide group as a substituent into the molecule of a tertiary phosphine results in the transfer of the mobile hydrogen atom to this group. The process can be both reversible and irreversible[224]:



Proton transfer to the phosphorus atom has been observed in acetonyldiphenylphosphine under the influence of tin tetrachloride[225]:

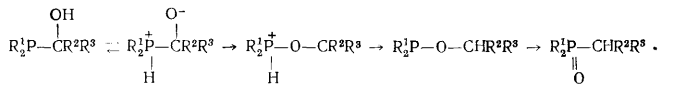


The observation of the prototropic diad phosphorus–carbon tautomerism emphasises the powerful influence of substituents on the properties of tertiary phosphines.

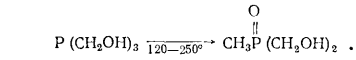
4. Rearrangements

The lability of the P–C bond and the close proximity in space of the substituents at the phosphorus atom in tertiary phosphines with function-group substituents can lead to rearrangements whose character depends on the nature of the solvents. The rearrangements of hydroxyalkylphosphines have been most thoroughly investigated. It has been suggested that the hydroxyalkylphosphine molecule is in equilibrium with the dipolar ion formed as a result of proton transfer to the phosphorus atom. This dipolar ion can rearrange to another dipolar ion containing the P–O–C group. The rearrangement is irreversible and the ion is stabilised by proton transfer to the carbon atom with formation of a phosphinite; the subsequent isomerisation yields

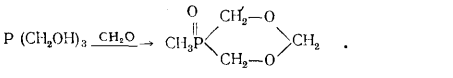
the compounds most stable in the given system—tertiary phosphine oxides[226]:



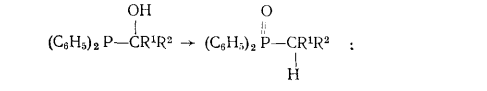
Tri-(hydroxymethyl)phosphine isomerises on heating to di(hydroxymethyl)methylphosphine oxide[227-231]:



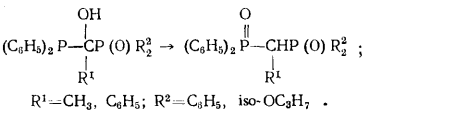
When paraformaldehyde is added, 5-methyl-5-oxo-1,3,5-dioxophosphorinane is formed[232]:



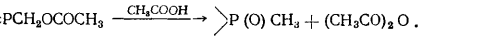
In the case of the hydroxyalkyl derivatives of diphenylphosphine, the rearrangement was observed for different C-substituted compounds[226,233]:



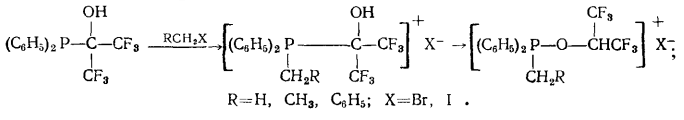
Replacement of the phenyl group at the phosphorus atom by the ethyl group does not affect the possibility of this rearrangement[226]. α-Phosphorus-substituted phosphinomethanols also give rise to rearrangement products on heating[234,235]:



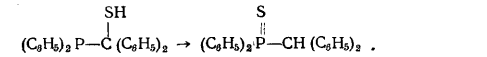
The isomerisation of hydroxyalkylphosphines to tertiary phosphine oxides can occur under the influence of acids and bases[233,236]. Acetoxymethylphosphines rearrange in an acid medium[237,238]:



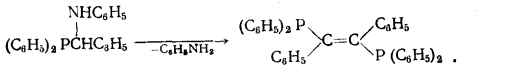
In the examples quoted above the oxygen atom is transferred to the phosphorus atom and the reaction cannot be arrested at the phosphinite formation stage. Phosphonium compounds with the P–O–C group have been obtained by treating with alkyl halides hydroxyalkylphosphines having trifluoromethyl groups at the carbon atom[236]:



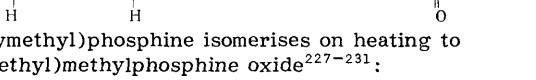
The study of mercaptoalkylphosphines has shown that they too are capable of rearranging to tertiary phosphine sulphides. The mechanisms of the rearrangements are apparently analogous. This follows from the conversion of α-mercaptobenzhydryldiphenylphosphine in benzhydryldiphenylphosphine sulphide[15]:



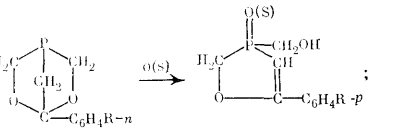
The organonitrogen analogues of hydroxyalkylphosphines are converted into 1,2-diphosphinoethylenes. This is accompanied by the formation of the corresponding arylamines[239]:



The rearrangement of α-halogenophosphines, formed on interaction of phosphinous acid chlorides with α-halogenomethyl sulphones in the presence of triethylamine or the sodio-derivatives of α-halogenodi(benzenesulphonyl)-methanes, to *P*-halogenoylides has been described[240,241]:

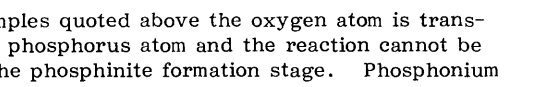


Many rearrangements are known for substituted phosphines, which can proceed under the conditions of oxidation or sulphur addition reactions. 4-Aryl-1-phospha-3,5-dioxabicyclo[2.2.1]heptane gives rise on oxidation or addition of sulphur to the oxide or sulphide of 4-aryl-1-hydroxymethyl-1-phospha-3-oxacyclopent-4-ene respectively[245,246]:



The migration of the phenyl group from the phosphorus atom to the carbon atom has been observed in the reactions of ferrocenyldiphenylphosphines, leading to the formation of phosphonium betaines and binylphosphonium salts[247]:

When benzyldi(α-hydroxybenzyl)phosphine oxide is heated with an equimolar amount of alkali in benzene, the sodium salt of dibenzylphosphinic acid is formed in an almost quantitative yield[248]:



Hydride transfer from the phosphorus atom to the carbon atom in the intermediate anion has been postulated in this reaction.

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Thus the introduction of substituents alters significantly the properties of tertiary phosphines; new pathways to the decomposition of the phosphonium compound appear and reactions with nucleophiles as well as rearrangements become characteristic of these compounds. The high and many-sided reactivity of tertiary phosphines with functional-group substituents together with the existence of a large number of convenient methods of their synthesis makes it useful to investigate this class of compounds.

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Arbuzov Institute of Organic
and Physical Chemistry,
Kazan Branch of the USSR Academy
of Sciences, Kazan