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P-Hetero-substituted Phosphorus Ylides

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The literature data on the methods of synthesis and properties of ylides containing various heteroatoms at the phosphorus atom in the P = C group are surveyed and described systematically.
The bibliography includes 134 references.

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I. INTRODUCTION

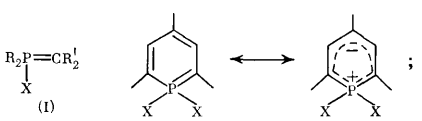
The interest in the chemistry of phosphorus ylides is due to the great theoretical and practical importance of these reactive compounds[1,2]. Phosphonium ylides are widely used in the laboratory and industrial Wittig synthesis of olefins and are employed in the synthesis of strained cycloalkanes, macrocyclic compounds, cyclic dienes and heavy metal complexes[3-10].

Structurally phosphorus ylides are carbanions stabilised by the neighbouring phosphonium group[1]:

$$R_3P{=}CR'_2 \longleftrightarrow R_3\overset{+}{P}{-}\overline{C}R'_2 .$$

The stability and reactivity of phosphorus ylides depend to a large extent on the substituents R' at the carbanionic centre. By varying these substituents, it is possible to obtain all possible types of *C*-substituted phosphorus ylides with exceptionally varied properties[1-10]. However, the substituents R at the phosphonium centre also exert a significant influence on the properties of ylides. Ylides containing heteroatoms attached to the phosphorus atom have especially interesting and frequently unusual properties; the chemistry of these compounds began to be investigated only in recent years. The principal results achieved in the synthesis and investigation of the properties of *P*-hetero-substituted phosphorus ylides (I) and published up to 1983 are the subject of the present review.

The review deals with acyclic *P*-hetero-substituted phosphorus ylides. Ylides containing a P=C bond in the ring, particularly λ^5-phosphorins, are not discussed in detail, since these compounds have specific chemical properties which resemble little those of acyclic phosphorus ylides:



(I)

X = Cl, Br, RS, R_2P, R_3Si, RO, HO, R_2N, RNH, H .

Electrophilic substitution reactions in the C(4)-position, comparable to the analogous reactions of other electron-enriched aromatic systems, for example, dimethylaniline, are characteristic of *P*-hetero-substituted λ^5-phosphorins. Their basicity and nucleophilicity are very low, they form stable radicals, give rise to stable π-complexes with heavy metal salts, etc.[11] Physicochemical studies confirming the unusual electronic structure of λ^5-phosphorins nevertheless make it possible to regard them as ylides in which the negative charge of the carbanionic component is delocalised over the ring[12,13].

II. METHODS OF SYNTHESIS

There exist several methods for the synthesis of *P*-hetero-substituted ylides. These compounds are usually obtained by the "oxidative ylidation" of phosphorus(III) compounds. The term "oxidative ylidation" implies reactions as a result of which the coordination number of the tervalent phosphorus atom increases and a P=C bond with a tetracoordinate phosphorus atom is formed[14]. Depending on the structure of the initial tervalent phosphorus compounds, their ylidation can proceed via two pathways: either a substituent X is introduced at the phosphorus atom of compound (II) with simultaneous deprotonation of the α-carbon atom or an alkylidene group is introduced in some way at the phosphorus atom of an X-substituted phosphine:

$$\underset{(II)}{R_2P{-}CHR'_2} \xrightarrow[-H^+]{[X]} \underset{(I)}{R_2P(X){=}CR'_2} \xleftarrow{I\diagdown\!\!\diagup CR'_2I} R_2PX .$$

The remaining methods of synthesis, especially the dehydrohalogenation of phosphonium salts and the conversion of one *P*-hetero-substituted phosphorus ylide into another, are used only in individual instances, but they sometimes have an advantage over "oxidative ylidation".

1. "Oxidative Ylidation" of Tervalent Phosphorus CH Acids

The "oxidative ylidation" of tertiary phosphines and phosphonites (II), containing a mobile hydrogen atom at the α-carbon atom and behaving as CH acids of tervalent phosphorus, must be regarded as the most flexible and general approach to the synthesis of *P*-hetero-substituted ylides[14-16]. Compounds (II) containing at the α-carbon atom only electron-accepting substituents R', enhancing the mobility of the hydrogen atoms and stabilising the ylide function, are ylidated most readily. However, in many instances it is possible to ylidate successfully also weak CH acids, such as, for example, trialkylphosphines. The phosphorus(III) CH acids are carbon analogues of the phosphorus(III) OH acids[14-20] and can be converted into ylides in the same way as the OH acids of tervalent phosphorus form compounds with a P=O group. In particular, the phosphorus(III) CH acids undergo reactions resembling the Atherton–Todd, Michaelis–Becker, etc. reactions characteristic of dialkyl phosphites. Certain alkylphosphines of type (II) isomerise to ylides with a P–H bond, analogous to the prototropic P(O)H forms of the phosphorus(III) OH acids, which emphasises still further the similarity of these types of organophosphorus compounds[18]:

$$R_2P{-}CHR'_2 \rightleftarrows R_2P(H){=}CR'_2 \quad R_2P{-}OH \rightleftarrows R_2P(H){=}O .$$

(a) Reactions of Compound (II) with Carbon Tetrahalides

Tertiary phosphines and phosphonites (II) containing electron-accepting substituents at the α-carbon atom are ylidated on interaction with carbon tetrachloride and alkylamines, aniline, or ammonia[15,16,19-22]. The reaction models the Atherton–Todd reaction, according to which dialkyl phosphites react with CCl_4 and alkylamines to form phosphoric acid amides[23]. The interaction of compound (II) with CCl_4 and alkylamines and also ammonia proceeds readily in ether at 0 °C, but the reaction with aniline must be carried out, in view of the low basicity of the latter, in the presence of triethylamine. The method employs readily available starting materials and makes it possible to vary widely the substituents at the phosphorus and carbon atoms of the P=C group:

$$R_2P{-}CHR'_2 \xrightarrow[-CHCl_3,\ -R''_2NH\cdot HCl]{CCl_4+R''_2NH} R_2P(NR''_2){=}CR'_2 \quad ;$$

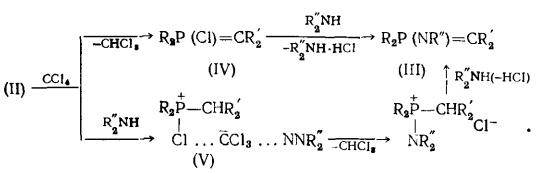
(II) (III), (50–70%)

R = Et, iso-Pr, Ph, EtO, iso-PrO; CR'_2 = $CHCO_2Et$, $CPhCO_2Me$, $C(CO_2Me)_2$, $CHSO_2CF_3$, $C(SO_2Ph)_2$; NR''_2 = NH_2, NHMe, NHPr-iso, NMe_2, NEt_2 ;

$$(iso\text{-}PrO)_2P{-}CH(CO_2Et)_2 \xrightarrow[-CHCl_3,\ -Et_3N\cdot HCl]{CCl_4+PhNH_2+Et_3N} (iso\text{-}PrO)_2P(PhNH){=}C(CO_2Et)_2 \quad .$$

Compounds(II) are converted into ylides (III) via the intermediate formation of *P*-halogenoylides (IV)[15,20] or via the complex (V)[21]. Depending on the reaction conditions, the first or second pathway is followed (Scheme 1).

Scheme 1



In the absence of amines, compounds (II) react with $CHal_4$ to form ylides with a halogen atom attached to the phosphorus atom[14,16,24-30]:

$$R_2P{-}CHR'_2 + CHal_4 \rightarrow R_2P(Hal){=}CR'_2 + CHHal_3 \quad ;$$

(II) (VI)

R = Et, iso-Pr, t-Bu, Ph, EtO, iso-PrO, Me_2N, Et_2N;

CR'_2 = CH_2, CHMe, CHPr, CHPr-iso, $CHSiMe_3$, CHSMe, CPh_2, fluorenylidene, cyclopentadienylidene, $C(SiMe_3)_2$, $CPhSiMe_3$, $C(CO_2Me)_2$, $C(CO_2Et)_2$, $C(SO_2Ph)_2$, $CHSO_2CF_3$;

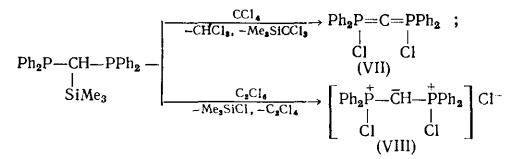
Hal = Cl, Br

The interaction of trialkylphosphines with carbon tetrachloride takes place readily on cooling to a temperature below 0 °C; less nucleophilic phosphonites react with carbon tetrachloride and are converted into *P*-chloroylides at an appreciable rate only in the presence of triethylamine, which exhibits a catalytic activity[14]:

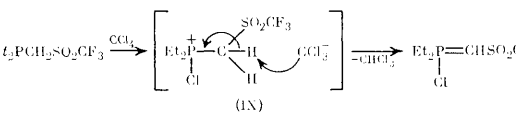
$$(EtO)_2P{-}CH(CO_2Et)_2 \xrightleftharpoons[+H^+]{B,\ -H^+} \left[(EtO)_2P{-}\bar{C}(CO_2Et)_2 \rightleftharpoons (EtO)_2\bar{P}{=}C(CO_2Et)_2\right] \xrightarrow[-CHCl_3]{CCl_4} (EtO)_2P(Cl){=}C(CO_2Et)_2 \quad .$$

However, phosphonites react with the very reactive carbon tetrabromide to form *P*-bromoylides even in the absence of triethylamine at −70 °C.[14] The yields of *P*-halogenoylides (VI) are usually high.

Interesting possibilities appear after the introduction of the trimethylsilyl group at the α-carbon atom in compound (II). Thus trimethylsilylbis(diphenylphosphino)methane gives rise to carbodiphosphorane (VII) on interaction with carbon tetrachloride as a result of the elimination of tribromotrimethylsilylethane and chloroform, while the reaction with hexachloroethane results in the formation of the ylide (VIII)[31,32]:



Compounds (II) are converted into *P*-halogenoylides owing to the presence of a mobile hydrogen atom at the α-carbon atom, as a result of which the anion $CHal_3^-$ readily deprotonates the quasi-phosphonium salt (IX) formed in the intermediate stage. Electron-accepting substituents at the α-carbon atom, which increase the mobility of the hydrogen atom, promote the formation of *P*-halogenoylides[14]:



However, weak CH acids such as trialkylphosphines can also be converted into *P*-halogenoylides, provided that there are bulky substituents at the phosphorus atom[28,29]:

$$t\text{-}Bu(R)PCH_2R' \xrightarrow[-CHHal_3]{CHal_4} t\text{-}Bu(R)P(Hal){=}CHR' \quad ;$$

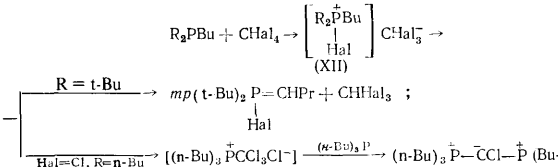
(X) (XI)

R = t-Bu, n-Bu, Et_2N, Me_2N; R′ = H, Me, n-Pr, iso-Pr; Hal = Cl, Br .

The "unstabilised" *P*-halogenoylides (XI) formed under these conditions are extremely reactive and are used for the synthesis of many interesting organophosphorus compounds.

Sterically unhindered tertiary phosphines, for example Me_3P or $n\text{-}Bu_3P$, do not form *P*-chlorides on interaction with CCl_4 but give rise to phosphoranylphosphonium salts (XIII)[33]. On the other hand, tertiary phosphines containing the t-butyl group are converted quantitatively into *P*-halogenoylides on interaction with carbon tetrahalides[28]. The influence of the steric shielding of the phosphorus atom on the pathway followed in the reactions of tertiary phosphines with carbon tetrahalides can be accounted for by Scheme 2 below:

Scheme 2



The interaction of a tertiary phosphine with $CHal_4$ results in the formation of the ion pair (XII), whose further reaction can proceed via two pathways: via the nucleophilic attack by $CHal_3^-$ on the phosphonium cation (anion exchange) or via the deprotonation of the α-carbon atom. The steric hindrance at the phosphorus atom generated by the t-butyl group is an obstacle to the interaction of $CHal_3^-$ with the phosphonium cation, as a consequence of which the deprotonation of the α-carbon atom becomes the dominant process. The mechanism has been confirmed by experimental observations[28].

The interaction of sterically hindered tertiary phosphines with carbon tetrabromide at −120 °C results in the formation of bright orange solid substances—bromophosphonium tribromomethanides (XIV)[28]. They exist at a very low temperature and, on increasing the latter to −90°– −60 °C, they are converted quantitatively into *P*-bromoylides. The stability of these unusual compounds is undoubtedly determined by the steric influence of the t-butyl groups at the phosphonium cation. Ion pairs of this type are also formed on interaction of sterically unhindered tertiary phosphines with carbon tetrahalides. However, in this case they behave as short-lived intermediates and can be "captured" by the proton-donating reagents only at the instant of their formation[34].

A conclusion concerning the structure of bromophosphonium tribromomethanides was reached on the basis of the study of their chemical reactions[28]. The reactions with deuterium chloride and chlorotrimethylsilane convincingly demonstrate the presence of the CBr_3^- anion:

$$(t\text{-Bu})_2PR + CBr_4 \xrightarrow{-120^\circ} (t\text{-Bu})_2\overset{+}{P}(Br)RCBr_3^- \ ;$$

R = t-Bu, n-Bu, Et_2N (XIV)

$$(XIV) \xrightarrow{-60^\circ,\ R=n\text{-Bu}} (t\text{-Bu})_2P(Br)=CHPr + CHBr_3 \ ;$$

$$(XIV) \xrightarrow{-120^\circ,\ DCl} (t\text{-Bu})_2(R)\overset{+}{P}ClBr^- + CDBr_3 \ ;$$

$$(XIV) \xrightarrow{-120^\circ,\ Me_3SiCl} (t\text{-Bu})_2(R)\overset{+}{P}ClBr^- + Me_3SiCBr_3 \ .$$

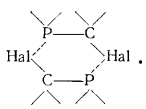
(b) The α-Halogenoalkylphosphine—P-Halogenoylide Rearrangement

The α-halogenoalkylphosphines (XV), formed on interaction of phosphinochloridous acids with halogenosulphonylmethanes, readily rearrange to *P*-halogenoylides (VI)[21,35]:

$$R_2PCl \xrightarrow{Na^+[HalCR'_2]^-} R_2P{-}\underset{(XV)}{CR'_2}{-}Hal \rightarrow \underset{(VI)}{R_2P(Hal)=CR'_2} \ ;$$

R = Et, iso-Pr, Ph; $CR'_2 = CHSO_2CF_3$, $C(SO_2Ph)_2$; Hal = Cl, Br .

The migration of the halogen atom from the α-carbon atom to the phosphorus atom (the C → P halogenotropic shift) increases the coordination number of the phosphorus atom and results in the formation of a P=C bond, i.e. "oxidative ylidation" takes place. The α-halogenoalkylphosphine (XV) contains a "positively charged" halogen to which the nucleophilic attack by the tervalent phosphorus atom may be directed, resulting in the abstraction of the halogen from the carbon atom. It is entirely likely that the transfer of the halogen from the carbon atom to the phosphorus atom proceeds via a six-membered transition state:



Electron-accepting substituents at the phosphorus atom, particularly halogen atoms, which make it less nucleophilic, prevent the rearrangement[36]:

$$Cl_3P + ClCH(CO_2Et)_2 \xrightarrow[-Et_3N\cdot HCl]{Et_3N} Cl_2P{-}\underset{Cl}{C}(CO_2Et)_2 \not\rightarrow Cl_3P{=}C(CO_2Et)_2 \ .$$

The α-halogenoalkylphosphine—*P*-halogenoylide rearrangement was first observed in a number of compounds containing sulphonyl groups at the α-carbon atom[21,35]. However, it was shown subsequently that certain silicon-containing α-chloroalkylphosphines also readily rearrange to *P*-chloroylides[37,38]:

$$Me_2PLi + Cl_2C(SiCl_3)_2 \rightarrow Me_2P{-}\underset{Cl}{C}(SiCl_3)_2 \rightarrow Me_2P{=}\underset{Cl}{C}(SiCl_3)_2 \ ;$$

$$R_2PCl + LiClC(SiMe_3)_2 \rightarrow R_2P{-}\underset{Cl}{C}(SiMe_3)_2 \rightarrow R_2P{=}\underset{Cl}{C}(SiMe_3)_2 \ ;$$

R = Ph, Me_2N .

(c) Disproportionation of Tertiary Phosphines with a Mobile Hydrogen Atom at the α-Carbon Atom

Tervalent phosphorus compounds with a mobile hydrogen atom at the α-carbon atom exhibit a distinct tendency to be converted into phosphorus ylides. Thus diethylbis(alkoxycarbonyl)methylphosphines and diethyltrifluoromethanesulphonylmethylphosphine disproportionate on heating with formation of the ylides (XVII) containing a phosphorus—phosphorus bond[14,39]:

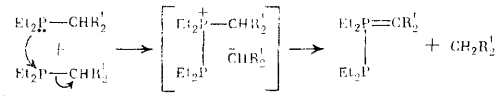
$$\underset{(XVI)}{2Et_2P{-}CHR'_2} \xrightarrow{120^\circ} \underset{(XVII)}{Et_2P{-}PEt_2{=}CR'_2} + CH_2R'_2 \ ;$$

$CR'_2 = CHSO_2CF_3$, $C(CO_2Me)_2$, $C(CO_2Et)_2$.

The disproportionation of compounds (XVI) is a reversible process. On heating with the simultaneous removal from the reaction sphere of the non-phosphorylated component $CH_2R'_2$, the equilibrium is fully displaced in the direction of the P—P ylides (XVII). Without heating and the removal of $CH_2R'_2$, the disproportionation of compounds (XVI) does not take place.

Scheme 3, taking into account the high lability of the P—P bond in compounds (XVI), explains the formation of P—P ylides (XVII).

Scheme 3



This lability is due to the effective stabilisation by the electron-accepting substituents R', formed on dissociation of the P—C bond of the carbanion CHR'_2, which becomes capable of playing the role of a readily eliminated group. Compounds (XVI) are cleaved at the P—C bond by alcohols, water, ketoenols, thiols, etc.[14]

The structure of the P—P ylides (XVII) is confirmed by spectroscopic data. The ^{31}P NMR spectra of the ylides (XVII) contain a double doublet of signals due to the tricoordinate and tetracoordinate phosphorus atoms. The constant $^1J_{PP}$ = 270–280 Hz corresponds to the spin–spin coupling of the phosphorus nuclei in the tetracoordinate phosphorus–tricoordinate phosphorus bond.

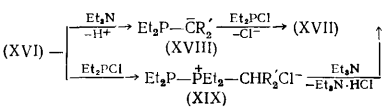
(d) Reactions of Tervalent Phosphorus CH Acids and Their Carbanions with Chlorine-containing Electrophiles

Tervalent phosphorus compounds (XVI) containing a mobile hydrogen atom at the α-carbon atoms form P—P ylides (XVII) also on interaction with chlorodiethylphosphine in the presence of triethylamine[14,20,40]. The reaction is carried out in ether at 0–10 °C:

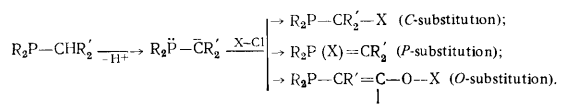
$$(XVI) + Et_2PCl \xrightarrow[-Et_3N\cdot HCl]{Et_3N} (XVII) \ .$$

A convenient method of synthesis of the P–P ylides (XVII) involves the reaction of malonic ester or trifluoromethanesulphonylmethane with two equivalents of chlorodiethylphosphine in the presence of an excess of triethylamine[14,39]. The tertiary phosphines (XVI), formed in the intermediate stage, can be obtained in high yields when the starting reactants are taken in proportions of 1:1.[14,25,40,41]

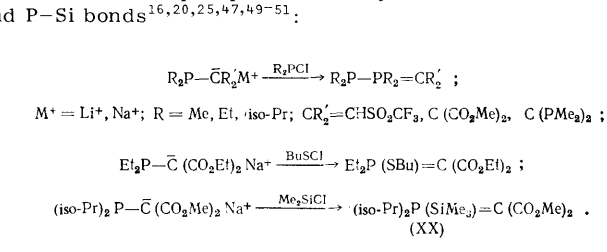
The P–P ylides (XVII) are apparently formed as a result of the *P*-phosphorylation of the α-phosphinocarbanion (XVIII) However, one cannot rule out also the electrophilic attack by chlorodiethylphosphine on the tervalent phosphorus atom of the tertiary phosphine (XVI) with subsequent dehydrochlorination of the phosphonium salt (XIX) (formed under these conditions) under the influence of triethylamine:



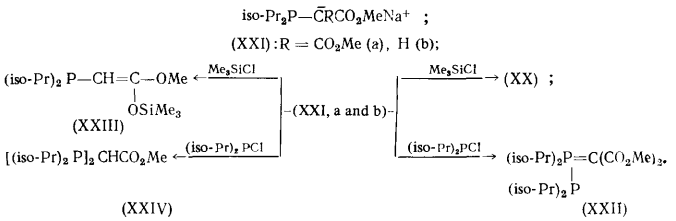
The α-phosphinocarbanions (XVIII), which are obtained by deprotonating alkylphosphines by various bases [lithium alkyls[20,42–45], sodium bis(trimethylsilyl)amide[46], sodium hydride[47], and even alkylamines[48]], can be converted in many instances into *P*-hetero-substituted phosphorus ylides. In principle, α-phosphinocarbanions can react with chlorine-containing electrophiles to form products substituted both at the carbon atom and at the phosphorus atom and, when the C=O group is present at the carbanionic centre, also products substituted at the oxygen atom:



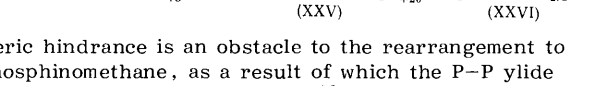
The mode of reaction of ambident α-phosphinocarbanions with chlorine-containing electrophiles (alkyl halides, tervalent phosphorus chlorides, sulphene chlorides, and chlorotrimethylsilane) is determined by kinetic and thermodynamic factors and depends primarily on the structure of the initial reactants. The presence of the electron-accepting groups CO_2R, SO_2R, and Me_2P at the α-carbon atom stabilises the ylide functional group, favouring the formation of products substituted at the phosphorus atom—ylides with P–P, P–S, and P–Si bonds[16,20,25,47,49–51]:



The influence of electron-accepting groups with substituents on the mode of reaction of α-phosphinocarbanions with chlorine-containing electrophiles is demonstrated by the following example. The carbanion (XXIa), containing two methoxycarbonyl groups, reacts with iso-Pr_2PCl and Me_3SiCl to form the ylides (XX) and (XXII)[47], while the carbanion (XXIb), with a single methoxycarbonyl group, gives rise to only the products (XXIII) and (XXIV) substituted at the C and O atoms[52]. The stabilisation of the *P*-substitution products by only one MeO_2C group in the latter case is insufficient:



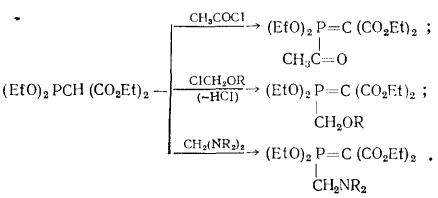
When bis(diphenylphosphino)methyl-lithium reacts with chlorodialkylphosphines at −78 °C, a P–P ylide (XXV) is formed and, on raising the temperature to 20 °C, rearranges to triphosphinomethane (XXVI)[49]. Evidently, under the conditions of kinetic control, the less stable *P*-substitution product is formed and is then converted into the thermodynamically more favourable *C*-substitution product:



Steric hindrance is an obstacle to the rearrangement to triphosphinomethane, as a result of which the P–P ylide (XXVII) is isolated in a pure state[49]:

Diethyl bis(ethoxycarbonyl)methylphosphonite readily forms ylides by interaction with acetyl chloride in the presence of bases[53,54], with α-chloroethers under the conditions of the Arbuzov reaction[55], and also with aminomethylenes under the conditions of the Kabachnik–Fields reaction[56] (Scheme 4):

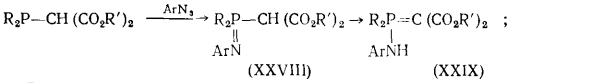
Scheme 4



(e) Prototropic Transformations of Phosphorylated CH Acids

The use of tervalent phosphorus compounds containing a mobile hydrogen atom at the α-carbon atom makes it possible to realise the extensive possibilities for their conversion into ylides as a result of reactions involving prototropic rearrangements.

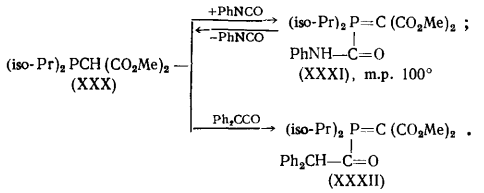
The Staudinger imination of bis(alkoxycarbonyl)methylphosphines and the analogous phosphonites by aryl azides yields the phosphazo-compounds (XXVIII), which readily rearrange to the ylides (XXIX) with the RNH group at the phosphorus atom[41,57–59] (for the phosphazo-ylide tautomerism, see Section III.4):



The driving force of this rearrangement is the endeavour by the system to form the least "acid" tautomeric form.

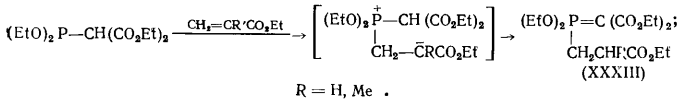
Phenyl isocyanate and diphenylketen readily add to the tertiary phosphine (XXX). The reaction proceeds with formation of the *P*-acyl-substituted ylides (XXXI) and

(XXXII)[25]:



The ylide (XXXI) is stable in the crystalline state, but in solutions it dissociates into the initial compounds. On cooling or removal of the solvent, the ylide (XXXI) is recovered from the solution in the crystalline form.

Diethyl bis(ethoxycarbonyl)methylphosphonite reacts with acrylic and methacrylic acid esters under the conditions of the Pudovik reaction with formation of the ylides (XXXIII)[60]:



It has been noted that in the presence of alkaline catalysts the yields of the ylides increase and the reaction is accelerated.

2. Introduction of an Alkylidene Group into Tervalent Phosphorus Compounds

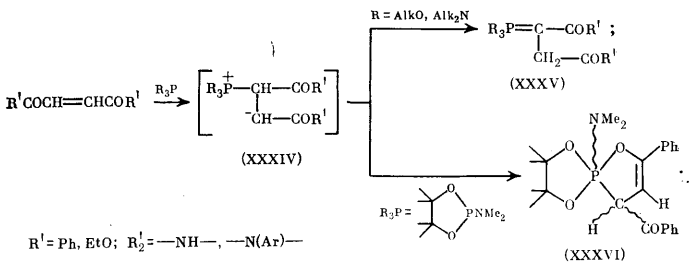
P-Hetero-substituted phosphorus ylides are formed when tervalent phosphorus acid derivatives interact with various compounds serving as sources of a substituted methylene fragment. Such sources can be carbenes, carbenoids, and various compounds with activated multiple bonds.

(a) Reactions of Tervalent Phosphorus Compounds with Alkenes and Alkynes

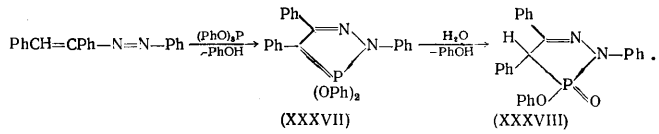
Compounds with an activated multiple bond readily react with tervalent phosphorus compounds and give rise to phosphorus ylides in many instances. Nucleophilic attack by the tervalent phosphorus atom on the electron-unsaturated carbon atom in the activated double bond produces a very reactive betaine (XXXIV), which readily rearranges to an ylide. An adequate mobility of the α-hydrogen atom is a condition which must be fulfilled for such a rearrangement. In the presence of the electron-accepting carbonyl group, the rearrangement of the betaine (XXXIV) to its less "acid" prototropic form, namely the ylide (XXXV), takes place readily. Thus the amides and esters of tervalent phosphorus acids add to maleimides[61-63], fumaric acid esters[64], and *trans*-dibenzoylethylene[65] with formation of the ylides (XXXV).

However, the presence of the five-membered dioxaphospholan ring favours the cyclisation of the betaine (XXXIV) to the phosphorane (XXXVI)[64] (Scheme 5).

Scheme 5

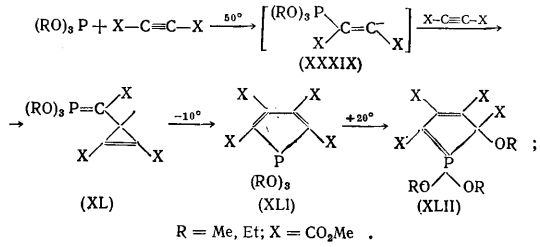


The ylides (XXXVII) with phenoxy-groups at the phosphorus atom have been obtained as a result of the [1 + 4]-cycloaddition of triphenyl phosphite to a conjugated azoalkene[66]. The chemical shift $\delta p = +43.7$ p.p.m. rules out a structure of the compound with a pentacoordinate phosphorus. The ylide (XXXVII) is very hygroscopic and is formed as a colourless solid product only after the complete removal of traces of moisture from the reaction mixture. In the presence of moisture, the ylide is instantly converted into the diazophosphole (XXXVIII):



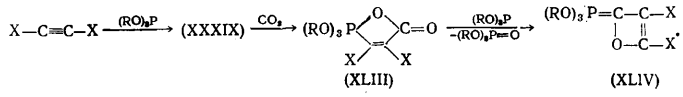
The reactions of acetylenedicarboxylic acid derivatives with tervalent phosphorus esters and amides proceeds in an interesting fashion. Thus the interaction of the methyl ester of this acid with trialkyl phosphites leads to the formation of the cyclic ylides (XLII) containing alkoxy-groups at the phosphorus atom[67,68]. NMR study of the reaction at a low temperature showed that the betaine (XXXIX) is formed initially and then its interaction with a second acetylenedicarboxylate molecule gives rise to the ylide (XL) with the cyclopropenyl group at the α-carbon atom. This ylide exists at −50 °C but, on raising the temperature to −10 °C, rearranges to the phosphorane (XLI), whose structure has been confirmed by the ^{31}P NMR spectrum ($\delta p = -37.4$ p.p.m.). At 20 °C the phosphorane is converted into the cyclic ylide (XLII)[67,68] via Scheme 6.

Scheme 6



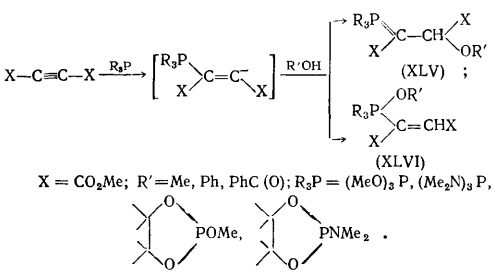
The ylides (XLII) have been obtained in the form of a crystalline substance and their structure has been convincingly confirmed by spectroscopic studies.

The betaine (XXXIX) interacts with carbon dioxide to form the phosphorane (XLIII) ($\delta p = -53.8$ p.p.m.), which is stable at a low temperature, but at 20 °C reacts with a second trialkyl phosphite molecule, gives up an oxygen atom to the latter, and is converted into the ylide (XLIV)[69]:



In the presence of hydroxylated reagents, the reaction of acetylenedicarboxylate ester with phosphites leads to the formation of ylides or phosphoranes. Acyclic phosphites give rise to the ylides (XLV), while five-membered cyclic phosphites yield the phosphoranes (XLVI)[70-72] (Scheme 7):

Scheme 7



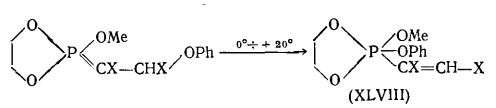
X = CO_2Me; R′=Me, Ph, PhC (O); R_3P = $(MeO)_3P$, $(Me_2N)_3P$,

Interesting transitions between the ylide and phosphorane structures, whose direction depends on the substituent R at the phosphorus atom and on the nature of the proton-donating reagent, have been observed with the aid of ^{31}P NMR. The rearrangement of the ylide to the phosphorane was observed in the interaction of trimethyl phosphite with acetylenedicarboxylate ester in the presence of a "trapping reagent"–methanol. At −40 °C the phosphorane can be detected in the reaction mixture, while at 20 °C it is converted into the ylide[73]:

$$(MeO)_4P{-}CX{=}CHX \xrightarrow{+20^\circ} (MeO)_3P{=}CX{-}CH\langle^{X}_{OMe} \quad .$$

(XLVII)

Conversely the reaction of acetylenedicarboxylate with cyclic phosphites and phenol at a low temperature gives rise to an ylide, which rearranges to the phosphorane (XLVIII) above 0 °C:



(XLVIII)

(b) Other Methods for the Introduction of the Methylene Group into Tervalent Phosphorus Compounds

A unique example of the synthesis of the ethoxycarbonyl ylide (XLIX) by displacing trimethylamine by an aminophosphine from a quaternary ammonium salt has been described[74]:

$$(Me_2N)_2PPh + Me_3\overset{+}{N}CH_2CO_2Et\ Cl^- \xrightarrow[-Me_3N\cdot HCl]{} (Me_2N)_2P{=}CHCO_2Et \quad .$$

Ph

(XLIX)

The formation of the trimethoxyphosphonium ylide (L) as a result of the interaction of tri(phenylthio)methyl-lithium with trimethyl phosphite has been reported[75]. The ylide (L) could not be isolated in a pure state, but its formation was demonstrated with the aid of the Wittig reaction. Under analogous conditions, the triphenylphosphonium ylide (LI) was obtained in the form of a pure crystalline substance:

$$(PhS)_3CLi + P(OMe)_3 \xrightarrow{-PhSLi} [(MeO)_3P{=}C(SPh)_2] \xrightarrow[-(MeO)_3P=O]{p\text{-}O_2NC_6H_4CHO}$$

(L)

$$\rightarrow p\text{-}O_2NC_6H_4CH{=}C(SPh)_2 \quad Ph_3P{=}C(SPh)_2 \quad .$$

(LI)

Compounds of tervalent phosphorus react with certain thioketones and their dimers to form the ylides (LII). The formation of a carbene in an intermediate stage, which then reacts with the second phosphite molecule, has been postulated. The ylides (LII) are stable liquids which can be vacuum-distilled[76]:

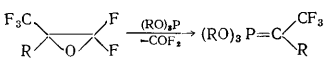
$$(CF_3)_2C{=}S + P(OR)_3 \xrightarrow[-(RO)_3P=S]{} [(CF_3)_2C{:}] \xrightarrow{P(OR)_3} (RO)_3P{=}C(CF_3)_2 \quad ;$$

(LII, a–c)

R = Me (a), Et (b), iso-Pr (c);

$$(CF_3)_2C\langle^{S}_{S}\rangle C(CF_3)_2 + P(OR)_3 \xrightarrow{(RO)_3PS} (LII) \quad .$$

It has been shown recently that the epoxy-derivatives of perfluorinated alkenes give rise to ylides on interaction with trialkyl phosphites[77]:



R = CF_3, CO_2R'

The amides of tervalent phosphorus acids react with *C*-ethoxycarbonyl- and *C*-acetyl-*N*-arylnitrile imines to form stable azomethylenephosphonium ylides (LIII)[78]:

$$(C_5H_{10}N)_2PR + R'{-}C{=}NNHPh \xrightarrow[-Et_3N\cdot HCl]{Et_3N} (C_5H_{10}N)_2P{=}C{-}N{=}N{-}Ph \quad ;$$

Cl R R′

(LIII)

R = $C_5H_{10}N$, Ph; R′ = CO_2Et, C (O) CH_3 .

3. The Synthesis of Ylides from Phosphonium Salts

The simplest method of synthesis of phosphorus ylides is the "salt method", which is widely used, particularly in the preparation of dialkylaminophosphonium ylides.

The phosphonium salts (LIV) are dehydrobrominated by sodium amide to form the ylides (LV) containing the unsubstituted methylene group; they are colourless, comparatively stable liquids which can be vacuum-distilled[79]. The benzylides (LVI) have been obtained by treating a phosphonium salt with butyl-lithium or sodium ethoxide[80,81]:

$$(Me_2N)_n(Me)_{4-n}\overset{+}{P}Br^- \xrightarrow[-NaBr]{NaNH_2/NH_3} (Me_2N)_n(Me)_{3-n}P{=}CH_2 \quad ;$$

(LIV) (LV)

$$(R_2N)_3\overset{+}{P}CH_2PhHal^- \xrightarrow[(-HHal)]{BuLi;EtONa} (R_2N)_3P{=}CHPh \quad ;$$

(LVI)

R = Me, Et; $n = 1-3$.

Stable ylides containing alkoxycarbonyl or diethylaminocarbonyl groups at the ylide carbon atom and primary or secondary amino-groups at the phosphorus atom have been obtained by treating the corresponding phosphonium salt with an aqueous solution of alkali, sodium ethoxide, or potassium t-butoxide[80–82].

The dehalogenation of trihalogenomethylphosphonium salts by triphenylphosphine or phosphorous acid tris(*N*,*N*-dimethylamide) constitutes a preparative method for the synthesis of dialkylaminophosphonium ylides containing a dihalogenomethylene group[83–85]:

$$(Me_2N)_3\overset{+}{P}CHal_3Hal^- \xrightarrow[-R_3PHal_2]{R_3P} [(Me_2N)_3P{=}CHal_2] \xrightarrow{R'_2C=O} R'_2C{=}CHal_2 \quad ;$$

R = Me_2N, Ph; Hal = Cl, Br, F .

Ylides are usually obtained, without the isolation of the phosphonium salts, by treating the phosphorous acid tris(*N*,*N*-dimethylamide) with carbon tetrahalide. This results in the formation of extremely reactive ylides, which are readily converted into ketones and olefins[86–88]:

$$2(Me_2N)_3P + BrCCl_3 \xrightarrow[-20^\circ \div -10^\circ]{} [(Me_2N)_3P{=}CCl_2] + (Me_2N)_3PClBr \quad .$$

Carbodiphosphorane (LVIII) has been obtained by treating the ylide (LVII) with phosphorous acid triamide[89]:

$$Ph_3P{=}C(Cl)(Cl){-}\overset{+}{P}Ph_2Cl^- \xrightarrow[-(Me_2N)_3PCl_2]{P(NMe_2)_3} Ph_3P{=}C(Cl){=}PPh_2$$
(LVII) (LVIII)

The "salt method" is hardly used for the synthesis of ylides with alkoxy-groups at the phosphorus atom in view of the instability of the alkoxyphosphonium salts.

A rare example of this kind has been described recently[90]. The formation of the ylides (LIX) proved to be possible as a result of the unique stability of vinyloxyphosphonium salts:

$$(R_2N)_2POR + BrCH_2CO_2Et \rightarrow (R_2N)_2\overset{+}{P}(OR')CH_2CO_2EtBr^- \xrightarrow[-NaBr]{NaH} \rightarrow (R_2N_2)P(OR')=CHCO_2Et$$
(LIX)

R = Me, Et; R′ =  .

The ylide (LXI) with the ethoxy-group at the phosphorus atom was detected among other products after the reaction of ethyl di-t-butylphosphinite with chloroacetonitrile. It has been suggested that the intermediate phosphonium compound (LX) is dehydrochlorinated by the phosphinite in the reaction. The Arbuzov dealkylation of the phosphonium salt (LX) takes place simultaneously[91]:

$$(t\text{-}Bu)_2POEt + ClCH_2CN \rightarrow (t\text{-}Bu)_2\overset{+}{P}(OEt)CH_2CNCl^- \rightarrow$$

$$\rightarrow \begin{cases} \xrightarrow{(t\text{-}Bu)_2POEt} (t\text{-}Bu)_2P(OEt){=}CHCN + (t\text{-}Bu)_2P(O)Cl \\ \text{(LXI)} \\ \xrightarrow{-(EtCl)} (t\text{-}Bu)_2P(O)CH_2CN \end{cases}$$

Polychlorophosphoranes react readily with bis(arenesulphonyl)methanes in the presence of triethylamine. The phosphonium salt (LXII) formed initially is dehydrochlorinated by triethylamine and is converted into the *P*-chloroylide (LXIII) with a high yield[92]. The reaction is preparatively very simple and makes it possible to obtain ylides with both one and two chlorine atoms at the phosphorus atom:

$$Ph_nPCl_{5-n} + CH_2(SO_2C_6H_4X\text{-}p)_2 \xrightarrow[-Et_3N\cdot HCl]{Et_3N} Ph_n\overset{+}{P}(Cl_{4-n}) - CH(SO_2C_6H_4X\text{-}p)_2Cl^-$$
(LXII)

$$\xrightarrow[-Et_3N\cdot HCl]{Et_3N} Ph_nP(Cl_{3-n}){=}C(SO_2C_6H_4X\text{-}p)_2$$
(LXIII)

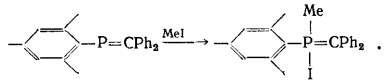
$n = 1,2$; X = H, Cl, Me, OMe .

4. The Conversion of Phosphorus Ylides of one Type into Phosphorus Ylides of Another Type

The conversion of ylides of one type into those of another provides extensive possibilities for the synthesis of *P*-hetero-substituted ylides. Thus *P*-halogeno-ylides readily exchange their mobile halogen atom for different groups in their reactions with nucleophiles, which makes it possible to introduce virtually any substituents at the phosphorus atom[14]. The hydrogen atoms at the ylide carbon atom are also readily substituted by other groups on interaction with chlorine-containing electrophiles[28,79]. The oxidative ylidation of tervalent phosphorus CH acids can be regarded to some extent as conversion of ylides of one kind into those of another. The CH acids are regarded as tautomeric forms of PH ylides[26,27]:

$$\left.\begin{array}{l} R_2P(Hal){=}CR'_2 \xrightarrow{X-H} \\ R_2P(X){=}CHR' \xrightarrow{R'-Cl} \\ R_2P{-}CHR'_2 \rightleftarrows R_2P(H){=}CR'_2 \xrightarrow[-H^+]{[X]} \end{array}\right\} \rightarrow R_2P(X){=}CR'_2 .$$

The synthesis of *P*-hetero-substituted ylides of one type into those of another type is discussed below in the section devoted to the properties of these compounds. The synthesis of *P*-hetero-substituted ylides from tervalent phosphorus compounds with a P=C bond is extremely interesting, although this method has been hardly developed further. A single example of the conversion of the acyclic phosphene (LXIV) into the ylide (LXV) with an iodine atom at the phosphorus atom is known[93]:



(LXIV) (LXV)

III. PROPERTIES

The properties of *P*-hetero-substituted phosphorus ylides are quite varied. The heteroatoms at the phosphorus atom of the P=C group alter the positive charge on the phosphonium cation and influence the nucleophilic properties of the ylides. In many instances, as a consequence of their mobility, the heteroatoms alter significantly the behaviour of ylides in chemical reactions. *P*-Hetero-substituted ylides therefore acquire properties which are lacking in triphenylphosphonium ylides. *P*-Hetero-substituted ylides are very reactive, are involved in many interesting reactions, and are valuable starting materials for the synthesis of many organic compounds.

1. Physical and Physicochemical Properties

In a pure state, the *P*-hetero-substituted phosphorus ylides are liquid or crystalline substances. Their stabilities differ greatly. Ylides having electron-accepting groups at the α-carbon atom capable of delocalising the negative charge of the carbanion are particularly stable. For example, the ylides (LXIII) with arenesulphonyl groups can be stored indefinitely and withstand heating to 200 °C.[14,21] However, unstable ylides, which exist only in solutions, are encountered. The "unstabilised" ylides, containing an unsubstituted methylene or alkylidene group, are oxidised very readily and hydrolysed in air[28,79,81].

P-Hetero-substituted phosphorus ylides have been investigated by various spectroscopic methods. The P=C group vibration frequencies have been observed in the infrared spectra of *P*-hetero-substituted ylides in the range 1000–1080 cm^{-1}.[18,28] A characteristic feature of ylides stabilised by carbonyl groups is the bathochromic shift of the absorption bands of these groups as a consequence of the conjugation with the negative charge of the ylide carbon atom[14,15,28,94,95]. The $\nu_S(SO_2)$ and $\nu_{as}(SO_2)$ absorption bands also undergo a bathochromic shift of approximately 70–80 cm^{-1} under the influence of the negative charge of the ylide carbon atom[14,21].

The ^{13}C and ^{31}P NMR spectra of *P*-hetero-substituted phosphorus ylides agree with their dipolar structure. The chemical shifts of the ^{31}P signals (Table 1) are located in a

weak field in direct proximity to the values of δp characterising the phosphonium cation $R_3\overset{+}{P}$ in phosphonium salts[28, 95,96]. On the other hand, the chemical shifts of the ^{13}C signals (relative to tetramethylsilane) are observed in a strong field in the region characteristic of the corresponding carbanions.

Table 1. The chemical shifts of the ^{31}P signals in the NMR spectra of *P*-hetero-substituted phosphorus ylides $RR'P(X)=CR''_2$.

X	R	R′	δp, p.p.m.	Refs.
H	Alk	Alk	20—40	[18, 25]
OH	Ph	Ph	47—50	[97, 98]
AlkO	AlkO	AlkO	50—57	[14, 65]
AlkO	Alk	Alk	82—92	[14, 37, 91]
AlkO	Ph	Ph	50—55	[65, 97, 98]
AlkNH	AlkO	AlkO	50—55	[14, 99]
AlkNH	AlkO	AlkO	40—45	[14, 99]
Alk_2N	AlkO	AlkO	55—60	[14]
Alk_2N	Alk	Alk	60	[22]
Alk_2N	Alk_2N	Alk_2N	59—65	[70, 100]
Me_3Si	iso-Pr	iso-Pr	37	[25, 46]
Alk_3P	Alk	Alk	14—30	[37, 46, 49]
Alk_3P	Ph	Ph	40	[49—51]
Cl	Me	Me	60	[37]
Cl	Alk	Alk	90—117	[27, 28, 101]
Cl	Alk_2N	Alk	95—105	[28]
Cl	Alk_2N	Alk_2N	60—70	[30, 38]
Cl	Ph	Ph	55—60	[38, 97, 98]
Br	t-Bu	t-Bu	100—126	[25, 26, 28]

Table 2. The tautomeric composition of dialkylbis(methoxycarbonyl)methylphosphines (in chloroform at 20 °C)[18,96].

R	R′	A, %	B, %
t-Bu	iso-Pr	39	61
t-Bu	s-Bu	35	65
t-Bu	Me_3SiCH_2	10	90
t-Bu	iso-Bu	67	33
t-Bu	n-Bu	65	35
n-Bu	n-Bu	85	15
iso-Bu	iso-Pr	70	30
t-Bu	Me_2N	100	0
t-Bu	Et_2N	100	0

2. Ylides with a P—H Bond

Alkylphosphines containing an α-hydrogen atom can be regarded as carbon analogues of tervalent phosphorus OH acids. Almost all the known OH acids of this kind exist in the tetracoordinate prototropic P(O)H form[102], which can be explained by the high energy of formation of the P=O bond ($E_{P=O}$ = 140 kcal mol^{-1}). On the other hand, the majority of alkylphosphines exist in the tricoordinate CH form owing to the inadequate thermodynamic stability of the PH ylide form. The ylide form can be stabilised by introducing two alkoxycarbonyl groups at the α-carbon atom as a consequence of the effective delocalisation of the negative charge of the ylide carbon atom over the conjugated bond system[18,25].

Thus dialkylbis(methoxycarbonyl)methylphosphines isomerise completely or partly to ylides with a P—H bond (Table 2):

$$\underset{(A)}{RR'P{-}CH(CO_2Me)_2} \rightleftarrows \underset{(B)}{RR'P(H){=}C(CO_2Me)_2}\ .$$

Dialkylbis(methoxycarbonyl)methylphosphines are stable substances which can be vacuum-distilled without decomposition and can be stored satisfactorily at the usual temperature. Some of them [compounds (LXVI)—(LXVIII)] have been obtained in the pure crystalline PH ylide form (B)[18,25]:

$$\text{t-Bu(R)}P{=}C(CO_2Me)_2 \quad (\text{H})$$

R= iso-Pr (LXVI), t-Bu (LXVII), Me_3SiCH_2 (LXVIII)

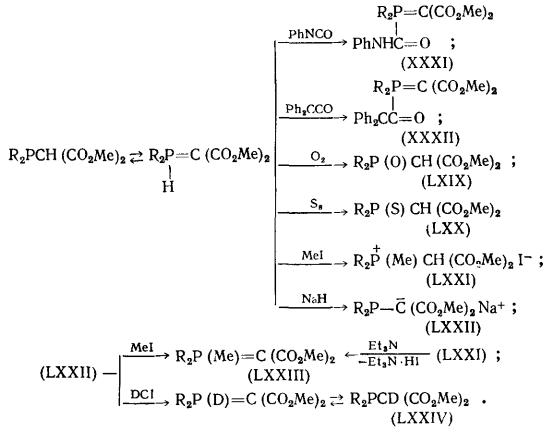
Dialkylbis(methoxycarbonyl)methylphosphines exist in solution as tautomeric mixtures of the prototropic forms (A) and (B), which has been demonstrated by spectroscopic studies. The signals of the protons of the CH and PH groups have been detected in the ^1H NMR spectra of these compounds. The signal of the proton of the PH group is split owing to the interaction with the phosphorus atom ($^1J_{PH}$ = 440 Hz). The signals of the CH form (singlet) and the PH form (doublet) with a coupling constant of 440 Hz are present in the ^{31}P NMR spectra. When the spin—spin coupling of the phosphorus nuclei with the protons is suppressed, the doublet is converted into a singlet, which confirms unambiguously the presence of a bond between the phosphorus atom and the hydrogen atom.

The tautomeric equilibrium (A) ⇌ (B) depends on the temperature and on the nature of the solvents and substituents at the phosphorus atom. The study of the thermodynamics of the tautomeric equilibrium led to the conclusion that the ylide form has a higher formation energy than the phosphine form [$\Delta H = -2.4 \pm 0.2$ kcal mol^{-1}, $\Delta S = -7.4 \pm 0.7$ e.u. for compound (LXVI) in chloroform][18].

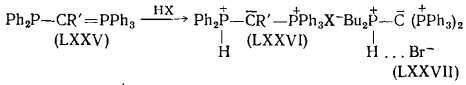
The results presented in Table 2 show that bulky and branched alkyl substituents stabilise the PH ylide form and displace the tautomeric equilibrium towards it. Examination of the Stuart—Briegleb models has led to the conclusion that bulky alkyl substituents are more favourable for the tetracoordinate PH ylide form, since the latter is sterically less hindered than the tricoordinate CH form[18,25]. It is quite evident that the influence of branched alkyl substituents on the position of the tautomeric equilibrium is associated with steric and not polar effects. According to modern ideas, alkyl groups (Me, Et, iso-Pr, t-Bu, etc.) are electrically neutral and differ only by their steric characteristics[103].

The chemical properties of ylides with a P—H bond are similar to those of other tervalent phosphorus CH acids as a consequence of the involvement of the tricoordinate form (A) in the tautomeric equilibrium[18,25,96]. They are oxidised, combine with sulphur, and are alkylated by alkyl halides with formation of phosphine oxides (LXIX), phosphine sulphides (LXX), and phosphonium salts (LXXI). At the same time dialkylbis(methoxycarbonyl)methylphosphines readily enter into oxidative ylidation reactions. The interaction with phenyl isocyanate and diphenylketen yields the *P*-substituted ylides (XXXI) and (XXXII). On interaction with sodium hydride, PH ylides are converted into the α-phosphinocarbanions (LXXII). The reaction of α-phosphinocarbanions with methyl iodide takes place at the phosphorus atom with formation of the ylide (LXXIII) (the "ylide variant" of the Michaelis—Becker reaction), while their reaction with deuterium chloride results in the formation of deuterated dialkylbis(methoxycarbonyl)methylphosphines (LXXIV), which consist of a tautomeric mixture of the CD and PD forms[18,25,96] (Scheme 8).

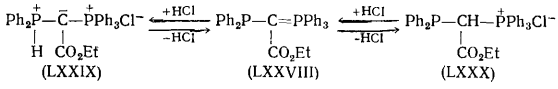
Scheme 8



The phosphinophosphonium ylides (LXXV), containing electron-accepting substituents at the α-carbon atom, are protonated by strong acids at the phosphorus atom[104-107]. X-Ray diffraction analysis of compound (LXXVII) not only confirmed the presence of the P–H bond but also showed that the proton retains to some extent its bond with the halogen[108-110]:



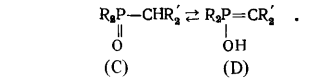
Detailed studies of the protonation of phosphinophosphonium ylides established that compound (LXXVIII) reacts with an excess of hydrogen chloride in methylene chloride at −80 °C with formation of the PH and CH forms of compounds (LXXIX) and (LXXX), between which equilibrium is established[109-112]:



These forms are unstable and exist only in solution at a low temperature, decomposing fully with cleavage of the P–C bond at −20 °C. The position of the tautomeric equilibrium (LXXIX) ⇌ (LXXX) depends on the temperature and the polarity of the solvent. The ratio of the CH and PH forms also depends on the concentration of hydrogen chloride, whence it follows that the interconversion of the forms occurs as a result of the reversible addition of HCl to and its elimination from the phosphinophosphonium ylide (LXXVIII). The involvement of hydrogen chloride in the prototropic equilibrium constitutes a significant difference between the tautomerism of the protonated phosphinophosphonium ylides and the phosphine–PH ylide tautomerism of dialkylbis(methoxycarbonyl)methylphosphines. The nature of the anion is also very important in this instance. For example, when hydrogen chloride is replaced by trifluoroacetic acid, protonation takes place only at the phosphorus atom of the phosphinophosphonium ylide (LXXVIII), the PH form is produced, and the CH form disappears[110].

3. Ylides with a P–O Bond

Ylides with an OH group are tautomeric forms of alkylphosphine oxides:



The majority of alkylphosphine oxides exist in the CH form (C) as a consequence of the high basicity of the ylide carbon atom. The tautomeric equilibrium (C) ⇌ (D) is displaced towards the OH form (D) in the case of diphenylbis(arenesulphonyl)methylphosphine oxides (LXXXI), which contain substituents with strong electron-accepting properties[97,98,113].

In the crystalline state these phosphine oxides exist in the pure CH phosphine oxide form while in solutions they consist of a tautomeric mixture of the OH ylide and the CH phosphine oxide forms (Table 3)[97,98]:

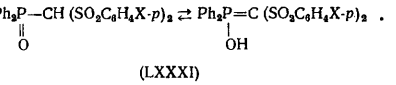
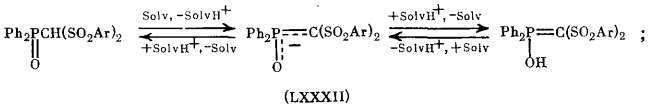


Table 3. The tautomeric composition of diphenylbis(benzenesulphonyl)methylphosphine oxides (LXXXI) (tetrahydrofuran at 25 °C)[96-98].

X	C, %	D, %
Cl	45	55
H	80	20
Me	90	10
MeO	96	4

The OH and CH forms can be readily detected by spectroscopic methods (infrared, ^{1}H, NMR, and ^{13}P NMR spectroscopy). The study of the process with the aid of dynamic NMR indicates a high rate of the interconversion of the tautomeric forms (the temperature at which the ^{31}P signals merge for the system in chlorobenzene is 100 °C for an external magnetic field strength of 81 MHz)[96]. The tautomeric equilibrium (C) ⇌ (D) is mobile and depends on the temperature and nature of the solvents and the substituents. The content of the ylide form increases with decrease of temperature and this form is evidently energetically more favourable. Electron-accepting substituents in the *para*-positions in the arenesulphonyl groups increase the content of the ylide form, because they enhance the delocalisation of the negative charge of the ylide carbon atom.

The study of the prototropic equilibrium in aqueous alcoholic solutions showed that a two-stage mechanism of the tautomeric transformation, with formation of the common anion (LXXXII), operates in these solvents, which have a high dissociating capacity:

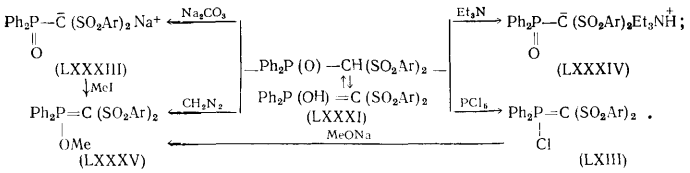


(LXXXII)

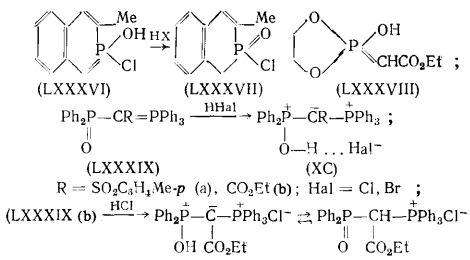
Solv = solvent.

Diphenylbis(arenesulphonyl)methylphosphine oxides have interesting properties, resembling those of the OH acids of tetracoordinate phosphorus. These extremely stable compounds are comparatively strong acids (pK_a = 3.55–3.68 in 50% alcohol). They readily dissolve in an aqueous solution of sodium carbonate, from which they can be recovered quantitatively on acidifying the solution; they react with triethylamine to form the stable triethylammonium salts (LXXXIV). The reaction of phosphine oxide with diazomethane leads to the formation of an *O*-methylated product—the ylide (LXXXV). The formation of the product (LXXXV) substituted at the oxygen atom is accompanied by the interaction of the sodium salt (LXXXIII) with methyl iodide. The reaction of compounds (LXXXI) with phosphorus pentachloride gives rise to the *P*-chloro-derivatives (LXIII) (Scheme 9).

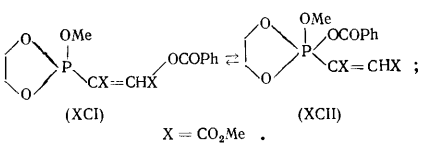
Scheme 9



The phosphine oxide–ylide tautomerism was first discovered and investigated in relation to diphenylbis(arenesulphonyl)-methylphosphine oxide[97,98,113]. Subsequently other OH ylides were also described. The cyclic *P*-hydroxy-λ^5-phosphorin (LXXXVI), which is stable in the crystalline state and which rearranges irreversibly to the more stable isomer (LXXXVII) with a P=O group in the presence of proton-donating reagents, has been synthesised[114]. It has been established[115] that the five-membered dioxaphospholan ring effectively stabilises the OH ylide form (LXXXVIII). The phosphine oxide phosphonium ylides (LXXXIX) are protonated by strong acids at the oxygen atom of the P=O group[106,116,117]. X-Ray diffraction analysis of compound (XCa) showed that the OH form is stabilised by a strong O–H...Br bond and that the H...Br distance is 2.24 Å, which is much less than the sum of the van der Waals radii (3.11 Å)[116]. The hydrochloride salt of the ylide (LXXXIXb) exists in the crystalline state in the OH form, while in solutions it is a mixture of the CH and OH forms in proportions of 1:1.8 (Mastryukova et al.[117]):



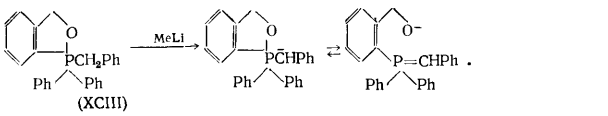
The tautomeric equilibrium between the ylide and phosphorane structures (XCI) ⇌ (XCII), which has been investigated by ^{31}P NMR,[71] is of considerable interest:



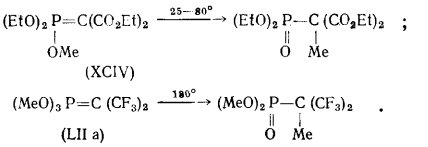
The position of the tautomeric equilibrium (XCI) ⇌ (XCII) depends on the nature of the solvent in the following way:

Solvent	(XCI)	(XCII)
CCl_4	18%	82%
CH_2Cl_2	37%	63%

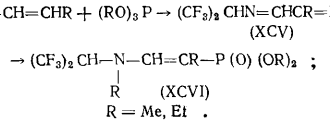
Another example of the ylide–phosphorane tautomeric equilibrium was found in the metallation of the phosphorane (XCIII) with a benzyl group[118]:



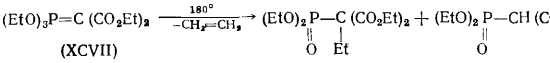
The ylides containing alkoxy-groups at the phosphorus atom are readily dealkylated and converted into phosphonates. Thus the alkoxyphosphonium ylides (LIIa) and (XCIV) rearrange on heating to phosphonates with migration of the alkyl group to the ylide carbon atom (the ylide version of the Pishchimuka reaction)[15,77]:



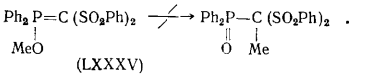
The ylides (XCV) are converted into the phosphonates (XCVI) already in their preparation reaction[119]:



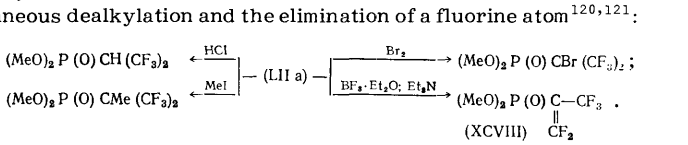
The ylides (XCVII) with ethoxy- or isopropoxy-groups at the phosphorus atom are more stable than the corresponding ylides (XCIV) with methoxy-groups. They are converted into phosphonates only on heating to 150–180 °C and the rearrangement is complicated by the elimination of an alkene[14]:



Electron-accepting substituents, which reduce the nucleophilicity of the ylide carbon atom, hinder the rearrangement. The ylide (LXXXV), containing the powerful electron-accepting benzenesulphonyl groups at the α-carbon atom, is stable and does not change on heating to 200 °C[14]:



Alkoxyphosphonium ylides are dealkylated on interaction with hydrogen chloride, bromine, and alkyl halides[14,16,76]. When the ylide (LIIa) was treated with boron trifluoride etherate, the "phosphorus analogue" of the perfluoromethacrylic ester (XCVIII) was obtained as a result of the simultaneous dealkylation and the elimination of a fluorine atom[120,121]:



Hydrolysis of ylides containing alkoxy-groups at the phosphorus atom proceeds both with elimination of one of the alkyl groups and with cleavage of the P=C bond[63,120].

Alkoxyphosphonium ylides normally undergo the Wittig reaction and their reactivities are probably comparable to those of triphenylphosphonium ylides. However, there are

very few data on this question[95]:

$$(\text{iso-PrO})_2(Et_2N)P{=}CHCO_2Et \xrightarrow{ArCH} ArCH{=}CHCO_2Et + (\text{iso-PrO})(Et_2N)PO \ ;$$
$$Ar = Ph,\ p\text{-}O_2NC_6H_4 \ .$$

4. Ylides with a P–N Bond

Ylides with dialkylamino-groups at the phosphorus atom are available and are very reactive, which aroused much interest in these compounds by investigators. The reactivity and stability of dialkylaminophosphonium ylides depend on the substituents at the ylide carbon atom. Dialkylaminophosphonium ylides stabilised by electron-accepting substituents are indeed very stable. The azomethylenephosphonium ylide (LIII) hydrolyses only after prolonged refluxing in aqueous alcoholic solution. This involves the cleavage of the P–N and not the P=C bond and the amine formed converts the ethoxycarbonyl group into a carbamoyl group[78]:

$$(C_5H_{10}N)_3P{=}\underset{\underset{CO_2Et}{|}}{C}{-}N{=}NPh + H_2O \rightarrow (C_5H_{10}N)_2P{-}\underset{\underset{O}{\|}}{\underset{|}{C}}{=}NNHPh + C_5H_{10}NH \rightarrow$$
(LIII)
$$\rightarrow (C_5H_{10}N)_2P{-}\underset{\underset{O}{\|}}{\underset{|}{C}}{=}N{-}NHPh + EtOH \ .$$
$$C(O)NC_5H_{10}$$

The ylide (XCIX) does not change even after heating at 140 °C for 4 h in 50% KOH, but it is reactive in the Wittig reaction[81]:

$$(Et_2N)_3P{=}CHCONEt_2 \xrightarrow{p\text{-}O_2NC_6H_4CHO} p\text{-}O_2NC_6H_4CH{=}CHCONEt_2 \ .$$

On the other hand, the unstabilised dialkylaminophosphonium ylides or the same ylides stabilised by weak electron-accepting substituents hydrolyse very readily and are oxidised by atmospheric oxygen. The ease of the reaction of the benzylide (LVIa) with atmospheric oxygen, in which it is converted into stilbene in a high yield, is so great that it actually interferes with its isolation in a pure form[81]:

$$[(Et_2N)_3P{=}CHPh] \text{ (LVI a)} \begin{cases} \xrightarrow{p\text{-}O_2NC_6H_4CHO} p\text{-}O_2NC_6H_4CH{=}CHPh \ ; \\ \xrightarrow{O_2} PhCH{=}CHPh + (Et_2N)_3PO \ . \end{cases}$$

The ylide (LV) having a methylene group reacts with chlorine-containing electrophiles, being converted in high yields into new types of dialkylaminophosphonium ylides (C) and (CI). The reaction is carried out with a reactant ratio of 2:1, since one ylide molecule is consumed in the dehydrochlorination of the intermediate phosphonium salt[79]:

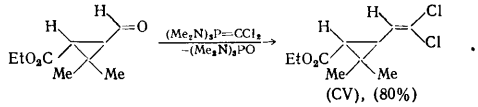
$$(Me_2N)_3P{=}CH_2 \begin{cases} \xrightarrow{PCl_3} \underset{-(Me_2N)_2(Me)\overset{+}{P}Cl^-}{} [(Me_2N)_3P{=}CH]_3P \ ; \\ \qquad\qquad (C) \\ \xrightarrow[-(Me_2N)_2(Me)P^+Cl^-]{R_2PCl} (Me_2N)_3{=}CHPR_2 \ ; \\ \qquad\qquad (CI) \end{cases}$$
$$R = Me, Et, OEt, NMe_2$$

Diazonium salts couple directly with dialkylaminophosphonium ylides. Phenyldiazonium fluoroborate reacts with the ylide (CII) to form the phosphonium salt (CIII), which can be converted into a new ylide (CIV) by treatment with sodium ethoxide[78]:

$$\underset{(CII)}{(C_5H_{10}N)_2P(Ph){=}CHCO_2Et} \xrightarrow{PhN_2^+BF_4^-} \underset{(CIII)}{(C_5H_{10}N)_2\overset{+}{P}(Ph)CHN{=}NPhBF_4^-} \rightarrow$$
$$\xrightarrow{C_2H_5ONa} \underset{(CIV)}{(C_5H_{10}N)_2P(Ph){=}C(CO_2Et){-}N{=}NPh} \ .$$

As reactants in the Wittig reaction, dialkylaminophosphonium ylides are more reactive than triphenylphosphonium ylides. The electron-donating dialkylamino-groups weaken the electron-accepting properties of the phosphonium group, as a result of which the negative charge on the ylide carbon atom increases. Under the influence of strongly nucleophilic dialkylaminophosphonium ylides, even inactive ketones are converted into olefins and in the reactions with reactive carbonyl compounds there is a significant increase in the yields of olefins. The use of dialkylaminophosphonium ylides frequently yields satisfactory results in those cases where the triphenylphosphonium ylides are unsuitable. The compounds $(Me_2N)_3P{=}CF_2$[83] and $(Me_2N)_3P{=}CCl_2$,[86] generated *in situ* from $(Me_2N)_3P$ and carbon tetrahalides, are good sources of the trifluoromethylene and dichloromethylene groups for reactions with inactive ketones. The conversion of the ethyl ester of *cis,trans*-caronaldehydic acid into an olefin with the aid of $(Me_2N)_3P{=}CCl_2$ made it possible to obtain a high yield of a chrysanthemic acid derivative (CV)—an analogue of the natural insecticide permethrin (NRDC 143)[87] (Scheme 10).

Scheme 10

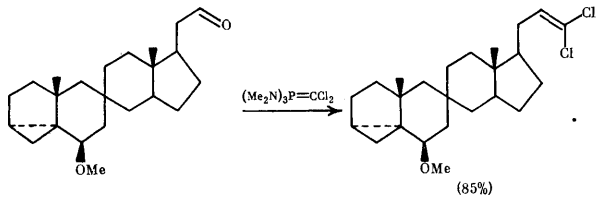


(CV), (80%)

Under analogous conditions, $Ph_3P{=}CCl_2$ gives a low yield of a highly contaminated compound (CV)[87].

It has been noted that the use of dimethylaminophosphonium ylides increases the stereospecificity of the Wittig reaction. It is significant, especially in studies with natural products, that, on treatment with these ylides, the optically active centres in the molecule are not involved and the compounds are not racemised[12,83] (Scheme 11).

Scheme 11



(85%)

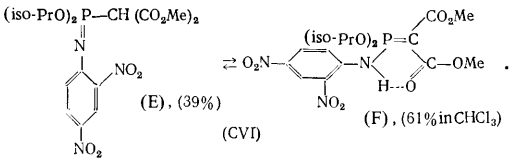
The ylides (F) containing NHR groups at the phosphorus atom are in a tautomeric equilibrium with the phosphazo-compound (E)[57,99]:

$$\underset{\underset{NR'''}{\|}}{R_2P{-}CHR'CO_2R''} \rightleftarrows \underset{\underset{NHR'''}{|}}{R_2P{=}CR'CO_2R''} \ .$$
(E) (F)

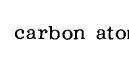
The phosphazo-ylide tautomerism (E) ⇌ (F) obeys the rules of the acid–base prototropic equilibria and shifts towards the form which is a weaker acid under the given conditions. The introduction of more electron-accepting substituents at the nitrogen atom of the $-N-\underset{|}{P}-C\diagup\diagdown$ triad increases the content of the phosphazo-form (E) and, conversely, electron-accepting substituents at the carbon atom favour the formation of the ylide form (F)[57,99].

Depending on the substituents at the nitrogen and carbon atoms, the phosphazo–ylide equilibrium (E) ⇌ (F) can be displaced towards the preferential formation of one of the tautomeric forms or the forms (E) and (F) are present in comparable amounts (Scheme 12).

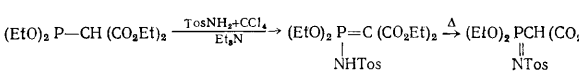
Scheme 12



(CVI)

Thus compound (CVI) exists in the ylide form in the crystalline state, while in solutions it is present as a mixture of two tautomers. The ratio of the forms (E) and (F) depends on the temperature and the solvent. The study of the thermodynamics of the phosphazo–ylide tautomerism showed that the tautomeric equilibrium (E) ⇌ (F) is influenced by two opposed factors. On the one hand, the conversion of the phosphazo-form into the ylide form with its conjugation chain results in an energy gain $\Delta H = -6 \pm 0.6$ kcal mol^{-1}. On the other hand, this entails an increase of the rigidity of the molecule (since the ylide form is fixed by a strong intramolecular hydrogen bond) and the entropy diminishes ($\Delta S = -21 \pm 2$ e.u.). According to the equation $\Delta G = \Delta H - T\Delta S$, the equality of ΔH and $T\Delta S$ determines the equilibrium position. The presence of a strong intramolecular hydrogen bond has been confirmed by infrared and ^{1}H NMR spectra[57, 99, 124]. The migration of the proton between the nitrogen and carbon atoms in the  triad takes place readily and the interconversion of the tautomers (E) ⇌ (F) takes place comparatively rapidly.

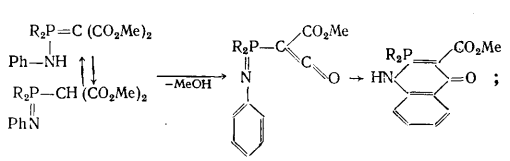
It has been reported[125] that the ylide with the tosylamide group at the phosphorus atom rearranges to the phosphazo-compound during the vacuum distillation of the reaction mixture formed in accordance with the equation



The conclusion that an ylide is formed and undergoes a rearrangement was reached on the basis of the presence in the infrared spectrum of the reaction mixture of an absorption band at 1650 cm^{-1}, which disappears on heating. The energy barrier to the prototropic rearrangement is unusually high, bearing in mind the high mobility of the NH proton of the tosylamide group, and apparently requires additional study and confirmation.

Anilinophosphonium bis(alkoxycarbonyl)methylides, which are stable under the usual conditions, evolve alcohol on heating to 150–180 °C and are converted into 2-phospha-4-quinolones (CVIII)[124]. The elimination of the alcohol results in the formation of the keten (CVII), whose cyclisation at the *ortho*-position of the benzene ring gives rise to 2-phospha-4-quinolone (Scheme 13).

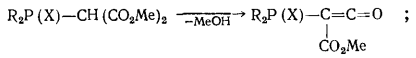
Scheme 13



(CVII) (CVIII)

R = EtO, iso-PrO, iso-Pr .

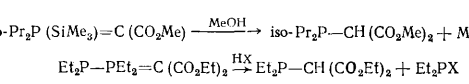
Under analogous conditions, the thermolysis of dialkylbis(methoxycarbonyl)methylphosphine oxides and phosphine sulphides leads to the formation of stable ketens[25]:



R = iso-Pr, t-Bu; X = O, S .

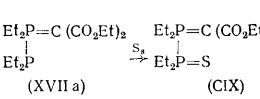
5. Ylides with P–Si, P–S, and P–P Bonds

The ylides containing the P–Si, P–S, and P–P bonds are stable liquids, capable of being vacuum-distilled, or crystalline substances. The P–P and P–Si ylides are readily cleaved at the phosphorus–element bond by various proton-donating reagents:



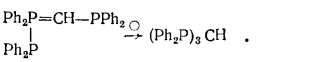
X = Cl, MeO, HO .

The P–P ylides are readily oxidised by atmospheric oxygen. The ylide (XVIIa) combines with sulphur via the tervalent phosphorus atom and is converted into the ylide (CIX) with the P(S)–P group; the P–P bond is then retained[14,48]:



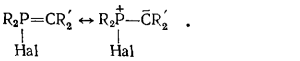
(XVII a) (CIX)

In certain cases, the P–P ylides rearrange to triphosphinomethanes as a result of the migration of the phosphino-group to the α-carbon atom[49]:



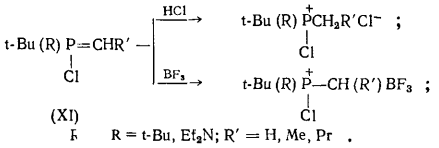
6. Ylides with Halogen Atoms at the Phosphorus Atom

P-Halogenoylides are promising reagents for organophosphorus synthesis. They are very reactive. The combination in one molecule of two active reaction centres (the nucleophilic centre consisting of the negatively charged carbon atom and the electrophilic centre consisting of the phosphonium carbanion to which the labile halogen atom is attached) is responsible for the wide variety and the specific features of the properties of these compounds:



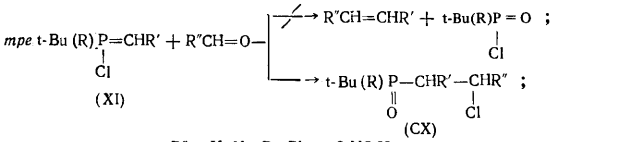
P-Halogenoylides react readily with both electrophiles and nucleophiles. Their reactivity in relation to electrophiles depends on the substituents at the carbanionic centre. The nucleophilicity and basicity of the *P*-halogenoylides containing powerful electron-accepting substituents R′ are low. Some of them (R′ = SO_2Ar) do not even give rise to stable phosphonium salts on interaction with hydrogen chloride. On the other hand, the "unstabilised" *P*-halogenoylides (XI, R′ = H or alkyl) are extremely reactive in relation to electrophiles. They combine with hydrogen chloride and boron trifluoride

via exothermic reactions and interact with carbonyl compounds, acid chlorides, etc.[27,28]:



(XI) R = t-Bu, Et_2N; R′ = H, Me, Pr .

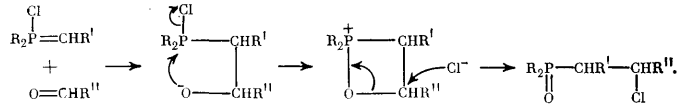
In contrast to triphenylphosphonium ylides, *P*-halogenoylides react with carbonyl compounds without the dissociation of the P=C bond, which results in the formation of organophosphorus products. *P*-Chloroylides do not form olefins on reaction with aldehydes, but give rise to β-chloroalkylphosphine oxides (CX)[101]. The reactions of *P*-chloroylides (XI) with aldehydes having different structures proceed at a low temperature and are accompanied by the evolution of heat. The yields of β-chloroalkylphosphine oxides (CX) are very high:



(XI) (CX)

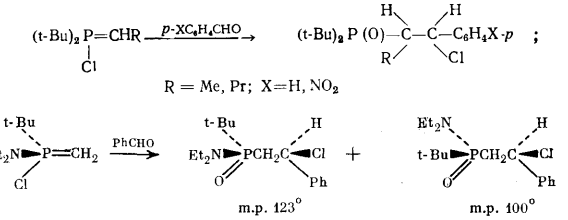
R″ = H, Me, Pr, Ph, *p*-$O_2NC_6H_4$.

The anomalous course of the reaction of *P*-chloroylides with aldehydes is due to the presence of the labile chlorine atom. As a consequence of the ability of the chlorine atom to ionise, an intermediate oxaphosphetanium salt (CXI) is formed. In contrast to the pentacoordinate intermediate compound in the Wittig reaction, this salt does not decompose into an olefin and a compound containing the P=O group, but is converted into a β-chloroalkylphosphine oxide as a result of the attack by Cl^- on the β-carbon atom via the mechanism of the Arbuzov rearrangement:



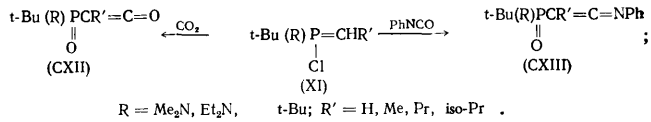
(CXI)

The reactions of *C*-alkyl-substituted *P*-chloroylides with aldehydes are stereoselective and lead to the formation of a single diastereoisomer of a β-chloroalkylphosphine oxide. However, the reactions of *P*-chloroylides having an asymmetrically substituted phosphorus atom are not distinguished by a high stereoselectivity and give rise to a mixture of diastereoisomers (in proportions of 1:2–2:3)[96,101]:



m.p. 123° m.p. 100°

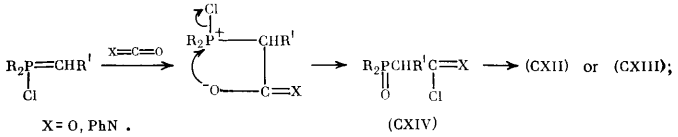
The *P*-chloroylides (XI) react with carbon dioxide and phenyl isocyanate to form phosphorylated ketones and *C*-phosphorus-containing keten imines (CXII) and (CXIII)[27]:



R = Me_2N, Et_2N, t-Bu; R′ = H, Me, Pr, iso-Pr .

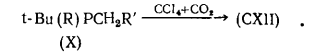
The reaction is carried out with an initial reactant ratio of 2:1, since one molecule of the ylide is consumed in the dehydrochlorination of the acid chloride (CXIV) formed at an intermediate stage (the reaction stops at the stage involving the formation of this acid chloride in the presence of a large excess of CO_2) (Scheme 14).

Scheme 14



X = O, PhN . (CXIV)

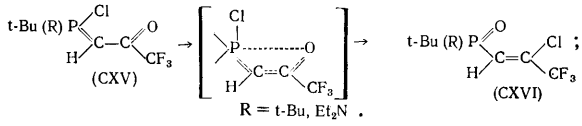
This method of synthesis of phosphorylated ketens and keten imines is preparatively fairly convenient. The initial *P*-chloroylides are formed from the tertiary phosphines (X) and CCl_4 and it is not obligatory to isolate them. The ketens (CXII) can be obtained directly from the tertiary phosphine (X) by treating it with CCl_4 and CO_2; the yields of the ketens are high:



(X)

The reactions of *P*-chloroylides containing a carbonyl group at the ylide carbon atom proceed via an analogous mechanism. The *P*-chloroylides (CXV), where there is a trifluoroacetyl group at the carbon atom, rearrange on heating to 120–150 °C to β-chlorovinylphosphine oxides (CXVI). The rearrangement takes place via a four-membered transition state, formed as a consequence of the intramolecular attack by the negatively charged oxygen of the C=O group on the positively charged phosphorus atom[126] (Scheme 15).

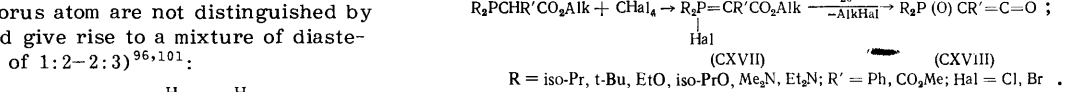
Scheme 15



(CXV) (CXVI)

R = t-Bu, Et_2N .

The *P*-halogenoylides (CXVII), containing an alkoxycarbonyl group, are converted into the phosphorylated ketens (CXVIII) even at room temperature and an alkyl halide is formed[25,127–129]:

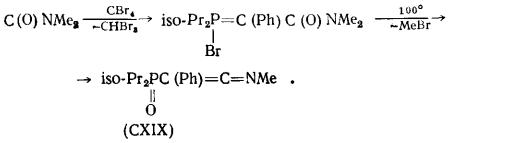


(CXVII) (CXVIII)

R = iso-Pr, t-Bu, EtO, iso-PrO, Me_2N, Et_2N; R′ = Ph, CO_2Me; Hal = Cl, Br .

The *P*-halogenylides (CXVII) are comparatively stable at 0 °C. They have been isolated in a pure state and characterised by the usual physical and chemical methods[14,25].

Diisopropyl-α-(*N*,*N*-dimethylcarbamoyl)benzylphosphine reacts with carbon tetrabromide to form a *C*-phosphorus-containing keten imine (CXIX) via the intermediate *P*-bromoylide[126]:



(CXIX)

The labile halogen atom attached to the $\overset{+}{P}$–C group in combination with the highly basic negatively charged ylide carbon atom determines the unusual "chlorinating" dehydrating

properties of *P*-chloroylides. Thus the reaction of the *P*-chloroylides (XI) with *N*-monosubstituted carboxylic acid amides results in the formation of imidoyl chlorides and phosphine oxides. The reactions take place in ether at a temperature below 0 °C and is accompanied by the evolution of heat[131]:

$$(XI) + PhC(O)NHR'' \rightarrow \begin{matrix} t\text{-Bu}(R)P(O)CH_2R' \\ + \\ PhC(Cl)=NR'' \end{matrix};$$

$$R = t\text{-Bu}, Et_2N;\ R = H, Pr;\ R'' = Ph, p\text{-}ClC_6H_4\ .$$

It has been suggested that the deprotonation of the amide by the ylide results in the formation of an ion pair containing the mesomeric anion $O-\bar{C}-NR'$. The attack by the phosphonium cation on the oxygen atom of this anion gives rise to a quasi-phosphonium salt, which decomposes into an imidoyl chloride and a phosphine oxide[131] via Scheme 16.

Scheme 16

$$PhC(O)NHR' + R_2P(Cl)=CH_2 \rightarrow R_2\overset{+}{P}(Cl)-CH_2 \rightarrow R_2\overset{+}{P}(Me)-O-C(Ph)=NR' \rightarrow$$
$$\rightarrow R_2P(O)Me + PhC(Cl)=NR'\ .$$

The primary amides of carboxylic acids are dehydrated by *P*-chloroylides (XI) and are converted into nitriles. Imidoyl chlorides are formed as intermediates and are dehydrochlorinated by the ylides to nitriles:

$$R''C(O)NH_2 \xrightarrow[-t\text{-}Bu(R)P(O)CH_2R']{(XI)} [R''CCl=NH] \xrightarrow[-t\text{-}Bu(R)(R'CH_2)PCl_2]{(XI)} R''C\equiv N\ .$$

The anilides of diphenylacetic and α-phosphorylated carboxylic acids react similarly with the *P*-chloroylides (XI) to form keten imines, while *N*,*N'*-disubstituted ureas are dehydrated by *P*-chloroylides to carbodiimides. The reaction of *P*-chloroylides (XI) with phosphaureas, providing a pathway to the synthesis of the heterocumulenes (CXX) with a dicoordinate phosphorus atom, are of special interest[96,131-133]:

$$R_2CHC(O)NHPh \xrightarrow{(XI)} R_2C=C=NPh\ ;$$

$$R_2 = Ph_2, \quad t\text{-}Bu_2P(O)C(Me)<\ ;$$

$$R-NHC(O)NH-Ph \xrightarrow{(XI)} R-N=C=N-Ph\ ;$$

$$R = Ph, \quad t\text{-Bu}\ ;$$

$$RPHC(O)NHBu\text{-}t \xrightarrow{(XI)} RP=C=NBu\text{-}t\ .$$

(CXX)

P-Halogenoylides serve as the starting materials for the synthesis of a wide variety of organophosphorus compounds containing P=C bonds, including those which are difficult to obtain in other ways. Thus bis(methylene)phosphoranes (CXXII), the first compounds of quinquevalent tricoordinate phosphorus with two P=C bonds, have been obtained with the aid of the *P*-chloroylide (CXXI)[134]:

$$R-P(Cl)-C(SiMe_3)_2 \xrightarrow[-LiCl,-Cl_2C(SiMe_3)_2]{LiCCl(SiMe_3)_2} R-P[C(SiMe_3)_2]_2\ ;$$

(CXXI) (CXXII)

$$R = C_6H_{11}, Ph, Me_2N\ .$$

In the reactions of *P*-chloroylides (XI) with chlorine-containing electrophiles (chlorotrimethylsilane, carboxylic acid chlorides, and tervalent phosphorus chlorides), the hydrogen atoms attached to the carbon atom of the P=C group are substituted and the new *P*-chloroylides (CXXIII)–(CXXVI), containing various substituents at the α-carbon atom, are formed[28] (Scheme 17).

Scheme 17

$$t\text{-Bu}(R)P(Cl)=CH_2 \xrightarrow{R'C(O)Cl} mpe\ t\text{-Bu}(R)P(Cl)=CHC(=O)R'\ ;$$
(CXXIII) ($R' = CCl_3, CF_3$)

$$\xrightarrow{Me_3SiCl} t\text{-Bu}(R)P(Cl)=CHSiMe_3\ ;$$
(CXXVI)

$$\xrightarrow{mpem\text{-}BuPCl_2} t\text{-Bu}(R)P(Cl)=CHP(Cl)Bu\text{-}t\ ;$$
(CXXV)

$$\xrightarrow[(R=Et_2N)]{(Me_2N_2)PCl,CCl_4} t\text{-Bu}\left(Et_2N\right)P(Cl)-CH=P(NMe_2)_2\ Cl^-\ ;$$
(CXXVI)

$$R = t\text{-Bu}, Et_2N\ .$$

The halogen atom at the phosphorus atom in *P*-halogenoylides is exchanged for different substituents on interaction with nucleophiles containing a mobile hydrogen atom. The *P*-halides stabilised by electron-accepting groups are converted with high yields into all possible types of *P*-substituted ylides on interaction with alkylamines, aniline, ammonia, lithium phosphides, alcohols, phenols, thiols, and lithium alkyls[14,16,20,21,35,37,130]. These reactions are preparatively very simple and lead to extensive prospects for the synthesis of ylides containing virtually any substituents at the phosphorus atom in the P=C group (Scheme 18).

Scheme 18

$$R_2P(Hal)=CR'_2 \xrightarrow{AlkOH+Et_3N} R_2P(OAlk)=CR'_2\ ;$$
$$\xrightarrow{PhCN} R_2P(OPh)=CR'_2\ ;$$
$$\xrightarrow{AlkSH+Et_3N} R_2P(SAlk)=CR'_2\ ;$$
$$\xrightarrow{R_2PLi} R_2P(R_2P)=CR'_2\ ;$$
$$\xrightarrow{NH_3} R_2P(NH_2)=CR'_2\ ;$$
$$\xrightarrow{AlkNH_2} R_2P(NHAlk)=CR'_2\ ;$$
$$\xrightarrow{Alk_2NH} R_2P(NAlk_2)=CR'_2\ ;$$
$$\xrightarrow{PhNH_2+Et_3N} R_2P(NHPh)=CR'_2\ ;$$

R = Alk, AlkO, Ph, Alk_2N; R' = CO_2R, SO_2Ph, $SiMe_3$, $SiCl_3$, Ph; Hal = Cl, Br.

On the other hand, the unstabilised *P*-halogenoylides (XI) are converted with high yields into the phosphonium salts (CXXVII)–(CXXX) on interaction with compounds containing a mobile hydrogen atom (alcohols, phenols, ketoenols, alkylamines, hydrazoic acid, etc.)[130]. The CH acidity of the phosphonium salts is low and they are not dehydrochlorinated under the reaction conditions and are not converted into ylides. The reaction therefore stops at the stage involving the formation of addition products and not substitution products, as in the case of the stabilised *P*-halogenoylides:

Scheme 19

$$t\text{-Bu}(R)\overset{+}{P}MeCl^- \xleftarrow{MeNH_2} t\text{-Bu}(R)P(NHMe)=CHR' \xrightarrow{AlkOH} t\text{-Bu}(R)\overset{+}{P}CH_2R'Cl^-\ ;$$
(CXXIX) (CXXVIII)

$$t\text{-Bu}(R)\overset{+}{P}CH_2R'Cl^- \xleftarrow{ArOH} t\text{-Bu}(R)P(Cl)=CHR' \xrightarrow{HN_3} t\text{-Bu}(R)\overset{+}{P}MeCl^-\ ;$$
(CXXVII) (XI) (CXXX)

$$(XI) \xrightarrow{ArOH} t\text{-Bu}(R)\overset{+}{P}CH_2R'OAr^- \rightarrow (CXXVII)\ .$$
(CXXXI)

The reactions of unstabilised *P*-chloroylides with compounds containing a mobile hydrogen atom take place in two stages. Initially the ylide carbon atom is protonated and the chlorophosphonium salt (CXXXI) is formed, after which the anion attacks the phosphonium cation to produce the phosphonium chloride (CXXVII). The chlorophosphonium salts (CXXXI) can be detected by spectroscopic methods[96,130].

It follows from the data examined here that the *P*-hetero-substituted phosphorus ylides can be used successfully in organic and organophosphorus synthesis. They successfully complement and significantly extend the applications of ylides as a whole. The introduction of various substituents not only at the carbon atom but also at the phosphorus atom of the P=C group makes it possible to control flexibly the properties of these reactive compounds.

REFERENCES

1. A.W.Johnson, "Chemistry of Ylides" (Translated into Russian), Izd.Mir, Moscow, 1969, p.9.
2. H.J.Bestmann and R.Zimmerman, in "Organic Phosphorus Compounds" (Edited by G.M.Kosolapoff and L.Maier), Wiley, New York, 1972, **3**, p.1.
3. H.Pommer, Angew Chem., 1977, **89**, 437.
4. G.Wittig, Acc.Chem.Res., 1974, **7**, 6.
5. K.Becker, Tetrahedron, 1980, **36**, 1717.
6. H.J.Bestmann, Angew.Chem., 1977, **89**, 361.
7. H.Schmidbauer, Acc.Chem.Res., 1975, **8**, 62.
8. V.V.Tyuleneva, E.M.Rokhlin, and I.L.Knunyants, Uspekhi Khim., 1982, **51**, 3 [Russ.Chem.Rev., 1982, **51**(1)].
9. US P.3686159 (1972).
10. D.B.Boyd and R.Hoffmann, J.Amer.Chem.Soc., 1971, **93**, 1064.
11. K.Dimroth, Fortsch.chem.Forsch., 1973, **38**, 1.
12. K.Dimroth, Acc.Chem.Res., 1982, **15**, 58.
13. K.Dimroth, S.Berger, and J.Kaletsch, Phosph.and Sulf., 1981, **10**, 305.
14. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1979, **49**, 104.
15. O.I.Kolodyazhnyi, L.A.Repina, and Yu.G.Gololobov, Zhur.Obshch.Khim., 1975, **45**, 541.
16. O.I.Kolodyazhnyi and V.P.Kukhar', in "Khimiya i Primenenie Fosforganicheskikh Soedinenii" (The Chemistry and Applications of Organophosphorus Compounds), Izd. Naukova Dumka, Kiev, 1981, p.63.
17. D.J.Peterson, J.Organomet.Chem., 1967, **8**, 199.
18. O.I.Kolodiazhnyi, Tetrahedron Letters, 1980, **21**, 2269.
19. O.I.Kolodyazhnyi, L.A.Repina, and Yu.G.Gololobov, Zhur.Obshch.Khim., 1974, **44**, 951.
20. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1975, **45**, 2556.
21. O.I.Kolodyazhnyi and V.P.Kukhar', Zhur.Org. Khim., 1977, **14**, 275.
22. L.A.Repina, R.A.Loktionova, and Yu.G.Gololobov, Zhur.Obshch.Khim., 1976, **46**, 2683.
23. F.R.Atherton, H.P.Openshaw, and A.R.Todd, J.Chem.Soc., 1945, 660.
24. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1977, **47**, 2159.
25. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1980, **50**, 1485.
26. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1980, **50**, 1885.
27. O.I.Kolodiazhnyi, Tetrahedron Letters, 1980, **21**, 3983.
28. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1981, **51**, 2466.
29. O.I.Kolodyazhnyi, "Tezisy XVII Vsesoyuznoy Konferentsii po Khimii Fosforganicheskikh Soedinenii" (Abstracts of Reports at the VIIth All-Union Conference on the Chemistry of Organophosphorus Compounds), Leningrad, 1982, p.51.
30. R.Appel, J.Peters, and R.Schmits, Z.anorg.Chem., 1981, **475**, 18.
31. R.Appel and K.Waid, Angew.Chem.Int.Ed., 1979, **18**, 169.
32. R.Appel, K.Geisler, and H.F.Schöler, Chem.Ber., 1979, **112**, 648.
33. R.Appel and H.F.Schöler, Chem.Ber., 1978, **111**, 2056.
34. R.Appel, Angew Chem.Int.Ed., 1975, **14**, 801.
35. O.I.Kolodyazhnyi, L.I.Shevchuk, and V.P.Kukhar', Zhur.Obshch.Khim., 1977, **47**, 723.
36. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1974, **44**, 1413.
37. G.Fritz et al., Z.anorg.Chem., 1981, **472**, 45.
38. R.Appel, M.Huppertz, and A.Westerhaus, Chem. Ber., 1983, **116**, 114.
39. O.I.Kolodyazhnyi, L.I.Shevchuk, and V.P.Kukhar', Zhur.Obshch.Khim., 1978, **48**, 223.
40. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1975, **45**, 2561.
41. O.I.Kolodyazhnyi, L.A.Repina, and Yu.G.Gololobov, Zhur.Obshch.Khim., 1974, **44**, 1275.
42. D.J.Peterson and J.U.Collins, J.Org.Chem., 1966, **31**, 2373.
43. K.Issleib and H.P.Abicht, J.prakt.Chem., 1970, **312**, 456.
44. H.H.Karsch, Z.Naturforsch., 1979, **34b**, 1178.
45. H.H.Karsch and H.Schmidbaur, Z.Naturforsch., 1977, **23b**, 762.
46. S.N.Zdorova, Z.S.Novikova, and I.F.Lutsenko, Zhur.Obshch.Khim., 1976, **46**, 1218.
47. O.I.Kolodyazhnyi and V.P.Kukhar', Zhur.Obshch. Khim., 1979, **49**, 949.
48. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1977, **47**, 956.
49. H.H.Karsch, Z.Naturforsh., 1979, **34b**, 1171.
50. R.Appel, W.Vender, and T.Knoll, Chem.Ber., 1979, **112**, 1094.
51. R.Appel and G.Haubrich, Angew.Chem.Int.Ed., 1980, **19**, 213.
52. Z.S.Novikova et al., Zhur.Obshch.Khim., 1976, **46**, 541.
53. D.M.Malenko and Yu.G.Gololobov, Zhur.Obshch. Khim., 1976, **46**, 194.
54. D.M.Malenko and Yu.G.Gololobov, Zhur.Obshch. Khim., 1979, **49**, 308.
55. D.M.Malenko et al., Zhur.Obshch.Khim., 1980, **50**, 1946.
56. Yu.G.Gololobov, D.M.Malenko, and L.A.Repina, Zhur.Obshch.Khim., 1980, **50**, 1206.
57. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1975, **45**, 546.
58. L.F.Kasukhin, M.P.Ponomarchuk, L.A.Repina, and Yu.G.Gololobov, Dokl.Akad.Nauk SSSR, 1975, **224**, 95.
59. Yu.G.Gololobov, I.N.Zhmurova, and L.F.Kasukhin, Tetrahedron, 1981, **37**, 437.
60. D.M.Malenko and Yu.G.Gololobov, Zhur.Obshch. Khim., 1978, **48**, 2793.
61. A.N.Pudovik, E.S.Batyeva, and Yu.N.Girfanova, Zhur.Obshch.Khim., 1975, **45**, 2618.
62. A.N.Pudovik, E.S.Batyeva, and Yu.N.Girfanova, Zhur.Obshch.Khim., 1975, **45**, 272.
63. A.N.Pudovik, E.S.Batyeva, and Yu.N.Girfanova, Zhur.Obshch.Khim., 1973, **43**, 1696.
64. Y.Leroux, D.El Manouni, and R.Burgada, Tetrahedron Letters, 1981, **22**, 3393.
65. F.Ramirez and O.P.Madan, Tetrahedron, 1966, **22**, 567.

66. G.Baccolini, P.E.Todesco, and G.Bartolle, Phosph. and Sulf., 1980, **9**, 203.
67. J.C.Tebby, S.E.Willets, and D.V.Griffiths, Chem.Comm., 1981, 420.
68. R.Burgada, Y.Leroux, and J.O.El Khoshnieh, Tetrahedron Letters, 1981, **22**, 3533.
69. V.Griffiths and I.C.Tebby, Chem.Comm., 1981, 607.
70. R.Burgada, Y.Leroux, and J.O.El Khoshnieh, Tetrahedron Letters, 1980, **21**, 925.
71. D.El Manouni, Y.Leroux, and R.Burgada, Compt. rend. C, 1981, **293**, 1065.
72. R.Burgada, Y.Leroux, and J.O.El Khoshnieh, Phosph. and Sulf., 1981, **10**, 181.
73. R.Burgada, Y.Leroux, and J.O.El Khoshnieh, in "Phosphorus Chemistry, Proc. 1981 Int.Conf.ACS Symposium Series", 1981, **171**, p.607.
74. R.F.Hudson and P.A.Chopard, Helv.Chim.Acta, 1964, **46**, 632.
75. D.Seebach, Chem.Ber., 1972, **105**, 487.
76. W.J.Middleton and W.H.Sharkey, J.Org.Chem., 1965, **30**, 1384.
77. A.A.Kadyrov, E.M.Rokhlin, and I.L.Knunyants, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 2653.
78. S.N.Konotopova et al., Zhur.Obshch.Khim., 1973, **43**, 987.
79. K.Issleib and M.Lishewski, J.prakt.Chem., 1970, **312**, 135.
80. L.I.Mizrakh et al., Zhur.Obshch.Khim., 1973, **43**, 987.
81. L.I.Mizrakh, L.Yu.Polonskaya, and T.M.Ivanova, Zhur.Obshch.Khim., 1978, **48**, 1900.
82. Yu.G.Gololobov et al., Zhur.Obshch.Khim., 1976, **46**, 1184.
83. D.G.Naae, H.S.Kesling, and D.J.Burton, Tetrahedron Letters, 1975, 3789.
84. M.J.van Hamme and D.J.Burton, J.Organometal. Chem., 1979, **169**, 123.
85. M.J.van Hamme and D.G.Burton, J.Fluorine Chem., 1970, **13**, 407.
86. W.G.Salmond, Tetrahedron Letters, 1977, 1239.
87. W.G.Taylor, Synthesis, 1980, 554.
88. G.G.Naae and D.J.Burton, Synth.Comm., 1973, **3**, 197.
89. R.Appel and H.D.Wihler, Chem.Ber., 1978, **111**, 2054.
90. T.V.Kim, E.I.Kiseleva, R.A.Loktionova, and Yu.G.Gololobov, Zhur.Obshch.Khim., 1980, **50**, 1889.
91. O.Dahl, J.Chem.Soc.Perkin Trans.I, 1978, 947.
92. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1977, **47**, 2390.
93. Th.A.van der Knaap and F.Bickelhaupt, Tetrahedron Letters, 1982, **23**, 2037.
94. I.E.Boldeskul et al., Zhur.Obshch.Khim., 1977, **47**, 2735.
95. O.I.Kolodyazhnyi, V.I.Yakovlev, and V.P.Kukhar', Zhur.Obshch.Khim., 1979, **49**, 2458.
96. O.I.Kolodyazhnyi, Doctoral Thesis in Chemical Sciences, Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev, 1982.
97. O.I.Kolodiazhnyi, Tetrahedron Letters, 1982, **23**, 499.
98. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1982, **52**, 1538.
99. O.I.Kolodyazhnyi and V.P.Kukhar', Zhur.Obshch. Khim., 1979, **19**, 1992.
100. J.Bellan, M.R.Marre, M.Sanchez, and R.Wolf, Phosph.and Sulf., 1981, **22**, 1231.
101. O.I.Kolodiazhnyi, Tetrahedron Letters, 1981, **22**, 1231.
102. R.F.Hudson, "Organic Chemistry", Vol.6, "Structure and Mechanism in Organophosphorus Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1967, pp.88, 106.
103. M.Charton, J.Amer.Chem.Soc., 1977, **99**, 5687.
104. G.H.Birum and C.N.Matthews, J.Amer.Chem.Soc., 1966, **88**, 4198.
105. O.I.Kolodyazhnyi, V.P.Lysenko, M.G.Tret'yak, R.A.Loktionova, and Yu.G.Gololobov, in "Khimiya Elementoorganicheskikh Soedinenii" (The Chemistry of Organoelemental Compounds), Izd.Nauka, Leningrad, 1976, p.188.
106. I.M.Aladzheva, O.V.Bykhovskaya, P.V.Petrovskii, and T.A.Mastryukova, Zhur.Obshch.Khim., 1982, **52**, 1095.
107. T.A.Mastryukova, I.M.Aladzheva, I.F.Leont'eva, V.A.Svoren', P.V.Petrovskii, and M.I.Kabachnik, Zhur.Obshch.Khim., 1977, **47**, 2449.
108. M.A.Antipin, Candidate's Thesis in Chemical Sciences, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1980.
109. T.A.Mastryukova et al., Tetrahedron Letters, 1980, **21**, 2931.
110. T.A.Mastryukova, I.V.Leont'eva, I.M.Aladzheva, P.V.Petrovskii, E.I.Fedin, and M.I.Kabachnik, Dokl.Akad.Nauk SSSR, 1979, **247**, 866.
111. T.A.Mastryukova, I.M.Aladzeva, I.V.Leont'eva, P.V.Petrovski, E.I.Fedin, and M.I.Kabachnik, Pure Appl.Chem., 1980, **52**, 945.
112. I.V.Leont'eva, Candidate's Thesis in Chemical Sciences, Institute of Organoelemental Compounds, USSR Academy of Sciences, Moscow, 1980.
113. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1976, **46**, 2386.
114. T.Klebach, C.Johnson, and F.Bickelhaupt, Rec.Trav.chim., 1979, **98**, 14.
115. V.V.Ovchinnikov et al., Zhur.Obshch.Khim., 1979, **49**, 2434.
116. I.M.Aladzheva et al., Zhur.Obshch.Khim., 1982, **52**, 2358.
117. T.A.Mastryukova, I.M.Aladzheva, O.V.Bykhovskaya, P.V.Petrovskii, M.Yu.Antipin, Yu.T.Struchkov, and M.I.Kabachnik, Dokl.Akad.Nauk SSSR, 1982, **264**, 1396.
118. I.Granoth, R.Alkabeth, E.Shirin, J.Margalit, and P.Bell, in "Phosphorus Chemistry. Proc. 1981 Int.Conf.ACS Symposium Series", 1981, Vol.171, p.435.
119. K.Burger and A.Meffert, Annalen, 1975, 316.
120. A.A.Kadyrov and E.M.Rokhlin, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 2583.
121. I.L.Knunyats, E.M.Rokhlin, and A.A.Kadyrov, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 237.
122. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1982, **52**, 2361.
123. H.Oediger and K.Eiter, Annalen, 1965, **682**, 58.
124. O.I.Kolodyazhnyi, L.A.Repina, V.P.Kukhar', and Yu.G.Gololobov, Zhur.Obshch.Khim., 1979, **49**, 1004.
125. L.A.Repina, R.A.Loktionova, and Yu.G.Gololobov, Zhur.Obshch.Khim., 1975, **45**, 2341.
126. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1982, **52**, 446.
127. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1979, **49**, 716.

128. O.I.Kolodyazhnyi and V.P.Kukhar', Zhur.Org.Khim., 1978, **14**, 1340.
129. O.I.Kolodiazhnyi, V.I.Yakovlev, and V.P.Kukhar, in "Phosphorus Chemistry. 1981 Int.Conf.ACS Symposium Series", 1981, Vol.171, p.247.
130. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1982, **52**, 1086.
131. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1982, **52**, 1314.
132. O.I.Kolodiazhnyi, Tetrahedron Letters, 1982, **23**, 4933.
133. O.I.Kolodyazhnyi, Zhur.Obshch.Khim., 1983, **53**, 1226.
134. R.Appel, J.Peters, and A.Vesterhaus, Angew. Chem., 1982, **94**, 76.

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