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Acyl Phosphites

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The review deals with an interesting new field among organophosphorus compounds—the chemistry of acyl phosphites. The possible ways of synthesising and the chemical properties of these highly reactive compounds have been examined together with the likely mechanisms of the reactions considered.
The bibliography includes 111 references.

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I. INTRODUCTION

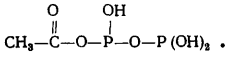
One of the results of the rapid development of the chemistry of organophosphorus compounds has been the discovery and detailed study of new classes of substances. In particular, one of such classes is acyl phosphites. Like other mixed anhydrides of phosphorus and carboxylic acids, acyl phosphites readily enter into phosphorylation and acylation reactions with nucleophilic agents. They react also with electrophilic agents owing to the presence of the unshared electron pair in the outer shell of the phosphorus atom. This property of acyl phosphites is responsible for the very wide range of reagents which react with them and makes them interesting objects for theoretical studies as well as important key substances in organophosphorus synthesis.

The majority of investigations of acyl phosphites have been carried out very recently and therefore there are no relevant reviews. This and also the appearance in the chemistry of acyl phosphites of certain new trends, characteristic also of other classes of organic derivatives of phosphorus, made it desirable to write the present article. The review is not merely a compilation. Together with a description of the advances in this field of chemistry, the authors make a critical assessment of certain experimental studies and put forward a number of general considerations concerning this subject.

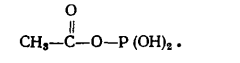
II. SYNTHESIS OF ACYL PHOSPHITES

1. The Reaction of Phosphorous Acid and Dialkyl Phosphites with Carboxylic Acid Anhydrides

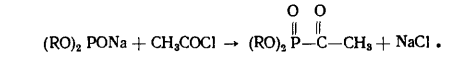
In order to elucidate the structure of phosphorous acid, in 1866 Menshutkin allowed it to react with acetyl chloride and obtained a substance to which he attributed the following structure:



Somewhat later Vvedenskii achieved the reaction of phosphorous acid with acetic anhydride and isolated a crystalline product, which he believed to be monoacetyl phosphite:

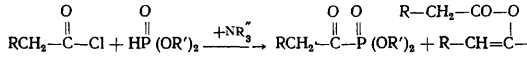


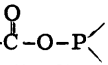
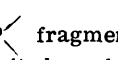
The same substance was obtained by Brooks[3] in a reaction of acetyl chloride with phosphorous acid under somewhat milder conditions than in Menshutkin's reaction. However, Cade[4] established on the basis of chemical and X-ray diffraction data that in fact the above workers did not obtain a mixed anhydride but acetylphosphonic acid: $CH_3C(O)PO(OH)_2$. Cade's conclusion concerning this reaction is consistent with the data of A. E. Arbuzov, who showed that sodium (and potassium) salts of dialkyl phosphites react with acetyl chloride to form 1-ketophosphonic acids[5]:



Ketophosphonates are obtained similarly also in the reaction with benzoyl chloride[6].

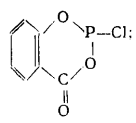
The reaction of carboxylic acid chlorides with dialkyl phosphites in the presence of tertiary amines has also been discussed in the literature. Here the products are not acyl phosphites, α-ketophosphonates and the corresponding enol carboxylates being isolated in a high yield[7]:

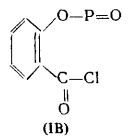


Thus so far it has not proved possible to find conditions under which phosphorous acid and salts of dialkylphosphorous acid react with carboxylic acid anhydrides to form  fragments and not . However, in view of the limited number of publications on this question, one cannot state categorically that there is no possibility of developing methods for the synthesis of acyl phosphites on the basis of such reactions.

2. Reaction of Phosphorus(III) Acid Chlorides with Carboxylic Acids and Their Salts

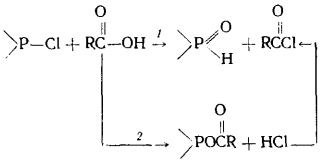
Acyl phosphites were obtained for the first time by Anshutz and Emery[8] by the reaction of phosphorus trichloride with salicylic acid. They discussed two possible structures of the products:


(IA)


(IB)

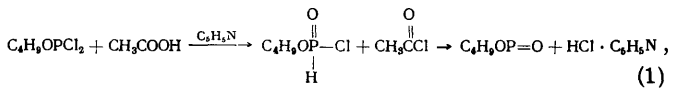
On the basis of preparative data for the reaction of carboxylic acids with phosphorous trichloride, which leads to acyl chlorides, the authors concluded that their compound has the structure (IB). This formula was attributed to compound (I) in the well known monograph of Kosolapoff[9]. Later Young[10] and Cade and Gerrard[11] established that the original conclusion was erroneous and the structure (IA) was assigned to the substance obtained by Anshutz and Emery. The data allowing this conclusion can be more usefully dealt with below in the section concerned with the reaction of amines with acyl phosphites (see p. 1059).

Further discussion of the preparation of acyl phosphites by the reaction of carboxylic acid with phosphorus(III) acid chlorides makes it necessary to consider the mechanism of this reaction. Cade and Gerrard[12] attempted to elucidate this problem. They attempted to discover whether there is a direct exchange of chlorine bound to the phosphorus atom for the hydroxy-group of the carboxylic acid (mechanism *1*) or whether chlorine is substituted by the acyloxy-group with formation of an acyl phosphite which reacts *in situ* with the hydrogen chloride liberated (mechanism *2*):



Bearing in mind that in the presence of pyridine acetyl chloride and acetic acid react to form acetic anhydride and pyridine hydrochloride[13] (this reaction takes place extremely rapidly even at −78°C), the authors carried out the reaction of dibutyl phosphorochloridite with two moles of acetic acid in the presence of one mole of pyridine. It was thought that, if the reaction proceeds via mechanism *1*, the acetyl chloride formed in the presence of pyridine should immediately react in the second stage with the residual mole of acid, forming acetic anhydride and pyridine hydrochloride. On the other hand, if the process proceeded via mechanism *2*, then the reaction products should contain acetyl dibutyl phosphite, pyridine hydrochloride, and one mole of unreacted acid.

Since Cade and Gerrard obtained a 92% yield of acetic anhydride, they considered it proved that the reaction of carboxylic acids with phosphorus(III) acid chlorides takes place via mechanism *1*. Attributing great importance to the formation of acetic anhydride in their experiments and failing to see another mechanism of its formation, these workers suggested that mechanism *1* obtains also when a carboxylic acid salt and pyridine are introduced into the reaction with phosphorochlorodites. In this connection the considerations they put forward concerning the mechanism of the reaction of butyl phosphorodichloridite with two moles of acetic acid and two moles of pyridine, which leads to the formation of diacetyl butyl phosphite[12], are noteworthy. They asserted that at the beginning there is "as usual" a direct exchange of one of the chlorine atoms of butyl phosphorodichloridite for a hydroxy-group with formation of acetyl chloride and butyl hydrogen phosphorochloridite, which decomposes into butyl metaphosphite and pyridine hydrochloride. Subsequently acetyl chloride reacts with another mole of acetic acid and forms acetic anhydride, which reacts with the metaphosphite to give diacetyl butyl phosphite:



(1)



(2)

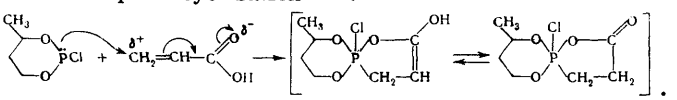
(3)

Cade and Gerrard saw a confirmation of this mechanism in the fact that the metaphosphite formed by the controlled hydrolysis of butyl phosphorodichloridite indeed reacted with acetic anhydride to form diacetyl phosphites. Thus, having discovered a new way of synthesising acetyl phosphite (unfortunately they quote only one example, which precludes the consideration of this reaction in a separate section), the authors omitted from all their discussions another way in which the actual products may be formed: namely by the reaction of equimolar amounts of acyl phosphite and carboxylic acid to give dialkyl phosphite and acetic anhydride[14] (see p. 1056). Having disregarded this possibility, Cade and Gerrard could not find an alternative mechanism for the formation of acetic acid anhydride in their experiments and therefore arrived at an incorrect conclusion concerning the reaction of carboxylic acids and their salts with phosphorus(III) acid chlorides.

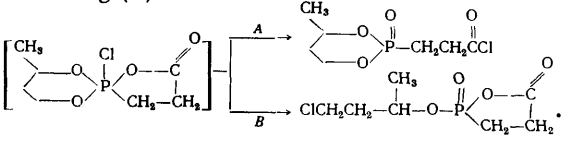
That the conclusion of Cade and Gerrard was incorrect was subsequently shown experimentally by Anderson and Young[15-17], who successfully employed dialkyl phosphorodichloridites in reactions with carboxylic acids in the presence of tertiary amines in order to obtain acyl phosphites.

The above analysis of the literature data shows that most probably the reaction of carboxylic acids and their salts with phosphorus(III) acid chlorides consist in a nucleophilic substitution of a chlorine atom bound to phosphorus for an acyloxy-group. When the usual aliphatic acids are employed, the hydrogen chloride liberated rapidly decomposes the acyl phosphite formed to the acyl chloride and acid phosphite and therefore mixed anhydrides cannot be obtained by this method. Cyclic acyl phosphites synthesised from acids having substituents with functional groups are more resistant to the action of hydrogen chloride. For example, salicylic acid reacts with phosphorus dichloride to form compound (IA) without a hydrogen chloride acceptor. Similarly mercaptoacetic acid gives a stable mixed anhydride[18,19]. Probably acyl phosphites based on other acids with specific structural factors can also be prepared in this way.

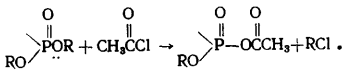
In a discussion of the general problem of the reaction of phosphorochloridites with carboxylic acids, it is necessary to consider in greater detail the studies on αβ-unsaturated acids carried out in recent years. A mechanism different from those analysed above has been proposed for this case. Acrylic and methacrylic acids react with cyclic glycol phosphorochloridites to form oligomeric products. The reaction proceeds readily and in some cases with liberation of heat. It is suggested that the mechanism of the process includes as the initial stage nucleophilic attack by the phosphorus atom on the β-carbon atom in the acid with subsequent cyclisation[20,21]:



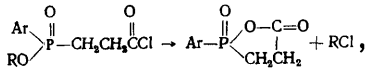
The authors believe that the cyclic product can isomerise in two ways: with opening of the anhydride ring (*A*) or the ester ring (*B*):



They assert[20,21] that the ester ring is opened since the infrared spectrum of the products has an intense band at 1720 cm^{-1}, which can only be due to the carbonyl group in the ester and not the acid chloride group; moreover the substance contains hardly any mobile chlorine. Thus, if the above mechanism is adopted, one may conclude that the quasiphosphonium chloride decomposes anomalously, since in such cases the chloride anion usually attacks the more electrophilic carbon of the carbonyl group (mechanism *A*). It is more likely that, if a bicyclic quasiphosphonium intermediate is in fact formed in this reaction, it decomposes via mechanism *A* with subsequent conversion into the product postulated in mechanism *B*. This hypothesis is consistent with the available data concerning the tendency of neutral phosphonates[22] and phosphates[23] to react with acetyl chloride:

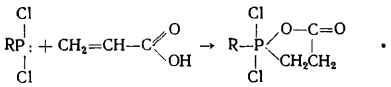


Moreover, the above hypothesis is confirmed directly by the latest work of Pudovik and coworkers, who quote data on the reaction of ester chlorides of phosphonous acids with $\alpha\beta$-unsaturated acids. They succeeded in isolating the chlorides of phosphonocarboxylic acids and in showing that they are unstable and readily undergo cyclisation[24,25]:

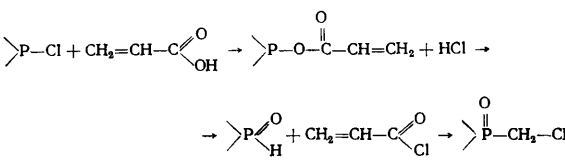


i.e. a reaction takes place, the possibility of which had not been taken into account in studies dealing with the reaction of alkylene phosphorochloridites with unsaturated acids[20,21].

In conclusion of the discussion of the reaction of phosphorus(III) acid chlorides with $\alpha\beta$-unsaturated acids, it is necessary to consider the results obtained in the investigation of the reaction of the unsaturated acids with dichlorophosphines. Here the only products isolated were the chloride anhydrides of phosphorylates carboxylic acids[26,27], the formation of which was explained by the mechanism already considered:



Thus one may say that, according to published data, the reaction of phosphorus(III) acid chlorides with $\alpha\beta$-unsaturated acids proceeds via a stage involving the formation of a cyclic compound. However, the formation of a cyclic adduct has been in no way proved. Moreover, the mechanism has not been confirmed by recent investigations either[28]. We believe that the formation of the final products can be accounted for by a simpler mechanism, which follows logically from the facts discussed above:



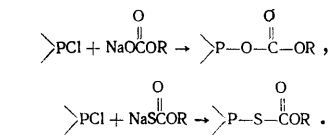
This course of the process explains why the reaction of phosphorochloridites with $\alpha\beta$-unsaturated acids of the type RCH=CHCOOH with substituents at the β-carbon atom takes place in an unusual way: thus crotonic and cinnamic acids do not form the above products and are only converted into their chlorides[29]. Probably in this case the reaction stops at an intermediate stage, since acid phosphites should add less readily to such chlorides owing to the steric and electrostatic effects of the hydrocarbon groups.

Summarising the discussion of the literature data on the reaction of phosphorus(III) acid chlorides with carboxylic acids, the following may be noted. At the present time there is no convincing proof for a particular mechanism of this reaction, but the known facts indirectly confirm that in all the syntheses which have been achieved the primary products are acyl phosphites. In some cases acyl phosphites were isolated in a pure form but usually they are decomposed by hydrogen chloride to acid phosphites and acyl chlorides.

For preparative purposes, acyl phosphites are best synthesised from phosphorus(III) acid chlorides and carboxylic acid salts. Optimum results are obtained when alkali metal salts are employed. Experimentally this method is distinguished by simplicity and ease of isolation of the required products. The reaction is of general importance. On the one hand, aliphatic and aromatic phosphorochloridites[30-34], phosphoramidochloridites[33], and phosphonous acid chlorides[33,35,36] and, on the other hand, salts of various aliphatic and aromatic acids enter into it.

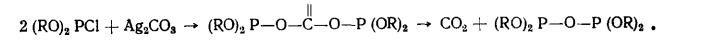
The reaction of phosphorochloridites with formic acid salts is of considerable interest, since it is known that formic anhydrides constitute a little investigated group of compounds in organic chemistry. Unfortunately the formyl phosphites obtained proved to be unstable, decomposing with liberation of carbon monoxide. The second decomposition product is acid phosphite[33]. Since this decomposition is not accompanied by other side processes, formyl phosphites are promising reagents for the synthesis of certain acid phosphites.

Dialkyl phosphorochloridites react also with salts of alkylcarbonic[37] and alkylthiocarbonic[38,39] acids:

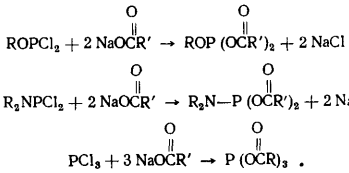


Phosphite-carbonates are of interest for the synthesis of completely esterified phosphorus(III) acids and natural acidophilic alcohols, since phosphorylation by phosphite-carbonates should be accompanied by the liberation of monoalkyl carbonates, which, by virtue of their extreme instability, decompose into alcohols and carbon dioxide—substances which are inert with respect to neutral phosphites.

When dialkyl phosphorochloridites react with silver carbonate, a symmetrical phosphite-carbonate is formed, which is also unstable and is readily decarboxylated to pyrophosphite[40]:



Apart from phosphorus(III) monochlorides, dichlorides[41] and also phosphorus trichloride[42] react with carboxylic acid salts, forming di- and tri-acyl phosphites, for example:



3. Reaction of Pyrophosphites with Carboxylic Acids

Acyl alkyl phosphites were obtained for the first time by the acidolysis of tetraethyl pyrophosphites using a method developed by A. E. Arbuzov and Alimov[43]. These investigators showed that pyrophosphite reacts with carboxylic acids with liberation of heat according to the following mechanism:

$$(C_2H_5O)_2P{-}O{-}P(OC_2H_5)_2 + RCOOH \rightarrow (C_2H_5O)_2P{-}\overset{O}{\overset{\|}{C}}R + (C_2H_5O)_2P(=O)H.$$

Anderson et al.,[44] who employed tetraethyl pyrophosphite for the synthesis of peptides, also stated that acyl phosphites are formed as intermediates. Despite its ease, this method of synthesis has many disadvantages. Firstly, it is not universal, since frequently it is difficult to separate by distillation the anhydride and the side product (acid phosphite). Secondly only half of the phosphorus bound to the organic group is usefully employed in this method. Moreover, one must remember that the initial pyrophosphites are frequently difficult to obtain. These reasons probably explain why the above method of synthesis of acyl phosphites has not found preparative application.

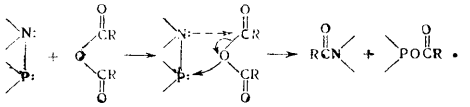
4. Reaction of Phosphorus(III) Acid Amides with Carboxylic Acids and Their Anhydrides

A novel synthesis of acyl phosphites distinguished by a high yield of the desired product is based on the reaction of the amides[45-49] and hydrazides[49] of phosphorus(III) acids with carboxylic acid anhydrides:

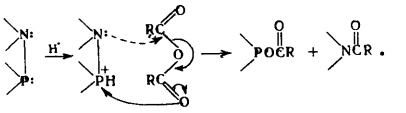
$$>P{-}NR_2 + (R'CO)_2O \rightarrow >P{-}O{-}\overset{O}{\overset{\|}{C}}R' + R'CONR_2.$$

A series of acyl phosphites and acyl phosphinites have been obtained in this way, but this method can hardly be recommended for preparative purposes, since the second reaction product (the acyl amide or acyl hydrazide) frequently has a boiling point close to that of the required product. In this case the separation of the products is extremely difficult. Moreover, in the reaction of triamide of phosphorous acid with 1, 2, or 3 moles of acetic anhydride, it was not possible to isolate acetyl phosphorodiamidite, diacetyl phosphoroamidite, or triacetyl phosphite respectively[46]. Formyl phosphites cannot be obtained by this method, since formic acid anhydride does not exist. It should also be noted that the amides and even more so the hydrazides of phosphorus(III) acids are in most cases more difficult to obtain than the chlorides (the latter are frequently employed as the starting materials for the synthesis of the amides). Thus the reaction of phosphorus(III) amides and hydrazides with mixed carboxylic acid anhydrides must be regarded as a new reaction of compounds with a phosphorus–nitrogen bond rather than as a preparative method for synthesising acyl phosphites.

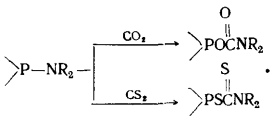
The study of the mechanisms of this process is of considerable interest. Recently the first mechanism was proposed, according to which the carbon in the carbonyl group is subjected to nucleophilic attack by the nitrogen atom with a free electron pair[46]:



This treatment of the mechanism is open to a number of objections. In particular, it contradicts the available data showing the greater nucleophilicity of the phosphorus(III) atom compared with the nitrogen atom in phosphorus(III) amides[50-52]. Bearing in mind what has been said above and also the observations according to which phosphoramidites frequently react in a protonated form[41,53], a different mechanism may be proposed for this reaction:



By the reaction of phosphoramidites with carbon dioxide and carbon disulphide, it proved possible to obtain mixed anhydrides of *NN*-substituted carbamic acids and phosphoramidous and phosphorodiamidous acids[54-56]:



However, the attempts to synthesise the trianhydrides of phosphorous and carbamic acids were unsuccessful.

In a study of carbonylation it was established that the reaction takes place successfully only in the presence of proton donors, for example amine hydrochlorides[57]. Probably the mechanism of this process is the same as that considered above for carboxylic acid anhydrides.

One of the preparative methods for the synthesis of carboxylic acid amides is the reaction of phosphoramidites with carboxylic acids[58]:

$$>P{-}NR_2 + R'COOH \rightarrow P(=O)H + R'\overset{O}{\overset{\|}{C}}NR_2.$$

A new application of this reaction, permitting the preparation of acyl phosphites, has been recently demonstrated[59]:

$$>P{-}NR_2 + 2\,R'COOH \rightarrow >P{-}O{-}\overset{O}{\overset{\|}{C}}R' + R'COOH \cdot HNR_2.$$

Probably this method will be of synthetic value in those cases where phosphorus(III) acid amides are more readily available than their chlorides.

5. Reaction of Acetyltrialkylsilanes with Phosphorous Acid Halides

In 1952 Anderson[60] reported that the exchange of a halogen linked to the phosphorus(III) atom for acyloxy-group takes place readily when trimethylsilyl α-monochloroacetate reacts with phosphorus tribromide:

$$2\,Me_3SiCOOCH_2Cl + PBr_3 \rightarrow 3\,Me_3SiBr + P(\overset{O}{\overset{\|}{C}}CH_2Cl)_3.$$

Later Orlov and Kaufman[61], who investigated this reaction with phosphorus trichloride, found that triacetyl phosphite is not formed and the process takes place by the following mechanism:

$$3\,R_3SiOAc + PCl_3 \rightarrow AcP(OSiR_3)_2 + 2\,AcCl + R_3SiCl.$$

It appears that Anderson's report is incorrect.

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Thus several types of reactions leading to mixed anhydrides of phosphorus(III) and carboxylic acids are known

at present. We believe that in most cases the most promising method of synthesising acyl phosphites is based on the reaction of sodium (or potassium) salts of carboxylic acids with phosphorus(III) acid chlorides. The method is fairly general and experimentally simple, giving high yields of the desired products.

III. CHEMICAL PROPERTIES OF ACYL PHOSPHITES

All the reactions of acyl phosphites, which are probably heterolytic processes, can be divided into two large groups on the basis of the reagents employed—electrophilic and nucleophilic. Such subdivision of the available data is of course arbitrary and is used merely to facilitate description.

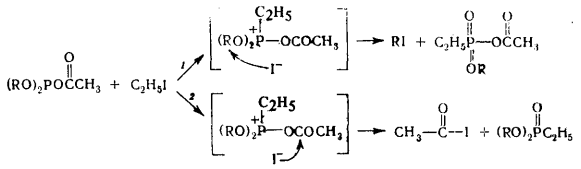
A. REACTIONS WITH ELECTROPHILIC AGENTS

1. Oxidation and Addition of Sulphur

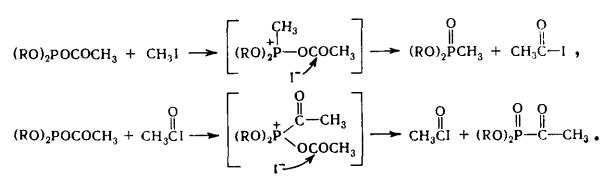
Like all compounds containing a phosphorus(III) atom, acyl phosphites are readily oxidised to acyl phosphates[30], combine with sulphur[43,45], and react with monohalogeno-compounds of copper with liberation of heat, forming crystalline products[43,62]. As was to be expected, derivatives containing phosphorus-carbon bonds are very reactive in these processes.

2. The Arbuzov Reaction

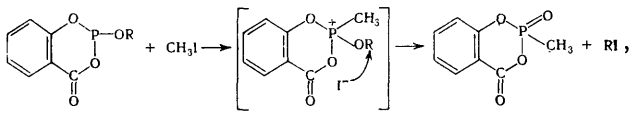
The fundamental process in the chemistry of organophosphorus compounds is the Arbuzov reaction. It has recently been applied to acyl phosphites. Since acyl phosphites contain both alkoxy- and acyloxy-groups at the phosphorus atom, it might have been expected that the process would involve the elimination of either an alkyl or an acyl halide:



In 1951 A. E. Arbuzov and Alimov reported[43] that the reaction of diethyl isovaleroyl phosphite with ethyl iodide gives a low yield of an isomerisation product via mechanism *1*. At the same time there is a high yield of a product the structure of which the authors did not establish. Later Pudovik and coworkers[63,64] showed that the intermediate complex decomposes predominantly via mechanism *2*, and the acid halide liberated reacts in turn with the acyl phosphite:

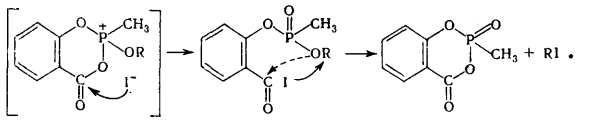


It is interesting that, when methyl iodide is introduced into the reaction, it remains almost completely unchanged. It is quite evident that in this case the process takes place via the Arbuzov mechanism and in the second stage of the reaction the iodide ions attack the more electrophilic centre—the carbon of the carbonyl and not the alkoxy-group. It is noteworthy that in the alkylation of salicylphosphorous acid esters by methyl iodide the overall situation changes. According to Nesterov and Sabirova[65], who achieved this reaction, the iodide ion attacks the carbon of the alkoxy-group which results in the formation of phosphonates in high yields:



where R = CH_3, C_2H_5, or iso-C_4H_9.

The authors of the above investigation believe that this mode of reaction is most likely, since "the C–O bond is polarised in the required direction in the alkoxy-group"[65]. This statement is not altogether clear. Another reaction mechanism, which does not contradict data showing a greater electrophilicity of the carbon atom in the carbonyl group compared with the carbon atom in the alkoxy-group, is more likely:

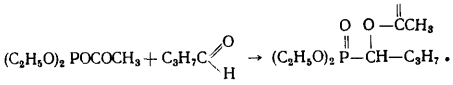


The studies confirming the possibility of the concluding stage of the reaction were discussed above (p. 1052).

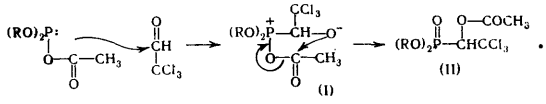
Above we considered the interaction of acyl phosphites with acyl halides as an intermediate stage in certain reactions. Later this process was investigated also as an independent reaction, using as the acyl chlorides the chlorides of mono-, di-, and tri-chloroacetic acids[66].

3. Reaction with Aldehydes and Ketones

In 1956 Alimov and Cheplanova reported that the reaction of acetyl diethyl phosphite and butyraldehyde results in the formation of α-acetoxybutyl diethyl phosphonate[67]:

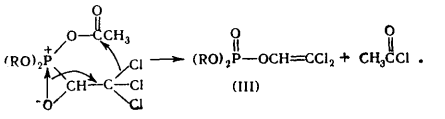


Subsequently other workers extended this reaction to new systems[34,68]. The reaction of α-halogenoaldehydes with acyl phosphites is similar to that of the simplest aldehydes[70,71]:



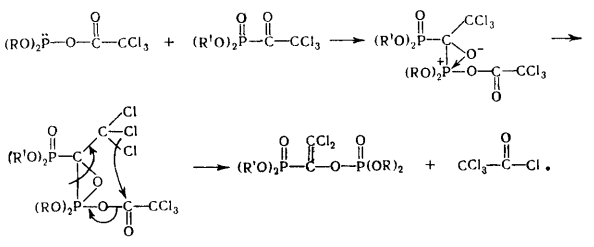
In this case the reaction takes place much more readily (with spontaneous liberation of heat). This was in fact to be expected, bearing in mind that the reaction begins with the nucleophilic attack by the phosphorus(III) atom on the carbon atom in the carbonyl group. The dipolar adduct (I)

formed in the first stage of the process has two electrophilic centres: the phosphorus atom and the carbon atom of the carbonyl group. Consequently in the second stage of the reaction the attack by the negatively charged oxygen atom may be directed either to the carbonyl group, with formation of a product having the phosphonate structure (II), or to the phosphorus atom, whereupon the mechanism of the Perkow reaction[71] may obtain with formation of a product having the enol phosphate structure (III):



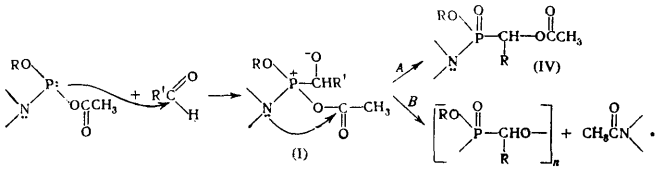
Indeed in some cases, for example in the reaction of acetyl di-isobutyl phosphite with chloral, $\beta\beta'$-dichlorovinyl di-isobutyl phosphate was isolated together with α-acetoxyphosphonate[71]. It is noteworthy that in the reaction of chloral with dialkyl phosphites, enol phosphates are formed preferentially[72]. This difference in the behaviour of trialkyl phosphites and acyl dialkyl phosphites can probably be explained by the presence in the molecules of the latter of a carbonyl group, which in the second stage of the process may be attacked by the negatively charged oxygen atom in preference to the phosphorus atom.

Pudovik and Gazizov obtained very interesting results in a study of the reaction of acyl dialkyl phosphites with trichloroacetylphosphonic acid esters[66]:



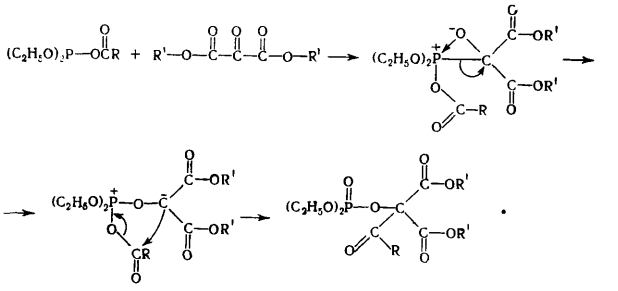
The mechanism of this reaction is different from that with chloral. Evidently the $(RO)_2P{=}O$ group, which replaces a hydrogen atom in chloral, increases the electrophilicity of the phosphonic acid centre. As a result, the attack by the anionic centre is directed to the phosphorus atom and not to the carbon atom in the carbonyl group, and the reaction proceeds via the Perkow mechanism. The occurrence of both competing reactions has been discovered when aldehydes were allowed to react with acetyl phosphoramidites[69].

Possibly in this case the reaction proceeds via a stage involving the formation of a dipolar ion of type (I), which either rearranges under the influence of the nucleophilic attack by the negatively charged oxygen atom on the carbon atom of the carbonyl group with formation of the phosphonate (IV) (mechanism *A*) or decomposes to acetamide and a phosphorus-containing polyester (mechanism *B*):



4. Reaction with α-Ketoacid Esters

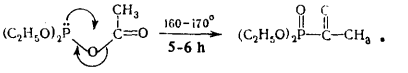
Acyl phosphites react with mesoxalic esters. Probably in this case the phosphorus(III) atom exhibits its nucleophilic properties[73]:



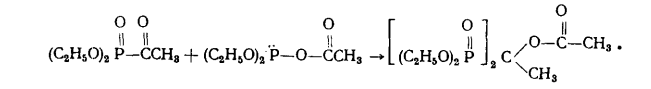
It must be emphasised that in this reaction the attack by the carbanionic centre of the intermediate compound is directed to the carbon atom of the carbonyl and not the alkoxy-group, as happens in the reaction of neutral phosphites with mesoxalic acid esters. Pyruvate and glyoxylate esters react with acyl phosphites similarly to mesoxalic acid esters[74].

5. Thermal Isomerisation

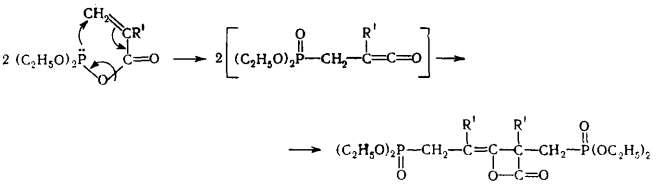
In contrast to acyl phosphates[32,75], acyl phosphites are not readily disproportionated on heating to pyrophosphites and carbon dioxide. However, they can undergo a rearrangement, the mechanism of which is as follows[32]:



This rearrangement is a kind of intramolecular version of the Arbuzov reaction. The diethyl acetylphosphonate formed reacts further with another molecule of acetyl diethyl phosphite with formation of methylbis(diethylphosphono)methyl acetate:



The isomerisation of acyl phosphites formed by $\alpha\beta$-unsaturated acids takes place in an unusual manner. In the first stage of the reaction a phosphorylated ketone is formed, which, being unstable, undergoes subsequent isomerisation[32]:

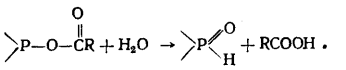


B. REACTIONS WITH NUCLEOPHILIC AGENTS

Acyl phosphites have two electrophilic reaction centres: the carbon atom in the carbonyl group and the phosphorus atom. This property of acyl phosphites leads to the expectation that two series of reaction products may be formed, the structure of which is determined by the mode of attack by the nucleophilic agent.

1. Hydrolysis

When water acts upon acyl phosphites, the latter decompose into the carboxylic and the corresponding phosphorous acids. The reaction is accompanied by the liberation of heat[43,62]:

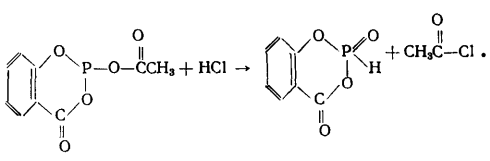


It is noteworthy that the formation of the final products may take place as a result of the attack by the hydroxy-group on both the phosphorus atom and the carbon atom in the carbonyl group. This problem still remains open.

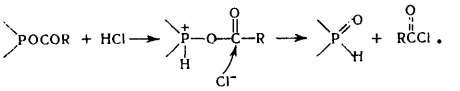
2. Reaction with Acids

Data have been published on the reaction of certain acyl phosphites with hydrogen chloride. It has been established that salicyl phosphorochloridite hardly changes in the presence of hydrogen chloride. However, butyl salicyl phosphate is cleaved with formation of butyl phosphorodichloridite[76]. The hydrochlorination of diacetyl trifluoromethyl phosphonite, resulting in the formation of acetic acid and dichlorotrifluoromethylphosphine, is formally analogous to this process[35]:

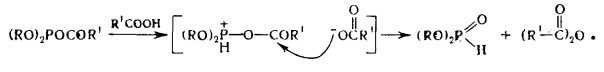
The mechanism of these reactions has not been investigated and the available data do not allow the appropriate analysis. However, we may conclude that the reactions considered are accompanied by the formation of phosphorus–chlorine bonds and are energetically favourable under the given conditions. Another result was obtained for reactions of hydrogen chloride with acetyl salicyl phosphite[77] and acetyl dialkyl phosphites[78]:



Evidently the latter syntheses proceed via a mechanism similar to that which was adopted for the alkylation of acyl phosphites:

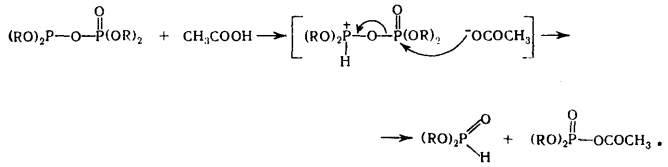


This mechanism is also consistent with the results of the reaction of acyl phosphites with carboxylic[14,33,79]†, dialkylphosphoric[80], and dialkylphosphorodithioic[81] acids:



† In a brief communication[47] it has been stated that acetyl ethylene phosphite reacts with benzoic acid to form benzoyl ethylene phosphite. The conditions of the synthesis and the yield and the constants of the product are not quoted. The reaction of acetyl diethyl phosphite with benzoic acid described in the same paper is striking. The authors assert that transacetylation also takes place in the first stage and subsequently diethyl phosphate and acetyl benzoate are formed. No factual data are given for this reaction either.

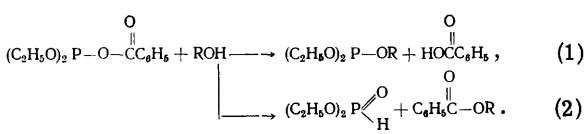
Probably the Arbuzov mechanism operates also in the reaction of neutral subphosphates with acetic acid[82]:



This process can be represented in a different way too: initially there is transacylation to acyl phosphite and dialkylphosphoric acid, which then react with one another to form the products isolated. However, ultimately these mechanisms do not differ significantly.

3. Reaction with Alcohols

One may expect that the alcoholysis of acyl phosphites will lead to the formation of either phosphorus(III) acid esters or carboxylic acid esters. A. E. Arbuzov and Alimov[43] showed that benzoyl diethyl phosphite reacts with alcohols to give a small yield of a phosphorylated product, i.e. of the possible modes of reaction the first actually occurs:



Subsequently certain additional data on this reaction were published[30,31,62,76,83,84]. They are mainly concerned with the fact that the reaction of acyl phosphites with alcohols yields both neutral phosphites and dialkyl phosphites. This result was explained by secondary dealkylation of the neutral phosphites formed initially[31,85].

The possibility, in principle, of this reaction at an elevated temperature has been demonstrated[86]. Therefore, in order to prevent the dealkylation side process, it is recommended that neutral phosphites be employed only in the presence of acid acceptors (triethylamine[31,85] or dialkyl phosphoramidites[83,85]). The authors of these hypotheses note themselves that the use of such procedures gives rise to considerable experimental difficulties in the isolation of the required products. Consequently this version of the method does not have fundamental advantages over the alcoholysis of phosphorochloridites, which also requires the application of an acceptor; moreover, phosphorochloridites are more readily available and are usually employed as the starting materials in the synthesis of acyl phosphites.

Thus the procedures for the phosphorylation of alcohols by acyl phosphites described in the early investigations are of no synthetic value.

Subsequently this reaction was studied in greater detail. In the first place the stability of the neutral phosphites with respect to carboxylic acids at room temperature was estimated. For this purpose, the most labile neutral esters (trimethyl phosphite and 1,3-butylene methyl phosphite) were kept at 20°C with acetic acid and the mixture was periodically analysed by gas chromatography. It was

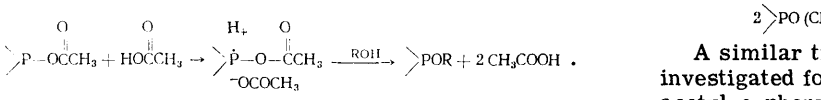
shown[79] that only after 48 h weak peaks due to methyl acetate appeared on the chromatogram. Consequently, under the phosphorylation conditions, acetic acid hardly reacts with neutral phosphites and the side process involving their dealkylation, which had been suggested previously, does not in fact occur.

On the basis of this experiment, it was concluded that acid phosphites are formed via another side process.

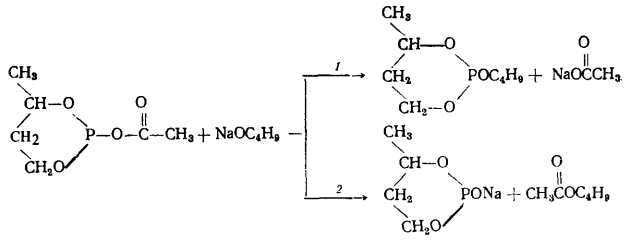
In the preceding section of this review, the reaction of carboxylic acids with acyl phosphites was discussed and it was concluded that such reaction takes place significantly more readily than the reaction of acids with neutral phosphites. This finding led to the conclusion[14,79] that in the earlier investigations of the alcoholysis of acyl phosphites the formation of hydrogen phosphites was not associated with the dealkylation of the neutral phosphites but with the deacylation of the phosphorylating agent. The carboxylic acid liberated by the reaction accumulates in the reaction medium and, when its concentration becomes equal to that of the alcohol, it can successfully compete with the latter for the phosphorylating agent. Evidently, in order to develop a preparative method for the synthesis of neutral phosphites, it is necessary to find conditions such that the alcohol reacts faster with the phosphorylating agent. Since acetyl dialkyl phosphites are deactivated by carboxylic acids at an appreciable rate only above 0°C while they react with alcohol also at lower temperatures, at 0°C the synthesis may be successfully employed to prepare neutral phosphites without the introduction of carboxylic acid acceptors. Experiments confirmed this hypothesis and the method thus developed has been used to prepare a series of neutral phosphites, the yield of which was in all cases higher than under conditions where acceptors are employed[33,79,87].

The mechanism of the alcoholysis of acyl phosphites is of considerable interest. In a study of this reaction it was concluded that, when the reactants are mixed, the process does not begin at once but only after an induction period and, once begun, the reaction proceeds exothermically. Hence it was suggested that the alcoholysis does not reduce merely to the reaction of the acyl phosphite and the alcohol but that the carboxylic acid also takes part[79].

We believe that the following mechanism of the alcoholysis is most likely. The process begins with the protonation of the mixed anhydride by the acid, probably due to the free electron pair of the phosphorus atom. The protonation is accompanied by the induction of a considerable positive charge at the phosphorus atom, which is subsequently subjected to nucleophilic attack by the alcohol, terminating with the formation of the neutral phosphite and carboxylic acid; the latter accumulates in the reaction medium and accelerates the process:

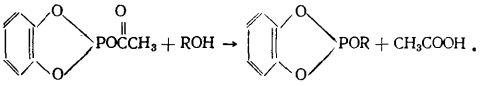


This mechanism has been confirmed experimentally by comparing the rates of reaction of acetyl 1,3-butylene phosphite with 2-octanol in the absence and in the presence of triethylamine. It was established that in the first case the process is much faster than in the second[74]. Experiments, in which the effect of the acid on the phosphorylating capacity of acyl phosphites was excluded, indirectly confirm this mechanism. Thus the reaction of acetyl 1,3-butylene phosphite with sodium butoxide results in the formation of a mixture of both phosphorylation and acetylation products, i.e. butyl 1,3-butylene phosphite and butyl acetate were obtained[79]:



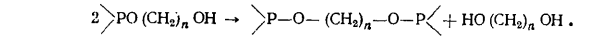
On the other hand, the acetate ester could not be isolated in the reaction between acetyl 1,3-butylene phosphite and butanol. Thus, in those cases where the reaction mixture contains an acid which is an effective protonating agent, the reaction proceeds virtually in one way, while in the absence of such acid there are two reaction mechanisms. If the reaction mixture contains an acid, it activates the phosphorylating centre and the reaction involves only that centre. If there is no acid, there is no activation either (or it takes place less effectively via the solvation of the reactant) and both phosphorylation and acylation, which previously took place to a lesser extent, occur.

The alcoholysis of acyl phosphites in the presence of acids is a convenient and effective method for the synthesis of a wide variety of neutral phosphite esters. Particularly satisfactory results were obtained when acetyl *o*-phenylene phosphite was employed[87]:

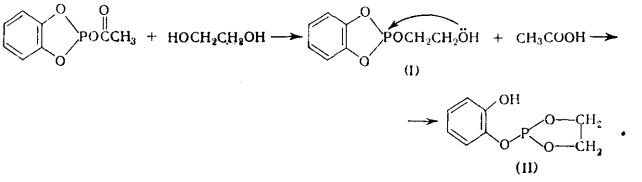


In this synthesis the yield of neutral phosphites reached 90%; this was explained by the enhanced stability (with respect to acetic acid) of the anhydride, which did not change on being kept for 24 h with an equimolar amount of the acid. Since *o*-phenylene phosphites are used industrially as stabilisers for certain materials[88,89], the explanation of the finding that they are formed readily and in high yields is very important. It should also be noted that the esters obtained in this way are purer than those synthesised by other procedures[89,90].

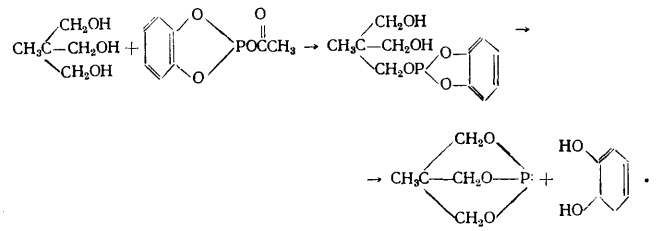
Like monohydric alcohols, glycols readily react with mixed anhydrides of dialkyl(aryl)phosphorous and carboxylic acids without the introduction of acceptors[87]. Diphosphites were obtained in this way in high yields. Esters containing a free hydroxy-group were synthesised in a low yield. This result can be accounted for by the disproportionation of the hydroxyalkyl phosphites (formed initially) under the conditions of their isolation:



A similar transphosphorylation reaction was recently investigated for acid hydroxyalkyl phosphites[91]. When acetyl *o*-phenylene phosphite reacted with ethylene glycol in proportions of 1 : 1, ethylene *o*-hydroxyphenyl phosphite (II) was obtained instead of the expected hydroxyethyl *o*-phenylene phosphite (I)[87]:



Intramolecular transesterification takes place very readily also when 2-hydroxymethyl-2-methyl-1,3-propanediol is phosphorylated by acetyl *o*-phenylene phosphite:

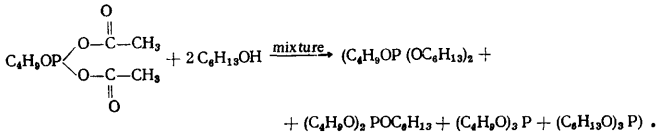


However, in the reaction with an excess of the anhydride the main product is the fully phosphorylated diol. Under analogous conditions, pentaerythritol is phosphorylated to give the tetraphosphite[87].

Acyl phosphites are highly effective in the phosphorylation of hydroxylated polymers. In this case the effect of acids on the process is particularly pronounced. Thus in the phosphorylation of hydroxylated macromolecular compounds [cellulose and poly(vinyl alcohol)] it was virtually impossible to obtain phosphorus-containing polymers when the experiments were carried out without added acid[92], whereas in similar syntheses with added acids such polymers are obtained readily and their phosphorus content reaches 14%.[93,94]

Di- and tri-acyl phosphites are also good phosphorylating agents for alcohols[41]. It might have been supposed that they would prove to be more promising for the synthesis of certain neutral phosphites than monoacetyl phosphites. This hypothesis was based on the following factors.

Firstly, the synthesis of di- and tri-acetyl phosphites takes place in one stage and experimentally does not differ from the synthesis of monoacyl phosphites. Secondly, the initial acid dichlorides and phosphorous trichlorides are more readily available than the monochlorides of dialkylphosphorous acid. Unfortunately only symmetrical phosphites could be obtained by this procedure in high yields. All the experiments undertaken to synthesise esters with different groups resulted in a mixture of neutral phosphites[41], for example:

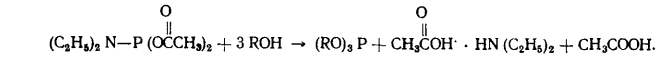


Many workers have concluded that asymmetric neutral phosphites disproportionate during their synthesis and suggested that the tendency towards "ester exchange" is a characteristic of the asymmetric neutral phosphites themselves. The reason for this phenomenon was never elucidated. The first step towards the determination of the mechanism of such disproportionation was taken by the present authors[41], who succeeded in establishing that the disproportionation of asymmetric phosphites takes place only in the presence of acid compounds or at least is sharply accelerated by them.

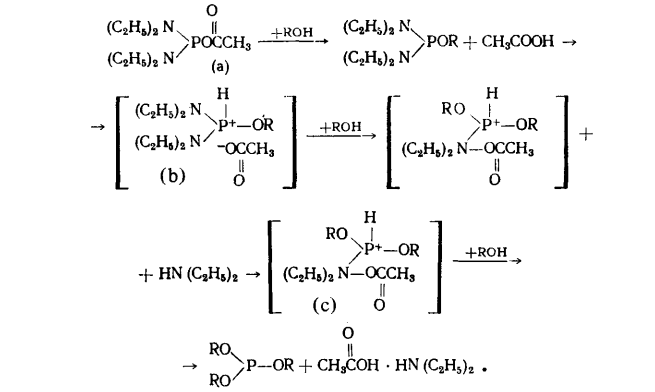
The results of the alcoholysis of acyl phosphoramidites merit special consideration. The reaction of acetyl *NNN'N'*-tetraethylphosphorodiamidite and alcohol in molar proportions of 1 : 3 at a temperature above 10°C gave a high yield of trialkyl phosphite[33]:



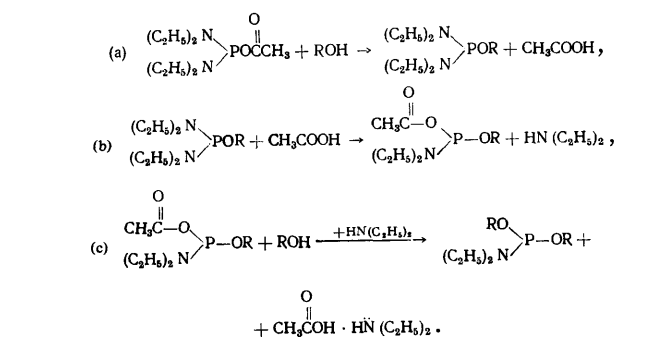
Fully esterified phosphorous acid is also formed under these conditions in the alcoholysis of diacetyl *NN*-diethylphosphoramidite[41]:



The reaction is exothermic and therefore, in order to avoid spontaneous heating, it is necessary to mix the reactants very cautiously with cooling. Such reaction conditions are consistent with the phosphorylation of alcohols by mixed anhydrides but not phosphorus(III) acid amides, which react with alcohols only on heating[95]. Consequently one may conclude that in the phosphorylation by amidoanhydrides, phosphoramidites and acetic acid are formed in the first stage and then interact with formation of new products, which are capable of readily phosphorylating alcohols. Probably these intermediates have the structure of quasiphosphonium salts:



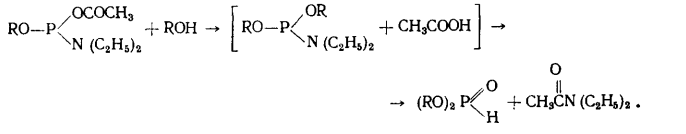
It is interesting that ammonium acetate is isolated only at the end of the reaction after the P–N bonds in the phosphoramidite have been fully replaced by P–O bonds. Probably this finding can be explained by the higher basicity of the phosphoramidite compared with the neutral phosphite, the quasiphosphonium complex of which with carboxylic acid is extremely unstable and readily decomposes into the initial compounds. In our cases the acid isolated is immediately converted into the salt by the diethylamine present in the reaction mixture. Probably the ready formation of neutral phosphites in the alcoholysis of acyl phosphoramidites cannot be represented by another mechanism, including the formation of acyl phosphite by the reaction of phosphoramidite and acetic acid produced in the first reaction stage (the possibility and scope of this reaction were demonstrated above—see Section II, 4):



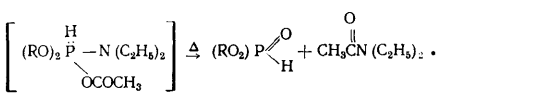
In this case the acetic acid bound in a salt with diethylamine can no longer participate in the formation of the next

anhydride bond and the product must be *NN*-dialkylphosphoramidite and not the neutral phosphite, as is in fact observed experimentally. One should also remember that the amine is much more nucleophilic than the alcohol and therefore if the occurrence of stage (b) involving the formation of acyl phosphoramidite and diethylamine is postulated, the amine will react with the phosphoramidite faster than the alcohol.

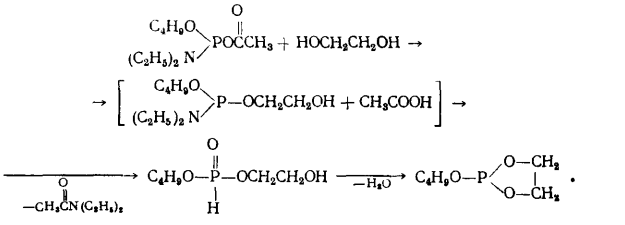
Yet another treatment of the mechanism of the alcoholysis of acetyl phosphoramidites[84] must be rejected. The authors conclude that the reaction of equimolar amounts of the phosphorus-containing reactant and alcohol yields dialkyl phosphite and *NN*-diethylacetamide via the following mechanism:



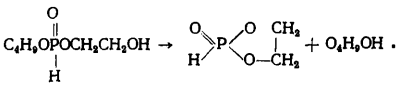
Probably in this case the phosphoramidite and acetic acid formed in the first stage are not produced in a pure form but are present as a quasiphosphonium compound. On heating, this adduct may decompose to acid phosphites and *NN*-diethylacetamide:



It was to be expected that, when the temperature of the process is controlled and a large amount of alcohol is employed, it should result in neutral and not acid phosphites‡. Unfortunately Evdakov et al.[84] did not arrive at this conclusion. Moreover, they carried out the reaction of acetyl butyl *NN*-diethylphosphoramidite with an equimolar amount of glycol (which corresponds to two moles of a monohydric alcohol in terms of the number of hydroxy-groups) and obtained butyl ethylene phosphite—a neutral ester of phosphorous acid. However, on the basis of their general mechanism of alcoholysis, including the formation of an acid phosphite as an obligatory stage, the authors put forward the following scheme for the process:

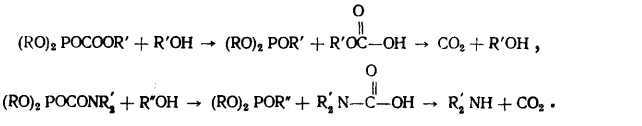


However, this postulate contradicts the logic of the chemistry of phosphites. It is known that diesters of phosphorous acid are not esterified by alcohols under the usual conditions[96,97] and in general the conversion of derivatives of phosphorous acid with a tetracoordinate phosphorus atom to derivatives with a tricoordinate phosphorus atom is extremely difficult. Moreover, the assertion that alkyl β-hydroxyethyl phosphites can be cyclised to alkyl alkylene phosphites contradicts also specific experimental data, since it has been shown that these compounds are cyclised by a transesterification and not a dehydration mechanism[91]:



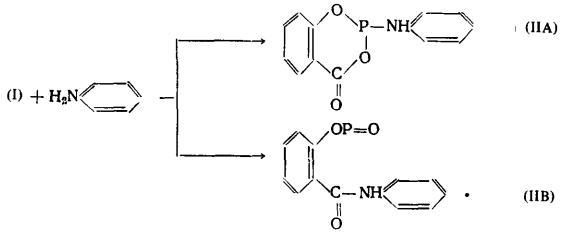
Thus the inclusion in the mechanism of the alcoholysis of acyl phosphoramidites of a stage involving the formation of an acid phosphite is unjustified. Probably protonation products are always formed§ and, depending on the specific conditions, these are converted into various compounds in accordance with the factors described above.

The range of acyl phosphites employed was very recently extended in a study of the phosphorylation of alcohols. Apart from the mixed anhydrides of phosphorus(III) acids and carboxylic acids, the corresponding derivatives of alkylcarbonic[37] and carbamic[57] acids have begun to be employed. The results obtained are extremely interesting: the synthesis takes place under mild conditions and, what is most important, acid does not accumulate in the reaction mixture:

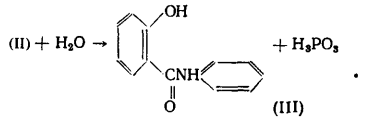


4. Reactions with Amines and Phosphines

In Section II, 2 it was stated that the reaction of salicylic acid with phosphorus trichloride yields a product to which one of the two structures (IA) or (IB) (see p. 1051) could be attributed. The reaction of compound (I) with aniline led to the isolation of a product (II), the structure of which may also be represented by two formulae, corresponding to those of compound (I):



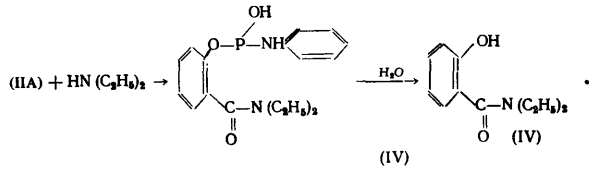
Since the hydrolysis of compound (II) yielded salicylanilide (III), the structure (IIB) was attributed to the product[8]:



‡ Subsequently[41] acetyl butyl *NN*-diethylphosphoramidite was allowed to react with two moles of butanol at 0°C and tributyl phosphite was obtained in a high yield. The second reaction product is diethylammonium acetate and not *NN*-diethylacetamide.

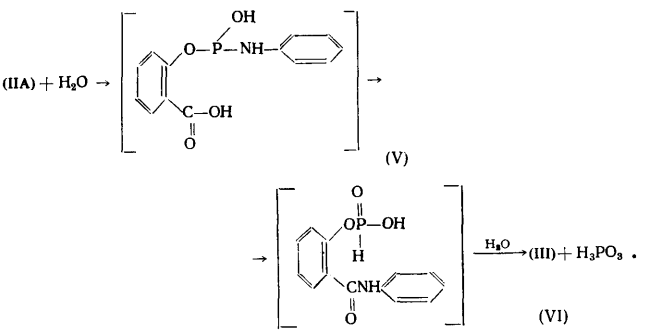
§ Acid catalysis is probably of general importance in the reactions of phosphorus(III) acid derivatives with nucleophilic agents. Thus in the presence of acetic acid, triamides react with three moles of alcohol and are converted into trialkyl phosphites at 0°C[53], whereas previously, without the use of acid, this synthesis was carried out at a temperature frequently exceeding 100°C.

However, the reaction of (II) with diethylamine and subsequent hydrolysis of the intermediate led to the isolation of *NN*-diethylsalicylamide (IV)[10]. The formation of (IV) is probably possible only when compound (II) includes an anhydride ring, i.e. has the structure (IIA):



(IV)

The isolation of salicylanilide in the hydrolysis of (II) is also consistent with the structure (IIA) and may be represented by the following mechanism:

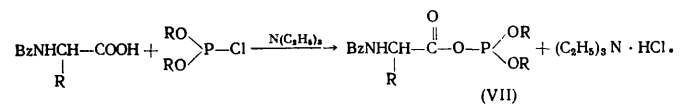


(V)

(VI)

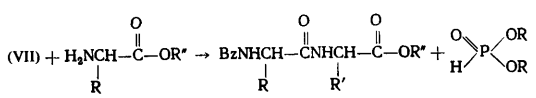
Above we stated that the amides of phosphorus(III) acids react vigorously with carboxylic acids to form carboxamides[58]. Therefore the conversion of (V) into (VI) agrees with expectation. Thus the demonstration of the cyclic structure of compound (I) yields information about the reaction of acyl phosphites and amines.

As we have seen above, the reaction of *N*-benzoylated α-aminoacids with phosphorus(III) chlorides leads to the formation of acyl phosphites:

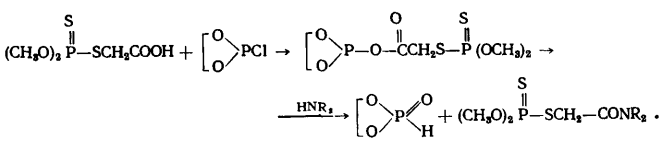


(VII)

These compounds react further with α-aminoacids, forming peptides[16]:



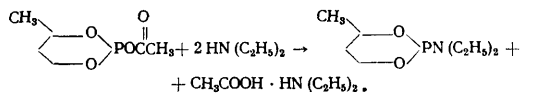
Amine acylation products were obtained in the synthesis of analogues of the insecticide Ragor[98]:



Thus the data quoted show that the ammonolysis of acyl phosphites gives high yields of acylation products and does not result in their phosphorylation. This finding is not trivial, since we know that acyl phosphites react with alcohols to form esters of phosphorous and carboxylic acids, i.e. act as phosphorylating agents.

It would be wrong to seek the cause of the difference between the reactions of acyl phosphites with alcohols and amines only in the different nature of the reactants employed and to use for this purpose one of the familiar concepts, for example those of Pearson[99], which have been recently resorted to in the interpretation of the results of the reactions of other phosphorus-containing mixed anhydrides with alcohols and amines[100].

The above considerations are based on the relevant experiments. An experiment was performed in which the mode of attack by the amine on the phosphorus atom in the acyl phosphite was definitely demonstrated. Indeed, at 0°C acyl phosphites react with twice the equimolar amount of diethylamine, so that one obtains a more than 50% yield of the phosphoramidite and the ammonium salt of the carboxylic acid[78,101], for example:

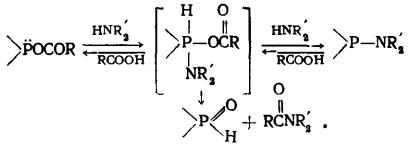


In a parallel experiment without temperature control the diethylamide of the carboxylic acid was obtained in high yield.

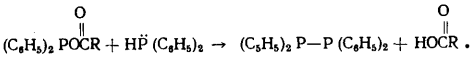
Probably the first stage of the reaction of acyl phosphites with amines involves an addition process similar to that which occurs when certain phosphorus(III) acid fluorides are treated with amines[102].

The addition product, which is essentially a quasiphosphonium salt, can undergo a nucleophilic substitution reaction if the reaction mixture contains an excess of the amine. In the absence of temperature control, the addition product decomposes with formation of the pure acid phosphite and the carboxylic acid amide.

The general scheme should be supplemented by the decomposition of the addition product on treatment with acid to the acyl phosphite and the ammonium salt. The overall process mechanism can be represented as follows:



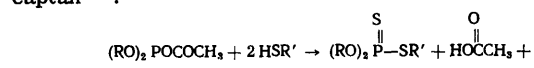
It is interesting to add to the above that, in contrast to the amine, according to the data of Trippett and coworkers, diphenylphosphine forms with acyl phosphinate diphosphine and a carboxylic acid even when the reactants are present in stoichiometric proportions[36]:



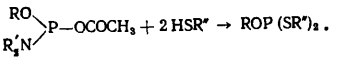
5. Reaction with Mercaptants

The reaction of acyl phosphites with mercaptants has been very little investigated despite the fact that it has a number of characteristic features compared with the alcoholysis of phosphonimidites. After the acyl phosphites had been treated for a long time with an equimolar amount of a mercaptan at 20°C under conditions excluding radical reactions, new products were not obtained[101,103]. When the reaction was carried out in the presence of triethylamine or sodium mercaptide was employed instead of the mercaptan, phosphorothioites were obtained[101].

Neutral phosphorodithioates were synthesised by treating acyl dialkyl phosphites with an excess of a mercaptan[104]:



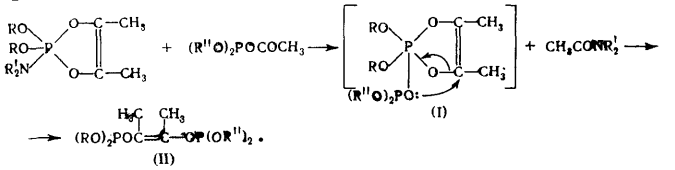
Probably in this case phosphorylation was accompanied by the desulphuration of the mercaptan, i.e. a process which is very familiar in the chemistry of phosphites[105,106]. The reaction of acyl phosphoramidites with mercaptans, which leads to neutral phosphorodithioites but not phosphorothioates, has also been described[104]:



The authors[104] did not analyse the causes of the difference in the mode of the two formally similar reactions.

6. Interaction with Aminophospholens

Aminophosphoranes with a phospholen ring are an interesting type of nucleophilic agent with several centres capable of undergoing attack by electrophilic agents. The reaction of aminophospholens with acyl phosphites has been described[107] and the following mechanism has been put forward:

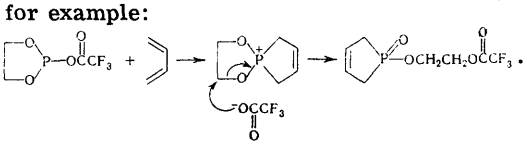


It is suggested that in the first stage the carbon atom of the carbonyl group undergoes nucleophilic attack with formation of acetamide and an intermediate pentacovalent compound(I), which undergoes further rearrangement to the final product (II). It is surprising that Mizrakh et al.[107] discussed the possibility of nucleophilic attack by nitrogen only and on only one electrophilic centre in acyl phosphites—the carbon atom of the carbonyl group. Nevertheless, having concluded that compound (II) is formed (yield 23%), the authors failed to prove rigorously its structure. For example, no data are quoted concerning the presence of a phosphorus(III) atom in the molecule. At the same time the absence of a phosphorus–carbon bond is not demonstrated either, although it is well known that it is always formed when dialkyl phosphite anions are alkylated by unsaturated compounds[108] (this in fact happens in the mechanism proposed). Moreover, it remains obscure why the dialkylphosphite anion attacks the carbon atom involved in the multiple bond and not the more electrophilic carbon atom of the alkoxy-group.

Thus at present it is impossible to include the reaction of acyl phosphites with aminophospholens among the known processes.

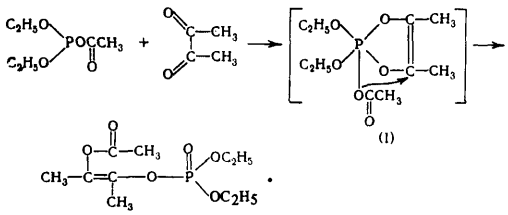
7. Reactions with Dienes

The reaction of acyl phosphites with conjugated dienes, the investigation of which began only very recently[109], can be considered in this section in a somewhat arbitrary fashion, for example:

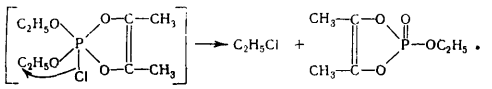


It has been noted that mixed anhydrides containing a trifluoroacetic acid residue react with dienes more readily than the corresponding acetic acid derivatives.

When diacetyl is employed as the diene, the reaction takes place readily also with mixed anhydrides incorporating non-halogenated carboxylic acids[110]:



The intermediate (I), the structure of which had been demonstrated by ^{31}P NMR[110], proved to be unstable, undergoing, according to the authors of the investigation, a rearrangement via the mechanism of the second stage of the Arbuzov reaction. However, the cause of the attack by the anion of the carbon atom of the multiple bond is not explained. At the same time this factor must be investigated in detail, since phospholen, which has a similar structure and is formed in the reaction between diacetyl and dialkyl phosphorochloridite[111], decomposes with elimination of alkyl chloride and not with ring opening:



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