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ORGANOPHOSPHORUS COMPOUNDS† OBTAINED FROM α-OXIDES

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† In this translation names of these compounds have been changed to conform to the 1952 rules of the Chemical Society and American Chemical Society, where authors' intentions are clear. In the Russian text derivatives of phosphonous and phosphinous acids are both referred to as phosphinites (Ed. of Translation).

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I. INTRODUCTION

The importance of organophosphorus compounds in chemical science and industry has grown during the post-war years. Many substances of this type are effective insecticides, medicinals, catalysts for various reactions, plasticisers, flameproofing agents for various materials, additives for improving the properties of lubricating oils, etc. This has naturally aroused interest in the development of simple and efficient methods for synthesising various types of organophosphorus compounds, as noted particularly by several authors at the Second All-Union Conference on the Chemistry and the Applications of Organophosphorus Compounds (Kazan, November 1959)[1-3].

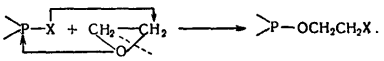
The present review deals with the reactions of cyclic oxides with some phosphorus compounds and also the properties, reactions, and applications of the products. The only short summary in this field, dealing with the addition of α-oxides to halogen compounds of phosphorus, was written by one of us in 1947[4]. During the past years many facts have accumulated, the applications of this reaction have been extended, and many new compounds of the β-substituted "organoelemental" type have been prepared. This trend in the chemistry of organophosphorus compounds has developed considerably during recent years in relation to the practical exploitation of organophosphorus compounds synthesised from α-oxides. Other methods for the preparation of such compounds have usually been less effective, and are difficult to use, even if they are possible at all. α-Oxides and phosphorus compounds usually undergo ready addition without the formation of by-products. In organic chemistry reactions of this type — the addition of ethylene oxide to alcohols, amines, and other compounds containing a reactive hydrogen atom — have for a long time been extensively used for the preparation of 2-hydroxyethyl compounds[5-9].

II. INTERACTION OF PHOSPHORUS COMPOUNDS CONTAINING REACTIVE HALOGEN ATOMS WITH α-OXIDES. PROPERTIES OF THE RESULTING PRODUCTS

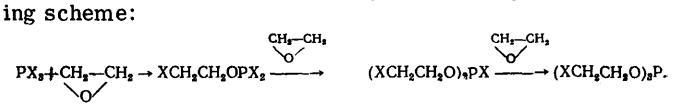
1. Addition of α-Oxides to Halogen Compounds of Tervalent Phosphorus

The addition of α-oxides (epichlorohydrin) to phosphorus trichloride was first described by Hanriot[10]; fifty-four years later Lommel and Engelhardt[11] patented the addition of ethylene oxide to PCl_3 for the preparation of chloroethyl esters of phosphorous acid. In neither case was the structure of the products of these reactions established.

The systematic investigation of this reaction was begun by Soviet scientists. Kabachnik and Rossiiskaya studied the reaction of phosphorus trichloride and tribromide and also of various ester chlorides of phosphorous acid with ethylene oxide[12-15]. Smooth addition of the components to one another was observed in all cases, the oxide ring opening with formation of a P–O–C link, while halogen, previously combined with the phosphorus, added to the β carbon atom



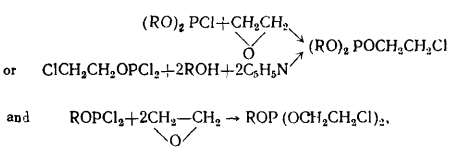
The valency of the phosphorus remains unchanged during this reaction. Addition of ethylene oxide to tervalent phosphorus halides takes place in stages according to the following scheme:



Products formed by the addition of one, two, and three molecules of the oxide to PCl_3 [12] and PBr_3 were isolated[13].

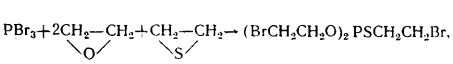
The process can be stopped at any desired stage, depending on the amount of ethylene oxide introduced, making it easy to obtain various derivatives of the 2-halogenoethyl phosphorous acids (see below).

Kabachnik, Rossiiskaya, and other investigators obtained also mixed esters of phosphorous acids containing either one or two 2-chloroethyl groups, according to the following schemes:

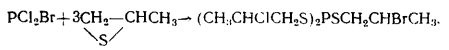


where R = phenyl[14], ethyl[15,16], some 1-cyanoalkyls[17], and other radicals[15,18].

Interesting mixed 2-halogenoalkyl esters of phosphorous acid with different bonds (P–O–C and P–S–C) or with different halogens were synthesised by De Witt[19] by the reaction of phosphorus tribromide with a mixture of ethylene oxide and ethylene sulphide:



and also by the reaction of phosphorus bromodichloride with propylene sulphide:



The preparation of such unsymmetrical compounds is sometimes complicated by disproportionation processes, which readily occur with some esters of tervalent phosphorus acids. For example, 2-chloroethyl diphenyl phosphite[14], 2-chloroethyl *o*-phenylene phosphite[14], and 2-chloroethyl cyanoalkyl phosphites[17] were synthesised in good yields, whereas the preparation of 2-chloroethyl diethyl phosphite yielded only a certain amount of this product together with other theoretically possible compounds — triethyl phosphite, bis-2-chloroethyl ethyl phosphite, and tris-2-chloroethyl phosphite[15,16] — formed by disproportionation. Similar behaviour was found in the synthesis of bis-2-chloroethyl phenyl phosphite[14] and dialkyl 2,2-dichloro-1-methylethyl phosphite[20]; incidentally, the preparation of 2-chloroethyl methyl phosphite from phosphorus trichloride and a mixture of methanol and ethylene chlorohydrin was also accompanied by formation of other possible products, dimethyl and bis-2-chloroethyl phosphites[21].

Ethylene oxide reacts extraordinarily readily with tervalent phosphorus halides with much heat evolution, the tribromide reacting more vigorously than phosphorus trichloride.

Another possible method for obtaining ester chlorides [phosphoro-chloridites and -dichloridites (Ed. of Translation)] and 2-chloroethyl esters of phosphorous acid (symmetrical and mixed) is by reaction of phosphorus trihalides with ethylene chlorohydrin. However, the accompanying evolution of hydrogen chloride makes this procedure less convenient, reduces the yields of products owing to partial rupture of ester links, and often requires special apparatus owing to the corrosive action of the hydrogen chloride evolved. Sometimes this last product must be combined with organic bases, which complicates the process.

The preparation of bis-2-chloroethyl hydrogen phosphite [bis-2-chloroethyl phosphonite? (Ed. of Translation)] may well be the only case in which the use of ethylene chlorohydrin provides a simpler process than that with ethylene oxide, the former reaction taking place in a single stage[21,22]

$$PCl_3+3HOCH_2CH_2Cl \rightarrow HPO(OCH_2CH_2Cl)_2+2HCl+ClCH_2CH_2Cl,$$

whereas the latter occurs in two stages, *via* tris-2-chloroethyl phosphite[23]

$$2PCl_3+6CH_2\!-\!CH_2 \rightarrow 2P(OCH_2CH_2Cl)_3 \xrightarrow{H_3PO_2} 3HPO(OCH_2CH_2Cl)_2.$$

However, in this case also the use of ethylene oxide is to be preferred, since both the above stages take place readily, with excellent yields, and without the formation of by-products.

The use of ethylene bromohydrin, by analogy with the chlorohydrin, to obtain 2-bromoethyl esters of phosphorous acid, *e.g.* $BrCH_2CH_2OPBr_2$ [really 2-bromoethyl phosphorodibromidite (Ed. of Translation)], is apparently impossible, since hydrogen bromide cleaves ester links far more readily than does hydrogen chloride[24]; it is for this reason that the reaction of phosphorus tribromide with alcohols is a universal method for preparing alkyl bromides.

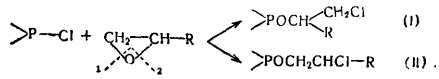
Hence for the preparation of 2-halogenoethyl derivatives of phosphorous acid the above reaction of ethylene oxide with phosphorus trihalides has no equal for simplicity and the ease with which it can be carried out.

Technically it is more convenient to pass gaseous ethylene oxide into the phosphorus trihalide than to carry out the reaction in the reverse order. The yields of the reaction products remain substantially unaffected by the order in which the components are added to one another. Although according to Efimova's results[25] the addition of PCl_3 to liquid ethylene oxide gives a higher yield (64.6%) of tris-2-chloroethyl phosphite than does bubbling gaseous ethylene oxide through phosphorus trichloride (56.5%), these results are not typical, since the vacuum distillation of the reaction product occurred in this case at high temperatures (owing to a poor vacuum), so that isomerisation of the tris-2-chloroethyl phosphite took place at an appreciable rate. In a good vacuum this substance distils almost quantitatively[23].

Until recently only 2-halogenoalkyl esters of phosphorous acid were known, *i.e.* compounds containing P–O or P–X bonds, where X represents a halogen. Comparatively recently, the addition of ethylene oxide to alkyl-[26-28] and aryl-phosphonous dichlorides[29-31] and to diethylphosphinous chloride[32] has been studied. These reactions, which were more vigorous than in the case of phosphorus trichloride, led to the preparation of mono- and bis-2-chloroethyl esters of methyl-,[26] ethyl-,[27,28] and phenyl-phosphonous acids[29-31] and the 2-chloroethyl ester of diethylphosphinous acid[32].

The comparatively little studied reactions of unsymmetrical α-oxides with tervalent phosphorus halides are interesting. The addition of propylene oxide[23,25,33-35], styrene oxide[23,36], epichlorohydrin[33], and glycidyl‡ phenyl ether [1-phenoxypropane-2,3-diol (Ed. of Translation)][33] to phosphorus trichloride has been described, as well as that of propylene oxide to methyl-,[36] ethyl-,[26] and phenyl-phosphonous dichloride[36] and of propylene sulphide to phosphorus tribromide and bromodichloride[19]. The reaction is fundamentally the same as with ethylene oxide, the oxide ring opening with formation of 2-halogenoalkyl esters or thioesters of phosphorous acid.

Theoretically the reaction can go in two ways, the radical of the α-oxide being attached to either an α or a β carbon atom in the reaction product:



Little experimental work has been done on this problem, and the results are inconclusive. Thus Shuikin and Bel'skii[35] obtained a good yield of 2-chloropropan-1-ol by hydrolysing the addition product of propylene oxide and phosphorus trichloride, which indicates the second type of reaction. Efimova[25] carried out the same investigation and isolated 1-chloropropan-2-ol (although without giving the yield), which can be obtained only by the first type of reaction. Nevertheless, most chemists consider from general principles that these processes are of the second type, *i.e.* that the oxide ring is opened at the bond between oxygen and the secondary carbon atom[19,23,33-36]:

$$>P\!-\!Cl+CH_2\!-\!CH\!-\!R \rightarrow >POCH_2CHCl\!-\!R.$$

The only case of the reaction of phosphorus trichloride with an α-oxide (*e.g.* epichlorohydrin) in the presence of aluminium chloride so far described[37] is one yielding the

‡ The term ***glycidyl*** used throughout this review derives from ***glycidol***, 2,3-epoxypropan-1-ol (Ed. of Translation).

dichloride of 3-chloro-2-hydroxypropylphosphonic acid $ClCH_2.CH(OH).CH_2.POCl_2$. The mechanism of this reaction was not given.

2. Some Properties of 2-Halogenoalkyl Derivatives of Tervalent Phosphorus Acids

Compounds containing the grouping $>P-O.CH_2.CH_2X$ (where X = Cl or Br) display all the properties characteristic of esters or ester halides of tervalent phosphorus acids. They can add on oxygen, sulphur, and halogens, the phosphorus becoming quinquevalent:

$$>POCH_2CH_2X+A \rightarrow >P(A)OCH_2CH_2X,$$

where A = O, S, Cl_2, or Br_2. Such addition occurs more readily with phosphonous esters than with derivatives of phosphorous acid. Thus tris-2-chloroethyl phosphite could be oxidised to the phosphate with potassium permanganate[38] and sodium hypochlorite[39], while bis-2-chloroethyl phenylphosphonite is readily oxidised to the phenylphosphonate ester even in the air[31].

The addition of sulphur to 2-chloroethyl phosphorodichloridite[40], bis-2-chloroethyl phosphorochloridite[41], bis-2-chloroethyl phenylphosphonite[31], tris-2-chloroethyl phosphite[42,43], and methylphosphonochloridite esters (the 2-chloroalkyl ester)[26] has been described. The action of chlorine on 2-chloroethyl *NN*-diethylphosphoramidochloridite was investigated by Malatesta and D'Atri[40]. 2-Halogenoethyl phosphites are hydrolysed quite readily, ultimately giving phosphorous acid[12,14].

The variety of behaviour of these 2-chloroethyl derivatives on storage (in absence of air or moisture) and on heating is noteworthy[12]. Among the three well-known substances:

$$\underset{(I)}{ClCH_2CH_2OPCl_2}, \quad \underset{(II)}{(ClCH_2CH_2O)_2PCl}, \text{ and } \underset{(III)}{(ClCH_2CH_2O)_3P},$$

I and III are quite stable on storage; I is stable when heated to 190°–200°, but begins to decompose at higher temperatures; III is stable at temperatures below 140°–150°, but at about 140° it begins to isomerise at an appreciable rate, as will be discussed in detail below. Product II is in general unstable, gradually changing into a mixture of I and III:

$$2(ClCH_2CH_2O)_2PCl \rightarrow ClCH_2CH_2OPCl_2+(ClCH_2CH_2O)_3P.$$

This process is accelerated on heating, and the decomposition becomes more complicated.

Various mixed 2-chloroethyl derivatives of phosphorous acid have been prepared using the reactivity of the chlorine atoms attached to phosphorus in 2-chloroethyl phosphorodichloridite. One or both of these atoms were replaced by fluorine by the action of metal fluorides[40,44] by diethylamino- and anilino-groups by the action of the amines[40], and by the corresponding alkoxy-groups by the action of ethanol in the presence of pyridine[15] and of cyanomethyl alcohol[17].

Walsh found that trialkyl phosphites, including those containing 2-chloroalkyl groups, are able to react with phosphorous acid to form dialkyl phosphonates[23]

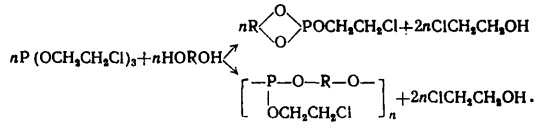
$$2P(OR)_3+H_3PO_3 \rightarrow 3HPO(OR)_2.$$

By this method Walsh obtained excellent yields of bis-2-chloroethyl, bis-2-chloropropyl, and bis-2-chloro-2-phenylethyl phosphonates. The hydrogen in these bis-2-chloroalkyl esters possesses the usual reactivity of compounds of this type. Aldehydes, for example, add to bis-2-chloroethyl phosphonate to form the corresponding bis-2-chloroethyl 1-hydroxyalkylphosphonates[45-47]. This offers great scope, little used as yet, for the synthesis of 2-halogenoalkyl esters of various phosphonic acids.

Tris-2-chloroethyl phosphite on moderate heating with alcohols and diols undergoes transesterification to other esters or polyesters of phosphorous acid[48,49] presumably according to such schemes as:

$$P(OCH_2CH_2Cl)_3+ROH \rightarrow ROP(OCH_2CH_2Cl)_2+ClCH_2CH_2OH,$$

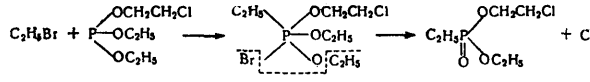
and



The Arbuzov rearrangement of tris-2-chloroethyl phosphite occurs under the influence of alkyl halides[21,25] acetyl chloride[21], halogenated ethers[25], and chlorine[50]. As anticipated, bis-2-chloroethyl esters of the corresponding phosphonic acids were obtained, while chlorine yielded bis-2-chloroethyl phosphorochloridate:

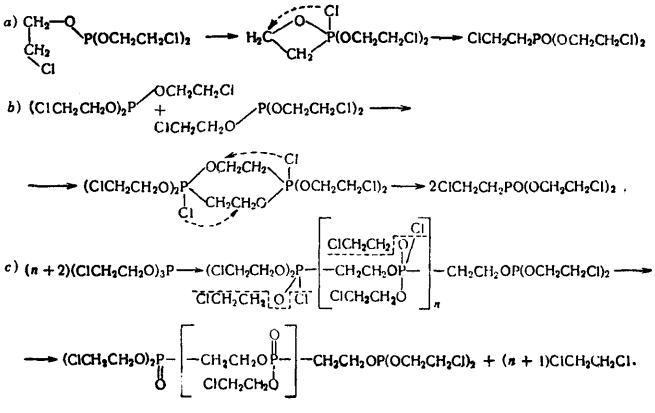
$$Cl_2+P(OCH_2CH_2Cl)_3 \rightarrow \begin{matrix}Cl\\Cl\end{matrix}\!\!>P(OCH_2CH_2Cl)_3 \rightarrow ClPO(OCH_2CH_2Cl)_2+ClCH_2CH_2Cl.$$

It is interesting that the Arbuzov rearrangement of 2-chloroethyl diethyl phosphite in the presence of ethyl bromide takes place in only one of the two theoretically possible ways, a mixed 2-chloroethyl ethyl ethylphosphonate being obtained[16]:



A remarkable property of 2-halogenoalkyl esters of tervalent phosphorus acids is their ability to undergo Arbuzov isomerisation merely on heating, without the addition of any halogen compounds or other agents[12,50]. In these cases the 2-halogenoethyl groups themselves act as the halogen-containing agents causing the rearrangement.

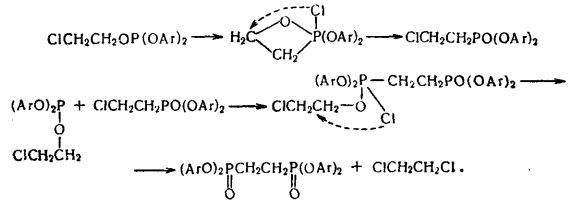
Kabachnik and Rossiiskaya investigated the course of the thermal isomerisation of tris-2-chloroethyl phosphite, and suggested that this isomerisation can take place both as an intramolecular[50] and as an intermolecular[50,51] process:



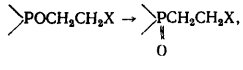
In the first two cases a single product, bis-2-chloroethyl 2-chloroethylphosphonate, is formed by the isomerisation; the third case results in non-volatile resinous products of polyester type, containing both C–O–P and C–P bonds. Such polyester resins may be formed to some extent also as a result of the thermal polycondensation of 2-chloroethyl esters of acids of phosphorus, which has been investigated by Korshak *et al.* (phosphonic esters)[52] and by Acker (a phosphorochloridic ester)[53].

Isomerisation of other 2-halogenoalkyl esters of tervalent phosphorus acids not containing Ar–O–P groups apparently occurs similarly[13,15,25,27-32,50].

Compounds containing such groups, *e.g.* mixed aryl 2-chloroethyl phosphites, however, isomerise according to a different mechanism, forming esters not of 2-chloroethylphosphonic but of ethylenediphosphonic acid[14] according to the following scheme:



Clearly, the former type of thermal isomerisation makes it easy to prepare organophosphorus compounds containing 2-halogenoethyl groups combined directly with the phosphorus. Thus 2-bromo- and 2-chloro-ethylphosphonic esters have been obtained from 2-halogenoethyl phosphites[13,15,50] ethyl-2-chloroethylphosphinic[27,28] and phenyl-2-chloroethylphosphinic esters from bis-2-chloroethyl ethyl- and phenyl-phosphonites[29-31] and 2-chloroethyldiethylphosphine oxide from 2-chloroethyl diethylphosphinite[32]. The common feature of all these reactions is

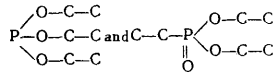


where X = Cl or Br.

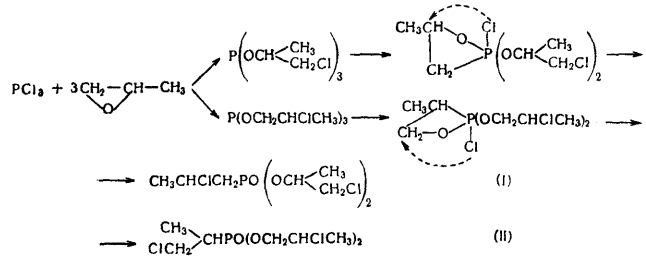
A peculiarity of the thermal isomerisation of 2-halogenoethyl esters of tervalent acids of phosphorus is that, up to a certain temperature (which is different in each case), the process is quite slow, but at some point, especially if local overheating is present, the reaction becomes comparatively rapid, sometimes with considerable heat evolution. This fact, first noted by Kabachnik and Rossiiskaya[50], presented serious danger even in work with small amounts of these substances, and of course hindered their extensive investigation.

A safe method for isomerising 2-chloroethyl esters of tervalent phosphorus was worked out by one of us[54-56] and independently by German chemists[57], who described the isomerisation of tris-2-chloroethyl phosphite in various solvents, which were boiling and well stirred. The agitation prevented local overheating, and the boiling of the solvent absorbed the heat of isomerisation evolved. Moreover, the presence of solvents diminished the probability of polycondensation, so that the yields of the isomeric product increased. For example, thermal isomerisation of tris-2-chloroethyl phosphite in the absence of solvent yielded 40% of the monomeric isomer, bis-2-chloroethyl 2-chloroethylphosphonate[50], whereas the yield increased to 65–70%[55] and sometimes even to 90%[57] when isomerisation was carried out in solvents. The solvents used should be inert towards the isomerising substances and should possess sufficiently high boiling points for isomerisation to take place at a satisfactory rate. In addition, the solvents must not form azeotropic mixtures with the products of isomerisation, nor must they have similar boiling points, so that they can be easily separated. Suitable solvents for the isomerisation of tris-2-chloroethyl phosphite are aromatic hydrocarbons[55,57], halogenated aromatic hydrocarbons[56,57], and some phosphoric esters[57]; ethylbenzene[27,28] can be used for bis-2-chloroethyl ethylphosphonite, decalin[30,31] for the corresponding phenylphosphonite, and toluene[32] for 2-chloroethyl diethylphosphinite.

The thermal isomerisation of the addition products of unsymmetrical α-oxides with phosphorus trihalides have been far less investigated than that of tris-2-halogenoethyl phosphites. A qualitative difference between these two processes involves the hydrocarbon skeletons, which are the same for the tris-2-halogenoethyl phosphites and their isomerisation products, consisting of three chains each of two carbon atoms



The isomerisation of any other tris-2-halogenoalkyl phosphite, however, shows a different pattern, for example



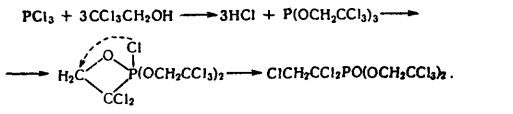
It can be seen from this scheme that during isomerisation the hydrocarbon skeleton of the acid part of the ester molecule changes its structure, while that of the ester part remains as before. This was shown by Efimova[25] for tri-(2-chloro-1-methylethyl) phosphite, and by Kuznetsov and Valetdinov[58] and Khairulin *et al.*[20] for tri-(2-chloro-1-chloromethylethyl) phosphite (this compound, obtained together with others by the action of PCl_3 on glycerol 1,3-dichloride, can be formed by the addition of epichlorohydrin to PCl_3 according to mechanism I).

The thermal isomerisation of 2-halogenoalkyl phosphites, like the usual Arbuzov rearrangement, depends on the readiness with which the components of alkyl halides add to the tervalent phosphorus atom in each individual compound. Steric factors and also the type of radical in the alkoxy-groups apparently play an important part.

Whereas tris-2-chloroethyl, tri-(2-chloropropyl), tri-(2-chloro-1-chloromethylethyl), and similar phosphites when heated isomerise quite readily into corresponding compounds of quinquevalent phosphorus, some mixed phosphorous esters containing cyanoalkoxy-groups do not isomerise and do not undergo radical redistribution[17].

The information on tris-2,2,2-trichloroethyl phosphite is contradictory: according to Gerrard *et al.*[59] this ester is incapable of thermal isomerisation, but according to Rydon

and Tonge[60] it is already converted into the normal isomerisation product, bis-2,2,2-trichloroethyl 1,1,2-trichloroethylphosphonate during preparation by the interaction of PCl_3 and trichloroethanol in the cold:



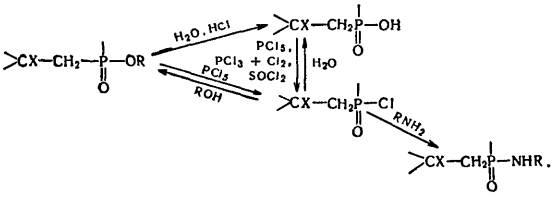
It is clear that thermal isomerisation of the addition products of α-oxides and phosphorus trihalides can be used to obtain more or less readily compounds containing one, two, or three phosphorus–carbon bonds (depending on the initial phosphorus compounds taken), where one of the radicals combined with phosphorus will necessarily be a 2-halogenoalkyl group. Compounds of this type form, in turn, starting materials for the preparation of halides of phosphinic acids and oxides of tertiary phosphines containing 2-halogenoalkyl and 1,2-unsaturated radicals.

3. 2-Halogenoalkylphosphonic Acids and Their Derivatives

Phosphorus–carbon, C–P, bonds are usually more stable, except in a very few cases, than bonds of the ester, C–O–P, type. It is not surprising, therefore, that treatment of 2-halogenoalkylphosphonic esters (among which bis-2-chloroethyl 2-chloroethylphosphonate has been studied the most thoroughly) with water, hydrochloric acid[50,51], hydrogen chloride[61,62], or phosphorus pentachloride[13,27-30,50,51,61,62] results in rupture of the C–O–P bonds, while the C–P bonds remain unchanged. In the first three cases 2-halogenoalkylphosphonic acids are obtained, and in the last case their chlorides. Phosphorus pentachloride splits off one ester group, especially a 2-chloroethyl group, very readily[27-30,50,51,62], while the second ester link reacts incompletely even on moderate heating. Preparation of the acid dichloride from bis-2-chloroethyl 2-chloroethylphosphonate therefore requires more severe conditions. For example, the ester has been heated with PCl_5 to 150°–160° under pressure[51]; PCl_5 has been added to the ester heated to the same temperature in the presence of some metal chlorides[61]; and the ester has first been converted into 2-chloroethylphosphonic acid with hydrogen chloride, and the acid subsequently treated with phosphorus pentachloride, a mixture of phosphorus trichloride and chlorine[61], or thionyl chloride[61].

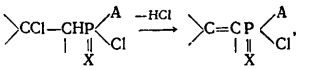
Chlorides of 2-halogenoalkylphosphonic acids, which contain reactive chlorine atoms in the molecule, more or less readily form the corresponding acids, esters, and amides on treatment with water[29,30,50,62,63], alcohols[27-30,62,63], or phenols[63,64], and amines[51,63] respectively.

These reactions of derivatives of 2-halogenoalkylphosphonic acids can be represented by the following scheme:



4. Compounds Containing αβ-Unsaturated Groups Attached to Phosphorus§

2-Halogenoalkyl radicals attached to phosphorus are quite inert towards acid reagents and towards heating for a short period up to about 300°. They are not stable at higher temperatures, especially in the presence of some metal salts, nor to the action of basic reagents. Kabachnik and Medved', Soborovskii and Zinov'ev, and subsequently others, have described the preparation of several chlorides of αβ-unsaturated phosphonic and phosphonothioic acids by dehydrochlorination¶ according to the following general scheme:

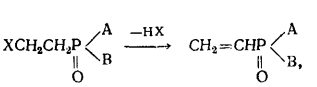


where X = O or S, and A = Cl, alkyl, or aryl.

Dehydrochlorination in the presence of barium salts or activated carbon at about 300°, for example, yielded chlorides of vinylphosphonic[66,67], propenylphosphonic[68], and ethylvinylphosphinic[27,28] acids, while dehydrochlorination with triethylamine has given the chlorides of vinylphosphonic[69], vinylphosphonothioic[70], and phenylvinylphosphinic[71] acids. Finally, the chloride of vinylphosphonic acid was synthesised in a different way, by treating esters of this acid with phosphorus pentachloride[72,73].

Hydrolysis of several chlorides of αβ-unsaturated phosphonic acids yielded the corresponding acids[67,71,74] and also the anhydride of vinylphosphonic acid[67].

Treatment of 2-halogenated alkylphosphonic esters or tertiary phosphine oxides with alcoholic alkalis[27-30,71,75,76], triethylamine[29,30,32,64,71,77-82], diethylamine in non-aqueous medium[83], or alkali-metal acetates[56,84], readily splits off hydrogen halide to form an αβ-unsaturated group attached to phosphorus, for example



where A and B are ester, alkyl, or aryl groups. In aqueous medium dialkylamines react differently with a 2-halogenoalkyl group attached to phosphorus, replacing halogen by dialkylamino groups: *i.e.* dialkylaminoethylphosphonic instead of unsaturated phosphonic esters are formed[76]:



If esters containing no 2-halogenoalkyl group in the alcoholic part of the molecule are subjected to dehydrohalogenation, all the above basic reagents act in the same way to give about the same yields of esters of αβ-unsaturated phosphonic acids. If, however, 2-chloroethyl groups are present in both acid and alcoholic parts of the ester molecule, as for example in bis-2-chloroethyl 2-chloroethylphosphonate, these basic reagents will have differing

§ The properties of such compounds and a series of methods for preparing them are given in a monograph written by one of us[65]. The present review includes a short account of methods for synthesising these compounds and material which has been published since the appearance of the monograph.

¶ The starting materials for the dehydrochlorination were obtained also by methods not discussed in the review.

effects. Alkali-metal acetates act selectively, reacting only with the 2-chloroethyl radical attached to phosphorus, practically without affecting the P–O–CH_2.CH_2Cl group. Alkalis, and to a lesser extent amines, react quite readily with both acid and alcoholic 2-chloroethyl groups, giving rise to side-reactions[56,84], which will be considered below. Here we note only that, by carrying out the reaction with triethylamine slowly, we can obtain satisfactory yields of 2-chloroethyl esters of vinylphosphonic[78] and arylvinylphosphinic[71] acids, whereas with alcoholic alkali only small yields of these substances can be isolated.

Esters and also amides of $\alpha\beta$-unsaturated phosphonic acids can be prepared in other ways, for example by treating chlorides of $\alpha\beta$-unsaturated phosphonic acids with alcohols[27,28,66,67], glycols[67], phenols[27,28,67], or amines[67].

Specific methods for the preparation of vinylphosphonic esters are the dehalogenation of 1,2-dihalogenoalkylphosphonic esters with zinc dust[79], and also (for divinyl vinylphosphonate) reaction of 2-chloroethylphosphonic dichloride with acetaldehyde and triethylamine[85,86].

$$ClCH_2CH_2POCl_2+2CH_3CHO+3N(C_2H_5)_3 \rightarrow CH_2=CHPO(OCH=CH_2)_2+3N(C_2H_5)_3\cdot HCl.$$

Among tertiary phosphine oxides containing $\alpha\beta$-unsaturated groups are diethylvinylphosphine, dipropylvinylphosphine, and ethylphenylvinylphosphine oxides, prepared by dehydrochlorination (by heat or with triethylamine) of the corresponding tertiary phosphine oxides containing 2-chloroethyl groups[32]. These and some other dialkylvinylphosphine oxides are synthesised by means of organomagnesium compounds[87].

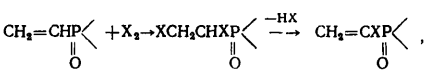
5. Properties of Compounds Containing $\alpha\beta$-Unsaturated Groups Attached to Phosphorus

These unsaturated organophosphorus compounds can add nucleophilic reagents at the double bond, take part in diene syntheses, in polymerisation and copolymerisation, and sometimes, depending on their structure, in polycondensation and polytransesterification reactions.

An account of these processes, studied mainly with vinylphosphonic esters, and of the properties of the products, has been given in the monograph[65] mentioned earlier, and we shall confine ourselves to a discussion of information not given there.

The addition of halogens at the double bond in derivatives of $\alpha\beta$-unsaturated phosphonic acids has been investigated. Kabachnik and Medved'[67,75] showed that bromine is readily added to diethyl vinylphosphonate to give the corresponding 1,2-dibromoethylphosphonate. This ester proved to be thermally quite unstable, and on heating (during vacuum distillation) it partially split off hydrogen bromide to form the bromovinylphosphonic ester. Similar behaviour was observed by Tsivunin and Kamai, who brominated and chlorinated ethylvinylphosphinyl chloride[28,88]. In both cases the halogens added smoothly at the double bond, but the stability of the products differed. The unstable bromination product split off hydrogen bromide during distillation, being converted into bromovinylethylphosphinic chloride. The chlorine addition product, on the other hand, was quite stable, and it could be dehydrochlorinated over a mixture of barium carbonate and activated carbon at 330°–350°.

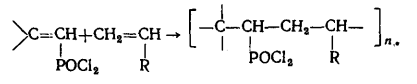
The position of the halogen remaining in the products of dehydrohalogenation has not yet been rigorously established, but all the investigators mentioned consider that it is located on the α carbon atom. Thus the above changes can be represented by the following scheme



where X = Cl or Br.

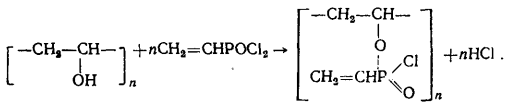
Addition of halogens to such a halogenovinyl group is very difficult[88]. The kinetics of the bromination of diethyl vinylphosphonate was investigated by Kabachnik and Balueva, who showed it to be a radical process[89].

Apart from halogenation it has been found, for example, that chlorides of $\alpha\beta$-unsaturated phosphonic acids can undergo polymerisation and copolymerisation[90-92] with formation of chlorides of polymeric phosphonic acids:



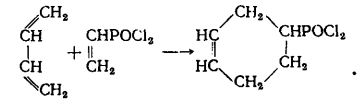
Such acid chlorides, of fairly high molecular weight, react readily with water, alcohols, silanols, and other hydroxy-compounds, the chlorine atoms being replaced by the corresponding groups[91,93]. It can be seen from the scheme above that as in polymers and copolymers of vinylphosphonic esters, the phosphorus atoms surround the main carbon chain and are directly linked to it in these compounds.

In the reaction of poly(vinyl alcohol) with the chloride of vinylphosphonic acid, however, the resulting carbon-chain polymers (of either linear or three-dimensional structure depending on the reaction conditions) contain the phosphorus linked to the carbon chains by bonds of ester type[94]:



The second chlorine atom can react with a hydroxyl group on the same or a different macrochain, leading in the latter case to cross-linking of the chains with formation of a three-dimensional macromolecule.

Chlorides of $\alpha\beta$-unsaturated phosphonic acids can take part in diene syntheses, forming chlorides of the corresponding cyclic $\gamma\delta$-unsaturated phosphonic acids[95], for example



Ester fluorides of alkoxyvinylphosphonic acids have been obtained by treating the acid dichlorides with alcohols and metal fluorides[96].

It has been found comparatively recently that derivatives of 2-chloroethyl- and especially vinyl-phosphonic acids can form the starting materials for the preparation of phosphorus-containing polyesters that may be toughened by heat treatment. The problem of producing such polyesters is of both

theoretical interest and practical importance. Until recently all known phosphorus-containing polyesters had linear structures[65], and there were no methods for preparing three-dimensional polyesters (apart from one not entirely clear patent specification[97]).

Most such linear polyesters possessed, together with their well-known useful properties (incombustibility, chemical stability, adhesion to many materials), not very high softening points, unless starting materials which were not readily available were used. This fact diminished the value of such polyesters. At present several methods are known for obtaining thermo-hardening phosphorus-containing polyesters based on derivatives of 2-chloroethyl- and vinyl-phosphonic acids.

The fundamental possibility of producing such polyesters was shown by Gefter and Rubtsova[98], who condensed 2-chloroethylphosphonic dichloride with aromatic diols. The resulting linear polyesters were subjected to heat treatment or the action of basic reagents, which caused dehydrochlorination of the 2-chloroethyl side-chains to vinyl groups. These latter groups polymerised, cross-linking the linear chains to form three-dimensional polyesters which were incombustible, infusible, and insoluble in organic solvents. This principle of two-stage preparation of hardenable polyesters (production of linear polyesters with unsaturated side-chains, and cross-linking of chains by means of the double bonds in the unsaturated groups) was later worked out in detail, especially its first stage.

Rubtsova *et al.* prepared the initial linear polyesters by reaction of the dihydroxy-compounds with the chloride of vinylphosphonic acid (polycondensation)[69,99] and also with the diphenyl ester of this acid (polytransesterification)[99,100]. They also refined the older method (see above)[98] of obtaining the initial linear polyesters (*via* the chloride of 2-chloroethylphosphonic acid[69,99]).

Kabachnik *et al.*[101] based their synthesis of linear polyesters containing vinyl groups in the side-chains on a different principle. They prepared a series of cyclic esters of vinylphosphonic acid (by the method described previously[67]) and polymerised them by ring-opening hydrolysis.

The linear polyesters obtained by any of the methods described form three-dimensional polymers by cross-linking of the unsaturated side-chains on heating with radical initiators. The hardened polyesters do not dissolve in organic solvents, do not burn in a naked flame, and do not melt, but merely soften somewhat on heating; above 250°–300°, however, they gradually char.

Among other new work must be mentioned that on the polymerisation and copolymerisation of dibutyl vinylphosphonate by the molecular beam method[102] and also a preliminary study of the polymerisation capacity of saturated and unsaturated (allyl) esters of ethylvinyl- and ethylchlorovinyl-phosphonic acids in the presence of radical initiators[27,28,88].

Alkyl ethylvinylphosphinates slowly polymerise into linear polymer gels of low molecular weight; the corresponding ethylhalogenovinylphosphinates show hardly any appreciable change in viscosity under similar conditions.

Allyl esters of ethylvinyl- and ethylchlorovinyl-phosphinic acids polymerise quite readily into tacky, rubber-like substances, which swell but do not dissolve in a number of organic solvents.

6. Addition of α-Oxides to Acid Halides of Quinquevalent Phosphorus

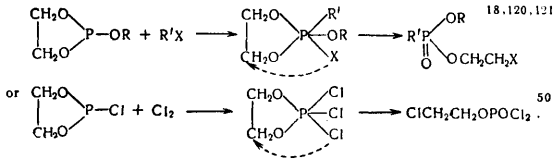
The reactions of α-oxides with acid halides of tervalent and quinquevalent phosphorus follow a fundamentally similar course, with opening of the oxide ring and formation of 2-halogenoalkyl derivatives of the phosphorus acid in both cases, the processes occurring in stages involving the addition of one, two, or three molecules of alkene oxide. However, the difference in valency of the phosphorus in the initial acid halides causes substantial differences in reactivity, and especially in the properties of the products. In contrast to the tervalent acid halides, the corresponding derivatives of quinquevalent phosphorus react less vigorously with α-oxides, and usually under the influence of catalysts — halides of metals or (less often) non-metals, organometallic compounds, metal alkoxides, tertiary amines, etc.

The addition has been described of ethylene oxide (more rarely of propylene oxide and epichlorohydrin) to phosphoryl chloride in the presence of small amounts of phosphorus trichloride[103]; the chlorides of aluminium[104,105], tin[104,105], antimony[104,105], nickel[104], cadmium[104], zinc[104], cobalt[104], lead[104], titanium[105–107], zirconium[106,107], and other metals; tetrabutyltin[105]; aluminium triethoxide[105]; titanium tetrabutoxide[105]; tertiary amines[108]; etc.

Among other acid halides which have been used are thiophosphoryl chloride[109]; the dichlorides of phenylphosphonic[105,110,111], substituted phosphoramidic[106,107], and other acids, and of aryl dihydrogen phosphates[106,107,111]; and monohalides of dimethylphosphinic[112] and other[111,113] acids and of diethyl[110] and dibutyl[106,107] hydrogen phosphates.

Among cyclic oxides which are rarely employed in the above reaction may be mentioned those of but-1-ene and but-2-ene[106], styrene[105], undecene[105], and stilbene[108], the glycidyl esters of unsaturated carboxylic acids[111], 1,3-diepoxybutane[105], and also hexitol mono- and di-anhydrides in which the free hydroxyl groups are protected[103].

Other methods also exist for obtaining 2-halogenoalkyl derivatives of the acids of quinquevalent phosphorus, such as, for example, reaction of alkene β-halogenohydrins with phosphorus pentahalides[22,58,114–119] (sometimes in the presence of organic bases) or the Arbuzov rearrangement of some cyclic derivatives of phosphoric acid according to the following general scheme:



The original method of preparing bis-2-chloroethyl phosphorochloridate from phosphorus trichloride, ethylene glycol, and chlorine[122] stands on its own:

$$2PCl_3+3HOCH_2CH_2OH \rightarrow 4HCl+ ClCH_2CH_2Cl+C_4H_{10}O_6P_2$$

(structure presumably $HOP(OCH_2CH_2O)_2POH$)

$$C_4H_{10}O_6P_2+2Cl_2 \rightarrow ClPO(OCH_2CH_2Cl)_2+HPO_3+HCl\,.$$

None of these methods is as suitable as the method which has been discussed.

The inadvisability of using alkene halogenohydrins instead of alkene oxides has been discussed above (see Section 1).

Arbuzov isomerisation of cyclic derivatives of phosphorous acid can be employed for the synthesis of a limited range of compounds, whereas the last method can be used for only one substance.

The addition of oxygen or sulphur to 2-halogenoalkyl derivatives of acids of tervalent phosphorus discussed above (see Section 2) is not, of course, a distinct method for synthesising 2-halogenoalkyl derivatives of acids of quinquevalent phosphorus.

7. Properties of 2-Halogenoalkyl Esters and Ester Halides of Acids of Quinquevalent Phosphorus

The presence of the phosphorus atom in its higher valency state makes these compounds relatively stable chemically and deprives them of many of the synthetic possibilities existing with 2-halogenoalkyl derivatives of acids of tervalent phosphorus, notably the ability to undergo addition reactions, Arbuzov rearrangement, thermal isomerisation, etc.

The characteristic $>CX-\underset{|}{CH}-O-P=O$ groups in these components behave peculiarly towards chemical reagents.

Upson found that treatment of 2-chloroethyl phenylphosphonates and 2-chloroethyl diethyl phosphate with alcoholic alkali, sodium carbonate, or triethylamine yields the corresponding vinyl esters or (depending on the conditions of dehydrochlorination) polymers of them[110].

Allen and his collaborators[123], however, were unable to repeat this, in spite of the simplicity of the experiments. A detailed account of Allen's results and arguments is beyond the scope of this review, and we will merely point out that he was able to prepare only small amounts of unsaturated compounds of somewhat indeterminate composition. Nevertheless, these workers accomplished the dehydrobromination of 2-bromoethyl diethyl phosphate to diethyl vinyl phosphate by means of such a specific reagent as sodium hydride.

Kabachnik showed that alcoholic alkali exerts its dehydrochlorinating action mainly on the acid portion of the bis-2-chloroethyl 2-chloroethylphosphonate molecule, forming bis-2-chloroethyl vinylphosphonate[75]. Alkali-metal salts of organic acids are even more effective[56,84]. Ward considers that the alcoholic alkali replaces chlorine by hydroxyl in the $ClCH_2CF_2O\underset{\|}{P}<$ group to form a 2-hydroxyethyl group[124]:

$$NH_2PO(OCH_2CH_2Cl)_2+2NaOH \rightarrow NH_2PO(OCH_2CH_2OH)_2+2NaCl.$$

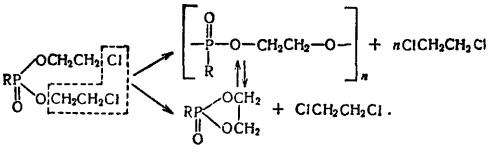
Tertiary amines react quite readily with 2-halogenoalkoxy groups attached to phosphorus[78,114] forming comparatively stable crystalline addition products of the same type as quaternary ammonium salts. Primary amines, however, react by replacing the halogen with an alkylamino group.

A reaction of such a type, that of bis-2-chloroethyl vinylphosphonate with ethanolamine and aminoheptanoic acid, yielded interesting compounds — a glycol and a dicarboxylic acid — containing phosphorus, nitrogen, and a double bond in the molecule[125], for example:

$$CH_2=CHPO(OCH_2CH_2Cl)_2+2NH_2CH_2CH_2OH \rightarrow$$
$$\rightarrow CH_2=CHPO(OCH_2CH_2\underset{HCl}{NHCH_2CH_2OH})_2 \xrightarrow{2C_6H_5ONa}$$
$$\rightarrow CH_2=CHPO(OCH_2CH_2NHCH_2CH_2OH)_2+2NaCl+2C_6H_5OH.$$

Acid reagents — hydrochloric acid, hydrogen chloride, phosphorus pentachloride — rupture the C–O–P bonds more or less easily, replacing the 2-halogenoalkoxy groups by hydroxyl[50,61,62] and chlorine[12,13,27-30,50,51,61,62] respectively. Substances containing 2-halogenoalkoxy groups attached to phosphorus undergo various (intramolecular or intermolecular) condensation reactions on heating.

Korshak and his coworkers showed that, when bis-2-chloroethyl alkyl- and aryl-phosphonates as well as tris-2-chloroethyl phosphate are heated above 200°, dichloroethane is evolved with the formation of a mixture of cyclic and linear products, between which an equilibrium probably exists[52]:



It cannot yet be stated definitely whether the primary process is intermolecular elimination of dichloroethane (formation of a linear polyester of low molecular weight) or the intramolecular reaction (formation of a cyclic ester), or whether they occur simultaneously. It may be noted that conversion of purified cyclic esters of phosphorus acids into linear polyesters occurs quite readily (for example with various catalysts, moderate heating, and sometimes simply on standing[65]), whereas the reverse process is possible only in the case of thermal degradation of the polyesters, *i.e.* under more severe conditions[52,126].

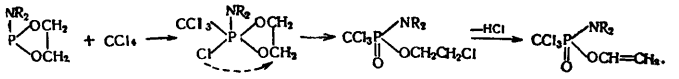
Acker[53] has described the liberation of dichloroethane and the formation of polyester chains in the thermal homopolycondensation of 2-chloroethyl phenyl phosphorochloridate.

A reaction of a different type was investigated by Lecoq, who showed that hydrogen chloride is evolved and cyclic ethylene hydrogen phosphate is formed when an aqueous solution of 2-chloroethyl dihydrogen phosphate is boiled[127]:

$$ClCH_2CH_2OPO(OH)_2 \xrightarrow{-HCl} CH_2O\diagdown\!\!\diagup P(O)OH.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2O\diagup\!\!\diagdown$$

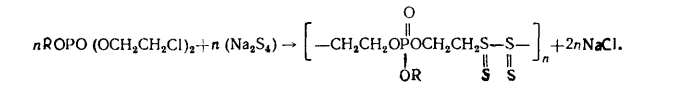
These reactions (or one of them) are the cause of the decomposition of various 2-halogenoalkyl esters of phosphorus acids when distilled at high temperatures (at atmospheric pressure or under a poor vacuum). There is, it is true, the patent of Winkle *et al.*[128], which is inconsistent with these results. According to this patent, interaction of some cyclic esters of substituted phosphoramidous acids with carbon tetrachloride at 200° leads to the formation of vinyl esters of trichloromethylphosphonamidic acids. The formation of such substances can apparently be represented

as a result of consecutive reactions — (1) Arbuzov rearrangement with opening of the ring and formation of 2-chloroalkoxy-groups attached to phosphorus, and (2) thermal dehydrochlorination of these groups:

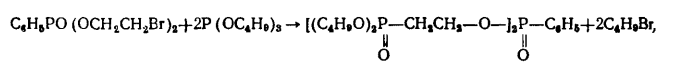


The hydrolysis of 2-halogenoalkyl phosphates has been investigated by German and French scientists. Dilute alkalis and acids in aqueous-alcoholic media have been found to split off 2-halogenoalkoxy-groups with comparative difficulty[38], and the halogens in these groups more easily[38], whereas the phenoxy-groups in 2-halogenoethyl diphenyl phosphates and bis-2-halogenoethyl phenyl phosphates are split off quite easily under these conditions[118,119]. Therefore 2-halogenoethyl diphenyl phosphates can be used to introduce $(OH)_2PO(OCH_2CH_2)$ groups into various organic compounds.

It has been found comparatively recently that the halogen atoms in 2-halogenoalkoxy-groups linked to phosphorus react quite readily with sodium and calcium polysulphides forming special "Thiokols"† containing phosphorus[2,20,129]



Bis-2-halogenoalkyl alkyl- and aryl-phosphonates have been used as special dihalogenoalkanes in the Arbuzov rearrangement of phosphorous or phosphonous esters, for example:



and for the Michaelis-Becker reaction[130].

2-Halogenoalkyl phosphorochloridates possess the normal reactivity characteristic of acid halides of phosphorus. They react with alcohols and amines to form alkyl 2-halogenoalkyl phosphates[114] and 2-halogenoalkyl *N*-mono- or *NN*-di-alkylphosphoramidates[131] respectively. Tertiary amines add readily to such ester chlorides (obviously at the P-Cl bond), forming hygroscopic crystalline products which are insoluble in inert solvents (ether, benzene, etc.) and which decompose on contact with water or alcohols[132].

Substantial differences in chemical behaviour are thus observed between 2-halogenoalkyl groups combined with quinquevalent phosphorus directly or through oxygen.

These differences are briefly as follows. (1) Basic reagents in non-aqueous media dehydrochlorinate 2-halogenoalkyl groups attached to phosphorus comparatively readily, converting them into $\alpha\beta$-unsaturated groups[27-30,56,64,69-72,75,84]. 2-Halogenoalkyl groups linked to phosphorus *via* oxygen under similar conditions have their halogens replaced by other groups[124,125], add on tertiary amines[78,114], or else do not react at all[56,84]. More severe action of certain basic reagents produces changes which have not yet been elucidated, resulting in polymeric or resinous substances[123]. (2) Acidic reagents — hydrochloric acid, hydrogen chloride, PCl_5 — rupture the C-O-P ester bonds more or less readily, replacing the 2-halogenoalkoxy-groups by hydroxyl or chlorine, but (up to certain temperatures) do not affect 2-halogenoalkyl groups attached to phosphorus[13,27-30,50,51,61,62,72,73]. (3) The action of high temperatures on 2-halogenoethyl groups attached to phosphorus results, especially in the presence of certain salts or of activated carbon, in their dehydrohalogenation with the formation of vinyl groups attached to the phosphorus[27,28,66-68]. 2-Halogenoalkoxy-groups, however, split off dichloroethane and hydrogen chloride and undergo other changes, but, except in one case[128], it has not been possible to isolate vinyl esters of phosphorus acids[52,53,127].

† Trade mark of Thiokol Chemical Corp. for various products; here denotes polysulphide synthetic rubbers (Ed. of Translation).

8. Reactions of α-Oxides with Phosphorus Halides Not Involving Formation of C-O-P Bonds

It was shown above that α-oxides and sulphides readily add to halides of tervalent and quinquevalent phosphorus (except PCl_5 and PBr_5) at the P-X bonds, forming 2-halogenoalkyl derivatives of the corresponding acids of phosphorus.

Similar reactions of β-oxides have not been described, while reaction of γ- and δ-oxides with such phosphorus halides is more difficult than, and of a different type from, that of α-oxides. Such reactions, studied mainly in the case of $POCl_3$, occur only in the presence of catalysts — zinc chloride, sulphuric acid, aluminium chloride, etc. The oxide ring is broken, but formation of a P-O-C bond is not observed. Under mild conditions a halogen-carbon bond is formed, the ring oxygen atom being preserved in the product molecule. Under more severe conditions two halogen-carbon bonds are produced with simultaneous elimination of the ring oxygen. The final products of these processes are thus halogenated ethers and dihalogenoalkanes. The latter are obtained also by the reaction of any cyclic oxides or their homologues with phosphorus pentachloride and pentabromide. We may note that PBr_3, PCl_5, and PBr_5 (in contrast to the less vigorous reagents, PCl_3 and $POCl_3$) undergo such reactions in the absence of any catalyst. Thus ethylene and trimethylene oxides react with phosphorus pentachloride to form 1,2-dichloroethane[133] and 1,3-dichloropropane[133a] respectively.

Treatment of tetrahydrofuran with phosphoryl chloride under mild conditions, with small additions of sulphuric acid or zinc chloride, yields mainly bis-4-chlorobutyl ether $Cl.[CH_2]_4.O.[CH_2]_4.Cl$ [134,135] (with phosphorus trichloride the yields are poor[134]) and to a less extent 1,4-bis-4'-chlorobutoxybutane $Cl.[CH_2]_4.O.[CH_2]_4.O.[CH_2]_4.Cl$.[134] If large quantities of zinc chloride are used in this reaction, 1,4-dichlorobutane is obtained[135], while the action on tetrahydrofuran of phosphorus tribromide[136] and of phosphorus and iodine[137] or phosphoric acid and potassium iodide[138] leads to the formation of 1,4-dibromo-[136] and 1,4-diiodo-butanes[137,138] respectively.

2-Methyltetrahydrofuran on treatment with phosphorus tribromide forms 1,4-dibromopentane[138a].

In no case was the formation of 3-halogenoalkyl esters of the phosphorus acids observed during these reactions, as suggested in Bretschneider's patent[108], and his statement that a γ-oxide (tetrahydrofuran) can react with phosphorus halides in the same way as α-oxides must be regarded as incorrect.

δ-Oxides react with phosphorus halides with still greater difficulty than do γ-oxides. Tetrahydropyran on treatment with phosphoryl chloride in the presence of sulphuric acid forms a mixture of comparatively small quantities of bis--5-chloropentyl ether and 1,5-dichloropentane[134]. Nevertheless, in the well-know Braun reaction this same δ-oxide and a substituted nitrogen analogue (*N*-benzoylpiperidine) react with phosphorus pentachloride and pentabromide under severe conditions to give respectively 1,5-dichloropentane[139,140] and 1,5-dibromopentane[140].

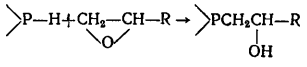
A few cases of reaction of phosphorus halides with furan, thiophen, and pyridine, which have aromatic properties, have been described[141,142] but do not come within the scope of the present review.

III. INTERACTION OF PHOSPHORUS COMPOUNDS CONTAINING A REACTIVE HYDROGEN ATOM WITH α-OXIDES. PROPERTIES OF THE PRODUCTS

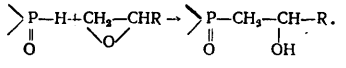
1. Addition of α-Oxides to Phosphorus Compounds (at a Phosphorus–Hydrogen Bond)

Comparatively little research has been done on reactions of this type.

During the addition of α-alkene oxides at a phosphorus–hydrogen bond the oxide ring is opened with formation of a phosphorus–carbon bond, and at the β-carbon atom a hydroxyl group is produced from the oxygen of the oxide and the hydrogen of the phosphorus compound, the valency of the phosphorus remaining unchanged:

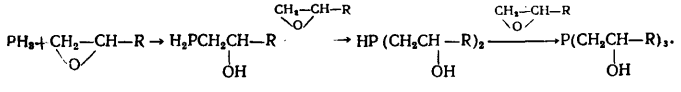


or

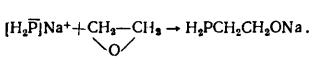


Two types of reactions of this nature have been described involving the addition of α-oxides to phosphine and to dialkyl hydrogen phosphites.

Knunyants and Sterlin[143] showed that the difficulty in reaction between phosphine and ethylene and propylene oxides lay in the very feeble dissociation of PH_3 under normal conditions. They were able to make these components combine with one another only under pressure and on heating, but even then the yields of the reaction products were not very high. The reaction obviously took place in stages:

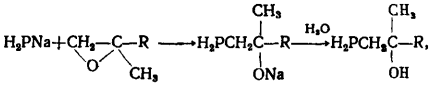


Products formed by addition of one and three (but not two) oxide molecules to the PH_3 were mainly obtained. When sodium dihydrogen phosphide in liquid ammonia was used instead of phosphine, reaction took place very readily and with good yields:



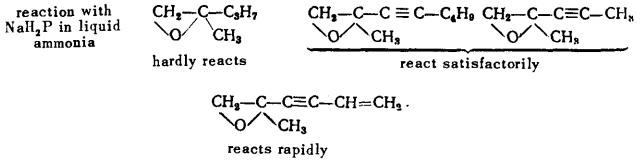
Decomposition of the resulting alkoxide with water gave free 2-hydroxyethylphosphine.

Sodium dihydrogen phosphide in liquid ammonia was used also by Perveev and Rikhter[144], who effected the addition of several acetylenic α-oxides to it



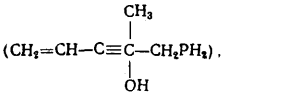
where R contains a triple bond.

If R were a saturated radical (propyl), such a reaction would be extraordinarily difficult[144]. The ability of substituted α-oxides to react with sodium dihydrogen phosphide is apparently governed primarily by the electronic state of the molecule of the particular oxide and only secondarily by steric factors. In fact the reactivity of the following four α-oxides increases with the occurrence and strengthening of conjugation between the multiple bonds in the substituent group and the oxide ring



The 2-hydroxyalkylphosphines known at the present time are colourless mobile liquids with the disagreeable odour characteristic of phosphines. Simple representatives of this group are readily soluble in water and pyridine, but less soluble in ether and benzene[143]. More complex members of this class dissolve well in several organic solvents, but do not dissolve in water[144].

Hydroxyalkylphosphines, and especially *O*-acyl derivatives of the lower members, oxidise easily[143]. When an attempt was made to replace hydroxyl by halogen in several 2-hydroxyalkylphosphines, the phosphorus–carbon bond was ruptured with the formation of phosphine itself and halogenated unsaturated hydrocarbons[143]. A 2-hydroxyalkylphosphine containing a conjugated double and triple bond



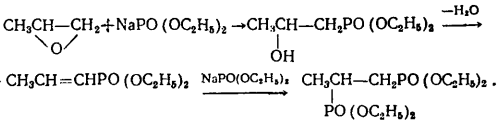
polymerised so rapidly that it could not be isolated, although it was very readily formed[144].

No other methods exist as yet for the synthesis of 2-hydroxyalkylphosphines. Compounds containing the reactive hydrogen attached to quinquevalent phosphorus react with α-oxides with still greater difficulty.

In the absence of catalysts, dialkyl hydrogen phosphites do not react at all with α-oxides. A qualitative experiment on the addition of ethylene oxide to sodium diethyl phosphite was carried out by Chelintsev and Kuskov[145].

Pudovik and Ivanov[16], Preis *et al.*[146], and Kreutzkampf[147] have shown that addition of α-oxides to sodium dialkyl phosphites does take place, but the yields are not very high. The addition of propylene oxide to sodium diethyl phosphite[146] is noteworthy, for tetraethyl propylene-1,2-diphosphonate was unexpectedly isolated. According to Preis *et al.*, the reaction proceeds normally at first, *i.e.* with the

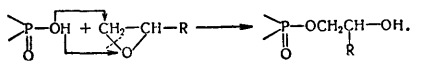
formation of diethyl 2-hydroxypropylphosphonate, which is then dehydrated, and a second molecule of the phosphite adds on to the double bond thus formed:



Sulphuric acid proved to be a feeble catalyst for the addition of α-oxides to dialkyl hydrogen phosphites[16]. Rather better yields were obtained for the addition of ethylene oxide, cyclohexene oxide, and 1-ethoxypropane-2,3-diol to several dialkyl hydrogen phosphites by heating a mixture of the components in the presence of boron trifluoride–diethyl ether under pressure[16].

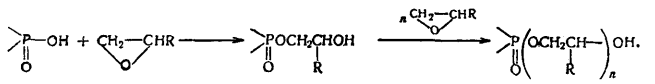
2. Addition of α-Oxides and Their Analogues to Hydroxyl Groups Attached to Phosphorus (at an Oxygen–Hydrogen Bond)

Compounds containing one or more hydroxyl groups combined with phosphorus are more or less strong acids. They usually react readily with α-oxides in the absence of any catalyst. If one molecule of alkene oxide adds on at an O–H bond, 2-hydroxyalkyl esters of the corresponding acids of phosphorus are formed. The oxide ring opens, the P–O–H bond is converted into a P–O–C bond, and a hydroxyl group is formed at the β carbon atom:



This main reaction is accompanied by some side-reaction, polymerisation of α-oxides under the influence of the acids of phosphorus. The addition has been reported of various α-oxides (principally those of ethylene and propylene) to phosphorous acid and its salt[148,149], phosphoric acid[148], its salts[148,150], and acid esters[151–153], including polymeric forms[154], and also to alkylphosphonic acids[155,156].

Since the substances obtained in this way always contain hydroxyl groups in the β position, this reaction can proceed stepwise by ring-opening and addition of the next oxide molecule, and so on



Such secondary processes takes place less readily in the presence of excess of the corresponding α-oxide[148,153,155,156], on heating[153,155,156], sometimes under pressure, in the presence of catalysts, for example aluminium hydrosilicate[155,156].

Dickey and McNally oxidised unsaturated ketones, acids, ethers, and esters, and treated the products (obviously containing α-oxide groups) with various phosphorus acids or their salts. The reactions went normally, *i.e.* with opening of the oxide ring and addition of the components to one another[157–159].

2-Hydroxyalkyl esters of phosphorus acids are more or less viscous oily liquids, soluble in water and the lower alcohols. The hydroxyl groups in these compounds can be replaced by chlorine by the action of phosphorus trichloride[148].

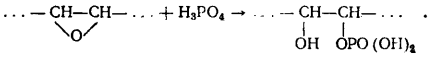
Sulphur and nitrogen analogues of α-oxides — ethylene sulphide[148], aziridine (ethyleneimine)[160], and the 2-methyl[148] and 2-ethyl[148] derivatives of the latter — have been added to phosphoric acid. The course of the reactions is similar, with mercapto- and amino-groups respectively replacing the hydroxyl groups in the final products. The properties of such compounds have hardly been investigated. It is known only that some 2-aminoalkyl esters are hard crystalline substances[160].

3. Addition of Polyepoxides to Hydroxyl Groups Attached to Phosphorus

Interesting and promising work has been carried out on the interaction of polyepoxides with phosphoric acid and its acid esters.

Polyepoxides are copolymers of unsaturated compounds containing one double bond with various proportions of epoxy compounds also containing one double bond in the molecule.

On moderate heating of a polyepoxide with phosphorus acids, the α-oxide ring of the polyepoxide is opened, and a macromolecular acid of phosphorus is formed according to the following general scheme:



Patents cover the reaction of phosphoric acid with dioxan solutions of the copolymers 1-allyloxypropane-2,3-diol/styrene[161,162], 1-allyl glycidyl ether/butyl methacrylate[163], glycidyl methacrylate/butyl methacrylate[163], etc.[161–164]

The interaction has also been described of alkyl- and aryl-phosphonic acids with glycidyl polyethers of dihydric and polyhydric phenols, polymers of allyl glycidyl ether, and other compounds of high molecular weight containing epoxy-groups[164]. These reactions are usually carried out in solution with the aim of minimising premature formation of three-dimensional polymers. Dioxan is the most suitable solvent, since it is miscible with water, and enables aqueous solutions of phosphoric acid to be used.

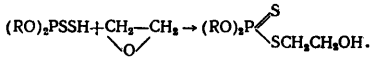
The polymeric acids of phosphorus thus obtained are soluble in dioxan, acetone, benzene, several other organic solvents, and sometimes, depending on the structure of the original polyepoxides, in water and aqueous alkalis. Polymeric phosphoric acids based on copolymers of allyl glycidyl ether and vinyl acetate, for example, are soluble in aqueous solutions of alkalis, while those based on copolymers of glycidyl methacrylate with other methacrylates are insoluble.

Depending on the extent of copolymerisation of the original monomers, the molecular weights of the polymeric phosphoric acids vary between 1500 and 50000 (mainly 2000–10000)[164], their consistency varying from semi-liquid to solid[164].

On being heated, or treated with diisocyanates, they are converted into three-dimensional polymers possessing hardness, strength [or stability (Ed. of Translation)], and good adhesion to many materials [161-165].

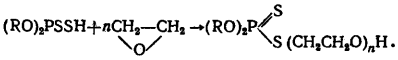
4. Addition of α-Oxides and Sulphides to Mercapto-Groups Attached to Phosphorus

α-Oxides add readily to *OO*-dialkyl hydrogen phosphorothiolothionates [166] and also to *OO*-alkaryl and *OO*-diaryl hydrogen phosphorothiolothionates [167]. The reactions are accompanied by the evolution of heat, but if the process is carried out slowly and at moderate temperatures the addition takes place practically quantitatively:



The resulting 2-hydroxyalkyl esters of substituted phosphoro- and phosphono-dithioic acids are viscous liquids which can be distilled in a vacuum (sometimes with slight decomposition). They are quite readily oxidised by nitric acid, and decomposed by alkalis. The 2-hydroxy-groups in them are acetylated by acetic anhydride and replaced by chlorine on careful treatment with phosphorus pentachloride.

If the alkene oxide is added rapidly, and the temperature is not controlled, the reaction mixture becomes very hot, and syrupy substances are formed which cannot be distilled in a vacuum. Kabachnik and his coworkers claim that stepwise addition of many oxide molecules then occurs [166]:

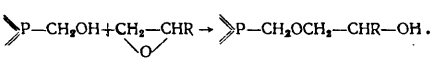


Cyclic 1,2-sulphides react similarly to, but less vigorously than the oxides [167,168]. The dialkyl *S*-2-mercaptoethyl phosphorothiolothionates $(RO)_2P(S)SCH_2CH_2SH$ formed in this reaction have in general similar properties to their hydroxy-analogues, but differ from the latter in their insolubility in water, lower thermal stability, and the ease with which the mercapto-group is methylated by diazomethane.

5. Addition of α-Oxides and Aziridine to Hydroxymethyl and *p*-Hydroxybenzyl Groups in Phosphorus Compounds

Tetrakishydroxymethylphosphonium chloride and trishydroxymethylphosphine oxide are quite widely known as flameproofing agents for various synthetic and natural materials [65]. It has recently become known that monomers for epoxide resins containing phosphorus have been produced on the basis of these interesting substances.

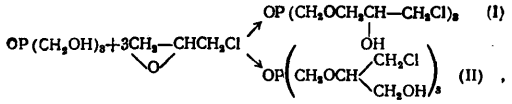
The hydroxymethyl groups in these compounds, the hydrogen in which is quite reactive, can add at the O–H bond to α-oxide compounds of normal type comparatively readily, ether links being formed in the phosphorus compound and hydroxyl groups in the β position relative to them



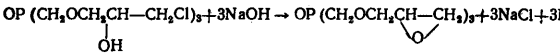
The reaction is carried out simply by boiling a mixture of the components, sometimes in the presence of acid catalysts.

Descriptions have appeared of the addition to tetrakishydroxymethylphosphonium chloride, to trishydroxymethylphosphine oxide, and to substances containing the group $\gg P-CH_2OH$, of ethylene oxide [169], epichlorohydrin [169-171], epibromohydrin [171], poly(glycidyl ether) ("Epon 562"‡) [171,172] poly(glycidyl dihydrophenol ether) ("Epon 1007"‡) [171], ethyleneimine [173-175], etc.

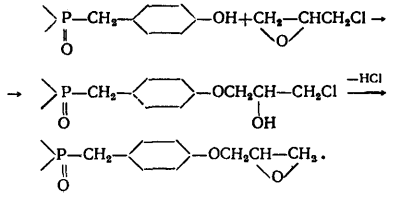
Monomers for phosphorus-containing epoxide resins (mentioned above) were prepared by adding epichlorohydrin to trishydroxymethylphosphine oxide in the presence of acid catalysts. Of the two possible compounds



only the first is formed. Dehydrochlorination and closure of the α-oxide ring occur readily on treatment with alkalis



As the accompanying equations show, this method enables us to obtain organophosphorus compounds containing epoxy-groups. Apart from the above phosphorus compounds, tertiary phosphine oxides containing one, two, or three *p*-hydroxybenzyl groups [176,177] were also subjected to this reaction. Their reactions with epichlorohydrin go as follows:



IV. INTERACTION OF PHOSPHORUS COMPOUNDS WITH α-OXIDES AND SULPHIDES INVOLVING THE LONE ELECTRON PAIR OF THE PHOSPHORUS ATOM

1. Addition of Components to One Another

Reactions of this type are almost uninvestigated. Scott patented a process for preparing dialkyl alkoxyalkylphosphonates by heating certain alkene oxides with trialkyl phosphites under pressure [178]

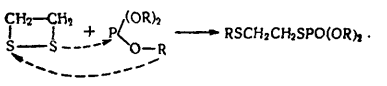


However, numerous investigations have shown that the α-oxides react with trialkyl phosphites in a different way (see Section 2). Scott's actual patent [178] (so far the only communication of this kind) did not give the yields of the

‡ Epon resins are condensation products of epichlorohydrin and bisphenol-A [2,2-bis-(4-hydroxyphenyl)propane], made by Shell Chemical Co. (Ed. of Translation).

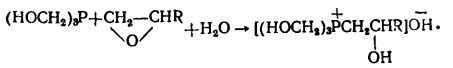
products obtained, and it therefore seems to us that addition of α-oxides to trialkyl phosphites (which is quite possible theoretically) occurs as a side-reaction and is not the main reaction.

Trialkyl phosphites react with cyclic disulphides with the formation of *OO*-dialkyl *S*-alkylthioalkyl phosphorothiolates[179]. This interesting reaction can be represented (in the simplest case) as follows:



The addition of α-oxides to trishydroxymethylphosphine has been described by Reuter *et al.*[180]. These reactions occur at 50°–100° in water, the lower alcohols, acetonitrile, dimethylformamide, etc. Two competing reactions are possible in a given case — addition of the alkene oxides to the hydroxymethyl groups at the O–H bonds (which was considered in Section 5 (Part III) or to the tervalent phosphorus — but it was found that the latter reaction takes place far more readily and practically completely.

Reuter and his coworkers patented the addition to trishydroxymethylphosphine of ethylene and propylene oxides, epichlorohydrin, glycidol, bivinyl dioxide, triglycidyl cyanurate, and polyepoxides. The process apparently corresponds to the following scheme:



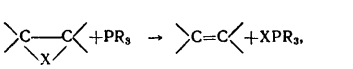
Quaternary phosphonium compounds can be obtained in this way.

2. Formation of Unsaturated Substances Together with Quinquevalent Organophosphorus Compounds

The possibility of synthesising these compounds results from the strong affinity of tervalent phosphorus for oxygen and sulphur. It was found that certain structures (α-oxides and sulphides) containing these latter elements readily give them up on reacting with certain compounds of tervalent phosphorus.

Culvenor and his coworkers, investigating the reaction of ethylene and propylene sulphides and of several other alkene sulphides with triethyl phosphite and tertiary phosphines, were the first to note that these organophosphorus compounds readily add sulphur to form triethyl phosphorothioate and tertiary phosphine sulphides respectively[181]. They did not study the transformations of the alkene sulphides.

Other investigators have found that, in these and similar reactions (with α-oxides), the cyclic components lose oxygen or sulphur and are converted into unsaturated compounds. Thus the general scheme of this reaction can be represented as



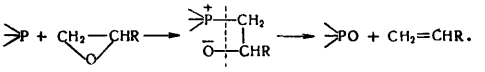
where X = O or S; and R = alkyl, aryl, or alkoxy.

Accounts have been published of the reaction of ethylene oxide with triethyl phosphite[182,183] and triallyl phosphite[183], propylene oxide with triethyl phosphite[182,183], 2,3-epoxybutane with tributylphosphine[184], styrene oxide with triethyl phosphite[183] and triphenylphosphine[185], and finally of the oxide of ethyl cinnamate with triphenylphosphine[185].

The analogous reactions of cyclic α-sulphides have been investigated no less thoroughly.

The interaction has been studied of ethylene sulphide and 2-methylpropylene sulphides with triethylphosphine[181]; of propylene sulphide with triethylphosphine[181], triphenylphosphine[186], and triethyl phosphite[187]; of 3-chloropropylene sulphide with triethylphosphine[181] and triethyl phosphite[187], and of but-2-ene sulphide with triphenylphosphine[184,188], tributylphosphine[188], and triethyl phosphite[188]. The reactions have also been studied of 3-methoxypropylene sulphide with triethyl phosphite[187] and of cyclohexene sulphide with triethylphosphine[181], triphenylphosphine[181,186], and triethyl phosphite[181,186].

Apparently the components first add to one another, with rupture of a C–O (C–S) bond and production of a C–P bond. This is followed by formation of a stable P=O (P=S) bond and rupture of the less stable second C–O (C–S) bond[185].



This reaction usually takes place very smoothly, the sulphides reacting more readily than the cyclic oxides with tervalent phosphorus compounds, sometimes simply when a mixture of the components is allowed to stand in the cold[181]. It goes practically to completion, and the yields are good in all cases.

It is interesting that interaction of triallyl phosphite with ethylene oxide yields only triallyl phosphate practically no epoxidation of the double bond being observed[183].

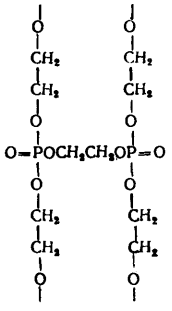
The formation of olefines in this reaction is accompanied by an interesting stereochemical phenomenon: whereas the *cis*-and *trans*-isomers of but-2-ene sulphide are practically entirely converted into *cis*- and *trans*-but-2-enes respectively[187,189], the oxygen analogues of this sulphide (namely *cis*- and *trans*-2,3-epoxybutane) give mixtures of isomers in which the stereoisomer of opposite structure to that of the original oxide predominates[184].

V. OTHER REACTIONS OF PHOSPHORUS COMPOUNDS WITH α-OXIDES

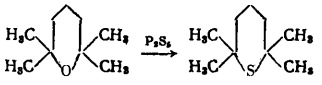
Ethylene oxide, propylene oxide, and epichlorohydrin add to phosphorus pentoxide[190], phosphorus pentasulphide[190], and also to the product formed by reaction of P_2S_5 with certain petroleum products[191]. Liquids or solids are formed depending on the reaction conditions.

The reactions of α-oxides with P_2O_5 and P_2S_5 occur quite readily on moderate heating of mixtures of the components, 3–7 moles of the alkene oxide being taken per mole of the phosphorus compound.

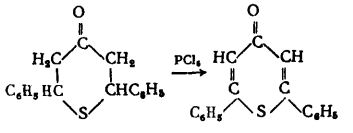
According to the patent literature[190] units of the following type are present in the substances (whose structure has not been completely elucidated):



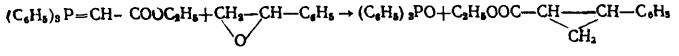
The action of phosphorus pentasulphide on 2,2,6,6-tetramethyltetrahydropyran does not involve addition, as in the case of α-oxides, but the replacement of oxygen by sulphur[142]



Substituted tetrahydrothiapyrones are dehydrogenated into thiapyrones by the action of PCl_5,[142]



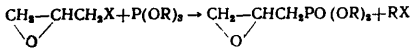
An interesting reaction has been described by Denney and Boskin: when cyclic oxides react with certain organophosphorus compounds of methylenephosphine type R.CH=P$\lessdot$, the CHR group is replaced by oxygen, and a cyclopropane ring is formed[192]:



VI. INTERACTION OF PHOSPHORUS COMPOUNDS WITH α-OXIDES AND THEIR ANALOGUES NOT INVOLVING THE OXIDE FUNCTION

1. Arbuzov Rearrangement and Michaelis-Becker Reaction of Phosphorous Esters with Halogenated α-Oxides and Their Analogues

The Arbuzov rearrangement of trialkyl phosphites under the influence of epihalogenohydrins has been studied[146,177,193-195]:



(X is halogen).

This reaction is carried out in a similar manner to an ordinary Arbuzov rearrangement, *i.e.* the trialkyl phosphite and the epihalogenohydrin are mixed, and the mixture is heated until the alkyl halide ceases to separate; the reaction product is isolated by vacuum distillation. Various 2,3-epoxypropylphosphonic esters have been prepared in this way.

2-Tetrahydrofurfurylphosphonic esters have been obtained in a similar manner from tetrahydrofurfuryl bromide[193]. Since all these reactions conform to the well-known rules of the Arbuzov rearrangement, they will not be discussed in greater detail here.

2,3-Epoxypropyl- and 2-tetrahydrofurfuryl-phosphonic esters have also been obtained by the reaction of epihalogenohydrins and 2-tetrahydrofurfuryl halides with sodium dialkyl phosphites[193,194], *i.e.* by the Michaelis-Becker reaction.

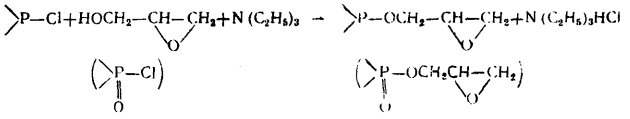
It is interesting that 2-bromotetrahydropyran reacts normally with sodium diethyl phosphite[193], whereas 2,3-dibromotetrahydropyran does not form an organophosphorus compound at all under these conditions, but undergoes dehydrobromination[193]. Rearrangements of trialkyl phosphites by more complex halogenated heterocycles (containing two oxygen atoms, nitrogen, etc.) have been systematised by Arbuzov.[196]

2. Reaction of Acid Halides of Phosphorus with Alcohols Containing Epoxy Groups

Little work has been done on this reaction. It is known to require more care than that of the corresponding acid halides with ordinary alcohols.

The α-oxide ring is readily opened by various reagents, and this side-reaction can sharply diminish the yield of the epoxyalkyl esters of the phosphorus acids.

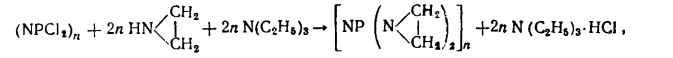
Patent specifications[197,198] have described the reaction of glycidyl alcohol with phosphorus trichloride phenyldichlorophosphine, and phosphoryl chloride, of 2,3-epoxybutane-1,4-diol with dimethylphosphinic and dibutylphosphinous chlorides, etc. Other alcohols containing α-oxide groups, such as 2,3- and also 3,4-epoxyhexanol and 4,5-epoxyoctanol, have been used in addition to the most readily available glycidyl alcohol. Triethylamine was used to combine with the hydrogen chloride liberated in these reactions:



The yields of the reaction products have not been stated. The organophosphorus compounds containing epoxy-groups resulting from this reaction and also the reaction discussed in Section 1 can be obtained by another method, the epoxidation of allyl or other unsaturated groups combined with phosphorus either directly or *via* oxygen. The epoxidation of allylphosphonic esters[195], tertiary phosphine oxides containing allyl groups[170,176,177], and also allyl esters of various phosphorus acids[198] has been reported.

3. Reaction with Aziridine of Phosphorus Compounds Containing a Reactive Chlorine Atom

This reaction and the products formed have been discussed elsewhere[65] and they will not be considered here. Among new work is that on the reaction of tri- and tetra--mers of phosphonitrilic chloride with aziridine in the presence of triethylamine[199]. The chlorine atoms are completely replaced by aziridine rings:

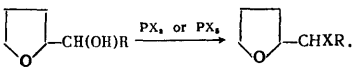


where n = 3 or 4.

4. Reactions Not Resulting in Formation of Organophosphorus Compounds

The relative stability of γ-oxides towards phosphorus halides has been pointed out in Section 8 (Part II). If however, hydroxyl is present in the γ-oxide molecule, it is readily replaced by halogen, but the corresponding ester of an acid of phosphorus (as in the case of glycidyl alcohol) is not formed.

The interaction of tetrahydrofurfuryl alcohol and its derivatives with phosphorus trichloride and tribromide (sometimes in the presence of pyridine) and also with phosphorus pentachloride has been described. Tetrahydrofurfuryl halides are formed in these cases[200-202]



Note that when sodium diethyl phosphite reacts with 2,3-dibromotetrahydropyran the latter is dehydrobrominated to 3-bromodihydropyran[193].

VII. APPLICATIONS OF ORGANOPHOSPHORUS COMPOUNDS OBTAINED BY THE PROCESSES DISCUSSED

Many compounds synthesised by these reactions have found use in a number of branches of the national economy, while other substances are undergoing production trials, and yet others have been recommended or patented for use in various branches of industry. Results are interesting, though not yet quite definite, and additional investigation is required.

Plasticisers

Phosphoric esters containing 2-halogenoalkyl groups have been widely explored as plasticisers for various polymeric materials[103-108,203-210].

Such esters as tris-2-chloroethyl phosphate§, tris-2,3--dichloropropyl phosphate, and tris-2-chloropropyl phosphate have found industrial application under various commercial names – "Celluflex CEF"§, "Cetamol Q", "Celluflex Fr-2"¶, "Cetamol P", etc. These esters are readily compatible (often in combination with other plasticisers) with poly(vinyl chloride), polyesters, cellulose acetate and nitrate, polyurethanes, phenol–formaldehyde plastics, and epoxy and other resins. These polymers thus acquire flame resistance and in some cases (for example cellulose derivatives) resistance to light, durability, and elasticity[204-208].

Various aryl 2-halogenoalkyl phosphates[106,107], phosphoric and phosphonic esters containing epoxyalkyl groups[195,198] products formed by addition of alkene oxides to phosphonic acids[155] and acid phosphoric esters[153], and also *OO*-dialkyl *S*-alkylthioalkyl phosphorothiolothionates[179] have been proposed as plasticisers.

Flameproofing Agents for Various Articles, Plastics, Textiles, etc.

It is well known that many phosphorus compounds make various materials flameproof (or more so)[3,65]. The compounds of various classes described here have also been used for this purpose. Almost all the plasticisers considered above increase the fire resistance of the polymers[103-108,153,195,203-210]. 2,3-Dibromoalkyl phosphates, especially tris-2,3-dibromopropyl phosphate, have proved particularly effective flameproofing agents for polystyrene foams[211-213]. The use has been patented of poly(bis-2--chloroethyl vinylphosphonate), which here acts as a special kind of plasticiser, to confer incombustibility on polycondensation resins[214]. Flameproof coatings have been obtained by the polymerisation of the addition products of acid halides of quinquevalent phosphorus to glycidyl esters of methacrylic and other unsaturated carboxylic acids[111].

Flameproof polymers can be produced by incorporating phosphorus in macromolecules using the acid chlorides and some esters of 2-chloroethyl- and vinyl-phosphonic acids. In contrast to the 2-halogenoalkyl phosphates, these compounds are not simply present in the mass of the polymer, but are chemically combined with it. The phosphorus enters the main polymer chains (in thermosetting phosphorus-containing polyesters[69,98-101]), or is located in the side-chains (in the case of copolymers of an acid chloride and vinylphosphonic esters[90-92,102,215]), or even in the cross--links between the linear chains of the organic polymers of, for example, unsaturated polyesters[216-219].

Since in these cases the phosphorus components are combined with the macromolecules by stable chemical bonds, the flameproof properties are practically unaffected by any treatment which does not destroy the polymer.

Products of the reaction of aziridine with phosphonitrilic chloride[199], phosphoryl chloride, or thiophosphoryl chloride[220-227] and of α-oxides or aziridine with tetrakishydroxymethylphosphonium chloride or trishydroxymethylphosphine oxide[169-175] (and their combinations with other substances) have proved useful for making various materials, and particularly textiles, flameproof. Solutions of 2-chloroethyl phosphoric acid[228], and also the addition products of phosphoryl chloride and its derivatives with glycidyl methacrylate, oleate, and crotonate[111], have been employed for the same purpose.

Recently Monsanto Chemical Co. has developed several compounds containing phosphorus and halogens under the general name "Phosgard", which confer good fire resistance on synthetic resins, fibres, wood, and paper[229]. The exact compositions of these compounds are not yet known, but it has been stated that the starting materials for them are in several cases 2-halogenoalkyl derivatives of phosphorous acid.

§ Tris-2-chloroethyl phosphate, made by Amcel Co. Inc., affiliated with Celanese Corp. of America (Ed. of Translation).

¶ Tris-dichloropropyl phosphate, made by Amcel Co. Inc., affiliated with Celanese Corp. of America (Ed. of Translation).

Additives for Motor Fuels

Several 2-halogenoalkyl phosphorothio-ites and -ates, phosphonothioates, and also (more rarely) phosphites and phosphates have proved to be effective additives for petrol and other fuels for internal combustion engines [19,34,38,42,43,108,109,230,231]. Their value lies in preventing the premature ignition of fuel, thereby raising its octane number, and they diminish the formation of carbon deposits. The Phosgard compounds (see above) have been proposed for the same purpose [229].

Additives for Lubricating Oils

2-Halogenoalkyl phosphites and phosphates, as well as their sulphur analogues, improve the quality of lubricating oils (in particular those used in friction units operating under very high loads) [108,109,232,233].

Among compounds which have proved useful additives for lubricating oils are bis-2-chloroethyl vinylphosphonate [217], Phosgard compounds [229], esters and thioesters of 2-chloroethylphosphonic acids [234], and products of the addition of α-oxides and sulphides to phosphoric acid [148], its acid esters [153], diaryl- and alkylaryl-phosphinodithioic acids [167], phosphorus pentasulphide [190], and finally to substances formed by reaction of petroleum hydrocarbons with P_2S_5. [191]

Stabilisers for Polymers

Salts of vinylphosphonic and alkylvinylphosphinic acids stabilise several polymers and copolymers (particularly those of vinyl chloride and acrylonitrile) towards light and heat [235-237].

Among antioxidants are several 2-halogenoalkyl esters of phosphorus, phosphoric, phosphonothioic, and phosphorothioic acids [103,108,238]. Cable plastics can be stabilised for tropical use with tris-2-chloroethyl phosphite and bis-2-chloroethyl 2-chloroethylphosphonate [239,240]. Epoxyalkyl esters [195,198] and "ethyleneimides" of phosphorus acids [241-243], and also *OO*-dialkyl alkylthioalkyl phosphorothioates [179], are good stabilisers for poly(vinyl chloride).

Textile-Finishing Agents

Products of the interaction of various α-oxide compounds with acids of phosphorus, their acid esters, and phosphates of aliphatic amines have found application in the textile industry mainly as antistatic agents [151,152,157-159,244].

It has been suggested that textiles should be treated with epoxyalkyl esters of phosphorus acids to make them crease-resistant [245].

Other Fields of Application and Prospects

Several 2-halogenoalkyl, vinyl, and alkylthioalkyl esters of acids of phosphorus have been suggested as insecticides [131,179,246-248].

2-Halogenoalkyl and also epoxyalkyl derivatives of phosphorus acids are intermediates in the synthesis of various organophosphorus monomers [3,65,195] and Thiokols [2,20,129].

Products of the addition of polyepoxides to phosphoric acid give hard and durable corrosion-resistant coatings for various materials [161-165].

Bis-2-chloroethyl hydrogen phosphite is apparently of interest for some biological investigations [249].

Finally, research on the preparation of organophosphorus compounds containing epoxy-groups [176,177,193-195,197,198] is extremely important and promising. In particular, it is suggested that such substances can be used to produce flameproof and very heat-resistant plastics [176,177,250].

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The reaction of phosphorus compounds with α-oxides provides then a very simple, convenient, and cheap method for obtaining various organophosphorus compounds containing 2-halogenoalkyl and hydroxyl groups, $\alpha\beta$-unsaturated radicals attached to the phosphorus, and also reactive epoxide and aziridine rings. The majority of such compounds are obtained in good yields, and are easily separable from the reaction mixture. They have already found some application, and will probably be more extensively used in the near future.

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EFFECT OF ANIONS ON THE KINETICS OF THE DISSOLUTION OF METALS

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The dissolution of metals in electrolyte solutions is electrochemical in nature, and its velocity depends not only on the usual variables of chemical kinetics — concentration and temperature — but also on the electrochemical properties of the system, primarily on the electrode potential and the structure of the electrical double layer at the metal–solution interface. This point, obvious to electrochemists, has often been neglected, and is not always taken into account now by workers on corrosion.

From the laws of electrochemical kinetics, the dependence of rate of dissolution on potential can be represented in the simplest case by the equation

$$i_1 = k_1 \exp\left(\beta \frac{F}{RT}\varphi\right), \quad (1)$$

where i_1 is the rate of dissolution expressed as an electric current, φ the electrode potential, β the transfer coefficient, and k_1 a constant depending on the nature of the metal and the state of its surface.

Eqn. (1) is valid for a process which can be written in the general form

$$M \rightarrow M^{n+} + ne. \quad (2)$$

In the spontaneous dissolution of a metal in an acid, reaction (2) is balanced by the simultaneous cathodic discharge of hydrogen ions:

$$2H^+ + 2e \rightarrow H_2, \quad (3)$$

the kinetics of which can be expressed by the equation

$$i_2 = k_2[H^+]\exp\left(-\alpha \frac{F}{RT}\varphi\right). \quad (4)$$

On combining Eqns. (1) and (4) we find that the dependence of the rate of spontaneous dissolution of a metal on the acid concentration should be given by the equation

$$v = k_3[H^+]\frac{\beta}{\alpha+\beta}, \quad (5)$$

which in several cases shows good agreement with experiment[1-3].

In many cases, however, the rate of dissolution of metals in acid electrolyte solutions depends not only on the concentration of hydrogen ions, which are directly involved in the process, but also on the nature and the concentration of the anions, which at first sight do not appear to take part in the process. Recent investigations in this laboratory[4-9] have shown that a change in the anionic composition of the solution can lead to a change both in the cathodic process (hydrogen evolution) and in the anodic process.

The activating effect of anions on the anodic process is often associated with their influence on the state of the passivating film, *i.e.* on the magnitude of the diffusion barrier. However, recent data indicate that anions are directly involved in the discharge and the formation of metal ions[8-14].

Kolotyrkin and Medvedeva[8] have shown that the dependence of the rate of anodic dissolution of cadmium on the potential in solutions containing halides is represented by a Tafel straight line having a slope of 0.035 V, which gives a value of 1.66 for β (reckoning that $\alpha + \beta = 2$), the position of this curve depending markedly on the nature and the concentration of the added halide. The curve for the dependence of rate of dissolution on KI concentration at a given electrode potential (Fig. 1) shows that, after a certain critical concentration of the salt, in this case 0.1 N, a tenfold increase in the salt concentration is accompanied by an almost thousandfold increase in the rate of the anodic process. Bromide and chloride solutions give similar results, but with the difference that replacement of I^- by Br^- and Cl^- resulted in an increase in the critical concentration of the added salt.

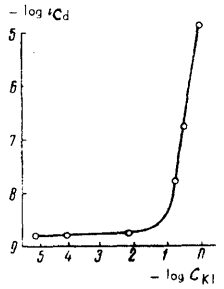


Fig. 1. Dependence of rate of dissolution of cadmium (at constant potential) in a solution of 1.0 N H_2SO_4 + x KI on the concentration of KI.