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α-Ketophosphonic Acid Esters—Synthesis, Structure, and Reactions

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Studies on the synthesis and properties of α-ketophosphonic acid esters (KPE)—a class of highly reactive organophosphorus compounds—are surveyed. Data are presented concerning instances of the anomalous course of the process in the synthesis of KPE by the Arbuzov reaction. The reactions of KPE with nucleophiles, including those which lead to the rupture of the phosphorus-carbon bond, are examined in detail. The problems of the stereochemistry of KPE are dealt with briefly. The bibliography includes 162 references.

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I. INTRODUCTION

For a long time, α-ketophosphonic acid esters (KPE) were comparatively little known and the chemistry of this unusual group of organophosphorus compounds began to be studied vigorously only in recent times. The experimental data for the properties of KPE obtained in the period 1962–71 have been partially surveyed in a short review[1]. Despite the lability of the phosphorus-carbon bond, KPE proved to be interesting key compounds in a number of syntheses based on the use of the increased reactivity of the carbonyl group, particularly in the preparation of α-aminophosphonic acids[2] and phosphorylcarbenes[3]. Even a superficial acquaintance with the chemical properties of KPE reveals an analogy with α-dicarbonyl compounds. On the other hand, the stereochemical aspects of the formation of the KPE molecule and its structure have been shown by the first studies[4,5] to be more varied compared with the same problems in the case of α-dicarbonyl compounds.

The synthesis of carbohydrate derivatives with a phosphorus–carbon bond using traditional methods for the formation of the latter is frequently accompanied by side reactions[6,7], one of the causes of which is the involvement in the reaction of the acetoxy-group of the protected monosaccharide. This feature was fully manifested also in the synthesis of carbohydrate-containing KPE, where the initial compounds were the chlorides of acetylated aldonic acids.

II. METHODS OF SYNTHESIS

The synthesis of KPE is based on the acylation of phosphite esters. Different versions of this reaction are distinguished by the nature of the acylating agent and the structure of the tervalent phosphorus acid derivative.

KPE (I) were first synthesised by Kabachnik et al.[8] from acyl chlorides and trialkyl phosphites:

$$\underset{}{RCOCl} + P(OR')_3 \rightarrow \underset{(I)}{RC(O)P(O)(OR')_2} + \underset{(II)}{[RC(O)OP(OR')_2]} + R'Cl \quad .$$

In subsequent years a large number of a wide variety of KPE were synthesised by the interaction of the full esters of phosphorous acid with aliphatic[9–19] and aromatic[20–25] carboxylic acid chlorides. The method of synthesis has undergone certain changes compared with the initial procedure[8] (reaction in an inert gas atmosphere[10,13,20] and in a number of instances the reverse order of mixing of the reactants[13,16,21]).

KPE can be obtained by the reaction of acyl halides with other derivatives of tervalent phosphorus acids—tetraethyl pyrophosphite[26], hypodiphosphites[27,28], and phosphoramidite esters[29–32]. Attempts have been frequently made to employ dialkyl phosphites and their salts for the synthesis of KPE, but their reaction with halides does not proceed unambiguously and the yield of KPE is only 10–30%. This is because the KPE formed initially react further with dialkyl phosphites to form diphosphoryl compounds[15,33,34]; in other cases the enolic form of the α-ketophosphonate is acylated by the initial acyl halide[35]. The chlorides of halogeno-substituted acids give rise to high yields of KPE on interaction with dialkyl phosphites. The chlorides of trichloroacetic[36], trifluoroacetic[37], and other perfluorocarboxylic acids[38] have been used in this reaction.

Apart from acyl halides, carboxylic acid anhydrides can be used to acylate phosphite esters. The interaction of acetic anhydride with triethyl phosphite leads to a 10% yield of diethyl acetylphosphonate[39]. The main reaction product is a compound without an active carbonyl group. Referring to earlier studies, the authors[39] attributed the structure of tetraethyl 1-hydroxyethylidenediphosphonate (III) to this compound. However, it was shown later[34] that, under the conditons of the reaction described, the diphosphonate (III) rearranges to the phosphonophosphate (IV):

$$\underset{\underset{OH}{|}}{CH_3C} - [P(O)(OC_2H_5)_2]_2 \xrightarrow{t^\circ} \underset{\underset{OP(O)(OC_2H_5)_2}{|}}{CH_3CHP(O)(OC_2H_5)_2} \quad .$$
(III) (IV)

Trialkyl phosphite reacts anomalously with phthalic anhydride–biphthalyl was obtained in 70% yield instead of the expected α-ketophosphonate[40].

Mixed anhydrides of carboxylic and dialkylphosphorous acids (II) are converted into KPE under the influence of alkyl iodides, acyl iodides, and iodine, which function as catalysts in this reaction. The reaction has been carried out[41,42] with the anhydrides of a number of aliphatic acids, including those with the iso-structure. The anhydrides of carboxylic acids apparently interact analogously with dialkyl phosphorochloridites[43], whereupon the mixed anhydride (V) formed in the first stage isomerises to the ketophosphonate under the catalytic influence of the acyl chloride (VI):

$$(C_3H_7CO)_2O + (RO)_2PCl \rightarrow \underset{(V)}{C_3H_7C(O)OP(OR)_2} + \underset{(VI)}{C_3H_7COCl} \quad ;$$

$$(V) + (VI) \rightarrow C_3H_7C(O)P(O)(OR)_2 \quad .$$

The formation of acetyl phosphonate $CH_3C(O)P(O)(OC_2H_5)_2$ (VII) by the reaction of acetyl acylals with diethyl phosphorochloridite can be explained satisfactorily[44] within the framework of the same mechanism.

KPE are frequently formed as intermediates in various reactions and their involvement in further chemical transformations has been confirmed by specific syntheses. The formation of the phosphonate (VII), which is then converted into the phosphonophosphate (IV), has been demonstrated[45,46] in the acetylation of dialkyl phosphite with vinyl acetate. The prototropic isomerisation of the esters of α-hydroxyallyl- and α-hydroxypropargyl-phosphonic acids to KPE has been observed recently[47,48]:

$$\underset{\text{(VIII)}}{CH_2{=}CHCH(OH)P(O)(OCH_3)_2} \xrightarrow{Na} \underset{\text{(IX)}}{CH_3CH_2C(O)P(O)(OCH_3)_2} .$$

The KPE (IX) formed in the intermediate stage acylates another molecule of the initial hydroxyacid ester (VIII).

The presence of halogen atoms in the α-position in the acyl halide frequently results in the reaction of the KPE (X) formed initially with the trialkyl phosphite via the mechanism of the Perkow reaction and the ultimate formation of unsaturated phosphonophosphates (XI):

$$\underset{X=Cl \text{ or } Br}{RCH(X)COX} + P(OR')_3 \rightarrow \underset{\text{(X)}}{[RCH(X)C(O)P(O)(OR')_2]} \xrightarrow{P(OR')_3} \underset{\text{(XI)}}{RCH{=}C\underset{\displaystyle OP(O)(OR')_2}{\underset{|}{P}}(O)(OR')_2} ;$$

Such a complex course of the reaction of the halides of α-halogeno-derivatives of acids with trialkyl phosphites, observed in a few instances, can be explained[11,36,49-52] on the basis of the modern interpretation of the mechanism of the Perkow reaction[53,54]. However, α-ketophosphonates of type (X) can be obtained not only from the halides of perhalogenocarboxylic acids and dialkyl phosphites[36-38] (see above), but also as a result of the reaction of hexafluorodimethylketen with dialkyl phosphite[55] or of the chlorides of chloroacetic acids with acetyl dialkyl phosphite[52].

The latter reaction has been used to elucidate the mechanism of the formation of unsaturated phosphonophosphates from α-halogenoacyl halides and trialkyl phosphites[52]. In principle, the interaction of chloroacetyl chloride with trialkyl phosphite, which leads to the unsaturated phosphonophosphate (XIV), could proceed either via chloroacetyl phosphonate (XII) (pathway *1*) or via chlorovinyl phosphate (XIII) (pathway *2*):

$$ClCH_2COCl + P(OR)_3 \rightarrow \left[\begin{array}{l} \xrightarrow{(1)} \underset{\text{(XII)}}{ClCH_2C(O)P(O)(OR)_2} \\ \xrightarrow{(2)} \underset{\displaystyle Cl}{\underset{|}{CH_2{=}COP(O)(OR)_2}} \quad \text{(XIII)} \end{array}\right] \rightarrow \underset{\displaystyle P(O)(OR)_2}{\underset{|}{CH_2{=}COP(O)(OR)_2}} \quad \text{(XIV)} .$$

When the less reactive acetyl diethyl phosphite is used, it is possible to isolate the chloro-substituted KPE (XIIa) together with a small amount of high-boiling products formed as a result of further reactions:

$$ClCH_2COCl + (C_2H_5O)_2P(O)COCH_3 \rightarrow \underset{\text{(XIIa)}}{ClCH_2C(O)P(O)(OC_2H_5)_2} .$$

Thus pathway 1—the initial Arbuzov reaction with subsequent Perkow reaction—is more probable.

In the synthesis of KPE by the classical version of the Arbuzov reaction phosphites of different structures have been used[11,17,28-32,52]. The study of the kinetics of this reaction with phosphoramidite esters in benzene and acetonitrile solutions showed[31] that its direction depends on the structure of the phosphoramidite: cyclic phosphoramidites are less reactive and tend to react anomalously when acted upon by benzoyl chloride. An analogous phenomenon has been described in a number of other studies[29,30,32]. It has been noted[32] that the direction of the reaction of phosphoroamidite esters with acetyl chloride depends on the environment of the phosphorus and nitrogen atoms—the introduction of more electron-donating groups at the phosphorus atom promotes the preferential formation of acetyl phosphonate. The full amides of phosphorous acid react with acetyl and benzoyl chlorides at the nitrogen atom and, when benzoyl chloride was used, it was possible to isolate[32] intermediate benzoylphosphonium halides.

On interaction with acyl chlorides in diethyl ether, fully *O*-triorganosilylated phosphorous acids give rise to KPE in high yields[56]. When mixed alkyl triorganosilyl phosphites are used in this reaction, the most electrophilic triorganosilyl group is always split off[17,18,57]:

$$(R_3SiO)_nP(OR')_{3-n} + R''COCl \rightarrow R''C(O)P(O)(OR')_{3-n}(OSiR_3)_{n-1} + R_3SiCl .$$

Among the specific methods for the synthesis of bis(triethylsilyl)acetylphosphonates, mention should be made of procedures based on the reactions of acetoxytriethylsilane under the influence of halogeno-derivatives of tervalent phosphorus[57,58].

The reactions of sulphur analogues of carboxylic and phosphorous acids have been less investigated. While trimethyl phosphite reacts with thiobenzoyl chloride via the standard mechanism[59], the interaction of acyl chlorides with phosphorothioites does not lead to the synthesis of thioanalogues of KPE.

III. STRUCTURE

The products of the reaction of trialkyl phosphites with acyl halides can have the structure of ketophosphonates (I) or the isomeric structure of mixed phosphites with a tervalent phosphorus atom (II). The structure (I) has proved to be fully consistent with the pronounced carbonyl functions of these compounds and the usually easy hydrolysis, leading to the regeneration of phosphorous acid, was fully accounted for by the isomeric phosphite structure (II). However, the first investigators of this reaction[8] were forced to recognise on the basis of the chemical properties (and later infrared spectroscopic studies) that the reaction products are α-ketophosphonates (I) and that the interaction therefore proceeds via the mechanism of the Arbuzov reaction. If one assumes a reaction mechanism involving the formation of phosphonium salts as intermediates (there is also evidence[60,61] for the formation of intermediate pentacovalent derivatives in some reactions), then evidently adducts with a tetrahedral configuration are formed as intermediates in this case[62]:

$$RCOCl + P(OR')_3 \rightarrow \left[\begin{array}{c} R \\ | \\ (R'O)_3\overset{+}{P}CCl \\ | \\ O^- \end{array}\right] \rightarrow (R'O)_3\overset{+}{P}COR\ Cl^- \rightarrow \underset{\text{(I)}}{RC(O)\overset{O}{\overset{\|}{P}}(OR')_2} .$$

Summarising the result of earlier studies[8,9,22], Hudson[63] claims that the phosphonates (I) are thermodynamically more stable that the isomeric phosphites (II). The formation of thermodynamically stable isomers is consistent with the concept that the transition states resemble the intermediate addition products, so that the energy of bond formation plays a decisive role.

Spectroscopic studies of KPE and in recent years comprehensive investigation of their chemical reactions confirmed the phosphonate structure of these compounds. The low frequency of the carbonyl vibrations is a consequence of the

conjugation between the C=O and P→O bonds and demonstrates[22] the absence of an oxygen atom between the acyl group and the phosphorus atom.

In the KPE containing cycloalkane and aliphatic acyl groups the absorption by the C=O and P→O groups varies over a short range. The introduction of the phenyl group[16], alkoxy- and thioalkoxy-groups[14], and halogens[52] in the β-position in the KPE displaces the frequency of the carbonyl vibrations to the region 1715–1733 cm^{-1}, while in KPE with a β,γ-unsaturated bond the C=O vibrations appear[10] at 1645 to 1660 cm^{-1}. A low absorption frequency of the C=O group (1639–1672 cm^{-1}) compared with α-diketones and aliphatic KPE (1685–1695 cm^{-1}) is observed in the series of aroylphosphonates[20,22,23,64] and the extreme values correspond respectively to *o*-chlorobenzoyl- and *p*-anisoyl-phosphonates.

The study of the infrared spectra of *para*- and *ortho*-substituted bis(triorganosilyl)benzoylphosphonates showed that the shift of the frequencies of the C=O groups depends on the electronic effects of the substituents in the aromatic ring and a correlation between the frequency shifts of the stretching vibrations of the carbonyl group with the Hammett σ constants was clearly observed[64].

The structure of the acyl group in KPE has a slight influence on the position of the P→O absorption band: in thiobenzoylphosphonate[59] the P→O group absorbs at 1280 cm^{-1}, while in alkoxyacetylphosphonate[14] it absorbs at 1260 to 1270 cm^{-1}. The structure of the ester groups at the phosphorous atom has a more significant influence and the phosphoryl group in alkyleneacylphosphonates[28] can absorb at 1280–1290 cm^{-1}.

The infrared spectra of the phosphonates obtained from the chlorides of mono- and di-chloroacetic acids contain, apart from the frequencies characteristic of the C=O and P→O groups, absorption bands at 1605 and 3000–3400 cm^{-1}. These data suggested[52] the occurrence of keto–enol tautomerism, which was subsequently confirmed by ^1H NMR[65]:

$$\underset{(87\%)}{ClCH_2C(O)P(O)(OR)_2} \rightleftarrows \underset{(13\%)}{ClCH{=}C(OH)P(O)(OR)_2}\ .$$

The ratio of the tautomers of dichloroacetylphosphonate is the same, while the phenylacetylphosphonate molecule is 82% enolised. The keto–enol equilibrium is apparently based[65] on the free energy of the enol form and not on the acid properties of the CH protons.

Chemists soon ceased to be satisfied with spectroscopic data as an additional confirmation of the structure of KPE and the problem of the study of their steric structure was posed. It proved to be complex, primarily because of two factors—the uncertainty of the function performed by the vacant 3*d* orbitals of the phosphorus atom and the possibility of different steric configurations—different relative positions of the carbonyl and the neighbouring phosphoryl group, in which the phosphorus atom can be asymmetric depending on the structure of the other two substituents. Apart from the importance of the study of the steric structure of KPE from the theoretical point of view, investigation of the nature of the mutual influence of adjacent phosphoryl and carbonyl groups is necessary to elucidate many anomalous reactions of KPE.

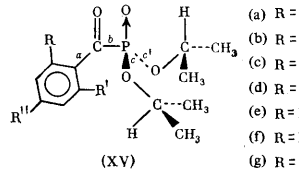
Remarkably low absorption frequencies of the carbonyl group in KPE have been observed by Berlin and Taylor[22], who explained this phenomenon by the reaction of the non-bonding orbital of the oxygen atom in the phosphoryl group with the π orbital of the carbon atom in the C=O group. The overlap of the orbitals then reaches a maximum when the P→O bond is at right angles to the plane in which the aromatic ring, the carbonyl carbon, and phosphorus are located. Thus Berlin and Taylor not only interpreted the spectroscopic characteristics of KPE from the standpoint of conjugation between the C=O and P→O groups, but also proposed a possible version of their relative positions in space. The additional interaction between the carbonyl group and the phosphoryl centre, presupposing the involvement of the 3*d* orbitals of the phosphorus atom, can be investigated by spectroscopic methods in KPE. Laskorin and coworkers[37,66] investigated different spectroscopic characteristics of ketophosphoryl compounds, in particular a series of dimethyl esters of acylphosphonic acids, differing from one another in the structure of the acyl group. It was noted that the decrease of ν(C=O) and the appreciable bathochromic shift of the $n \rightarrow \pi^*$ transition in dimethylacylphosphonates compared with the corresponding ketones indicate the conjugation of the carbonyl group with the phosphorus atom. After comparing ultraviolet, infrared, and ^1H NMR spectroscopic data, the authors[66] concluded that the effective positive charge on the phosphorus atom increases with increasing electronegativity of the acyl residue in dimethylacylphosphonates and that the carbonyl group is involved in conjugation with the 3*d* orbitals of the phosphorus atom to a greater extent.

The same workers[5] made a detailed study of different spectroscopic characteristics of KPE in order to detect the conformers whose existence had been suggested[67]. Different sterically hindered KPE, containing bulky substituents at the carbonyl group and the phosphorus atom, were synthesised. Their infrared spectra showed that they do not exhibit the *cis-trans* isomerism involving the P(O)–C(O) bond, since the ν(C=O) frequency is not split. A detailed study of the ultraviolet and ^1H NMR spectra of KPE showed[5] that the dynamic equilibrium between the isomers cannot be observed by spectroscopic methods. The occurrence of $p_\pi - d_\pi$ conjugation in KPE was again confirmed; the adoption of this concept implies that the rotation about the C–P bond cannot be free.

The first investigators[68] of the electronic spectra of the acylphosphonates also expressed the view that there is a significant conjugation in the P(O)–C(O) system. Ultraviolet spectroscopic data have been frequently invoked to characterise KPE [4,37,66–70] (the bathochromic shift of the $n \rightarrow \pi^*$ transition relative to the corresponding methyl ketone reaches 68 nm). In the studies enumerated above correlations are presented between the bathochromic shift of the $n \rightarrow \pi^*$ transition, as a measure of the $p_\pi - d_\pi$ conjugation, and the structure of the acyl group.

The application of NMR to the conformational analysis of KPE is at present restricted to several investigations[4,5,67], although the ^{31}P NMR spectra of diethyl acetylphosphonate had been published in still earlier studies[33]. The ^1H NMR spectra published in various communications[4,5,10,13,15,32,37,65–67,71,72] are of interest from the standpoint of the study of the spin–spin coupling constants between the P and H nuclei. In the case of dialkyl acetylphosphonates J_{P-H} for the methyl group adjoining the carbonyl group is 5 Hz, which is significantly less than *J* for trimethyl phosphate (11.2 Hz), dimethyl methylphosphonate (CH_3, $J = 17.5$ Hz; OCH_3, $J = 11$ Hz), and trimethyl phosphite ($J = 11$ Hz).

Clark et al.[4] used NMR for the conformational analysis of KPE in relation to diisopropyl esters of aroylphosphonic acids (XV, a-i):



(XV)

(a) R = R′ = R″ = H
(b) R = R″ = H, R′ = CH_3
(c) R = R′ = H, R″ = CH_3
(d) R = R′ = CH_3, R″ = H
(e) R = R″ = H, R′ = OCH_3
(f) R = R′ = H, R″ = OCH_3
(g) R = R′ = OCH_3, R″ = H
(h) R = R″ = H, R′ = Cl
(i) R = R′ = H, R″ = Cl

it was suggested[4] that the bulky isopropyl groups influence the preferred conformation of the system in which the angle between the C=O and P→O bonds can vary as a function of the nature of the substituents in the aromatic ring. A splitting, unusual for KPE, of the doublets due to the methyl group in the isopropyl group in consequence of their non-equivalence has been observed in the ^{1}H NMR spectra measured at temperatures from -50° to +100 °C. In compounds (XV, a, c, f, and i) the non-equivalence of the protons is observed between -50° and +20 °C, in the esters (XV, d, g, and h) between -50° and +100 °C, and in the compounds (XV, b and e) only at temperatures below -20 °C and at approximately +100 °C. Furthermore, the non-equivalence of the methylidyne protons of the isopropyl groups follows from the ^{31}P NMR spectra of the esters (XV, b and c). This fact suggests that, whatever the angle between the C=O and P→O bonds, the rotation about the P–O bond in these compounds (*c* and *c'*) must be restricted. On the basis of NMR data, the determination of dipole moments, infrared absorption, and theoretical calculations, the authors[4] concluded that the possibility of the existence of the system in a preferred conformation and of a restricted rotation about the C–P and possibly P–O bonds is ruled out. The authors[4] state that the earlier conclusion[73] that acylphosphonates exist as equilibrium systems of *s-cis*- and *s-trans*-isomers cannot be correct for the isopropyl esters (XV) according to their dipole moments. The C(O)–P(O) system does not need to be coplanar to achieve the overlap of the *d* and *p* orbitals of different sizes which ensure the d_π–p_π conjugation. The authors claim that the dihedral OPCO angle in the system can assume a series of values for which conjugation is achieved between the C=O and P→O bonds.

The study of the mass spectra of KPE showed[74] that, on electron impact, fragmentation evidently begins with ionisation of the oxygen of the carbonyl group and the dissociation of the P–C bond in consequence of the formation of the stable ion R–C ≡ O$^+$ (the latter is formed from the unstable KPE molecular ion). Among the fragments produced, other ions as well as keten and carbon monoxide were detected, but the formation of a fragment containing carbonyl and phosphoryl groups with simultaneous dissociation of other bonds at the phosphorus atom could never be observed. The P(O)–C(O) bond is least stable in KPE and this structural feature is reflected in a wide variety of chemical reactions of KPE.

IV. CHEMICAL PROPERTIES

The phosphorus–carbon bond, readily formed in the synthesis of α-ketophosphonates, is also readily ruptured under the influence of various nucleophiles. The decomposition of KPE under the influence of a weak nucleophile such as water is one of the chemical reactions observed for these compounds. The reactions of KPE with nucleophiles have been successfully classified by Pudovik and Gareev[75], who proposed a mechanism for the reactions of acetylphosphonate with compounds of type XH (or XNa) and diazoalkanes. The authors state that, when proton-containing compounds react with acetylphosphonate, the latter is cleaved at the P–C bond with formation of an acetic acid derivative and dialkyl phosphite. On the other hand, if the nucleophile is aprotic, the dissociation of the P–C bond is accompanied by the migration of the phosphorus-containing fragment. Numerous experimental facts confirm that the reactions take place generally via these pathways.

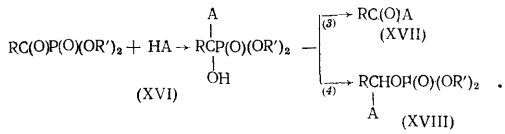
1. Interaction with Proton-Containing Compounds

The hydrolysis of KPE, which leads to a carboxylic acid, can be carried out in a neutral medium[76], but it proceeds faster and reaches completion in the presence of acids[8,22] and alkalies[8,22]. Bertin and Taylor[22] made the first attempt to elucidate the mechanisms of the alkaline and acid hydrolyses by making a detailed study of the decomposition of *p*-anisoylphosphonate. The authors state that the alkaline hydrolysis proceeds more readily and explain this phenomenon by the fact that in the acid hydrolysis the protonation of the phosphoryl group is reversible and the positive charge on the phosphorus atom hinders attack on the carbonyl group. They do not rule out an alternative mechanism, i.e. the slow protonation of the carbonyl group with subsequent rapid attack by water on the carboxonium cation. The formation of an intermediate in the alkaline catalysis resembles the hydrolysis of carboxylic acid esters. However, the true mechanism of the hydrolysis of acylphosphonates is probably more complex[77].

Acylphosphonates and halogeno-substituted KPE react with alcohols in an acid medium[78] or in the presence of a tertiary amine[79], forming unstable adducts; the latter decompose into the corresponding carboxylic acid esters and dialkyl phosphites. Benzoylphosphonate behaves as a benzoylating agent in reactions with thiophenoxides[21]. The rupture of the phosphorus–carbon bond is observed when KPE are acted upon by various amines–aniline[79,80], dialkylamines in the presence of a catalyst (magnesium bromide),[24] and liquid ammonia[81].

In the above reactions with water, alcohols, and amines KPE play the role of acylating agents. It has been shown[24] for dimethylbenzoylphosphonate that these reactions (which the authors[24] called "direct benzoylation") are accelerated by magnesium chloride and bromide. A similar catalytic effect for magnesium salts had been observed earlier in a study of the interaction of Grignard reagents with phosphonates[82].

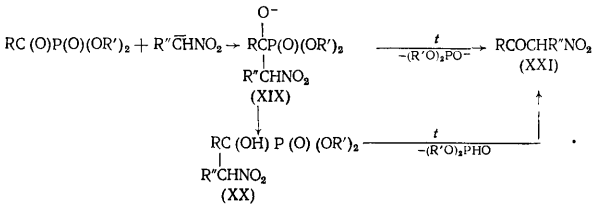
However, the reactions of KPE with proton-containing compounds can proceed also via different pathways, where the addition of the elements of HA to the carbonyl group leads to the formation of the α-hydroxyphosphonic acid ester (XVI). Under the conditions of alkaline catalysis, depending on the nature of A, the latter either decomposes with formation of the corresponding acylated compounds (XVII) or rearranges to a phosphoric acid derivative (XVIII):



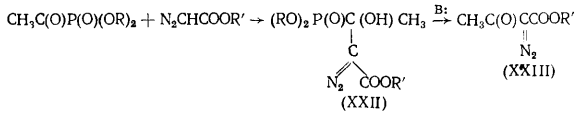
Reactions via pathway *3* are known as "indirect acylation" and have been thoroughly investigated[24] in relation to the reaction of benzoylphosphonate with *N*-magnesium derivatives of amines. The adducts formed under these conditions, containing a hydroxy-group and a substituted amino-group attached to the same carbon atom, proved to be unexpectedly stable; they can be distilled without decomposition. Under the influence of sodium methoxide, the adduct decomposes with liberation of dialkyl phosphite and an acylated amine. It has been suggested[47,48] that the same mechanism is valid for the acylation of β,γ-unsaturated *d*-hydroxyphosphonic acid esters [for example (VIII)] by α-ketophosphonates (IX), which are formed as a result of protoropic isomerisation when esters of type (VIII) are acted upon by metallic sodium.

Apart from the reactions discussed above, in which KPE behave as *O*- and *N*-acylating agents, it has been shown in recent studies[75,83,84] that they can acylate the carbon atoms

in nitroalkanes, alkylmagnesium bromides, and diazoacetic ester. In these reactions the α-hydroxyacid ester formed initially decomposes in the presence of bases at the carbon–phosphorus bond with elimination of the phosphorus-containing group and the *C*-acylated nucleophile. The acylated nitroalkane[83] (XXI) can be formed from the corresponding α-hydroxy-β-nitroalkylphosphonates (XX) while from the intermediate anion (XIX):

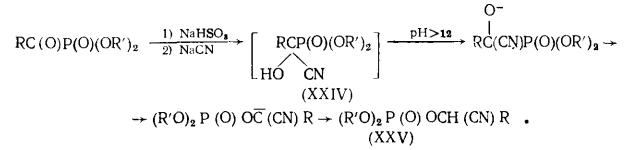


When acetylphosphonate condenses with diazoacetic ester, the product is the ester (XXII),[85,86] stable under neutral conditions, which decomposes under the influence of basic compounds (sodium methoxide, amines, diazomethane) [75] with formation of the ester of 1-diazo-2-oxobutanoic acid (XXIII):



In their study of the stability of compounds containing the O=P–C–OH fragment in the molecule, Pudovik and Gareev[75] suggested that the decomposition of α-hydroxyphosphonates is due to the mobility of the hydrogen atom of the hydroxy-group and the highly nucleophilic properties of the oxygen atom of the phosphoryl-group. The reactions of α-hydroxyphosphonate derivatives, formed when benzoylphosphonate interacts with Grignard and Reformatskii reagents, can be assigned to the same group of reagents (pathway *3*)—the adducts are cleaved with formation of alkyl phenyl ketones and benzoylacetate esters respectively[24,84].

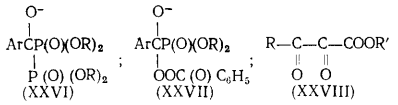
The conditions for the rearrangement[87,88] of α-hydroxyphosphonates to phosphoric acid derivatives (pathway *4*) have now been thoroughly investigated. The first reactions of this type were observed by Hall and Stephen when sodium cyanide was allowed to react with bisulphite compounds of KPE. Instead of the expected α-cyano-α-hydroxyphosphonic acid esters (XXIV), the isomeric phosphates (XXV) were obtained:



The pyrolysis of the phosphates (XXV) has been studied recently and the nitriles of α,β-unsaturated carboxylic acids were obtained in high yields[89]. The reactions of KPE with partially esterified phosphorus acids have been studied in fair detail. Such reactions sometimes accompany as side processes reactions involving the synthesis of α-ketophosphonate as the desired product. It was believed for a long time that the interaction of acetylphosphonate with sodium dialkyl phosphite and with dialkyl phosphite in the presence of amines leads to the hydroxydiphosphonate (III). The study of ^{31}P NMR spectra showed[33] that the products contain two non-equivalent phosphorus atoms. Under mild conditions (0 °C), it was possible to isolate diphosphonates of type (III), which are converted on distillation into the phosphonophosphates (IV). The conditions for the rearrangement were studied in greater detail by Pudovik and coworkers[34,45,46]. The phosphonophosphate (IV) has been obtained as a side product on heating acetylphosphonate with ethanol in the presence of triethylamine. The rearrangement to phosphates takes place readily[90] when dialkyl phosphites react with β-halogeno-substituted α-ketophosphonates without a catalyst.

In the case of asymmetric hydroxydiphosphonates (such diphosphonates have been obtained by the reaction of dialkyl acylphosphonates with derivates of ethylphosphinothioic[20] or dialkylphosphorothioic[91,92] acids as well as ethyl *N*,*N*-diethylphosphoramidite[93]) the structure of the isomerisation products (phosphates) was established by chemical and additional physicochemical methods[93].

In the course of the phosphonate–phosphate rearrangement the dialkoxyphosphono-group migrates from carbon to oxygen. α-Hydroxydiphosphonates obtained from aroylphosphonates isomerise particularly readily; the unstable intermediate ion (XXVI), containing three electron-accepting groups, is then stabilised by conversion into a phosphate:

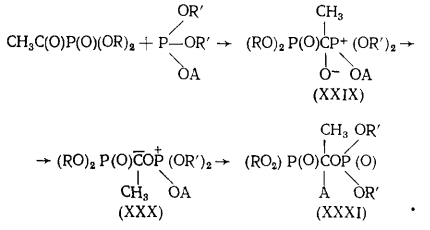


The preferred migration of the dialkoxyphosphono-group compared with the aryl group is observed in the oxidation of aroylphosphonates by perbenzoic acid[94]. The mixed anhydride of dialkylphosphorous and substituted benzoic acids is formed in high yield in this reaction from the intermediate addition product (XXVII).

2. Reactions with Aprotic Nucleophiles

For the majority of reactions of KPE with aprotic reagents, the attack of the nucleophile is directed to the carbon atom of the carbonyl group. The dipolar ion formed can be stabilised in different ways; however, the migration of the electrophilic group (frequently the dialkoxyphosphono-group) is characteristic of all cases of stabilisation.

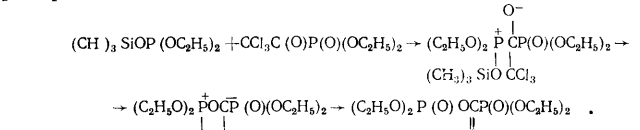
Part of the review of Konovalova and Pudovik[95] is devoted to the reactions of KPE and α-dicarbonyl compounds with trialkyl phosphites. They draw attention to the lower reactivity of KPE in the reaction with phosphites compared with α-ketocarboxylic acid esters (XXVIII) [96] and to a different course of the reaction. The interaction of trialkyl phosphites with the esters (XXVIII) usually leads to compounds having the 1,3,2-dioxophospholan structure, while KPE give rise to the phosphonophosphates (XXXI, A = alkyl). The reaction, occurring at 100–120 °C, probably begins with attack by the phosphite on the carbon atom of the carbonyl group and in the resulting zwitter-ion (XXX) the alkyl group migrates to the carbanionic centre of the molecule[97,98]:



When trimethylsilyl phosphite reacts with acetylphosphonate, the product is a diphosphonate[99]. Evidently[100] in this case the dipolar ion (XXIX, A = Si(CH$_3$)], which has

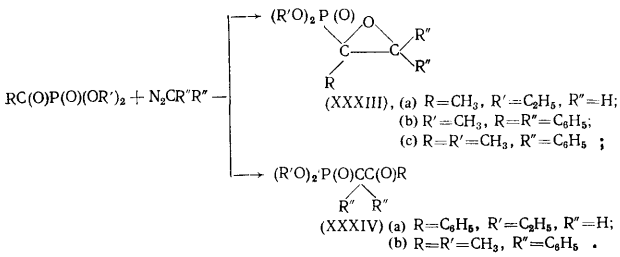
a harder electrophilic centre A, is rapidly stabilised as a result of the migration of the trimethylsilyl group and not the dialkoxyphosphono-group. The intermediate ion [XXIX, $A = C(O)CH_3$], formed by the interaction[101] of acetylphosphonate with acetyl phosphite, isomerises analogously.

The interaction of triethyl phosphite with β-halogeno-substituted KPE proceeds in a complex manner[36,52], discussed previously, with formation of a mixture of compounds including unsaturated phosphates. The reaction of trichloroacetyl phosphonate with mixed phosphites (trimethylsilyl and acetyl diethyl phosphite) is exothermic and leads to the same compound (XXXII). It has been suggested that, in the reaction with trimethylsilyl phosphite[102], the zwitter-ion is converted by the mechanism of the Perkow reaction into the phosphono-phosphate (XXXII):



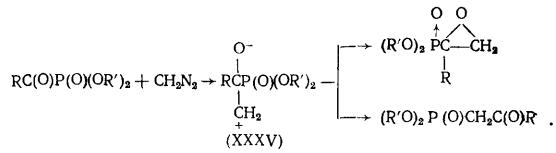
Aldehydes, which have a potentially mobile hydrogen atom in the formyl group (trichloroacetaldehyde, benzaldehyde), react with KPE via a mechanism of the type of benzoin condensation at 80 °C in the presence of piperidine. At a higher temperature the resulting "benzoins" isomerise to phosphates[103,104]. When trichloroacetylphosphonate was allowed to react with chloral, the product was an unsaturated phosphate[105], formed evidently from the initial "benzoin" anion as a result of the elimination of the chloride ion.

The reactions of KPE with diazoalkanes take place in different ways. Data have been published[106] on the interaction between certain KPE and diazomethane. The reaction of acetylphosphonate with diazomethane leads to the oxiran derivative (XXXIIIa) and benzoylphosphonate is converted into the β-ketophosphonate (XXXIVa). Acetyl- and benzoyl-phosphonates react with diphenyldiazomethane at 80 °C via one pathway with formation[107] of the epoxy-compounds (XXXIII, b and c). When the reaction of acetylphosphonate with diphenyldiazomethane was carried out at 0 °C, a mixture of products was obtained[108], consisting of derivatives of oxiran (XXXIIIc) and β-ketophosphonate (XXXIVb):



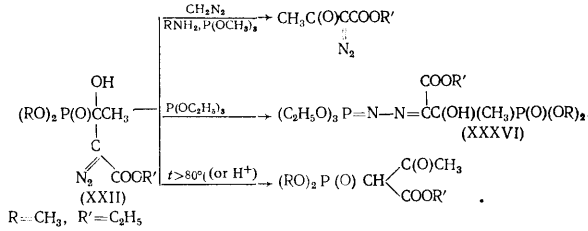
The authors[108] suggest that in the latter case both products are formed from the same intermediate ion. It was later shown[109] that, when benzoylphosphonate is acted upon by a threefold excess of diazomethane, the only reaction product is a compound to which the structure of the methyl ether of the enolic form of the β-ketophosphonate was attributed on the basis of spectroscopic data; evidently the carbonyl form enolises under the influence of diazomethane as a base. Under analogous conditions, diazoethane does not promote the enolisation of the corresponding ketophosphonate.

The mechanism of the reactions of KPE with diazoalkanes can be treated in different ways from the standpoint of the possible pathways leading to the formation of intermediates[109,110], but there is no doubt about the formation of a bond between the carbon atoms of the diazo-component and the carbonyl group of KPE [110]. The elimination of molecular nitrogen results subsequently in two pathways leading to the stabilisation of the ion (XXXV); for $R = CH_3$, both pathways operate, while for $R = C_6H_5$ only the second pathway is active:



In the transformation of the dipolar ion (XXXV, $R = C_6H_5$) to the stable β-ketophosphonate, the phosphorous-containing fragment migrates to the electron-deficient carbon atom. Contrary to expectation, the interaction of dimethyl acetylphosphonate with diazoethane leads to an oxiran derivative and not a β-ketophosphonate. On the basis of data obtained in the study of this reaction, it was concluded[111] that the nature of the final product of the reaction of KPE with diazoethane is independent of the type of substituent at the carbonyl group of the initial ketophosphonate.

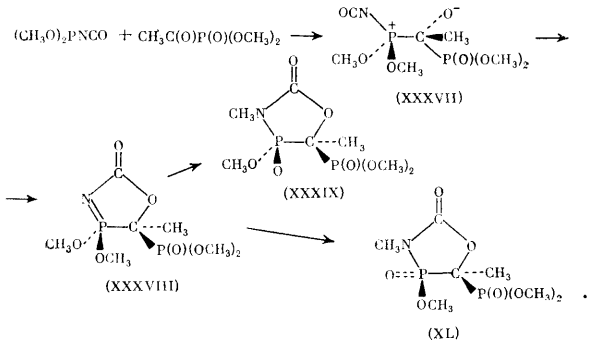
As already mentioned previously, the condensation of diazoacetate ester with acetylphosphonate led unexpectedly to the formation of a product of the aldol type (XXII), [86] which undergoes interesting reactions. Under the influence of diazomethane[75] or trimethyl phosphite[112] as bases, the ester (XXII, $R = CH_3$, $R' = C_2H_5$) is cleaved at the carbon–phosphorus bond with liberation of dimethyl phosphites. Under these conditions, the reaction with triethyl phosphite leads to the phosphazine system (XXXVI),[112] which is cleaved hydrolytically with elimination of triethyl phosphate. On heating above 80 °C or under the influence of acids, the ester (XXII) undergoes 1,2-fragmentation of a new type, which yields dialkoxyphosphonylacetoacetic ester. The mechanism of the formation and the structure of the latter have been studied in detail[113–115]:



A series of studies by Japanese workers were devoted to the investigation of KPE with thiazolium and benzimidazolium salts. A derivative of 2-substituted 1,4-thiazine was obtained from benzoylphosphonate and thiamine in the presence of bases[21,116,117]. Subsequently the reaction was extended to different *N*-substituted thiazolium salts[118–123] and 1,3,4-oxadiazolium salts[124], and in some cases intermediate isomerisation products were isolated[121]. It has been suggested that in all cases the nucleophilic thiazolium centre adds to the carbon atom of the carbonyl group in KPE. This is followed by isomerisation to a phosphate, which hydrolyses on treatment with alkali with formation of an enol. Ring expansion then takes place as a result of the insertion of a new carbon atom with formation of a 1,4-thiazine derivative. The reactions of KPE with benzimidazolium salts yielded adducts[125], which do not give rise to quinoxaline derivatives on alkaline hydrolysis.

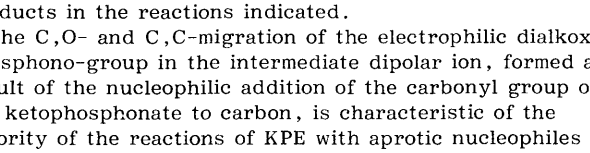
The interaction of KPE with phosphoroisocyanatidites results in the formation of zwitter-ions [for example, (XXXVII)], the pathway leading to the stabilisation of which

is determined by the presence of several reaction centres. In the case of dialkyl phosphoroisocyanatidites, three structural isomers are formed[126,127] (demonstrated by infrared spectroscopy). A detailed study of the reaction[128] between dimethyl phosphoroisocyanatidite and acetylphosphonate at reduced temperatures made it possible to observe a new type of isomerisation of the zwitter-ion to the intermediate (XXXVIII) with subsequent conversion into a mixture of two configurational isomers of the substituted phosphaoxazolidinone, (XXXIX) and (XL), with a P–C bond in the ring:



The reaction of dialkyl phosphoroisocyanatidites with chloro-substituted acetylphosphonates does not proceed unambiguously. Whereas the only product of the interaction with trichloroacetylphosphonate is[129] a phosphonophosphate, resulting from the Perkow reaction, the interaction with mono- and di-chloroacetylphosphonate under analogous conditions leads[130] to a mixture of products. One of these is a phosphonophosphate and the other is a substituted phosphaoxazolidinone with a P–O–C linkage in the ring. A similar feature was noted in the behaviour of chloro-substituted acetylphosphonates in relation to alkyl phosphorodi-isocynatidites[65,131]. The migration of the alkyl group to the nitrogen atom is characteristic of the formation of cyclic products in the reactions indicated.

The C,O- and C,C-migration of the electrophilic dialkoxyphosphono-group in the intermediate dipolar ion, formed as a result of the nucleophilic addition of the carbonyl group of the ketophosphonate to carbon, is characteristic of the majority of the reactions of KPE with aprotic nucleophiles examined above. However, one can postulate also direct attack by phosphorus on the oxygen atom of the carbonyl group in the reaction of KPE with phosphoramidite[132]:



The complex-forming properties of KPE have been studied inadequately. The formation of a complex on interaction of dimethyl benzoylphosphonate with aluminium chloride has been reported[24]. Molecular complexes[133] of aroylphosphonates with tin and titanium tetrahalides have been described; it has been established by infrared spectroscopy that the metal in the complex is coordinated to the carbonyl and phosphoryl groups. Diethyl acylphosphonates behave as bidentate ligands in the reaction[134,135] with 3*d* metal perchlorates. The reaction between aroylphosphonates and nickel complexes with cyclo-octa-1,5-diene proceeds via a different pathway: the arolyphosphonates are cleaved at the C–P bond[136].

The synthesis of free α-ketophosphonic acids from the esters involves certain difficulties because of the hydrolytic instability of the phosphorus–carbon bond in the KPE molecule mentioned above. In a study of the use of aroylphosphonates as alkylating agents for the synthesis of *p*-toluenesulphonic acid esters, Golborn[137] isolated also acylphosphonic acids. Zygmunt et al.[138] reviewed briefly data on the dealkylation of acylphosphonates and suggested that the dealkylation can be carried out with the aid of trimethylsilyl iodide. KPE are silylated under mild conditions; the resulting trimethylsilyl α-ketophosphonate esters are readily hydrolysed by water under neutral conditions.

3. Reactions Involving the Substitution of the Carbonyl Oxygen

The traditional qualitative reactions of ketones are also undergone by KPE, which form phenylhydrazones and oximes. The methods for the preparation of arylhydrazones are various–heating with arylhydrazine in absolute alcohol, the addition of an ethereal solution of the KPE to solid *p*-nitrophenylhydrazine, and reactions in the presence of sulphuric acid. It is remarkable that β-halogeno-substituted KPE do not form[66,76] *p*-nitrophenylhydrazones and oximes. This fact has been explained[66] by the reduced amount of double bond character in the carbonyl group owing to the p_π-d_π conjugation with the phosphorus atom. KPE oximes (more rarely phenylhydrazones) have been used as the starting compounds in the synthesis of various α-aminophosphonic acids[2]. Apart from aluminium amalgam[23], diborane[139] and hydrogen over Raney nickel[16] have been used as reducing agents.

The conversion of acetylphosphonates into derivatives of α,β-unsaturated phosphonic acids has been described[140]. When acetylphosphonates react with cyanoacetic ester in the presence of amines, it is possible to obtain either the corresponding α-hydroxyphosphonates or their dehydration products, depending on the reaction temperature. α-Hydroxyphosphonates, obtained by the condensation of acetylphosphonate with malonodinitrile, are readily dehydrated[140].

Dialkylphosphonodiazoalkanes have been synthesised by the decomposition of the tosylhydrazones of aliphatic KPE;[10,141,142] subsequently this method was extended[143] to aroylphosphonates. It has been suggested[71] that diazoalkylphosphonates be synthesised from the tosylhydrazones of KPE by treatment with sodium borohydride in methanol. A review has been devoted to the chemistry of aryldiazoalkylphosphonates[3].

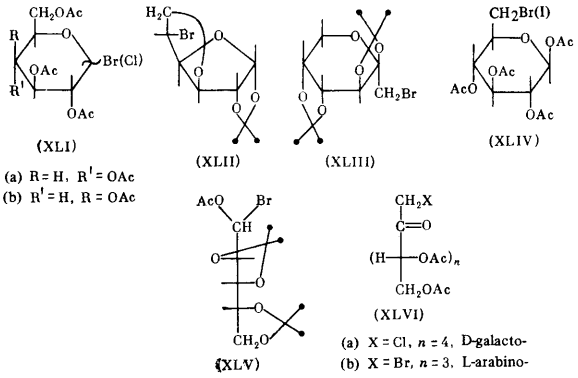
The photochemical reactions of aroylphosphonates[70,144] are distinguished by a wide variety of reaction products. This behaviour is determined by the structure of the aroylphosphonate and the coreactant in the photochemical reaction. When diethyl benzoylphosphonate is irradiated with the light of a mercury lamp, a trioxan derivative is formed as a result of trimerisation; isopropyl and butyl esters undergo the pinacol rearrangement under these conditions. In methanol solution methyl benzoate is formed from these esters. Irradiation of substituted azirine in the presence of benzoylphosphonate leads to a satisfactory yield of a phosphonate-substituted oxazoline, whereupon the diatomic C–O bond is inserted in the ring[144].

The conversion of KPE into alkylphosphonates can be achieved by reducing α-diazoalkylphosphonates with sodium borohydride in boiling tetrahydrofuran[71] or by electrochemical reduction[145].

V. CARBOHYDRATE-CONTAINING α-KETOPHOSPHONIC ACID ESTERS

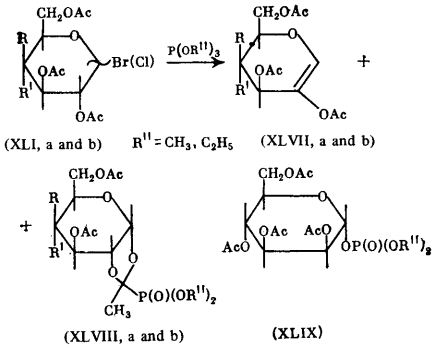
Numerous examples in which the usual organic reactions take place via non-standard pathways are known in carbohydrate chemistry. The Arbuzov reaction, applied to

halogen-containing monosaccharides in order to obtain carbohydrate derivatives with a phosphorus–carbon bond, is no exception in this sense. In the classical version of the Arbuzov reaction the principal types of halogeno-derivatives of monosaccharides (XLI)–(XLVI) have been used:



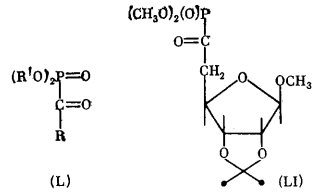
Among these compounds, only (XLIV) and (XLV) yield the "normal" products of the Arbuzov reaction–the corresponding carbohydrate-containing phosphonates[146–148]; compound (XLII) is reduced[149] by triethyl phosphite; acetohalogenoses (acetylated 1-halogeno-monosaccharides), for example, (XLI, a and b), react to form anomalous compounds, while compound (XLIII) does not react with trialkyl phosphites even under severe conditions. Acetylated non-cyclic halogenoketoses (XLVI) undergo the Perkow reaction on treatment with triethyl phosphite to form vinyl phosphates[150].

In the general case the interaction of acetohalogenoses with trialkyl phosphites results in a mixture of compounds[6,7,151], the ratios of which depend on the configuration of the initial halogenose:



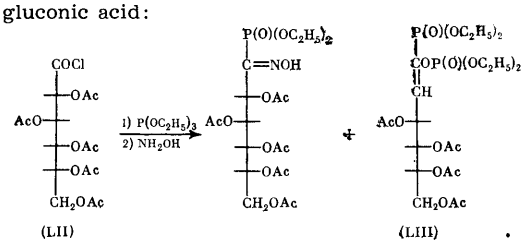
Compounds (XLVIII, a and b) are formed from the acetohalogenoses (XLI, a and b) and trialkyl phosphites in 12–15% yield and by the Michaelis–Becker reaction (using the mercury and silver salts of dialkylphosphorous acids) in 20 to 80% yield. The glucal (XLVIIa) and the phosphate (XLIX) were isolated after the reaction of α-acetobromomannose with trialkyl phosphites. The probable mechanism of the formation of acetylphosphonates (XLVIII) under the conditions of the Arbuzov reaction is believed[151] to involve the formation of an intermediate acetoxonium ion, which combines with triethyl phosphite and then eliminates ethyl halide. It is remarkable that in the acetylphosphonates (XLVIII) the carbon–phosphorus bond is stable and the conversion of these phosphonates into the glycal (XLVII) has not been observed in any one instance. Compound (XLVIII) is a cyclic ketal of acetylphosphonate and exhibits a stability characteristic of KPE ketals[152] with respect to the action of alkaline agents. It has been suggested that α-ketophosphonates are formed in the oxidation of carbohydrate-containing α-hydroxyphosphonates by sodium periodate[153].

The synthesis of carbohydrate-containing α-ketophosphonate (L) (R is a polyol residue with protected hydroxy-groups) from the chlorides of acetylated aldonic acids was first reported by Zhdanov et al.[154]; the synthesis of compound (LI) from the chloride of uronic acid and trimethyl phosphite was described subsequently[72]:



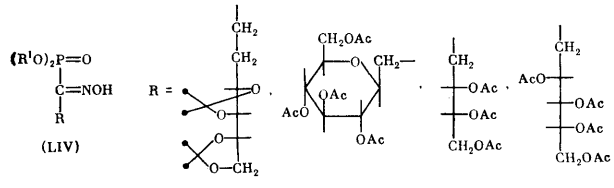
The esters (L) have been isolated in low yields as hydroxyimino-derivatives. The principal reaction products are[155] diphosphoryl-containing compounds, the structure of which has been established with the aid of NMR and infrared specta; the alkyl esters of aldonic acids have also been obtained.

Diphosphorylcarbohydrate reaction products, with non-equivalent phosphorus atoms, an olefinic bond, and a smaller number of acetyl groups than in the initial acid halide, are formed via the Perkow reaction mechanism. α-Ketophosphonates with highly reactive carbonyl groups and an acetoxy-group activated by α-carbonyl and β-phosphoryl functional groups are obtained in the first stage and react with the excess phosphite. The α,β-unsaturated phosphonophosphates formed have been isolated as isomeric compounds. Thus compound (LIII) is formed from the chloride of acetylated D-gluconic acid:



Similarly compound (LII) reacts with tri-isopropyl phosphite and the chlorides of D-galactonic and D-arabonic acids react with triethyl phosphite[155]. It is of interest to note that the Perkow reaction observed for carbohydrate-containing α-ketophosphonates takes place under very mild conditions (at 25 to 30 °C), while in the case of the carbonyl forms of monosaccharides the enol phosphates are formed only on heating with triethyl phosphite to 85–140 °C.[156,157]

The interaction of trialkyl phosphites with the chlorides of desonoic acids gives high yields of carbohydrate-containing α-ketophosphonates, which have been identified as the oximes (LIV).[158] Such phosphonates are phosphorus analogues of 2-oxo-3-deoxyaldonic acids:



Carbohydrate-containing phosphonic acids, obtained from compounds of type (LIV) after removing the protecting groups at the phosphorus atom and in the carbohydrate residue, can apparently be used as substrates and inhibitors in the study of their interaction with a number of enzymes[159, 160]. This conclusion is based on convincing data[161] for the inhibition of pyruvate dehydrogenase by the phosphonate analogue of pyruvate and for the inhibition of acetyl-CoA synthetase when the substrate is acted upon by adenosine 5'-chloroacetylphosphonate[162].

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