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Acyclic Alkoxy- and Aryloxy-phosphoranes

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The review gives a systematic account of the methods of synthesis, physical properties, structure, and reactivity of pentacoordinate phosphorus compounds having an acyclic structure and containing alkoxy- and aryloxy-substituents. The bibliography includes 91 references.

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I. INTRODUCTION

Phosphorus is undoubtedly outstanding among other Group V elements of the Periodic System as regards the number of compounds with different coordinations of the central atom which really exist and are being investigated. The compounds of pentacoordinate phosphorus (phosphoranes) occupy a special place in organophosphorus chemistry. Fundamental research into the mechanisms of the reactions of organophosphorus compounds has yielded convincing evidence for the existence of intermediates with pentacoordinate phosphorus in reactions of compounds of tricoordinate and tetracoordinate phosphorus.[1-6] The concept of metastable hydroxyphosphorane derivatives $(RO)_{5-n}P(OH)_n$, formed as intermediates, has been dominant in the study of the biochemical role of phosphate-containing coenzymes, for example ATP.[7-10]

The ability of the phosphorus atom to form covalent bonds with five ligands has long been known in the inorganic chemistry of phosphorus. The high stability of PF_5 and other fluorophosphoranes has received a detailed theoretical justification.[11-13] On the other hand, the chemistry of stable pentaorganophosphoranes, i.e. compounds in which the phosphorus atom is linked by σ-bonds to five organic substituents, has been developing vigorously only during the last 25 years. Among the studies which have stimulated the detailed investigation of organophosphoranes, mention must be made of the investigation of the mechanism of the hydrolysis of cyclic phosphates,[14] which made it possible for the first time to discover the important role which the presence of a cyclic fragment in the molecule plays in the stabilisation of organophosphoranes. Ramirez[1,15] established the rules governing the formation of cyclic alkoxyphosphoranes and the principles of their molecular structure and pointed out the possibility of their synthetic employment.

Until recently, much less was known about pentaorganophosphoranes with an acyclic structure despite the fact that the closest models of the intermediates in the majority of the reactions of organophosphorus compounds (OPC), including biochemical processes, are precisely phosphoranes with a phosphorus atom not involved in a ring.

In the series of acyclic pentaorganophosphoranes, alkoxy- and aryloxy-phosphoranes are best known. Several relatively unstable acyclic alkoxyphosphoranes with arylthio-groups[16,17] or dialkylamino-groups[18] as well as several penta(perfluoroalkyl)phosphoranes[19,20] and penta-arylphosphoranes[21] are known.

The increased stability of acyclic alkoxy- and aryloxyphosphoranes compared with their thia- and aza-analogues can apparently be explained by the greater electronegativity of the oxygen atom compared with the oxygen atoms attached to sulphur and nitrogen atoms. On the other hand, the electronic and steric properties of the substituents at the oxygen atoms could influence the stability and reactivity of the same phosphoranes. In order to elucidate the factors influencing the properties of acyclic alkoxyphosphoranes, methods have been developed in recent years for the synthesis of a wide variety of compounds of this type and their reactivity has been investigated in reactions with organic compounds of different classes. The results of these studies are surveyed in the present review.

II. METHODS OF SYNTHESIS

The methods of synthesis of alicyclic penta-alkoxy- and penta-aryloxy-phosphoranes, as well as alicyclic alkoxy- and aryloxy-organophosphoranes, can be usefully divided into three groups in terms of the coordination of the phosphorus in the initial compounds used for the synthesis. Many of these phosphoranes have been obtained from compounds of pentacoordinate and tricoordinate phosphorus and many fewer from compounds of tetracoordinate phosphorus.

1. Synthesis from Halogenophosphoranes

The reaction of phosphorus pentachloride and phenol proceeds, according to Anshutz[22] and Zhmurova and Kirsanov,[23] via a stage involving the formation of dichlorotriphenoxyphosphorane (I) and leads to an organophosphorus compound of a new type—pentaphenoxyphosphorane (II):

$$3C_6H_5OH + PCl_5 \xrightarrow{-2HCl} \underset{(I)}{(C_6H_5O)_3PCl_2}$$

$$(C_6H_5O)_3PCl_2 + 2C_6H_5OH \xrightarrow{-2HCl} \underset{(II)}{(C_6H_5O)_5P} .$$

However, ^{31}P NMR [24] showed that these reactions yield not compound (II) but a mixture of dichlorotriphenoxyphosphorane (I) and other compounds.

Analytically pure pentaphenoxyphosphorane (II) was obtained only in the presence of a base—γ-collidine:[24]

$$PCl_5 \xrightarrow[2)\ 5C_6H_5OH]{1)\ 5(CH_3)_3C_5H_2N,\,0^\circ C} \underset{(II)}{(C_6H_5O)_5P} + 5\,(CH_3)_3C_5H_2N\cdot HCl .$$

Other substituted pentaphenoxyphosphoranes $(ArO)_5P$ with Ar = *o*-$CH_3C_6H_4$, *p*-$CH_3C_6H_4$, *o*-Cl_6H_4, or *p*-ClC_6H_4,[25] as well as penta(perfluorophenoxy)phosphoranes [26] have been obtained analogously.

A method consisting in the reaction of halogenophosphoranes with alcohols or phenols in the presence of bases and also with alkoxides, phenoxides, or alkoxy- and aryloxy-silanes has been used successfully for the synthesis of a whole series of acyclic alkoxy- and aryloxy-phosphoranes. Apart from PCl_5, the halogenophosphoranes employed were PF_5, alkyl-, and aryl-fluoro-phosphoranes,[27,28] alkoxychloro- and alkoxyfluoro-phosphoranes,[27,29–32] dibromotriphenyl- or dibromotributyl-phosphoranes,[33,34] and tris(trifluoromethyl)-fluoro- or tris(trifluoromethyl)chloro-phosphoranes [35,36] (Table 1):

$$(CH_3)(CF_3)_3PF + CH_3OSi(CH_3)_3 \xrightarrow{-(CH_3)_3SiF} (CH_3)(CF_3)_3POCH_3$$
(III)

$$R^1R^2_2PX_2 + 2R^3OM \xrightarrow{-2MX} R^1R^2_2P(OR^3)_2$$
(IV) — (XIX)

When phosphorus pentachloride is treated with perfluoro-t-butyl hypochlorite penta(perfluoro-t-butoxy)phosphorane is formed in a quantitative yield.[37]

2. Synthesis from Compounds of Tetracoordinate Phosphorus

There are very few methods of synthesis of acyclic alkoxy- or aryloxy-phosphoranes from compounds of tetracoordinate phosphorus. Methyl- or aryl-aryloxy-phosphoranes containing two, three, or four aryloxy-groups [compounds (XX)–(XXVI) and (XXIX)] are formed, for example, when methyl- or aryl-aryloxyphosphoniatrifluoromethanesulphonates (XXVII) [38–40] or trichlorophenylphosphonium chloride (XXVIII) [39] are treated with the corresponding phenoxides:

$$R_n\overset{+}{P}(OAr)_{4-n}\bar{O}SO_2CF_3 + ArOM \xrightarrow{-CF_3SO_3M} R_nP(OAr)_{5-n}$$
(XXVII) (XX) — (XXIV)

R=CH_3, $n=1$, Ar=C_6H_5 (XX), 2,6-$(CH_3)_2C_6H_3$ (XXI), 2-$CH_3C_6H_4$ (XXII), 4-$CH_3C_6H_4$ (XXIII); R=CH_3, $n=2$, Ar=2-$CH_3C_6H_4$ (XXIV)

$$CH_3(C_2H_5)_n\overset{+}{P}(OC_6H_5)_{3-n}\bar{O}SO_2CF_3 \xrightarrow[-CF_3SO_3M]{C_6H_5OM} CH_3(C_6H_5)_nP(OC_6H_5)_{5-n}$$
(XXV), (XXVI)

$n=1$ (XXV), 2 (XXVI)

$$C_6H_5\overset{+}{P}Cl_3Cl^- + 4C_6H_5OH \xrightarrow{2,6\text{-lutidine}} C_6H_5P(OC_6H_5)_4$$
(XXVIII) (XXIX)

It has been established [41] that the alkoxytetramethylphosphoranes (XXX) and (XXXI) and the alkoxymethyltriphenylphosphoranes (XXXII)–(XXXIV) are formed as a result of the addition of alcohols to trimethylphosphinomethylene (XXXV) or triphenylphosphinomethylene (XXXVI) respectively:

$$R_3P{=}CH_2 + R^1OH \rightarrow R_3P\begin{matrix}CH_3\\OR^1\end{matrix}$$

R=CH_3 (XXXV), C_6H_5 (XXXVI) R=CH_3, R^1=CH_3 (XXX), C_2H_5 (XXXI); R=C_6H_5, R^1=CH_3 (XXXII), C_2H_5 (XXXIII), $(CH_3)_2CH$ (XXXIV)

The formation of acyclic alkoxy- and aryloxy-phosphoranes is possible in principle also as a result of the addition of suitable reagents to the P=O double bond. However, although several examples of addition to the phosphoryl group, involving both an increase of the coordination number of phosphorus [42] and proceeding without change in coordination,[43–48] are known at present in the chemistry of organophosphorus compounds, the only rigorously demonstrated instance of the synthesis of a pentacovalent phosphorane structure among

Table 1. The synthesis and properties of the alkoxyphosphoranes $R^1R^2_2PX_2+2R^3OM \xrightarrow[-2MX]{} R^1R^2_2P(OR)^3_2$ (IV)—(XIX)

No. of compound	R^1	R^2	R^3	X	M	M.p., °C, b.p., °C (mmHg)	δ, p.p.m.[c]	Refs.
(IV)	C_6H_5	C_6H_5	CF_3CH_2	Br	Na	—[a]	—	[33, 34]
(V)	C_6H_5	C_6H_5	$C_6H_5C(CF_3)_2$	Br	Na	124—126	—	[33]
(VI)	C_4H_9	C_4H_9	CF_3CH_2	Br	Na	—[a]	—	[34]
(VII)	CF_3	CF_3	CH_3	Cl, F	$Si(CH_3)_3$	—[a]	—74.5	[35]
(VIII)	$(CF_3)_2CHO$	CH_3	$(CF_3)_2CH$	Cl	Li	46—49	—20,3	[30]
(IX)	$(CF_3)_2CHO$	CF_3	$(CF_3)_2CH$	Cl	Li	45 (0,01)	—72.8	[30]
(X)	C_6H_5	$(CF_3)_2CHO$	$(CF_3)_2CH$	Cl	Li	91	—65.0	[30]
(XI)	C_6H_5	CF_3CH_2O	CF_3CH_2	F	$Si(CH_3)_3$	62	—58.7	[28]
(XII)	CH_3	$(CF_3)_2CHO$	$(CF_3)_2CH$	Cl	Li	33—37	—53.0	[30]
(XIII)	CH_3	CF_3CH_2O	CF_3CH_2	F	$Si(CH_3)_3$	—[a]	—	[28]
(XIV)	$(CF_3)_2CHO$	$(CF_3)_2CHO$)	$(CF_3)_2CH$	Cl	Li	25—28	—84.0	[29]
(XV)	CF_3CH_2O	CF_3CH_2O	CF_3CH_2	F	$Si(CH_3)_3$	44 (0.15)[b]	—76.6[b]	[27]
(XVI)	$HCF_2CF_2CH_2O$	$HCF_2CF_2CH_2O$	$HCF_2CF_2CH_2$	Cl, Br	H	88—89 (0,05)	—77.0	[32]
(XVII)	$H(CF_2CF_2)_2CH_2O$	$H(CF_2CF_2)_2CH_2O$	$H(CF_2CF_2)_2CH_2$	Cl, Br	H	159—161 (0,05)	—76.0	[32]
(XVIII)	CCl_3CH_2O	CCl_3CH_2O	CCl_3CH_2	Cl, Br	H	104—106	—79.6	[31]
				F	$Si(CH_3)_3$	122—124	—79.0	[27]
(XIX)	CCl_3CH_2O	CCl_3CH_2O	C_6H_5	Cl, Br	H	—[a]	—85.1	[31]

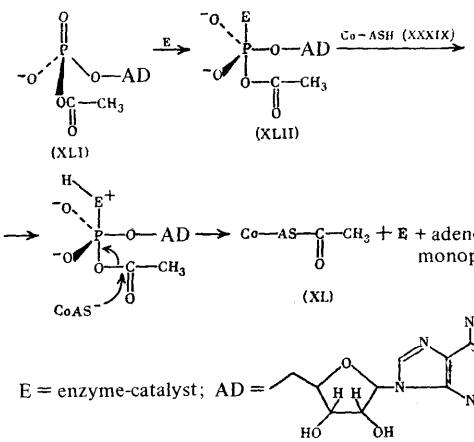
[a] Not isolated in a pure state. [b] Data quoted by Denney et al.[16] [c] In ^{31}P NMR (relative to 85% H_3PO_4).

the acyclic compounds is the reaction of tris(trifluoromethyl)-phosphine oxide (XXXVII) with hexamethyldisiloxane:[49,50]

$$(CF_3)_3P{=}O + (CH_3)_3SiOSi(CH_3)_3 \rightarrow (CF_3)_3P[OSi(CH_3)_3]_2$$
(XXXVII) (XXXVIII)

The phosphorane (XXXVIII) formed under these conditions is a low-boiling liquid, which has been isolated in a pure state by vacuum distillation.

It is noteworthy that the hydroxyphosphorane concept, based on the hypothesis that processes involving adenosine triphosphate proceed via an intermediate with a pentacoordinate phosphorus atom,[8,9] formed as a result of the addition of the enzyme to the P=O bond, has become widely adopted at the present time in biochemistry. For example, in the conversion of the coenzyme A (CoASH) (XXXIX) into the acetylcoenzyme A (XL), the adenyl acetate (XLI) formed initially reacts with the enzyme E catalysing this process and is converted into the pentacoordinate intermediate (XLII). As a result of proton transfer from the mercapto-group of coenzyme A (XXXIX) to the apical atom through which the enzyme is linked to the phosphorus followed by attack on the carbonyl group by the coenzyme anion, acetylcoenzyme A (XL) is subsequently obtained:[9]



3. Synthesis from Compounds of Tricoordinate Phosphorus

As a result of the studies of Denney and co-workers, the method of synthesis of acyclic alkoxyphosphoranes from compounds of tervalent phosphorus and dialkyl peroxides has come to be widely known since 1964. The first representative of acyclic penta-alkoxyphosphoranes, namely pentaethoxyphosphorane (XLIII), was obtained by the reaction of triethyl phosphite with diethyl peroxide.[51] Subsequently pentamethoxyphosphorane (XLIV) was also obtained by the same method.[52] However, these compounds were not isolated in a pure state—they contained an admixture of trialkyl phosphates:

$$(AlkO)_3P + AlkOOAlk \rightarrow (AlkO)_5P;\ Alk = C_2H_5\ (XLIII),\ CH_3\ (XLIV).$$

Having studied systematically the reaction of diethyl peroxide with compounds of tervalent phosphorus, Denney and co-workers[53–55] found the optimum conditions for the synthesis and isolation of a whole series of diethoxyphosphoranes (XLV)–(LIII):

$$R^1R^2_3P + C_2H_5OOC_2H_5 \rightarrow R^1R^2_3P(OC_2H_5)_2$$
(XLV) – (LIII)

$R^1 = R^2 = C_6H_5$ (XLV), C_4H_9 (XLVI), CH_3 (XLVII), $(CH_3)_2CH$ (XLVIII), CH_3O (XLIX); $R^1 = C_2H_5O$, $R^2 = C_6H_5$ (L); $R^1 = CH_3$, $R^2 = C_6H_5$ (LI); $R^1 = C_6H_5$, $R^2 = C_2H_5O$ (LII), CH_3 (LIII)

Denney and Jones[55] suggest two possible mechanisms for the formation of phosphoranes from dialkyl peroxides.

The direct formation of alkoxyphoshorane in a single stage via a transition state in which both oxygen atoms are linked to the phosphorus atom:

$$(AlkO)_3P + AlkOOAlk \rightarrow \left[(AlkO)_3P\begin{matrix}\cdot OAlk\\ |\\ \cdot OAlk\end{matrix}\right] \rightarrow (AlkO)_5P\ .$$

A two-stage mechanism involving substitution at the oxygen atom of the dialkyl peroxide with formation of the tetra-alkoxyphosphonium cation–alkoxide anion ion pair, which is subsequently converted into the penta-alkoxyphosphorane:

$$(AlkO)_3P + AlkOOAlk \rightarrow (AlkO)_4\overset{+}{P}AlkO^- \rightarrow (AlkO)_5P$$

The reactivity of phosphites and phosphines in relation to diethyl peroxide is the opposite of their reactivity in nucleophilic substitution reactions with C_2H_5I.[55] These data make it possible to give preference to the single-stage mechanism of the formation of the phosphorane in which the tervalent phosphorus atom is inserted, as a biphilic reagent, in the oxygen–oxygen bond.

The disadvantages of using dialkyl peroxides are the difficulty of obtaining them, their explosive nature, and also the limited set of such compounds. The reactions with dialkyl peroxide take place slowly [for example, in the synthesis of pentaethoxyphosphorane (XLIII) the reaction lasts 20 days at room temperature[55]] and the phosphoranes are always formed not in a pure state but in a mixture with the oxidation products of the initial organophosphorus compound: phosphates, phosphonates, phosphinates, or tertiary phosphine oxides.[51–55]

The method of synthesis of acyclic alkoxyphosphoranes involving the reaction of derivatives of tervalent phosphorus with alkyl benzenesulphenates is free from many of these disadvantages. When this method involving the reaction of two moles of alkyl benzenesulphenate with tervalent phosphosus compounds under mild conditions is used, the corresponding alkoxyphosphoranes (IV), (XI), (XV), (XLIII)–(XLV), (L), (LII), and (LIV)–(LXI) are formed in high yields:[16,56–59]

$$(C_6H_5)_{3-n}P(OAlk)_n + 2AlkOSC_6H_5 \rightarrow (C_6H_5)_{3-n}P(OAlk)_{n+2} + (C_6H_5S)_2$$
(IV), (XI), (XV), (XLIII) – (XLV), (L), (LII), (LIV) – (LXI)

$n = 0$, Alk = CF_3CH_2 (IV), CH_3CH_2 (XLV);
$n = 1$, Alk = CH_3CH_2 (L), CF_3CH_2 (LXI);
$n = 2$, Alk = CF_3CH_2 (XI), CH_3CH_2 (LII), cyclo-C_5H_9 (LIX), $(CH_3)_3CCH_2$ (LX);
$n = 3$, Alk = CF_3CH_2 (XV), CH_3CH_2 (XLIII), CH_3 (XLIV), $(CH_3)_2CH$ (LIX), $(CH_3)_3CCH_2$ (IV), cyclo-C_5H_9 (LVI), cyclo-C_6H_{11} (LVII), $C_6H_5CH_2$ (LVIII) .

It has been suggested[56–60] that the mechanism of this reaction involves the direct insertion of phosphorus in the S–O bond analogous to the reaction with dialkyl peroxides[55,61] with a certain degree of donation of the free electron pair of sulphur to the phosphorus orbitals in the transition state and the formation of alkoxyarylthiophosphorane (LXII) as an intermediate. Such mixed alkoxyarylthiophosphoranes have been isolated in the reactions of alkyl benzenesulphenates with cyclic phosphites[56,62] and in other cases in reactions with acyclic tris(2,2,2-trifluoroethyl) [16] and tris(1-trifluoromethyl-2,2,2-trifluoroethyl) phosphites.[63] The alkoxyarylthiophosphorane (LXII) then reacts with another molecule of benzenesulphenate to form a dialkoxyphosphorane and diphenyl

disulphide (pathway *a*):

$$R_3P + ROSAr \rightarrow \underset{(LXII)}{R_3P\langle^{SAr}_{OR}} \begin{cases} \xrightarrow{ROSAr} R_3P(OR)_2 + ArSSAr \quad (a) \\ \rightarrow R_3\overset{+}{P}OR + ArS^- \rightarrow R_3P{=}O + ArSR \quad (b) \end{cases}$$

The other pathway in the reactions of tervalent phosphorus compounds with alkyl benzenesulphenates involves the formation of a phosphoryl compound and an alkyl aryl sulphide, apparently as a result of the dissociation of the mixed alkoxyarylthiophosphorane (LXII) into an ion pair and its subsequent reactions (pathway *b*). For example, diethoxyphenylphosphine reacts with ethyl benzenesulphenate to form 65% of tetraethoxyphenylphosphorane (LXII) and 35% of diethyl phenylphosphonate.[59] On the other hand, the reactions of mixed alkylarylphosphines[55] and tributylphosphine[60] with alkyl benzenesulphenates proceed only via pathway *b*. Apparently, the presence of electron-donating alkyl groups promotes the stabilisation of the phosphonium cation.[54] If, on the other hand, the rate of the reaction of the mixed alkoxyarylthiophosphorane with another molecule of alkyl benzenesulphenate is higher than the rate of its dissociation, pathway *a* operates.

Apart from the two general methods of synthesis of acyclic alkoxyphosphoranes from tricoordinate phosphorus compounds described above, several individual instances of the synthesis of phosphoranes of this type are also known.

Pentakis(2,2,2-trifluoroethoxy-1-trifluoromethyl)phosphorane (XIV) has been obtained by the reaction of the phosphite (LXIII) with the bis(1,1,1,3,3,3-hexafluoroisopropyl) ester of sulphoxylic acid (LXIV):[64]

$$\underset{(LXIII)}{4\,[(CF_3)_2CHO]_3P} + \underset{(LXIV)}{S[OCH(CF_3)_2]_2} \rightarrow \underset{(XIV)}{[(CF_3)_2CHO]_5P} + 2\,[(CF_3)_2CHO]_3P{=}S + [(CF_3)_2CHO]_3P{=}O + (CF_3)_2CHOCH(CF_3)_2 \quad .$$

The reaction of chloroform with sodium methoxide and trimethyl phosphite leads to the formation of tetramethoxydimethoxymethylphosphorane (LXV):[65]

$$(CH_3O)_3P + CHCl_3 + 3CH_3ONa \rightarrow \underset{(LXV)}{(CH_3O)_4PCH(OCH_3)_2} + 3NaCl \quad .$$

Aryl phosphonites and aryl phosphinates react with derivatives of acrylic acid in the presence of alcohols to form alkoxyphosphoranes (LXVI):[66]

$$R_nP(OR^1)_{3-n} + CH_2{=}CHX \rightleftarrows \underset{(LXVII)}{R_n\overset{+}{P}(OR^1)_{3-n}(CH_2\bar{C}HX)} \xrightleftharpoons{R^2OH} \rightleftarrows R_n\overset{+}{P}(OR^1)_{3-n}(CH_2CH_2X) \rightleftarrows \underset{OR^2}{R_nP(OR^1)_{3-n}(CH_2CH_2X)}$$

$$\underset{-OR^2}{R_n\overset{+}{P}(OR^1)_{3-n}(CH_2CH_2X)}$$

(LXVI)

$n = 1, 2$; $R = C_6H_5$; $R^1 = CH_3$, C_2H_5;
$R^2 = CH_3$, C_2H_5, $(CH_3)_3C$;
$X = COOC_2H_5$, CN

$n = 2$; $R = n\text{-}(CH_3)_3COC_6H_4$; $R^1 = R^2 = (CH_3)_3C$; $X = COOC_2H_5$.

It has been suggested[66] that the betaine (LXVII) formed as an intermediate is protonated by alcohol and the alkoxide anion then carries out a nucleophilic attack on the positively charged phosphorus atom with formation of the phosphoranes (LXVI).

III. NMR SPECTRA AND STRUCTURE

The signals of the phosphorus nuclei in the ^{31}P NMR spectra of acyclic alkoxy- and aryloxy-phosphoranes are in the range $\delta p = -20.3 - -92.0$ p.p.m. (relative to 85% H_3PO_4). The chemical shifts at the highest fields are characteristic of penta-alkoxy- and penta-aryloxy-phosphoranes. When one, two, or three alkoxy-groups are replaced by an aryl group and especially by the methyl group, the chemical shift undergoes an appreciable downfield displacement (Table 2). It may be that such displacement is caused by the distortion of the symmetry of the electron distribution around the pentacoordinate phosphorus induced by the difference between the electronegativities of the alkyl(aryl) and alkoxy-substituents. With a decrease in the difference between the electronegativities of the substituents—in the case of the phosphoranes (VII), (IX), and (XXXVIII) containing CF_3 groups at the phosphorus atom—there is almost no downfield displacement of the signal. A similar hypothesis has been used to account for the downfield displacement of the signals in the ^{31}P NMR spectra of tetracoordinate phosphorus compounds.[67] An exception in the series considered is that of alkoxytetramethylphosphoranes (XXX) and (XXXI), whose chemical shifts occur at the lowest fields (Table 2).

Table 2. ^{31}P NMR spectra of alkoxy- and aryloxy-phosphoranes.

Formula	δp, p.p.m.	Refs.
$P(OCH_3)_5$ (XLIV)	−66.0	[57]
$P(OC_6H_5)_5$ (XLIII)	−70.9	[51]
$P(OCH_2CF_3)_5$ (XV)	−76.6	[16]
$P[OCH(CF_3)_2]_5$ (XIV)	−84.5	[29]
$P(OCH_2CF_2CF_2H)_5$ (XVI)	−77.0	[32]
$P(OCH_2CF_2CF_2CF_2CF_2H)_5$ (XVII)	−76.0	[32]
$P(OCH_2CCl_3)_5$ (XVIII)	−79.6	[31]
$P(OC_6H_5)_5$ (II)	−85.4; −84.2[a]	[70]
$C_6H_5P(OC_6H_5)_4$ (LII)	−55.0	[54]
$C_6H_5P(OCH_2CF_3)_4$ (XI)	−61.7	[16]
$C_6H_5P[OCH(CF_3)_2]_4$ (X)	−65.0	[30]
$CH_3P[OCH(CF_3)_2]_4$ (XII)	−53.0	[30]
$(C_6H_5)_2P(OC_6H_5)_3$ (L)	−41.0	[54]
$(C_6H_5)_2P(OCH_2CF_3)_3$ (LXI)	−42.5	[16]
$(CH_3)_2P[OCH(CF_3)_2]_3$ (VIII)	−20.3	[30]
$(CF_3)_2P[OCH(CF_3)_2]_3$ (IX)	−72.8	[30]
$(C_6H_5)_3P(OC_6H_5)_2$ (XLV)	−54.0	[53]
$(C_6H_5)_2P(OCH_2CF_3)_2$ (IV)	−58.2	[16]
$(C_6H_5)_2(CH_3)P(OC_6H_5)_2$ (LI)	−47.0	[54]
$(C_6H_5)(CH_3)_2P(OC_6H_5)_2$ (LIII)	−40.0	[54]
$(CH_3)_3P(OC_6H_5)_2$ (XLVII)	−39.0	[54]
$(CF_3)_3P(OCH_3)_2$ (VII)	−64.5	[35]
$(CF_3)_3P[OSi(CH_3)_3]_2$ (XXXVIII)	−92.8	[50]
$(CH_3)_4POCH_3$ (XXX)	−88.0	[41]
$(CH_3)_4POC_2H_5$ (XXXI)	−92.0	[41]

[a] In the solid state.

It has been suggested that penta-alkoxyphosphoranes have the structure of a trigonal bipyramid (TBP). However, ^1H, ^{13}C, and ^{19}F NMR studies of a series of these compounds [compounds (IV)–(VII), (XV), and (XVIII)][26,57,68,69] demonstrated the equivalence of the alkoxy-groups even at low temperatures. This has been explained[57] by the very low barrier to permutational isomerisation of the phosphoranes investigated.

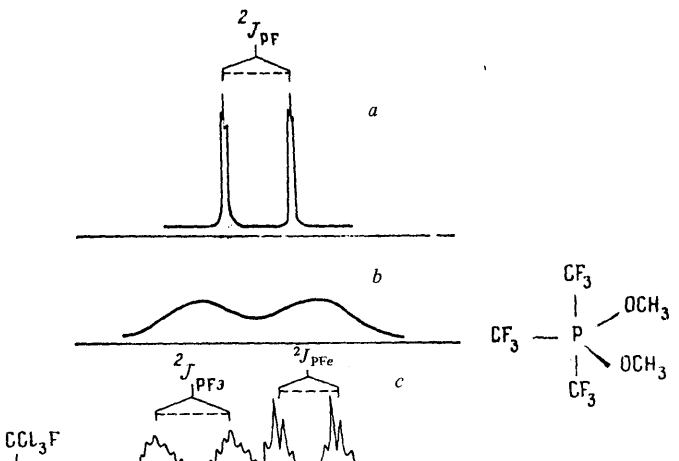
It has been established by X-ray diffraction[71] that pentaphenoxyphosphorane in the crystalline state has the structure of a TBP with the phosphorus atom at the centre. The two axial P–O bonds (1.602, 1.596, and 1.600 Å). It has been suggested that the electrons of the apical oxygen atoms are less involved in the p, d_π conjugation with the phosphorus atom than the electrons of the equatorial oxygen atoms and are mainly delocalised over the benzene rings. The five benzene rings are distributed in the TBP in such a way that the intramolecular repulsion is a minimum.

In the case of tetrakix(2,6-dimethylphenoxy)methylphosphorane (XXI) [38] and tetrakis(1,1,1,3,3,3-hexafluoroisopropoxy)methylphosphorane (XII), [30] the rate of pseudorotation is reduced to such an extent that, in the ^1H NMR spectra of the phosphorane (XXI) at −65 °C and in the ^1H and ^{19}F NMR spectra of the phosphorane (XII) even at 25 °C, the alkoxy-substituents are found to be non-equivalent owing to their location in the axial or equatorial positions.

The study of the ^1H and ^{19}F NMR spectra of a series of alkyl- and aryl-phosphoranes (XLV), (XLVI), and (L) at different temperatures showed that the rate of the pseudotransformation is a function of the number of alkyl or aryl groups linked directly to the phosphorus. The pseudotransformation is retarded when the number of these groups increases. [55]

The trigonal-bipyramidal structure of trialkoxy- and triaryloxy-phosphoranes, in which two alkoxy- or aryloxy-groups occupy axial positions and one occupies an equatorial position, has been established spectroscopically for triethoxydiphenylphosphorane (L) at −60 °C, [56] dimethyltri(2-methylphenoxy)phosphorane (XXIV) at −95 °C, [38] diphenyltris(2,2,2-trifluoro-1-trifluoromethylethoxy)phosphorane (VIII) at 25 °C. [30]

The activation energies for the intramolecular pseudorotation of the ligands are 5.8, 12.0, and 14.0 kcal mol^{-1} respectively for the phosphoranes (XXIV), (L), and (LXI).



^{19}F NMR spectra of dimethoxytris(trifluoromethyl)phosphorane (VII) in CCl_3F: [35] *a*) t = 33°, $^2J_{PF}$ = 96 Hz; *b*) t = −60 °C; *c*) t = −80 °C, $^2J_{PF_e}$ = 108 Hz and $^2J_{PF_a}$ = 88 Hz.

Dimethyltris(2,2,2-trifluoro-1-trifluoromethylethoxy)phosphorane (VIII) has apparently an even higher isomerisation barrier, because the coalescence temperature for this compound is 60 °C. [30] The ^1H NMR spectra of the phosphoranes (XLV) and (LI) (Table 2) do not change in the temperature range from −60° to 120 °C or to 60° respectively. It has been suggested [54] that in these compounds and also in the phosphorane $(C_6H_5)_3(OCH_2CF_3)_2$ (V) [34] the alkoxy-groups occupy axial positions and the phenyl and alkyl groups occupy equatorial positions. The invariance of the NMR spectra over a wide temperature range can apparently be explained by the high energy barrier to pseudorotation.

In contrast to the phosphoranes (IV), (XLV), and (LI), the alkoxy-groups in dimethoxytris(trifluoromethyl)phosphorane (VII) are in the equatorial positions, which follows from the analysis of the ^{19}F NMR spectra (see Figure). At room temperature, the CF_3 groups are equivalent and appear in the ^{19}F NMR spectrum as a doublet of heptets. When the temperature is reduced to −80 °C, two signals with an intensity ratio of 2 : 1 are observed in the ^{19}F NMR spectrum—a doublet of quartets with δ_F = −63.6 p.p.m. and relatively small spin–spin coupling constants ($^2J_{PF}$ = 88 Hz), which are characteristic of axial CF_3 groups, and a doublet of heptets with δ_F = −61.7 p.p.m. and relatively higher values of the spin–spin coupling constants ($^2J_{PF}$ = 108 Hz) characteristic of equatorial CF_3 groups. [35]

An analogous trigonal bipyramidal structure with two axial CF_3 groups has been determined by ^{19}F NMR also for tris(trifluoromethyl)bis(trimethylsiloxy)phosphorane (XXXVIII) [49,50] and also for methoxymethyltris(trifluoromethyl)phosphorane (III). [36]

Analysis of the ^{13}C and ^1H NMR spectra of methoxytetramethylphosphorane (XXX) [41,72] at different temperatures enabled the authors to demonstrate that this compound has a trigonal bipyramidal structure in which the methoxy-group and one of the methyl groups occupy axial positions and the remaining three methyl groups occupy equatorial positions.

IV. CHEMICAL PROPERTIES

1. Thermal Stability

The majority of acyclic penta-alkoxyphosphoranes containing alkyl substituents with the normal structure are liquids which have not been isolated in a pure state. Heating or an attempt to distil them *in vacuo* lead to decomposition. [51,52,54,57] Penta-alkoxyphosphoranes decompose slowly also at room temperature. Thus pentaethoxyphosphorane (XLIII) does not change during storage in a refrigerator for 7 days [57] but decomposes at 20 °C with formation of triethyl phosphate, ethanol, diethyl ether and probably ethylene: [51]

$$\underset{\text{(XLIII)}}{(C_2H_5O)_5P} \xrightarrow{20^\circ C} (C_2H_5O)_3P{=}O + C_2H_5OH + C_2H_5OC_2H_5 + CH_2{=}CH_2 .$$

Among the penta-alkoxyphosphoranes investigated, pentabenzyloxyphosphorane (LVIII) shows the lowest stability, decomposing fully in the course of two days at room temperature. [57]

The stability of acyclic penta-alkoxyphosphoranes increases somewhat for compounds with branched alkyl substituents. Crystalline pentaneopentyloxyphosphorane (LV), pentacyclopentyloxyphosphorane (LVI), and pentacyclohexyloxyphosphorane (LVII), which are stable for several months at temperatures in the range 0–10 °C, have been isolated in a pure state. [57]

The thermal stability of penta-alkoxyphosphoranes increases to a much greater extent following the enhancement of the electron-accepting properties of the alkyl substituents. Thus pentakis(2,2,2-trifluoro-1-trifluoromethylethoxy)phosphorane (XIV), [29] pentakis(2,2,2-trifluoroethoxy)phosphorane (XV), [27] and pentakis(ααω-trihydropolyfluoroalkoxy)phosphoranes (XVI) and (XVII) [32] distil *in vacuo* without decomposition, while pentakis(2,2,2-trichloroethoxy)phosphorane (XVIII) is a crystalline substance stable on heating to 130 °C in the

course of 1 h.[31] All the known penta-aryloxyphosphoranes as well as the alkyl- and aryl-aryloxyphosphoranes (XX), (XXIII)–(XXVI), and (XXIX) are thermally stable, which is apparently also caused by the electron-accepting properties of the aryloxy substituents. In solutions, these phosphoranes are weakly dissociated (the equilibrium constant is less than 10^{-7}):[40,73]

$$(ArO)_5P \rightleftarrows (ArO)_4\overset{+}{P} + ArO^- .$$

The replacement of one, two, or three alkoxy-groups by alkyl or aryl-groups as a rule diminishes the thermal stability of the alkoxy-phosphoranes. Thus tributylbis(2,2,2-trifluoroethoxy)phosphoranes (VI) decomposes even at room temperature in 24 h with formation of 20% of bis(2,2,2-trifluoroethyl) ether.[34]

It has been shown by ^1H and ^{31}P NMR [54] that the phosphoranes (XLVI), (XLVII), and (LIII) exist in solutions even at 20 °C in equilibrium with the phosphonium form. The equilibrium has been explained[54] by the fact that the alkyl and aryl substituents at the phosphorus atom stabilise the phosphonium cation:

$$R_nP(CH_3)_{3-n}(OC_2H_5)_2 \rightleftarrows R_n\overset{+}{P}(CH_3)_{3-n}(OC_2H_5) + C_2H_5O^-$$
$$R = n\text{-}C_4H_9,\ n=3\ (XLVI);$$
$$R=C_6H_5,\ n=1\ (LIII),\ n=0\ (XLVII)$$

The high thermal stability of dimethoxymethyltetramethoxyphosphorane (LV), which does not decompose until 125 °C via a mechanism unusual for acyclic alkoxyphosphoranes (involving the formation of a tervalent phosphorus compound), is noteworthy:[65]

$$\underset{(LXV)}{(CH_3O)_4PCH(OCH_3)_2} \xrightarrow{\Delta} (CH_3O)_3P + HC(OCH_3)_3 .$$

The thermal stability increases most significantly on passing to phosphoranes containing only one alkoxy-group. The alkoxytetramethylphosphoranes (XXX) and (XXXI) [41] and the alkoxymethyltriphenylphosphoranes (XXXII)–(XXXIV) have been isolated pure by vacuum distillation or crystallisation. They do not decompose until 130–140 °C:[74]

$$\underset{(XXX),\ (XXXI)}{(CH_3)_4P(OAlk)} \xrightarrow{130°C} (CH_3)_3P{=}O + AlkCH_3$$

$$(C_6H_5)_3P\begin{matrix}CH_3\\OAlk\end{matrix} \xrightarrow{140°C} (C_6H_5)_2PCH_3 + C_6H_5OAlk$$
$$(XXXII)-(XXXIV) .$$

2. Hydrolysis

All the acyclic penta-alkoxy- and penta-aryloxy-phosphoranes as well as alkoxy- or aryloxy-organylphosphoranes, with the exception of $(C_6H_5)_3P[OC(CF_3)_2C_6H_5]_2$ (V),[33] are extremely readily hydrolysed by atmospheric moisture with dissociation of the P–O bond. The hydrolysis of penta-alkoxy- and penta-aryloxy-phosphoranes leads to the formation of alcohols and phenols and phosphates:[9,25,29,32,37,75,76]

$$(RO)_5P + H_2O \rightarrow (RO)_3P{=}O + 2ROH$$
$$R=(CF_3)_2CH\ (XIV);\ H(CF_2)_nCH_2,\ n=2\ (XVI),$$
$$4\ (XVII);\ C_6H_5\ (II);\ CH_3\ (XLIV);\ C_2H_5\ (XLIII) .$$

The products of the hydrolysis of the alkoxy- or aryloxy-alkyl(aryl)phosphoranes (IV), (XXI), (XLV), (L), and (LII), containing four, three, or two alkoxy-groups, are phosphonates, phosphinates, or tertiary phosphine oxides respectively.[34,38,54,56] The hydrolysis of methoxytetramethylphosphorane (XXX) and the alkoxymethyltriphenylphosphoranes (XXXII)–(XXXIV), containing only one alkoxy-group, proceeds with the dissociation of both P–O and P–C bonds:[41]

$$\underset{(XXX)}{(CH_3)_4POCH_3} + H_2O \rightarrow (CH_3)_3P{=}O + CH_4 + CH_3OH$$

$$(C_6H_5)_3P\begin{matrix}CH_3\\OR\end{matrix} + H_2O \rightarrow CH_3(C_6H_5)_2P{=}O + C_6H_6 + ROH$$
$$(XXXII)-(XXXIV) .$$

The P–C bond is ruptured also on hydrolysis of the phosphoranes (VII) (XXXVIII) containing trifluoromethyl groups at the phosphorus atom:[35,50]

$$\underset{(VII)}{(CF_3)_3P(OCH_3)_2} + 2H_2O \rightarrow (CF_3)_2PO_2H + CF_3H + 2CH_3OH$$

$$\underset{(XXXVIII)}{(CF_3)_3P[OSi(CH_3)_3]_2} + H_2O \rightarrow (CF_3)_2PO_2H + CF_3H + [(CH_3)_3Si]_2O .$$

The kinetics and mechanism of the hydrolysis of acyclic alkoxy- and aryloxy-phosphoranes have been investigated[25] in relation to pentaphenoxyphorane (III) and certain substituted penta-aryloxyphosphoranes. The rate of reaction in neutral and alkaline media depends greatly on the electronic and steric properties of the substituents in the aromatic ring (Table 3).

Table 3. The influence of substituents on the rate of hydrolysis of penta-aryloxyphosphoranes at 25 °C in 75% aqueous dimethoxyethane.[25]

Rate constant, s^{-1}	$P(OC_6H_5)_5$	$P(OC_6H_4CH_3\text{-}o)_5$	$P(OC_6H_4CH_3\text{-}n)_5$	$P(OC_6H_4Cl\text{-}o)_5$	$P(OC_6H_4Cl\text{-}n)_5$
k_{H_2O}	0.202	$1.1\cdot10^{-5}$	0.0197	0.106	390
k_{H^+}	16.4	1.3	79	—	—
k_{OH^-}	11.4	$7.5\cdot10^{-4}$	3.4	—	—

These effects are less pronounced in an acid medium. Kinetic data and especially the appreciable steric effects enabled the authors to suggest that the hydrolysis of pentaphenoxyphosphoranes in neutral and alkaline media also takes place via an intermediate in which the coordination number of phosphorus rises to six:[25]

$$\underset{(II)}{(C_6H_5O)_5P} + H_2O \xrightarrow{k_1} (C_6H_5O)_5\overline{P}OH + H^+$$

$$(C_6H_5O)_5\overline{P}OH \xrightarrow{k_2} (C_6H_5O)_3P{=}O + C_6H_5OH + C_6H_5O^- .$$

The entropies (-188 J mol^{-1} K^{-1}) and enthalpies (22.5 kJ mol^{-1} of activation obtained for the hydrolysis of pentaphenoxyphosphorane (II) in 25% aqueous dioxan also led the authors[75] to the conclusion that this is a multistage process involving the formation of a hexacoordinate intermediate.

3. Reactions with Alcohols

The mode of reaction of alkoxyphosphoranes with alcohols is determined by the nature of the substituents both in the phosphorane and alcohol molecules. In the reaction of pentaethoxy phosphorane (XLIII) with five moles of propyl alcohol, the exchange of ethoxy-groups for propoxy-groups is observed. This apparently results in the formation of the mixed phosphoranes (LXVIII), since treatment of the reaction

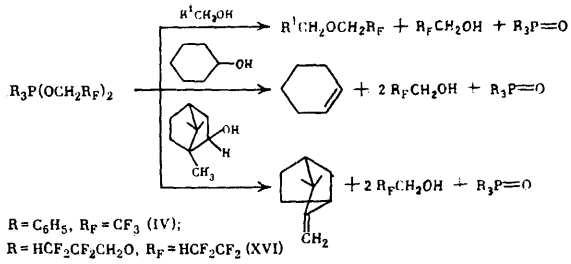
mixture with benzoic acid entails the formation of ethyl benzoate and propyl benzoate in equal amounts:[76]

$$(C_2H_5O)_5P + n\,CH_3CH_2CH_2OH \underset{-nC_2H_5OH}{\rightleftharpoons} \underset{\text{(XLIII)}}{}$$

$$\rightleftarrows (C_2H_5O)_{5-n}P(OCH_2CH_2CH_3)_n \xrightarrow{C_6H_5\overset{O}{\overset{\|}{C}}-OH} \underset{\text{(LXVIII)}}{}$$

$$\rightarrow C_6H_5\overset{O}{\overset{\|}{C}}-OC_2H_5 + C_6H_5-\overset{O}{\overset{\|}{C}}-OCH_2CH_2CH_3$$

With enhancement of the electron-accepting properties of the substituents in ethoxyphosphoranes, their tendency to alkylate alcohols also increases. The ethers $ROCH_2P_F$ ($R = C_4H_9$, C_5H_{11}, C_8H_{17}, $C_6H_5CH_2$, or $C_6H_5CH_2CH_2$) are formed when bis(2,2,2-trifluoroethoxy)triphenylphosphorane (IV)[33,34] and pentakis(2,2,3,3-tetrafluoropropoxy)phosphorane (XVI)[69] react with the corresponding primary alcohols. In their reactions with cyclic secondary alcohols (cyclohexanol or borneol), the phosphoranes (IV) and (XVI) exhibit dehydrating properties, as a result of which one observes the preferential formation of olefins:[33,34,69]



$R = C_6H_5$, $R_F = CF_3$ (IV);
$R = HCF_2CF_2CH_2O$, $R_F = HCF_2CF_2$ (XVI)

2-Phenylethanol interacts with the phosphorane (IV) to form 70% of the ether $C_6H_5CH_2CH_2OCH_2CF_3$ and 11% of styrene:[33,34]

$$(C_6H_5)_3P(OCH_2CF_3)_2 + ROH \xrightarrow[-CF_3CH_2OH]{20^\circ C} \left[(C_6H_5)_3P\begin{matrix}OR\\ OCH_2CF_3\end{matrix}\right] \rightarrow$$
(IV)

$$\rightarrow \left[(C_6H_5)_3\overset{\delta+}{P}\begin{matrix}O-R\\ \delta-\\ O-CH_2CF_3\end{matrix}\right] \begin{matrix}\xrightarrow{(a)} (C_6H_5)_3P{=}O + ROCH_2CF_3\\ \xrightarrow{(b)} (C_6H_5)_3P{=}O + \text{⟨=⟩} + CF_3CH_2OH\end{matrix}$$

It has been suggested[33,34] that, as a result of attack on the phosphorus atom, one of the trifluoroethoxy-groups is exchanged in the first stage for an alkoxy-group. Then, as a result of nucleophilic attack by the trifluoroethoxide anion on the α-carbon atom of the alkyl group (pathway *a*), ethers are produced. In the cyclic secondary alcohols, the trifluoroethoxide anion apparently attacks the β-carbon atom (pathway *b*), which leads to the formation of olefins.

The possibility of the initial attack by the alkoxide anion on the alkoxyphosphorane molecule precisely at the phosphorus atom has been demonstrated by the formation of compounds of hexacoordinate phosphorus in the reactions of phosphoranes (II), (XI), (XV), (XLIII), (XLIV), and (LXX) with alkoxides or phenoxides:[16,39,69,77]

$$(C_6H_5)_n P(OR)_{5-n} + ROM \rightarrow (C_6H_5)_n \tilde{P}(OR)_{5-n}\,M^-$$
$n = 0$, $R = CH_3$ (XLIV), C_2H_5 (XLIII), C_6H_5 (II), CF_3CH_2 (XV);
$n = 1$, $R = CF_3CH_2$ (XI);
$n = 2$, $R = CF_3CH_2$ (LXI);
$M^+ = K^+$, Na^+, $(C_2H_5)_3\overset{+}{N}H$

Acyclic phosphoranes containing at least two alkoxy-groups react with 1,2-glycols to form phosphoranes containing one or two five-membered or six-membered rings.[16,65,69,78] This mode of reaction is apparently associated with the stabilising influence of these rings on the phosphorane structure:[79,80]

$$R^1R^2_3P(OR^3)_2 + HOCH_2CH_2OH \xrightarrow[-2R^3OH]{} R^1R^2_3P\begin{matrix}O\\ O\end{matrix}\!\!>$$
(XV), (XVI), (XLIII), (XLV), (XLVI), (L)–(LIII)

$R^1 = R^2 = OC_2H_5$, C_6H_5, CF_3CH_2O, $HCF_2CF_2CH_2O$;
$R^1 = OC_2H_5$, CH_3, $R^2 = C_6H_5$;
$R^1 = C_6H_5$, $R^2 = OC_2H_5$, CH_3;
$R^1 = (CH_3O)_2CH$, $R^2 = OCH_3$

$$R^1P(OR^2)_4 + 2HOCH_2CH_2OH \xrightarrow[-4R^2OH]{} R^1P\left(\begin{matrix}O\\ O\end{matrix}\!\!>\right)_2$$
(XV), (VLIII), (LXV), (LII)

$R^1 = C_2H_5O$, C_6H_5, CH_3, CF_3CH_2O, $(CH_3O)_2CH$
$R^2 = CH_3O$, C_2H_5O, CF_3CH_2O

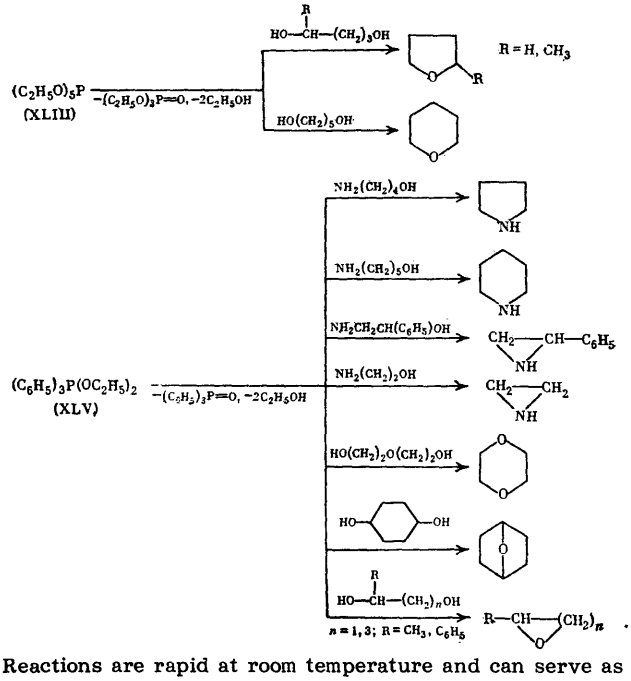
$$(C_6H_5)_nP(OC_2H_5)_{5-n} + HOCH_2C(CH_3)_2CH_2OH \xrightarrow[-2C_2H_5OH]{} \rightarrow (C_6H_5)_n(C_2H_5O)_{3-n}P\begin{matrix}O-CH_2\\ O-CH_2\end{matrix}\!\!>\!C(CH_3)_2$$

$n = 0$ (XLIII), $n = 1$ (LII), $n = 2$ (L)

$$(C_6H_5)_nP(OC_2H_5)_{5-n} + 2HOCH_2C(CH_3)_2CH_2OH \xrightarrow[-4C_2H_5OH]{} R^1P\left(\begin{matrix}O-CH_2\\ O-CH_2\end{matrix}\!\!>\!C(CH_3)_2\right)_2$$
$n = 0$ (XLIII),
$n = 1$ (LII)

$R^1 = C_2H_5O$, C_6H_5

The reactions of the alkoxyphosphoranes (XLIII) and (XLV) with diols containing more than three methylene groups and also with aminoalcohols entail the dehydration of the latter and the formation of heterocycles, probably as a result of the decomposition of the intermediate unstable phosphoranes:[78,81–83]



Reactions are rapid at room temperature and can serve as a convenient preparative method for the synthesis of simple heterocycles.

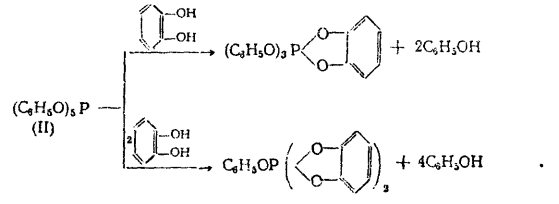
4. Reactions with Phenols

Pentamethoxy- and pentaethoxy-phosphoranes (XLIV) and (XLLIII) react with various phenols at room temperature, as a result of which phenol ethers are formed in high yields:[76,84]

$$(RO)_5P + ArOH \rightarrow (RO)_3P{=}O + ArOR + ROH$$
$R = CH_3$ (XLIV), C_2H_5 (XLIII)

Pentakis(polyfluoroalkoxy)phosphoranes (XVI) and (XVII) interact with phenols only at 150–160 °C, but phenol alkylation products are not then formed. According to ^{31}P NMR data, when equimolar amounts of the phosphorane (XVII) and phenol are heated, nucleophilic substitution of the polyfluoroalkoxy-group by the phenoxy-group takes place and an equilibrium mixture of the initial phosphorane (XVII) and a mixed phenoxytetrakis(polyfluoroalkoxy)phosphorane is formed.[59]

In the reaction of pentaphenoxyphosphorane (II) with catechol, the phenoxy-groups are substituted and cyclic phosphoranes are formed:[85]

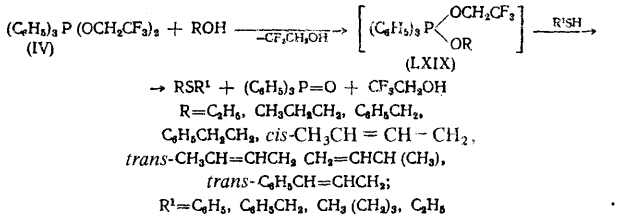


5. Reactions with Thiophenols and Mercaptans

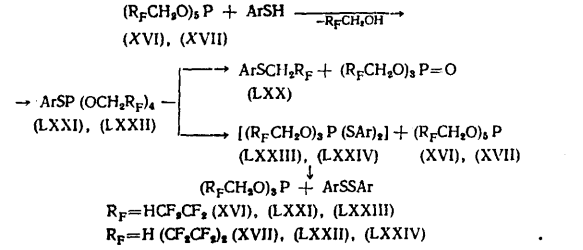
Acyclic alkoxyphosphoranes alkylate thiophenols and mercaptans at room temperature. The product of the alkylation of thiophenol by pentamethoxyphosphorane (XLIV), namely methyl phenyl sulphide, is formed in 90% yield:[84]

$$\underset{\text{(XLIV)}}{(CH_3O)_5P} + C_6H_5SH \rightarrow C_6H_5SCH_3 + (CH_3O)_3P{=}O + CH_3OH$$

The alkoxy(2,2,2-trifluoroethoxy)triphenylphosphoranes (LXIX), formed as intermediates in the reactions of the phosphorane (IV) with alcohols, are also convenient alkylating agents for thiophenols and mercaptans:[34,86]



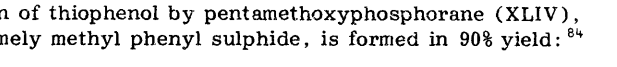
In contrast to compound (IV), pentakis(polyfluoroalkoxy)-phosphoranes (XVI) and (XVII) react with thiophenols only on heating. The yields of the alkylation products, i.e. aryl polyfluoroalkyl sulphides (LXX), then diminish with increase of the length of the polyfluoroalkyl chain.[17] The reactions of the phosphoranes (XVI) and (XVII) with thiophenols take place as a result of the initial attack by the thiophenol on the phosphorus atom with formation of arylthiotetrakis(polyfluoroalkoxy)phosphoranes (LXXI) and (LXXII).[17] The way subsequent reactions take place depends on the length of the polyfluoroalkyl chain of the substituent.



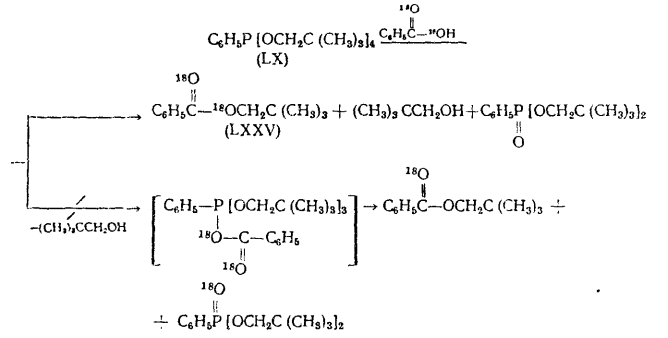
The arylthiophosphorane (LXXI) is largely converted into the sulphide (LXX) and phosphate via the mechanism of the second stage of the Arbuzov reaction and disproportionates to the phosphoranes (XVI) and (LXXIII) only to a slight extent. However, the arylthiophosphorane (LXXII) is to a considerable extent converted into the di(arylthio)phosphorane (LXXIV) together with decomposition via the mechanism of the Arbuzov rearrangement. Compound (LXXIV) is unstable and decomposes under the reaction conditions to a phosphite and a disulphide, which has been confirmed by a special experiment.[17,69]

Reactions with Acids

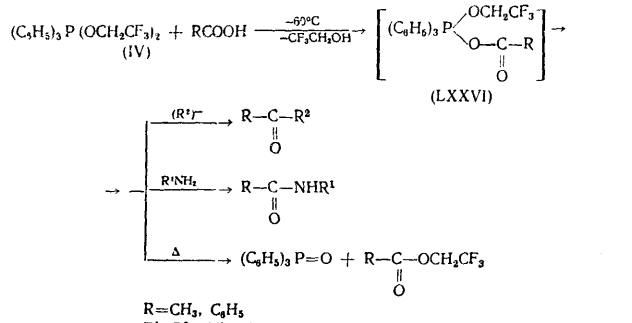
Acyclic alkoxyphosphoranes react vigorously with carboxylic acids at room temperature to form products of the alkylation of the latter—esters:[33,34,53,54,59,76,84]



It has been shown[59] that in the reaction of tetraneopentylphenylphosphorane (LX) with [^{18}O]-labelled benzoic acid, both isotopic ^{18}O atoms are located in the molecule of the ester (LXXV), i.e. the acid attacks the α-carbon atom of the alkoxy-substituent:

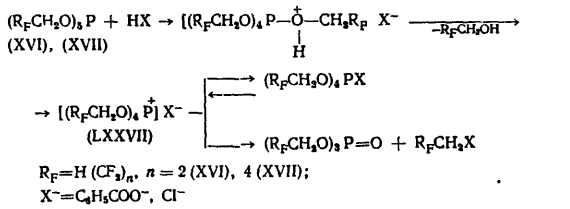


However, it is not clear from the above data[59] whether the attack takes place in the first stage of the reaction or whether it is preceded by the formation of intermediate compounds of pentacoordinate phosphorus, as has been suggested, for example, by workers[34] who investigated the reaction of bis-(2,2,2-trifluoroethoxy)triphenylphosphorane (IV) with acids. In this case the reactive acyloxyphosphorane (LXXVI) is apparently formed initially. This hypothesis is based on the fact that the products of the reaction of the phosphorane (IV) with acetic and benzoic acids at a low temperature are acylating agents, which convert amines into acid amides and alkyl or aryl anions into ketones:[34]



On the other hand pentakis(polyfluoroalkoxy)phosphoranes (XVI) and (XVII) do not react with acetic and benzoic acids on heating to 100 °C in the course of 4 h. 2,2,3,3-Tetrafluoropropyl benzoate is formed only after prolonged heating of the reactants at 170 °C.[69]

Bearing in mind the ability of the oxygen atom in alkoxyphosphoranes to be protonated by acids,[87,88] one may put forward a general mechanism of the reactions of acyclic alkoxyphosphoranes with acids, consisting in the protonation of oxygen and subsequent splitting off of the alcohol and the formation of the phosphonium salt (LXXVII), which may exist in equilibrium with the acyloxyphosphorane. The decomposition of the salt (LXXVII) actually leads to the final reaction products:

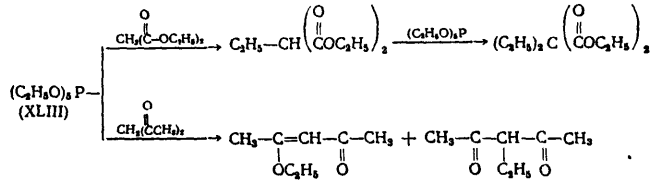


R_F=H $(CF_2)_n$, n = 2 (XVI), 4 (XVII);
X^-=$C_6H_5COO^-$, Cl^-

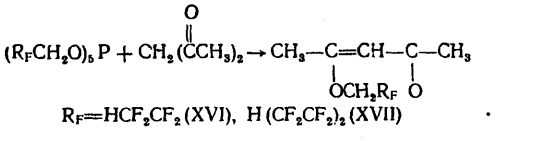
Evidently the difference between the reactivities of the alkoxyphosphoranes (IV), (XLIII), (XLVII), (L), (LII), and (LX) and of the polyfluoroalkoxyphosphoranes (XVI) and (XVII) in relation to acids is associated with the influence of the polyfluoroalkyl substituents, which weakens the nucleophilic properties of the oxygen, hindering its protonation.

7. Reactions with CH Acids

Pentaethoxyphosphorane (XLII) ethylates diethylmalonic ester at the carbon atom and acetylacetone at the oxygen atom. An insignificant amount of the *C*-alkylation product is also formed in the latter case:[76]



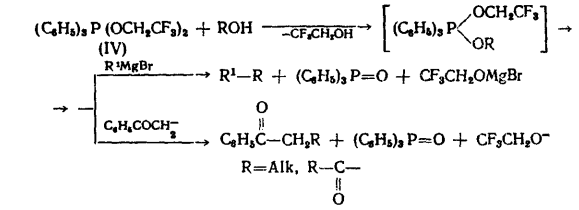
Pentakis(polyfluoroalkoxy)phosphoranes (XVI) and (XVII) react with acetylacetone to form vinyl ethers only:[89]



R_F=HCF_2CF_2 (XVI), $H(CF_2CF_2)_2$ (XVII)

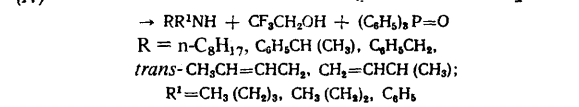
8. Reactions with Carbanions

Succesive treatment of bis(2,2,2-trifluoroethoxy)triphenylphosphorane (IV) with an alcohol or acid and then with a Grignard reagent or the enolate anion results in the formation of compounds with a C–C bond—alkanes or ketones. It is believed[34] that the carbanion executes a nucleophilic attack on the intermediate highly reactive alkoxy- or acyloxy-phosphorane:



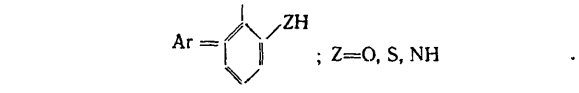
9. Reactions with Amines and Carboxylic Acid Amides

The structure of the products of the reactions of alkoxyphosphoranes with primary amines is determined by the nature of the substituents at the phosphorus atom. When bis(2,2,2-trifluoroethoxy)triphenylphosphorane (IV) is treated with an alcohol and then a primary amine, the latter is alkylated and a secondary amine is formed:[34]



R = n-C_8H_{17}, $C_6H_5CH(CH_3)$, $C_6H_5CH_2$, *trans*-$CH_3CH{=}CHCH_2$, $CH_2{=}CHCH(CH_3)$;
R^1=$CH_3(CH_2)_3$, $CH_3(CH_2)_2$, C_6H_5

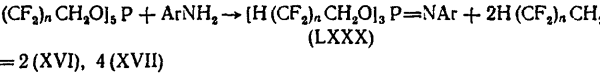
Primary arylamines are alkylated also in the reaction with bis(2,2,2-trifluoro-1-trifluoromethylethoxy)triphenylphosphorane (LXXVIII):[90]



Ar = ; Z=O, S, NH

The secondary amines (LXXIX) thus produced have been used successfully for the synthesis of heterocyclic systems.[90]

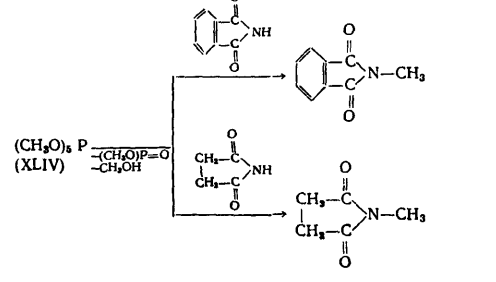
In contrast to the examples quoted above, the reactions of pentakis(polyfluoroalkoxy)phosphoranes (XVI) and (XVII) with primary arylamines lead to tris(polyfluoroalkoxy)phosphazobenzenes (LXXX):[69]



n = 2 (XVI), 4 (XVII)

There are very few data on the reactions of acyclic alkoxyphosphoranes with compounds containing a secondary amino-group.

Pentamethoxyphosphorane (LXIV) reacts with phthalimide and succinimide to form *N*-methylated compounds:[84]



Detailed study of the reaction of pentakis(2,2,3,3-tetrafluoropropoxy)phosphorane (XVI) with secondary amines [91] showed that a compound of hexacoordinate phosphorus with an acyclic structure, namely dialkylammonium pentakis(2,2,3,3-tetrafluoropropoxy)piperidino(morpholino)phosphorate (LXXXI), is formed initially even at 20 °C as a result of the attack by the amine on the phosphorus atom. The phosphorates (LXXXI) are crystalline compounds stable at 20 °C. When they are heated to 150 °C, the nucleophilic substitution of the 2,2,3,3-tetrafluoropropoxy-group takes place and the mixed piperidino(morpholino)tetrakis(2,2,3,3-tetrafluoropropoxy)phosphorane (LXXXII) is produced. The latter alkylates a second amine molecule and the final products of the reaction of the phosphorane (XVI) with piperidine or morpholine on heating are therefore the tertiary amine (LXXXIII), the phosphoramidate (LXXXIV), and tetrafluoropropanol:

$$(HCF_2CF_2CH_2O)_5P + 2Alk_2NH \xrightarrow{20^\circ C} (HCF_2CF_2CH_2O)_5\bar{P}NAlk_2H_2\overset{+}{N}Alk_2 \xrightarrow{\Delta}$$
(XVI) (LXXXI)

$$\xrightarrow{-HCF_2CF_2CH_2OH} (HCF_2CF_2CH_2O)_4PNAlk_2 +$$
(LXXXII)

$$+ HNAlk_2 \xrightarrow{\Delta} (CHF_2CF_2CH_2O)_2\overset{O}{\overset{\|}{P}}-NAlk_2 + HCF_2CF_2CH_2NAlk_2 +$$
(LXXXIV) (LXXXIII)

$$+HCF_2CF_2CH_2OH;\ NAlk_2 = \text{morpholino, piperidino}$$

10. Reactions with Aldehydes and Ketones

Bis(2,2,2-trifluoroethoxy)triphenylphosphorane (IV) reacts with aliphatic aldehydes at room temperature to form bis(2,2,2-trifluoroethyl)acetals: [31]

$$(C_6H_5)_3P(OCH_2CF_3)_2 + RCHO \rightarrow (C_6H_5)_3P{=}O + RCH(OCH_2CF_3)_2$$
(IV)

$$R = (CH_3)_2CH,\ n\text{-}C_5H_{11},\ n\text{-}C_6H_{13}.$$

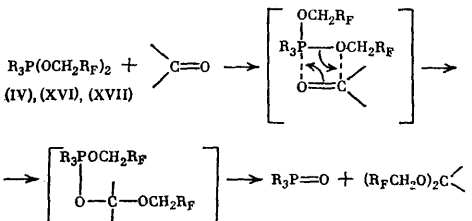
Pentakis(polyfluoroalkoxy)phosphoranes (XVI) and (XVII) alkylate on heating formaldehyde and also aldehydes and ketones with electron-accepting substituents but do not react with the usual aliphatic aldehydes and ketones even at 200 °C: [89]

$$(R_FCH_2O)_5P + R{-}\overset{O}{\overset{\|}{C}}{-}R^1 \rightarrow R{-}\overset{R^1}{\overset{|}{C}}(OCH_2R_F)_2 + (R_FCH_2O)_3P{=}O$$

$R_F = HCF_2CF_2$ (XVI), $H(CF_2CF_2)_2$ (XVII)

$R = R^1 = H$; $R = Ar$, $R^1 = H$; $R = C_6H_5CH{=}CH$, $R^1 = H$; $R = CH_3CH{=}CH$, $R^1 = H$; $R = R^1 = CF_3$

It has been suggested [34,89] that the alkylation proceeds via a four-membered cyclic transition state, which is produced as a result of the initial attack by the positively charged carbon atom of the carbonyl group on the oxygen atom of the polyfluoroalkoxyphosphorane:



$R = C_6H_5$, $R_F = CF_3$ (IV); $R = H(CF_2CF_2)_nCH_2O$, $R_F = H(CF_2CF_2)_n$, $n = 1$ (XVI), $n = 2$ (XVII)

The significant difference between the reactivities of the phosphorane (IV), on the one hand, and the phosphoranes (XVI) and (XVII), on the other, can apparently be explained by the weakening of the nucleophilic properties of the oxygen of the polyfluoroalkoxy-group in the molecules of compounds (XVI) and (XVII), as a result of which the attack on the carbon atom of the carbonyl group is possible only after an increase of the positive charge on the latter.

The literature data examined show that the methods of synthesis of derivatives of acyclic hydroxyphosphoranes known at present make it possible to obtain compounds containing substituents with different electronic and steric properties at the phosphorus atom; this alters in its turn their chemical properties within extremely wide limits.

Acyclic alkoxyphosphoranes are extremely reactive reagents, suitable for the synthesis of various classes of organic compounds. Special mention should be made of the advantages of alkoxyphosphoranes as alkylating agents: the alkylation takes place under mild conditions in the absence of basic or acid catalysts and does not require the use of protecting groups; the reaction does not result in the formation of acids or bases, which are in many instances undesirable.

Since vigorous investigation of the chemical properties of acyclic alkoxyphosphoranes began only recently, many reactions have been examined in relation to a limited number of examples. There is no doubt that further study of acyclic alkoxy- and aryloxy-phosphoranes will greatly expand the range of synthetic applications of these reactive compounds and will also lead to the discovery of new facts, which will extend our understanding of the nature of phosphorus compounds.

REFERENCES

1. F.Ramirez and I.Kogi, in "Trudy V Konferentsii 'Khimiya i Primenenie Fosfororganicheskikh Soedinenii'" (Proceedings of the Vth Conference on 'The Chemistry and Applications of Organophosphorus Compounds'), Izd.Nauka, Moscow, 1974, p.138.
2. B.A.Arbuzov and N.A.Polezheva, Uspekhi Khim., 1974, **43**, 933 [Russ.Chem.Rev., 1974(5)].
3. S.A.Terent'eva, M.A.Pudovik, and A.N.Pudovik, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 1152.
4. D.Houalla, T.Mouheich, M.Sanchez, and R.Wolf, Phosphorus, 1975, **5**. 229.
5. G.Kemp and S.Trippett, J.Chem.Soc., Perkin Trans.I, 1979, 879.
6. D.Houalla, M.Sanchez, R.Wolf, and F.H.Osman, Tetrahedron Lett., 1978, 4675.
7. F.Ramirez, Y.F.Chaw, and Y.F.Marecek, Phosphorus Sulfur, 1979, **7**, 241.
8. M.V.Wimmer and I.A.Rose, Ann.Rev.Biochem., 1978, **47**, 1031.
9. W.G.Voncken and H.M.Buck, Rec.trav.Chim., 1974, **93**, 210.
10. P.M.Van Ool and H.M.Buck, Rec.trav.Chim., 1984, **103**, 119.
11. R.J.Gillespie and R.S.Nyholm, Quart.Rev.Chem.Soc., 1957, **11**, 339.
12. R.J.Gillespie, J.Chem.Soc., I, 1952, 1002.
13. R.J.Gillespie, J.Chem.Educ., 1970, **47**, 18.
14. F.H.Westheimer, Acc.Chem.Res., 1968, **1**, 70.
15. F.Ramirez, Synthesis, 1974, 90.
16. D.B.Denney, D.Z.Denney, P.J.Hammond, and Y.-P.Wang, J.Amer.Chem.Soc., 1981, **103**, 1785.

17. Yu.G.Shermolovich, N.P.Kolesnik, V.V.Vasil'ev, V.E.Pashinnik, and L.N.Markovskii, Zhur.Obshch. Khim., 1981, **51**, 542.
18. L.N.Markovskii, A.V.Solov'ev, and Yu.G.Shermolovich, Zhur.Obshch.Khim., 1980, **50**, 2184.
19. H.Schmidbaur and G.E.Zybill, Chem.Ber., 1981, **114**, 3589.
20. R.G.Cavell and K.I.The, Inorg.Chem., 1978, **17**, 355.
21. D.Hellwinkel, Chem.Ber., 1966, **99**, 3642.
22. L.Anshutz, Annalen, 1927, **454**, 77.
23. I.N.Zhmurova and A.V.Kirsanov, Zhur.Obshch.Khim., 1959, **29**, 1687.
24. F.Ramirez, A.J.Bigler, and C.P.Smith, J.Amer.Chem. Soc., 1968, **90**, 3507.
25. W.C.Archie, Jr. and F.H.Westheimer, J.Amer.Chem. Soc., 1973, **95**, 5955.
26. D.B.Denney, D.Z.Denney, and L.-T.Liu, Phosphorus Sulfur, 1982, **13**, 1.
27. F.Jeanneaux and J.G.Riess, Nouv.J.Chim., 1979, **3**, 263.
28. D.D.Poulin, C.Demay, and I.G.Riess, Inorg.Chem., 1977, **16**, 2278.
29. D.Dakternieks, G.-V.Röschenthaler, and R.Schmutzler, J.Fluor.Chem., 1978, **11**, 387.
30. D.Dakternieks, G.-V.Röschenthaler, and R.Schmutzler, J.Fluor.Chem., 1978, **12**, 413.
31. L.M.Markovskii, A.V.Solov'ev, V.E.Pashinnik, and Yu.G.Shermolovich, Zhur.Obshch.Khim., 1980, **50**, 807.
32. L.N.Markovskii, N.P.Kolesnik, and Yu.G.Shermolovich, Zhur.Obshch.Khim., 1979, **49**, 1764.
33. T.Kubota, T.Kitazume, and N.Ishikawa, Chem.Lett., 1978, 889.
34. T.Kubota, S.Miyashita, T.Kitazume, and N.Ishikawa, J.Org.Chem., 1980, **45**, 5052.
35. K.I.The and R.G.Cavell, Inorg.Chem., 1976, **15**, 2518.
36. K.I.The and R.G.Cavell, Inorg.Chem., 1977, **16**, 2887.
37. Q.-C.Mir, R.W.Shreeve, and J.M.Shreeve, Phosphorus Sulfur, 1980, **8**, 331.
38. C.L.Lerman and F.H.Westheimer, J.Amer.Chem.Soc., 1976, **98**, 3533.
39. C.L.Lerman and F.H.Westheimer, J.Amer.Chem.Soc., 1976, **98**, 179.
40. D.I.Phillips, I.Szele, and F.H.Westheimer, J.Amer. Chem.Soc., 1976, **98**, 184.
41. H.Schmidbaur, H.Stühler,, and W.Buchner, Chem. Ber., 1973, **106**, 1238.
42. F.Ramirez, M.Nowakowski, and J.F.Marecek, J.Amer. Chem.Soc., 1976, **98**, 4330.
43. V.D.Romanenko, V.I.Tovstenko, and L.N.Markovskii, Zhur.Obshch.Khim., 1979, **49**, 1907.
44. S.Antczak and S.Trippett, J.Chem.Soc., Perkin Trans. I, 1978, 1326.
45. V.V.Malovik, V.A.Bondar', N.O.Chernukho, and G.F.Solodushchenko, Zhur.Obshch.Khim., 1980, **50**, 2618.
46. T.Kh.Gazizov, Yu.I.Sudarev, I.Kh.Shakirov, V.N.Smirnov, and A.N.Pudovik, Zhur.Obshch.Khim., 1982, **52**, 769.
47. A.Aaberg, T.Gramstad, and S.Husebye, Tetrahedron Lett., 1979, 2263.
48. J.Chojnowski, M.Cypryk, and J.Michalski, J.Organometal.Chem., 1978, **161**, 31.
49. R.G.Cavell and R.D.Leary, Chem.Comm., 1970, 1520.
50. R.G.Cavell, R.D.Leary, and A.J.Tomlinson, Inorg. Chem., 1972, **11**, 2578.
51. D.B.Denney and H.M.Relles, J.Amer.Chem.Soc., 1964, **86**, 3897.
52. D.B.Denney and S.T.D.Gough, J.Amer.Chem.Soc., 1965, **87**, 138.
53. D.B.Denney, D.Z.Denney, and L.A.Wilson, Tetrahedron Lett., 1968, 85.
54. D.B.Denney, D.Z.Denney, B.C.Chang, and K.L.Marsi, J.Amer.Chem.Soc., 1969, **91**, 5243.
55. D.B.Denney and D.H.Jones, J.Amer.Chem.Soc., 1969, **91**, 5821.
56. L.L.Chang and D.B.Denney, Chem.Comm., 1974, 84.
57. L.L.Chang, D.B.Denney, D.Z.Denney, and R.J.Kazior, J.Amer.Chem.Soc., 1977, **99**, 2293.
58. D.B.Denney, R.Melis, and A.D.Pendse, J.Org.Chem., 1978, **43**, 4672.
59. D.A.Bowman, D.B.Denney, and D.Z.Denney, Phosphorus Sulfur, 1978, **4**, 229.
60. D.B.Denney, D.Z.Denney, and D.M.Gavrilolic, Phosphorus Sulfur, 1981, **11**, 1.
61. D.B.Denney, D.Z.Denney, C.D.Hall, and K.L.Marsi, J.Amer.Chem.Soc., 1972, **94**, 245.
62. D.B.Denney, D.Z.Denney, P.J.Hammond, C.Huang, and K.S.Tseng, J.Amer.Chem.Soc., 1980, **102**, 5073.
63. D.B.Denney, D.Z.Denney, P.J.Hammond, L.-T.Liu, and Y.-P.Wang, J.Org.Chem., 1983, **48**, 2159.
64. G.-V.Röschenthaler, Z.anorg.Chem., 1981, **479**, 158.
65. L.V.Nesterov and N.E.Krepysheva, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 1451.
66. P.D.Beer, R.C.Edwards, C.D.Hall, J.R.Jennings, and R.J.Cozens, Chem.Comm., 1980, 351.
67. J.H.Letcher and J.R.Wan Wazer, in "Topics in Phosphorus Chemistry", Intersci.Publ., New York–London–Sydney, 1967, Vol.5, p.75.
68. F.Jeanneaux and J.G.Riess, Nouv.J.Chim., 1979, 3, 263.
69. N.P.Kolesnik, Candidate's Thesis in Chemical Sciences, Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev, 1984.
70. L.W.Dennis, V.J.Bartuska, and G.E.Maciel, J.Amer. Chem.Soc., 1982, **104**, 230.
71. R.Sarma, F.Ramirez, B.McKeever, J.F.Marecek, and S.Lee, J.Amer.Chem.Soc., 1976, **98**, 581.
72. H.Schmidbaur, W.Buchner, and F.H.Köhler, J.Amer. Chem.Soc., 1974, **96**, 6208.
73. J.S.Sigal and F.H.Westheimer, J.Amer.Chem.Soc., 1979, **101**, 5329.
74. L.V.Nesterov and N.E.Krepysheva, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 1453.
75. A.Queen, A.E.Lemire, and A.F.Janzen, Int.J.Chem. Kinet., 1981, **13**, 411.
76. D.B.Denney and L.Saferstein, J.Amer.Chem.Soc., 1966, **88**, 1839.
77. D.B.Denney, D.Z.Denney, and C.-F.Ling, J.Amer. Chem.Soc., 1976, **98**, 6755.
78. B.C.Chang, W.E.Conrad, D.B.Denney, D.Z.Denney, R.Edelman, R.L.Powell, and D.W.White, J.Amer.Chem. Soc., 1971, **93**, 4004.
79. K.Burger, in "Organophosphorus Reagents in Organic Synthesis", Acad.Press, London, 1979, p.467.
80. F.Ramirez, Acc.Chem.Res., 1968, **1**, 168.
81. D.B.Denney, R.L.Powell, and A.Taft, Phosphorus, 1971, **1**, 151.
82. D.B.Denney, D.Z.Denney, and J.J.Cigantino, J.Org. Chem., 1984, **49**, 2831.
83. P.L.Robinson, C.N.Barry, S.W.Bass, and S.A.Evans, J.Org.Chem., 1983, **48**, 5398.
84. D.B.Denney, R.Melis, and A.D.Pendse, J.Org.Chem., 1978, **43**, 4672.
85. F.Ramirez, A.J.Bigler, and C.P.Smith, Tetrahedron, 1968, **24**, 5041.

86. T.Kubota, S.Mijashita, T.Kitazume, and N.Ishikawa, Chem.Lett., 1979, 845.
87. M.M.C.F.Castelijus, P.Schipper, and H.M.Buck, Chem.Comm., 1978, 382.
88. E.Grochowski, B.D.Hilton, R.J.Kupper, and C.J.Michejda, J.Amer.Chem.Soc., 1982, **104**, 6876.
89. Yu.G.Shermolovich, N.P.Kolesnik, Z.Z.Rozhkova, and L.N.Markovskii, Zhur.Obshch.Khim., 1982, **52**, 2526.
90. T.Kubota, K.Yamamoto, and T.Tanaka, Chem.Lett., 1983, 167.
91. Yu.G.Shermolovich, N.P.Kolesnik, and L.N.Markovskii, Zhur.Obshch.Khim., 1980, **50**, 826.

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