Translated from *Uspekhi Khimii* **60** 799–834 (1991) U.D.C. 547.241

P-Halogen-substituted phosphorus ylids

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ABSTRACT. Literature data on methods of obtaining ylids containing halogen atoms on the phosphorus atom of the P=C group are arranged systematically and reviewed.

The bibliography contains 125 references.

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I. Introduction

Phosphorus ylids are important reactants and are widely used in organic synthesis.[1] Among the various types of these compounds synthesised in recent years there is significant interest in *P*-hetero-substituted phosphorus ylids,[2–4] particularly in ylids containing halogen atoms on phosphorus, or *P*-halogenated ylids as they are usually called. The presence of labile halogen atoms determines the properties of these compounds, which are interesting from theoretical and preparative aspects.[2–7] With the aid of *P*-halogenated ylids such valuable substances for organic synthesis as phosphorus-containing ketenes, thioketenes, vinylphosphine oxides, allylphosphine oxides, etc. have been obtained. *P*-Halogenated ylids participate in various cycloaddition and heterocyclisation reactions and possess high phosphorylating ability.

In addition *P*-halogenated ylids are also convenient subjects for studying important theoretical problems of structure and reactivity of organophosphorus compounds.

Recently published review papers on *P*-halogenated ylid chemistry comprise material from only the author's work.[2,8–10] Latterly a significant number of publications has appeared describing new methods of synthesis and disclosing interesting properties of *P*-halogenated ylids as a result of which there is a need to review all the available information on this important type of organophosphorus compound. Results of investigations on *P*-halogenated ylid chemistry published up to 1990 are correlated in this review.

II. Synthetic methods

Detailed investigations on *P*-halogenated ylids have enabled convenient methods for their synthesis to be devised based on the following conversions. 1. 'Oxidative ylidation' of compounds of trivalent phosphorus comprising increasing the phosphorus coordination number to four by adding halogen and forming a P=C bond.[2] Such reactions include 1,2(C→P)-halogenotropic rearrangements and reactions of tertiary alkylphosphines with carbon tetrahalides to form *P*-halogenated ylids containing one atom of chlorine or bromine on the phosphorus atom. 2. The formation of a P=C multiple bond in a halophosphorane or halophosphonium salt by an elimination reaction. Various *P*-chloro- and *P*-fluoroylids were synthesised by this means, including some containing several halogen atoms on phosphorus. 3. Reactions of *P*-halogenated ylids with chlorine-containing electrophiles which proceed with replacement of hydrogen atoms at the α-carbon by various groups.

The methods listed have enabled *P*-halogenated ylids of practically any strucure to be obtained by simple operations using starting materials available in the laboratory.

1. Rearrangement of α-haloalkylphosphines into *P*-halogenated ylids

A halogen atom at the α-position of tertiary alkylphosphines is distinguished by high lability as a result of which it may possibly migrate to the phosphorus atom [1,2(C→P)-halogenotropic shift]. The valency of the phosphorus atom is increased as a result of halogen atom migration, a P=C bond is formed and the α-haloalkylphosphines (A) are converted into *P*-halogenated ylids (B).

$$\underset{\text{(A)}}{R_2P(X)-CR_2'} \longrightarrow \underset{\text{(B)}}{R_2P(X)=CR_2'},$$

X = Br, Cl.

Halogenotropy in a P–C diad depends on the substituents R and R′ on the phosphorus and carbon atoms, which influence the thermodynamic stability of the halogenotropic isomers (A) and (B). Consequently not only 1,2(C→P) but also 1,2(P→C)-halogenotropic rearrangements (see below) are possible with a particular choice of substituents. However α-haloalkylphosphines containing electron-accepting substituents on the α-carbon atom, stabilising the ylid function as a rule, are readily converted into *P*-halogenated ylids and in this case a 1,2(C→P)-halogenotropic rearrangement is a reliable means of obtaining them.

Halo-bis-(benzenesulphonyl)methanes, being comparatively strong CH-acids, react with chlorodiphenylphosphine in the presence of triethylamine in tetrahydrofuran at 0 °C with the formation of tertiary α-haloalkylphosphines (I). Compounds (I) rearrange smoothly into *P*-halogenated ylids (II), which are isolated in good yield as stable crystalline compounds and are used as reagents in various chemical conversions.[11]

$$Ph_2PCl + XCH(SO_2Ph)_2 \xrightarrow[-Et_3N\cdot HCl]{Et_3N} \underset{\text{(I)}}{Ph_2PC(X)(SO_2Ph)_2} \longrightarrow \underset{\text{(II)}}{Ph_2P(X)=C(SO_2Ph)_2}$$

X = Br, Cl.

The reaction of di-organochlorophosphines with metallochloromethanes (III) or (V) stabilised by sulphonyl or trimethylsilyl groups proceeds readily.[2,11–13] The resulting α-chloroalkylphosphines (IV) and (VI) are very unstable and rearrange into *P*-chloroylids at low temperature. For example, α-chloroalkylphosphine (VI), which was observed by its ^{31}P NMR (signal at δ_P 86.1 p.p.m.), exists at −110 °C in toluene but even at −90 °C is converted quantitatively into ylid (VII) (δ_P 65.5 p.p.m.).[13]

$$R_2PCl + LiCHSO_2CF_3 \xrightarrow[-LiCl]{} \underset{Cl}{\underset{|}{R_2PCHSO_2CF_3}} \longrightarrow \underset{Cl}{\underset{|}{R_2P{=}CHSO_2CF_3}},$$

(III) (IV) 60—75%

R = Et, iso-Pr, Ph,

$$(Me_2N)_2PCl + LiCHSiMe_3 \xrightarrow[-LiCl]{} \underset{Cl}{\underset{|}{(Me_2N)_2PCHSiMe_3}} \longrightarrow$$

(V) (VI)

$$\longrightarrow \underset{Cl}{\underset{|}{(Me_2N)_2P{=}CHSiMe_3}}.$$

(VII), 64%

Compounds of trivalent phosphorus containing a trichloromethyl group are comparatively stable. Lutsenko and co-workers obtained bis-(dimethylamino)trichloromethylphosphine, which is stable at room temperature, by an exchange reaction of dichloro(trichloromethyl)phosphine with diethylamine. The product was purified by distillation in vacuum and was then converted into *P*-chloroylid (VIII) by boiling in dichloromethane.[14]

$$Cl_2PCCl_3 \xrightarrow[-Me_2NH\cdot HCl]{Me_2NH} (Me_2N)_2PCCl_3 \longrightarrow \underset{Cl}{\underset{|}{(Me_2N)_2P{=}CCl_2}}.$$

(VIII)

Pinchuk and co-workers have carried out the analogous rearrangement of bis-(diethylamino)trichloromethylphosphine (X) into ylid (XI).[15,16] Phosphine (X) was obtained by the reaction of chloro-bis-(diethylamino)phosphine with hexamethyltriaminophosphine and carbon tetrachloride. As was shown previously by Riesel[17] the ion pair (IX) is formed, containing the CCl_3^- anion, which is capable of reacting with chlorine-containing electrophiles. In this case the ion pair interacts with chloro-bis-(diethylamino)-phosphine with the formation of phosphine (X). Ylids (VIII) and (XI) were not isolated in a pure state. However their structures were confirmed spectroscopically and by hydrolysis.

$$(Me_2N)_3P + CCl_4 \longrightarrow \underset{(IX)}{[(Me_2N)_3\overset{+}{P}Cl\ CCl_3^-]} \xrightarrow{(Et_2N)_2PCl} \underset{(X)}{(Et_2N)_2PCCl_3} \longrightarrow$$

$$\longrightarrow \underset{(XI)}{(Et_2N)_2P(Cl){=}CCl_2} \xrightarrow{H_2O} (Et_2N)_2P(O)CHCl_2.$$

The *C*-silicon-substituted *P*-chloroylids (XIII) and (XIV) were obtained by reacting carbosilanes with lithio- or silylphosphines. α-Haloalkylphosphines (XII) rearrange into *P*-chloroylids extremely readily but they were not recorded spectroscopically. Nonetheless the formation of α-haloalkylphosphines is not in doubt as follows convincingly from the reaction scheme.[18,19]

$$Cl_{4-n}C(SiCl_3)_n \xrightarrow{Me_2PLi} Me_2PC(Cl_{3-n})(SiCl_3)_n \longrightarrow \underset{Cl}{\underset{|}{Me_2P{=}C(Cl_{2-n})(SiCl_3)_n}},$$

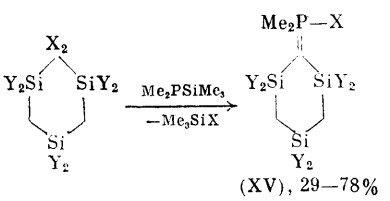
(XII) (XIII)

$n = 1, 2,$

$$Cl_2C(SiMe_3)_2 \xrightarrow[-Me_3SiCl]{Me_2PSiMe_3} Me_2PC(Cl)(SiMe_3)_2 \longrightarrow \underset{Cl}{\underset{|}{Me_2P{=}C(SiMe_3)_2}}.$$

(XIV)

The reaction of *C*-dihalo-1,3,5-trisilacyclohexanes with silylphosphines on boiling in dimethoxyethane gives *P*-halogenated ylids (XV) with fission of the Si—P bond. These are stable crystalline substances or liquids distillable in vacuum.[19] The structures of the *P*-chloroylids were proved by X-ray structural analysis. Compounds (XV) are molecules planar in structure with shortened lengths for the P=C and Si—C bonds as a result of delocalisation of the negative charge on the ylid carbon atom around the ring.[20]



(XV), 29—78%

X = Br, Cl; Y = Cl, F, Me.

In certain cases *P*-chloroylids (XVI) and (XVIII), formed by 1,2 (C→P)-chlorotropic rearrangement, then undergo a prototropic or silylotropic rearrangement being converted into imidophosphonic chlorides (XVII) and (XIX).[21–24]

$$Cl_2PCHCl_2 \xrightarrow{RNH_2 + Et_3N} (RNH)_2PCHCl_2 \longrightarrow \underset{NR}{\underset{\|}{\ }}$$

$$\longrightarrow \underset{Cl}{\underset{|}{[(RNH)_2P{=}CHCl]}} \longrightarrow \underset{Cl}{\underset{|}{RNH{-}PCH_2Cl}},$$

(XVI) (XVII)

R = Alk,

$$\underset{Cl}{\underset{|}{Et_2NPCHCl_2}} \xrightarrow{(Me_3Si)_2NLi} \underset{(Me_3Si)_2N}{\underset{|}{Et_2NPCHCl_2}} \longrightarrow \left[\underset{(Me_3Si)_2N}{\underset{|}{\overset{Cl}{\overset{|}{Et_2NP{=}CHCl}}}}\right] \longrightarrow$$

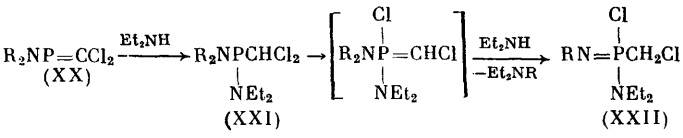
(XVIII)

$$\longrightarrow \underset{Me_3SiN}{\underset{\|}{\overset{Cl}{\overset{|}{Et_2NPCH(Cl)SiMe_3}}}}$$

(XIX)

The phospha-ethylene (XX) is converted into trimethylsilylimidophosphonic chloride (XXII) on boiling in tetrahydrofuran with an excess of diethylamine. Seemingly diethylamine adds to the phospha-ethylene with the formation of dichloromethylphosphine (XXI) which rearranges to an unstable *P*-chloroylid. The latter gives

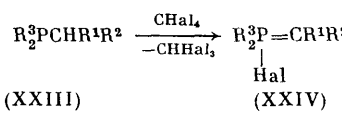
ylid (XXII) as a result of a silylotropic rearrangement and desilylation.[25,26]



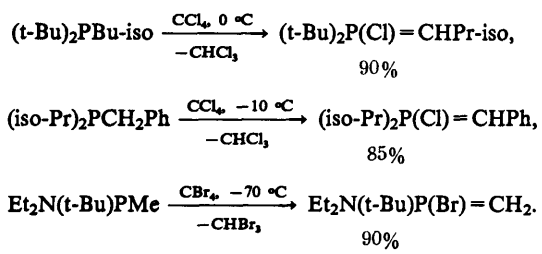
R = Me_3Si.

2. Reactions of tertiary alkylphosphines with carbon tetrahalides

The reaction of tertiary alkylphosphines with carbon tetrahalides was first studied in the last century.[27,28] However *P*-halogenated ylids were not obtained from this reaction for a long time.[29–32] The reaction, which is very sensitive to conditions, proceeded only to the formation of a mixture of compounds difficult to identify.[32] Only in 1975–1977 was it established that by observing an appropriate temperature regimen and choice of solvent, tertiary alkylphosphines (XXIII) react with carbon tetrachloride or tetrabromide with the formation of *P*-halogenated ylids (XXIV).[33–36]

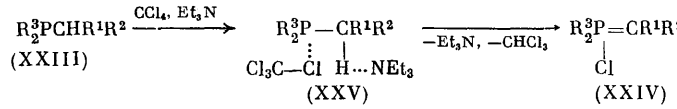


The interaction of compounds (XXIII) with carbon tetrahalides (CCl_4,[33,34] $CBrCl_3$, CBr_4 [34–37]) is usually carried out in pentane, diethyl ether[33–37] or dichloromethane[39] below 0 °C. Reaction with carbon tetrachloride occurs below 0 °C, and with CBr_4 and $CBrCl_3$ at −70 °C. The yields of *P*-halogenated ylids are high as a rule. *P*-Halogenated ylids are not isolated from the reaction mixture for preparative work, which appreciably simplifies handling. In this event it is sufficient to add carbon tetrachloride to the alkylphosphine in ether in order to obtain a reagent which is very reactive and ready to use.[9] However where necessary (for example for spectroscopic investigations) *P*-halogenated ylids may be purified by distillation in vacuum or by crystallisation from inert solvents.[9,40–43]



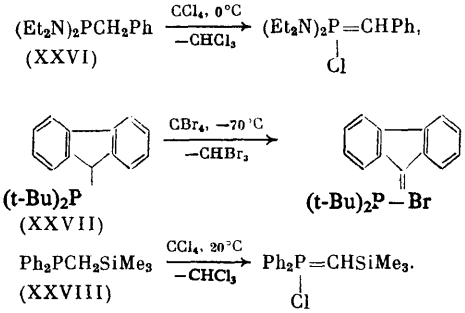
The substituents R^1 and R^2 in compound (XXIII) may be electron acceptors, groups, increasing the CH-acidity,[35–37,39–41] electron-neutral or electron-donating groups.[33,34,37,38] Compounds of trivalent phosphorus, containing at the α-carbon atom, alkyl groups, hydrogen atoms or trimethylsilyl or phenyl groups, which stabilise the ylid function, interact most actively with carbon tetrahalides. Yields of ylids obtained in this way are very high.[34,38,43–45] Strong electron-accepting groups at the α-carbon atom may reduce the nucleophilicity of the trivalent phosphorus atom since the rate of their interaction with carbon tetrahalides is reduced. For example, the introduction of one, two or three atoms of chlorine or bromine at the α-carbon atom of tertiary alkyl phosphines successively slows the reaction with carbon tetrachloride down to a complete stop. Electronegative alkoxycarbonyl or arylsulphonyl groups at the α-carbon atom of tertiary alkylphosphines also reduce the rate of interaction of the trivalent phosphorus atom with carbon tetrachloride.[35,40] However the reaction rate may in this case be increased by the addition to the reaction medium of tertiary amines the catalytic action of which is explained by participation in the formation of an intermediate reaction complex (XXV) (Scheme 1).[35,44] For example, compounds (XXIII) react readily with carbon tetrachloride in the presence of triethylamine in ether below 0 °C being converted in high yield into *P*-chloroylids (XXIV). In the absence of triethylamine at 20 °C the interaction is effected extremely slowly.[35]

Scheme 1

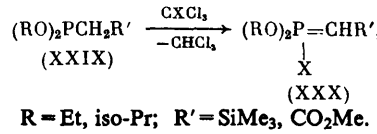


CR^1R^2 = $CHCO_2Me$, $C(CO_2Me)_2$, $CHSO_2CF_3$, $C(SO_2Ph)_2$; R^3 = Alk, Ph, AlkO.

Among tertiary alkylphosphines, compounds of the type of (XXVI)–(XXVIII) containing alkyl, phenyl or dialkylamino groups on the trivalent phosphorus atom react readily with carbon tetrahalides.[38,39,43–46]



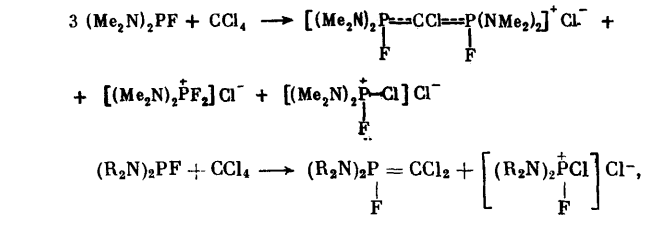
Esters of alkylphosphonous acids (XXIX) react slowly even with an excess of carbon tetrachloride at 20 °C (R′ = $SiMe_3$, 14 h) while with CBr_4 or $CBrCl_3$ they react in ether at −70 °C and give high yields of *P*-bromoylids (XXX).[35–37,40,44]



R = Et, iso-Pr; R′ = $SiMe_3$, CO_2Me.

Acid chlorides and bromides of trivalent phosphorus do not react directly with carbon tetrahalides although fluorotetraalkyldiamino-phosphines react slowly with carbon tetrachloride at a ratio of 1:3

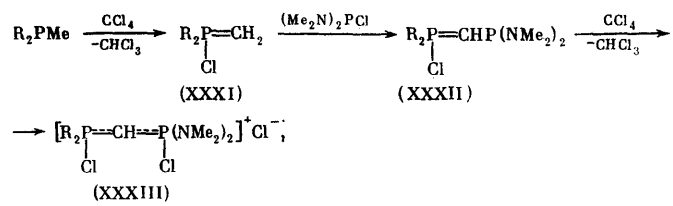
(R = Me) or 2:1 (R = Et, n-Pr) giving *P*-fluoroylids and phosphonium salts.[47]



R = Et, iso-Pr.

Tertiary alkylphosphines give *P*-chloroylids (XXXIII) in high yield with an excess of carbon tetrachloride in the presence of chloro-bis-(dimethylamino)phosphine. As shown in Scheme 2 ylids (XXXI) are formed initially and are converted by reaction with the chlorophosphine into ylids (XXXII) containing a trivalent phosphorus atom. Reaction of the latter with CCl_4 gives *P*-chloroylid (XXXIII).[34]

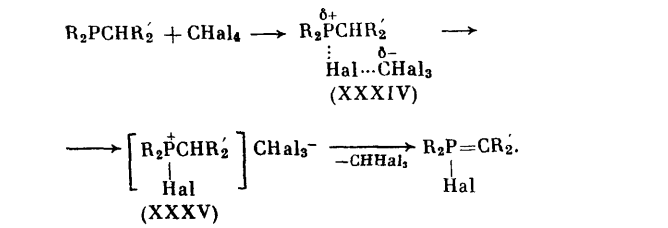
Scheme 2



R = t-Bu, Et_2N.

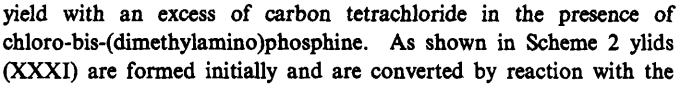
It is assumed at present that the mechanism of the reaction of trivalent phosphorus compounds with carbon tetrahalides with few exceptions[48,49] has an ionic character.[50,51] The mechanism of the reaction of tertiary alkylphosphines with $CHal_4$ is not exceptional in this regard, although the presence of a labile hydrogen atom on the α-carbon determines some of its special features (Scheme 3).[34]

Scheme 3



Nucleophilic attack of the trivalent phosphorus by a halogen atom of the carbon tetrahalide leads through the intermediate formation of complex (XXXIV) to heterolytic fission of the readily polarised bond of $CHal_4$ and the formation of an ion pair (XXXV) containing trichloromethyl anion (Scheme 3). The highly basic $CHal_3$ anion deprotonates the α-carbon atom of the intermediate, the CH-acidity of which is fairly high due to the strong positive inductive effect of the phosphonium group, as a result of which halogenoform is eliminated and a *P*-halogenated ylid is formed.[9,34,52]

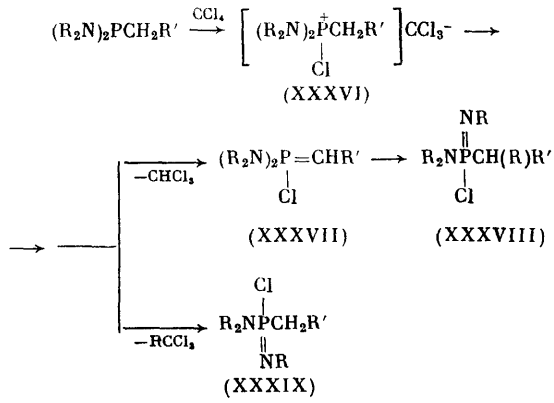
Scheme 3 demonstrates the reaction of sterically hindered trialkylphosphines with carbon tetrabromide as a result of which phosphonium salts containing tribromomethyl anion and stable at low temperature (−120 °C in pentane) are formed. The stability of the phosphonium salt is explained by steric hindrance to nucleophilic attack by the tribromomethyl anion on the phosphonium cation or on the α-proton. On increasing the temperature to −60 °C the phosphonium salts are converted into the corresponding *P*-bromoylids with elimination of chloroform. The structure of the phosphonium salts, particularly the presence in them of CBr_3 anion, was demonstrated by chemical reactions. Deuterobromoform was obtained on reacting the salts with deuterium chloride and tribromotrimethylsilylmethane was formed with chlorotrimethylsilane.[34]



R = D, Me_3Si.

The route of the reaction of compounds of trivalent phosphorus (XXIII) with carbon tetrahalides and the character of the resulting products depends on the solvent.[53] Neilson and co-workers have shown that on reacting aminoalkyl-bis-(trimethylsilyl)phosphines with carbon tetrachloride in nonpolar solvents, chloroform is eliminated and *P*-chloroylids (XXXVII) are formed which then rearrange into iminophosphoranes (XXXVIII). However on carrying out the reaction in dichloromethane, trichlorotrimethylsilylmethane is eliminated and iminophosphoranes (XXXIX) are formed (Scheme 4). The dependence of the reaction route on the nature of the solvent is determined by the polarity of the medium on ion pair (XXXVI). In a polar solvent the ion pair separates and consequently the CCl_3^- anion attacks the exposed trimethylsilyl group. On the other hand in a nonpolar solvent a tighter ion pair (XXXVI) exists and consequently reaction of CCl_3 anion with the neighbouring hydrogen on the α-carbon atom and elimination of chloroform are readily effected.[54]

Scheme 4

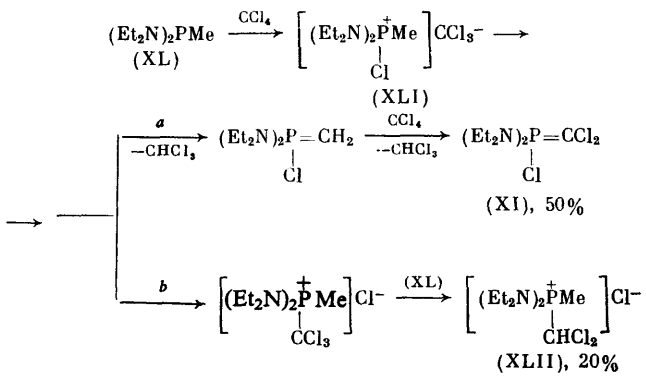


R = Me_3Si; R′ = H, Alk.

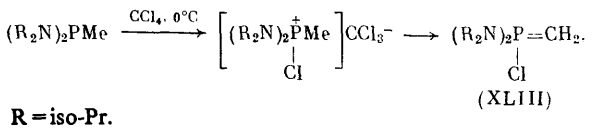
The reaction of compounds of trivalent phosphorus with carbon tetrahalides may under certain conditions occur with no elimination of halogenoform and no *P*-halogenated ylid formation but with attack of the trichloromethyl anion on the phosphonium cation and

formation of trichloromethylphosphonium salts.[55–57] The first reaction route occurs more frequently than the relatively rare second. As shown in Scheme 5, the reaction of bis-(diethylamino)methylphosphine (XL) with an excess of carbon tetrachloride occurs simultaneously in the two directions *a* and *b*, as a result of which a certain quantity of phosphonium salt (XLII) is formed in addition to ylid (XI).[57]

Scheme 5

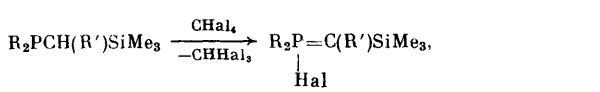


Branched groups on the phosphorus atom, which cause steric hindrance, hinder attack to $CHal_3^-$ on the phosphonium cation of ion pair (XLI). Consequently, in contrast to compound (XL), the reaction of bis-(diisopropylamino)methylphosphine with carbon tetrachloride in ether at 0 °C at a reactant ratio of 1:1 gives *P*-chloroylid (XLIII) in quantitative yield.[58] Tertiary alkylphosphines containing bulky t-butyl or isopropyl groups are smoothly converted into *P*-chloroylids. The groups mentioned not only facilitate ylid formation but also increase their stability.[9,33,34]



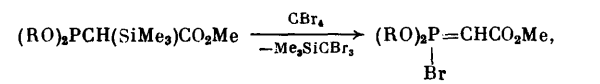
R = iso-Pr.

Tertiary alkylphosphines containing trimethylsilyl groups on the α-carbon atom very often react with carbon tetrahalides and are usually converted into ylids (XLIV).[20,34,37–40,46]

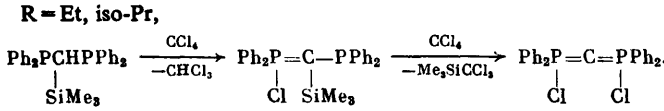


Hal = Br, Cl; R = Me_2N, Et_2N, $(iso\text{-}Pr)_2N$, Me, t-Bu, Ph, EtO, iso-PrO; R′ = $SiMe_3$, Ph.

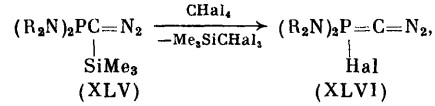
In certain cases trivalent phosphorus compounds containing trimethylsilyl groups on the α-carbon atom react with carbon tetrahalides with elimination of trihalotrimethylsilylmethane and not haloform. Trivalent phosphorus compounds containing a trimethylsilyl group at the sp^2-hybridised carbon atom are particularly readily desilylated.[59,60]



R = Et, iso-Pr,

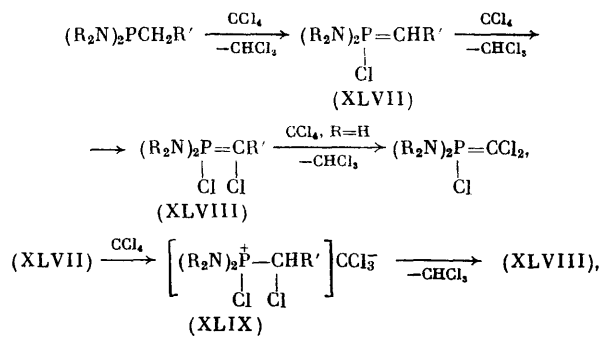


Compound (XLV) eliminates trihalotrimethylsilylmethane on reaction with carbon tetrahalides being converted into *P*-halogenated ylids (XLVI) containing a diazo group on the ylid carbon atom.[61,62] Ylids (XLVI) are hygroscopic red oily liquids containing an absorption band at 2035 cm^{-1} in the IR spectrum. They are stable in solution for several days and are very reactive (see below).



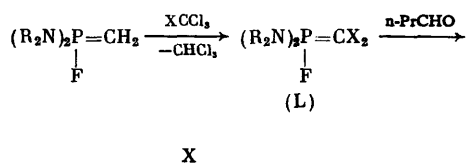
Hal = Br, Cl, R = iso-Pr.

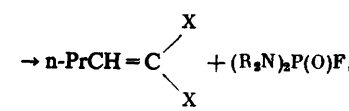
P-Chloroylids formed by reaction of trivalent phosphorus compounds with carbon tetrachloride may react with a second molecule of CCl_4, exchanging a hydrogen atom on the α-carbon atom by an atom of chlorine. Thus reaction of bis-(dialkylamino)-alkylphosphines with an excess of carbon tetrachloride gives *C*-chloro-substituted *P*-chloroylids in yields of 70–80%.[57,63] Nucleophilic removal of a chlorine atom from carbon tetrachloride by the ylid carbon atom with the formation of ion pair (XLIX) is proposed, which is then converted into ylid (XLVIII) by elimination of chloroform.



R_2N = Et_2N, $C_5H_{10}N$; R′ = H, Me, n-Pr, iso-Pr, Cl.

Exchange of hydrogen atoms on the ylid carbon atom by chlorine or bromine occurs on reaction of *P*-fluoroylids with carbon tetrachloride or tetrabromide in ether at −10 to +20 °C. *C*-Halogen-substituted ylids (L) are used in the synthesis of 1,1-dihaloolefins.[57]





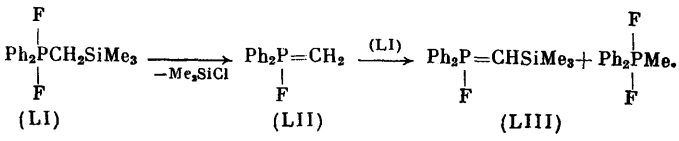
X = Br, Cl; R = Et, $C_5H_{10}N$.

The ability of *P*-halogenated ylids to react with carbon tetrachloride is appreciably reduced on introducing electron-accepting groups onto the ylid carbon atom thus reducing its nucleophilicity.[57]

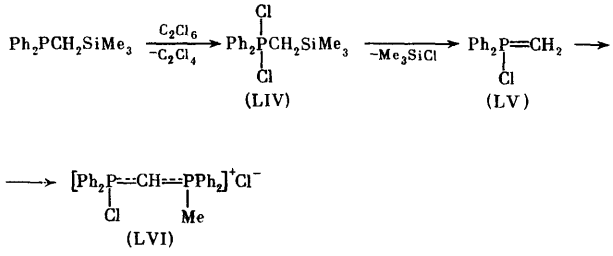
3. Synthesis of *P*-halogenated ylids from halophosphoranes

A comparatively simple method of obtaining *P*-halogenated ylids is the elimination of X—Hal (X = H, Hal, Me_3Si) from halophosphoranes or halophosphonium salts.[44–47]

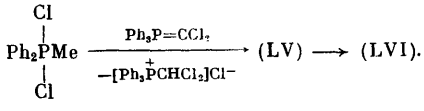
Difluorotrimethylsilylphosphorane (LI) eliminates fluorotrimethylsilane at room temperature with the formation of *P*-fluoroylid (LII) which enters into a transylidation reaction with difluorophosphorane (LI) being converted into *C*-silicon-substituted *P*-fluoroylid (LIII).[64]



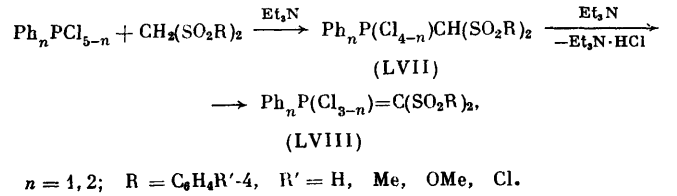
The dichlorophosphorane (LIV) formed from the reaction of diphenyltrimethylsilylmethylphosphine with hexachloroethane is converted into ylid-phosphonium salt (LVI). It is proposed that elimination of chlorotrimethylsilane from the dichlorophosphorane (LIV) gives *P*-chloroylid (LV) which dimerises and forms salt (LVI).[65] The difference in behaviour of *P*-chloro- and *P*-fluoroylids (LII) and (LV) is seemingly explained by the instability of the *P*-chloroylid.[65]



The dimerisation of ylid (LV) resulting on dehydrochlorination of dichloromethyldiphenylphosphorane with triphenylphosphonium-dichloromethylylid proceeds in a similar manner.[66]

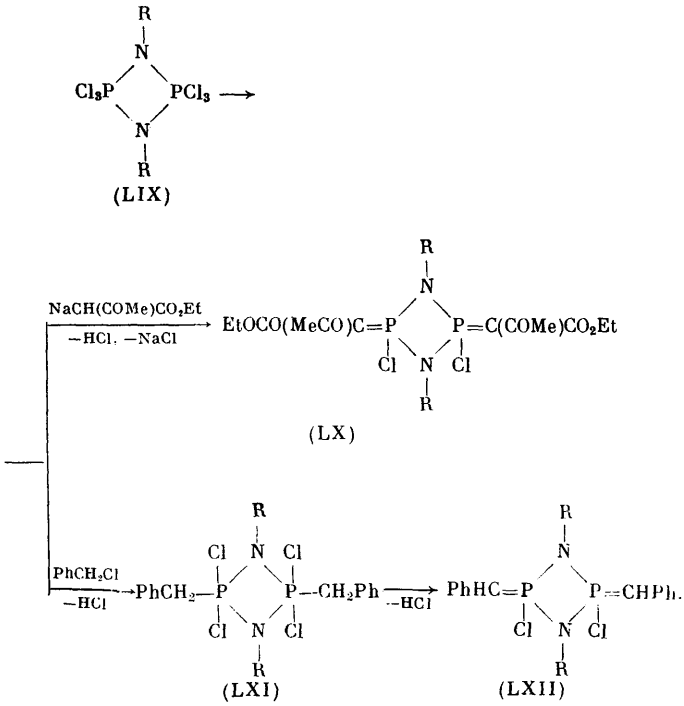


Polychlorophosphoranes react with bis-(arylsulphonyl)methanes in the presence of triethylamine through the formation of phosphonium salts (LVII) to give *P*-chloroylids with one or two chlorine atoms on phosphorus (LVIII).[67,68]

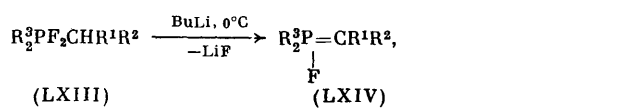


$n = 1, 2$; $R = C_6H_4R'$-4, $R' = H$, Me, OMe, Cl.

The reaction of dimers of trichlorophosphazo compounds (LIX) with sodio acetoacetic ester in boiling benzene as reported by Salman and co-workers proceeds with separation of hydrogen chloride and gives *P*-chloroylids with exocyclic P=C bonds (LX) in 4–56% yield. In precisely the same way the *P*-chloroylids (LXII) are formed in 12–48% yield on extended boiling in benzene of compounds (LIX) with an exess of benzyl chloride, hydrogen chloride being eliminated. It was proposed that phosphonium salts (LXI) are formed initially, which spontaneously eliminate hydrogen chloride, and are converted into *P*-chloroylids (LXII). The formation of ylids in the presence of HCl is remarkable, since these compounds are strong bases readily adding and firmly retaining hydrogen chloride.[69]



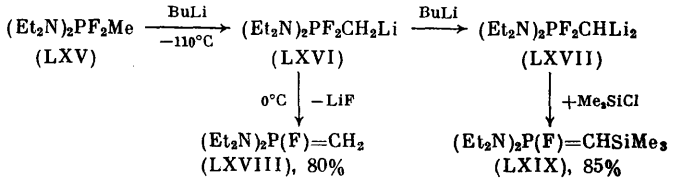
In several cases dihalophosphoranes were not converted into *P*-halogenated ylids on treatment with organometallic compounds. The main obstacle to successfully obtaining *P*-halogenated ylids in this way is the competing substitution of the halogen at phosphorus by an alkyl group. Nonetheless dehydrohalogenation of difluorophosphoranes (LXIII) with butyllithium or lithium hexamethyldisilazane proceeded quite smoothly and enabled the preparation of *P*-fluoroylids (LXIV) containing various substituents R^1, R^2 and R^3 on the phosphorus and carbon atoms of the P=C bond. To achieve high yields of *P*-fluoroylids (LXIV) it was necessary to carry out the reaction in ether at 0 °C, since a reduction of temperature down to −60 to −80 °C strongly reduced the yields and purity of the compounds.[64,70]



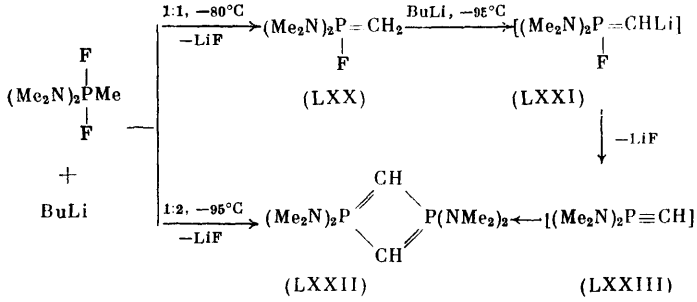
R^1, R^2 = H, Me, n-Pr, iso-Pr; R^3 = t-Bu, Et_2N.

Reaction of the difluorophosphorane (LXV) with butyllithium gives the *C*-substituted difluorophosphorane (LXVI) which eliminates lithium fluoride at −20 to 0 °C but is stable at lower temperatures. At −60 °C and below, compound (LXVI) is readily

metallated by a second molecule of butyllithium with the formation of the dilithio-substituted difluorophosphorane (LXVII). On reaction of the difluorophosphorane with one equivalent of butyllithium a mixture is formed of mono- and dilithio-substituted difluorophosphoranes (LXVI) and (LXVII). In addition a portion of the difluorophosphorane (LXV) remains unreacted and after elimination of lithium fluoride leads to a complex mixture of final reaction products. On reacting difluorophosphorane (LXV) with two equivalents of chlorotrimethylsilane the *C*-silylated *P*-fluoroylid (LXIX) is obtained in high yield.[64]



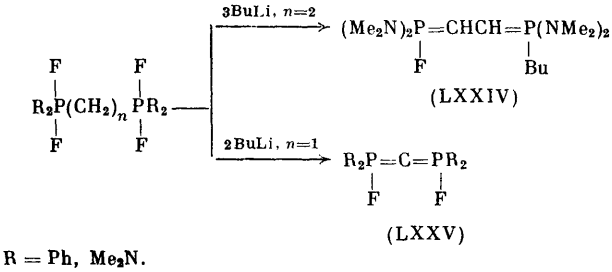
At a reactant ratio of 1:1 butyllithium dehydrofluorinates bis-(dimethylamino)methyldifluorophosphorane in pentane at −80 °C giving the *P*-fluoroylid (LXX) in 61.2% yield,[71,72] while on reacting the difluorophosphorane with two equivalents of butyllithium in pentane at −95 °C the diphosphacyclobutadiene (LXXII) is formed.[6,73,74]



It is proposed that butyllithium metallates the ylid carbon atom of the *P*-fluoroylid (LXX) with formation of compound (LXXI) which eliminates lithium fluoride and is converted into the phospha-acetylene (LXXIII). Dimerisation of the phospha-acetylene gives the diphosphacyclobutadiene.[72] It should be noted however that exchange of a hydrogen atom on the α-carbon of the P=C bond by lithium is achieved with great difficulty even at +20 °C or on heating. This is even less probable at −90 °C. The constitution of the diphosphacyclobutadiene was confirmed by X-ray structural analysis which showed particularly the planar structure of the cyclic portion of the molecule with completely uniform P−C bonds, the length of which were 172.5 pm.[72]

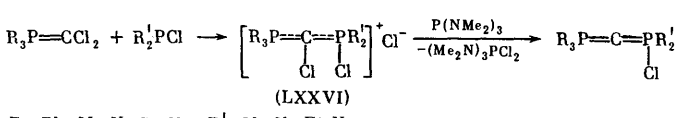
Diphosphacyclobutadiene (LXXII) is a reactive compound and readily participates in various cycloaddition reactions.[75−78]

The reaction of bis-(difluorophosphoranyl)ethane with butyllithium proceeds with dehydrofluorination of one difluorophosphorane group and replacement of a fluorine atom by a butyl group at the other, as a result of which the bis-ylid (LXXIV) is formed in good yield.[79] At the same time carbodiphosphoranes (LXXV) are obtained on reaction of bis-(difluorophosphoranyl)methane with butyllithium, the structure of which was shown by X-ray structural analysis.[80,81]



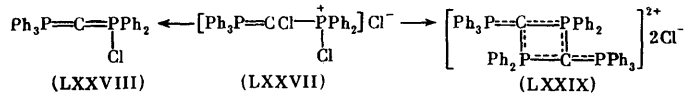
R = Ph, Me_2N.

Phosphoric acid triamides, possessing high dehalogenating ability, were used with success for converting halogenalkylphosphonium salts into *P*-halogenated ylids. For example, the dechlorination of the phosphonium salts (LXXVI) with tris-(dimethylamino)phosphine in dichloromethane at room temperature gives carbodiphosphoranes in high yield.[82]

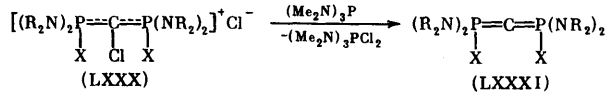


R = Ph, Me_2N, Et_2N ; R' = Me_2N, Et_2N.

The initial reaction conditions influence its course. Appel and co-workers established that the dechlorination of the salt (LXXVII) with tris-(dimethylamino)phosphine in toluene at −78 °C gives the chloropentaphenylcarbodiphosphorane (LXXVIII),[83] while in dichloromethane at room temperature the dimer of product (LXXVIII), viz. diphosphacyclobutadiene, is formed.[84] The structure of dimer (LXXIX) was established by X-ray structural analysis. Compound (LXXIX) contains a centrosymmetric cation with uniform endocyclic and exocyclic P−C bonds because all four phosphorus atoms participate in the delocalisation of the negative charge of the ylid carbon atom.[85]

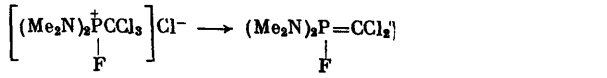


Symmetrical *P*-halogen-substituted carbodiphosphoranes (LXXX) were obtained by the dechlorination of the halogenophosphonium salts (LXXXI) and tris-(dimethylamino)phosphine.[86−88]



R = Me, X = F; R = Me, Et, n-Pr, X = Cl.

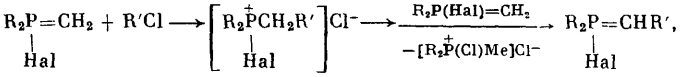
The dehalogenation of trichloromethylphosphonium salts with tris-(dimethylamino)phosphine gives *P*-halogenated ylids, containing a dichloromethylene group, in good yield.[47]



4. Other methos of synthesising *P*-halogenated ylids

Hydrogen atoms and trimethylsilyl groups on the α-carbon atom of *P*-halogenated ylids are distinguished by a high lability and are readily replaced by various groups on interaction with electrophiles. Consequently reactions of *P*-halogenated ylids, having hydrogen or silicon on the α-carbon atom, with various chlorine-containing electrophiles is a convenient means of obtaining new *C*-substituted *P*-halogenated ylids of more complex structure than the starting materials.

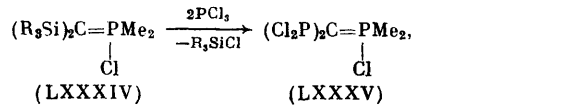
The reaction of *P*-chloro- and *P*-fluoroylids with chlorotrimethylsilane and with acid chlorides of carboxylic, carbonic and phosphoric acids proceeds readily. Intermediate phosphonium salts (LXXXII) substituted at the α-carbon atom are formed in this way, the dehydrochlorination of which with a second molecule of the starting ylid gives new *P*-halogenated ylids (LXXXIII).[2,9] Dehydrochlorination of the phosphonium salt (LXXXII) occurs more readily the greater the electron-accepting ability of the group R′. Yields of *P*-halogenated ylids (LXXXII) containing trimethylsily, acyl, alkoxycarbonyl or phosphino groups at the α-carbon atom are between 50–85%.[9,34,71,89]



(LXXXII) (LXXXIII)

Hal = Cl, F; R′ = Me_3Si, $R_2''P$, R″C(O), AlkOCO.

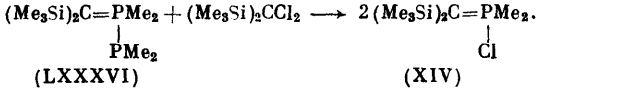
On reacting ylids (LXXXIV) with phosphorus trichloride in benzene at room temperature the Si–C bond is readily broken and *P*-chloroylids with two dichlorophosphine groups on the phosphorus atom (LXXXV) are formed in good yield.[90]



(LXXXIV) (LXXXV)

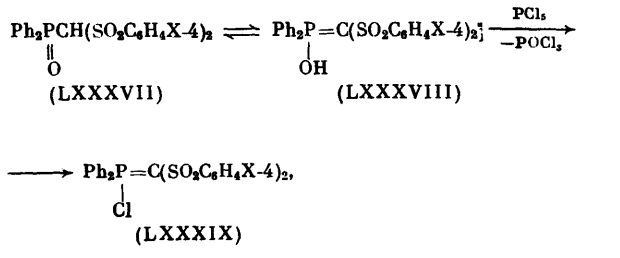
R_3Si = Cl_3Si, $Cl_2Si(CH_2SiCl_2)_2C$, $Me_2Si(CH_2SiMe_3)_2C$.

The ylid (LXXXVI) containing a very labile P–P bond is converted in good yield into the *P*-chloroylid (XIV) on reaction with dichloro-bis(trimethylsilyl)methane.[19]



(LXXXVI) (XIV)

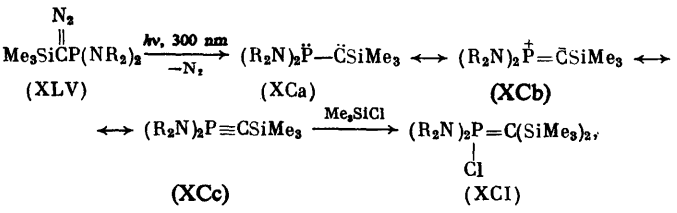
Ylids with OH groups on phosphorus (LXXXVIII), which are prototropic isomers of bis-(arylsulphonyl)methylphosphine oxides (LXXXVII), form *P*-chloroylids (LXXXIX) on boiling with phosphorus pentachloride in benzene.[68]



(LXXXVII) (LXXXVIII) (LXXXIX)

X = H, Me, OMe, Cl.

It has been reported that photolysis of phosphinodiazomethane (XLV) in benzene solution at room temperature in the presence of an excess of chlorotrimethylsilane gives the *P*-chloroylid (XCI) in almost quantitative yield.[91–94]

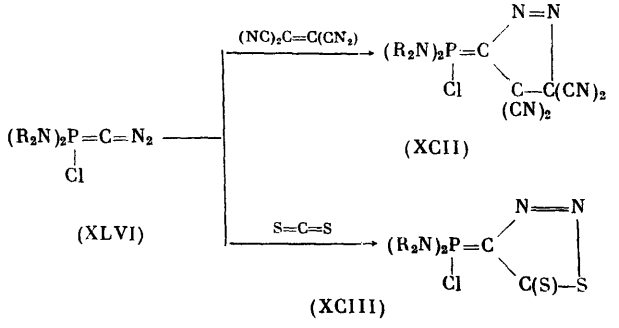


(XLV) (XCa) (XCb) (XCc) (XCI)

R = iso-Pr.

The carbene (XCa) is formed on photolysis of phosphinodiazomethane and has a certain degree of 'phospha-acetylene' character as a result of the contribution of resonance structures to the ground state of the molecule. The presence of an electron-rich trivalent phosphorus atom on the electron-deficient carbon atom determines the displacement of the lone pair of electrons on the phosphorus atom towards the carbon atom with addition of its electrons to the octet and formation of the dipolar structure (XCb), which makes the 1,2-addition of trimethylchlorosilane possible. Recently Bertrand and co-workers succeeded in obtaining the phosphinocarbene (XC) in stable form by flash photolysis of the phosphinodiazomethane (XLV) at 250 °C in vacuum and purified it by vacuum distillation [b.p. 75–80 °C (0.01 mmHg)].[94,95] According to its NMR spectrum the phosphinocarbene (XCI) partially possesses the structure of a phosphorovinyl-ylid and consequently enters into the various addition and cycloaddition reactions typical of a multiple bond. A characteristic is the low field ^{13}C chemical shift, δ_C 142.754 p.p.m., a doublet with $^1J_{CP}$ 159.3 Hz belonging to a two-coordinated carbon atom.

The phosphacumulene-ylid (XLVI) reacts with tetracyanoethylene and also with carbon disulphide forming *P*-chloroylids (XCII) and (XCIII) in quantitative yield. These are products of [2+2]-cycloaddition at the diazo group.[61,62]

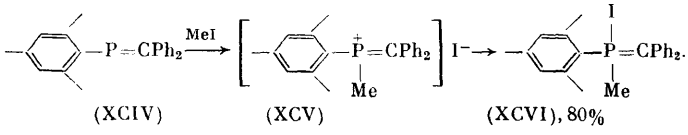


(XLVI) (XCII) (XCIII)

R = iso-Pr.

Bickelhaupt and co-workers have shown that phospha-ethylene (XCIV) is converted into β-iodoylid (XCVI) in 80% yield on heating with an excess of methyl iodide in the dark. The reaction occurs by 1,1-addition of methyl iodide to the phosphorus atom. They

proposed that the phosphoniumalkene (XCV) is formed by nucleophilic attack of methyl iodide at the two-coordinated phosphorus atom and is then converted into the ylid (XCVI).[96]



(XCIV) (XCV) (XCVI), 80%

III. Physical and spectral properties

P-Halogenated ylids are crystalline substances or liquids. The majority of *P*-halogenated ylids are colourless and only some of them are coloured. For example, fluorenylids are intensely red and diphenylmethylids are an orange colour.[34]

The stability of *P*-halogenated ylids to heat depends on their structure. The most stable *P*-halogenated ylids store well in an inert atmosphere and are distillable in vacuum without decomposition. The less stable *P*-chloroylids can be distilled in vacuum in many cases and store well in an inert atmosphere at 0 °C. The still less stable *P*-bromoylids are successfully isolated and purified only in those cases when they contain electron-accepting groups at the α-carbon atom. The *P*-iodoylids are unstable compounds. Possibly for this reason only one stable *P*-iodoylid (XCV) is known which has been isolated and identified.[96] The stability of *P*-halogenated ylids is increased with increasing electron-accepting properties of the substituents at the α-carbon atom, reducing the negative charge centred on this atom, and also by introducing bulky substituents (e.g. t-butyl, isopropyl, diisopropylamino groups, etc.) at the phosphorus and carbon atoms, creating steric hindrance. Such substituents screen the P=C bond and hinder nucleophilic attack of the ylid carbon atom onto the positively charged phosphorus atom.

The structure of *P*-halogenated ylids has been investigated in detail by various spectroscopic methods including IR, UV, ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR and also by X-ray structural analysis.[18,19,72,80,85]

The ^{31}P chemical shifts for *P*-halogenated ylids are very close to the δ_P values of the corresponding phosphonium salts and depend on the substituents at phosphorus (to a larger degree) and carbon (to a lesser degree), viz. δ_P 50–70 (R = Alk_2N), 40–60 (R = Me), 90–100 (R = iso-Pr), 95–110 (R = t-Bu), 55 (R = Ph), 60 p.p.m. (R = AlkO). Signals of phosphorus nuclei of *P*-halogenated ylids are doublets, $^{1}J_{PF}$ 1000–1100 Hz.

The ^{13}C chemical shifts of the P=C carbon atom are in the region of δ_C 20–80 p.p.m. and are doublets with large values of the $^{1}J_{CP}$ constant of 150–200 Hz, which is in agreement with the carbanion character of the ylid carbon atom.

X-Ray structural analysis shows the effective delocalisation of the negative charge of the ylid carbon atom of *P*-halogenated ylids with atoms or groups of atoms added to it. The ylid portion of the majority of molecules studied has a planar structure. For example, in the molecule of (LXXV) the N–P–C–P–N bond system lies in one plane and the C–P–C angle is 134.8°.[80] The lengths of phosphorus–carbon multiple bonds of *P*-halogenated ylids are shortened.

IV. Chemical properties

P-Halogenated ylids are highly reactive entering into numerous conversions. The chemical properties of *P*-halogenated ylids are very unusual due to the presence in the molecule of a highly polar P=C bond and a labile halogen atom. Characteristic reactions for *P*-halogenated ylids occur with carbonyl compounds, proceeding with retention of the phosphorus–carbon bond, chlorotropic rearrangements in the P–C diad, conversions with reduction in the phosphorus coordination number and several other properties not met in the case of triphenylphosphonium ylids.

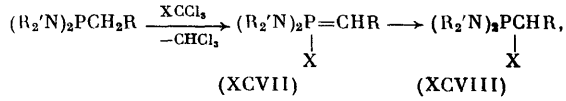
1. Conversions of *P*-halogenated ylids proceeding with a reduction in the phosphorus coordination number

A significant negative charge is centered on the α-carbon atom of *P*-halogenated ylids weakening the P–Hal bond. Consequently transition of a tetracoordinated into a tricoordinated phosphorus atom, which is extremely rare in organophosphorus chemistry, becomes possible.

a) Halogenotropy in the P–C diad

Halogen atoms in the P–C diad are capable of migrating between the phosphorus and carbon atoms as a result of which the interconversion of *P*-halogenated ylids and α-haloalkylphosphines may be effected. Various examples were shown in section II of conversions of α-haloalkylphosphines into *P*-halogenated ylids which were accompanied by the transition of three-coordinated into four-coordinated phosphorus and, as is known, give a significant energy gain.[97] It must be borne in mind that in this the electrically neutral four-coordinated α-carbon atom is converted into a negatively charged three-coordinate ylid carbon atom. But such a transition is one the other hand energetically unprofitable. Consequently changes in energies of coordination transitions of phosphorus and carbon atoms are mutually counterbalanced by one another. Therefore by varying the substituents on the phosphorus and carbon atoms of the P–C diad it is possible to influence the thermodynamic stability of the halogenotropic isomers and to create conditions for 1,2(C→P)- or 1,2(P→C)-migrations of halogen atoms.

1,2(P→C)-Chlorotropic rearrangements have been detected in the case of *P*-chloroylids containing diisopropylamino groups on the phosphorus atom. Bis-diisopropylamides of alkylphosphonous acids react with carbon tetrachloride with the formation of *P*-chloroylids (XCVII) stable in solution below 0 °C, which were observed by ^{13}C and ^{31}P NMR spectra. Above 0 °C, ylids (XCVII) are converted quantitatively into α-chloroalkylphosphines (XCVIII).[57,99] The reaction of bis-(diisopropylamino)alkylphosphines with bromotrichloromethane proceeds analogously. The resulting *P*-bromoylids (XCVII) are converted into the α-bromoalkylphosphines (XCVIII) significantly more rapidly than are the corresponding *P*-chloroylids. Nonetheless they were observed by ^{31}P NMR. α-Haloalkylphosphines (XCVIII) were isolated as crystalline substances in good yield.



(XCVII) (XCVIII)

X = Br, Cl; R = H, Me, n-Pr, iso-Pr, R′ = iso-Pr.

Bis-(diisopropylamino)methylphosphines with an excess of CCl_4 or $CBrCl_3$ in ether at 0 °C give *P*-halogenated ylids (XCIX) which readily rearrange into dihalomethylphosphines (C).[57]

$$(R_2N)_2PMe \xrightarrow[-CHCl_3]{XCCl_3} (R_2N)_2P(X)=CH_2 \xrightarrow[-CHCl_3]{XCCl_3} (R_2N)_2P(X)=CHX \longrightarrow$$

(XCIX)

$$\longrightarrow (R_2N)_2PCHX_2,$$

(C)

X = Br, Cl, R = iso-Pr.

Chlorotropic migrations (CI)⇄(CII) depend on the substituent at the carbon atom of the P–C diad in such a way that electron-accepting substituents (Ph, $SiMe_3$) favour a displacement of the chlorotropic equilibrium to the side of *P*-chloroylids (CI) but electron-donors (H, Me, n-Pr, iso-Pr) favour the side of chloroalkylphosphines (CII).[98–101]

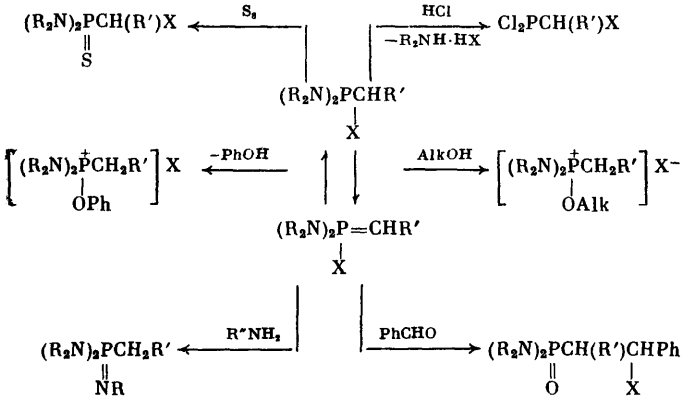
$$(R_2N)_2P(Cl)=CHR' \rightleftharpoons (R_2N)_2PCHR'(Cl)$$

(CI) (CII)

R = iso-Pr; R' = H, Me, n-Pr, iso-Pr, Cl, Br, Ph, $SiMe_3$.

The α-chloroalkylphosphines (CII) display chemical properties characteristic of both compounds of trivalent phosphorus and of *P*-halogenated ylids, as a result of which they are considered as 'masked' *P*-chloroylids.[58,98] The chemical properties of α-chloroalkylphosphines (CII) correspond to the existence of a reversible phosphorus–carbon diad chlorotropy (C)⇄(CII). As is shown in Scheme 6, the α-haloalkylphosphines (CI), being compounds of trivalent phosphorus, add sulphur with the formation of α-haloalkylthiophosphonic acid derivatives and are split at the P–N bond by hydrogen chloride giving acid chlorides of phosphonic acid.[58] Like *P*-halogenylids, the α-haloalkylphosphines (CI) add alcohols and phenols with the formation of R-oxyphosphonium salts, they react with primary alkylamines and aniline being converted into imidophosphonic acid derivatives and give 2-chloroalkylphosphonic acid derivatives on reaction with carbonyl compounds.[58,98,101]

Scheme 6



X = Br, Cl; R = iso-Pr; R' = H, Alk, Cl, Br.

Kinetic measurements, carried out with ^{31}P NMR, showed that the 1,2(P→C)-chlorotropic rearrangement obeyed a first order reaction rate equation exactly at various concentrations of *P*-chloroylid and at various temperatures. The rate constant for the rearrangement increased in proportion to the increase in ionising ability of the solvent: $CH_3CN > Cl_2CHCHCl_2 > CHCl_3 > CH_2Cl_2 \gg C_6H_6 > C_6H_{14}$. Based on the kinetic characteristics and on the activation parameters, it was established that the 1,2(P→C)-chlorotropic rearrangement proceeds through the formation of phosphonium cation (CIII) resulting from dissociation of the ylid at the P–Cl bond. Stabilisation of the phosphonium cation was achieved by effective delocalisation of the positive charge by branched diisopropylamino groups.[58,100]

$$(R_2N)_2P(Cl)=CHR \longrightarrow [R_2N)_2P^+=CHR\ Cl^-] \longrightarrow (R_2N)_2PCHR(Cl),$$

(CIII)

R = iso-Pr.

Kinetic investigations of the reverse 1,2(C→P)-chlorotropic rearrangement have been carried out using the chloromethylphosphine (CIV) as an example.

$$t\text{-}Bu(R_2N)PCH_2Cl \rightarrow t\text{-}Bu(R_2N)P(Cl)=CH_2$$

(CIV) (CV)

R = n-Bu.

Compound (CIV) is stable in nonpolar solvents (diethyl ether, hexane) however it is readily converted into ylid (CV) in dissociating solvents of the type of acetonitrile > tetrachloroethane > chloroform > dichloromethane. Kinetic investigations showed that the 1,2(C→P)-chlorotropic rearrangement of (CIV)→(CV), just like the 1,2(P→C)-chlorotropic rearrangement, obeyed a first order reaction rate equation. Analysis of the activation parameters for the rearrangement (E_a 77 kJ mol^{-1} and $\Delta S^{\neq}$ −67 kJ K mol^{-1}, at 30 °C in benzene + 15% chloroform) and the dependence of the rate constants on the dissociating ability of the solvent enabled a conclusion to be drawn on the decisive effect of solvolysis on the rearrangement, under the influence of which there was heterolytic fission of the C–Cl bond of chloromethylphosphine (Scheme 7).

Scheme 7

$$(R_2PCH_2Cl)_{solv} \rightleftharpoons (R_2PCH_2^+Cl^-)_{solv} \rightleftharpoons \left(R_2\overset{+}{P}=CH_2\ Cl^-\right)_{solv} \rightleftharpoons \left(R_2P(Cl)=CH_2\right)_{solv}$$

The values of the main kinetic characteristics and activation parameters for the 1,2(P→C)- and 1,2(C→P)-chlorotropic rearrangements proceeding through the same phosphonium intermediates and having a reversible character, were very close.

Dissociation of chloromethylphosphines at the C–Cl bond with the formation of phosphonium chlorides recalls the behaviour of chloromethylamines, existing in the ionised state as iminium

chlorides,[102] with the only difference that chloromethylphosphines are not as strongly ionised as chloromethylamines.

$$R_2NCH_2Cl \rightleftharpoons [R_2N{=}CH_2]Cl^-,$$

$$R_2PCH_2Cl \rightleftharpoons [R_2\overset{+}{P}{=}CH_2]Cl^-.$$

The formation of phosphinium salts from *P*-halogenated ylids is confirmed by various experimental data. *P*-Chloroylids (CVI) containing an alkoxy group on the α-carbon atom as a result of a 1,2(P→C)-migration of chlorine rearrange to α-chloroalkylphosphines or are converted into acylphosphines with loss of alkyl chloride. The structure of ylids (CVI) existing in solution below 0 °C was demonstrated by NMR and by chemical methods.[8,103]

$$(t\text{-Bu})_2PCH(R)OAlk \xrightarrow[-CHCl_2]{CCl_4} (t\text{-Bu})_2P(Cl){=}C(R)OAlk \rightarrow$$

(CVI)

$$\rightarrow \begin{cases} \xrightarrow{R=H} (t\text{-Bu})_2PCH(Cl)OAlk \\ \xrightarrow{R=Ph} (t\text{-Bu})_2PC(Cl){=}O\,Ph \end{cases}$$

Conjugation of the free electron pairs of oxygen with the P=C multiple bond stimulates fission of chloride ion and favours the formation of an intermediate phosphinium cation (CVII) which, depending on attack by chloride ion on the α-carbon or on the alkoxy group, is converted into an α-chloroalkylphosphine or eliminates alkyl chloride with the formation of acylphosphine. The formation of the cation is facilitated by effective delocalisation of the positive charge in the P–C–O triad.[8]

$$R_2P(Cl){=}C(R')-OAlk \longrightarrow \left[R_2\overset{+}{P}{=}C(R')-OAlk \leftrightarrow R_2P-C(R'){=}\overset{+}{O}Alk \right] Cl^-$$

(CVII)

b) Conversion into compounds of three-coordinate pentavalent phosphorus and two-coordinate phosphorus

Precisely the same as ylids with alkoxy groups (CVI) the *P*-chloroylids (CVIII) containing a dialkylamino group at the α-carbon atom are ionised with fission of the P–Cl bond. However in this case, as a result of more effective delocalisation of the positive charge in the P–C–N triad, stable phosphonium cations (CIX) are formed and were isolated as crystalline compounds.[104]

$$(t\text{-Bu})_2PCH_2NAlk_2 \xrightarrow[-CHCl_3]{CCl_4} (t\text{-Bu})_2P(Cl){=}CHNAlk_2 \rightarrow (t\text{-Bu})_2\overset{+}{P}{=}CH-NAlk_2\ Cl^-$$

(CVIII) (CIX)

Alk = Me, Et.

Compounds (CIX) are very soluble in polar and with difficulty in nonpolar solvents. They readily exchange chloride anion for perchlorate anion on reaction with sodium perchlorate in aqueous solution. The structure of phosphonium cations (CIX) was confirmed by the NMR spectroscopy. The values δ_P 21 p.p.m. corresponds to a three-coordinate phosphorus atom, and δ_C 207 p.p.m., a doublet with $^1J_{CP}$ 14 Hz to a sp^2-hybridised carbon atom on phosphorus. The δ_H signal at 10.5 p.p.m., a doublet with $^1J_{HP}$ 3 Hz, belongs to a proton on carbon in a P=C group.[8]

The synthesis of another phosphonium cation (CX) has been reported recently.[95]

$$\underset{(XC)}{(R_2N)_2\overset{+}{P}{=}\overline{C}SiMe_3} \xrightarrow{CF_3SO_2OSiMe_3} \underset{(CX)}{[(R_2N)_2\overset{+}{P}{=}C(SiMe_3)_2]CF_3SO_3^-},$$

R = iso-Pr.

On adding an excess of trimethylsilyl triflate to an ethereal solution of the carbene (XC) a salt-like product (CX) was isolated as a yellow crystalline substance. The ^{31}P chemical shift δ_P 76.5 p.p.m., a doublet with $^1J_{CP}$ 87.6 Hz, is in agreement with the proposed structure. The structure of the phosphinium cation (CX) was confirmed by X-ray structural analysis.

Various types of cations of three-coordinate pentavalent phosphorus are known which are obtained by the action of aluminium chloride on the acid chlorides of oxo-, thiono-, seleno- and iminophosphoric acids. Certain of them exist in the crystalline state as dimers as shown by X-ray structural analysis.[105]

$$Y_2P(Cl){=}X \xrightarrow{AlCl_3} [Y_2\overset{+}{P}{=}X]AlCl_4^- \rightleftharpoons \left[\begin{array}{c} Y \\ Y \end{array}\!\!>\overset{+}{P}<\!\!\begin{array}{c} X \\ X \end{array}\!\!>\overset{+}{P}<\!\!\begin{array}{c} Y \\ Y \end{array} \right] AlCl_4^-,$$

Y = Cl, NMe_2, NEt_2; X = O, NR, CR_2, S, Se.

It is assumed that phosphinium cations are generated by fission of the P–Cl bond in *P*-chloroylids by aluminium chloride. However this idea, with the exception of a short communication,[106] has not yet been developed.

$$(R_2N)_2P(Cl){=}CHSiMe_3 \xrightarrow{AlCl_3} [(R_2N)_2PCH(SiMe_3)]^+AlCl_4^-,$$

R = iso-Pr.

Appel obtained bis-(methylene)phosphoranes by dehalogenation of *P*-chloroylid (CXI) with a lithio-organic compound. These are compounds of three-coordinate pentavalent phosphorus containing two P=C multiple bonds. Bis-(methylene)phosphoranes (CXII) are stable compounds which enables their purification by crystallisation from inert solvents or by vacuum distillation.[107,108]

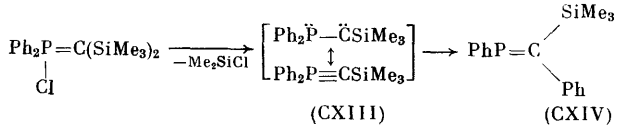
$$RPCl_2 \xrightarrow{LiCCl(SiMe_3)_2} RP[CCl(SiMe_3)_2]_2 \longrightarrow \underset{(CXI)}{RP(Cl)(Cl){=}C(SiMe_3)_2} \longrightarrow$$

$$\xrightarrow{LiCCl(SiMe_3)_2} \underset{(CXII)}{RP{=}C(SiMe_3)_2}$$

R = Alk, Ph, AlkO, AlkS, Alk_2N.

Conversions of *P*-chloroylids are also known which occur with reduction of the phosphorus coordination number to two. Thermolysis of a *P*-chloroylid containing two trimethylsilyl groups

on the α-carbon led to the formation of the phospha-alkene (CXIV). It was proposed that elimination of trimethylchlorosilane from the *P*-chloroylid initially gave a compound of three-coordinate pentavalent phosphorus, viz. the phospha-acetylene (CXIII), which was converted into a compound of two-coordinate phosphorus (CXIV) by migration of a phenyl group to the α-carbon atom (by a type of Curtius rearrangement).[5]



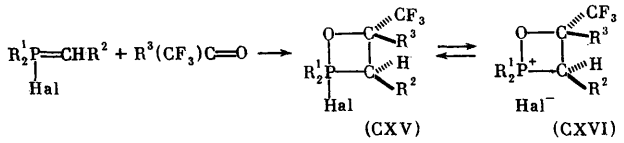
(CXIII) (CXIV)

2. Reactions of *P*-halogenated ylids with carbonyl compounds

The reactions of *P*-halogenated ylids with carbonyl compounds are highly original. *P*-Halogenated ylids react with carbonyl compounds 'anomalously' without fission of the phosphorus–carbon bond, which opens wide possibilities for the synthesis of every kind of phosphorus-containing alkene. In addition *P*-halogenylids form comparatively stable products by [2+2]-cycloaddition of the C=O group to the P = C$^-$ bond.

a) [2+2]-Cycloaddition reactions

P-Chloro- and *P*-bromoylids with ketones containing a trifluoromethyl group with the formation of stable [2+2]-cycloaddition products, 2-chloro- or 2-bromo-1,2λ^5-oxaphosphetanes (CXV) which were isolated in yields close to quantitative as crystalline substances or as liquids distillable in vacuum.[8,42,109,110]



(CXV) (CXVI)

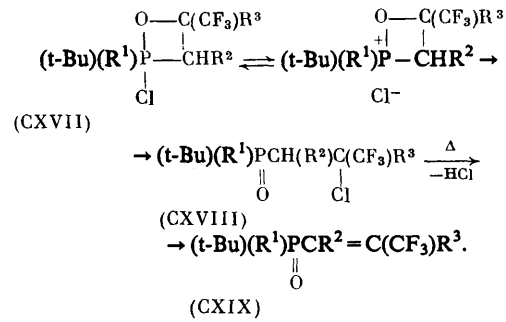
Hal = Br, Cl; R^1 = iso-Pr, t-Bu, Et$_2$N; R^2 = H, Me, Ph; R^3 = Ph, C$_6$H$_4$OMe-4, C$_6$H$_4$F-4.

The [2+2]-cycloaddition of *P*-halogenated ylids to ketones proceeds stereoselectively and leads predominantly to the formation of one of the possible diastereomers of 2-halooxaphosphetanes (CXV). It was established by NMR that the ratio of diastereoisomers of 2-halooxaphosphetanes containing asymmetric atoms at C(3) and C(4) was within the limits 95:5 to 90:10. If phosphorus is one of the asymmetric atoms in the molecule then the stereoselectivity of the reaction is low. The ratio of disastereomers after completion of the reaction was approximately 6:4. However on heating, as a result of permutational changes in the molecule, the ratio of diastereomers grew to a value of 95:5 in favour of the thermodynamically more stable diastereomer.[109,110]

2-Halo-1,2λ^5-oxaphosphetanes (CXV) dissociate in solution at the P–Hal bond with the formation of cyclic phosphonium salts (CXVI), as a result of which an equilibrium is established between the forms (CXV) ⇄ (CXVI) with five- and four-coordinate phosphorus atoms. Dissociation of 2-halooxaphosphetanes is enhanced with a reduction of the electron-accepting properties of substituents R^3 and also with a growth in solvent polarity.[110]

The stability of 2-halooxaphosphetanes changes in the same sequence of substituents R^3 at the endocyclic carbon atoms at position 4. The most stable are compounds, containing strong electron-accepting groups at C(4), drawing off electron density from the oxygen atom as a result of which the three-centre apical bond O–P–Hal is strengthened. 2-Chlorooxaphosphetanes (CXVII) containing two CF$_3$ groups at the α-carbon atom, are converted into vinylphosphonates (CXIX) with elimination of hydrogen chloride only at a temperature of 160–190 °C.[42,110]

2-Chloroxaphosphetanes, having less electron-accepting substituents at C(4), are dissociated to a large extent and correspondingly are converted into vinylphosphine oxide at a lower temperature. The 2-chlorooxaphosphatane (CXVII) (R^1 = t-Bu, R$_2$ = H, R^3 = C$_6$H$_4$OMe-*p*) is transformed quantitatively into the 2-chloroalkylphosphine oxide (CXVIII) at 20 °C in the course of several days. On heating compound (CXVIII) elimination of hydrogen chloride was observed and the (*E*)-olefin (CXIX) was obtained in high yield.[42]



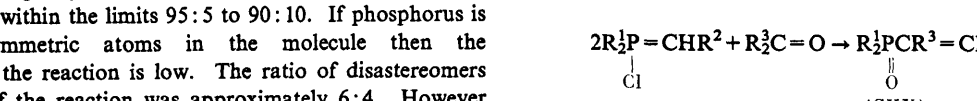
(CXVII) (CXVIII) (CXIX)

2-Bromooxaphosphetanes are more strongly dissociated at the phosphorus–halogen bond than 2-chlorooxaphosphetanes and consequently are less stable. Usually they are gradually converted at room temperature into vinylphosphine oxides.[110]

b) Synthesis of phosphorus-containing alkenes

P-Chloroylids are more reactive than triphenylphosphonium ylids. Unstabilised *P*-chloroylids (R^2 = H, Alk) are particularly reactive and react readily with alkyl- and arylaldehydes below 0 °C with the formation of various types of phosphorus-containing alkenes.[8]

The reaction of *P*-chloroylids with aldehydes or ketones proceeds at a ratio of starting materials of 2:1. In this one molecule of *P*-chloroylid is consumed in binding hydrogen chloride isolated in the reaction process, as a result of which a phosphonium salt (CXXI) is formed in addition to olefins (CXX) and is separated in solid form and is readily removed by filtration.[8,42]

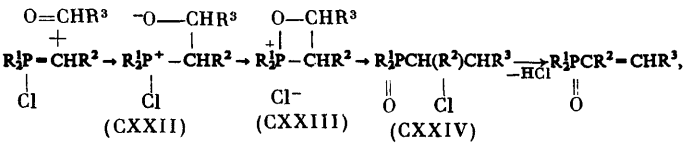


(CXX) (CXXI)

R^1 = Alk, Alk$_2$N; R^2 = H, Me, Ph; R$^3_2$C = Ph$_2$C, Ar(CF$_3$)C.

It was established by NMR spectroscopy at low temperature that *P*-chloroylids add aldehydes with the formation of zwitter-ions (CXXII), which are then converted into 2-chlorooxaphosphetanes (CXXIII). Compound (CXXIII) is strongly dissociated at the P–Cl bond and exists predominantly as cyclic phosphonium salt. They are stable in solution at −60 °C, but on increasing the temperature are

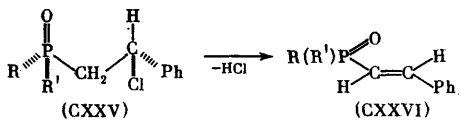
readily rearranged into 2-chloroalkylphosphine oxides (CXXIV). Compounds (CXXIV) are dehydrochlorinated by an excess of the initial *P*-chloroylid with the formation of vinylphosphine oxides.



(CXXII) (CXXIII) (CXXIV)

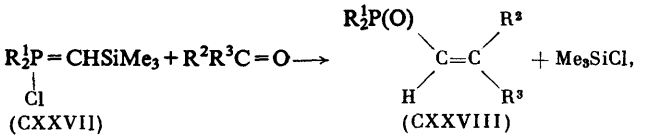
R^1 = Alk, Alk_2N; R^2 = H, Alk, Ph; R^3 = Alk, Ar.

In several cases the reaction of *P*-chloroylids with aldehydes occurs with the formation of 2-chloroalkylphosphine oxides (CXXIV) which are stable at room temperature and were purified by crystallisation from nonpolar solvents. On heating they lose hydrogen chloride and are converted in high yield into vinylphosphine oxides of (*E*)-configuration. 2-Chloroalkylphosphine oxides (CXXV) are usually obtained as *threo*-diastereomers and only in comparatively rare cases was a mixture of two diastereomers formed.[111] However elimination of HCl from these diastereomers occurs stereoselectively with the formation of only (*E*)-vinylphosphine oxides (CXXVI).



(CXXV) (CXXVI)

C-Silicon-containing *P*-chloroylids (CXXVII) react with aldehydes and ketones with elimination of chlorotrimethylsilane. The reaction proceeds at a ratio of initial reactants of 1:1 and gives vinylphosphine oxides (CXXVIII) in high yield.[112]

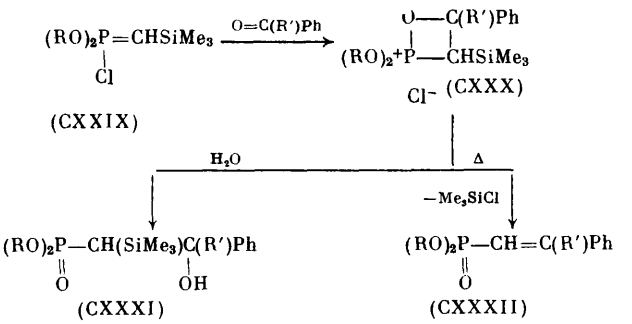


(CXXVII) (CXXVIII)

R^1 = Alk, AlkO, Alk_2N; R^2 = H, CF_3; R^3 = Alk, $C_6H_4R^4$-*p*; R^4 = H, OAlk, Cl, Br, CHO, CH=CHP(O)R_2.

Various aldehydes and ketones and dialdehydes react with *P*-chloroylids (CXXVII). On reacting *P*-chloroylids (CXXVII) with dialdehydes, one or two carbonyl groups were successfully 'olefinated' depending on the initial ratio of reactants. In all cases olefins of (*E*)-configuration were obtained with a high degree of stereoselectivity.[8,112]

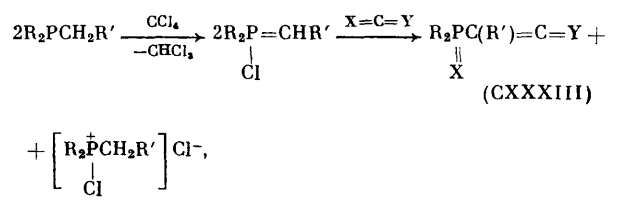
The cyclic phosphonium salts (CXXX) were obtained by reacting *P*-chloroylids (CXXIX) with aldehydes and ketones. Compounds (CXXX) were hydrolysed with the formation of 2-hydroxyalkylphosphine oxides (CXXXI) and on heating were converted into (*E*)-vinylphosphine oxides (CXXXII).[40]



(CXXIX) (CXXX) (CXXXI) (CXXXII)

R = Et, iso-Pr; R′ = H, CF_3.

There is significant preparative interest in the reaction of *P*-chloroylids with carbon dioxide, carbon disulphide and isocyanates leading to the formation of phosphorus-containing ketenes, thioketenes and ketenimines.[33,42] The reaction of *P*-chloroylids with CO_2, CS_2 and RNCO proceeds at an initial ratio of starting materials of 2:1 and leads to the formation of phosphorus-containing heterocumulenes and chlorophosphonium chlorides. Phosphorus-containing heterocumulenes (CXXXIII) are conveniently obtained preparatively by a 'one-pot' method without isolating *P*-chloroylids by sequentially treating tertiary alkylphosphines with CCl_4 initially and then with CO_2, CS_2 or RNCO.[9,33,42,113]

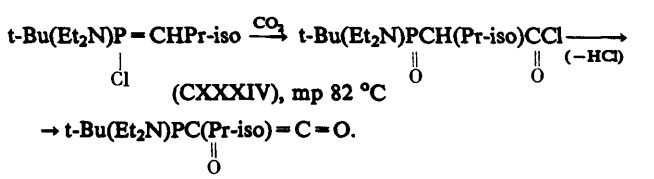


(CXXXIII)

X = O, S; Y = O, S, NPh; R = t-Bu, Et_2N; R′ = H, Me, n-Pr, iso-Pr.

The phosphorus-containing heterocumulenes (CXXXIII) are distinguished by high stability on storage and on vacuum distillation, which is explained by the steric and electronic influence of the phosphoryl grouping. For example, thioketenes are unchanged on storage for several years.

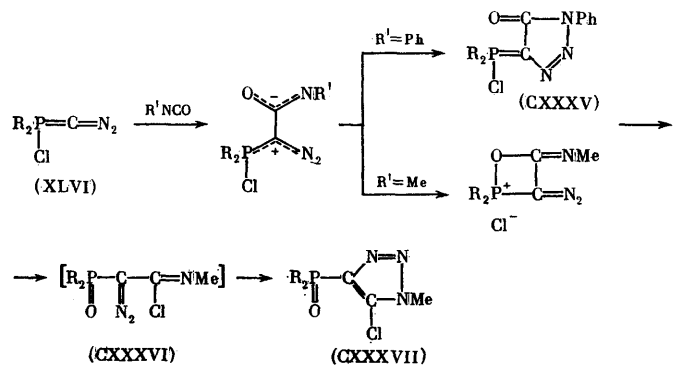
It was established that the reaction of *P*-chloroylids with CO_2 proceeds through the formation of acid chlorides (CXXXIV) of carboxylic acids which were isolated in a pure state and were then converted by the action of triethylamine into phosphorus-containing ketenes.[9]



(CXXXIV), mp 82 °C

Phosphorus-containing ketenes and thioketenes are very reactive and enter into a variety of addition and cycloaddition reactions.[113]

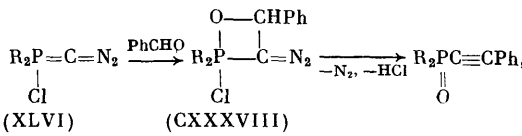
Phosphacumulene-ylids (XLVI) give addition products at the diazo group with isocyanates, the *P*-chloroylid (CXXXV) being formed with phenyl isocyanate and the triazenophosphonate (CXXXVI) with methyl isocyanate. It was proposed that initially nucleophilic attack of the ylid carbon atom on the carbonyl carbon gives a betaine, which depending on the relationship of the oxygen atom (or NR group) to nitrogen or phosphorus, is converted into products of 1,4- and 1,5-cyclisation. The unstable 1,4-cycloadduct is transformed initially into an α-diazoimine as a result of a 1,3-halogenotropic shift and then into the triazenophosphonate (CXXXVII).[61]



(XLVI) (CXXXV) (CXXXVI) (CXXXVII)

R = (iso-Pr)$_2$N.

Benzaldehyde gives the 2-chlorooxaphosphetane (CXXXVIII) with the ylid (XLVI) which readily eliminates hydrogen chloride and a molecule of nitrogen being converted into an acetylene phosphonate. This reaction is the first example of the direct formation of a carbon–carbon triple bond under the conditions of the Wittig reaction.[61]



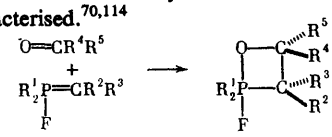
(XLVI) (CXXXVIII)

R = iso-Pr.

c) Reaction of *p*-fluoroylids with carbonyl compounds

P-Fluoroylids add carbonyl compounds with the formation of 2-fluoro-1,2λ^5-oxaphosphetanes (CXXXIX) which are distinguished by their higher stability compared with 2-chlorooxaphosphetanes. Usually 2-fluorooxaphosphetanes are successfully isolated without difficulty and are purified by vacuum distillation. The stability of 2-fluorooxaphosphetanes is explained by the higher electronegativity of the fluorine atom in comparison with the electronegativities of chlorine and bromine. Consequently the P–F bond of 2-fluorooxaphosphetanes is stable and they do not dissociate with the formation of cyclic phosphonium salts as do the 2-chlorooxaphosphetanes.[70]

Various stable products of [2+2]-cycloaddition of 2-fluoroylids with alkyl and aryl isocyanates, alkyl and aryl ketones, carbon dioxide and isocyanates have been synthesised and characterised.[70,114]

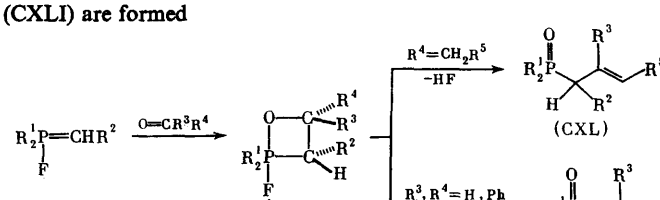


(CXXXIX)

R^1 = Alk, Ph, Alk$_2$N; CR^{2}R^3 = CH$_2$, CHAlk, CAlk$_2$, CHPh, CHSiMe$_3$, CCl$_2$, CBr$_2$; CR^{4}R^5 = C=O, C=NPh, CHAlk, CAlk$_2$, CHPh, CPh$_2$, CH$_2$CH=CR$_2$.

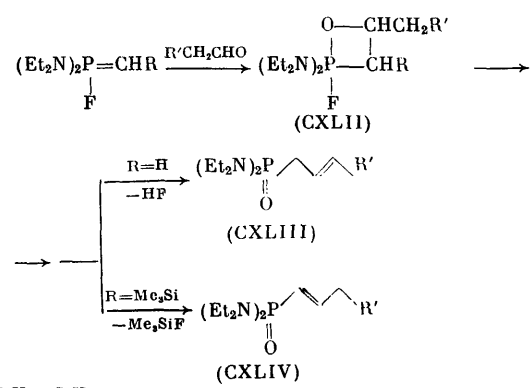
The reaction of *P*-fluoroylids with aldehydes and ketones is stereoselective and gives predominantly *threo*-diasteroisomers of 2-fluorooxaphosphetanes (CXXXIX),[64,70] the structure of which was demonstrated by spectroscopic methods. The content of *erythro*-diastereomers was small and did not exceed 5–10%.

On heating, 2-fluorooxaphosphetanes lost hydrogen fluoride and depending on structure were converted into allyl- or vinylphosphine oxides.[64,70,114,115] Allylphosphine oxides (CXL) are formed when there are hydrogen atoms on the carbon atom next to C(4) and a 1,4-elimination of HF can take place. If 1,4-elimination of HF cannot be effected because of structural features of the molecule than a 1,2-elimination of HF occurs and vinylphosphine oxides (CXLI) are formed



(CXL) (CXLI)

The reaction usually leads to the formation of isomers of allylphosphine oxides containing the maximum number of alkyl groups on the multiple C=C bond and is a convenient means of obtaining them. The route of the reaction may be guided in the direction of forming vinylphosphine oxides (CXLIV), which are isomers of the allylphosphine oxides (CXLIII), if a trimethylsilyl group is introduced at position C(3) of the oxaphosphetane ring. Silicon-containing 2-fluorooxaphosphetanes (CXLII) are obtained by the reaction of *C*-silyl-substituted *P*-fluoroylids with aldehydes. 1,2-Elimination of Me$_3$Si from fluorooxaphosphetanes (CXLII) proceeds with the formation of stereochemically pure (*E*)-vinylphosphine oxides (CXLIV).[64,114]

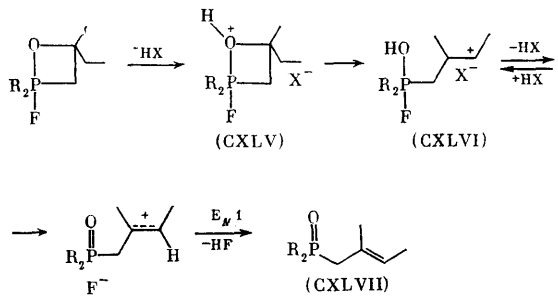


(CXLII) (CXLIII) (CXLIV)

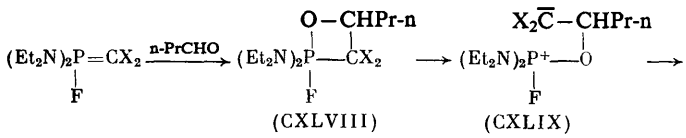
R = C$_5$H$_{11}$, C$_6$H$_{13}$.

Lewis and Brønsted acids actively catalyse the conversion of 2-fluorooxaphosphetanes into allylphosphine oxides. In addition the reaction is autocatalytic since the hydrogen fluoride eliminated catalyses the transition of 2-fluorooxaphosphetanes into allylphosphine oxides.[114] Acids protonate the oxygen atom of 2-fluorooxaphosphetanes with the formation of oxonium salts (CXLV), which readily convert into carbenium intermediates (CXLVI), the deprotonation of which under E_N 1 elimination conditions gives allylphohphine oxides (CXLVII) (Scheme 8). The formation of carbenium intermediates (CXLVI) was shown by chemical methods.[64,115]

Scheme 8



P-Halogenated ylids react with carbonyl compounds with the formation of phosphorus-containing alkenes as a rule. There is a single exception. 2-Fluorooxaphosphetanes (CXLVIII), containing chlorine or bromine atoms at C(3), decompose on heating with fission of the P–C bond and the formation of 1,1-diahloalkenes and fluorophosphine oxides. It is proposed that the electronegative halogen atoms favour transfer of the CX_2 group to an axial position as a result of which the phosphorus–carbon bond is broken and anion (CXLIX) is formed.[63,64]



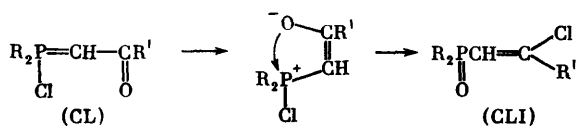
$\rightarrow X_2C{=}CHPr\text{-}n + (Et_2N)_2P(O)F,$

X = Br, Cl.

3. Conversions of *P*-halogenated ylids, containing C=O groups on the α-carbon

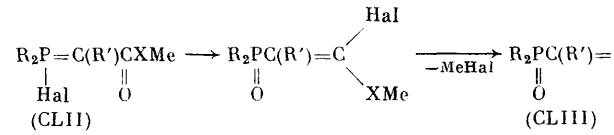
Conversions accompanied by transfer of the carbonyl oxygen to the phosphorus atom are characteristic of *P*-chloro- and *P*-bromoylids containing a carbonyl group at the α-carbon.

P-Chloroylids (CL) in which there is an acyl group at the α-carbon rearrange on heating into β-chlorovinylphosphine oxides (CLI). The rearrange-ments are effective intramolecularly by attack of the negatively charged oxygen atom of the C=O group on the positively charged phosphorus atom.[116]



R = t-Bu, Alk_2N; R′ = Alk.

The conversion of *P*-halogenated ylids (CLII) containing an alkoxycarbonyl group at the α-carbon proceeds by an analogous reaction scheme. They are converted at room temperature or on gentle heating into phosphorylated ketenes with separation of alkyl halide.[39,41,117] *P*-Bromoylids (CLII) with a dimethylaminocarbonyl group at the α-carbon are more stable. However they also split off methyl bromide on heating to 100 °C and phosphorus-containing ketenimines are formed in good yield.[116]

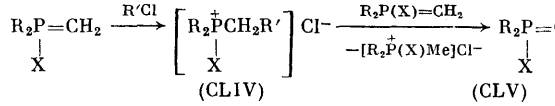


Hal = Br, Cl; X = O, NMe; R = iso-Pr, t-Bu, EtO, iso-PrO, Me_2N, Et_2N; R′ = Ph, CO_2Me.

4. Reactions of *P*-chloroylids with electrophiles

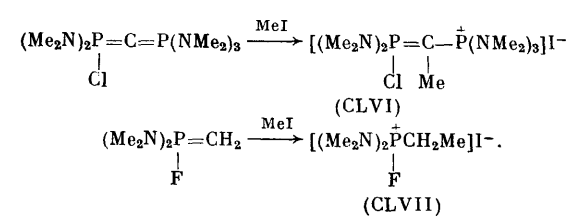
The P=C bond of *P*-halogenated ylids is strongly polarised as a result of which a significant negative charge is centred on the carbon atom. Consequently *P*-halogenated ylids readily add various electrophiles with the formation of the corresponding phosphonium salts or betaines.

Phosphonium salts (CLIV) formed by reaction of *P*-halogenated ylids with such electrophiles as chlorotrimethylsilane, chloroformates, or acid chlorides of carboxylic and phosphoric acids and having an electron-accepting substituent R′ at the α-carbon are readily dehydrochlorinated by the initial *P*-halogenated ylid, being converted into *C*-substituted *P*-halogenated ylids (CLV).[8,33,71]



X = Cl, F; R = Alk, Alk_2N; R′ = Me_3Si, RP(Cl), $(Me_2N)_2P$, $CF_3C(O)$, MeOCO, EtOCO.

At the same time the phosphonium salts (CLVI) and (CLVII) formed by the interaction of *P*-halogenated ylids with alkyl halides are not dehydrohalogenated by the initial ylid even in excess because the alkyl group reduces the lability of the hydrogen atoms at the α-carbon.[75,84,118]



P-Halogenated ylids usually add Lewis acids (boron trifluoride, aluminium chloride) with the formation of betaines (CLVIII).[33] It has however been reported that phosphinium cations may be

formed by this.[100] The reaction of *P*-chloroylids with gaseous chlorine leads to the formation of phosphonium salts (CLIX).[88]

$$\underset{\underset{X}{|}}{R_2P{=}CHR'} \xrightarrow{MX_3} \underset{\underset{X}{|}}{R_2\overset{+}{P}CH(R')}\bar{M}X_3,$$

(CLVIII)

$$\underset{\underset{Cl}{|}}{(R_2N)_2P{=}CCl_2} \xrightarrow{Cl_2} \left[\underset{\underset{Cl}{|}}{(R_2N)_2\overset{+}{P}CCl_3}\right]Cl^-,$$

(CLIX)

X = Cl, F.

5. Reactions of *P*-halogenated ylids with nucleophilic reagents

a) Nucleophilic replacement of the halogen atom

The labile halogen atom of *P*-halogenated ylids, located on the electrophilic, positively charged phosphorus atom is capable of ready replacement by various groups on interaction with nucleophiles. Preparatively these reactions are very simple and open wide possibilities for the synthesis of ylids containing practically any substituent at phosphorus.

P-Chloro- and *P*-bromoylids react smoothly with lithium and magnesium alkyls in organic solvents below 0 °C and form *P*-alkyl-substituted phosphorus ylids in good yield.[18,35,116]

$$\underset{\underset{X}{|}}{R_2P{=}CR_2'} \xrightarrow[-MX]{AlkM} \underset{\underset{Alk}{|}}{R_2P{=}CR_2'},$$

R = Ph, Me, t-Bu; CR_2' = $CHSiMe_3$, $C(SiCl_3)_2$, $C(SO_2Ph)_2$; M = Li, MgBr.

The reaction of *P*-chloroylids with lithium phosphides proceeds readily. The *p*-chloroylid (XIV) containing trichlorosilyl groups on the α-carbon selectively exchanges the chlorine atom on phosphorus for a dimethylphosphine group on interaction with lithium dimethylphosphide. The trichlorosilyl groups are unaffected by this. In addition, during reaction of ylid (XIV) with lithium trimethylsilylmethylphosphide, the P–P-ylid (CLX) is formed which readily reacts with a second molecule of P–Cl-ylid and is converted into a double ylid with a P–P bond (CLXI).[119]

$$\underset{\underset{Cl}{|}}{Me_2P{=}C(SiCl_3)_2} \xrightarrow{R(Me)PLi}$$

(XIV)

$$\longrightarrow R(Me)P{-}P(Me)_2{=}C(SiCl_3)_2 \xrightarrow[-Me_3SiP(Me)Cl]{R = Me_3Si} (Cl_3Si)_2C{=}\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{P}}{-}\underset{\underset{Me}{|}}{\overset{\overset{Me}{|}}{P}}{=}C(SiCl_3)_2,$$

(CLX) (CLXI)

R = Me, Me_3Si.

P-Chloroylids exchange the chlorine atom for an amino group on interaction with primary and secondary alkylamines, ammonia or aniline. Ylids (CLXII) containing a hydrogen atom at nitrogen exist in a state of prototropic tautomeric equilibrium with the corresponding iminophosphoranes (CLXIII).[9,43,120–122]

$$\underset{\underset{Cl}{|}}{R_2P{=}CR_2'} \xrightarrow[-Alk_2NH\cdot HCl]{Alk_2NH} \underset{\underset{Alk_2N}{|}}{R_2P{=}CR_2'}$$

$$\underset{\underset{Cl}{|}}{R_2P{=}CR_2'} \xrightarrow[-R''NH_2\cdot HCl]{R''NH_2} \underset{\underset{R''NH}{|}}{R_2P{=}CR_2'} \rightleftharpoons \underset{\underset{R''N}{||}}{R_2PCHR_2'}$$

(CLXII) (CLXIII)

Symmetrically substituted hexa(dimethylamino)carbodiphosphorane (CLXV) is obtained in high yield by the reaction of *P*-chlorocarbodiphosphorane (CLXIV) with lithium dimethylamide in toluene at 20 °C.[84]

$$\underset{\underset{Cl}{|}}{(Me_2N)_2P{=}C{=}P(NMe_2)_3} \xrightarrow[-LiCl]{Me_2NLi} (Me_2N)_3P{=}C{=}P(NMe_2)_3.$$

(CLXIV) (CLXV)

The labile halogen atom of *P*-chloro- or *P*-bromoylids are successfully replaced by alkoxyl, phenoxyl or thioalkyl groups by the action of alcohols, phenols or mercaptans in the presence of triethylamine, which leads to various types of *P*-substituted phosphorus ylids (CLXVI). Ylid (XIII, n = 2) exchanges the chlorine atom on phosphorus and one chlorine atom on silicon by methoxyl groups on reaction with methanol in the presence of diethylamine with the formation of ylid (CLXVII).[18]

$$\underset{\underset{Hal}{|}}{R^1{}_2P{=}CR^2_2} \xrightarrow[-Et_3N\cdot HHal]{R^3XH+Et_3N} \underset{\underset{R^3X}{|}}{R^1{}_2P{=}CR^2_2},$$

(CLXVI)

R^1 = Alk, AlkO, Ph; CR^2_2=$C(CO_2Me)_2$, $CHCO_2Me$, $C(SO_2Ph)_2$;

R^3 = Alk, Ph; Hal = Br, Cl; X = O, S,

$$\underset{\underset{Cl}{|}}{Me_2P{=}C(SiCl_3)_2} \xrightarrow[-Et_2NH\cdot HCl]{MeOH+Et_2NH} \underset{\underset{MeO}{|}}{\overset{\overset{SiCl_3}{|}}{Me_2P{=}C{-}Si(OMe)Cl_2}}.$$

(XIII) (CLXVII)

Ylids (CLXVII) are formed in high yield on interacting *P*-chloroylids with sodium alkoxides or phenoxides. It is necessary to carry out the reaction at an equimolar reactant ratio since an excess of alkoxide or phenoxide converts ylids (CLXVIII) into phosphine oxides.[11]

$$\underset{\underset{Cl}{|}}{R_2P{=}CR_2'} \xrightarrow{RONa} \underset{\underset{RO}{|}}{R_2P{=}CR_2'} \xrightarrow[-R_2O]{RONa} \left[\underset{\underset{O}{||}}{R_2P{-}\bar{C}R_2'}\right]Na^+ \xrightarrow{H^+} \underset{\underset{O}{||}}{R_2PCHR_2'},$$

(CLXVIII)

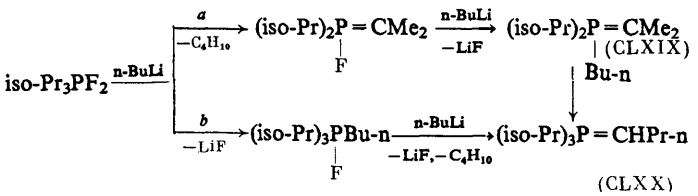
R' = SO_2Ph.

The hydrolysis of *P*-halogenated ylids proceeds extremely readily and even on interaction with moist air or the calculated amount of water they are, as a rule, converted in quantitative yield into the corresponding phosphine oxides. The hydrolysis reaction is

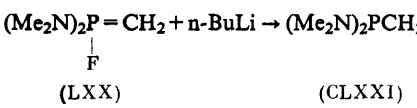
frequently used to prove the structure of *P*-halogenated ylids.[11,61,65,67,96,122]

There is no known convincing example of the replacement of fluorine by an alkyl group when interacting *P*-fluoroylids with lithium alkyls. It has been reported[123] that difluorotriisopropylphosphorane reacts with butyllithium with the formation of butylidenetriisopropylphosphorane (CLXX). It has been proposed that the reaction proceeds by route *a*, i.e. through the formation of *P*-fluoroylid, exchanging the fluorine atom for butyl, and subsequent rearrangement of the resulting ylid (CLXIX). However it is certain that there was no *P*-fluoroylid as intermediate. Consequently it may be suggested that the reaction proceeds by route *b* (Scheme 9).

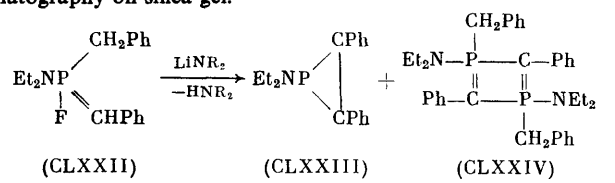
Scheme 9



Furthermore on reacting *P*-fluoroylids directly with lithium alkyls replacement of fluorine by the alkyl group does not occur. For example, the reaction of *P*-fluoroylid (LXX) with butyllithium gives a compound of trivalent phosphorus (CLXXI) only.[80]



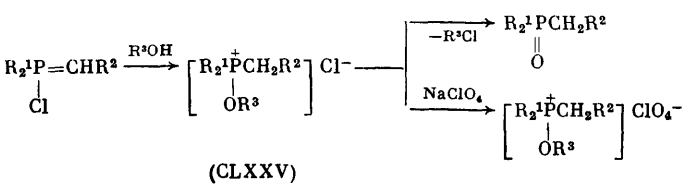
No product of nucleophilic replacement of fluorine was observed on reaction of *P*-fluoroylid (CLLXXII) with lithium amide. Only a mixture of diphenylphosphirane (CLXXIII) and diphosphetane (CLXXIV) was isolated which was separated by preparative chromatography on silica gel.[12]



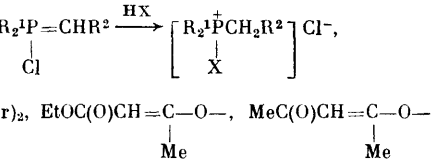
R = $SiMe_3$.

b) Addition reactions

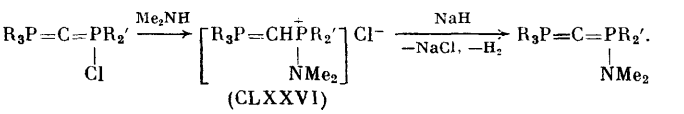
P-Chloroylids add alcohols in ether or pentane below 0 °C, being quantitatively converted into unstable alkoxyphosphonium salts (CLXXV), difficult to achieve by other routes. Salts (CLXXV) were isolated as colourless crystalline substances or viscous liquids insoluble in nonpolar solvents. On heating, alkoxyphosphonium salts (CLXXV) were converted into phosphine oxides, and on reaction with aqueous sodium perchlorate solution gave stable alkoxyphosphonium perchlorates.[58,124]



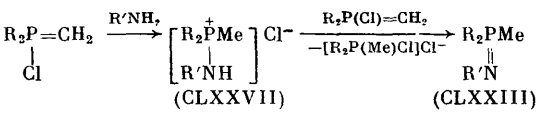
Phosphonium salts differing in structure were obtained on reacting *P*-chloroylids with hydrogen halides, hydrazoic acid, ketoenols and CH-acids. Yield of phosphonium salts were very high in all cases so the given reaction may serve as a preparative method.[33,34,124]



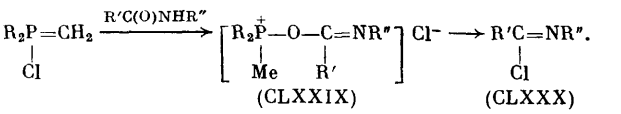
P-Chloroylids add alkyl- and dialkylamines with the formation of aminophosphonium salts. Phosphonium salts [of type (CLXXVI)] containing a dialkylaminogroup may be converted into *P*-substituted phosphorus ylids by the action of butyllithium or sodium hydride.[9,43,84,125]



Phosphonium salts (CLXXVII), resulting on interaction of *P*-chloroylids with primary alkylamines or aniline, are dehydrochlorinated by an excess of the initial *P*-chloroylid, being converted into iminophosphoranes (CLXXVIII). The reaction of *P*-chloroylids with amides of sulphonic and phosphoric acids also leads to the formation of iminophosphoranes (CLXXVIII).[125]



The reaction of *P*-chloroylids with carboxylic acid amides proceeds through the formation of an *O*-phosphorylated intermediate (CLXXIX) as a result of which imidoyl chlorides (CLXXX) are formed. Compounds (CLXXX) having substitutents R′ = Ph_2CH or R″ = H are readily dehydrochlorinated by the initial *P*-chloroylids to ketenimines or nitriles. In this case *P*-chloroylids show themselves to be dehydrating agents.[125]



* * *

Such are the main achievements in the chemistry of phosphorus *P*-halogenated ylids. It may be concluded from the material considered that the accessibility, convenient means of preparation and the ability to take part in various conversions, justify the attention which is paid to *P*-halogenated ylids and guarantee further progress in this region of the chemistry of organophosphorus compounds.

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