Translated from *Uspekhi Khimii*, **43**, 933-973 (1974) U.D.C. 547.40-2 : 547.451

Cyclic Oxyphosphoranes

B.A.Arbuzov and N.A.Polezhaeva

The review deals with a new interesting field in the chemistry of organophosphorus compounds—cyclic derivatives of pentacoordinate phosphorus containing at least one endocyclic P-O bond and not containing halogens.
The principal types of cyclic oxyphosphoranes with four-, five-, and six-membered rings, spirophosphoranes, and phosphoranes of the condensed and prismatic types have been examined. The methods of synthesis and chemical reactions of cyclic phosphoranes are described: condensation with carbonyl compounds, hydrolysis, alcoholysis, thermal stability, etc. Physicochemical studies on phosphoranes have been undertaken to establish their structures and to investigate their stereochemistry. X-ray diffraction, infrared spectroscopy, ^{1}H NMR, and ^{31}P NMR have been used for these purposes. The groups linked to phosphorus are capable of permutational isomerisation which can occur via the mechanism of the Berry pseudorotation or via turnstile rotation.
The bibliography includes 264 references.

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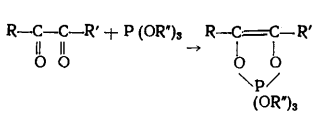
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I. INTRODUCTION

Organic derivatives of the hypothetical phosphorus hydride PH_5 (phosphorane) are called phosphoranes. Derivatives of hydroxyl-containing substances with the general formula $R_nP(OH)_{5-n}$ ($n = 0-4$) are regarded as oxyphosphoranes; when $n = 0-3$, they can be treated as derivatives of the ortho-forms of the corresponding phosphoryl compounds $R_nP(O)(OH)_{3-n}$, where $n = 0-3$. The stability of phosphoranes increases on passing from a cyclic to monocyclic and bicyclic compounds.

The present review deals with cyclic phosphoranes containing at least one endocyclic P–O bond. Halogen-containing phosphoranes are excluded.

Cyclic phosphoranes have been vigorously investigated in the last 15 years. The formation of 1 : 1 adducts of α-dicarbonyl compounds with trialkyl phosphites was discovered independently in 1958–1960 by three groups of investigators: Kukhtin[1,2], Birum and Dever[3,4], and Ramirez and coworkers[5,6].



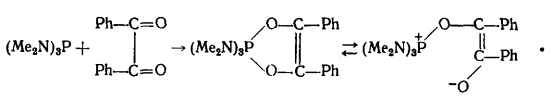
These adducts possess a set of interesting chemical and physical properties, lacked by the classes of organophosphorus compounds known previously, which led to their vigorous investigation by chemical and spectroscopic methods[7,8]. These studies showed that the adducts were unsaturated cyclic oxyphosphoranes. The relative ease of formation of such compounds and the wide variety of reactions which they undergo suggest that cyclic phosphoranes have a very promising future as chemical intermediates. Moreover, cyclic phosphoranes are ideal systems for the investigation of the stereochemistry of pentacoordinate phosphorus[9-13]

II. SYNTHESIS OF CYCLIC PHOSPHORANES

1. Synthesis of Phosphoranes by the Reaction of Phosphorus(III) Acid Derivatives with Carbonyl Compounds

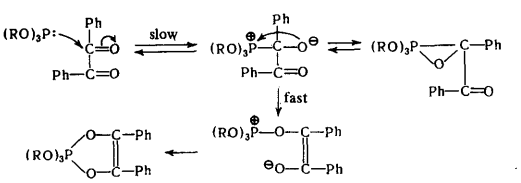
1,3,2-Dioxaphospholens are formed when trialkyl phosphites react with α-dicarbonyl compounds of the aliphatic[14-19], alicyclic[20,21], and aromatic[22-27] series. Phosphonites, phosphinites[19,28], dialkyl phosphoramidites[29-32], and dialkyl phosphonamidites[29,33,34] also form phosphoranes on interaction with α-dicarbonyl compounds. Cyclic phosphites and phosphoramidites react with α-diketones to form spirophosphoranes: 1,3,2-dioxaphospholen-spiro-1,3,2-dioxaphospholans[8,35,36], 1,3,2-dioxaphospholen-spiro-1,3,2-diazaphospholans[35,37], and 1,3,2-dioxaphospholen-spiro-1,3,2-dioxaphosphorinanes[36].

On reaction with certain α-dicarbonyl compounds tris(dimethylamino)phosphine gives rise to an equilibrium mixture of a phosphorane and a dipolar ion[9,37,38]:

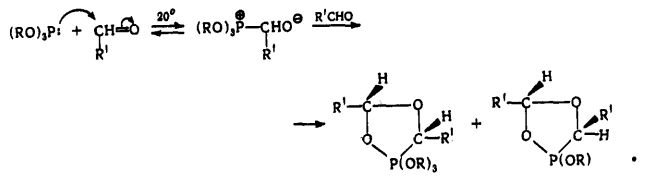


A similar equilibrium has been observed for the phenanthrenequinone–tertiary phosphine adduct[9,39].

The following mechanism has been proposed on the basis of a kinetic study of the reactions of trialkyl phosphites with benzil[40-42] and acyclic[43] and cyclic[21] α-diketones:

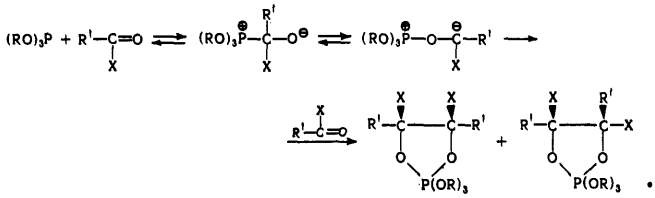


Under mild conditions, aliphatic aldehydes react with trialkyl phosphites to form diastereomeric 1,4,2-dioxaphospholans[44]:

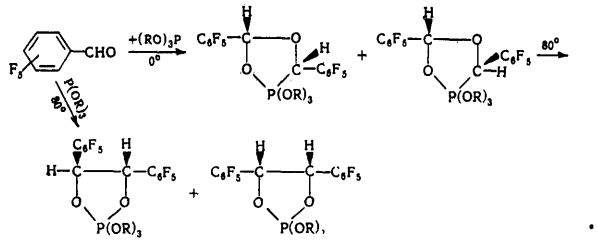


1,4,2-Dioxaphospholans are formed when dimethylketen[45] reacts with esters and ester-amides of tervalent phosphorus.

Aromatic aldehydes and ketones activated by electron-accepting groups[8,32,39,46-55], hexafluoroacetone[28,56,57], fluorenone[58,59], and indantrione[60] react with trialkyl phosphites to form 1,3,2-dioxaphospholans:

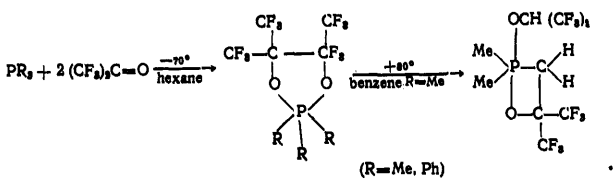


The rearrangement of the adduct with a P–C–O linkage formed initially into one with a P–O–C linkage was demonstrated for pentafluorobenzaldehyde[9,39]:



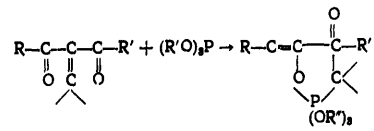
When cyclic phosphites and phosphorous triamides are employed, the products are 1,3,2-dioxaphospholan-spiro-1,3,2-dioxaphospholans[61] and 1,3,2-dioxaphospholan-spiro-1,3,2-diazaphospholans[62,63]. 1,3,2-Dioxaphospholans can also be obtained by the oxyphosphorane condensation of 1,3,2-dioxaphospholens with carbonyl compounds (see the Section on chemical properties).

Aromatic phosphines react with hexafluoroacetone to form 1,3,2-dioxaphospholans[39], while phosphines containing a fairly mobile hydrogen atom in the α-position relative to the phosphorus atom react with hexafluoroacetone to form 1,3,2-dioxaphospholans at −70° and 1,2-oxaphosphetans[64,65] at +80°C (see the Section on the thermal decomposition of phosphoranes):



(R=Me, Ph)

The reactions of trialkyl phosphites with certain $\alpha\beta$-unsaturated carbonyl compounds lead to the formation of 1,2-oxaphospholens; the reactions with methyl vinyl ketone[66], acrolein[67,68], and dibenzylidenecyclohexanone[69,70] take place in this way. Trialkyl phosphites react more readily with $\alpha\beta$-unsaturated carbonyl compounds in which the conjugated system is activated by electron-accepting groups. 1,2-Oxaphospholens have been obtained by the reaction of trialkyl phosphites with alkylidene derivatives of acetylacetone[66,71-73], acetoacetic[72-75] and benzoylacetic[76] esters, benzylidenephenylsulphonylacetophenone[77], and acetyl-*p*-quinone[78]:



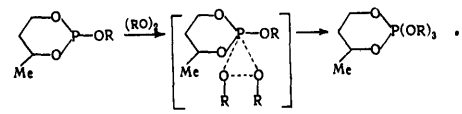
Stable 1,2-oxaphospholens are also obtained when phenylphosphonite and diphenylphosphinite are employed[66,79]. Allenic α-ketones[80] react with phosphites, phosphonites, and phosphinites and the products are also 1,2-oxaphospholens.

The $-N=N-\overset{|}{C}=O$, $-N=\overset{|}{C}-\overset{|}{C}=O$, and $\diagdown C=N-\overset{|}{C}=O$ conjugated systems can be involved in the formation of cyclic phosphoranes: phenylbenzoyldi-imide and azodiformic ester form 1,3,4,2-oxadiazaphospholens[81-83], α-ketoimine gives rise to 1,3,2-oxazaphospholen[84], and 1,1,1,3,3,3-hexafluoro-*N*-acyliminopropane yields 1,4,2-oxazaphospholen[85].

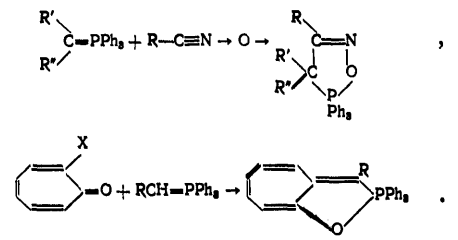
The synthesis of phosphoranes by the reaction of tervalent phosphorus acid derivatives with carbonyl compounds is described in greater detail in the literature[86,87].

2. Other Methods of the Synthesis of Phosphoranes

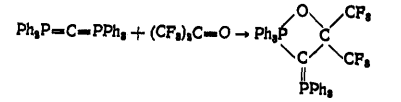
Cyclic phosphoranes of different types can be obtained with the aid of the so called peroxide method. It consists in the treatment of cyclic phosphites[88,89], phosphonites, phosphinites, and amidoesters[90] with alkyl peroxides. The method is general:



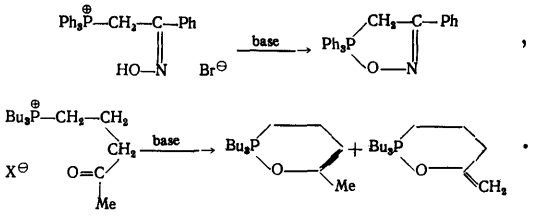
1,3-Dipolar addition to methylenephosphoranes leads to the formation of oxaphospholens. Such reactions take place with nitrones[91,92], nitrile oxides[93-96], epoxides[97], and 2-halogenotropones[98,99]:



In the reaction with phosphorus ylides, hexafluoroacetone yields 1,2-oxaphosphetan[100-103]:

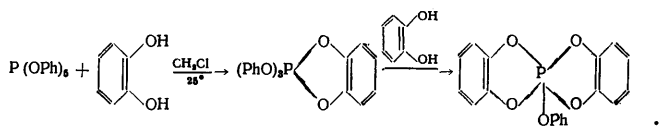


Phosphonium salts containing a hydroxy-group in the γ- or δ-position form phosphoranes on treatment with bases[104-109]:



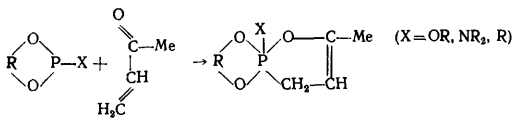
Oxazaphospholens have been obtained by the reaction of trialkyl phosphites with $\alpha\beta$-unsaturated β-nitroacid esters[110] and with 2,6-dimethylaryl 2-nitrophenyl ethers[111].

Cyclic phosphoranes can be obtained by an exchange reaction[112-115] from acyclic phosphoranes and bicyclic phosphoranes can be synthesised from monocyclic phosphoranes (see also the reactions of phosphoranes with glycols):

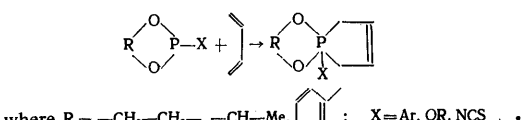


3. Synthesis of Spirophosphoranes and Phosphoranes of the Condensed and Cage Types

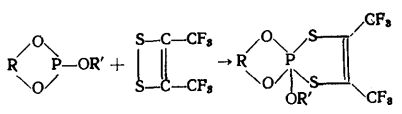
As already mentioned above, spirophosphoranes can be obtained by the interaction of five- and six-membered cyclic phosphites, phosphoramidites, and amides with α-dicarbonyl[8,35-37] and monocarbonyl[61-63] compounds. The reaction of cyclic derivatives of phosphorus(III) with $\alpha\beta$-unsaturated carbonyl compounds takes place similarly[84,116-120]:



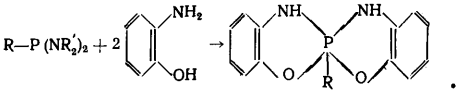
The condensation of the glycol and catechol esters of alkylphosphonous[121] and arylphosphonous acids[122-124] and of the methyl ether and isocyanate of catecholphosphorous [(*OO'*-phenylene)phosphorous] acid[125,126] with 1,3-diene hydrocarbons leads to 1,3,2-dioxaphospholan-spiro-2-phospholens:



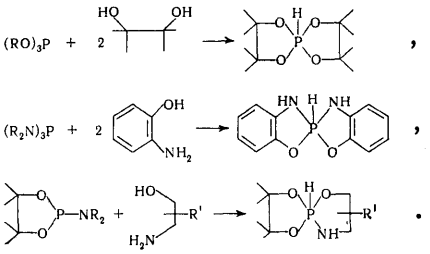
The condensation of cyclic phosphites with 3,4-bis(trifluoromethyl)-1,2-dithietans leads to stable phosphoranes containing sulphur[127]:



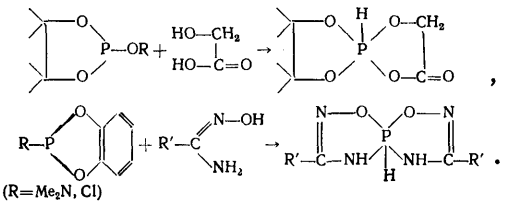
Certain derivatives of tervalent phosphorus form with *o*-aminophenols 1:2 adducts containing a pentacoordinate phosphorus atom[128]:



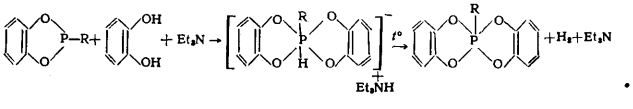
Spirophosphoranes with a P–H bond constitute an interesting group of compounds. They are formed when β-glycols and β-aminoalcohols react with phosphites[129-133] phosphorochloridites[129,134], phosphorus trichloride[129,135,136], tris(dimethylamino)phosphine[135,136,138-142], and cyclic phosphoramidites[143-145]:



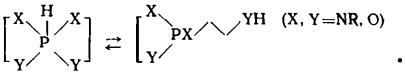
Analogous spirophosphoranes are obtained from derivatives of cyclic phosphites and α-hydroxyacids[146] or amidoximes[147-149]:



The reactions of cyclic phosphorus(III) derivatives with β-glycols and β-aminoalcohols, leading to the formation of spirophosphoranes, takes place only in a neutral or acid medium. In the presence of amines, ammonium salts with a hexacoordinate phosphorus atom are formed[148,150,151], from which spirophosphoranes can be obtained by treatment with acid or on heating:

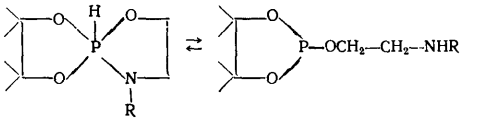


A tautomeric phosphite $\rightleftharpoons$ spirophosphorane equilibrium is characteristic[137,152,155,156] of spirophosphoranes with a P–H bond derived from glycols[131,137,152] or aminoalcohols[140,153,154]:



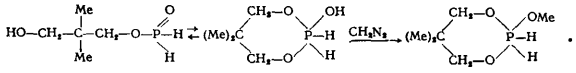
The equilibrium position depends on the temperature and the nature of the substituent in the ring and at the nitrogen atom. When X=Y=O, the equilibrium at room temperature is almost completely displaced towards spirophosphoranes[141,146]. The form with a pentacoordinate phosphorus atom is more characteristic of unsaturated or aromatic systems than of saturated rings or rings with alkyl substituents[154,157]. In asymmetric spirophosphoranes the less substituted ring is opened preferentially[157].

The dependence of the equilibrium position on the substituent at the nitrogen atom can be seen from the following example:

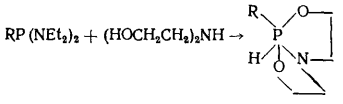


R	H	Me	Et	Ph
Spirophosphorane, %	90	25	3	0

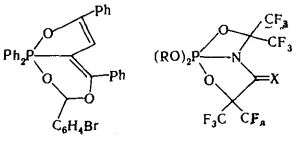
A report has been published[158] on the synthesis of a phosphorane with two P–H bonds:



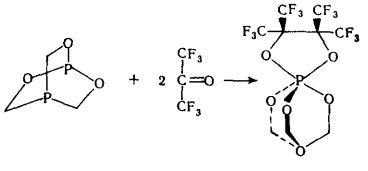
A phosphorane of the condensed type with a P–H bond is formed when aminophosphine reacts with diethanolamine[159]:



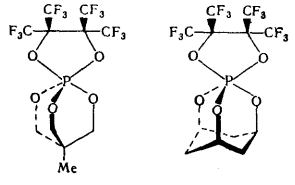
Condensed phosphoranes of the analogous type without P–H bonds have also been described[114,160,161]:



A cage phosphorane[12], which does not react further at the phosphine phosphorus atom, has been obtained by the reaction of a bicyclic phosphite–phosphine with hexafluoroacetone:



Another cage and adamantanoid phosphoranes have been obtained similarly[12,162].



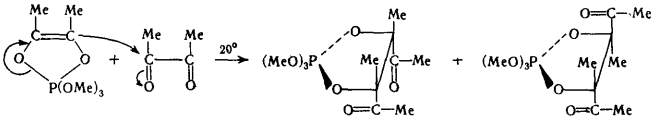
Cage phosphoranes are less stable owing to ring strain and intramolecular twisting in the trigonal bipyramid than the corresponding monocyclic and bicyclic phosphoranes. For this reason the above cage phosphoranes were obtained only with hexafluoroacetone and analogous compounds from, for example, diacetyl could not be synthesised.

III. CHEMICAL PROPERTIES

1. The Oxyphosphorane Condensation

1,3,2-Dioxaphospholens are very reactive. They can condense with carbonyl compounds to form 1,3,2-dioxaphospholans. This new method for the formation of carbon–carbon bonds has been called the oxyphosphorane condensation[7,8,46,163–166].

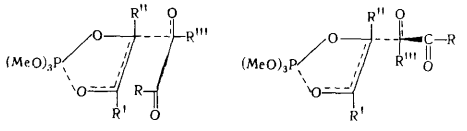
The reaction is nucleophilic addition of the unsaturated carbon atom to the carbonyl group. The condensation can proceed both stereoselectively (with formation of two isomers) and stereospecifically (with formation of one isomer only). For example, 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholen reacts smoothly with diacetyl to form two diastereomeric 1,3,2-dioxaphospholans[167]:



meso (80%) $\delta^{31}P = +54{,}8$ p.p.m. racemate (20%) $\delta^{31}P = +52{,}8$ p.p.m.

These two forms differ in their ^{31}P and ^{1}H spectra. The nucleus of the phosphorus atom is more effectively screened in the meso-form than in the racemate.

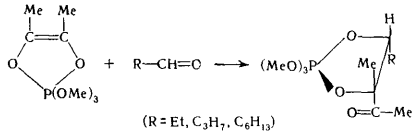
The reaction may proceed[23,168] via the transition states



in which the P–O bond of the phospholen is ruptured and new P–O and C–C bonds of the phospholan are formed.

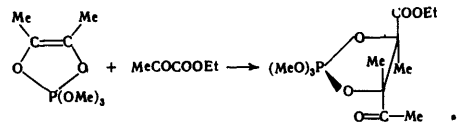
Two factors determine the proportions of the isomers formed: (1) the steric factor, according to which the least bulky groups are closest to one another and (2) the electronic factor associated with the favourable dipole–dipole interaction between the carbonyl groups when these are present.

The following compounds undergo the oxyphosphorane condensation with 1,3,2-dioxaphospholens: benzil, 1-phenylpropanedione (the benzoyl group is attacked exclusively), and phenylglyoxal (the reaction involves the aldehyde group)[168]. Propionaldehyde, butyraldehyde, and heptanal[7] react stereospecifically with formation of only one distereomer, in which the methyl and alkyl groups are in the *trans*-positions relative to one another, i.e. the stereochemistry of the products is determined by steric factors:



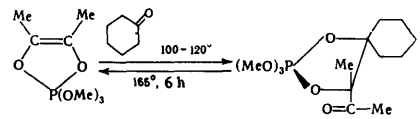
The following compounds undergo condensation with phospholens: benzaldehyde, phthalic and terephthalic aldehydes[169], and others[170,171]. Methyl pyruvate gives rise to two isomers, the product in which the two methyl groups are in the *trans*-positions relative to one another predominating, i.e. the steric repulsion between these two

groups exceeds the dipole–dipole attraction of the acetyl and methoxycarbonyl groups:

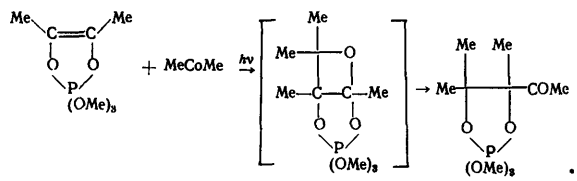


Acenaphthenequinone[7], *p*-benzoquinone[38,172,173], and hexafluoroacetone[174] readily condense with 1,3,2-dioxaphospholens.

Monoketones (cyclobutanone, cyclohexanone, acetophenone, *p*-nitroacetophenone, and $\alpha\alpha\alpha$-trifluoroacetophenone[174]) are less reactive than monoaldehydes and the reaction requires relatively high temperatures (100–120°C), which makes it unsuitable, since under these conditions the thermal decomposition of 1,3,2-dioxaphospholans begins:

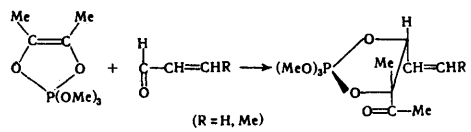


Cyclopentanone, acetone, butanone, 3-hexanone, and benzophenone do not enter into the oxyphosphorane condensation. Acetone can undergo photocondensation[175] with 1,3,2-dioxaphospholens. It has been established[176] that the reaction proceeds via the intermediate formation of oxetans:



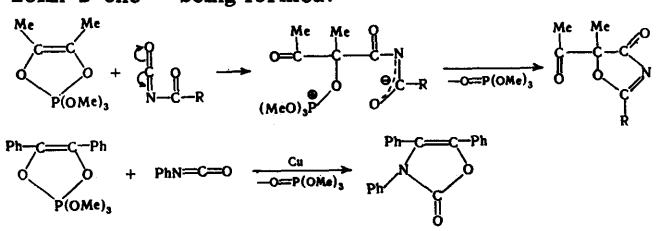
The reactivity of 1,3,2-dioxaphospholens in the oxyphosphorane condensation decreases on passing from dicarbonyl compounds to monoaldehydes and then to ketones. Electron-accepting substituents accelerate this reaction.

$\alpha\beta$-Unsaturated aldehydes[177,178] add to phospholens via the C=O group, and not in the 1,4-positions, with formation of only one stereoisomer:



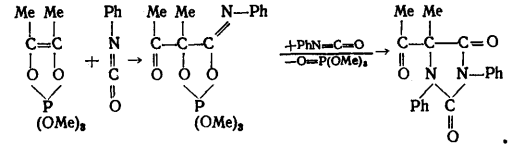
The attempts to condense a phospholen with $\alpha\beta$-unsaturated ketones were unsuccessful.

Systems with cumulative double bonds such as acyl or aryl isocyanates react with phospholenes, a trialkyl phosphate being eliminated and 2-oxazolin-4-one[179] or 4-oxazolin-2-one[180] being formed:

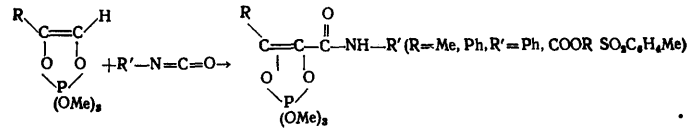


The latter reaction is catalysed by copper and probably proceeds via the intermediate formation of benzoylphenylcarbene, which reacts further with phenyl isocyanate.

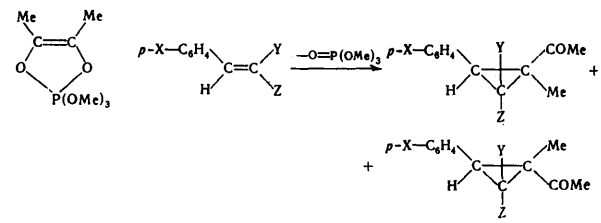
When aryl isocyanate adds to a phospholen without a catalyst, a dioxaphospholan is formed initially and then reacts further with a second molecule of phenyl isocyanate to form a hydantoin derivative[181,182]:



When there is a hydrogen atom at the double bond of the phospholen, the reaction with isocyanates takes place with retention of the phospholen ring[183]:



1,3,2-Dioxaphospholens can condense with olefins containing an electrophilic double bond. The reaction products are substituted cyclopropanes[184,185]:

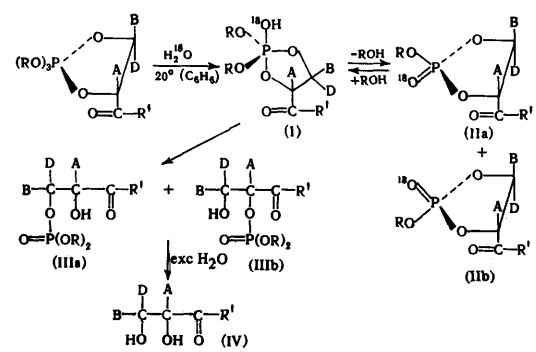


Keten[186] and carbon suboxide[187] react with phospholens at the C=O group. 1,2-Oxaphospholens do not undergo phosphorane condensation with carbonyl compounds[44].

The synthetic possibilities of the oxyphosphorane condensation are very great. Apart from the synthesis of new derivatives with a pentacoordinate phosphorus atom and certain cyclic compounds without a phosphorus atom (as stated above), this reaction leads to a series of new cyclic phosphates, open-chain phosphate esters, and hydroxycarbonyl compounds without phosphorus. All these compounds can be obtained from phosphoranes via hydrolysis.

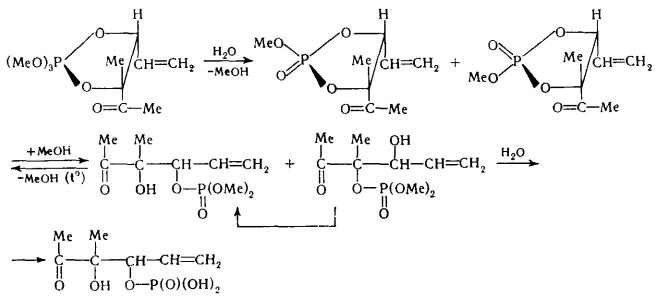
2. Hydrolysis of Phosphoranes

All 1,3,2-dioxaphospholans are extremely sensitive to hydrolysis. There is a possibility of the formation of three types of products: cyclic phosphates, open-chain phosphates, and diols without phosphorus:

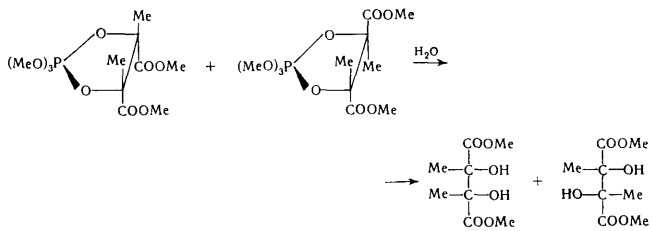


The first stage in the hydrolysis of 1,3,2-dioxaphospholans involves one equivalent of water and the nucleophilic substitution of a methoxy-group by a hydroxy-group[177]. The axial methoxy-group is apparently the first to be exchanged. The intermediate cyclic phosphorane (I) yields the cyclic phosphates (IIa) and (IIb)[165,170,188], which are diastereoisomers at the phosphorus atom. By employing heavy water, it has been shown that ^{18}O enters the phosphoryl group. The methanol formed in the hydrolysis reacts with the cyclic phosphates, yielding the acyclic phosphates (IIIa) and (IIIb) via the same intermediate (I). An excess of water leads to the formation of the corresponding diol (IV)[168,189,190]. The ease of removal of phosphorus from cyclic products depends on the nature of the groups linked to the five-membered ring.

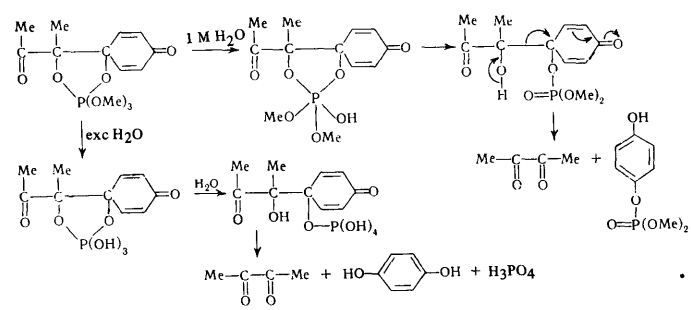
For example, the hydrolysis of 4α-acetyl-2,2,2-trimethoxy-4β-methyl-5α-vinyl-1,3,2-dioxaphospholan[177,178] leads to diastereomeric cyclic phosphates and further to acyclic phosphates. Phosphorus cannot be removed from the molecule even by an excess of water in the presence of an acid: the final hydrolysis product is a phosphate monoester:



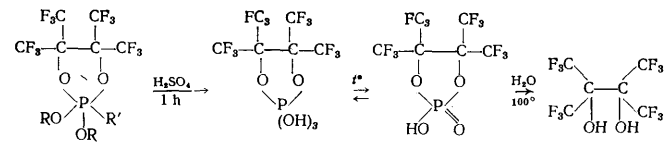
Diastereomeric 1,3,2-dioxaphospholans[46], obtained by the interaction of pyruvate ester with trimethyl phosphite, yield tartaric acid derivatives on hydrolysis[186]:



Thus hydrolysis of 1,3,2-dioxaphospholans makes it possible to obtain various polyhydroxycarbonyl compounds which are difficult to obtain by other procedures. In certain cases the hydrolysis of phospholans results in the cleavage of the C–C bond[172,173]:

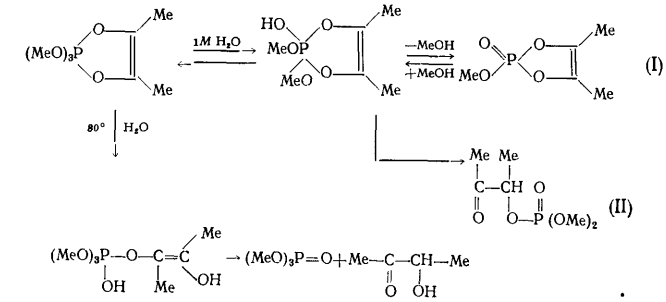


The mechanisms of the hydrolysis by 1 M water and an excess of water are different. The presence in the 1,3,2-dioxaphospholan ring of powerful electron-accepting substituents such as CF_3 makes them chemically inert and their hydrolysis proceeds only when they are acted upon by concentrated sulphuric acid[31,56]:



(R′=OR, NEt_2)

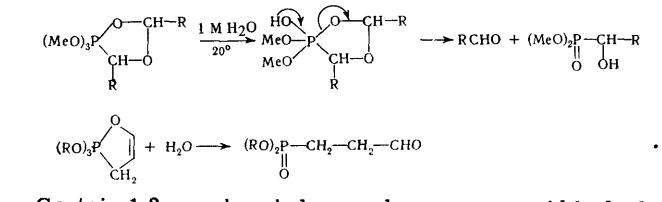
The hydrolysis of 1,3,2-dioxaphospholens proceeds similarly to that of 1,3,2-dioxaphospholans with formation of intermediates of the same type. For example, 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholen[191] is hydrolysed by one equivalent of water to a cyclic or acyclic phosphate (I or II):



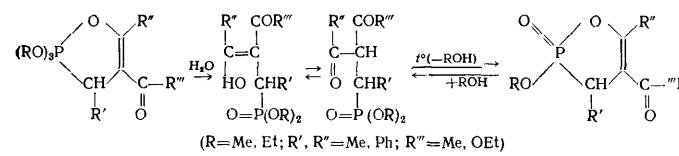
Trimethyl phosphate and acetoin are formed (at 80°C) via a different mechanism, since the phosphates (I) and (II) are not hydrolysed to acetoin under these conditions.

One of the most interesting aspects of the chemistry of cyclic oxyphosphoranes is their hydrolysis and alcoholysis. There is a striking similarity between these reactions and the analogous reactions of cyclic phosphates. The study of the hydrolysis of five-membered cyclic phosphates has shown[192,193] that compounds with a pentacoordinate phosphorus atom are involved in these reactions as intermediates. The hydrolysis of five-membered cyclic dioxyphosphoranes and the hydrolysis and alcoholysis of cyclic phosphates proceed via the formation of the same intermediates.

Phosphoranes containing a P–C bond in the ring are hydrolysed to the corresponding acyclic phosphonates[44,67,68]:

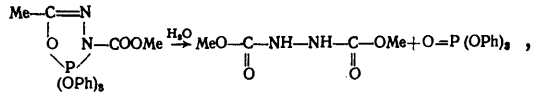


Certain 1,2-oxaphospholens undergo very rapid hydrolysis (sometimes even by atmospheric moisture) with formation of the corresponding ketophosphonates; in certain cases it is possible to isolate the labile enolic phosphonate[44,69,70]. When the products of the hydrolysis of 1,2-oxaphospholens are distilled, the alcohol is split off with formation of a cyclic phosphonate[73–75]:

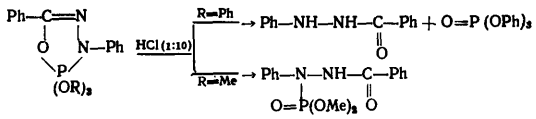


(R=Me, Et; R′, R″=Me, Ph; R‴=Me, OEt)

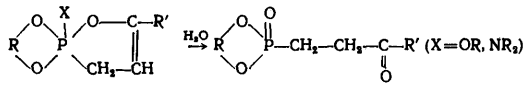
The sensitivity of 1,2-oxaphospholens to hydrolysis can vary within wide limits. While the adduct of triphenyl phosphite with azodiformic ester[83] is more hygroscopic than P_2O_5, the adducts of trialkyl phosphites with phenylbenzoyldi-imide[82,83] are hydrolysed,



only in the presence of hydrochloric acid:



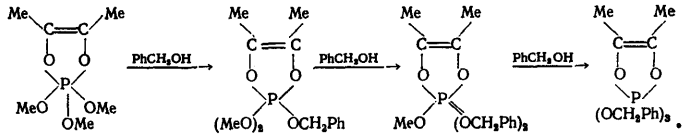
The 1,2-oxaphospholen ring is more sensitive to hydrolysis than the 1,3,2-dioxaphospholan or 1,3,2-dioxaphosphorinane rings. This is clearly seen for spirophosphoranes as an example[116,118]:



When spirophosphoranes obtained by the condensation of cyclic phosphonites with 1,3-dienes are hydrolysed, the ester linkage is broken[123,126].

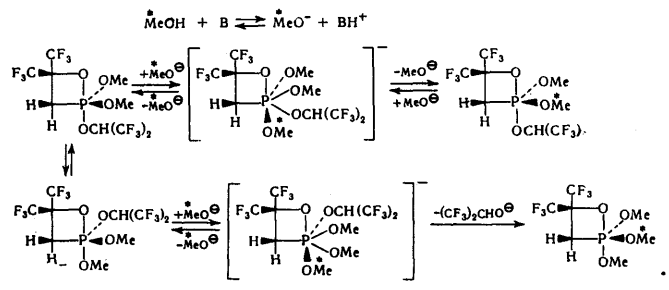
3. Alcoholysis of Phosphoranes

Phosphoranes are capable of undergoing nucleophilic substitution at the pentacoordinate phosphorus atom; the reaction proceeds with the retention of the phospholen ring. It is assumed that in a basic medium the process proceeds via a transition state with a hexacoordinate phosphorus atom[194,195]:



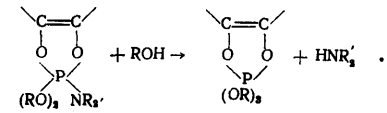
The reaction takes place in steps and the proportions of the products depend on the amount of the initial alcohol and the duration of heating. The rate of substitution depends on the concentration of the base.

The study of this substitution in 1,2-oxaphosphetans showed[115,198] that the nucleophilic RO^- species approaches the phosphorus atom from the equatorial side opposite the equatorial group being removed; the transition state has an octahedral symmetry with a linear distribution of the entering and leaving groups:

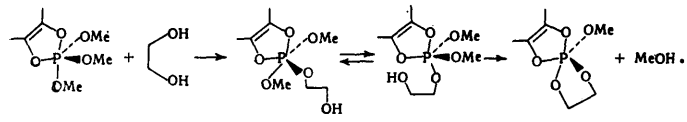


Hexafluoroisopropyl alcohol is more acid than methanol and therefore its anion is more suitable as the leaving group. The relative rates of substitution and of permutational isomerisation[10,12] of phosphoranes (see below) determine the course of this reaction.

When an alcohol is allowed to react with an aminophosphorane, the dialkylamine group is exchanged[30]:

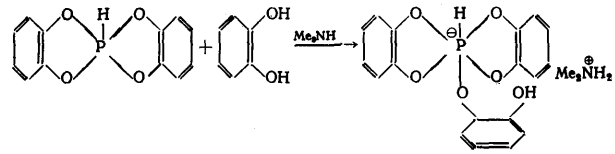


The reaction of ethylene glycol with phosphoranes is exothermic[115]. After the substitution of one equatorial group and subsequent permutation isomerisation, a second equatorial methoxy-group is substituted with formation of a spirophosphorane in which there is an axial-equatorial distribution of the two rings:

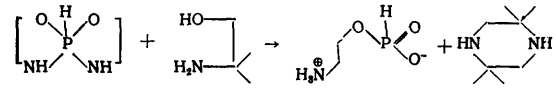


The driving force of this reaction is the appreciable increase of the stability of the resulting spirophosphorane (compared with 1,3,2-oxaphospholen) as a result of the decrease of intramolecular tension, which is smaller in bicyclic phosphoranes.

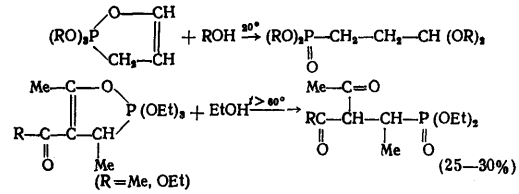
On reaction with β-aminoalcohols or β-glycols in the presence of bases, spirophosphoranes with a P–H bond form compounds with a hexacoordinate phosphorus atom[151]:



Salts of another type can be formed[197]:

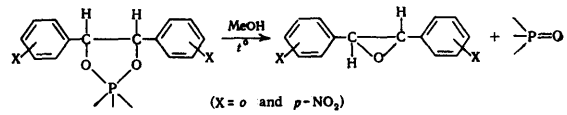


1,2-Oxaphospholen rings are opened by an alcohol[67,68,73]:

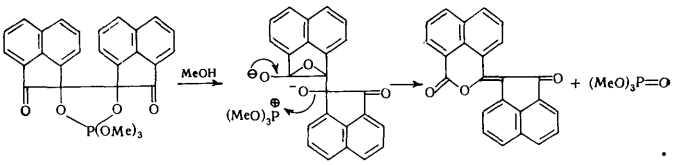


The thermal alcoholysis of 1,3,2-dioxaphospholans leads to the disruption of the phospholan ring. The reactions proceed with the formation of trialkyl phosphates and are frequently accompanied by molecular rearrangements.

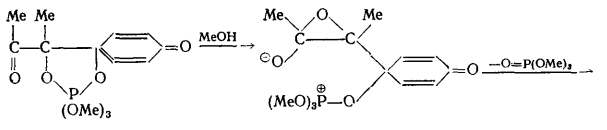
Methanolysis of phosphoranes with two hydrogen atoms and two phenyl groups in the phospholan ring leads to the formation of *trans*-epoxides[63,198]:



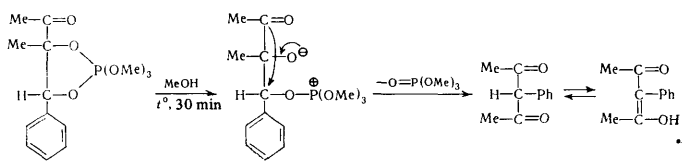
Methanolysis proceeds in a different manner when there are acyl substituents in the phospholan ring[163,164]:



The enol acetate formed on solvolysis can react with the alcohol[172]:



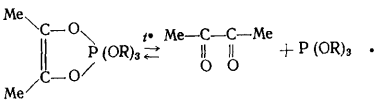
On treatment with hot methanol, 4-acetyl-2,2,2-trimethoxy-4-methyl-5-phenyl-1,3,2-dioxaphospholan loses trimethyl phosphate with a simultaneous skeletal carbon rearrangement, leading to a 1,2-shift of the acetyl group[169]:



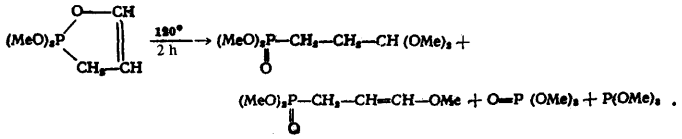
Possibly the high dielectric constant of the solvent (methanol) plays a decisive role in the thermal alcoholysis reactions.

4. Thermal and Photochemical Decomposition of Phosphoranes

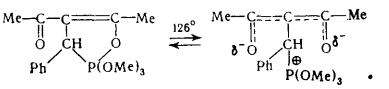
The majority of cyclic phosphoranes are thermally stable up to 100–120°C in an atmosphere of nitrogen[15] and many can be distilled *in vacuo*[5-7]. When certain 1,3,2-dioxaphospholens[14,77,199] and 1,2-oxaphospholens[73] are distilled, their partial dissociation into the initial compounds is observed:



When the simplest 1,2-oxaphospholen is heated, a complex mixture of substances is obtained[68], from which trimethyl phosphite, trimethyl phosphate, the dimethyl acetal of phosphonopropionaldehyde, and a small amount of an enol ether have been isolated; the latter is formed as a result of the thermal decomposition of the acetal[200] during distillation:

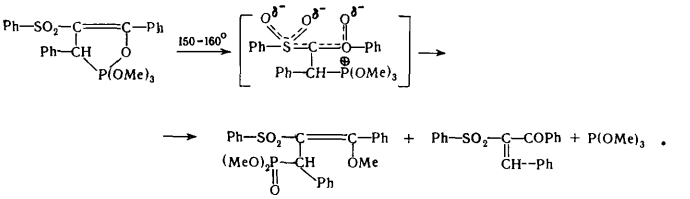


In the course of a study of the stereochemistry of cyclic phosphoranes in solution by ^{1}H NMR it was found[9,11,66] that above 110°C the ring P–O bond in 1,2-oxaphospholens is dissociated. The phosphorane ring is converted into a dipolar ion; the signals of the Me–C= and Me–C(O)– groups in the ^{1}H NMR spectrum merge at 126°C.

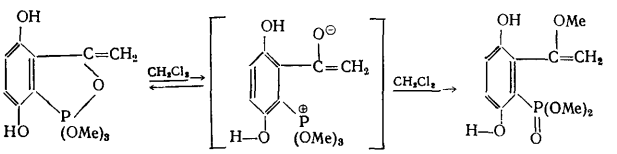


This process is reversible when it occurs below the decomposition and isomerisation temperatures. The temperature at which the Me–C= and Me–C(O)– peaks merge can serve as a measure of the stability of this phospholen system. In the spectrum of the analogous 1,2-oxaphospholen with ethoxy-groups at the phosphorus atom instead of the methoxy-groups the peaks merge at a temperature 15 deg lower. This can serve as an illustration of the importance of steric effects and intramolecular [packing? (Ed. of Translation)] density in the determination of the relative stabilities of compounds with pentacoordinate and tetracoordinate phosphorus. The adduct with EtO groups, which is more sterically strained, is less stable than the MeO adduct.

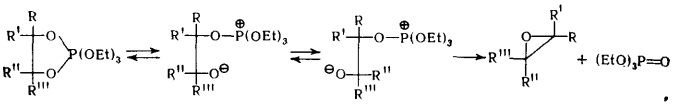
The dissociation of 1,2-oxaphospholen into a dipolar ion has been demonstrated by ^{31}P NMR spectroscopy[77]. The dipolar ion formed isomerises to an enol ether; the reaction is accompanied by the dissociation of the phosphorane (or the dipolar ion) into the initial compounds:



The isomerisation to an enol ether proceeds in the dipolar ion stage, while cyclic phosphoranes do not show a tendency to undergo this reaction; this has been demonstrated in a large number of instances[201]. Cases have been described where phosphoranes in polar solvents are in equilibrium with the dipolar form, the latter undergoing a rapid rearrangement as a result of dealkylation[58,78]:



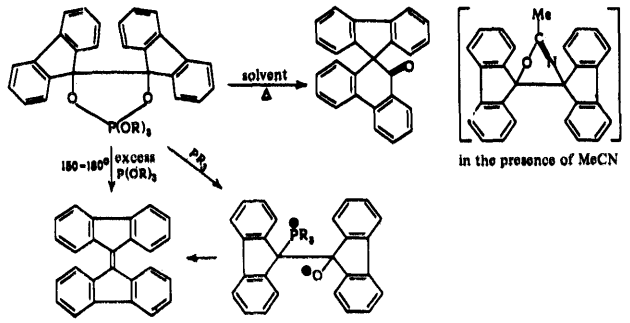
1,3,2-Dioxaphospholans undergo stereospecific thermolysis with formation of *trans*-epoxides. The temperature at which phospholans are decomposed depends on the ring substituents[49,54,89,169]:



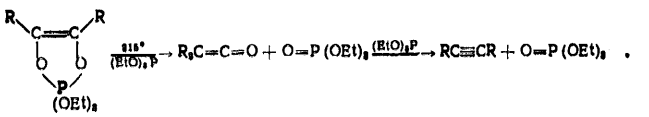
A similar course of the reaction, leading to the formation of epoxides, has been suggested for the highly exothermic interaction of tris(dimethylamino)phosphine with

aromatic aldehydes having electron-accepting substituents [63,202]. Such thermal decomposition of the phosphorane into an epoxide and a phosphate is analogous to the second stage of the Wittig reaction.

The 2 : 1 fluorenone–trialkyl phosphite adducts split off the trialkyl phosphate with a simultaneous rearrangement of the pinacol type on heating in different solvents [58,59,203-206]. The same rearrangement occurs when phospholan is dissolved in anhydrous acetonitrile with formation of an oxazoline in 17% yield [205]. On heating with an excess of the phosphite or phosphine, deoxygenation takes place [206]. The thermal stability of this 1,3,2-dioxaphospholan depends on the nature of the alkoxy-group linked to the phosphorus atom.

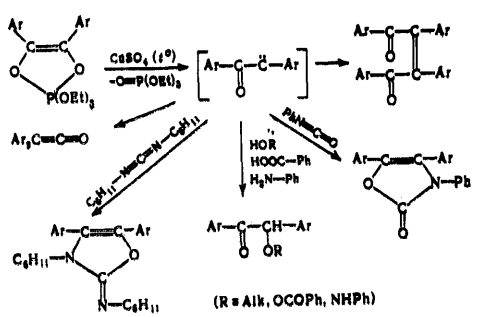


When 1,3,2-dioxaphospholens are heated in the presence of an excess of phosphite, deoxygenation with formation of a trialkyl phosphate and a diaryl- or alkylaryl-acetylene is also observed [207,208]. The intermediate formation of a disubstituted keten in this reaction has been demonstrated:

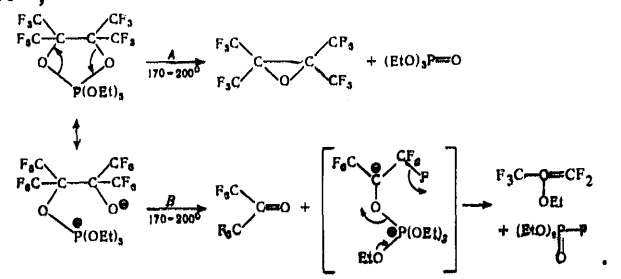


Dialkylacetylenes have not been obtained in the analogous reaction, although the corresponding phosphates are formed.

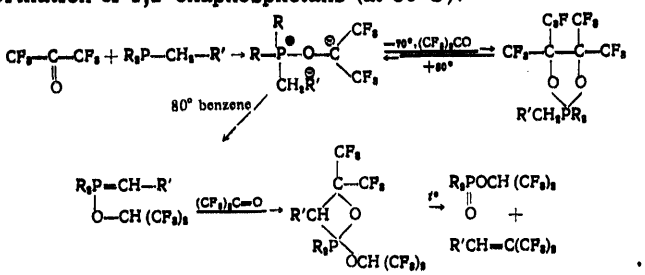
In the presence of copper or its salts 1,3,2-dioxaphospholen is decomposed at a lower temperature. The course of this reaction can be satisfactorily accounted for [180] on the assumption that a carbene is formed initially:



The thermal stability of the 2 : 1 adducts of hexafluoroacetone with various phosphorus(III) derivatives depends on the nature of the groups linked to the phosphorus atom. While 1,3,2-dioxaphospholans having alkoxy-groups at the phosphorus atom decompose at about 170°C into epoxyperfluorotetramethylethane and 2-ethoxyperfluoropropene [57],

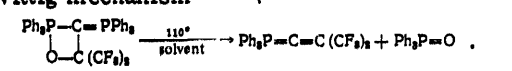


the adducts of hexafluoroacetone with phosphines containing active hydrogen in the α-position relative to the phosphorus atom undergo a rearrangement [64] with the formation of 1,2-oxaphosphetans (at 80°C):

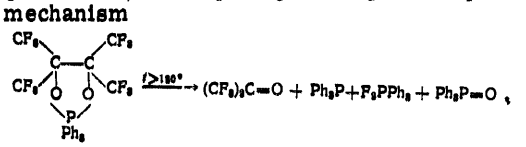


The process includes the cleavage of the 1,3,2-dioxaphospholan formed at a low temperature into a dipolar ion and hexafluoroacetone. The 1,2-oxaphosphetan formed decomposes at a higher temperature into an olefin and phosphinate in accordance with the second stage of the Wittig reaction.

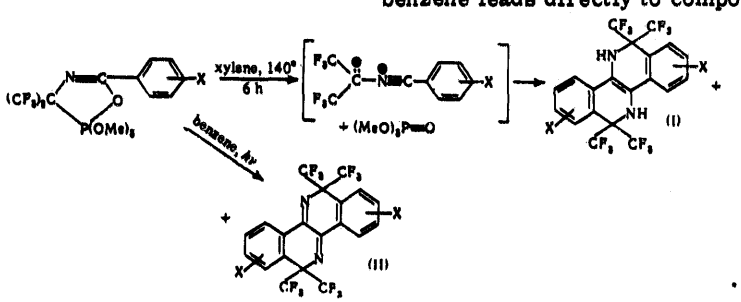
The decomposition of the 1,2-oxaphosphetan proceeds via the Wittig mechanism [101,102]:



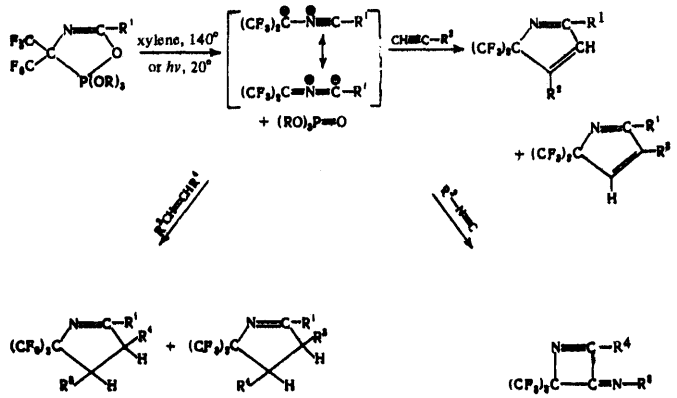
The adduct of hexafluoroacetone and triphenylphosphine is stable up to 120°C, decomposing at a higher temperature via the mechanism



The thermal elimination of phosphate is observed when 1,4,2-oxazaphospholen is refluxed in xylene [209]. The dimer (I) formed under these conditions is readily oxidised to compound (II). Photolysis of the oxazaphospholen in benzene leads directly to compound (II):

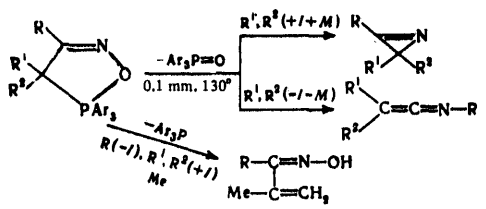


The nitrile imides formed on thermal and photochemical[210] decomposition of 1,4,2-oxazaphospholen can be detected with the aid of dipolarophiles; this results in the formation of products of 3 + 2 and 3 + 1 cycloadditions[210-215]:

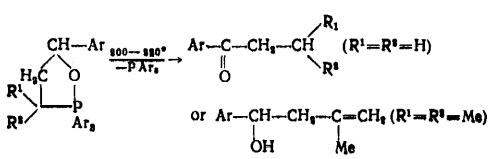


When asymmetric alkenes and alkynes were used, products with both orientations of the dipolarophile relative to the 1,3-dipole were obtained. Interaction with fumarate and maleate esters leads to identical products (epimerisation).

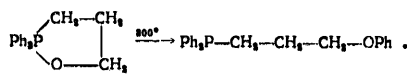
1,5,2-Oxazaphospholens having three phenyl substituents at the phosphorus atom undergo thermal decomposition with formation of either triphenylphosphine or its oxide[96]. The mode of reaction depends on the inductive ($\pm I$) and mesomeric ($\pm M$) effects of the substituents in the phospholen ring[95]:



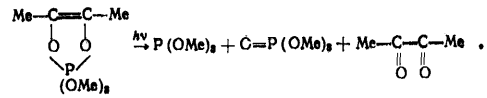
Pyrolysis of certain 1,2-oxaphospholans leads to the elimination of triphenylphosphine[97]:



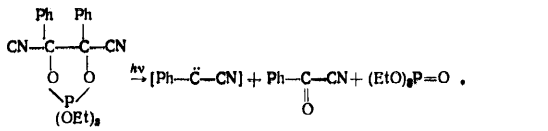
Phospholans of similar structure do not split off triphenylphosphine even at 300°C; a rearrangement, probably via an intramolecular mechanism, to 3-phenoxypropionyldiphenylphosphine takes place on heating[105]:



Photolysis of 1,3,2-dioxaphospholens leads to the formation of a trialkyl phosphite, a trialkyl phosphate, and an α-diketone. The phosphite/phosphate ratio depends on the wavelength of the irradiating light[216]:

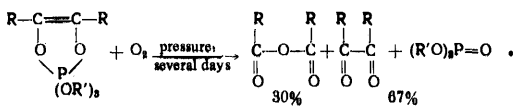


1,3,2-Dioxaphospholans can undergo photocycloelimination[54] (5 → 2 + 2 + 1):

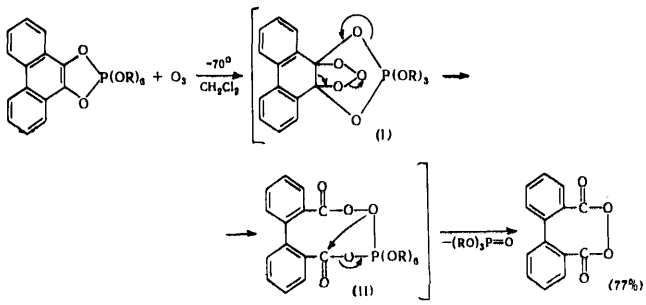


5. Oxidation of 1,3,2-Dioxaphospholens

When acted upon by molecular oxygen, the phospholen ring undergoes a rearrangement of its carbon skeleton with simultaneous dephosphorylation[5,217]:



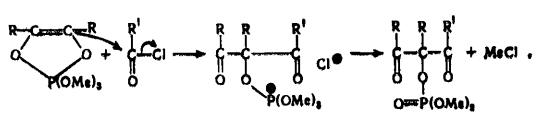
When a phospholen is treated with ozone at a low temperature, peroxide compounds are formed together with phosphates[217,218]:



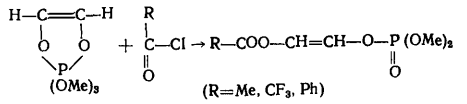
The authors believe that the process proceeds via the intermediate formation of an ozonide (I), which subsequently rearranges to the product (II); the latter splits off phosphate with formation of a peroxide.

6. Interaction of Phosphoranes with Electrophilic Reagents

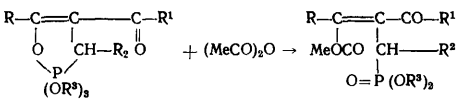
The interaction of 1,3,2-dioxaphospholens with electrophilic reagents is one of the reactions leading to the opening of the phosphorane ring. The interaction of phospholens with carboxylic acid chlorides[189] can yield polyfunctional carbonyl-containing phosphates, which are of biological interest. Various α-hydroxy-β-dicarbonyl compounds can be obtained by the hydrolysis of the phosphates formed; this is the reason for the synthetic possibilities of the reaction:



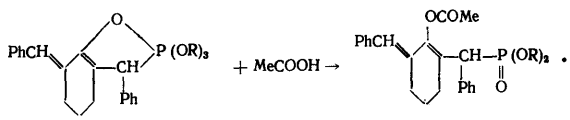
While phospholens with alkyl substituents at the unsaturated carbon atoms undergo *C*-acylation, phospholens with a labile hydrogen atom undergo *O*-acylation[219]:



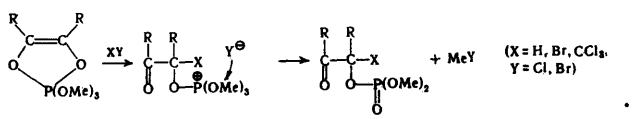
O-Acylation products are obtained when carboxylic acid anhydrides interact with 1,3,2-dioxaphospholens[220] and 1,2-oxaphospholens[68-70,73-76,118]:



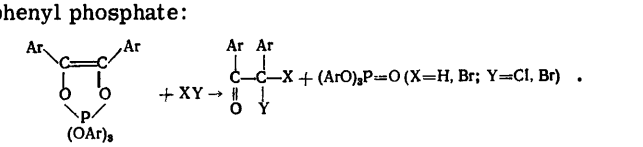
The formation of an enol acetate when a 1,2-oxaphospholen was acted upon by acetic acid was noted in one instance[69,70]:



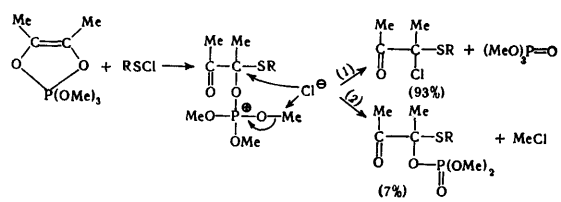
1,3,2-Dioxaphospholens interact with dry HCl,[6,26,186,219] with bromine[6,186,221], and with $CBrCl_3$ (photolysis in the presence of $CBrCl_3$).[222] Under these conditions, phosphates are formed when there are alkoxy-groups attached to the phosphorus atom:



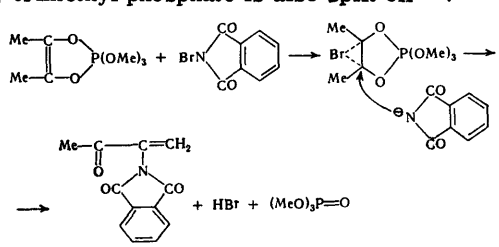
When phenoxy-groups, which are incapable of forming ArY are attached to the phosphorus atom, the intermediate phosphonium product decomposes with elimination of triphenyl phosphate:



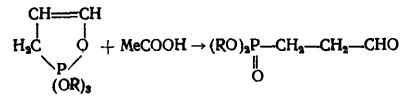
The interaction of phospholens with sulphenyl chloride takes place similarly[223-225], but the authors believe that an anionic attack is more likely:



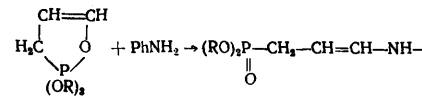
When 1,3,2-dioxaphospholen reacts with *N*-bromophthalimide, trimethyl phosphate is also split off[226]:



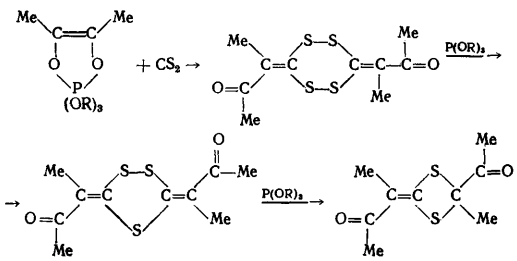
The interaction of certain 1,2-oxaphospholens with acetic acid has been investigated[68,77]:



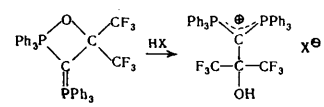
as well as the interaction with aniline[227]:



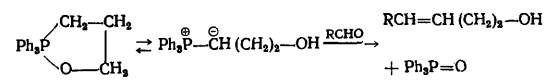
The phospholen ring is disrupted when acted upon by carbon disulphide[228]. The sulphur can be removed from the resulting tetrathi-ine by an excess of phosphite:



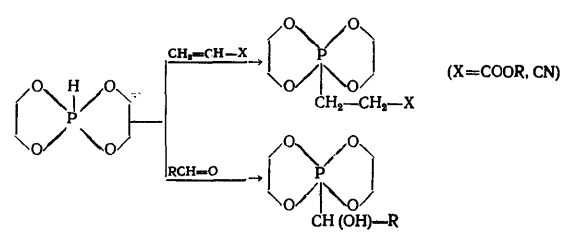
Phosphoranes with three phenyl substituents at the phosphorus atom differ in their chemical properties from phosphoranes with alkoxy-groups. For example, on interaction with HX, 1,2-oxaphosphetans give rise to salts[101]:



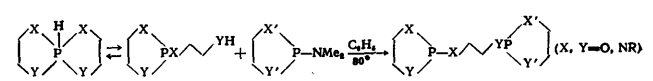
1,2-Oxaphospholans can react as ylides with aldehydes, yielding γδ-unsaturated alcohols[229]:



Spirophosphoranes with a P–H bond add to electrophilic multiple bonds[230] and interact with aldehydes[231] like dialkylphosphorous acids:



The chemical properties of spirophosphoranes containing a P–H bond are in many ways determined by the phosphorane ⇌ phosphite equilibrium. Intermolecular isomerisation takes place when asymmetric phosphoranes are heated[131,132,143]. The formation of a diphosphite in the subsequent reaction constitutes chemical proof of the existence of the phosphite ⇌ phosphorane equilibrium[232]:



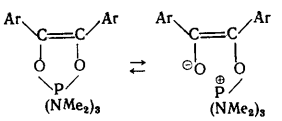
IV. PHYSICAL PROPERTIES. STEREOCHEMISTRY OF PENTACOORDINATE PHOSPHORUS COMPOUNDS

All the physicochemical studies on phosphoranes were undertaken to establish their structures and stereochemistry. Cyclic phosphoranes are ideal systems for the investigation of the stereochemistry of pentacoordinate phosphoranes. The problem of valence in compounds for which a phosphorane structure is proposed can be solved by combination of X-ray diffraction, ^{1}H and ^{31}P NMR, and infrared spectroscopic methods.

1. ^{31}P NMR Spectra

The principal argument in support of the pentacovalence of phosphorus is the high positive chemical shift ($\delta^{31}P$) of these compounds in ^{31}P NMR spectra relative to 85% orthophosphoric acid[7,15]. This implies that the phosphorus nucleus in phosphoranes is more screened than in the standard. In compounds with a dipolar structure and a positive charge on the phosphorus nucleus the phosphorus atom is highly descreened and $\delta^{31}P$ has a high negative value[233]. In those cases where phosphorane $\rightleftharpoons$ dipolar ion equilibrium obtains $\delta^{31}P$ has an intermediate value, since the equilibrium is attained rapidly relative to the NMR time scale. In such cases $\delta^{31}P$ depends on the polarity of the solvent: in non-polar solvents the equilibrium is displaced towards the phosphorane structure and $\delta^{31}P$ becomes more positive; in polar solvents the equilibrium is displaced towards the dipolar form and the chemical shift is displaced towards lower fields.

The benzil–tris(dimethylamino)phosphine adduct has been isolated in two crystalline forms[9,37,38], one of which corresponded to a phosphorane and the other to a dipolar ion. In solution the two forms exist in equilibrium:



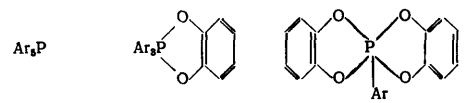
$\delta^{31}P$ = + 29.9 p.p.m. (1 M in hexane)
+13.1 p.p.m. (1 M in CH_2Cl_2)

A similar dependence of $\delta^{31}P$ on the solvent has been noted for adducts of phenanthrenequinone with diethylphenylphosphine and ethyldiphenylphosphine[9,39].

The ^{31}P NMR spectra of phosphoranes have fine structure owing to the interaction of phosphorus with adjacent protons: $^{3}J_{P-O-C-H} \simeq 10-13$ Hz and $^{2}J_{P-C-H} \simeq 20-24$ Hz.

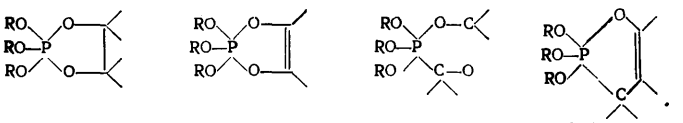
Most of the cyclic oxyphosphoranes have $\delta^{31}P$ in the range +50 ± 30 p.p.m. The dependence of this quantity on the structure of the ring and on the electronegativity of the substituents is not very pronounced. As a rule, the replacement of methoxy-groups at the phosphorus atoms by phenoxy-groups greatly increases $\delta^{31}P$.[36,83]

On passing from acyclic phosphoranes to monocyclic and bicyclic phosphoranes, $\delta^{31}P$ falls[9]:



+ 85.6 p.p.m. + 60.8 p.p.m. + 29.8 p.p.m.

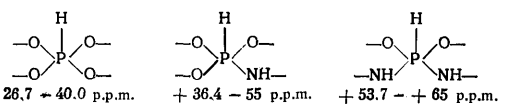
2,2,2-Trialkoxy-1,3,2-dioxaphospholans have $\delta^{31}P$ ranging from +44 to +62 p.p.m.[23] The replacement of one P–O bond in the phosphorane ring by P–C decreases $\delta^{31}P$.



+ 54.8 p.p.m. + 48.9 p.p.m. + 34.1 p.p.m. + 27.8 p.p.m.

The introduction of a second 1,3,2-dioxaphospholen or a 1,3,2-dioxaphospholan ring reduces $\delta^{31}P$, while the introduction of the 1,3,2-dioxaphosphorinane ring does not appreciably alter the chemical shift. The substitution of an endocyclic oxygen atom by nitrogen leads to a slight increase of $\delta^{31}P$ (about 5 p.p.m.), while the replacement of an exocyclic oxygen atom by nitrogen reduces $\delta^{31}P$ by 2–4 p.p.m.[36]

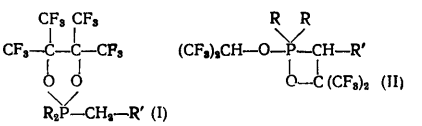
The majority of spirophosphoranes with a P–H bond have $\delta^{31}P$ = +26 – +55 p.p.m.; the values of $\delta^{31}P$ increase when O in the ring is replaced by N:



+ 26.7 – 40.0 p.p.m. + 36.4 – 55 p.p.m. + 53.7 – + 65 p.p.m.

If the molecule contains phenyl substituents, $\delta^{31}P$ decrease. In certain spirophosphoranes containing substituted nitrogen in the ring $\delta^{31}P$ may be between +60 and +100 p.p.m.[143,156] The differences between the chemical shifts of diastereomers are between 1 and 5 p.p.m.[7]

A high positive value of $\delta^{31}P$ constitutes important but not unique evidence of the pentacovalence of phosphorus in cyclic phosphoranes. The chemical shifts of certain phosphoranes are negative. For example $\delta^{31}P$ of 1,3,2-dioxaphospholans obtained by the condensation of hexafluoroacetone with tertiary phosphines[10,11,39,64] vary from −11.7 p.p.m. (for R = Et) to +53.2 p.p.m. (for R = OEt).



Chemical shifts for the phosphorus nucleus in 1,3,2-dioxaphospholans (I) and 1,2-oxaphosphetans (II).

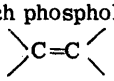
R	$\delta^{31}P$ R_3P	$\delta^{31}P$ (I)	$\delta^{31}P$ (II)	R	$\delta^{31}P$ R_3P	$\delta^{31}P$(I)	$\delta^{31}P$ (II)
Me	+62	+3.2	+23.7	Ph	+5.7	+21.6	—
Et	+19.1	−11.7	+15.7	OEt	−138.5	+53.2	—
n-Bu	+32.6	−7.3	+17.2	OMe	−140.0	+50.1	—

The following observation has been made (see Table): if the signal of the initial phosphorus(III) compound is in the high field region, then $\delta^{31}P$ for the 1,3,2-dioxaphospholan (I) obtained from it is displaced towards lower fields and conversely[11]. In 1,2-oxaphosphetans (II) $\delta^{31}P$ are more positive than in the corresponding 1,3,2-dioxaphospholans (I). Low values of $\delta^{31}P$ have been reported for

certain spirophosphoranes obtained by the condensation of cyclic derivatives of tervalent phosphorus with acrolein[118] (+2 p.p.m.), methyl vinyl ketone[119] (+0.62 p.p.m.), and 3,4-bis(trifluoromethyl)-1,2-dithietan[127] (between −16.5 and −17.5 p.p.m.).

2. Infrared, Raman, and Ultraviolet Spectra

A characteristic feature of compounds with pentacoordinate phosphorus atom is a shift of the stretching vibration band of the P–O–R group towards higher wavenumbers (1090–1075 cm^{-1})[15] compared with the analogous band in compounds with a tetracoordinate phosphorus atom. In the spectra of phosphoranes with aryloxy-groups at the phosphorus atom the P–O–Ar stretching vibration bands are at 1215–1200 cm^{-1}.

The position of the olefin band in the spectra of phospholens depends strongly on the substituents at the double bond and varies from 1664–1645 cm^{-1} [23,27] to 1740 cm^{-1}.[15] In controversial cases the problem of whether or not the band belongs to the stretching vibrations of the double bond can be solved by Raman spectroscopy[15,73]. If a carbonyl group is present in the α-position relative to the double bond in phospholens, there is an interaction between the vibrations and the wave-numbers ν(C=O) and ν(C=C) are markedly distorted[71]. The infrared and Raman spectra indicate the presence of two forms of such phospholens with different mutual orientations of the  and C=O groups[73].

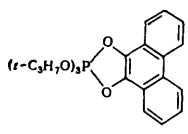
Spirophosphoranes with a P–H bond have a broad band at 2380 ± 30 cm^{-1}.[141,234,235]

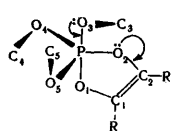
The ultraviolet spectra of 1,3,2-dioxaphospholens[23] and 1,2-oxaphospholens[73,74,76] with a carbonyl or alkoxycarbonyl group in the α-position relative to the double bond are characterised by an intense absorption over a broad section of the spectrum from 220 to 340 nm. The positions of the maxima depend on the substituent in the phospholen ring.

The dipole moments of oxaphospholens are 2–4 D.[6,14,67] The atomic refraction of the phosphorus in phospholen is 3.95.[236]

3. X-Ray Diffraction Analysis

The X-ray diffraction analysis of the two allotropic forms of the 1,3,2-dioxaphospholen obtained by the interaction of phenanthrenequinone with tri-isopropyl phosphite showed that the molecule has a slightly distorted trigonal bipyramidal structure with an axial-equatorial placement of the 1,3,2-dioxaphospholen ring[25,65,160,237,238]. The axial P–O bonds in the ring are longer by 0.1 Å than the equatorial P–O bonds. The exocyclic P–O bonds are somewhat shorter than the endocyclic bonds. This is related to the more intense $p_\pi - d_\pi$ interaction of phosphorus with the exocyclic oxygen atoms. The axial P–O bonds are weaker and more polarisable than the equatorial bonds and are therefore preferred by electronegative substituents.



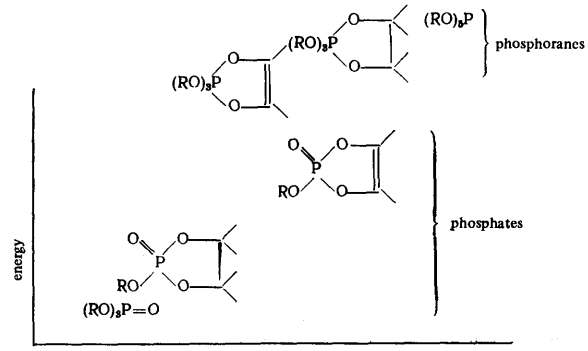


Certain bond lengths and angles in the phenanthrenequinone–tri-isopropyl phosphite adduct[9,11].

Bond length, Å		Angle in degrees			
$P-O_1$	1.753	O_1-P-O_2	89.3	$P-O_1-C_1$	111.9
$P-O_2$	1.649	O_2-P-O_3	88.6	$P-O_2-C_2$	114.2
$P-O_3$	1.641	O_3-P-O_4	91.3	$P-O_3-C_3$	121.8
$P-O_4$	1.601	O_4-P-O_5	93.1	$P-O_4-C_4$	129.8
$P-O_5$	1.586	O_5-P-O_1	117.2	$P-O_5-C_5$	127.5
O_1-C_1	1.347	O_4-P-O_5	117.2		
O_2-C_2	1.433	O_5-P-O_2	125.5		
C_1-C_2	1.333	$O_1-C_1-C_2$	113.9		
O_3-C_3	1.463	$O_2-C_2-C_1$	110.3		

The fact that α-dicarbonyl compounds form 1,3,2-dioxaphospholens with trialkyl phosphites but not with tris(dimethylamino)phosphine can be accounted for by the lower electronegativity of nitrogen (less favourable for the axial position) and the more stringent steric requirements of the dimethylamino-group compared with alkoxy-groups.

The O–P–O and P–O–C angles are capable of undergoing considerable distortion. The trigonal bipyramid is very tightly packed owing to the very short distances between certain non-bonded atoms (down to 2.63 Å). The contraction of the trigonal bipyramid can explain the higher stability of five-membered cyclic phosphoranes compared with acyclic phosphoranes, in contrast to the higher stability of acyclic phosphates compared with five-membered cyclic phosphates, although on the whole phosphoranes have a higher energy than the corresponding phosphates. This is clearly illustrated in the figure below[9,11].



This phenomenon plays a major role in the chemistry of biologically active compounds. Nucleophilic reagents (water, alcohol) add to the P=O group of five-membered cyclic phosphates (but not acyclic phosphates) with formation of intermediate unstable compounds containing a pentacoordinate phosphorus atom[177,178,188,191,192,239–245].

The existence of stable oxyphosphoranes supports the hypothesis that metastable oxyphosphoranes are intermediates in the reaction of tetracoordinate phosphorus[246]. The entering and leaving groups are then located in the axial positions.

4. Permutational Isomerisation

The ligands in the trigonal bipyramid can undergo intramolecular shifts (permutational isomerisation) more or less readily, which occur either via bond deformation (regular process) or via bond dissociation and recombination (irregular process)[162,247].

As a result of permutational isomerisation, the groups occupying the axial and equatorial positions change places, which leads to the formation of a new bipyramid. If all the five groups linked to the phosphorus atom are different, we have twenty chiral isomers, i.e. ten pairs of enantiomers in relation to the configuration at the phosphorus atom. If two ligands are equivalent, the number of isomers decreases to ten, namely six chiral and four achiral isomers. If three ligands are equivalent, we have four achiral isomers.

However, virtually all the ligands linked to the phosphorus atom occupy a definite position in the trigonal bipyramid, which is determined by the electronegativity, steric requirements, and the involvement of the *d* orbitals of phosphorus in the formation of the bonds. All this can be expressed in terms of the general polarity rule[162,247-250].

If any one group cannot occupy an axial position owing to steric or electronic factors, the number of isomers is reduced to twelve. A similar situation obtains if the substituent cannot occupy an equatorial position. Four- and five-membered rings occupy an axial-equatorial position in the trigonal bipyramid[9,25,65,160], while both axial-equatorial and diequatorial positions are possible for a six-membered ring.

Regular permutational isomerisation of acyclic phosphoranes can occur via six different mechanisms[250,251]. It has been shown theoretically[252] and by calculations based on infrared and Raman spectra[253] that the Berry pseudorotation mechanism is the most probable[254]. In a pseudorotation two pairs of axial and equatorial ligands change places via an intermolecular process consisting of the bending of the bonds with deformation of the angles at the central atom. This mechanism is consistent with the experimental data and has undoubted advantages over other mechanisms proposed as alternatives (pseudorotation is discussed in Refs. 248, 253, and 255).

In order to account for permutational isomerisation in cage phosphoranes, a new process called turnstile rotation has been proposed[256]. In turnstile rotation one axial and one equatorial ligand constitute a "pair" and the remaining ligands constitute a "trio". The process consists of a slight deformation of angles at the central atom and in the rotation of the "pair" in relation to the "trio" in opposite directions. On rotation by 60°, a single turnstile rotation (TR) is executed; it can be continued for a further 60° whereupon double turnstile rotation $(TR)^2$ takes place, etc. Ramirez and coworkers[13,246] give preference to this mechanism in the interpretation of the permutational isomerisation of all cyclic phosphoranes.

In turnstile rotation four- and five-membered rings play only the role of the "pair", the remaining ligands playing the role of the "trio", while six-membered rings can play the role of both the "pair" and the "trio". (Turnstile rotation is considered in greater detail in the literature[12,162,247].)

In both pseudorotation and turnstile rotation the axial and equatorial ligands are exchanged in pairs with retention of the position of the third. In turnstile rotation the ligand whose position is retained always forms part of the "trio". For each pseudorotation, there are four equivalent turnstile rotations. However, there are fundamental differences between these mechanisms. Only in turnstile rotation are all the ligands involved in internal motion about the axis passing through the central atom. The geometries, skeletal symmetries, and potential energies of these processes are different[162].

There is no unanimous view in the literature concerning the mechanism of permutational isomerisation in phosphoranes in general and in cyclic phosphoranes in particular. The pseudorotation and turnstile rotation mechanisms must be regarded as the most probable. It is impossible to give preference[257] to either on the basis of experimental data.

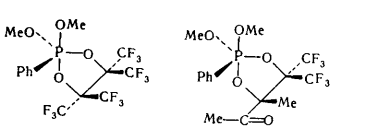
Both these processes presuppose a unimolecular mechanism. A bimolecular process including the formation of either the phosphorane dimer or a complex of the phosphorane with the solvent as the transition state or a metastable excited state has been proposed recently[258] for compounds of the type RPF_4.

5. ^{1}H NMR Spectra. Stereochemistry of Cyclic Phosphoranes

Much information about the structures of phosphoranes and their stereochemistry has been obtained from ^{1}H NMR spectra. The ^{1}H NMR spectra of many 2,2,2-trimethoxy-1,3,2-dioxaphospholens, investigated in the temperature range from +30° to −60°C, contain only one doublet due to the methoxy-groups linked to the phosphorus atoms with $^3J_{P\text{-}O\text{-}C\text{-}H} \simeq 10\text{–}13$ Hz. These results show that the methoxy-groups in the axial and equatorial positions change places, i.e. they are equivalent relative to the NMR time scale. This exchange of ligand positions cannot be inhibited even at fairly low temperatures (−90°C)[7-9,79].

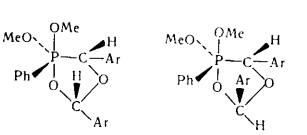
When there are different substituents at the phosphorus atom, the exchange of ligand position is retarded at a higher temperature, as demonstrated by ^{19}F NMR.[259]

A similar phenomenon occurs in 2,2,2-trimethoxy-1,3,2-dioxaphospholans, which give rise to only one doublet due to the methoxy-groups in the ^{1}H NMR spectra at all the temperatures investigated, regardless of molecular symmetry. When there are two methoxy-groups at the phosphorus atom, the ^{1}H NMR spectrum of the phospholan shows a single methoxy-group doublet, provided that the phospholan ring (but not the molecule as a whole) has a plane of symmetry. If there is no plane of symmetry, the ^{1}H NMR spectrum shows two methoxy-group doublets[11]:



one MeO group doublet — two MeO group doublets

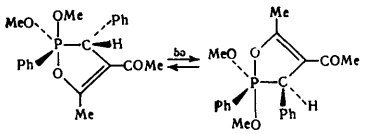
The exchange of ligand positions in 2,2,2-trimethoxy-1,4,2-dioxaphospholans is inhibited at −140°C. At this temperature three methoxy-group doublets appear in the ^{1}H NMR spectrum: the equatorial groups give rise to signals in a lower magnetic field than the axial groups; the $^3J_{PH}$ are higher for the equatorial groups than for the axial groups[44,260]. The *cis*-H/H isomers of 1,4,2-dioxaphospholans with two methoxy-groups at the phosphorus atom are "frozen" at a higher temperature (−42°C), while in the *trans*-H/H isomer the "freezing" occurs at −90°C,[10,11] i.e. the *cis*-isomer is more "rigid" in the sense that the exchange of ligand positions in it is inhibited at a higher temperature.



cis-H/H — *trans*-H/H

The ^{1}H NMR spectra of the diastereomeric 1,3,2-dioxaphospholans and 1,4,2-dioxaphospholans do not differ only in the region of the methoxy-groups. When the molecule contains phenyl substituents, the hydrogen or the methyl group in the *cis*-position relative to such a substituent absorbs in higher fields than the same groups in the *trans*-position[11,51,63,174].

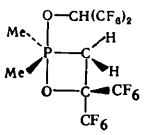
1,2-Oxaphospholens are frozen at −65°C[9-11,66,79,261,262]. 1,2-Oxaphospholens with two methoxy groups at the phosphorus atom exist in solution in the form of two diastereomers. They have different δ^{31}P values in solution at +30°C and for this reason do not undergo stereomutation under these conditions. Each of the two forms has two methoxy-group signals.



$\delta^{31}P = +16.7$ p.p.m. $\delta^{31}P = +13.3$ p.p.m.

The analogous 1,2-oxaphospholen with two phenyl groups at the phosphorus atom is "frozen" at +25°C. It exists in only one configuration[79].

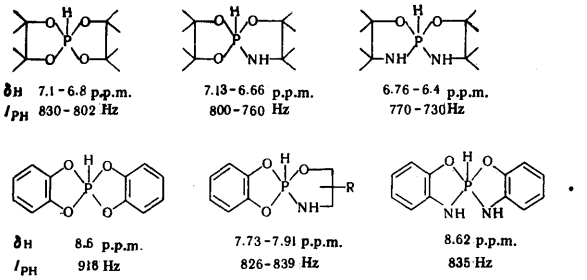
The relative rigidity of the 1,2-oxaphosphetan system was demonstrated by the fact that the ^{1}H NMR spectrum of this phosphorane does not change in the temperature range from −60° to +80°C.[10,39,64]



The isomer illustrated here is most stable, i.e. here the two oxygen atoms occupy the axial positions. The ^{19}F and ^{1}H NMR spectra are consistent with this structure: there is a singlet with $\delta^{19}F = +0.4$ p.p.m. relative to CF_3COOH and a doublet with $\delta^{19}F = -3.9$ p.p.m. and $I_{HF} = 5.8$ Hz. The two equatorial methyl groups give rise to a doublet with $\delta = 1.98$ p.p.m. and $^2J_{PH} = 15$ Hz and the protons of the phosphetan ring give rise to a doublet with $\delta = 4.04$ p.p.m. and $^2J_{PH} = 20.7$ Hz.

Spirophosphoranes obey the same rules as other cyclic phosphoranes. The rings assume the axial-equatorial position in the trigonal bipyramid[144,234]. Depending on the ring substituents, there are different numbers of diastereomers[153]. The diastereomers differ in their ^{31}P and ^{1}H NMR spectra at room temperature. At elevated temperatures the rate of interconversion of the diastereomeric forms increases and they cannot be distinguished on the basis of their NMR spectra[157]. The situation simplifies when there is nitrogen in the ring, since the more electronegative oxygen always occupies the axial position. Such molecules are "frozen" even at room temperature[234]. Spirophosphoranes with four oxygen atoms in the ring undergo permutational isomerisation even at −70°C.[263]

The ^{1}H NMR spectra of all spirophosphoranes with a P–H bond show the chemical shift of the P–H proton in the region 6.5–8.5 p.p.m. When the ring oxygen is replaced by the less electronegative nitrogen, the δH shift to higher fields; the position is reversed when there are benzene rings in the molecule[141,143,144,234,264]. J_{PH} increases when the ring is condensed with an aromatic nucleus[235]:

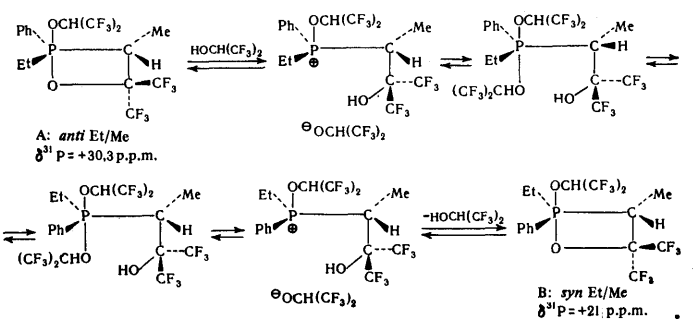


It decreases when oxygen in the ring is replaced by nitrogen. The substitution of H at the nitrogen atom by Me increases I_{PH} and shifts δH to lower fields[154].

6. Irregular Permutational Isomerisation

The base-catalysed irregular permutational isomerisation of oxyphosphoranes can proceed via the intermediate formation of compounds with a hexacoordinate phosphorus atom (see the alcoholysis of phosphoranes described above). An acid-catalysed irregular permutational isomerisation process[12,162,247], proceeding via the formation of a tetracoordinate intermediate, was discovered recently.

The 1,2-Oxaphosphetans A and B are diastereomers differing in the configuration at the phosphorus atom. They are stable in the absence of moisture and are not interconverted at a temperature below that of the Wittig reaction. Their interconversion via the regular process is forbidden, since it requires either the placement of the four-membered ring in the diequatorial position or the location of the P–C bond in the axial position. In the presence of hexafluoroisopropyl alcohol as the catalyst they undergo stereomutation, which proceeds via an irregular process associated with ring opening.



The following general rules can be formulated on the basis of the stereochemical study of cyclic oxyphosphoranes: (1) the more electronegative substituents occupy axial positions in the trigonal bipyramid; (2) four- and five-membered rings occupy the axial-equatorial position.

When these requirements are met, phosphoranes are obtained in which there is fairly rapid exchange of ligand positions, provided that the above rules hold for all the intermediate positions in the trigonal bipyramid. The exchange of ligand positions in cyclic oxyphosphoranes can be "frozen" at certain temperatures; 1,2-oxaphospholens constitute a more rigid system than 1,3,2-dioxaphospholans and 1,4,2-dioxaphospholans. In the latter

case some of the diastereomers (*cis*-H/H conformation) are more rigid than others (*trans*-H/H conformation). Certain four-membered cyclic phosphoranes are more stable than the corresponding five-membered phosphoranes. The steric effects and the electronegativities constitute important factors in determining the relative stabilities of pentacoordinate and tetracoordinate phosphorus. The importance of the static and dynamic stereochemistry of phosphoranes is great, since the compounds with pentacoordinate phosphorus are intermediates in the reactions of many derivatives of tetracoordinate phosphorus and can be used in the interpretation of the biochemistry of phosphorus.

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