U.D.C. 547.558.1

Reactions of Derivatives of Phosphorus(III) Acids with Carbonyl Compounds

I.V.Konovalova and A.N.Pudovik

The review describes the reactions of fully esterified phosphorous acids, phosphoramidites, and the mixed anhydrides of dialkylphosphorous and carboxylic acids with carbonyl compounds not containing halogens: unsaturated and saturated aldehydes and ketones, α-diketones, and carbonyl compounds activated by ethoxycarbonyl, phosphoryl, nitrile, or any other electronegative group. The modes and mechanisms of these extremely varied and interesting reactions, which are important for progress in the chemistry of organophosphorus compounds and theoretical organic chemistry, have been examined.
The bibliography includes 188 references.

CONTENTS

I. Introduction 411
II. Reactions of derivatives of phosphorus(III) acids with aldehydes and ketones 411
III. Reactions of derivatives of phosphorus(III) acids with aldehydes and ketones activated by electronegative groups 417

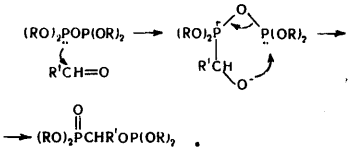
I. INTRODUCTION

One of the most important and interesting reactions in the chemistry of organophosphorus compounds is the Arbuzov reaction (A.E. Arbuzov) in which fully esterified phosphorus(III) acids react with alkyl halides and other halogen-containing organic compounds. However, in recent years there has arisen another extremely interesting and promising trend in the research on the chemistry of organophosphorus compounds involving reactions of fully esterified phosphorous acids, phosphoramidites, and mixed anhydrides with various organic compounds not containing halogen atoms. These reactions lead to the formation of compounds with a tetra- or penta-coordinate phosphorus atom. Reactions of this type proved to be extremely varied owing to the fact that the phosphorus atom exhibits biphilic properties under these conditions, which allows both electrophilic and nucleophilic interactions. Vigorous study of these reactions greatly extended synthetic possibilities in organic chemistry, led to the discovery of a number of extremely interesting types of reactions of organophosphorus compounds, and resulted in the introduction of many new features in the investigation of their mechanisms. A particularly large number of studies have been made on the reactions of derivatives of phosphorus(III) acids with various carbonyl compounds, which are the most important and interesting reactions of this type. Despite their specificity, in many cases they may be regarded as varieties of the Arbuzov reaction, proceeding via a general two-stage mechanism in which the first or both phases of the Arbuzov reaction take place. It is noteworthy that individual reactions of carbonyl compounds, mainly with phosphites, have been described in monographs dealing with particular aspects of the chemistry of organophosphorus compounds published abroad in previous years[1,2] and also in reviews and research reports in which the results of the investigators' own work are discussed[3-8]. In the present review, the authors' aim was to examine fully and systematically the reactions of derivatives of phosphorus(III) acids with carbonyl compounds without halogen atoms which have been described in the literature. Reactions of this type with phosphorus(III) acid chlorides were discussed in the review of Pudovik and Khairullin[9].

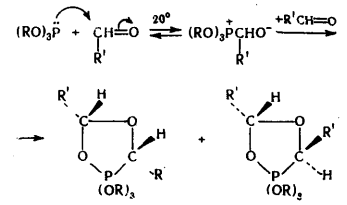
II. REACTIONS OF DERIVATIVES OF PHOSPHORUS(III) ACIDS WITH ALDEHYDES AND KETONES

1. Reactions with Saturated Aldehydes and Ketones

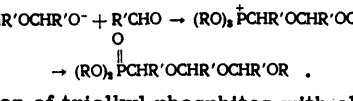
The reactions of phosphorus(III) acid esters with aldehydes were investigated for the first time by Arbuzov and Alimov, who established that pyrophosphites react with aldehydes to form products containing tri- and tetracoordinate phosphorus atoms[10]:



At room temperature aliphatic aldehydes react extremely slowly with trialkyl phosphites[11]. As a result of attack by the phosphorus atom on the carbon atom of the carbonyl group, an unstable 1:1 adduct is formed, further reaction of which with a second aldehyde molecule leads to diastereoisomeric 1,2,4-dioxaphospholans[11]:



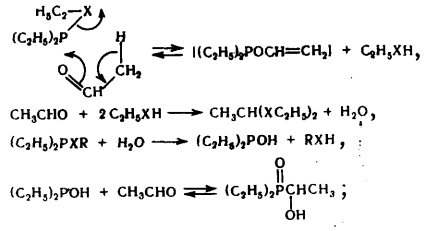
In the presence of an excess of the aldehyde, a 3:1 adduct is formed, which is stabilised by conversion via intramolecular dealkylation into the corresponding phosphonate[4]:



The reaction of trialkyl phosphites with aliphatic aldehydes at an elevated temperature also takes place with formation of products resulting from the addition of two

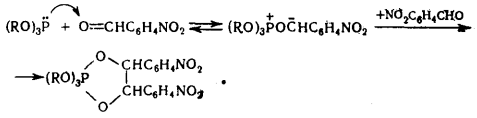
and three aldehyde molecules and having a linear structure[12].

The esters of diethylphosphinous and diethylphosphinothious acids react differently with acetaldehyde: the products are α-hydroxyethyldiethylphosphine, and diethylphosphine oxides and the diethylmercaptal or diethylacetal of acetaldehyde[13]. According to the authors, these reactions involve nucleophilic substitution with formation of a cyclic transition complex:

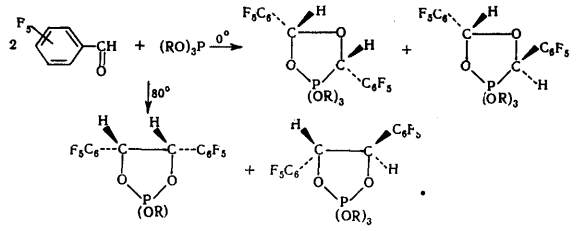


where X = O or S and R = C_2H_5 or CH = CH_2.

In contrast to data published previously[14], Ramirez showed that *o*- and *p*-nitrobenzaldehydes condense under mild conditions with trialkyl phosphites to form 1,3,2-dioxophospholans[15]. He postulates that the presence of electronegative substituents in the aldehyde molecule may be responsible for the direct attack of the phosphorus atom on the oxygen atom of the carbonyl group, which leads to the formation of an intermediate adduct with a P — O — C linkage:

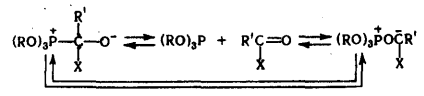


However, the possibility of the attack by the phosphorus atom also on the carbon atom of the carbonyl group, by analogy with unsubstituted aldehydes, resulting in the formation of an intermediate adduct having a P — C bond, which subsequently rearranges further to an adduct with a P — O — C linkage, is not ruled out in these reactions. This hypothesis is confirmed by the reaction of pentafluorobenzaldehyde with trialkyl phosphites which takes place with formation of 1,4,2-dioxophospholans at a low temperature and 1,3,2-dioxaphospholans at an elevated temperature[16,17]:

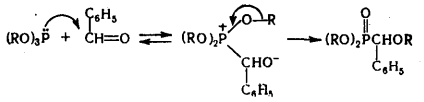


On dissolution, 1,4,2-dioxophospholan may be converted into 1,3,2-dioxaphospholan. It is suggested that this process involves the dissociation of the P — O and C — O bonds in 1,4,2-dioxaphospholan with regeneration of the aldehyde molecule and the formation of a 1 : 1 adduct with a P — C — O linkage, which rearranges into a 1 : 1 adduct with a P — O — C linkage; this adduct subsequently reacts with an aldehyde molecule to form 1,3,2-dioxaphospholan.

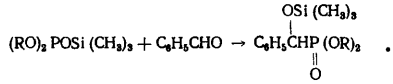
Thus it proved possible to demonstrate for pentafluorobenzaldehyde the initial formation of an adduct with a P — C — O linkage and its transformation into one with a P — O — C linkage. The mechanism proposed is probably general for reactions of tervalent phosphorus with activated carbonyl compounds. Possibly in these reactions there is equilibrium between the initial reactants and the adducts with P — C — O and P — O — C linkages[18]:



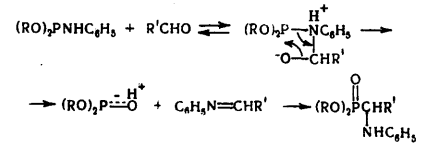
m-Nitrobenzaldehyde and aromatic aldehydes with electropositive substituents are inert with respect to trialkyl phosphites below 100°C.[15] At elevated temperatures aromatic aldehydes react with trialkyl phosphites via a mechanism involving the Arbuzov rearrangement with formation of alkoxyalkylphosphonic acid esters[19]:



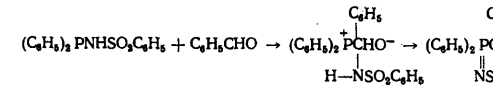
These reactions are accompanied by the oxidation of phosphites to phosphates[20]. Reactions of aromatic aldehydes with alkyl trialkylsilyl phosphites take place similarly[21]:



The reactions of aldehydes with phosphoramidites are extremely interesting and varied. Dialkyl *NN*-dialkylphosphoramidites and phenylphosphonamidous acids[24] react with aldehydes to form esters of α-aminoalkylphosphonic acids[25]. Evdakov postulated that in these reactions the phosphorus atom attacks the carbon atom of the carbonyl group, but subsequently Hudson and other investigators showed that in most cases these reactions involve the initial attack by the nucleophilic nitrogen atom on the carbon atom of the carbonyl group. Dialkyl *N*-phenylphosphoramidites react with aldehydes similarly. The intermediates formed are dialkyl phosphites and Schiff bases, the interaction of which leads to the final reaction product[26-28]:

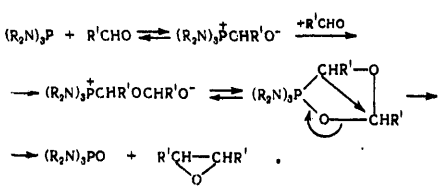


Earlier another reaction mechanism was suggested for dialkyl *N*-phenylphosphoramidites[29,30]. Pudovik and Batyeva showed that the reaction of *N*-diphenylphosphinobenzenesulphonamide and benzaldehyde takes place differently. In the benzenesulphonamide the nucleophilic activity of the nitrogen atom is reduced owing to the electron-accepting group linked to it, as a result of which the reaction takes place via the phosphorus atom[31]:



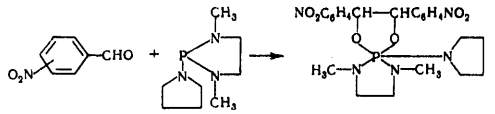
Phosphorous tris(dialkylamides) react with aliphatic, aromatic, and heterocyclic aldehydes with formation of various products. When there are electropositive substituents in the aldehyde, a 1 : 1 adduct having a dipolar structure and a P — C bond is formed. The presence of electronegative substituents promotes the interaction of the 1 : 1 adduct with a second aldehyde molecule to form *NNN*-tris(dialkyl)phosphoramides and epoxy-compounds.

It is suggested that the epoxy-compounds are formed via an intermediate 1,4,2-dioxaphospholan[32]:

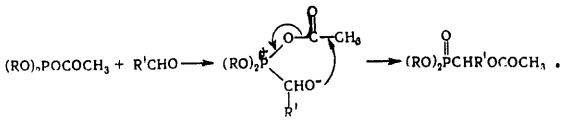


According to Ramirez[18], the formation of an epoxide in the reaction of phosphorous tris(dimethylamide) with nitrobenzaldehyde takes place via intermediate 2:1 adducts which have the structure of dipolar ions with a P—O—C linkage.

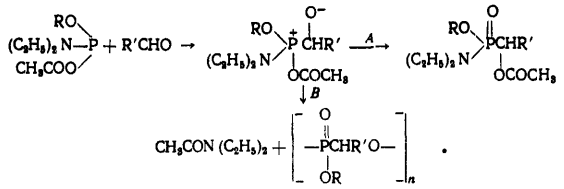
When nitrobenzaldehyde reacts with cyclic phosphorous triamides, stable spiro-1,3,2-dioxaphospholans are formed[18]:



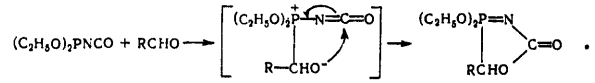
Mixed anhydrides of phosphorous and carboxylic acids readily react with aldehydes via a mechanism involving the Arbuzov rearrangement with formation of acyl derivatives of α-hydroxyalkylphosphonic acid esters[33-36]. In this case the attack by the negatively charged oxygen atom in the intermediate dipolar ion is directed to the electrophilic and sterically accessible carbon atom of the acetyl group:



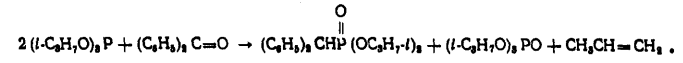
When phosphoramidoacetatidites react with aliphatic aldehydes, the reaction takes place predominantly according to mechanism *A*, while with benzaldehyde mechanism *B* obtains[36]:



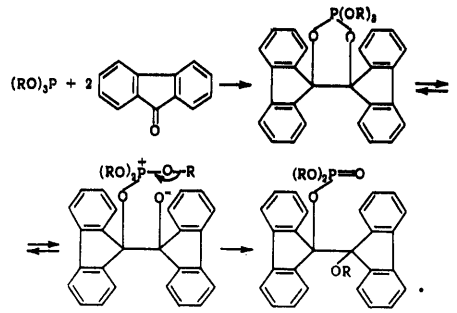
Diethyl phosphoroisocyanatidite reacts with benzaldehyde, *p*-chloro-, *p*-bromo-, and *p*-methoxy-benzaldehydes, and butyraldehyde to form cyclic esters of alkyldiethoxyphosphazocarbonic acid and polymeric 1:1 adducts; the cyclic bromobenzyldiethoxyphosphazocarbonic acid ester is converted on heating into a polymeric adduct[37]:



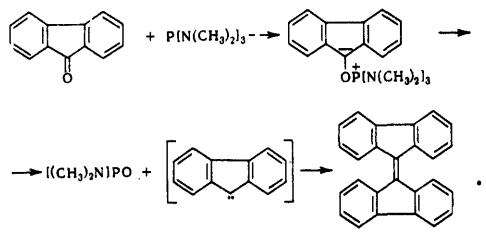
In many cases ketones react with trialkyl phosphites somewhat differently than aldehydes. Thus the reactions of tri-isopropyl phosphite with benzophenone and 4,4′-dichlorobenzophenone take place slowly on prolonged heating with formation of tri-isopropyl phosphate, di-isopropyl diphenylmethylphosphonate, and propene[38]:



Fluorenone reacts with trialkyl phosphites at room temperature to form 1,3,2-dioxaphospholans. In a polar solvent the phospholan may exist partly in an open-chain dipolar form and may be converted into phosphate as a result of dealkylation[39]:

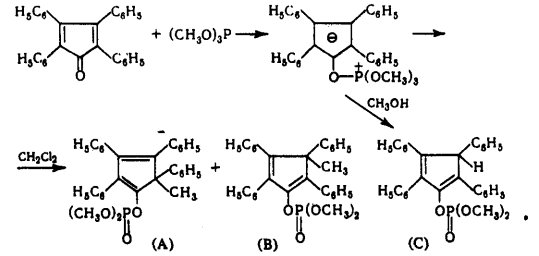


In the reaction with tri-isopropyl phosphite, tri-isopropyl phosphate and phenanthrone were isolated[38], while in the presence of an excess of phosphite the reaction proceeds via a mechanism analogous to that described above for benzophenone[38]. The reaction of fluorenone with phosphorous tris(dialkylamide) results in the formation of *NNN*-tris(dialkyl)phosphoramide and dibiphenyleneethylene, the latter probably resulting from the dimerisation of a carbene[40]:



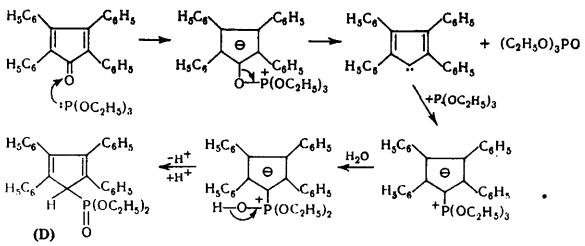
Cyclic phosphorous triamides form with fluorenone spiro-1,3,2-dioxaphospholans[40].

The mode of reaction of trialkyl phosphites with tetraphenylcyclopentadienone depends on the conditions[41,42]: a mixture of isomeric enol phosphates (A) and (B) is formed in dichloromethane and in methanol the product is compounds (C)[41]:

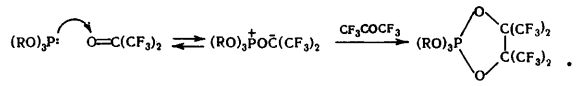


When tetracyclone reacts with trialkyl phosphites in aqueous ethanol, a more complex mixture of products is

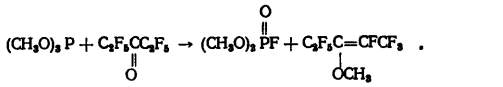
formed, the main component of which is the phosphonate (D). The proposed reaction mechanism includes the formation of a carbene and an ylide as intermediates[42]:



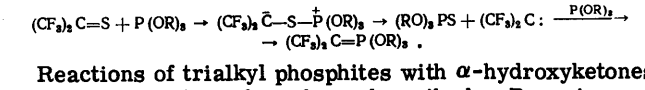
The reaction of derivatives of phosphorus(III) acids with perfluoroketones takes place very readily. Hexafluoroacetone reacts with trialkyl phosphites, phosphonites, phosphinites[43-46], *NN*-dialkylphosphoramidites[47], phosphorous tris(dialkylamides)[40,46], and cyclic phosphorous triamides[40] at low temperatures with formation of 1,3,2-dioxaphospholans:



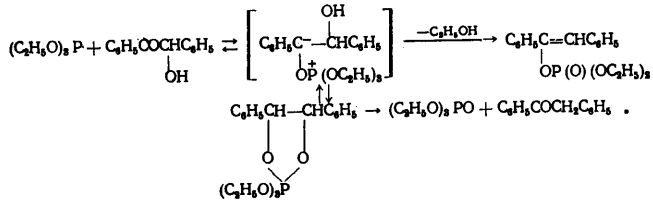
At an elevated temperature perfluoroketones form with trialkyl phosphites dialkyl phosphorofluoridites and enolic ethers derived from ketones[48]:



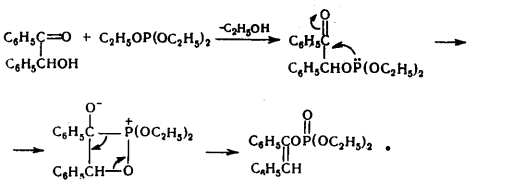
A more complex mixture is formed at an elevated temperature with phosphorous tris(dialkylamides)[46,49]: the main product is bis(dialkylamino)difluorophosphorane[46]. Trialkyl phosphites were found to react differently with hexafluorothioacetone[50]:



Reactions of trialkyl phosphites with α-hydroxyketones and their derivatives have been described. Benzoin reacts with triethyl phosphite at 180°C: the formation of an intermediate dipolar ion, which is stabilised by conversion into an enol phosphate with elimination of an alcohol or is converted into 1,3,2-dioxaphospholan, has been suggested. 1,3,2-Dioxaphospholan decomposes under the reaction conditions into triethyl phosphate and deoxybenzoin[51]:

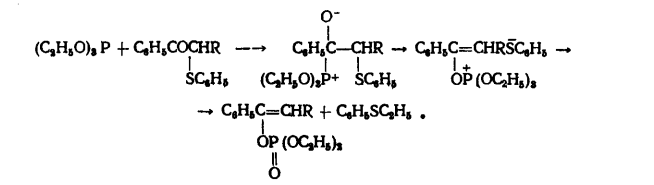


An enol phosphate is formed in the reaction of benzoin with triethyl phosphite in the presence of sodium[52]. In this case a somewhat different mechanism has been proposed:

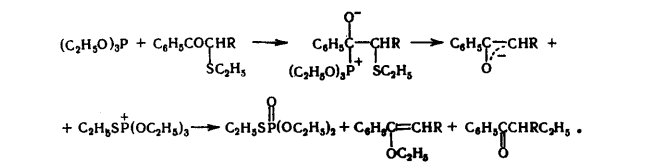


Benzoin acetate also reacts with the phosphite to form an enol phosphate[51].

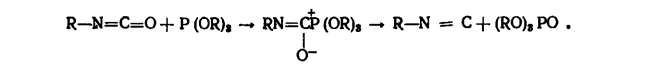
Depending on their structure, α-ketosulphides react with triethyl phosphite in two ways[53]. If the alkyl(aryl)-thio-group can be split off as an anion, the corresponding enol phosphate and ethyl phenyl sulphide are formed:



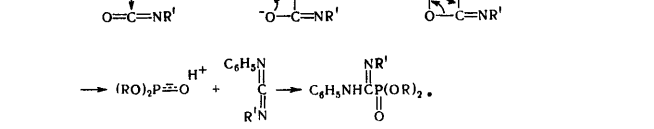
In the case of benzyl ethyl sulphide, the ethylthio-group is split off as an anion with greater difficulty and the reaction proceeds preferentially with formation of a vinyl ether or ketone derivatives[53]:



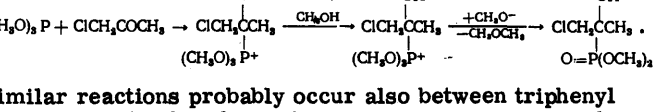
The reactions of isocyanates with trialkyl phosphites result in the formation of trialkyl phosphates and isonitriles[54]:



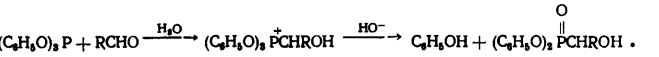
Dialkyl *N*-phenylphosphoramidites react with aromatic isocyanates to form dialkyl *NN'*-diphenylamidinophosphonates[55]. The reaction proceeds according to a mechanism involving the initial attack by the nitrogen atom on the carbon atom of the carbonyl group:



When the reactions of aldehydes and ketones with trialkyl phosphites are carried out in the presence of proton-donating agents, the intermediate dipolar ions are stabilised by the addition of a proton; the subsequent intramolecular dealkylation leads to the formation of α-hydroxyalkylphosphonates[56]:



Similar reactions probably occur also between triphenyl phosphite and aldehydes and ketones in an aqueous medium[2,57]:



When carbonyl compounds react with trialkyl phosphites in the presence of phosphorus trichloride or other acid chlorides, the intermediate addition product reacts with them to form tris-(α-dialkoxyphosphonoalkyl) phosphites[58]:

Ivanov showed recently that trialkyl phosphites are capable of condensing with formaldehyde and compounds containing a mobile hydrogen atom in the methylene group, forming the corresponding phosphonomethyl derivatives[59-61]:

$$(RO)_3P + CH_2O + HCHXY \rightarrow (RO)_2\overset{\overset{O}{\|}}{P}CH_2CHXY + ROH .$$

Aliphatic and aromatic aldehydes and furfural undergo this reaction. It is suggested that it proceeds according to the following mechanism[60]:

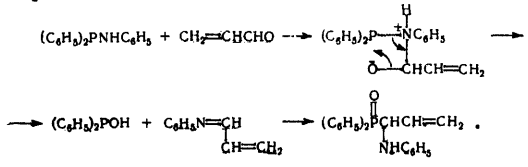
$$(RO)_3P + R'CHO \rightleftarrows (RO)_3\overset{+}{P}CHR'O^- \rightarrow [(RO)_3\overset{+}{P}CHR'OH] \rightarrow$$

$$\rightarrow [(RO)_3\overset{+}{P}CHR'CHXY]OH^- \rightarrow (RO)_2\overset{\overset{O}{\|}}{P}CHR'CHXY + ROH .$$

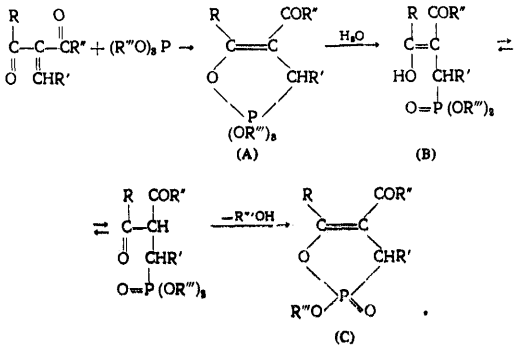
2. Reaction with $\alpha\beta$-Unsaturated Aldehydes and Ketones

The reactions of phosphites and phosphoramidites with $\alpha\beta$-unsaturated aldehydes and ketones proved to be extremely interesting; in many cases it was possible to follow clearly the formation of intermediate dipolar ions and to elucidate the effect of structural factors on their stability. Extensive studies in this field have been carried out by B. A. Arbuzov and coworkers. In a study of the reaction of triethyl phosphite with the simplest unsaturated aldehyde—acrolein—they showed that under mild conditions the reaction leads to the formation of 2,2,2-trialkoxy-Δ^4-oxaphospholen[62-64]. The earlier hypothesis of the isomerisation of Δ^4-phospholens to esters of γ-alkoxyalkenylphosphinic acids was not confirmed[65-67].

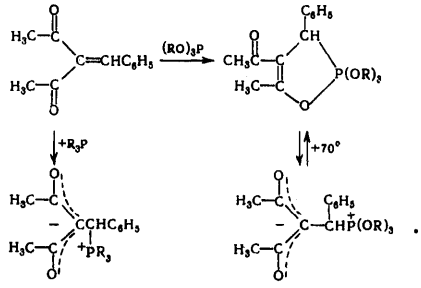
Pudovik and Batyeva showed that in reactions of $\alpha\beta$-unsaturated aldehydes with diphenylphosphinous anilide, products with the phospholan structure are not formed. The reactions probably take place with initial attack by the nitrogen atom on the carbonyl carbon atom and leads to the formation of α-arylamino-γ-aryl(alkyl)allyl(diphenyl)phosphine oxides[28]:



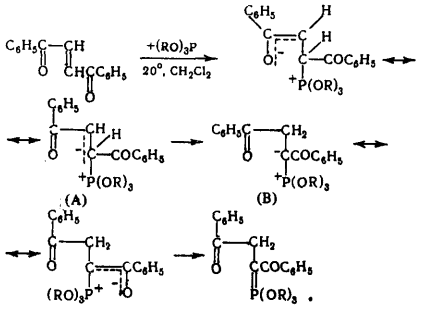
The reaction of trialkyl phosphites with ethylideneacetylacetone and with ethylidene- and benzylidene-acetoacetic esters leads to very stable 1,2-oxaphospholens[68,69]. On hydrolysis, the phospholen rings (A) are opened and the enols (B) are formed; on vacuum distillation, these split off an alcohol molecule and are converted into cyclic phosphonates (C)[70]:



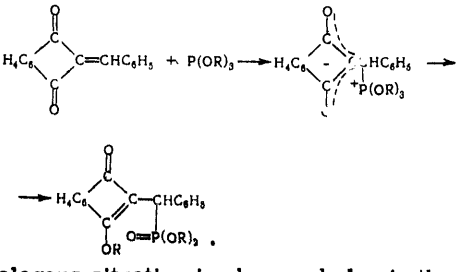
Stable phospholens with a P—C bond in the ring were also obtained by Ramirez in the reaction of 3-benzylidenepentane-2,4-dione with triethyl phosphite[71], phenylphosphonite, and diphenylphosphinite[72]. The study of the NMR spectra of solutions of the phospholens showed that at 70°C they are in equilibrium with dipolar ions, while at 125°C they have been fully converted into the dipolar form. Stable dipolar ions are formed by the reaction of 3-benzylidenepentane-2,4-dione with tertiary phosphines[73]:



The products of the reaction of trialkyl phosphites, phosphonites, and phosphinites with dibenzoylethylene have the structure of alkylidenephosphoranes[74-77] and not Δ^4-oxaphospholens as suggested earlier[78,79]. The reaction proceeds via the dipolar ion (A) which isomerises as a result of proton migration to the more stable dipolar ion (B):

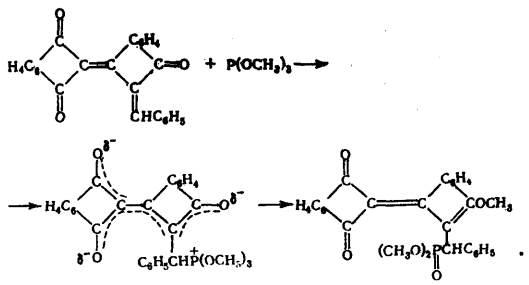


The reaction of dibenzoylethylene with a trialkyl phosphite in alcoholic solution and at an elevated temperature yields a complex mixture of products containing a trialkyl phosphate, 2,5-diphenylfuran, 1,2,3,4-tetrabenzoylbutane, and 1,2-dibenzoylethane[78,79]. The products of the addition of trialkyl phosphites to 2-benzylideneindan-1,3-dione at a low temperature exist in the form of dipolar ions, isomerising readily to esters of the enolic form of 1,3-dioxoindan-2-ylbenzylphosphonic acid[80]. At room temperatures the esters are formed immediately[81,82]:



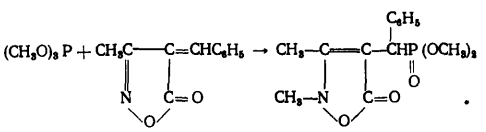
An analogous situation is observed also in the reaction of trimethyl phosphite with 2-benzylidene-3(2*H*)-thianaphthenone-1,1-dioxide[83,83]. As a result of the increase in the length of the conjugated chain and the equalisation

of electron density, even more stable dipolar ions are formed in the reactions of trialkyl phosphites with benzylidenebindone[82], 5-benzylidenebarbituric acid, and 5-benzylidene-1,3-diphenylbarbituric acid[84]

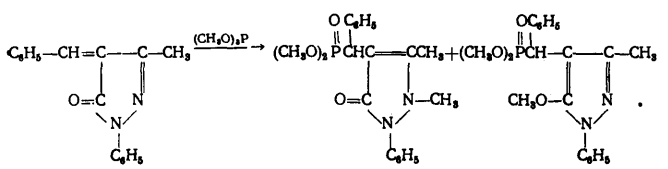


The reactions of phosphorous tris(dimethylamide) with 2-benzylideneindandione, 1,3,2-benzylidene-3(2*H*)-thianaphthenone-1,1-dioxide, benzylidenebindone, 5-benzylidenebarbituric acid, and 5-benzylidene-1,3-diphenylbarbituric acid also yielded stable crystalline dipolar ions with a P — C bond, the structure of which has been demonstrated by infrared, ultraviolet, and NMR spectroscopy and by dipole moment measurements[82,84,85].

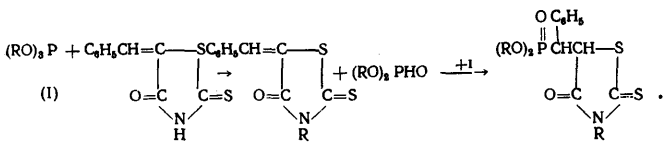
Heterocyclic carbonyl compounds containing a semicyclic double bond in the α-position relative to the carbonyl group do not form dipolar ions or phospholens on reaction with trialkyl phosphites. The reaction with 4-benzylidine-3-methyl-5-isoxazolone involves the $-N=C-C=C-$ system of conjugated bonds and leads to phosphonates[86]:



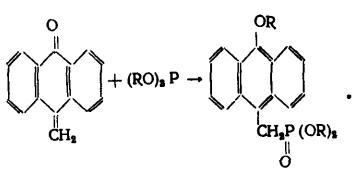
In the reaction with 4-benzylidene-3-methyl-1-phenyl-5-pyrazolone, trimethyl phosphite adds simultaneously to the $>C=C-C=N-$ and $>C=C-C=O$ bonds[87]:



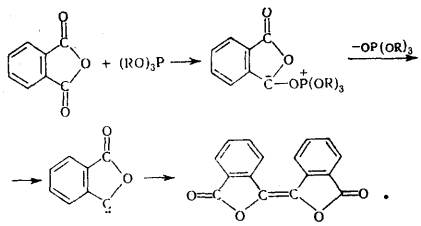
In the reaction with benzylidenerhodanine, the latter was found to be *N*-alkylated, the dialkyl phosphite formed in this process adding to the benzylidene double bond[88]:



Trialkyl phosphites react with methyleneanthrone via the conjugated system incorporating the methylene group[89]:

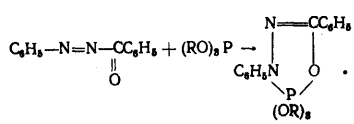


Phthalic anhydride does not react with trialkyl phosphites at room temperature; after prolonged heating, biphthalyl is formed[90]. The intermediate formation of a carbene which subsequently isomerises to biphthalyl is postulated. An alternative mechanism involves the formation of an epoxide, which is reduced by phosphite to an olefin[91]:

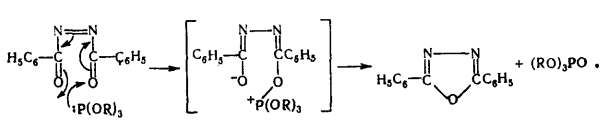


Similarly, thiophthalic anhydride undergoes reductive dimerisation by triethyl phosphite with formation of *trans*-bithiophthalide[91]. The reaction of thiophthalic anhydride with phosphorous tris(diethylamide) takes place via a different mechanism and leads to a mixture of lactones and thiolactones[91]. Dimethyl- and diphenylmaleic anhydrides react with triethyl phosphite to form the corresponding bifurandiones[92].

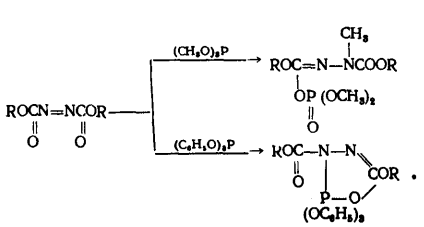
B. A. Arbuzov and coworkers showed that the conjugated system $-N=N-C=O$ may be also involved in the formation of cyclic phosphoranes[93,94]:



In the reaction of azodibenzoyl with trialkyl phosphites, the intermediate dipolar ions decompose into a trialkyl phosphate and diphenylfurodiazole owing to the difficulty of the closure of a seven-membered phosphorane ring[94,95]:

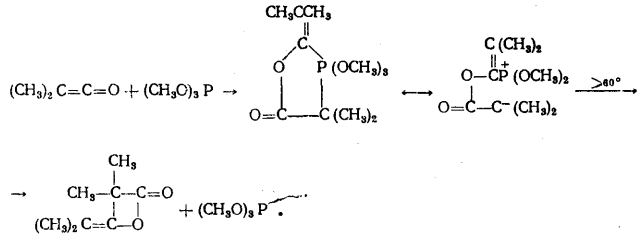


According to the data of Ginsburg and Yakubovich[95], the reaction of diethyl azodicarbonate with trimethyl and triphenyl phosphites yields linear phosphates and cyclic phosphoranes: their structure was recently confirmed by infrared and NMR spectroscopy[94]:

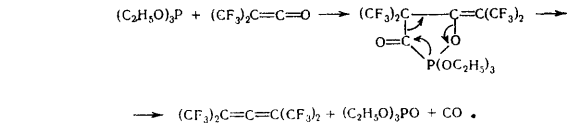


Ketens readily enter into reactions with phosphites, but the addition products are frequently unstable and undergo further reactions. Dimethylketen forms with

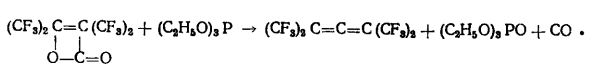
trimethyl phosphite a 2 : 1 adduct with a cyclic phosphorane structure, which is converted at 60°C into a dimer of dimethylketen and trimethyl phosphite[97,96]:



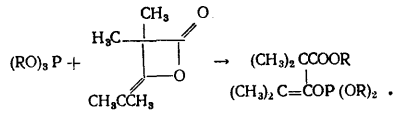
The product of the reaction of trimethyl phosphite with diphenylketen probably also has a phosphorane structure[96-98]. Bis(trifluoromethyl)keten reacts with triethyl phosphite to form tetrakis(trifluoromethyl)allene, triethyl phosphate, and carbon monoxide[99]:



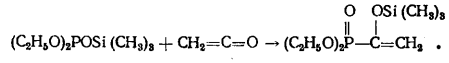
Possibly the first stage in this reaction is the formation of a β-lactone dimer, since this dimer yields the same products on reaction with triethyl phosphite[99]:



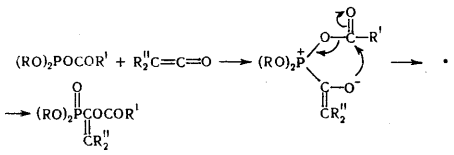
Dimethylketen dimers form with trialkyl phosphites 1 : 1 adducts containing a tervalent phosphorus atom. The reactions involve ring opening and migration of the alkoxy-group[100]:



Trialkylsilyl dialkyl phosphites react with ketens very readily[21]:



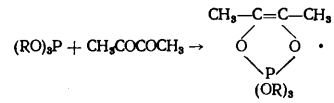
The reactions of mixed anhydrides of dialkylphosphorous and carboxylic acid anhydrides with keten and diphenylketen result in the formation of α-acyloxyvinylphosphonic acid esters[101,102]:



III. REACTIONS OF DERIVATIVES OF PHOSPHORUS(III) ACIDS WITH ALDEHYDES AND KETONES ACTIVATED BY ELECTRONEGATIVE GROUPS

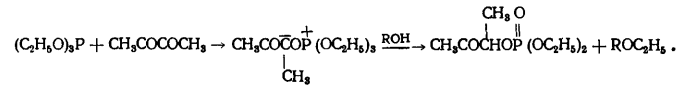
1. Reactions with α-Diketones

The reactions of trialkyl phosphites with α-dicarbonyl compounds have been investigated by a number of workers using diacetyl, the simplest α-diketone, as an example[103-107]. They take place very vigorously and result in the formation of 1 : 1-adducts for, which Ramirez et al.[107] and Kukhtin et al.[108] suggested and later proved the structure of 1,3,2-dioxaphospholens:

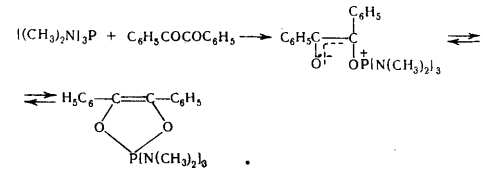


1,3,2-Dioxaphospholens are formed when trialkyl phosphites react with benzil, phenanthrenequinone[109,110], pentane-2,3-dione[106,107,111], dibenzoyl ketone[112], phenylglyoxal[112], 1,2-naphthoquinone[109,113], cyclohexane-1,2-dione[114], methylphenylglyoxal[115], and *o*-chloranil[109], and also when *NN*-dialkylphosphoramidites and phenyl- and methyl-phosphinous amides react with diacetyl[24,116], benzil[46,117], and cyclohexane-1,2-dione[118]. Cyclic phosphites and phosphoramidites form with α-diketones stable spirodioxaphospholens[5,119-121].

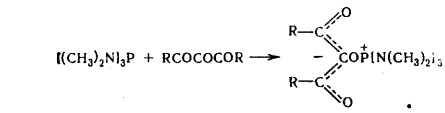
The reactions of trialkyl phosphites with α-diketones in proton-donating solvents lead to the corresponding phosphates, which confirms the intermediate formation of dipolar ions[122]:



In many cases it proved possible to demonstrate that 1,3,2-dioxaphospholens are in equilibrium with the dipolar ions. Thus phosphorous tris(dialkylamides) form with benzil a 1 : 1 adduct having the dioxaphospholen structure, which in solution is in equilibrium with the open-chain dipolar form. These data were obtained from a study of ^{31}P NMR spectra[120,121,123].

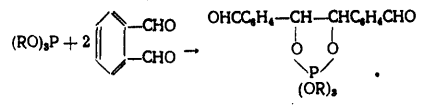


In benzene the main product is 1,3,2-dioxaphospholen but in methylene chloride the equilibrium is displaced towards the open-chain dipolar form[5,121]. The products of the reaction of phosphorous tris(dialkylamide) with dibenzoyl ketone[124] and 9,10-phenanthrenequinone[124] are generated only in the dipolar form[124]:

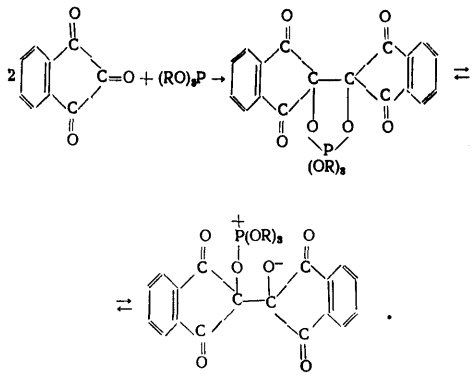


In reactions of phosphorous tris(dialkylamides) with polycarbonyl compounds, the cyclic phosphorane structure predominates over the dipolar structure on passing from α-diketones to *o*-quinones and triketones. An increase of the degree of delocalisation of the negative charge at the carbon atom promotes the formation of the open-chain dipolar form[121]. The stability of the dioxaphospholen structure increases on passing from acyclic phosphoramidites to five-membered cyclic phosphoramidites[125]. In the reaction of trialkyl phosphites with acenaphthenequinone[126], isatin[127], and phthalalhyde[128], 1 : 1 adducts were not isolated, since at the dipolar ion stage

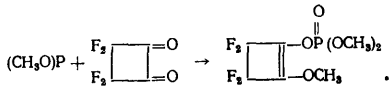
they react rapidly with a second molecule of the carbonyl compound and form 1,3,2-dioxaphospholans:



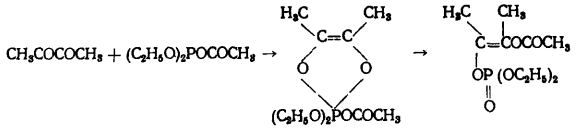
In the reaction with indantrione, 1,3,2-dioxaphospholans are in equilibrium with dipolar ions[129]:



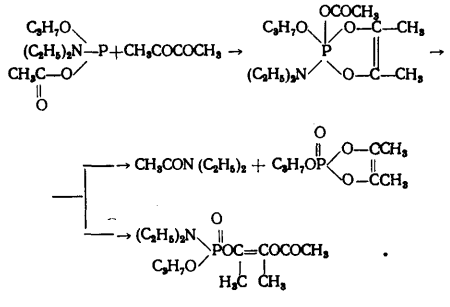
In the reactions of trialkyl phosphites with alloxan[130] and tetrafluorocyclobutane-1,2-dione[48], the intermediate dipolar ions are stabilised as a result of dealkylation to enol phosphates:



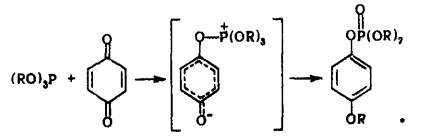
Dialkyl phosphoracetatidites react with α-diketones like trialkyl phosphites and phosphoramidites. The intermediate products of the addition of diethyl phosphoracetatidite to diacetyl—1,3,2-dioxaphospholen with a pentaco-ordinate phosphorus atom—was detected by ^{31}P NMR.[131] However, the presence of the anionoid acetyl group makes dioxaphospholens unstable and they react further via the mechanism of the second stage of the Arbuzov rearrangement with ring opening and the formation of an $\alpha\alpha$-endiol phosphate[36,131]:



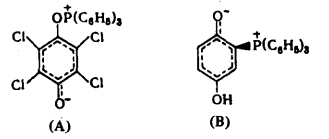
When phosphoramidoacetatidites react with α-diketones, two competing processes occur; the process leading to the retention of the dioxaphospholen ring predominates[36]:



The reactions of trialkyl phosphites with *p*-quinones are of considerable interest. *p*-Benzoquinone, 2,5-dimethylbenzoquinone, duroquinone, 1,4-naphthoquinone, anthraquinone, and 1,8-dichloroanthraquinone react with trialkyl phosphites via the 1,6-conjugated system with formation of *p*-alkoxyphenyl dialkyl phosphates[24,27,89,109,132-139] and not via a 1,4-addition mechanism as suggested previously[140,141]:



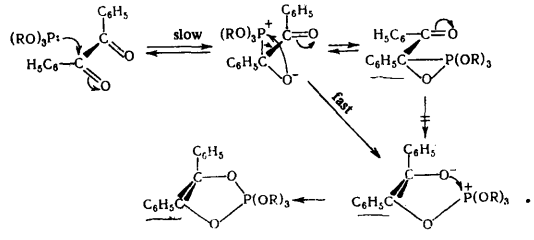
The intermediate dipolar ions were not isolated owing to their rapid conversion into phosphate esters. A stable dipolar ion (A) with a P—O—C linkage is formed when triphenylphosphine reacts with chloroanil and in the reaction of triphenylphosphine with *p*-benzoquinone the product is a dipolar ion (B) with a P—C bond[142,143]:



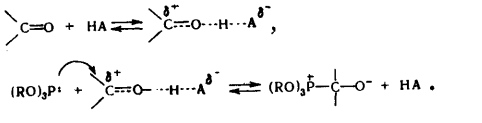
In the reaction of chloroanil with tri-isoalkyl phosphites, the substitution of all the chlorine atoms by di-isoalkoxyphosphono-groups was observed[144].

A spectrophotometric kinetic study of the reactions of trialkyl phosphites with benzil in anhydrous dioxan and benzene showed that the reaction is of second order with an activation energy of 8.41 kcal mole^{-1} and an activation entropy of −47.5 e.u.[145]. The rate of reaction increases in the following series of trialkyl phosphites: $(CH_3O)_3P < (s\text{-}C_4H_9O)_3P < (C_2H_5O)_3P < (iso\text{-}C_3H_7O)_3P$, which agrees with the increasing nucleophilicity of the phosphorus atom in these compounds.

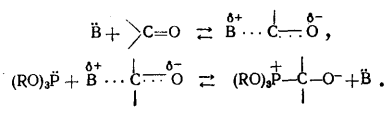
In the reaction involving tri-s-butyl phosphites, the steric effect has a significant influence. The following reaction mechanism was proposed on the basis of the results:



The nucleophilic attack by the phosphorus atom on the carbonyl carbon atom determines the rate of reaction. When an acid is added, the carbonyl group is activated by the formation of a hydrogen bond and the rate increases:



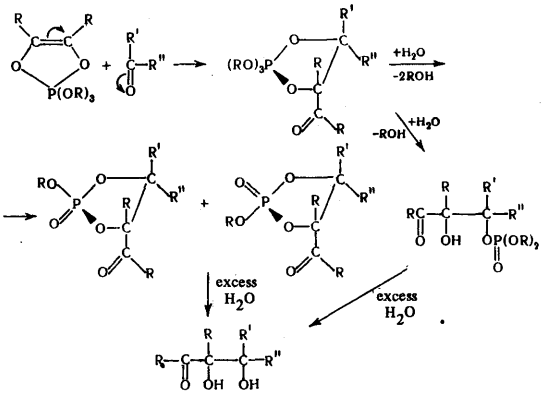
When a base adds to the carbonyl carbon atom it reduces its electrophilicity, which results in a lowering of the rate of reaction:



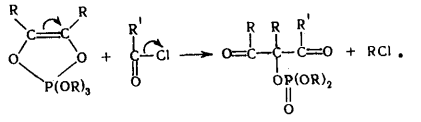
The low activation energy shows that the rate-determining stage does not require much energy and probably does not involve the dissociation of the P — C bond. The high negative activation entropy indicates a high degree of orientation of the transition state. The relatively slight dependence of the rate of reaction on solvent polarity can be accounted for by the fact that the transition state resembles an ion pair with a minimal charge separation owing to $2s - 3p$ bonding between the oxygen and phosphorus atoms. The conversion of the ion with a P — C bond into one with a P — O — C linkage takes place as a three-centre rearrangement with nucleophilic attack by the negatively charged oxygen on the phosphorus atom. The rearrangement of the ion with intermediate formation of a three-membered ring is less likely since the energy barrier preventing the complete dissociation of the P — C bond is higher.

However, there is as yet no unanimity concerning the mechanism of the reactions of phosphites, phosphoramidites and mixed anhydrides with dicarbonyl compounds. Together with the hypothesis of the initial attack by the phosphorus atom on the carbonyl carbon atom with subsequent isomerisation of the dipolar ion with a P — C bond, developed in the work of Ogata and Yamashita[145] discussed above and in the present authors' earlier investigations[146,147], it has been suggested in the literature, mainly in the publications of Ramirez, that there is a possibility of an initial attack by the phosphorus atom on the oxygen atom with direct formation of a P — O — C linkage. Such attack is most likely in the reactions of phosphites with quinones and also in the reactions of phosphorous tris(dialkylamides) with α-dicarbonyl compounds[38]. The possibility of synchronous or almost synchronous transfer of the lone electron pair of the phosphorus atom to the conjugated system of the α-diketone with subsequent incorporation of π electrons in the phosphorus d orbitals has also been suggested. Depending on the groups surrounding the phosphorus atom, the latter can exhibit in the initial reaction step both nucleophilic and electrophilic properties[131]. It is extremely probable that, depending on the nature of the reactants and the conditions, these reactions can involve different mechanisms.

1,3,2-Dioxaphospholens formed from α-diketones and phosphites are extremely reactive. They enter into condensation reactions involving the carbonyl groups of symmetrical[148-150] and asymmetric α-diketones[151], monoaldehydes[151-153], phthalaldehyde and terephthalaldehyde[154], monoketones[155], $\alpha\beta$-unsaturated aldehydes[156,157], phenyl isocyanate[158], p-quinones[159], and keten[160] with formation of 1,3,2-dioxaphospholans. Cyclic and linear phosphoric acid esters and also polyoxycarbonyl compounds were obtained from the latter by hydrolysis and alcoholysis[152,161-163]. The nucleophilic addition of 1,3,2-dioxaphospholens to the carbonyl group of mono- and polycarbonyl compounds constitutes a new stereoselective method of formation of a carbon — carbon bond; it has been called the oxyphosphorane condensation[156,157]:



The 1,3,2-dioxaphospholen ring opens on interaction with carboxylic acid chlorides, phosgene[161], bromine[164], oxygen[107], and ozone[165,166]:

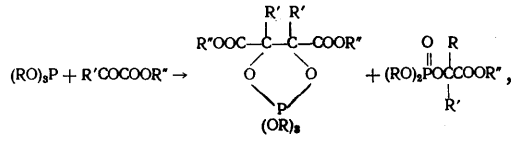


On irradiation with light, 1,3,2-dioxaphospholens decompose into a trialkyl phosphite, an α-diketone, and a trialkyl phosphate[167]. When acted upon by an excess of a trialkyl phosphite at 215°C, they give rise to a trialkyl phosphate and diaryl- or alkylaryl-acetylenes[98]. In the reactions with alcohols, there is partial exchange of substituents in the alkoxy-groups[168].

Ramirez has made interesting studies on the structure and stereochemistry of dioxaphospholens[4,5,8].

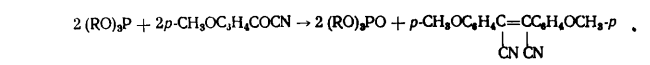
2. Reactions with Aldehydes and Ketones Activated by Alkoxycarbonyl, Phosphoryl, and Nitrile Groups

Reactions of derivatives of phosphorus(III) acids with carbonyl compounds in which the carbonyl group is activated by electron-accepting substituents are of considerable interest. The present authors' studies showed that the reactions of trialkyl phosphites with pyruvate, glyoxylate, and mesoxalate esters take place in two ways. At a low temperature trialkyl phosphites react preferentially with two molecules of the carbonyl compound forming 1,3,2-dioxaphospholans; at an elevated temperature, the corresponding α-substituted dialkyl alkyl phosphates are formed together with the dioxaphospholans[146,147,169-171]:

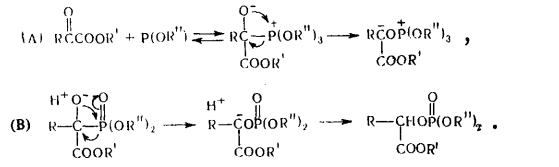


where R′ = H, CH_3, or COOAlk, and R, R″ = alkyl.

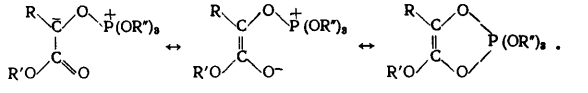
In reactions of trialkyl phosphites with pyruvate[172] and mesoxalate esters[5], Ramirez observed the formation of dioxaphospholans alone. Knunyants and coworkers demonstrated the formation of 1,3,2-dioxaphospholans in reactions of phosphites with trifluoropyruvate esters[173]. The reactions of trialkyl phosphites with the nitriles of benzoylformic and *p*-nitro-, *p*-chloro-, and *p*-methylbenzoylformic acids[174] also give rise to 2:1 adducts with the dioxaphospholan structure. The nitrile of *p*-anisoylformic acid gives an unstable addition product, as a result of which a trialkyl phosphate and $\alpha\alpha$-dicyano-*pp'*-dimethoxystilbene were isolated from the reaction mixture[174]:



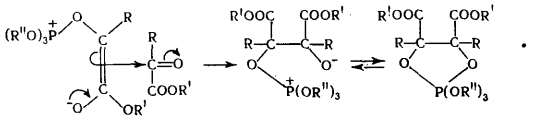
We suggested[146,147] that in reactions of trialkyl phosphites with α-ketoesters the rate-limiting process is nucleophilic attack by the lone electron pair of the phosphorus on the carbon atom of the carbonyl group as the most electrophilic centre in the molecule, which results in the formation of a dipolar ion [reaction (A)] with a P — C bond. Next there is a rapid intramolecular rearrangement of the type of nucleophilic substitution at the phosphonium centre with formation of a dipolar ion having a P — O — C linkage. This reaction resembles the phosphonate — phosphate rearrangement (B) of α-hydroxyalkylphosphonate esters, which was investigated in detail by the present authors for carbonyl compounds of the same type; the decisive role of electron-accepting substituents in this rearrangement has been demonstrated[175,176]:



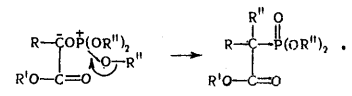
This mechanism has found definite confirmation in the work of Ogata and Yamashita[145], mentioned above, who investigated the kinetics of the reactions of trialkyl phosphites with benzil. However, there is as yet no direct proof for this mechanism, which does not allow a complete elimination of the possibility that these reactions take place also via the oxygen atom of the carbonyl group. The resulting dipolar ion with a P — O — C linkage can be stabilised further in two ways: (a) there is a possibility of the conversion of this ion into the more stable enolate — phosphonium system with a definite contribution by a pentacovalent structure[2]:



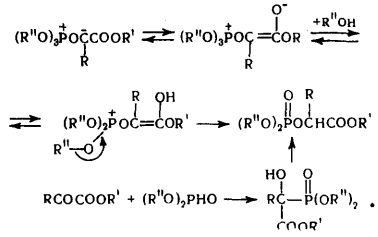
As a result of the attack by the carbon atom of the enolate group on the carbonyl group of a second α-ketoester molecule, a new dipolar ion is formed and stabilised by conversion into 1,3,2-dioxaphospholan:



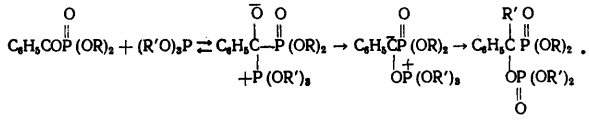
(b) The dipolar ion can also be stabilised in a different way—as a result of dealkylation in accordance with the second stage of the Arbuzov rearrangement:



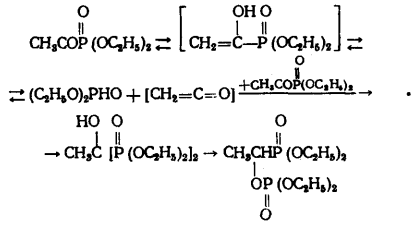
When reactions of trialkyl phosphites with pyruvate esters are carried out in proton-donating solvents (acetic acid, methanol), the dipolar ions are stabilised as a result of protonation with subsequent dealkylation to the corresponding phosphates; the formation of dioxaphospholans is not observed[177]:



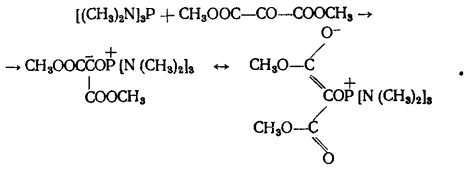
The phosphates formed proved to be identical with those obtained in the isomerisation of dialkyl α-alkoxycarbonyl-α-hydroxyalkylphosphonates[178]. The tendency towards the formation of phospholans in the reactions of phosphites with carbonyl compounds depends on the structure of the carbonyl compounds and diminishes in the series $RCOCOOR' > HCOCOOR' > R'OOC - CO - COOR' \gg RCOP(OR')_2$. The esters of α-ketophosphonic acids are relatively unreactive in reactions with trialkyl phosphites—they do not form products of the phospholan type. The esters of benzoylphosphonic acids react with trialkyl phosphites after prolonged heating of the reaction mixture. In contrast to earlier data[179], the present authors showed that the intermediate dipolar ions are stabilised as a result of their intramolecular dealkylation and conversion into dialkyl α-phenyl-α-dialkoxyphosphonoalkyl phosphates[180]:



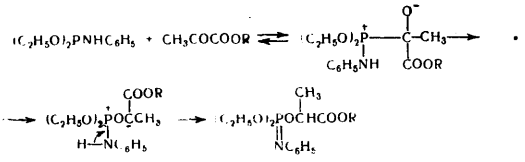
The reactions of phosphites with acetylphosphonic ester takes place similarly[181]. At a high temperature, thermal cleavage of the acetylphosphonic ester and the formation of diethyl α-(diethoxyphosphono)ethyl phosphate predominate[181]:



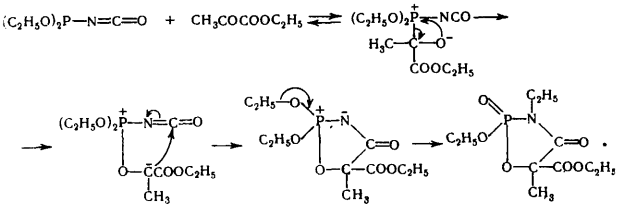
The mode of reaction depends also on the structure of the phosphorus(III) derivative. Thus, on passing from trialkyl phosphites to phosphoramidites and aminophosphines, the tendency towards the formation of dioxaphospholans is reduced[169,182]. One of the causes responsible for this decrease may be steric hindrance arising in the trigonal-bipyramidal configuration and increasing when the alkoxy-substituents at the phosphorus atom are replaced by dialkylamino-substituents. This lowers the stability of the phospholan structure relative to the open-chain dipolar form. Accordingly, the product of the addition of phosphorous tris(dialkylamide) to mesoxalate ester exists in the form of a dipolar ion[124] and not in the form of phospholen as suggested previously[183]:



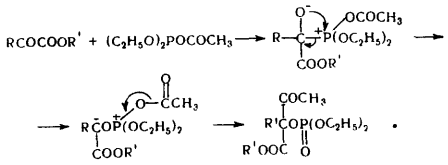
In the reaction of phosphorous tris(dialkylamides) with pyruvate and glyoxylate esters, only oxidation products were isolated[184]. The formation of 1,3,2-dioxaphospholans was not observed also in the reactions of pyruvate esters with dialkyl *N*-phenylphosphoramidites. In this case the dipolar ions are stabilised as a result of the migration of the anilino-proton to the carbanion with formation of dialkyl α-alkoxycarbonylalkyl *N*-phenylphosphorimidites[185]:



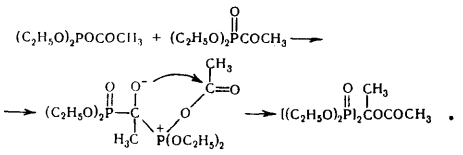
The present authors showed that pyruvate esters react vigorously with diethyl phosphoroisocyanatidite. In this case the dipolar ion is stabilised as a result of the attack by the carbanion on the electrophilic carbon atom of the isocyanate group and leads to the closure of a five-membered ring. Subsequent dealkylation yields an addition product—2-ethoxy-5-ethoxycarbonyl-3-ethyl-5-methyl-2-oxa-2-phosphaoxazolidin-4-one[186]:



Mixed anhydrides of phosphorous and carboxylic acids react with α-ketoesters in only one way with formation of substituted dialkyl α-acetylalkyl phosphates. In this case the dipolar ion is stabilised as a result of the migration of the acetyl group to the carbanion[187]:



The reactions of mixed anhydrides of diethylphosphorous and carboxylic acids with α-ketophosphonates yielded alkylbis(diethoxyphosphono)methyl acetates[101,188]:



REFERENCES

1. R. F. Hudson, "The Structure and Mechanism in Organophosphorus Chemistry" (Translated into Russian), Izd. Mir, Moscow, 1967, p. 209.
2. A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus", Elsevier Publishing Co., New York, 1967, p. 49.
3. A. N. Pudovik, I. V. Konovalova, and I. M. Aladsheva, "Abstracts of Congress Lectures and Scientific Papers, Presented at the XIXth International Congress of Pure and Applied Chemistry", London, 1963, p. 181.
4. F. Ramirez, Pure Appl. Chem., 9, 337 (1964).
5. F. Ramirez, Bull. Soc. chim. France, 8, 2443 (1966).
6. R. G. Harvey and E. R. DeSombre, "Topics in Phosphorus Chemistry" (Edited by M. Grayson and E. J. Griffith), Interscience Publ. New York, 1964, Vol. 1, p. 57.
7. B. A. Arbuzov, "Chimie organique du Phosphore", Centre National de Recherche Scientifique, Paris, 1970, p. 3.
8. F. Ramirez., "Chimie organique du Phosphore", Centre National de Recherche Scientifique, Paris, 1970, p. 61.
9. A. N. Pudovik and V. K. Khairullin, Uspekhi Khim., 37, 745 (1968) [Russ. Chem. Rev., No. 5 (1968)].
10. A. E. Arbuzov and P. I. Alimov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 530 (1951).
11. F. Ramirez, A. V. Patwardhan, and S. R. Heller, J. Amer. Chem. Soc., 86, 514 (1964).
12. V. A. Ginsburg and A. N. Yakubovich, Zhur. Obshch. Khim., 30, 3979 (1960).
13. E. A. Krasil'nikova, N. A. Moskva, A. I. Razumov, Zhur. Obshch. Khim., 40, 2001 (1970).
14. V. A. Kukhtin and K. N. Kirillova, Zhur. Obshch. Khim., 31, 2226 (1961).
15. F. Ramirez, S. B. Bhatia, and C. P. Smith, Tetrahedron, 23, 2067 (1967).
16. F. Ramirez, C. P. Smith, and J. Pilot, J. Org. Chem., 33, 3787 (1968).
17. F. Ramirez, Accounts Chem. Res., 1, 168 (1968).
18. F. Ramirez, A. Gulati, and C. P. Smith, J. Org. Chem., 33, 13 (1968).
19. V. S. Abramov, Dokl. Akad. Nauk SSSR, 95, 991 (1954).
20. B. A. Arbuzov and V. M. Zoroastrova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1030 (1960).
21. Z. S. Novikova and I. F. Lutsenko, Zhur. Obshch. Khim., 40, 2129 (1970).
22. V. P. Evdakov, L. I. Mizrakh, and L. Yu. Sandalova, Dokl. Akad. Nauk SSSR, 162, 573 (1965).
23. L. I. Mizrakh, L. Yu. Sandalova, and V. P. Evdakov, USSR P. 199877 (1966); Byul. Izobret., No. 16 (1967).
24. V. P. Evdakov, L. I. Mizrakh, and L. Yu. Sandalova, Zhur. Obshch. Khim., 37, 1875 (1967).

25. L. Yu. Sandalova, L. I. Mizrakh, and V. P. Evdakov, Zhur. Obshch. Khim., 35, 1314 (1965).
26. A. N. Pudovik, S. A. Terent'eva, and E. S. Batyeva, Dokl. Akad. Nauk SSSR, 175, 616 (1967).
27. R. F. Hudson, R. J. G. Searle, and F. H. Devitt, J. Chem. Soc., B, 789 (1966).
28. A. N. Pudovik and E. S. Batyeva, Izv. Akad. Nauk SSSR, Ser. Khim., 2391 (1968).
29. V. S. Abramov and N. A. Il'ina, Dokl. Akad. Nauk SSSR, 125, 1027 (1959).
30. V. S. Abramov and N. A. Il'ina, Dokl. Akad. Nauk SSSR, 132, 823 (1960).
31. A. N. Pudovik, E. S. Batyeva, and V. D. Nesterenko, Zhur. Obshch. Khim., 40, 502 (1970).
32. V. Mark, J. Amer. Chem. Soc., 85, 1884 (1963).
33. P. I. Alimov and I. V. Cheplanova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 939 (1956).
34. A. N. Pudovik, T. Kh. Gazizov, Yu. Yu. Samitov, and T. V. Zykova, Dokl. Akad. Nauk SSSR, 166, 615 (1966).
35. A. N. Pudovik, T. Kh. Gazizov, Yu. Yu. Samitov, and T. V. Zykova, Zhur. Obshch. Khim., 37, 706 (1967).
36. L. I. Mizrakh, L. Yu. Sandalova, and V. P. Evdakov, Zhur. Obshch. Khim., 38, 1107 (1968).
37. R. I. Tarasova, N. M. Kislitsyna, and A. N. Pudovik, Zhur. Obshch. Khim., 41, 1992 (1971).
38. A. C. Poshkus and J. E. Herweh, J. Org. Chem., 29, 2567 (1964).
39. J. I. Borowitz and M. Anshel, Tetrahedron Letters, 1517 (1967).
40. F. Ramirez, A. S. Gulati, and C. P. Smith, J. Amer. Chem. Soc., 89, 6283 (1967).
41. M. J. Gallagher and I. D. Jenkins, J. Chem. Soc., Chem. Zentr., 2605 (1969).
42. A. J. Floyd, K. C. Symes, G. J. Fray, G. E. Gymer, and A. W. Oppenheimer, Tetrahedron Letters, 1735 (1970).
43. N. P. Gambaryan, Yu. A. Cheburkov, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1526 (1964).
44. E. M. Rokhlin, Yu. V. Zeifman, Yu. A. Cheburkov, N. P. Gambaryan, and I. L. Knunyants, Dokl. Akad. Nauk SSSR, 161, 1356 (1956).
45. F. Ramirez, C. P. Smith, A. S. Gulati, and A. V. Patwardhan, Tetrahedron Letters, 2151 (1966).
46. F. Ramirez and C. P. Smith, Tetrahedron Letters, 3651 (1966).
47. V. P. Evdakov, L. I. Mizrakh, and L. Yu. Sandalova, Zhur. Obshch. Khim., 37, 1818 (1967).
48. D. W. Wiley and H. E. Simmons, J. Org. Chem., 29, 1876 (1964).
49. V. Mark, Tetrahedron Letters, 3139 (1964).
50. W. J. Middleton and W. Sharkey, J. Org. Chem., 30, 1384 (1965).
51. F. Mukaijama, F. Kumamoto, and T. Nagaoka, Tetrahedron Letters, 5563 (1966).
52. Haus-Georg Henning, Tetrahedron Letters, 2585 (1966).
53. T. Mukaijama, T. Nagaoka, and S. Fukuyama, Tetrahedron Letters, 2461 (1967).
54. T. Mukaijama, H. Nambu, and M. Okamoto, J. Org. Chem., 27, 3651 (1962).
55. A. N. Pudovik and E. S. Batyeva, Zhur. Obshch. Khim., 38, 285 (1968).
56. P. A. Chopard, V. M. Clark, R. F. Hudson, and A. J. Kirby, Tetrahedron, 21, 1961 (1965).
57. V. S. Abramov and N. A. Semenova, Zhur. Obshch. Khim., 28, 3056 (1958).
58. G. H. Birum, US P. 3014944 (1961); Chem. Abs., 56, 11622 (1962).
59. B. E. Ivanov and L. A. Kudryavtseva, Izv. Akad. Nauk SSSR, Ser. Khim., 480 (1969).
60. B. E. Ivanov, L. A. Kudryavtseva, and T. G. Bykova, Izv. Akad. Nauk SSSR, Ser. Khim., 889 (1969).
61. B. E. Ivanov, L. A. Kudryavtseva, T. G. Bykova, and T. A. Zyablikova, Izv. Akad. Nauk SSSR, Ser. Khim., 1851 (1969).
62. B. A. Arbuzov, O. D. Zolova, V. S. Vinogradova, and Yu. Yu. Samitov, Dokl. Akad. Nauk SSSR, 173, 335 (1967).
63. B. A. Arbuzov, V. S. Vinogradova, and O. D. Zolova, Izv. Akad. Nauk SSSR, Ser. Khim., 2290 (1968).
64. R. C. Harvey, Tetrahedron, 22, 2561 (1966).
65. G. Kamai and V. A. Kukhtin, Dokl. Akad. Nauk SSSR, 112, 868 (1957).
66. G. Kamai and V. A. Kukhtin, Zhur. Obshch. Khim., 27, 2376 (1957).
67. G. Kamai and V. A. Kukhtin, Zhur. Obshch. Khim., 28, 939 (1958).
68. B. A. Arbuzov, N. A. Polezhaeva, V. S. Vinogradova, and Yu. Yu. Samitov, Dokl. Akad. Nauk SSSR, 173, 93 (1967).
69. B. A. Arbuzov, E. N. Dianova, and V. S. Vinogradova, Izv. Akad. Nauk SSSR, Ser. Khim., 1109 (1969).
70. B. A. Arbuzov, N. A. Polezhaeva, and V. S. Vinogradova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2281 (1967).
71. F. Ramirez, O. P. Madan, and S. R. Heller, J. Amer. Chem. Soc., 87, 731 (1965).
72. F. Ramirez, J. Pilot, O. P. Madan, and C. P. Smith, J. Amer. Chem. Soc., 90, 1275 (1968).
73. F. Ramirez, J. Pilot, and C. Smith, Tetrahedron, 24, 3735 (1968).
74. F. Ramirez, O. P. Madan, and C. P. Smith, J. Amer. Chem. Soc., 86, 5339 (1964).
75. F. Ramirez, O. P. Madan, and C. P. Smith, Tetrahedron Letters, 201 (1965).
76. F. Ramirez, O. P. Madan, and C. P. Smith, J. Org. Chem., 30, 2284 (1965).
77. F. Ramirez, O. P. Madan, and C. P. Smith, Tetrahedron, 22, 567 (1966).
78. V. A. Kukhtin and K. M. Orekhova, Zhur. Obshch. Khim., 30, 1526 (1960).
79. R. C. Harvey and E. V. Jensen, Tetrahedron Letters, 1801 (1963).
80. B. A. Arbuzov, T. D. Sorokina, N. P. Bogonostseva, and V. S. Vinogradova, Dokl. Akad. Nauk SSSR, 171, 605 (1966).
81. A. Mustata, M. M. Sidky, and F. M. Soliman, Tetrahedron, 23, 99 (1967).
82. B. A. Arbuzov, T. D. Sorokina, V. S. Vinogradova, and A. A. Musina, Izv. Akad. Nauk SSSR, Ser. Khim., 2727 (1969).
83. B. A. Arbuzov, T. D. Sorokina, and V. S. Vinogradova, Dokl. Akad. Nauk SSSR, 177, 1337 (1967).
84. B. A. Arbuzov, T. D. Sorokina, and V. S. Vinogradova, Izv. Akad. Nauk SSSR, Ser. Khim., 573 (1971).
85. B. A. Arbuzov, T. D. Sorokina, V. S. Vinogradova, and G. N. Sergeeva, Izv. Akad. Nauk SSSR, Ser. Khim., 865 (1972).
86. B. A. Arbuzov, E. N. Dianova, V. S. Vinogradova, and Yu. Yu. Samitov, Dokl. Akad. Nauk SSSR, 173, 1321 (1967).
87. B. A. Arbuzov, E. N. Dianova, V. S. Vinogradova, and A. A. Musina, Izv. Akad. Nauk SSSR, Ser. Khim., 1530 (1969).
88. B. A. Arbuzov, V. M. Zoroastrova, and N. D. Ibragimova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1972 (1967).

89. B. A. Arbuzov, V. M. Zoroastrova, and N. D. Ibragimova, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 704 (1967).
90. F. Ramirez, H. Yamanaka, and O. H. Basedow, J. Amer. Chem. Soc., 83, 173 (1961).
91. J. H. Markgraf, C. J. Heller, and N. L. Avery, J. Org. Chem., 35, 1588 (1970).
92. C. W. Bird and D. Y. Wong, Chem. Comm., 932 (1969).
93. B. A. Arbuzov, N. A. Polezhaeva, V. S. Vinogradova, and Yu. Yu. Samitov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1605 (1967).
94. B. A. Arbuzov, N. A. Polezhaeva, and V. S. Vinogradova, Izv. Akad. Nauk SSSR, Ser. Khim., 2525 (1968).
95. V. A. Ginsburg, M. N. Vasil'eva, S. S. Dubov, and A. A. Yakubovich, Zhur. Obshch. Khim., 30, 2854 (1960).
96. W. G. Bentrude and W. D. Johnson, J. Amer. Chem. Soc., 90, 5924 (1968).
97. E. U. Elam, J. Org. Chem., 32, 215 (1967).
98. F. Mukaijama, H. Hambu, and F. Kumamotto, J. Org. Chem., 29, 2243 (1964).
99. Yu. E. Aronov, Yu. A. Cheburkov, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1758 (1967).
100. W. G. Bentrude and E. R. Witt, J. Amer. Chem. Soc., 85, 2522 (1963).
101. A. N. Pudovik and T. Kh. Gazizov, Zhur. Obshch. Khim., 38, 140 (1968).
102. A. N. Pudovik and T. Kh. Gazizov, Dokl. Akad. Nauk SSSR, 175, 1073 (1967).
103. V. A. Kukhtin and K. N. Orekhova, Zhur. Obshch. Khim., 30, 1208 (1960).
104. V. A. Kukhtin, Dokl. Akad. Nauk SSSR, 121, 466 (1958).
105. G. H. Birum and J. L. Dever, J. Amer. Chem. Soc., Abstracts of 134th Meeting, 1958, p. 101.
106. G. H. Birum and J. L. Dever, US P. 2 961 455 (1960); Chem. Abs., 55, 8292 (1961).
107. F. Ramirez, R. B. Mitra, and N. B. Desai, J. Amer. Chem. Soc., 82, 2651 (1960).
108. V. A. Kukhtin, K. M. Kirillova, and R. R. Shagidullin, Zhur. Obshch. Khim., 32, 649 (1962).
109. F. Ramirez, S. Bhatia, A. Patwardhan, E. Chen, and C. Smith, J. Org. Chem., 33, 20 (1968).
110. F. Ramirez, J. Amer. Chem. Soc., 89, 2268 (1967).
111. F. Ramirez and N. B. Desai, J. Amer. Chem. Soc., 85, 3252 (1963).
112. F. Ramirez, A. V. Patwardhan, and C. P. Smith, J. Org. Chem., 30, 2575 (1965).
113. K. M. Kirillova and V. A. Kukhtin, Zhur. Obshch. Khim., 32, 2338 (1962).
114. V. A. Kukhtin, T. N. Voskoboeva, and K. M. Kirillova, Zhur. Obshch. Khim., 32, 2333 (1962).
115. V. A. Kukhtin and K. M. Kirillova, Zhur. Obshch. Khim., 35, 544 (1965).
116. V. A. Kukhtin and I. P. Gozman, Dokl. Akad. Nauk SSSR, 158, 157 (1964).
117. V. P. Evdakov, L. I. Mizrakh, and L. Yu. Sandalova, USSR P. 199 880 (1966); Byul. Izobret., No. 16 (1967).
118. L. Yu. Sandalova, L. I. Mizrakh, and V. P. Evdakov, Zhur. Obshch. Khim., 36, 1451 (1966).
119. F. Ramirez, M. Nagabhushanam, and C. P. Smith, Tetrahedron, 24, 1785 (1968).
120. F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, Tetrahedron Letters, 3053 (1966).
121. F. Ramirez, A. V. Patwardhan, H. G. Kugler, and C. P. Smith, Tetrahedron, 24, 2275 (1968).
122. G. H. Birum and J. L. Dever, US P. 3 014 949 (1961); Chem. Abs., 56, 10190 (1962).
123. R. Burgada, Bull. soc. Chim. France, 347 (1967).
124. F. Ramirez, A. V. Patwardhan, and C. P. Smith, J. Amer. Chem. Soc., 87, 4973 (1965).
125. F. Ramirez, A. V. Patwardhan, H. J. Kugler, and C. P. Smith, J. Amer. Chem. Soc., 89, 6276 (1967).
126. F. Ramirez and N. Ramanathan, J. Org. Chem., 26, 3041 (1961).
127. A. Mustafa, M. M. Sidky, and F. M. Soliman, Tetrahedron, 22, 393 (1966).
128. F. Ramirez, S. Bhatia, A. Patwardhan, and C. Smith, J. Org. Chem., 32, 2194 (1967).
129. A. Mustafa, M. M. Sidky, and Salah M. A. Zayed, Annalen, 712, 116 (1968).
130. F. Ramirez, S. B. Bhatia, and C. P. Smith, J. Org. Chem., 31, 4105 (1966).
131. Ya. A. Levin, I. P. Gozman, and S. G. Salikhov, Izv. Akad. Nauk SSSR, Ser. Khim., 2609 (1968).
132. F. Ramirez and S. Dershowitz, J. Org. Chem., 22, 856 (1957).
133. F. Ramirez, J. Amer. Chem. Soc., 81, 587 (1959).
134. F. Ramirez, E. H. Chen, and S. Dershowitz, J. Amer. Chem. Soc., 81, 4338 (1959).
135. N. I. Rizpolozhenskii, L. V. Stepashkina, and R. R. Shagidullin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 3006 (1967).
136. F. Ramirez and S. Dershowitz, J. Org. Chem., 23, 778 (1958).
137. F. Ramirez, V. P. Catto, D. Rhum, and S. Dershowitz, Tetrahedron, 22, 637 (1966).
138. V. A. Kukhtin, K. M. Orekhova, and N. S. Garif'yanov, Zhur. Obshch. Khim., 31, 1157 (1961).
139. J. S. Meek and L. L. Kon, J. Org. Chem., 33, 2942 (1968).
140. E. C. Ladd and M. B. Harvey, US P. 2 609 376 (1952); Chem. Abs., 47, 7540 (1953).
141. V. A. Kukhtin and K. M. Orekhova, Dokl. Akad. Nauk SSSR, 124, 819 (1959).
142. F. Ramirez and S. Dershowitz, J. Amer. Chem. Soc., 78, 5614 (1956).
143. F. Ramirez, D. Rhum, and C. Smith, Tetrahedron, 21, 1941 (1965).
144. F. T. Rut, US P. 2 935 518 (1960); Chem. Abs., 54, 19 598 (1960).
145. Yoshiro Ogata, Mitsuji Yamashita, J. Amer. Chem. Soc., 92, 4670 (1970).
146. A. N. Pudovik and I. V. Konovalova, Zhur. Obshch. Khim., 34, 3848 (1964).
147. A. N. Pudovik and I. V. Konovalova, Zhur. Obshch. Khim., 35, 1591 (1965).
148. F. Ramirez, J. Amer. Chem. Soc., 85, 3465 (1963).
149. F. Ramirez and N. Ramanathan, J. Amer. Chem. Soc., 85, 3056 (1963).
150. F. Ramirez, N. Ramanathan, and N. Desai, J. Amer. Chem. Soc., 84, 1317 (1962).
151. F. Ramirez, A. Patwardhan, and C. Smith, J. Org. Chem., 31, 474 (1966).
152. F. Ramirez, N. Ramanathan, N. Desai, C. V. Greco, and S. R. Heller, J. Amer. Chem. Soc., 87, 549 (1965).
153. F. Ramirez, J. Amer. Chem. Soc., 87, 543 (1965).
154. F. Ramirez, S. Bhatia, A. Patwardhan, and C. Smith, J. Org. Chem., 32, 3547 (1967).
155. F. Ramirez, A. Patwardhan, and C. P. Smith, J. Org. Chem., 31, 3159 (1966).

156. F. Ramirez, H. Kugler, A. Patwardhan, and C. Smith, J. Org. Chem., 33, 1185 (1968).
157. F. Ramirez, H. J. Kugler, and C. P. Smith, Tetrahedron, 24, 3153 (1968).
158. F. Ramirez, S. Bhatia, and C. Smith, J. Amer. Chem. Soc., 89, 3030 (1967).
159. F. Ramirez, H. Kugler, and C. Smith, Tetrahedron, 24, 1931 (1968).
160. F. Ramirez, S. Bhatia, and C. Smith, J. Amer. Chem. Soc., 89, 3026 (1967).
161. F. Ramirez, S. Bhatia, A. Bigler, and C. Smith, J. Org. Chem., 33, 1192 (1968).
162. F. Ramirez, J. Amer. Chem. Soc., 87, 670 (1965).
163. F. Ramirez, N. B. Desai, and N. Ramanathan, J. Amer. Chem. Soc., 85, 1874 (1963).
164. F. Ramirez, K. Tasaka, N. B. Desai, and C. P. Smith, J. Org. Chem., 33, 25 (1968).
165. F. Ramirez, S. B. Bhatia, R. B. Mitra, Z. Hamlet, and N. Desai, J. Amer. Chem. Soc., 86, 4394 (1964).
166. F. Ramirez, N. B. Desai, and R. B. Mirta, J. Amer. Chem. Soc., 83, 492 (1961).
167. W. G. Bentrude, Chem. Comm., 174 (1967).
168. F. Ramirez, K. Tasaka, N. B. Desai, and C. P. Smith, J. Amer. Chem. Soc., 90, 751 (1968).
169. A. N. Pudovik, I. V. Gur'yanova, S. P. Perevezentseva, and T. V. Zykova, Zhur. Obshch. Khim., 37, 1317 (1967).
170. A. N. Pudovik, I. V. Gur'yanova, and S. P. Perevezentseva, Zhur. Obshch. Khim., 38, 942 (1968).
171. A. N. Pudovik, I. V. Gur'yanova, and S. P. Perevezentseva, Zhur. Obshch. Khim., 39, 1532 (1969).
172. F. Ramirez, N. B. Desai, and N. Ramanathan, Tetrahedron Letters, 323 (1963).
173. I. L. Knunyants, N. P. Gambaryan, and V. G. Tyuleneva, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2662 (1967).
174. F. Mukaijama, J. Kuwajima, Ohnok, Bull. Chem. Soc. Japan, 38, 1954 (1965).
175. A. N. Pudovik, I. V. Konovalova, and L. G. Dedova, Dokl. Akad. Nauk SSSR, 153, 616 (1963).
176. A. N. Pudovik, I. V. Gur'yanova, L. V. Banderova, and G. V. Romanov, Zhur. Obshch. Khim., 38, 143 (1968).
177. A. N. Pudovik, I. V. Gur'yanova, and S. P. Perevezentseva, Zhur. Obshch. Khim., 39, 2424 (1969).
178. A. N. Pudovik, I. V. Konovalova, and L. G. Dedova, Zhur. Obshch. Khim., 33, 483 (1963).
179. J. J. Cadogan and B. J. Bungan, J. Chem. Soc., 1527 (1963).
180. A. N. Pudovik, I. V. Gur'yanova, and S. P. Perevezentseva, Zhur. Obshch. Khim., 37, 1090 (1967).
181. A. N. Pudovik and I. V. Konovalova, Zhur. Obshch. Khim., 33, 3100 (1963).
182. A. N. Pudovik, I. V. Gur'yanova, S. P. Perevezentseva, and S. A. Terent'eva, Zhur. Obshch. Khim., 39, 337 (1969).
183. R. Burgada, Compt. rend., 258, 4789 (1964).
184. A. N. Pudovik, I. V. Gur'yanova, V. P. Kakurina, and N. P. Anoshina, Zhur. Obshch. Khim., 41, 1227 (1971).
185. A. N. Pudovik, I. V. Gur'yanova, and L. Kh. Rakhmatullina, Zhur. Obshch. Khim., 40, 1485 (1970).
186. A. N. Pudovik, I. V. Gur'yanova, and V. P. Kakurina, Zhur. Obshch. Khim., 41, 1976 (1971).
187. A. N. Pudovik, I. V. Gur'yanova, S. P. Perevezentseva, and T. V. Zykova, Zhur. Obshch. Khim., 39, 2421 (1969).
188. A. N. Pudovik, T. Kh. Gazizov, and A. N. Pashinkin, Zhur. Obshch. Khim., 36, 951 (1966).

Ul'yanov-Lenin Kazan
State University