Translated from *Uspekhi Khimii*, **51** 412-437 (1982)

α-Alkoxy-compounds of Phosphorus and Some of Their Analogues

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Data on the methods of synthesis of α-alkoxyalkyl derivatives of organophosphorus compounds are presented and their chemical properties and principal applications are examined.
The bibliography includes 305 references.

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I. INTRODUCTION

The α-alkoxyalkyl derivatives belong to the large class of derivatives of organophosphorus compounds with functional group substituents, which have been vigorously investigated in recent years. Novel and convenient methods of synthesis have been proposed for these compounds and certain practical applications have been discovered. However, there are no reviews in the Soviet and foreign literature devoted to the chemistry of these compounds, which was the reason why the present review was undertaken.

II. METHODS OF SYNTHESIS

α-Alkoxyalkyl derivatives of organophosphorus compounds are synthesised by several procedures which can be divided into two groups. The first group includes methods involving the α-alkoxyalkylation of tervalent phosphorus compounds, while the second comprises methods in which various groups in organophosphorus compounds are converted into α-alkoxy-groups.

1. α-Alkoxylation of Tervalent Phosphorus Compounds

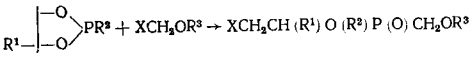
(a) Alkylation of the Fully Esterified Tervalent Phosphorus Acids by α-Halogenoalkyl Ethers

The esters of α-alkoxyalkylphosphonic[1-26] and alkyl(aryl)-phosphinic[24,27,28] acids, including compounds containing various functional groups in the hydrocarbon substituents, are obtained by this method:

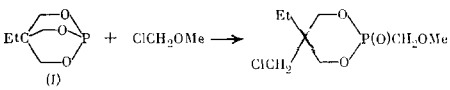
$$R^1P(OR^3)_2 + XCH(R^5)OR^4 \xrightarrow[-R^3X]{\Delta} R^1(R^3O)P(O)CH(R^5)OR^4 ,$$

where R^1 is a C_1-C_4 alkoxy-group, including one containing a halogen, OCH_2CH_2OMe, OCH_2CH_2OEt, OC_6H_4Y, Me, Et, Ph, or ClC_6H_4, Y = Cl, NO_2, CN, or Me_2NSO_2, R^2 = a C_1-C_5 alkyl group, including one containing a halogen, R^3 = H, C_1-C_7 alkyl, Ph, CH_2Br, COMe, COOMe, COOEt, $CONH_2$, CONHEt, CONO, or $P(O)(OBu)_2$, R^4 = C_1-C_{18} alkyl, $(CH_2)_n$–Ph, $ZCH{=}CHCH_2$, or $ZCH{=}CHCH_2CH_2$ (n = 0, 1, or 2 and Z = H, Cl, Br, or C_1-C_5 alkyl), R^3R^4 = $-OCH_2CH_2-$, $(CH_2)_m$ (m = 3 or 4) $-O-$Cl, or $-CH_2CH_2-$, and X = Cl or Br.

4,5-Unsubstituted and monosubstituted 2-alkoxy(diethylamino)-1,3,2-dioxaphospholans[29-34] and the bicyclic phosphite (I) [35] react with ring opening:

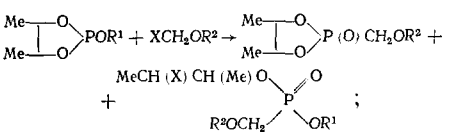


R^1 = H, Me; R^2 = NEt_2, OEt, OCH_2CH_2Y, Y = Cl, F, OEt;
R^3 = C_1-C_4 alkyl; X = Cl, Br, I



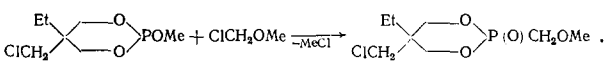
(I)

2-Alkoxy-4,5-dimethyl-1,3,2-dioxaphospholans interact with alkyl chloromethyl ethers to form a mixture of two substances[31]:



R^1 = Et, CH_2CH_2Cl; R^2 = C_1-C_3 alkyl; X = Cl, Br .

The reaction of 5-chloromethyl-5-ethyl-2-methoxy-1,3,2-dioxaphosphorinane with chloromethyl methyl ether proceeds with retention of the ring[34].



The methoxymethylation of tetraethyl methoxycarbonylmethylenediphosphonite is accompanied by the keto–enol migration of the ethoxy(methoxymethyl)phosphinyl group[36,37]:

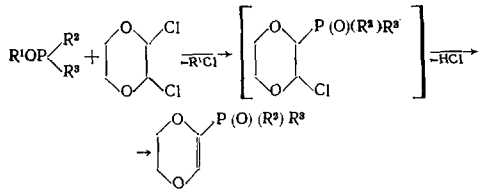
$$[(EtO)_2P]_2CHCOOMe + 2MeOCH_2Cl \xrightarrow[-2EtCl]{} EtO(MeOCH_2)P(O)CH{=}C(OMe)OP(O)(OEt)CH_2Me .$$

The alkylation of triethylphosphite with bishalogenodimethyl ethers yielded the corresponding diphosphonate[38]:

$$2(EtO)_3P + XCH_2OCH_2X \xrightarrow[-2EtCl]{} (EtO)_2P(O)CH_2OCH_2P(O)(OEt)_2 ;$$
X = Cl, Br .

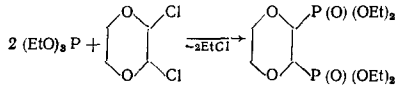
In the interaction of 2,3-dichloro-1,4-dioxan with 1 mole of trialkyl phosphite, phosphonite, or phosphinite the alkylation

product undergoes spontaneous dehydrochlorination[39,40]:

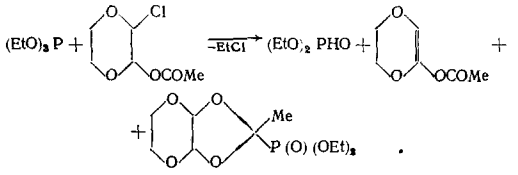


$R^1 = C_2—C_4$ alkyl; R^2, $R^3 = OR^1$, Et, Ph, ClC_6H_4 .

The reaction of 2,3-dichloro-1,4-dioxan with an excess of triethyl phosphite leads to 2,3-bis(diethoxyphosphinyl)-1,4-dioxan[5]:



The interaction of triethyl phosphite with 3-acetoxy-2-chloro-1,4-dioxan leads to a mixture of products[41]:

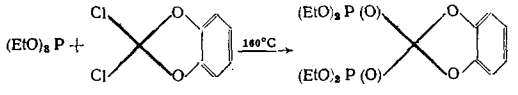


Mainly one or two chlorine atoms, depending on the reaction ratio, are substituted preferentially in trichloromethyl phenyl and dichloromethyl methyl ethers when these interact with trialkyl phosphites[9,26]:

$$(R^1O)_3P + Cl_2CR^2OR^3 \xrightarrow[1:1]{} (R^1O)_2P(O)CClR^2OR^3$$
$$\xrightarrow[2:1]{} [(R^1O)_2P(O)]_2CR^2OR^3$$

$R^1 = Et, Bu$; $R^2 = Cl$, $R^3 = Ph$; $R^2 = H$, $R^3 = Me$.

Bisphosphorylated benzodioxole has been obtained by the reaction of 2,2-di-chloro-benzo[*d*]dioxole with an excess of triethyl phosphite[5]:



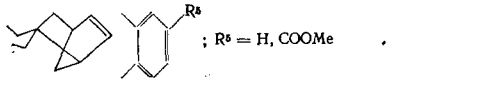
When ethoxymethyltrimethylammonium chloride is used instead of α-chloroethers, the alkoxylation reaction proceeds only under severe conditions[42]:

$$(EtO)_3P + Et_3\overset{+}{N}CH_2OEtCl^- \xrightarrow{140°C} (EtO)_2P(O)CH_2OEt + Et_4\overset{+}{N}Cl^-$$.

Under analogous conditions, tervalent phosphorus acid esters are alkylated by the methoiodides of dimethylformamide acetals[43,44]:

$$R^1_2POR^2 + Me_3\overset{+}{N}CH(OR^3)OR^4I^- \rightarrow R^1_2P(O)CH(OR^3)OR^4 + Me_3N + R^2I$$

$R^1 = OMe, OEt, OPr\text{-}iso, Ph$; $R^2 = Me, Et, iso\text{-}Pr$; $R^3 = R^4 =$ $= C_1—C_6$ alkyl; $R^3R^4 = (CH_2)_2$,



; $R^5 = H, COOMe$.

When alkyl phosphoroisocyanatidites are alkylated, the completion of the reaction requires prolonged refluxing of the mixture or the presence of a catalyst ($FeCl_3$):[45–47]

$$(R^1O)_nP(NCO)_{3-n} + ClCHR^3OR^2 \xrightarrow{-R^1Cl} (R^1O)_{n-1}(OCN)_{3-n}P(O)CHR^3OR^2$$

$n = 1, 2$; R^1, $R^2 = Me, Et$; $R^3 = H, Cl, CCl_3$, MeOC (O), EtOC (O) .

Alkylation of the ethyl ester of diphenylphosphinothious acid is complicated by oxidation-reduction processes and leads to a mixture of products[48]:

$$Ph_2PSEt + ClCHR^1OR^2 \xrightarrow{-EtCl} Ph_2P(S)CHR^1OR^2 + Ph_2P(S)SEt +$$
$$+ Ph_2\overset{+}{P}(CHR^1OR^2)_2\,Cl^-$$

$R^1 = H, Me$; $R^2 = C_1—C_4$ alkyl.

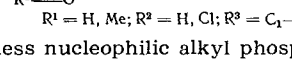
(b) Alkylation of Ester-Chlorides of Tervalent Phosphorus Acids

By virtue of the ready heterolysis of the carbon–halogen bond, α-halogenoethers are some of the most reactive alkylating agents. However, in the reactions with highly nucleophilic derivatives of tervalent phosphorus considered above this feature of the chemical properties of α-halogenoethers is manifested only by some acceleration of the alkylation reaction or by its occurrence under milder conditions, compared with those required, for example, by alkyl halides.

The situation is different when the less nucleophilic ester-halides of tervalent phosphorus acids are used in the alkylation reactions; whereas the latter are only sluggishly alkylated by alkyl halides or not at all, they are capable of reacting effectively with α-halogenoalkyl ethers via the Arbuzov reaction. Thus dialkyl halogenophosphites[49–53] and 2-chloro-1,3,2-dioxaphospholans[31–33,54,55] interact to form the ester-halides of alkoxyalkylphosphonic acids:

$$(R^1O)_2PX + ClCR^2R^3OR^4 \xrightarrow{-R^1Cl} (R^1O)XP(O)CR^2R^3OR^4$$

$R^1 = Et, Bu, Am$; $R^2 = H, Cl, Me, COOMe$; $R^3 = H, Cl$; $R^4 = Et, Bu$; $X = Cl, F$



$R^1 = H, Me$; $R^2 = H, Cl$; $R^3 = C_1—C_4$ alkyl; $X = Cl, Br$

The less nucleophilic alkyl phosphorodichloridites (difluoridites) are alkylated by α-chloroethers only in the presence of electrophilic catalysts—$FeCl_3$, $AlCl_3$, BF_3, etc.:[7,56–64]

$$R^1OPX_2 + R^2OCR^3R^4Cl \xrightarrow[-R^1Cl]{} R^2OCR^3R^4P(O)X_2$$

$R^1 = Me, Bu$; $R^2 = C_1—C_4$ alkyl, $PhCH_2$, CH_2Cl; $R^3 = H, CCl_3, CO_2Me$; $R^4 = H, Cl$; $X = Cl, F$.

All the halogen atoms in bis-α-chloroethyl and α,α-di-iodoethyl methyl ethers are substitutes when the latter interact with methyl phosphorodichloridite[56]:

$$2MeOPCl_2 \xrightarrow[MeOCl_2Me]{MeCHClOCHClOMe} Cl_2P(O)CH(Me)OCH(Me)P(O)Cl_2$$
$$\rightarrow Cl_2P(O)C(Me)(OMe)P(O)Cl_2$$.

Together with alkyl phosphorodichloridites, acetyl phosphorochloridites or acetyl phosphonochloridites, obtained as intermediates when a mixture of ethyl(phenyl)dichlorophosphine or ethyl phosphorodichloridite and an α-chloro-ether is acted upon by acetic anhydride, also react with α-chloroalkyl ethers[64,65]:

$$RPCl_2 + (MeCO)_2O \xrightarrow{-MeCOCl} R(Cl)POCOMe \xrightarrow{ClCHMeOEt}$$
$$\rightarrow [R(Cl)\overset{+}{P}(OCOMe)CHMeOEtCl^-] \xrightarrow{-MeCOCl} R(Cl)P(O)CHMeOEt$$.

$R = Et, Ph, OEt$

The chlorides of tervalent phosphorus acids and some of their derivatives also react with acetals and the orthoesters of carboxylic acids to form α-alkoxyalkyl derivatives of phosphorus. As a result of the exchange of the alkoxy-group between the acid chloride and the acetal or orthoester, α-chloroalkyl ethers and neutral esters or ester-chlorides of

tervalent phosphorus acids are formed initially and their interaction ultimately yields α-alkoxyalkyl compounds of phosphorus.

Phosphorus trichloride[67,68], alkyl phosphorodichloridites[68–70], diaryl phosphorochloridites[71,72], dialkyl phosphorochloridites[70–78], phenyldichlorophosphine[78,79], ethyldichlorophosphine and diethylaminoethylchlorophosphine[80], diethyl- and diphenyl-chlorophosphines[69,71,75,76,78,79,81], and aryl(alkyl) chlorophenylphosphonites[79] have been made to undergo this reaction:

$$R^1(R^2)PCl + R^3R^4C(OR^5)OR^6 \xrightarrow{-R^5Cl} R^1(R^2)P(O)CR^3R^4OR^5$$

R^1 = Cl, Et, Ph, OAlk, OAr; $R^2 = R^1$, NEt_2; R^3 = H, Me, OEt;

R^4 = H, Me, Et, Pr, Ph, CH_2CH_2OAlk, , Me_2$(Me)CH_2$—,

; $R^3R^4 = (CH_2)_5$; R^5 = Alk, cyclo-C_6H_{11}, $CH_2CH{=}CH_2$,

CH_2CH_2OBu, CH_2CH_2Cl, CH_2CO_2Alk; $R^6 = R^5$, CH_2COAlk.

A mixture of trialkyl phosphite and phosphorus trichloride in proportions of 2 : 1 can be used in these reactions instead of dialkyl phosphorochloridites[20,72,75,82]. The interaction of phosphorus trichloride with three moles of an orthoester or an acetal[20,69,72–74,82–85] and also the reaction of alkyl(aryl) phosphorodichloridites[69,74,82] and phenyldichlorophosphine[69,78,79] with two moles of an acetal or an orthoester lead to the same products:

$$PCl_3 + 3R^1O(R^2O)CR^3R^4 \xrightarrow[-R^2Cl]{ZnCl_2} (R^2O)_2P(O)CR^3R^4OR^1 + 2ClCR^3R^4OR^1$$

R^1 = Alk, $CH_2CH{=}CH_2$, CH_2CH_2Cl; $R^2{=}R^1$, CH_2COOMe; R^3 = H, Me, Et; R^4 = H, OR^1

$$ROPCl_2 + 2CHR^1(OR^2)OR^3 \xrightarrow{-R^2Cl} RO(R^3O)P(O)CHR^1OR^2 + ClCHR^1OR^2$$

R = Et, Bu, Ph; R^1 = H(Me, OEt; R^2 = Et,Bu; $R^3{=}R^2$, CH_2COOMe

$$PhPCl_2 + 2R^1CH(OR^2)OR^3 \xrightarrow{-R^2Cl} Ph(R^3O)P(O)CHR^1OR^2 + ClCHR^1OR^2$$

R^1 = H, Me, OEt, R^2 = Alk, $CH_2{-}CH{=}CH_2$; $R^3 = R^2$, CH_2COOMe.

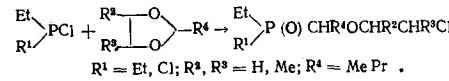
The reaction of phenyldichlorophosphine with methylal is accompanied by an oxidation-reduction process and leads to di(methoxymethyl)phenylphosphine oxide[79]:

$$2PhPCl_2 + 2(MeO)_2CH_2 \rightarrow PhP(O)(CH_2OMe)_2 + 2MeCl + PhPOCl_2.$$

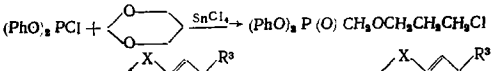
The interaction of dimethylformamide acetal with phosphorus trichloride leads to a mixture of products[86]:

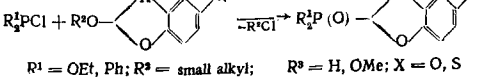
$$PCl_3 + 3(MeO)_2CHNMe_2 \rightarrow [(MeO)_2P(O)]_2CHNMe_2 + (MeO)_3P + (MeO)_2P(O)CH(OMe)_2 + HCONMe_2 + Me_4\overset{+}{N}Cl^- + MeCl$$

In the reactions of cyclic acetals with tervalent phosphorus acid halides the ring is opened[72,87,88], while in the reactions of cyclic orthoesters the ring is retained[78,89,90]:

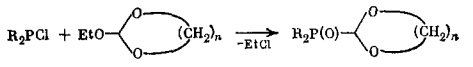


R^1 = Et, Cl; R^2, R^3 = H, Me; R^4 = Me Pr.



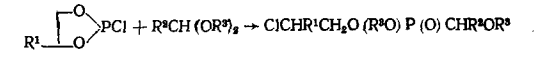


R^1 = OEt, Ph; R^2 = small alkyl; R^3 = H, OMe; X = O, S

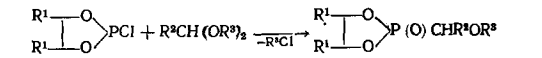


R = OEt, Ph; n = 2, 3.

The reactions of acetals and orthoesters with alkylene phosphorochloridites proceed both with ring opening[34,72,77,82,91] and with retention of the ring in the latter compounds[72,77]:

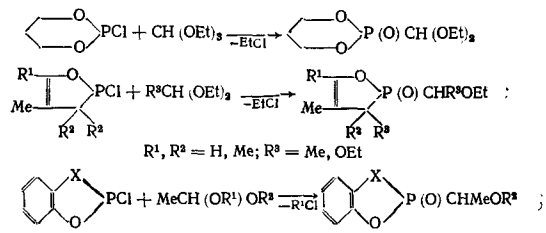


R^1 = H, Me; $R^2 = R^1$, OR^3; R^3 = Me, Et, Pr, CH_2CH_2OEt, $CH_2CHEtBu$, $(CH_2)_nCl$, n = 2, 4;



R^1, R^2 = Me, R^3 = Me, Et, Pr; R^1, R^2 = H, $R^3 = CH_2{-}CH{=}CH_2$.

Propylene phosphorochloridite[78], chloro-oxaphospholens[92], o-phenylene phosphorochloridite, and salicyl phosphorochloridite[70,93] interact with acetals and an orthoester with retention of the ring:



R^1, R^2 = H, Me; R^3 = Me, OEt

R^1 = Me, Et; R^2 = Et, CH_2COEt; X = O, COO.

Acyl phosphites[73], including those obtained by the reaction[94]

$$(EtO)_2POC(O)Me + HC(OEt)_3 \rightarrow (EtO)_2P(O)CH(OEt)_2 + MeC(O)OEt$$

$$PCl_3 + (RO)_2CHMe + (MeCO)_2O \rightarrow RO(Cl)P(O)CHMeOR + 2MeCOCl$$

R = Bu, Pr, Et,

interact with orthoesters similarly to phosphorochloridites.

The interaction of aryldichlorophosphines[95,96], alkyldichlorophosphines[97,98], and dialkyl phosphorochloridites[96,99,100] with acetalacylals proceeds with formation of a mixture of acid chlorides, ester-chlorides, ester-anhydrides, and acid esters of α-alkoxyethylarylphosphinic or α-alkoxyethylphosphonic acids. The interaction of dialkyl phosphorochloridites with an acetal-orthoformate also leads to a mixture of products[101].

(c) Alkylation of Chlorophosphines and Phosphoramidochloridites with α-Halogenoalkyl Ethers

Under mild conditions, dialkyl(aryl)chlorophosphines are alkylated by α-halogenoalkyl esters[102–107]:

$$R^1_2PCl + R^2CHClOR^3 \rightarrow R^1_2(Cl)\overset{+}{P}CH(R^2)OR^3Cl^-;$$

(II)

R^1 = Et, Ph, C_6H_4Me; R^2 = H, Me, CH_2Cl; R^3 = small alkyl or halogenoalkyl.

When complex (II), which is stable at low temperatures, was treated with hydrogen sulphide, the corresponding phosphine sulphides were obtained[102–104], while treatment with water, aqueous alcohol, acetic acid, alcohol, or a pyridine–water mixture yielded phosphine oxides[102–106]:

$$(II) \xrightarrow{H_2S} R^1_2P(S)CHR^2OR^3$$

$$(II) \xrightarrow{ROH} R^1_2P(O)CHR^2OR^3;$$

R = H, Bu, MeCO.

The more readily available complex of diphenylchlorophosphine and aluminium chloride can be used in this reaction instead of free diphenylchlorophosphine[108,109].

Ethyl *N*,*N*-diethylphosphonamidochloridite reacts similarly with alkyl chloromethyl ethers in the cold, forming a complex whose decomposition with hydrogen sulphide or sulphur dioxide is accompanied by deamination[110–113]:

$$Et_2N(Et)PCl + ClCH_2OR \rightarrow Et_2N(Cl)\overset{+}{P}(Et)CH_2ORCl^- \rightarrow$$
$$\rightarrow \begin{cases} \xrightarrow{H_2S} Et(Cl)P(S)CH_2OR \\ \xrightarrow{SO_2} Et(Cl)P(O)CH_2OR \end{cases}$$
R = small alkyl.

Phosphorodiamidous chlorides are alkylated by alkyl halogenomethyl ethers also with formation of quasi-phosphonium salts, whose decomposition with hydrogen sulphide or alcohols in the presence of tertiary amines leads to the diamides of alkoxymethylphosphonothioic acids[114,115]; the decomposition of the phosphonium salts with alcohols in the absence of a hydrogen chloride acceptor leads to amidoesters, while decomposition with alcohols and hydrogen chloride results in the formation of the diesters of alkoxymethylphosphonic acids[113,115–117,119]:

$$(Et_2N)_2PCl + X\,CH_2OR \rightarrow (Et_2N)_2\overset{+}{P}(Cl)CH_2ORX^- \rightarrow$$
$$\rightarrow \begin{cases} \xrightarrow{Et_3N+H_2S} (Et_2N)_2P(S)CH_2OR \\ \xrightarrow{Et_3N+R^1OH} (Et_2N)_2P(O)CH_2OR \\ \xrightarrow{R^1OH} Et_2N(R^1O)P(O)CH_2OR \\ \xrightarrow{R^1OH+HCl} (R^1O)_2P(O)CH_2OR \end{cases}$$
R, R^1 = small alkyl; X = Cl, Br, I .

The complexes of aryldichlorophosphines and aluminium chloride readily interact with alkyl chloromethyl ethers; after the alcoholysis of the reaction products, the esters of alkoxymethylarylphosphinic acids were isolated[120]:

$$ArPCl_2 \cdot AlCl_3 + ROCH_2Cl \rightarrow [ROCH_2(Ar)\overset{+}{P}Cl_2][AlCl_4]^- \xrightarrow{R^1OH} \rightarrow ROCH_2(Ar)P(O)OR^1$$
Ar = Ph, $CH_3C_6H_4$; R, R^1 = small alkyl.

(d) Alkylation of Tervalent Phosphorus Acid Salts with α-halogenoalkyl Ethers

When sodium, potassium[1,9,16,21,38,40,121–124], or silver[125] dialkyl phosphites were heated at 100 °C with α-chloroalkyl ethers, the corresponding phosphonates and diphosphonates were obtained:

$$(R^1O)_2POM + XCH_2(OR^2)R^3 \rightarrow (R^1O)_2P(O)CHR^3OR^2 + MX \xrightarrow[-R^1X]{\Delta} \rightarrow MO(R^1O)P(O)CHR^3OR^2$$
$$2(R^1O)_2POM + XCH_2OCH_2X \rightarrow [(R^1O)_2P(O)CH_2]_2O + 2MX$$
R^1 = C_1–C_4 alkyl, CH_2CH_2OAlk, $CH_2CH{=}CH_2$, Ph; R^2 = C_1–C_4 alkyl, CH_2Ph; R^3 = H, P(O)$(OBu)_2$; R^2R^3 = $(CH_2)_4$, –CHMe, $-CH_2CH_2CHCl-$;
X = Cl, Br, I; M = Na, K, Ag .

The reaction of sodium, potassium, and halogenomagnesium salts of phosphinous acids with alkyl chloromethyl ethers on refluxing in tetrahydrofuran results in the formation of the corresponding phosphine oxides[126–131]:

$$R^1_2POM + ClCH_2OR^2 \rightarrow R^1_2P(O)CH_2OR^2 + MCl$$
R^1 = Et, Bu, CH_2Ph; R^2 = C_1–C_{10} alkyl, $-CH_2-$(tetrahydrofuran-2-yl),
CH_2CH_2OMe, $(CH_2CHR^3O)_nAlk$; R^3 = H, Me; n = 1, 3;
M = Na, K, MgBr .

The alkoxymethylation of lithium phenylphosphides[132] and the product of the metallation of tetramethylphosphorodiamidous chloride[133] with alkyl halogenomethyl ethers resulted in the formation of the corresponding phosphines and amides of phosphonic acids:

$$Ph_2PLi \rightarrow \begin{cases} \xrightarrow{ClCH_2OMe} Ph_2PCH_2OMe \\ \xrightarrow{ClCH_2OCH_2Cl} Ph_2PCH_2OCH_2PPh_2 \end{cases}$$
$$(Me_2N)_2PCl + Na \rightarrow (Me_2N)_2PNa \xrightarrow{BrCH_2OR[O]} \rightarrow (Me_2N)_2P(O)CH_2OR$$
R = C_1–C_4 alkyl.

(e) Other Methods for the α-Alkoxyalkylation of Tervalent Phosphorus Compounds

α-Alkoxyalkylphosphonates can be sometimes obtained by prolonged heating of trialkyl(aryl) phosphites with aldehydes[134–136]:

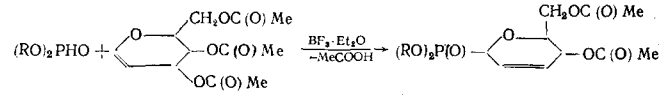
$$(R^1O)_3P + R^3CHO \rightarrow (R^1O)_2P(O)CHR^3OR^1$$
R^1 = Et, Ph; R^3 = H, C_1–C_3 alkyl, $CH_2CH{=}CH_2$, Ph; *p*-MeC_6H_4 .

A chloroform–sodium methoxide mixture alkylates neutral phosphites under mild conditions[137]:

$$R^1O(R^3O)POR^3 + CHCl_3 + MeONa \rightarrow R^1O(R^3O)(R^3O)P(OMe)CH(OMe)_2$$
R^1R^3 = $(CH_2)_2$, R^3 = Me; R^1 = R^3 = R^3 = Me .

Incompletely esterified tervalent phosphorus acids are α-alkoxyalkylated by acetals[138], vinyl ethers[139], keten acetals[140], and the orthoesters of carboxylic[141–144] and carbonic[118] acids:

$$(R^1O)_2PHO + (R^2O)_2CHC_6H_4R^3 \xrightarrow[-R^2OH]{180–210\,^\circ C} (R^1O)_2P(O)CH(OR^2)C_6H_4R^3$$
R^1 = Et, Bu; R^2 = Et; R^2_2 = CH_2CH_2; R^3 = H, OH, NO_2



R = Me, Et

$$(EtO)_2PHO + CH_2{=}C(OEt)_2 \rightarrow (EtO)_2P(O)CMe(OEt)_2$$
$$R^1R^2P(X)H + R^3C(OR^4)_3 \xrightarrow[-R^4OH]{} R^1R^2P(X)CR^3(OR^4)_2$$
R^1 = OAlk, Et, ClC_3H_1; R^2 = OMe, OEt, Et; R^3 = H, Me, OEt;
R^4 = Me, Et, Pr; X = O, S .

Phosphorylated formals are formed also by the interaction of phosphorous and hypophosphorous acids with an excess of orthoformate[145–149]:

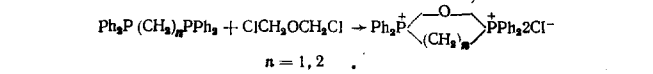
$$H(X)P(O)OH + CH(OR)_3 \rightarrow H(X^1)P(O)OR \xrightarrow[-ROH]{CH(OR)_3} (RO)_2CH(X^1)P(O)OR$$
X = X^1 = H; X = OH, X^1 = OR; R = C_1–C_3 alkyl.

Treatment of dialkyl phosphites and diarylphosphine oxides with dimethylformamide methylal leads to phosphinylated aminoacetals[150]:

$$R_2PHO + Me_2NCH(OMe)_2 \rightarrow R_2P(O)CH(NMe_2)OMe + MeOH$$
R = EtO, iso-PrO, Ph.

Phosphonium[23,151,152] and cyclic bisphosphonium salts[132] have been obtained by the alkylation of phosphines with α-chloroalkyl ethers[132]:

$$Ph_2P + ClCHR^1OR^2 \rightarrow Ph_2\overset{+}{P}CHR^1OR^2Cl^-$$
R^1 = H; R^2 = Me, Bu; R^1R^2 = $(CH_2)_3$,



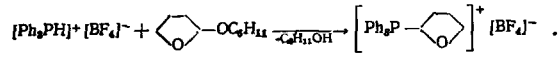
n = 1, 2 .

The alkylation of triphenylphosphine with 1,2-dibromoethyl ether is accompanied by dehydrobromination[153]:

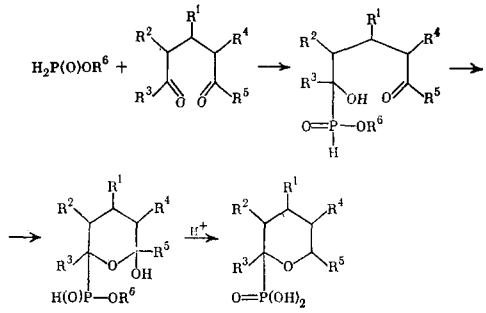
$$Ph_3P + BrCH_2CHBrOEt \xrightarrow[-HBr]{} Ph_3\overset{+}{P}C(OEt){=}CH_2Br^-$$

The interaction of triphenylphosphonium tetrafluoroborate and α-cyclohexyloxytetrahydrofuran also leads to an

α-alkoxyalkylphosphonium salt[23]:

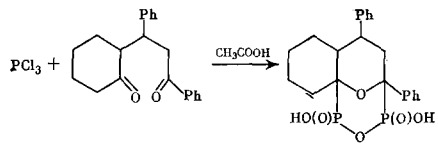


Tetrahydropyranylphosphonates are obtained on heating 1,5-diketones with hypophosphorous acid or alkyl hypophosphites[154–157]:

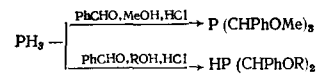


R^{1-5} = H, Ph; $R^2R^3 = (CH_2)_4$; R^6 = H, Et, Bu, CH_2Ph .

The anhydride of tetrahydropyranyldiphosphoric acid has been isolated together with other products in the reaction of 1,5-diketones with phosphorus trichloride in acetic acid[158]:



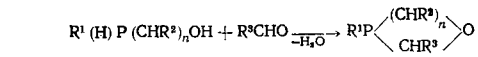
Phosphine[159] and diphenylphosphine[160] react with benzaldehyde and alcohols in the presence of hydrogen chloride to form α-alkoxybenzylphosphines:



R = C_2-C_4 alkyl;

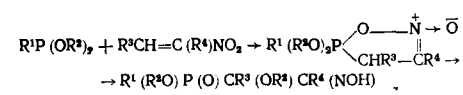
$$Ph_2PH + PhCHO + MeOH \xrightarrow{HCl} Ph_2PCHPhOMe + H_2O \quad .$$

1,3-Oxaphosphorinanes, 1,3-oxaphospholans, and 1,3-oxaphosphepans have been obtained by the reaction of alkyl-ω-hydroxyalkylphosphines with aldehydes[161–166]:



R^1 = Ph, *t*-Bu, C_8H_{17}; R^2 = H, Me, Et, Ph; R^3 = Ph, *t*-Bu; n=2–4

The addition of trialkyl phosphites and dialkyl phosphonites to α,β-unsaturated nitro-compounds with subsequent isomerisation of the intermediate phosphoranes leads to the oximes of α-alkoxy-β-ketophosphonates and phosphinates[167,168]:



R^1 = OR^3, Ph, Me; R^2 = Me, Et; R^3 = Me, Ph, C_6H_4X; R^4 = H, Me .

2. Methods for the Conversion of Substituted Alkyl Groups in Organophosphorus Compounds into α-Alkoxyalkyl Groups

(a) Substitution Reactions of Chloro(sulphonyloxy)methyl Derivatives of Organophosphorus Compounds

This method is of limited importance for the synthesis of compounds with a single α-alkoxyalkyl group at the phosphorus atom, because the methods of synthesis of such compounds described above are more effective. Thus the alkoxylation of arenesulphonyloxymethylphosphonates is accompanied by side reactions involving the transesterification and dealkylation of the ester groups at the phosphorus atom, which lowers the yield and hinders the isolation of the desired products[169]:

$$R^1SO_2OCH_2P(O)(OR^2)_2 + R^3ONa \rightarrow R^3OCH_2P(O)(OR^2)_2 + R^3OCH_2P(O)(ONa)OR^2 + R^3OCH_2P(O)(OR^3)OR^2$$

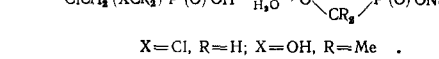
R^1 = Ph, Me; R^2 = iso-Pr, Bu; R^3 = Pr, Bu, C_6H_{13}, $CH_2CHBuEt$, $CH_2P(O)$(O-Pr-iso)$_2$.

However, this method may be convenient for the synthesis of compounds with two and three α-alkoxyalkyl groups at the phosphorus atom because of the relatively ready availability of, for example, bis- and tris-chloromethyl(hydroxymethyl) derivatives of organophosphorus compounds. Thus bis-alkoxymethylphosphinates[127,170–173] and trisalkoxymethylphosphine oxides[173] have been obtained by this method:

$$(ClCH_2)_nP(O)R^1_{3-n} + nR^2ONa \rightarrow (R^2OCH_2)_nP(O)R^1_{3-n} + nNaCl$$

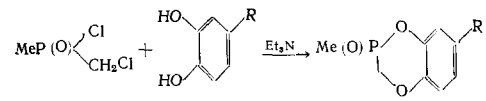
n = 1–3; R^1 = OMe, OEt, OPr, Me, CH_2Cl, Ph; R^2 = C_1–C_8, alkyl, CH_2CH_2OMe, CH_2CH_2OBu .

The interaction of bischloromethyl-[174] and α-hydroxyalkylchloromethyl-phosphinic acids[174,175] with an aqueous solution of sodium hydroxide leads to 1,3-oxaphosphetans:



X = Cl, R = H; X = OH, R = Me .

The reaction of catechol with the chloride of (chloromethyl)-methylphosphinic acid leads to benzo-1,4,2-dioxaphosphorinanes[176]:



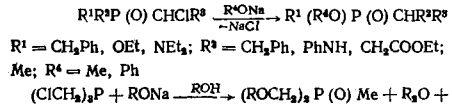
R = H, Me .

The alkylation method has been used to obtain aryloxymethyl derivatives of organophosphorus compounds[171–173,177–181]:

$$(XCH_2)_nP(O)R^1_{3-n} + R^2_mC_6H_{5-m}ONa \xrightarrow{-NaX} (R^2_mC_6H_{5-m}OCH_2)_nP(O)R^1_{3-n}$$

R' = OH, OMe, OEt, OBu, Me; R^2 = Me, Cl, Br, NO_2, COOMe; n = 1 – 3; m = 0 – 3; X = Cl, $OSO_2C_6H_4R^3$; R^3 = Cl, H, Me, NO_2 .

However, in certain cases the reaction of an α-halogenoalkyl derivative of the organophosphorus compound with an alkoxide or phenoxide proceeds differently—with formation of products of nucleophilic[182–184] or pseudoallyl [in the case of phosphorus(III) compounds] rearrangements[185–189]:



R^1 = CH_2Ph, OEt, NEt_2; R^2 = CH_2Ph, PhNH, CH_2COOEt; R^3 = H, Me; R^4 = Me, Ph

$$(ClCH_2)_2P + RONa \xrightarrow{ROH} (ROCH_2)_2P(O)Me + R_2O + NaCl$$

R = C_1 – C_{10} alkyl.

The Darzens reaction constitutes a convenient method of synthesising α,β-epoxyalkyl derivatives of organophosphorus compounds[190–193]:

$$(ClCH_2)_nP(O)(OR^1)_{3-n} + R^2R^3CO \xrightarrow{R^4M} (R^2R^3C{-}CH)_nP(O)(OR^1)_{3-n}$$

R^1 = Me, Et; R^2 = H, Me; R^3 = Et, —CH⟨ ⟩, iso-Pent, Ph, *p*-MeC_6H_4, *p*-C_6H_4OMe; $R^2R^3 = (CH_2)_5$, *o,o'*-$C_6H_4C_6H_4$; R^4 = EtO, t-BuO, H; M=Na, K; n = 1,2 .

The reaction of chloromethylphosphonate with dimethyl sulphide, followed by the conversion of the sulphonium salt into an ylid and its subsequent treatment with an aldehyde, is a variant of this reaction[194]:

$$ClCH_2P(O)R^1R^2 + Me_2S \rightarrow [Me_2\overset{+}{S}CH_2P(O)R^1R^2]\,Cl^- \xrightarrow{NaCH_2S(O)Me} \rightarrow [Me_2\overset{+}{S}\overset{-}{C}HP(O)R^1R^2] \xrightarrow{MeCHO} MeCH{-}CHP(O)R^1R^2 + Me_2S$$

R^1 = OEt, OPr, SEt; $R^2 = R^1$, N(Ph)Me .

(b) Alkylation of α-Hydroxyalkyl Derivatives of Organophosphorus Compounds

The preparative advantages of this method are due to the ready availability of α-hydroxyalkyl derivatives of organophosphorus compounds. Thus treatment of the sodium salts of such compounds[195–205] with alkyl halides yielded a series of alkoxymethyl derivatives of organophosphorus compounds:

$$R^1_nP(O)(CH_2ONa)_{3-n} \xrightarrow[-NaX]{R^2X} R^1_nP(O)(CH_2OR^2)_{3-n}$$

R^1 = alkyl, alkoxy; R^2 = alkyl, CH_2COOEt, $CH_2CH{-}CH_2$, $CH_2CH_2OCH{=}CH_2$, $CH_2SiR^3R^4_2$ (R^3 = Me, Et; $R^4 = R^3$, OEt); $CH_2C{\equiv}CH$, C(Me)(COOEt)$_2$, C(Me)$_2$C≡CH, C(Me)$_2$C≡C—CH=CH_2; X = Cl, Br; n = 0 – 2 .

Certain hydroxymethyl derivatives of organophosphorus compounds are alkylated directly in the presence of sodium alkoxide or a sodium hydroxide solution[206–210]:

$$(R^1O)_2P(O)CH_2OH + Me_2SO_4 + R^2ONa \rightarrow (R^1O)_2P(O)CH_2OMe + Na_2SO_4 + R^2OH$$

$$(HOCH_2)_nP(O)(OH)_{3-n} + R^1X + R^2ONa \xrightarrow{H+} (R^1OCH_2)_nP(O)(OH)_{3-n} + NaX + R^2OH$$

R^1 = small alkyl . $CH_2CH{=}CH_2$; $R^2 = R^1$, H; X = Cl, Br; n = 2,3

The esters and nitriles of acrylic and methacrylic acids also behave as alkylating agents[211]:

$$(R^1O)_2P(O)CHR^4OH + CH^2{=}CR^2R^3 \xrightarrow{R^1ONa} (R^1O)_2P(O)CHR^4OCH_2CHR^2R^3$$

R^1 = Me, Et, iso-Pr; R^2 = HMe; R^3 = CN, COOMe; R^4 = H, Me, Et .

The α,β-epoxy-derivatives of organophosphorus compounds are obtained by treating the corresponding halogenohydrins with bases[212–216]:

$$XCHR^1CR^2(OH)P(O)R^3R^4 \xrightarrow{B} R^1CH{-}CR^2P(O)R^3R^4$$

R^1 = H, Me, Ph; R^2 = H; $R^1R^2 = (CH_2)_4$; R^3 = OH, ONH_4, C_1—C_4 alkoxy-group, Ph; $R^4 = R^3$, $OCHMeCO_2Alk$; B=NaOH, KOH, anion-exchange resin; X = Cl, Br

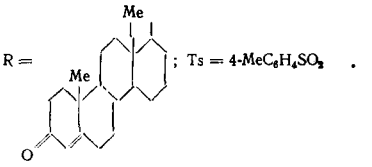
The initial halogenohydrins are usually obtained by the addition of dialkyl phosphites to α-halogenocarbonyl compounds; it is possible to combine the addition and cyclisation stages by adding dialkyl phosphite to the α-halogenocarbonyl compounds in the presence of sodium alkoxide[217–218] or sodium dialkyl phosphite[218–226]:

$$R^1R^2CXC(O)R^3 + (R^4O)_2PONa \rightarrow [R^1R^2CXC(ONa)R^3P(O)(OR^4)_2] \xrightarrow{-NaX} \rightarrow R^1R^2C{-}CR^3P(O)(OR^4)_2$$

R^1 = H, Me; $R^2 = R^1$, Ph; R^3 = Me, Et, t-Bu, Ph, C_6H_4OMe; $R^2R^3 = (CH_2)_4$; R^4 = Me, Et, Bu, CH_2Ph .

An α-tosyloxyketone has also been used in the latter reaction instead of α-halogenoketones[227]:

$$RC(O)CH_2OTs + (EtO)_2PONa \rightarrow (EtO)_2P(O)CH{-}CHR$$



; Ts = 4-$MeC_6H_4SO_2$.

2-Dialkoxy-2-alkylphosphinyltetrahydrofurans have been obtained by a similar method[223,226]:

$$R^1C(O)CH_2CH_2CH_2Cl + (R^2O)_2PONa \rightarrow (R^2O)_2P(O)C(ONa)R^1CH_2CH_2CH_2Cl \rightarrow \xrightarrow{-NaCl} (R^2O)_2P(O)\text{-}\langle R^1, O \rangle$$

R^1 = Me, Et; R^2 = Et, Bu .

When an attempt is made to epoxidise 2-chloro-1-hydroxyethane-1,1-diphosphonic acid with alkali[228,229], the following rearrangement takes place,

$$ClCH_2(HO)C(PO_3H_2)_2 \xrightarrow[2)H+]{1)NaOH} H_2O_3PCH_2C(O)PO_3H_2 .$$

α,β-Epoxypropylphosphonates have been obtained by treating α-chloroethoxymethylphosphonates (obtained from hydroxymethylphosphonates, acetaldehyde, and hydrogen chloride), with a zinc–copper alloy or phenyl-lithium[230,231]:

$$(RO)_2P(O)CH_2OH + MeCHO \xrightarrow{HCl} (RO)_2P(O)CH_2OCHClMe \xrightarrow{PhLi} \rightarrow (RO)_2P(O)CH{-}CHMe$$

R = Me, Et

The hydroxymethyl groups of bishydroxymethylphosphinic acid are alkylated by epoxyethane[232]:

$$(HOCH_2)_2P(O)OH + CH_2{-}CH_2 \rightarrow (HOCH_2CH_2OCH_2)_2P(O)OCH_2CH_2OH .$$

(c) Other Methods

Epoxyphosphonates are obtained by the epoxidation of the double bond in the α,β-alkenyl derivatives of organophosphorus compounds by biochemical methods[233], peracids[234,235], metal peroxides[236], t-butyl peroxide[237], and hydrogen peroxide in an alkaline medium or in the presence of tungstic

acid salts[235,237–240]:

$$R^1CH{=}CR^2P(O)R^3_2 \xrightarrow{[O]} R^1CH(O)CR^2P(O)R^3_2$$

$R^1 = H$, Me, Ph, OR^4; $R^2 = H$, Me; $R_2 = OH$, ONa, ONH_4, OMe, OEt, OCH_2CH_2Cl, Ph, $C{\equiv}CPh$; $R^4 = Et$, Bu, iso-Bu; $R^1R^2 = (CH_2)_3$, $(CH_2)_4$

$$MeCH{=}CH(R^1O)P(O)OP(O)(OR^1)R^3 + H_2O_2 \xrightarrow{OH^-} MeCH(O)CH(R^1O)P(O)OP(O)(OR^1)R$$

$R^1 = Na$; $R^1_2 = Ca$; $R^2 = OMe$, OEt, OPr, $OCH_2CH_2R^3$, OCH_2COOMe, Me, Ph, CH_2Ph, CH_2COOMe; $R^3 = OMe$, CN, $\overset{+}{N}Me_3$, $CH_2\overset{+}{N}H_2CHMe_2$, $CH_2\overset{+}{N}Me$, CH(Me)OMe.

α-Methyl(phenyl)-β,β-diphenylepoxyethylphosphonates have been synthesised by the reaction of α-ketophosphonates with diphenyldiazomethane[241,242]:

$$(MeO)_2P(O)C(O)R + Ph_2CN_2 \rightarrow (MeO)_2P(O)CR(O)CPh_2$$

$R = Me$, Ph, C_6H_4X, $X = Me$, Cl, Br.

α-Phosphorylated ketals have been obtained by converting α-keto-derivatives of organophosphorus compounds into ketals with the aid of triethyl orthoformate[244]:

$$R^2O(R^1)P(O)C(O)Me + CH(OEt)_3 \xrightarrow{H_2SO_4} R^2O(R^1)P(O)C(OEt)_2Me$$

$R^1 = OBu$, Opent, Ph; $R^2 = Pr$, Bu, Pent.

III. PROPERTIES AND APPLICATIONS

1. Chemical Properties

(a) Substitution Reaction at the Phosphorus Atom

The dichlorides of alkoxymethylphosphonic acids are converted into the dichlorides of alkoxymethylphosphonothioic acids by reaction with phosphorus pentasulphide[58,60,245]. The chlorides of ethylalkoxymethylphosphinic acids and the dichlorides and ester-chlorides of alkoxymethylphosphonic and alkoxymethylphosphonothioic acids readily react with alcohols[7,16,50,58,60,64,110–112], alkoxides[60], and mercaptans[7,60], are converted into fluorides by treatment with arsenic trifluoride[52], are converted into amides by treatment with secondary amines[16,110,112], and are hydrolysed by water to acids[110,112], which are esterified by trialkyl phosphites on heating[146,147,176,208]. The ester-chlorides of alkoxymethylphosphonic acids are readily converted into anhydrides on heating; when the latter react with alcohols or phenols, the monoesters of alkoxymethylphosphonic acids are obtained[68,248]:

$$nR^1O(Cl)P(O)CH_2OR^1 \xrightarrow[-R^1Cl]{\Delta} -[-O-P(O)CH_2OR^1]_n \xrightarrow{nR^2OH} \rightarrow R^2O(HO)P(O)CH_2OR^1$$

$R^1 = C_1$—C_8 alkyl; $R^2 = R^1$, Ph, $C_6H_4NO_2$-*p*.

The diethyl ester of (2-acetoxyethoxy)methylphosphonic acid readily cyclises on heating[249]:

$$MeC(O)OCH_2CH_2OCH_2P(O)(OEt)_2 \xrightarrow{\Delta} \text{(1,3,2-dioxaphosphorinane)}P(O)OEt + MeCOOEt$$

Dibutylethoxymethylphosphine oxide has been obtained by the reaction of diethyl ethoxymethylphosphonate with butyllithium[250].

Like other alkyl esters of phosphonic acids, alkoxymethylphosphonates hydrolyse in an alkaline medium with formation of salts of the monoesters of alkoxymethylphosphonic acids[203], while on refluxing with hydrochloric acid they hydrolyse to alkoxymethylphosphonic acids[4,26,203].

Diethyl diethoxymethylphosphonate is converted, on treatment with hydrobromic acid, into diethoxymethylphosphonic acid, while its treatment with gaseous dry hydrogen chloride is accompanied by the partial dissociation of the C–P bond and leads to a mixture of diethyl phosphite and diethyl ethoxychloromethylphosphonate[90].

The reaction of α-alkoxyalkylphosphonates with an equimolar amount of phosphorus pentachloride yields the ester-chlorides of the corresponding acids in satisfactory yields[19,52].

When an excess of phosphorus pentachloride is used, the C–P bond is cleaved and a complex mixture of products is obtained instead of the expected acid dichloride[251,252]. Analogous processes occur on treatment of α-alkoxyalkylpyrophosphonates and α-alkoxyalkylphosphine oxides with phosphorus pentachloride[252].

When alkylalkoxymethyl derivatives of organophosphorus compounds are acted upon by alkalies under severe conditions, the alkoxymethyl groups are split off[174,189]:

$$(C_8H_{17}OCH_2)_2P(O)Me + KOH \rightarrow C_8H_{17}OCH_2(Me)P(O)OK + C_8H_{17}OMe$$

$$\text{(1,3,2-dioxaphosphorinane)}P(O)R + NaOH \rightarrow MeOCH_2(R)P(O)ONa$$

$R = OH$, Me.

The phenyl groups are split off preferentially in the interaction of quaternary α-alkoxyalkylphenylphosphonium salts with potassium or sodium hydroxide[23,79,152]:

$$Ph_2R^1\overset{+}{P}CHR^2OR^3X^- \xrightarrow{MOH} PhR^1P(O)CHR^2OR^3 + PhH + MX$$

$R^1 = Ph$, Me; $R^2 = H$; $R^3 = Me$; $R^2R^3 = (CH_2)_3$; $X = Cl$, I, BF_4; $M = Na$, K.

α-Alkoxyethyltriphenylphosphonium chloride and α-alkoxy-β-bromoethyltriphenylphosphonium bromide are cleaved by water in a different manner[253–255]:

$$Ph_3\overset{+}{P}CH(OR)MeCl^- \xrightarrow[-HCl]{H_2O} Ph_3P + [MeCH(OH)OR]$$

$$Ph_3\overset{+}{P}CH(OR)CH_2BrBr^- \xrightarrow[-2HBr]{H_2O} Ph_3PO + [ROCH{=}CH_2]$$

$R = Et$, Bu.

When the diethyl esters of α,β-epoxyalkylphosphonic acids are heated with alcoholic solutions of sodium dialkyl phosphites, the diethoxyphosphinyl group is split off and dialkyl esters of β-ketophosphonic acids are formed[256]:

$$(EtO)_2P(O)CHR^1CHMe + (R^2O)_2PONa \rightarrow [(EtO)_2P(O)CR^1(ONa)CHMeP(O)(OR^2)_2] \rightarrow$$

$$\rightarrow (EtO)_2PONa + R^1C(O)CHMeP(O)(OR^2)_2$$

$R^1 = H$, Me; $R^2 = Et$, iso-Pr, Bu.

The reduction of alkoxymethyldiphenylphosphine oxides with lithium aluminium hydride or trichlorosilane yielded the corresponding phosphines, which were converted by alkylation into phosphonium salts[79,152]. A cyclic bisphosphonium salt has been synthesised by the alkylation of the bisdiphenylphosphinomethyl ether with ethylene bromide[132]:

$$Ph_2PCH_2OCH_2PPh_2 + BrCH_2CH_2Br \rightarrow \text{(1,3,2-dioxaphosphorinane-2,2-diyl)}(Ph_2\overset{+}{P}PPh_2) \cdot 2Br^-$$

On heating and treatment with acids, zinc chloride, or boron trifluoride etherate, α,β-epoxydiphosphonates[193,212,243,257–259] and 2-methoxy-2-diphenylphosphinyl-1-phenyl-1-propanol [260] are converted into β-keto-derivatives of organophosphorus compounds as a result of α → β migration:

$$(R^1O)_2P(O)CR^2{-}CR^3R^4 \rightarrow (R^1O)_2P(O)CR^3R^4C(O)R^2$$

$R^1 = Me$, Et; $R^2 = H$, Me, t-Bu, Ph, *p*-XC_6H_4; $X = OMe$, Me, Cl, Br; $R^3 = H$, Ph; $R^4 = H$, Me, Ph; $R^3R^4 = (CH_2)_n$, *o*, *o*'-$C_6H_4C_6H_4$; $n = 3, 5$

$$Ph_2P(O)C(Me)(OMe)CH(Ph)OH \xrightarrow{CF_3COOH} Ph_2P(O)CH(Ph)C(O)Me$$

(b) Substitution Reaction at the α-Carbon Atom

Treatment of alkoxymethyltriphenylphosphonium chloride with alkyl(aryl)-lithium or alkoxides leads to an ylid, which reacts with aldehydes and ketones to form triphenylphosphine oxide and alkyl vinyl ethers[151,261,262]:

$$Ph_3\overset{+}{P}CH_2OR^1Cl^- \xrightarrow[-B\cdot HCl]{B} Ph_3P{=}CHOR^1 \xrightarrow{R^2R^3CO} R^2R^3C{=}CHOR^1 + Ph_3PO$$

R^1 = Me, Bu, Ph, *p*-MeC_6H_4; $R^2 = R^1$, H; $R^3 = R^1$; $R^2R^3 = (CH_2)_n$; $n = 4-7$.

Alkoxyethylphosphonates are also suitable for the synthesis of the latter[14,16,17,25,26,263]:

$$(R^1O)_2P(O)CH(A)OR^2 \xrightarrow[-RH]{1)MR;2)R^3R^4CO} (R^1O)_2P(O)CA(OR^2)CR^3R^4OM \xrightarrow{\Delta} \rightarrow R^3R^4C{=}C(A)OR^2 + (R^1O)_2P(O)OM$$

R^1 = Me, Et, Bu; $R^2 = R^1$, Ph, CH_2CH_2OMe; A = P(O)$(OR^1)_2$, COOR^1, $CONH_2$, CONHPr, C(O)Me, CON⟨⟩O, Ph, H; $R^3 = R^1$, H, Ph; $R^4 = R^2$, H, ⟨⟩, *p*-XC_6H_4; X = OMe, Me, Cl; $R^3R^4 = (CH_2)_n$; $n = 4, 5$, MR = Li, iso-Pr_2NLi, NaH, t-BuOK, n-BuONa.

When α-methoxyethyldiphenylphosphine oxide was allowed to react with lithium di-isopropylamide and then with benzaldehyde, 2-methoxy-2-diphenylphosphinyl-1-phenyl-1-propanol was isolated[260]:

$$Ph_2P(O)CH(Me)OMe \xrightarrow[2)PhCHO;H_2O]{1)\ iso\text{-}Pr_2NLi} Ph_2P(O)C(Me)(OMe)CH(Ph)OH$$

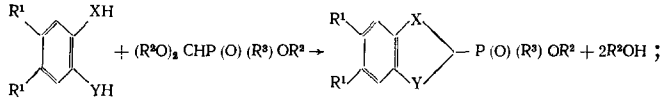
Metallation of alkoxymethylphosphonates followed by treatment with chlorotrimethylsilane, chloromethyl ethyl ether[250], sulphur, and methyl iodide[264] yielded α-substituted phosphonates:

$$(Me_2N)_2P(O)CH_2OEt \xrightarrow[-BuH]{BuLi} (Me_2N)_2P(O)CHLiOEt \xrightarrow[-LiCl]{RCl} (Me_2N)_2P(O)CHROEt$$

R = $SiMe_3$, CH_2OEt .

Chlorination of dialkyl methoxymethylphosphonates with sulphuryl chloride leads to α-chloromethyoxymethylphosphonates[9].

Reactions involving the substitution of α-alkoxy-groups are also known. Thus cyclic phosphorylated formals and aminomercaptals are obtained by the transacetalisation of phosphorylated dialkylformals with *o*-bisphenols[265] and *o*-aminothiophenol[266]:

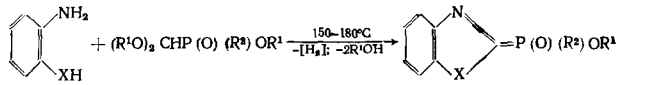


$$+ (R^3O)_2CHP(O)(R^3)OR^2 \rightarrow$$

$$- P(O)(R^3)OR^2 + 2R^2OH$$

R^1 = H; $R^1_2 = (CH)_4$; R^2 = Et, Pr, Bu; R^3 = OEt, OBu, Ph, *p*-MeC_6H_4; X = Y = O; X = NH, Y = S .

When *o*-aminophenol and *o*-phenylenediamine are used in this reaction, phosphorylated derivatives of benzoxazole and benzimidazole are obtained as a result of the oxidation of the transacetalisation products during isolation[267–268]:



$$+ (R^1O)_2CHP(O)(R^3)OR^1 \xrightarrow[-[H_2]; -2R^1OH]{150-180^\circ C}$$

$$= P(O)(R^2)OR^1$$

X = NH, O; R^1 = small alkyl; R^3 = Ph, *p*-MeC_6H_4, OR^1 .

α-Dialkylamino-α-methoxymethyl derivatives of organophosphorus compounds interact with thionyl chloride to form phosphorylated ammonium salts[150,269] and also with dialkyl phosphites and diphenylphosphine oxide to form dialkylaminomethanebisorganophosphorus compounds[150]:

$$(EtO)_2P(O)CH(NMe_2)OMe \xrightarrow[-R_2PHO]{SOCl_2} \begin{matrix}(EtO)_2P(O)CH{=}\overset{+}{N}Me_2Cl^- \\ (EtO)_2P(O)CH(NMe_2)P(O)R_2\end{matrix}$$

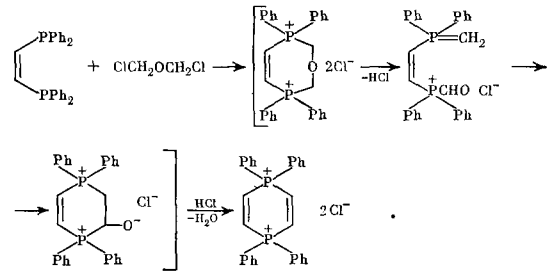
R = OEt, Ph.

α-Alkoxy-β-halogenoethylphosphonates are readily dehydrochlorinated by sodium hydroxide[3], while 2-dialkoxyphosphinyl-3-chloro-1,4-dioxans and α-alkoxy-β-chloroethylphosphine oxides eliminate hydrogen chloride even in the course of distillation[39,40,104,106].

α-Ethoxyvinyltriphenylphosphonium bromide readily combines with thiophenol via its double bond[153]:

$$Ph_3\overset{+}{P}C(OEt){=}CH_2Br^- + PhSH \rightarrow Ph_3\overset{+}{P}CH(OEt)CH_2SPhBr^-$$

The rearrangement occurring in the alkylation of *cis*-bisdiphenylphosphinoethylene with bischloromethyl ether has been described[270]:



2-Diphenylphosphinyl-2-methoxy-1-methyl-3-tosyloxypentane isomerises in an acetate solution as a result of the 2 → 3 migration of the methoxy-group[260]:

$$Ph_2P(O)C(OMe)(CHMe_2)CH(Me)OTs \xrightarrow{AcOH-AcONa} \rightarrow Ph_2P(O)CH(COMe)CHMe_2 + Ph_2P(O)CH(CHMe_2)C(OMe){=}CH_2$$

Ts = 4-$MeC_6H_4SO_2$.

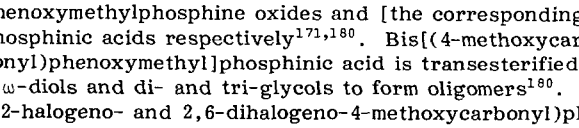
(c) Other Reactions

Propargyloxymethylphosphonates enter into the Mannich reaction[198]:

$$(R^1O)_2P(O)CHR^2OCH_2C{\equiv}CH + CH_2O + HNR^3_2 \xrightarrow{(AcO)_2Cu} \rightarrow (R^1O)_2P(O)CHR^2OCH_2C{\equiv}CCH_2NR^3_2$$

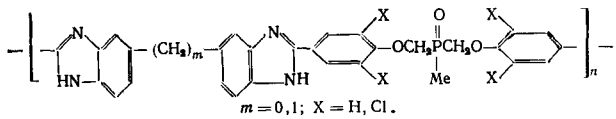
R^1 = Et, Pr, Bu; R^2 = H, Me; R^3 = Et; $R^3_2 = (CH_2)_5$.

On treatment with formaldehyde, the disodium salt of phenoxymethylphosphonic acid is hydroxymethylated, while the free acid is converted into a polymer[272]:



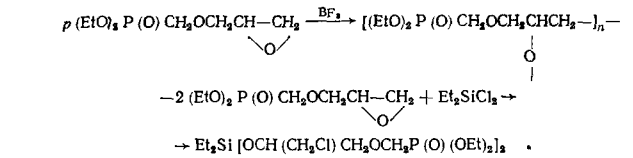
On treatment with sodium hydroxide in alcohol, bis[(4-methoxycarbonyl)phenoxymethyl]phosphine oxides and the corresponding phosphinic acids are converted into carboxyphenoxymethylphosphine oxides and [the corresponding] phosphinic acids respectively[171,180]. Bis[(4-methoxycarbonyl)phenoxymethyl]phosphinic acid is transesterified with 1,ω-diols and di- and tri-glycols to form oligomers[180]. Bis-[(2-halogeno- and 2,6-dihalogeno-4-methoxycarbonyl)phenoxymethyl]methylphosphine oxides and the carboxylic acids obtained from them by hydrolysis respectively undergo transesterification or esterification with ethylene glycol, diethylene glycol, and 1,2-propylene glycol to form thermostable self-extinguishing resins[273–275].

The condensation of bis[(4-methoxycarbonyl)phenoxymethyl]methylphosphine oxide or bis[(4-carboxy-2,6-dichloro)phenoxymethyl]methylphosphine oxide with 3,3'-diaminobenzidine tetrahydrochloride or 3,3',4,4'-tetra-aminodiphenylmethane yields resins with a high thermal stability[276]:



$m = 0,1$; X = H, Cl.

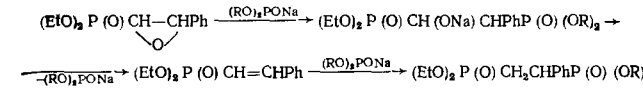
2,3-Epoxypropylenoxymethylphosphonate polymerises on treatment with boron trifluoride[196] and on heating interacts with dichlorodiethylsilane with opening of the oxiran ring[277]:



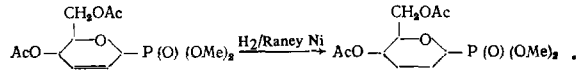
Treatment of epoxyphosphonates with an alcoholic solution of boron trifluoride etherate or sulphuric acid leads to β-alkoxy-α-hydroxyethylphosphonates[237].

The oxiran ring in α,β-epoxyphosphonates is opened to form α-hydroxyphosphonates with β-functional substituents on treatment with an aqueous solution of sulphuric acid, aniline, ammonia[278], water, amines, alcohols, mercaptans, potassium cyanide, and malonates[229,279-283].

Epoxyphosphonates interact with sodium dialkyl phosphite, forming bisphosphonates[284]:



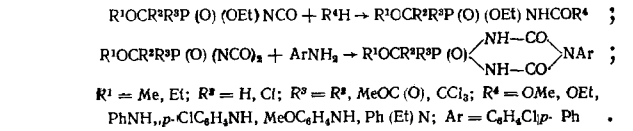
The multiple carbon–carbon bond in unsaturated glycosyl phosphonates is readily hydrogenated under the usual conditions[285]:



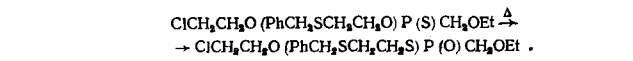
(−)-*cis*-α,β-Epoxypropylphosphonic acid has been isolated from the racemic mixture by resolving the latter with the aid of α-phenylethylamine[286,287].

The β-chloroethyl esters of alkoxymethylphosphonic acids are converted into the β-mercaptoethyl esters on treatment with sodium sulphide and subsequent acidification, while treatment with sodium mercaptide leads to β-alkylthioethyl esters[288]. Alkylation of the silver salt of *cis*-α,β-epoxypropylphosphonic acid with halogeno-derivatives yielded the corresponding esters[289].

α-Alkoxymethylphosphonoisocyanitidates readily combine with alcohols and amines[47]:



When phosphonothionates are heated, the thione–thiol rearrangement takes place[288]:

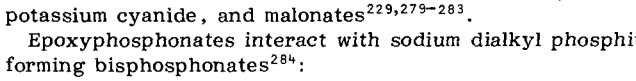


2. Applications of α-Alkoxyalkyl Derivatives of Organophosphorus Compounds

α-Alkoxyalkyl derivatives of organophosphorus compounds have been recommended in several fields. One of these involves their use as pesticides. Certain esters of alkoxymethylphosphono(di)thioic acids have been tested for this purpose. They were found to exhibit a high insectidal activity and a comparatively low toxicity for warm blooded animals[7,56,58,60,104]:

The second application is in medicine: certain compounds of this class, for example mixed alkyl and *p*-nitrophenyl esters of α-methoxyalkylphosphonic acids, have an antienzymatic activity and an insignificant toxicity for mammals and have been recommended for therapy[230]. The esters of bisallyloxymethylphosphinic acid are able to suppress the activity of the central nervous system[210] and are therefore of definite therapeutic interest.

Among α-epoxy-derivatives of organophosphorus compounds, an effective antibiotic has been discovered—1-*R*,2-*S*-1,2-epoxypropylphosphonic acid[191,287,292]; its derivatives, for example, its salts with aminoacids[241], and epoxypropylpyrophosphonic acids also have a high bactericidal activity [240,293]:



The third application involves the use of alkoxymethylphosphine oxides as extractants[294], for example, for uranium and thorium, particularly when the latter are to be extracted from sulphuric acid solutions[189,205]:



The most effective extractants are alkoxymethyldialkylphosphine oxides, whose extracting capacity approaches that of trialkylphosphine oxides[294]. In the above series trisalkoxymethylphosphine oxides are the least effective, but even their activity exceeds by three orders of magnitude that of tributyl phosphate[205].

The fourth practical application involves the use of the products of the polycondensation of bisaryloxymethylphosphinic acids with formaldehyde as ion-exchange resins[177,178,272], which proved to be selective in relation to certain polyvalent ions.

Carboxyalkoxymethylphosphonic acids, for example, $H_2O_3PCH_2OCH_2COOH$, have been recommended as complexones for the prevention of the deposition of salts[202,203].

The fifth application involves the use of di(tri)halogenoalkoxy(phenoxy)methylphosphonates[6,8,181] and the products resulting from the addition of alcohols, mercaptans, amines, cyanides, sulphides, etc. to α-epoxyphosphonates[278-283] as fire-proofing additives to polymers and textiles.

The possibility of using α-alkoxyalkylphosphonates, α-alkoxyalkylphosphinates, and α-alkoxyalkylphosphine oxides as solvents which effectively solvate alkali metal cations[85,127,188,271,295,296], plasticisers[2,85,170], phytopharmaceutical preparations[8], monomers[177,272], etc. has been indicated. It has also been noted that higher alkoxymethylphosphinic acids have effective surface-active properties[4,297].

After the present review had been sent to the editors, several publications describing the synthesis and properties of α-alkoxyalkyl compounds of phosphorus appeared.

Phosphorus ylids have been obtained by the alkylation of the phosphorus atom in the *C*-phosphorylated malonic ester with alkyl chloromethyl ethers[298] and diethoxymethyl acetate[299].

The interaction of chlorodiphenylphosphine with a series of dimethyl acetals led to the synthesis of α-methoxyalkyldiphenylphosphine oxides[300]. Bis(α-diphenylphosphinyl)benzyl ether has been obtained, together with other products, by heating chlorodiphenylphosphine with benzaldehyde[301].

The alkylation of hypophosphorous acid by orthoformates in the presence of toluene-*p*-sulphonic acid, leading to a mixture of bisdialkoxymethylphosphinate and alkyl dialkoxymethylphosphonite, has been described[302].

The reactions of primary and secondary phosphines with alcohols and aromatic aldehydes in the presence of toluene-*p*-sulphonic acid have been investigated[303]. It has been shown that, depending on the type of substituents in the aromatic ring, either α-alkoxybenzylphosphines or benzylidenebisphosphines are obtained.

A study has been made of the thermal cleavage of 1-alkoxy-2-bromoethyl and α-alkoxyalkyl derivatives of triorganophosphonium salts, involving the formation of triorganophosphine oxide in the former case and triorganophosphine in the latter case[304].

When electrophiles (hydrogen bromide, tetrapropyldiborane) are added to (α-alkoxyvinyl)triphenylphosphonium salts, the directing influence of the alkoxy-group predominates over that of the positively charged phosphorus atom[305].

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