Russian Chemical Reviews **66** (3) 225 – 254 (1997) © 1997 Russian Academy of Sciences and Turpion Ltd

UDC 547.241

Methods of preparation of *C*-substituted phosphorus ylides and their application in organic synthesis

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Abstracts. Methods of preparation of phosphorus ylides substituted at the carbon atom of the P = C group with atoms of various elements and their application in organic synthesis are systematised and generalised. The bibliography includes 508 references.

I. Introduction

During recent years the chemistry of phosphorus ylides substituted at the carbon atom of the P = C group with atoms of various elements has been extensively developed.[1–14] Owing to these studies, phosphorus ylides containing elements of almost all groups of the Periodic Table have been synthesised, convenient preparative techniques of such ylides have been elaborated, and areas of their practical application in organic synthesis have been discovered. Chemical properties of *C*-substituted ylides are extremely diverse, which is due to the variety of the properties of the substituent elements and their different effects on the electron density distribution in ylide molecules.

The stability of *C*-substituted ylides has made them fascinating and convenient objects for theoretical studies, particularly, for the study of the nature of the element – carbocation bond. Depending on the nature of the element, this bond can be covalent or coordinate with various extents of negative charge transfer from the carbanion to the element.

$$R_3P{=}CH_2{-}E \longleftrightarrow R_3P^+{-}C^-H{\leftarrow}E \longleftrightarrow R_3P^+{-}CH{=}E^-.$$

Thus the elements of the higher periods which possess vacant orbitals (silicon, phosphorus, sulfur, arsenic, *etc.*) interact with the ylide carbanion by a $p_\pi - d_\pi$-mechanism, which results in a decrease in the electron density on the α-carbon atom and partial element – carbon double bonding. On the other hand, the elements with σ-donor properties, *e.g.* mercury, increase the electron density on the ylide carbon, thus increasing further the already high nucleophilicity of ylides. Also certain elements, especially transition metals, can form additional coordinate bonds with the ylide carbon atom. Sometimes, the distribution of the electron density in the ylide molecule is simultaneously affected by two or even three different factors, their relative contribution depending on the nature of the element and the surrounding ligands.

However, *C*-substituted phosphorus ylides attract particular interest as reagents for organic synthesis, and thus find increasing application in laboratory practice and industry. For example, *C*-silicon phosphorus ylides served as the basis for a series of preparative syntheses of medicinals, pheromones, and other types of phosphorus ylides. *C*-Phosphino phosphorus ylides are important ligands in transition-metal complexes. *C*-Halogeno phosphorus ylides are of interest for the preparation of halogenoalkenes. *C*-Nitrogen ylides are of considerable importance, especially in the synthesis of antibiotics. Active catalysts of alkene polymerisation based on *C*-transition metal-substituted ylides have been proposed. Complexes of phosphorus ylides with gold salts have been recommended for the treatment of certain diseases.

Unfortunately, numerous papers and patents on applications of *C*-substituted phosphorus ylides in various fields of organic synthesis have not hitherto been generalised. Only some topics concerning the synthesis and chemical properties of *C*-substituted phosphorus ylides have so far been discussed in monographs[4,5,8,13] and reviews.[1–3,10–12] However, the scope of the topics covered was very narrow, which is due to the specific character of these publications. Also, *C*-substituted phosphorus ylides are regarded there as a particular case of phosphorus ylides in general. The present review is meant to fill the gap; its aim is to demonstrate the broad synthetic potentialof the *C*-substituted phosphorus ylides and to disclose the effect of the nature of the element at the ylide carbon atom on their reactivity. The present report summarises the data on the application in organic synthesis of phosphorus ylides substituted at the α-carbon atom by atoms of elements of Groups I – VII of the Periodic Table.

II. Phosphorus ylides substituted at the α-carbon atom by atoms of Groups I – IV elements of the Periodic Table

The influence of σ-donor inductive and π-acceptor mesomeric effects of the elements is clearly exemplified by ylides † containing metals and metalloids of the main subgroups of Group I – IV of the Periodic Table at the α-carbon atom. The elements with *s*-donor properties increase the electron density on the ylide carbon atom, thus exchanging the nucleophilicity and reactivity of the ylides, as for instance, in the case of *C*-lithiated ylides. On the contrary, such elements with as germanium and silicon,

† Hereinafter, P-ylides are considered.

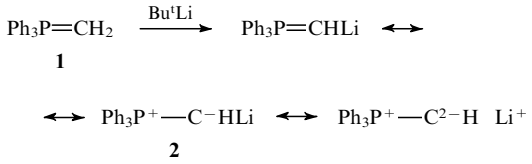
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Received 28 February 1996
Uspekhi Khimii **66** (3) 246 – 277 (1997); translated by M I Yanovskaya

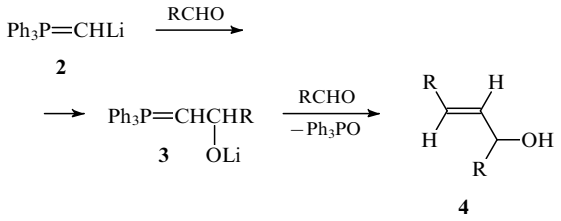
decrease the electron density on the α-carbon atom to form partial element–carbon double bonding by a $p_\pi - d_\pi$-mechanism which results in a lowering of the nucleophilicity of the ylide. In many cases, these two opposite effects act together, and their relative contribution depends on the nature of the element and the surrounding ligands. The chemistry of ylides containing lithium, boron, silicon, tin, and other elements at the α-carbon atom has recently received considerable attention.

1. Ylides containing Group IA and IIA elements

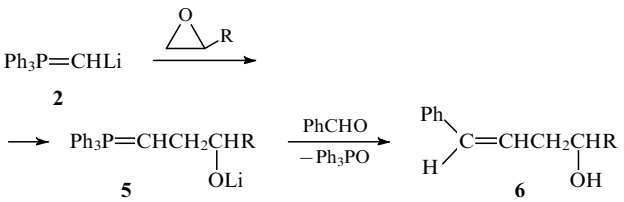
The synthesis of ylides containing alkali metals at the ylide carbon atom presents a challenging problem. According to the definition of A.Johnson [8] ylides are carbanions stabilised by the positively charged heteroatom. The introduction of Group I metals to the ylide carbon considerably increases the electron density on this atom: the ylide carbanion thus becomes a dicarbanion. Quantum-chemical calculations performed by McDowell and Streitwieser [15] and by Bestmann [16] demonstrated that lithium methylides should possess high nucleophilicity and reactivity. Due to the presence of a highly ionised C–Li bond they are associated in solutions. The theoretical calculations were confirmed experimentally by Corey and Kang,[17] who, pursuing the goal of preparation of 'hyperactive phosphorus ylides', have synthesised lithium triphenylphosphonium methylide **2** by reaction of *tert*-butyllithium with triphenylphosphonium methylide **1** in THF at −78°C to −40°C.



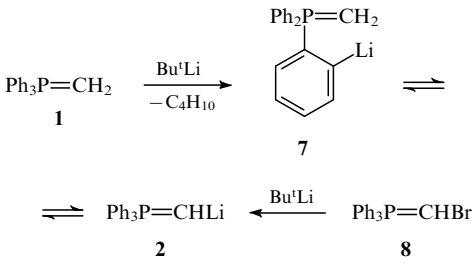
Ylide **2** manifests interesting chemical properties. It proved to be much more reactive than the initial triphenylphosphonium methylide. For example, the sterically hindered ketone, fenchone, does not react with triphenylphosphonium methylide on heating to 50°C but can be easily alkenated by lithium methylide at −50 °C to −20 °C, to give in 1h the exomethylene derivative (yield 87%).[17] Lithium methylide **2** exchanges the metal atom for different groups in reactions with chlorine-containing electrophiles. It could also be introduced into a double Wittig reaction with aldehydes (SCOOPY-alkenation). In reactions with aldehydes, lithium methylide **2** first forms alkoxide anions **3**, which can enter into the Wittig reaction with the second molecule of a carbonyl compound to form *trans*-allylic alcohols **4**.[17]



Reaction of α-lithiated ylide **2** with epoxides is even more interesting as regards synthetic applications: it also results in alkoxide anions **5** which react with aldehydes to give unsaturated alcohols **6**:

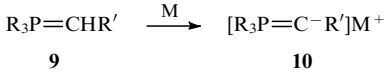


Another method of synthesis of the ylide **2** was proposed by Schlosser.[18, 19] He obtained ylide **2** by reaction of *C*-bromo ylide **8** with *tert*-butyllithium in hexane at −75 °C. However the spectroscopic characteristics of the ylide **2** obtained by Schlosser differed from those of the ylide prepared earlier by Corey.[17] Schlosser has proved by low-temperature NMR that the reaction of triphenylphosphonium methylide with alkyllithium is accompanied by ortho-lithiation of the benzene ring and the formation of the lithiated ylide **7**.[20]



Later, Corey [21] published a detailed procedure for the synthesis of methylide **2** by reaction of triphenylphosphonium lithium methylide **1** with *tert*-butyllithium and demonstrated the high reactivity of the reagent in reactions with various electrophiles. Corey rationalised (although, without convincing evidence) the difference in the spectral characteristics of the ylides prepared by the different methods by the existence of a tautomeric equilibrium **2** ⇌ **7**.[21]

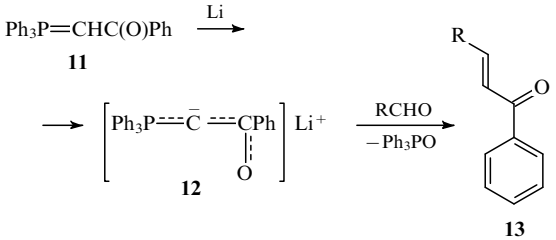
It should be noted that the 'hyperactive' *C*-lithium methylides did not find extensive synthetic application, which is due to the difficulties associated with their preparation. However, the metallated ylides **10** are relatively readily formed from the stabilised phosphorus ylides **9** with electron-withdrawing substituents at the α-carbon atom. This method is quite frequently used to increase the reactivity of phosphorus ylides.[22–27]



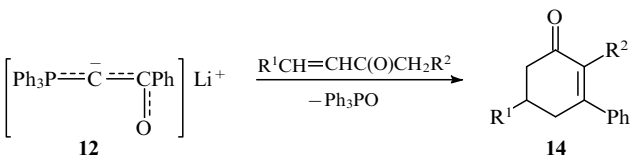
R′ = C(O)Ph, SO_2Ph, CN;

M = Li, Na, K.

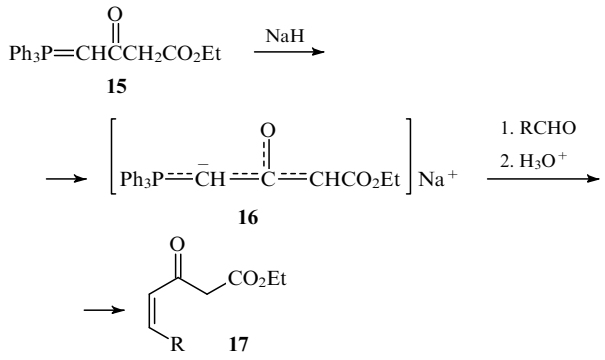
For example, triphenylphosponium phenacylide **11** reacts with aldehydes with difficulty and does not react with ketones at all. However, the highly reactive ylide **12,** which is formed in the reaction of **11** with lithium in HMPT-benzene mixture, alkenates aldehydes and ketones and gives the dienone **13**:[22, 23]



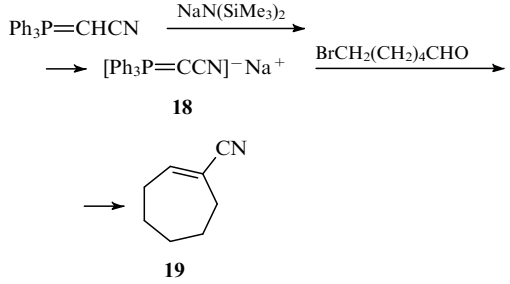
Lithium ylide **12** adds to α,β-unsaturated ketones according to the Michael reaction thus giving the substituted cyclohexanone **14**.[24]



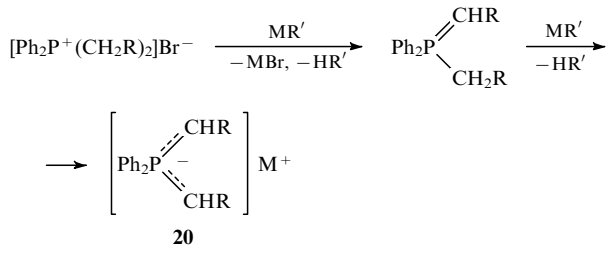
The stabilised ylide **15** demonstrates low reactivity towards aldehydes, while its sodium derivative **16** readily enters into the Wittig reaction with carbonyl compounds to give the conjugated unsaturated β-oxoesters **17** with *Z*-configuration.[25, 26]



The sodium derivatives of triphenylphosphonium cyanomethylide **18** synthesised by Bestmann and Schmidt [27] were used for the preparation of cyclic compounds *e.g.*, **19**.

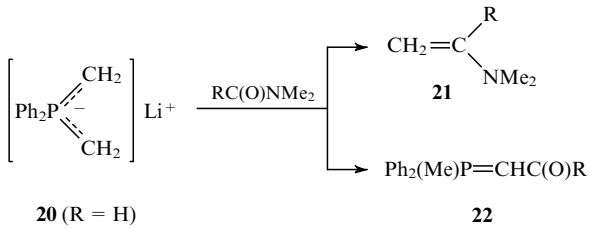


α-Carbon metallated ylide carbanions of the type **20**, which can be obtained by direct addition of 2 equiv. of a base to a phosphonium salt or of 1 equiv. of base to a phosphorus ylide, have recently found an important synthetic application. Some ylide carbanions **20** were isolated in the form of crystalline (colourless or coloured) compounds. Highly reactive tricarbanions were obtained by reaction of trialkylphosphonium ylides with excess of butyllithium.[14,21–38] The structures of ylide carbanions **20** were determined by X-ray structural analysis [39,40] and NMR spectroscopy.[40]

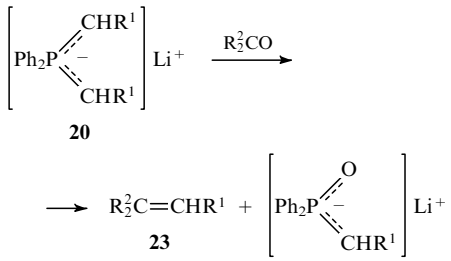


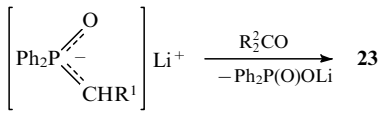
R = H, Ph, CN, CO_2Me;
MR′ = KH, NaH, $NaNH_2$, LiAlk.

Ylide anions can serve as the initial compounds for the synthesis of other *C*-substituted phosphorus ylides, because the metal atoms in them are readily substituted for various groups in reactions with electrophiles.[41] Some examples of such syntheses are given in the present review. Ylide anions react even with those electrophiles which do not react, or react with difficulty, with other phosphorus ylides. For instance, they alkenate carboxyamides to give enamines **21** or acyl ylides **22** depending on the reaction conditions. Analogously, the reaction of ylide anions **20** with carboxylic esters yields vinylic ethers or acyl ylides.[14]

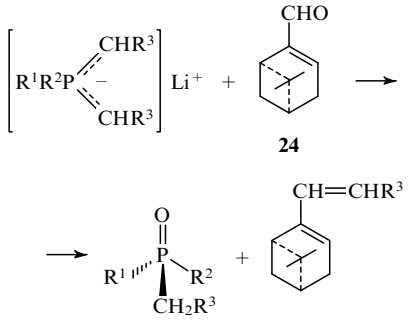


In their reactivity, ylide anions **20** are not inferior in rank to 'hyperactive' *C*-lithium methylides **2** synthesised by Corey and Schlosser, and they are considerably superior in availability and stability. Thus, ylide anions **20** (R = H) [42–53] react at room temperature with sterically hindered ketones (di-*tert*-butyl ketone, fenchone), which cannot be alkenated by triphenylphosphonium methylide. The ratio of ylide anion **20** to the carbonyl compound in this reaction is 1 : 2, therefore the yields of alkenes **23** can reach 180% – 200% with respect to the phosphorus ylide.[50]

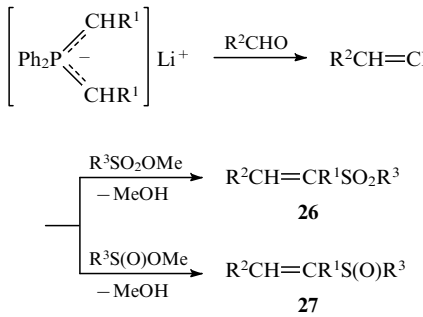




Reaction of ylide anions with chiral aldehydes **24** is accompanied by asymmetric induction, which results in optically active tertiary phosphine oxides **25**.[14]



Reactions of ylide anions with aldehydes and carbonates, thiocarbamates, isocyanates, carbodiimides, sulfonates and sulfinates are documented.[42–53] The two latter reactions give *E*-isomers of the unsaturated sulfones and sulfoxides **26** and **27**.[50,52]

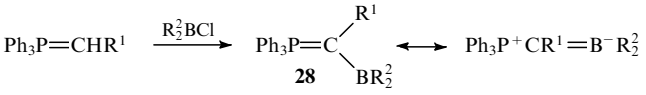


Free ylides containing Group II metals (beryllium, magnesium) at the α-carbon atom have not hitherto been obtained.

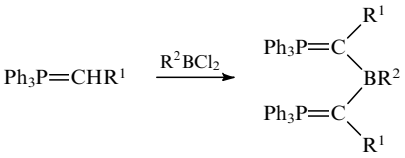
According to the quantum-chemical calculations for the molecule of the simplest ylide $H_3P=CHBeH$, it has planar structure.[16]

2. Ylides containing Group IIIA elements

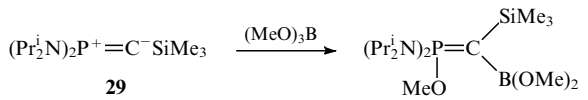
Compounds of elements of Group IIIA of the Periodic Table are strong Lewis acids and readily react with phosphorus ylides.[54–58] Reactions of triphenylphosphonium alkylides and benzylides with dialkylchloroboranes in benzene are accompanied by transylidation and result in α-dialkylboryl-substituted ylide **28**, which was isolated in the crystalline form. The NMR spectra of the ylide **28** indicate its mesomeric structure.[58–60] Phosphorus ylides react with alkyl-dichloroboranes to give bis(ylidyl) alkylboranes.



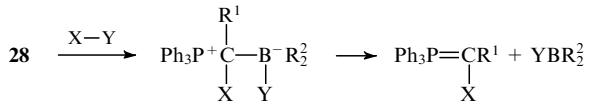
R^1 = Alk, $PhCH_2$.



C-Boron substituted ylide **30** was isolated by Bertrand *et al.*[61] by the addition of trimethyl borate to phospinecarbene **29**:

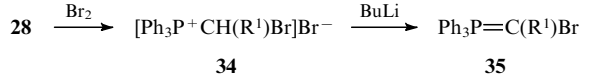


C-Boron substituted ylides **28** are characterised by high reactivity. They readily react with polar compounds X–Y to give ylides **32** and boranes *via* the intermediate onium complexes **31**.

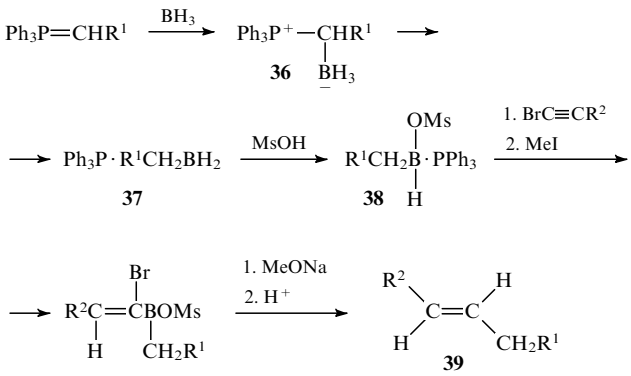


Reaction of the ylide **28**, (R = Alk), with deuteriomethanol gives deuterated ylides **33**, which has been used for the preparation of deuterated olefins. In reaction with bromine, the phosphonium salts **34** were obtained; when treated with butyllithium, they yield *C*-bromo-substituted phosphorus ylides **35**.[60]





Bestmann and coworkers [57, 62] have elaborated stereoselective methods for the synthesis of *E*-olefins, in particular pheromones, based on products of hydroboration of phosphorus ylides. The key step in the synthesis is the reaction of phosphorus ylide with borane. Betaine **36** thus formed undergoes rearrangement into the adduct of monoalkylborane with triphenylphosphine **37**. The latter is converted to *E*-olefin **39** with 99% stereochemical purity by a series of successive reactions.

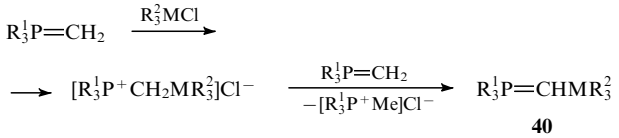


The attempts to synthesise phosphorus ylides with aluminium, gallium, indium, and thallium at the α-carbon atom have failed. The corresponding ylides were unstable and were converted into dimers and oligomers with the structure of metallacycles.[1, 3, 63–65]

3. Ylides containing Group IVA elements

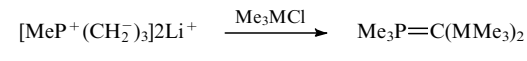
C-Silyl-substituted phosphorus ylides are of considerable preparative importance. The interest in these compounds is due to their availability, stability, and high reactivity. *C*-Germanium- and *C*-tin-substituted phosphorus ylides are less studied.

For the synthesis of *C*-substituted phosphorus ylides **40**, reactions of simple phosphorus ylides containing hydrogen atoms at the α-carbon atom with silicon, germanium, and tin halides (at a 2:1 ratio of the reagents) are most often used.[66, 67] Numerous examples of the synthesis of cyclic and acyclic *C*-silyl-substituted phosphorus ylides by this method have been reported.[1, 66–73]



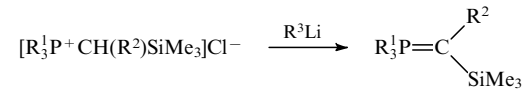
M = Si, Ge, Sn.

Reactions of carbanions **41** with organic, germanium, tin, and lead halides in a 1:1 ratio lead to the formation of *C*-mono- or *C*-dimetal-substituted phosphorus ylides **42** in high yields, which allow a more economical use of the initial phosphorus ylides.[74–77]

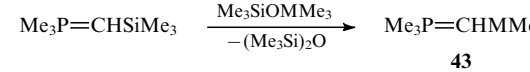


M = Ge, Si, Sn, Pb.

C-silyl-substituted ylides are often prepared by treating the corresponding phosphonium salts with organolithium compounds.[66–78]



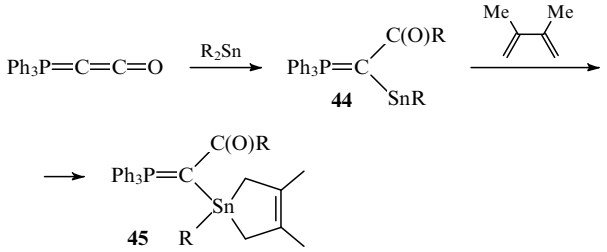
The reaction of trimethylphosphonium trimethylsilylmethylide with heterosiloxanes provides a simple and convenient route to germanium-, tin-, and lead-containing ylides **43.** The driving force of this reaction is the formation of disiloxane.[74, 79]



M = Ge, Sn, Pb.

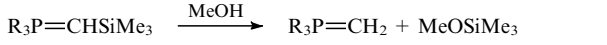
Silicon-containing phosphorus ylides can be also prepared by the reaction of phosphorus alkylides with silacyclobutane derivatives as a result of the insertion of the ylide carbon atom into the Si–C bond.[80–82]

Ketene ylides add the derivatives of two-coordinate tin, and are converted into ylides **44** in high yields. The latter readily enter into the [1 + 4]-cycloaddition reaction with dienes to form *C*-tin-substituted ylides **45**.[83]



Phosphorus ylides stabilised by silicon, germanium, and tin atoms are thermally stable and can be purified by distillation *in vacuo* or crystallisation from organic solvents. Silicon atoms at the ylide carbon atom reduce the basicity and nucleophilicity of the corresponding phosphorus ylides by stabilising the carbanion, which follows, for instance, from transylidation.[66, 78–82, 84] The stabilising effect of the silicon atom was previously attributed to the participation of *d*-orbitals in delocalisation of the negative charge on the ylide carbon atom.[1, 52, 66, 78] At present, however, the concept of electrostatic interaction and charge redistribution at the ylide carbon atom is more popular. It is suggested that increase in the space around the carbanion centre and the corresponding decrease in the repulsion between the high electron density on the ylide carbon atom and the valence shell bonding electrons of the elements of the third period should be considered.[85] The interaction between the phosphorus atom and the ylide carbon atom is regarded as a negative hyperconjugation, which results in the shift of electron density from the occupied *p*-orbital of the ylide carbanion to the vacant *s*-orbital of the phosphorus ligand. In this case, the role of the *d*-orbitals of the heteroatom is reduced to the polarisation function.[86] This point of view is supported by physicochemical studies and quantum-chemical calculations.[1, 52, 66, 87–91]

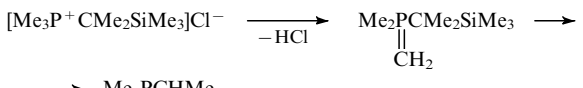
The trimethylsilyl group at the ylide carbon atom is characterised by high mobility and in this sense it may be considered as an analogue of the proton. *C*-silicon-substituted phosphorus ylides can be easily desilylated by reaction with hydroxyl compounds, *e.g.*, with alcohols, which is a convenient method for the preparation of ylides **46** of high purity.[74]

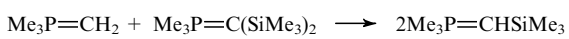


46

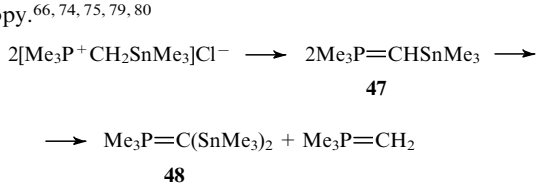
R = Alk, Ph.

The silyl groups in the *C*-silylated ylides migrate to other carbanionic centres of the molecule, thus lowering their nucleophilicity, which confirms the validity of the comparison of the silyl groups at the ylide carbon atom with the proton.[74] The migration of the silyl groups of the silylated ylides can occur by both intramolecular and intermolecular (disproportionation) processes.[66, 74, 79, 80]

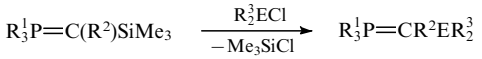




The Me_3Sn, Me_3Ge, Me_3Pb groups migrate equally readily in the molecules of phosphorus ylides. Therefore, *C*-monostannyl-substituted phosphorus ylides, which readily disproportionate into distannyl-substituted ylides **48**, could not be isolated in the individual form. They were identified only by spectroscopy.[66, 74, 75, 79, 80]

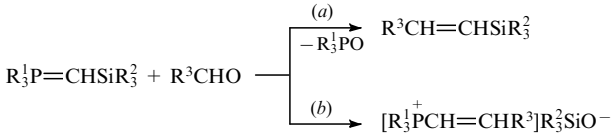


Trimethylsilyl groups at the α-carbon atom in phosphorus ylide **49** can be exchanged for various substituents by reactions with chlorine-containing electrophiles (chlorophosphines, phosphorus trichloride, chloroarsines, and chlorostibines) to yield phosphorus-, arsenic-, and antimony- substituted ylides **50**.[66, 74, 92–94] Different silicon-containing heterocycles,[52, 67] cyclic as well as acyclic bifunctional ylides[54, 63–65] were obtained by reaction of phosphorus ylides with chlorosilanes.

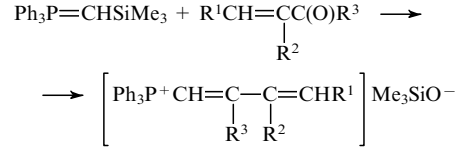


E = P, As, Sb.

C-Silyl-substituted phosphorus ylides react with carbonyl compounds both according to Wittig (route *a*) and Peterson (route *b*) pathways.[56, 95–97] A mixture of products is usually formed, and therefore this reaction is of limited synthetic importance.



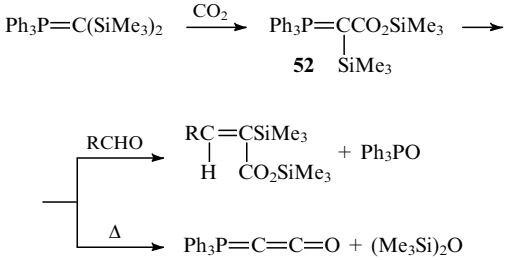
However in some cases the reactions of *C*-silyl-substituted phosphorus ylides with carbonyl compounds occur regioselectively. Thus, triphenylphosphonium trimethylsilylmethylide reacts with unsaturated carbonyl compounds to form conjugated phosphonium salts **51** in yields of 50% – 100%.[98]



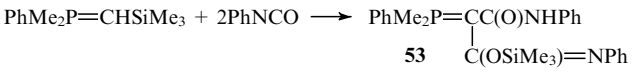
51

R^1 = H, Ph; R^2 = H, Me; R^3 = H, Me.

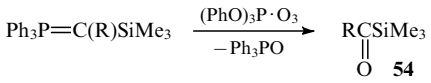
The reaction of bis-silylilated phosphorus ylides with carbon dioxide results in silylated acyl ylides **52**, which react with aldehydes to give silyl esters of α,β-unsaturated carboxylic acids in good yields and with high stereoselectivity. Thermolysis of ylides **52** results in ketene ylides.[99, 100]



The silylated phosphorus ylides give adducts with isocyanates **53**,[99] isothiocyanates, carbon disulfide.

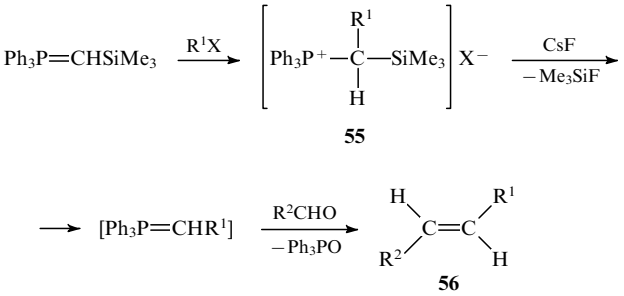


The acyl silanes **54** were obtained by oxidation of silylated ylides with the triphenyl phosphite-ozone adduct.[101–103]

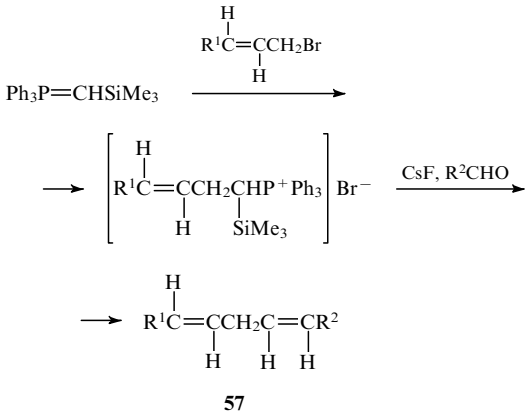


R = $SiMe_3$, Ph, 4-BrC_6H_4, 4-$MeOC_6H_4$.

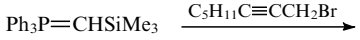
C-Silyl-substituted ylides exhibit high nucleophilicity in reactions with alkyl halides. The α-silyl-substituted phosphonium salts thus formed undergo smooth cleavage under the action of cesium fluoride with the formation of new phosphorus ylides.[104–108] This reaction has served as the basis for the development of convenient methods for the synthesis of diverse natural compounds, including homoconjugated pheromones.[105–108] for example, the reaction of triphenylphosphonium trimethylsilylmethylide with alkyl halides results in the *C*-silyl-substituted phosphonium salts **55**, which are converted to *Z*-alkenes **56** with elimination of trimethylsilyl fluoride in reactions with cesium fluoride in the presence of aldehydes.[95, 101]

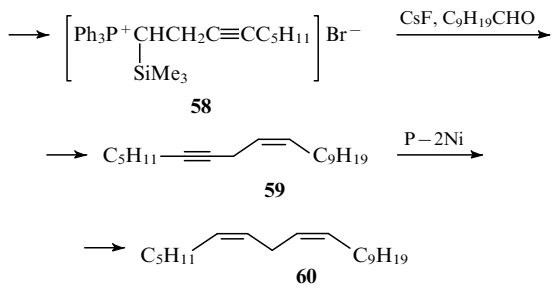


Alkylation of *C*-silyl-substituted ylides with allylic bromides was used in the preparation of *Z*,*E*-dienes **57**.[100]

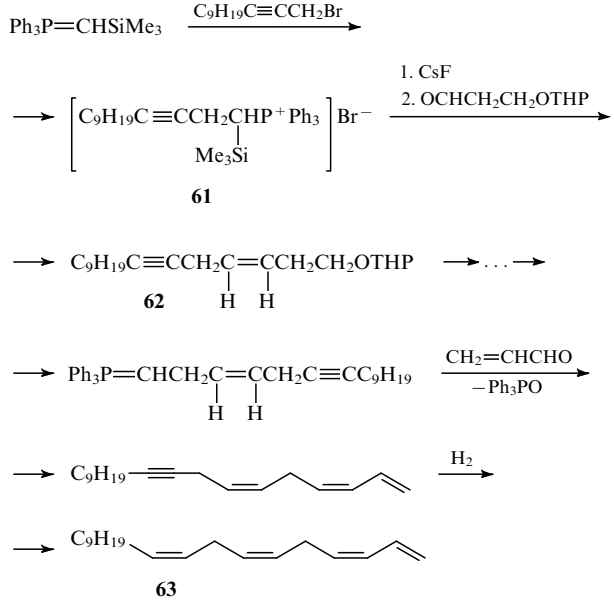


The alkylation of *C*-silylated ylides with acetylenic alkyl halides and subsequent desilylation of the phosphonium salts formed **58** by cesium fluoride in the presence of an aldehyde produces enynes **59** with a 98% *Z*-stereoselectivity. Reduction of the latter with P-2 nickel leads to *Z*,*Z*-dienes **60** containing C=C bonds separated by a methylene group.[100]



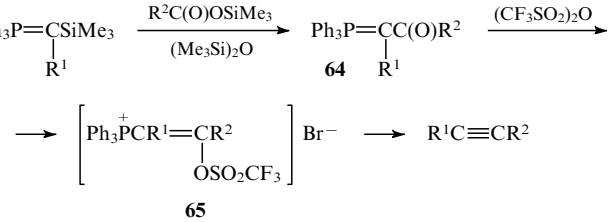


Using this reaction, Bestmann *et al.*[109, 110] obtained *Lepidoptera* pheromones in particular (*Z*,*Z*)-nonadeca-6,9-diene, which is a component of the *Bupalus piniarius* pheromone complex. The silyl-containing phosphonium salt **61** was obtained by the alkylation of triphenylphosphonium trimethylsilylmethylide by 1-bromododeca-2-yne; its desilylation by cesium fluoride in the presence of the aldehyde resulted in the enyne **62**. The latter was converted into tetraene **63** which is a component of *Operophtera brumata* pheromone.[100, 109]

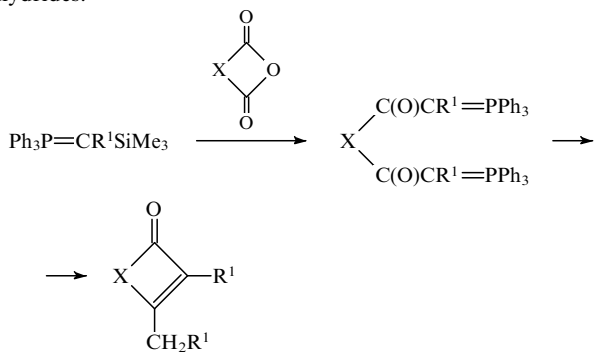


THP is tetrahydropyran-2-yl.

The reaction of *C*-silyl-substituted phosphorus ylides with trimethylsilyl carboxylates is accompanied by the elimination of hexamethyldisiloxane and therefore provides a convenient method for the synthesis of acyl ylides **64**. Acylylides **64** were used by Bestmann *et al.*[71, 102, 105, 106, 110] in the synthesis of *N*-*tert*-butoxycarbonyl-substituted merukatinone,[111] the starting material for the preparation of medicinals and also of 1,2-disubstituted acetylenes.[104] Synthesis of acetylenes involved the treatment of the acyl ylides **64** with trifluoromethane sulfonic anhydride and the *O*-substituted vinylphosphonium salts **65** formed were reduced with sodium amalgam.



The reaction of *C*-silyl-substituted phosphorus ylides with carboxylic acids proceeds in a similar manner. Cycloalkenones **66** containing 5–8 atoms in the ring were also prepared in high yields by reactions of *C*-silyl-substituted phosphorus ylides with acid anhydrides.[71]



R^1 = H, Alk; X = $(CH_2)_n$ (n = 2–5), CH_2OCH_2, CH_2SCH_2.

The reaction of *C*-silyl-substituted phosphorus ylides with silyl carboxylates has served as the basis for the development of a method of synthesis of ceramide, leucotriene A_4 [111–113] and the components of the *Manica ribuda* ant pheromone.[105]

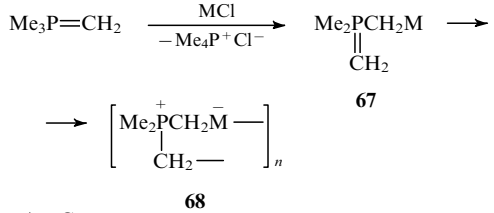
C-Silyl-substitued phosphorus ylides are used as ligands in transition metal complexes. Stable organometallic complexes, with metal–carbon bonds are formed in reactions of *C*-silyl-substituted phosphorus ylides with halides of copper(I), silver, gold, and their phosphine complexes.[114–116] Neutral complexes of iron, chromium, molybdenum, and tungsten were also synthesised.[117–122] Examples of *C*-silyl-substituted complexes are discussed in the next section and in reviews.[1–4]

III. Phosphorus ylides substituted at the α-carbon atom by transition metal atoms

Transition metal atoms at the ylide carbon atom substantially affect its negative charge, and consequently, the properties of the ylides. Three main mechanisms describing the interaction of transition metals with the ylide carbanion may be distinguished. Transition metals with *s*-donor properties, such as mercury, increase the electron density on the ylide carbon atom and enhance the nucleophilicity of the ylides. The electron density on the α-carbon atom decreases if the electron interaction of transition metals with the ylide carbanion, is of d_π–p_π type and the metal–carbon bond acquires partially double character. The relative contribution of these two opposite effects depends on the nature of the metal atom and the surrounding ligands. Finally transition metals can form additional coordinate bonds with the ylide carbon atoms, which may lead to dimerisation or oligomerisation of the organometallic complexes.

1. Ylides containing atoms of Group IB, IIB

The reactions of phosphorus ylides with copper, gold and silver halides are accompanied by the formation of the ylides **67**, which are easily dimerised into linear and cyclic complexes **68** due to high coordination number of the metal atoms.[115, 116, 123–125]

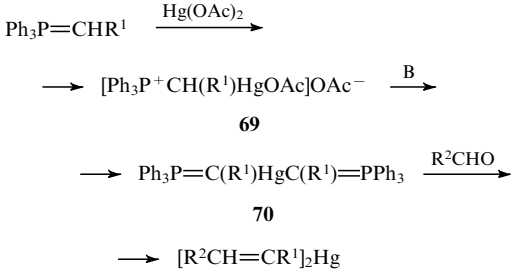


67

68

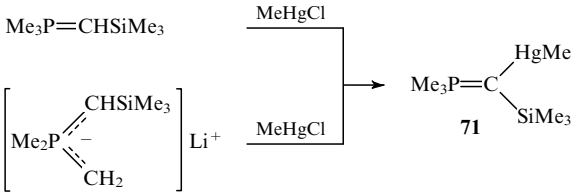
M = Ag, Cu.

Therefore it was impossible to isolate true ylides of the type **67**. In contrast, *C*-mercury-substituted phosphorus ylides are monomers. As has been mentioned, mercury atoms increase electron density at the ylide carbon due to their *s*-donor properties. Therefore, it is necessary that a second substituent at the α-carbon atom should compensate the electron-donating effect of the metal atom in order to stabilize mercurated ylides. Benzoyl, cyano- or methoxycarbonyl groups may serve as such substituents. For instance, phosphorus ylides $Ph_3P{=}CHR^1$ add mercuric acetate (or chloride) to form compounds **69**; their subsequent reaction with liquid ammonia or sodium methoxide leads to the *C*-mercurated phosphorus ylides **70**, which enter into the Wittig reaction with aldehydes.[126, 127]

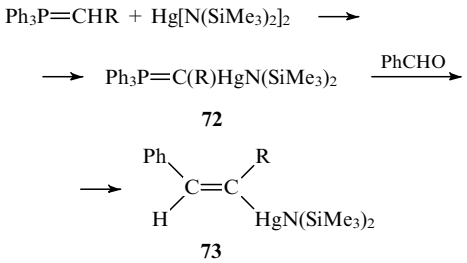


R^1 = CN, COPh, CO_2Me; B = NaOMe/MeOH, NH_3.

C-mercurated ylides **71** were obtained by the reaction of methylmercury chloride with an excess of *C*-silylated phosphorus ylide or its anion. The ylides **71** are stable liquids, which can be distilled *in vacuo*.[128]



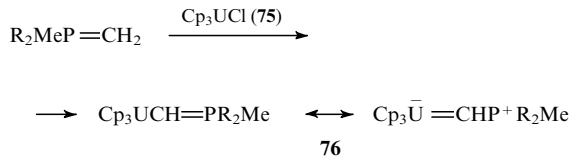
The *C*-mercury-substituted ylides **72,** which readily enter into the Wittig reaction to form the compounds **73,** were obtained by the reaction of phosphorus ylides $Ph_3P{=}CHR$ with mercury hexamethyldisilazide in inert solvents.[129]



Other Group IIB metals, zinc and cadmium, give ylide complexes of the type $[Ph_3PCR_2MCl]^+Cl^-$ (M = Zn, Cd) (**74**). Although the latter cannot be regarded as true ylides, they readily enter into the Wittig reaction and are widely used for the preparation of alkenes,[130–143] for instance, halogenoalkenes (see Section III.3).[54, 141–143]

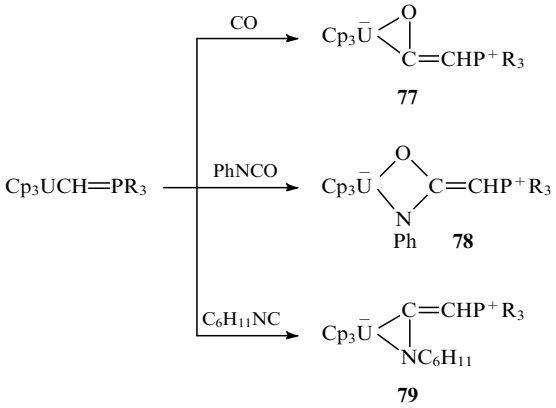
2. Ylides containing atoms of the actinide metals

The uranium complex Cp_3UCl **75** readily undergoes transylidation under the action of phosphorus ylides and their lithium derivatives to form pyrophoric, green crystalline complexes sensitive to moisture and atmospheric oxygen. On the basis of X-ray [144–146] and electron diffraction [147] data, the metallocene ylide structure **76** was ascribed to these compounds. Shortening of the U–C and C–P bonds indicates the delocalization of the negative charge in the U–C–P fragment.[145, 147]

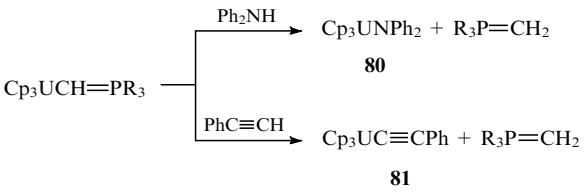


R = Me, Ph.

The metallocene ylides exhibit nucleophilic properties in reactions with polar unsaturated compounds.[146] Insertion reactions into the metal–carbon bond are characteristic of the uranocene ylides.[148]

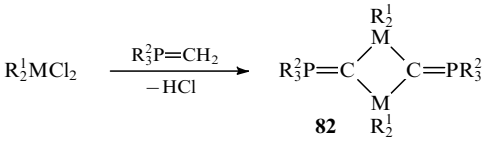


The uranocene ylides enter into metathesis reactions with compounds containing active hydrogen atoms.[149, 150]



3. Phosphorus ylides containing the Group IVB metal atoms

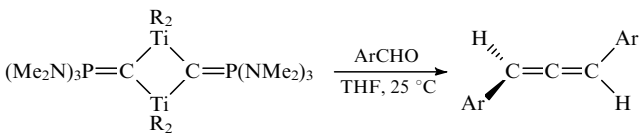
The group IVB transition metals (titanium, zirconium, and hafnium) stabilize the ylide carbanion as do the non-transition elements of this group, silicon and tin. Therefore, the preparation procedures, structures, and properties of phosphorus ylides, which contain metal atoms of Group IVA and IVB at the ylide carbon atoms, are similar. For instance, the four-membered cyclic bis-ylides **82** containing titanium or zirconium atoms at the ylide carbon atoms are obtained in the same way as cyclic silyl-substituted phosphorus ylides. The X-ray structural study of phosphorus ylides **82** has shown that they have a centrosymmetric structure.[116, 151, 152]



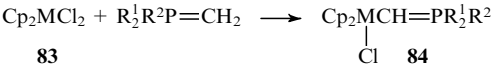
M = Ti, Zr, Hf;

R^1 = Me_2N, Cl, Et; R^2 = Me, Et_2N, $(CH_2)_2PMe_2$.

The titanium-containing cyclic ylides enter into the Wittig reaction with aromatic aldehydes to form the corresponding 1,3-diarylallenes which is a promising way for their synthesis.[153]



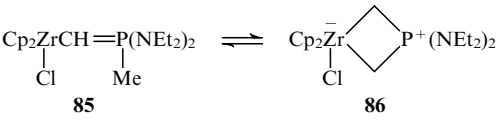
The transylidation reaction of bis(cyclopentadienyl)titanium, -zirconium, and -hafnium dihalides **83** with phosphorus ylides results in *C*-metallated ylides **84** containing halogen at the metal atom and exhibiting special chemical properties.[154–160]



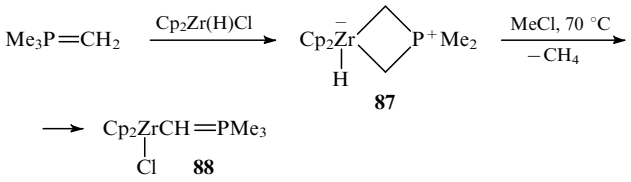
M = Ti, Zr, Hf;

R^1 = R^2 = Ph, Et_2N; R^1 = Et_2N, R^2 = Me.

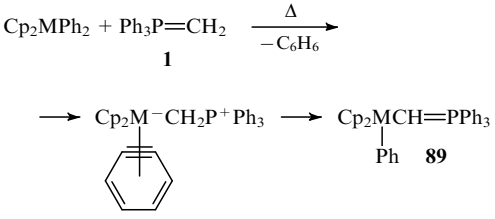
For example, the zirconocene ylide **85** exists in a ring-chain, prototropic tautomeric equilibrium with the chelate complex **86**. The position of the tautomeric equilibrium depends on the nature of the solvent.[156]



A zirconium hydride complex reacts with trimethylphosphonium methylide to give a four-membered cyclic ylide complex **87**, which is converted to zirconium ylide **88** on heating with methyl chloride.[156–158]

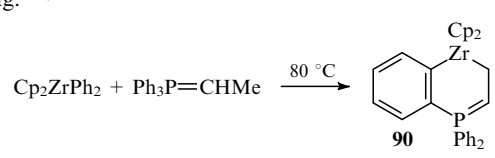


The metallocene ylides of titanium, zirconium and hafnium **89** are formed in the reactions of triphenylphosphonium methylide **1** with the thermally generated (η^2-ethene)- and (η^2-aryne)metallocenes. These reactions are accompanied by the replacement of the aryne ligand by phosphorus ylide and by a proton shift from the ylide methylene to the aryne ligand.[159, 160]

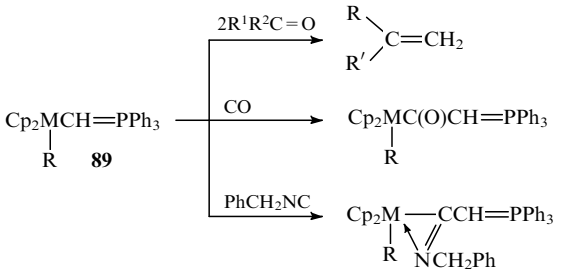


M = Ti, Zr, Hf.

When biscyclopentadienyl diphenylzirconium was heated with triphenylphosphonium ethylide, the cyclic metallocene ylide **90** was formed as a result of *ortho*-metallation of the benzene ring.[161, 162]



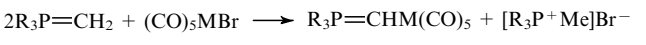
The nucleophilicity of the metallocene ylides **89** is lowered because of the high electron-acceptor ability of the transition metals.[161] Nevertheless, the metallocene ylides **89** react with ketones.[125] Carbon monoxide and isocyanides readily insert into the zirconium–carbon bond of ylides **89**.[160–165]



M = Ti, Zr, Hf.

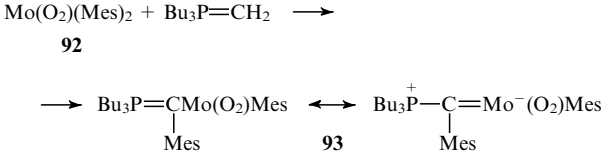
4. Ylides containing the Group VIB – VIIIB metal atoms

Phosphorus ylides containing atoms of Group VI – VIII transition metals are characterised by high stability on storage and the ability to exist in a free, non-associated form. Recent detailed studies of the phosphorus-ylide complexes of Group VI – VIII transition metals allowed convenient procedures for their synthesis to be elaborated. The simplest method involves the substitution of ligands in the transition metal complexes by the phosphorus-ylide ligand.[158, 166–174] For instance, bromopentacarbonyl complexes of manganese and rhenium undergo transylidation with phosphorus ylides to give the *C*-metal-substituted phosphorus ylides **91**.[158, 166]

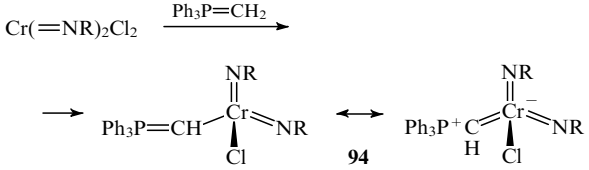


M = Mn, Re.

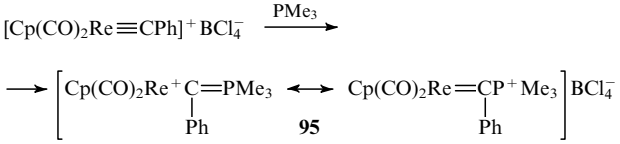
The dioxomolybdenum ylide **93** was synthesised by the reaction of the dioxomolybdenum complex **92** with tributylphosphonium methylide.[168, 169]



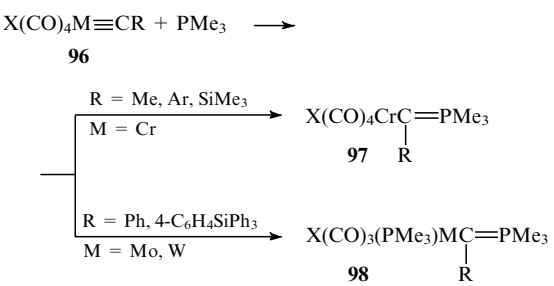
The first complex of hexavalent chromium **94**, which has high reactivity, was synthesised by the transylidation reaction of a bisalkylimide chromium complex with 2 equivalents of triphenylphosphonium methylide.[170]



The phosphorus ylide **95** was synthesised by addition of trimethylphosphine to a cationic rhenium complex. The bond between the rhenium atom and the ylide carbon atom in compound **95** is shortened because of the effective delocalisation of the negative charge on the ylide carbon atom by the transition metal.[171–178]

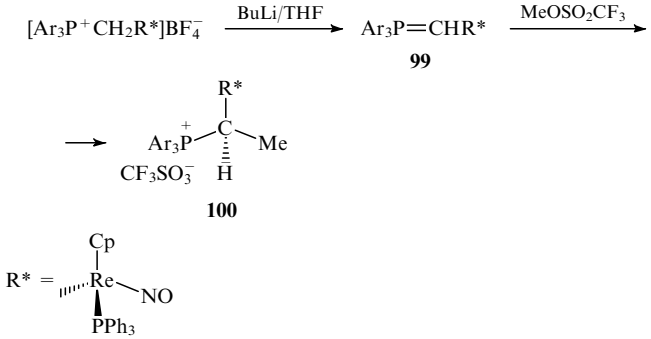


Tertiary phosphines add to chromium, molybdenum, and tungsten carbyne complexes even at −60 °C to form stable metal-substituted phosphorus ylides **97** and **98**.[171, 172]

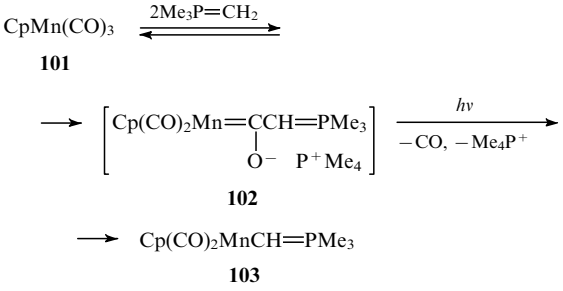


X = Cl, Br, I.

The phosphorus ylides containing Group VI – VIII elements at the α-carbon atom may be obtained by the salt method.[173, 179] This method was used to prepare optically active phosphorus ylides **99** with a chiral rhenium atom, their treatment with methyl triflate in THF at −78 °C produced the (*S*,*S*,*R*,*R*)-α-rhenium-substituted phosphonium salt **100** [166] as a result of asymmetric induction at the α-carbon atom.



The manganese complex **101** reacts with trimethylphosphonium methylide to give the mesomeric, anionic manganese-substituted phosphorus ylide **102** as the adduct which is in equilibrium with the starting compound. Photolysis of the compound **102** occurs with the elimination of carbon monoxide and results in a neutral ylide **103** with a manganese atom at the α-carbon atom.[180–183]

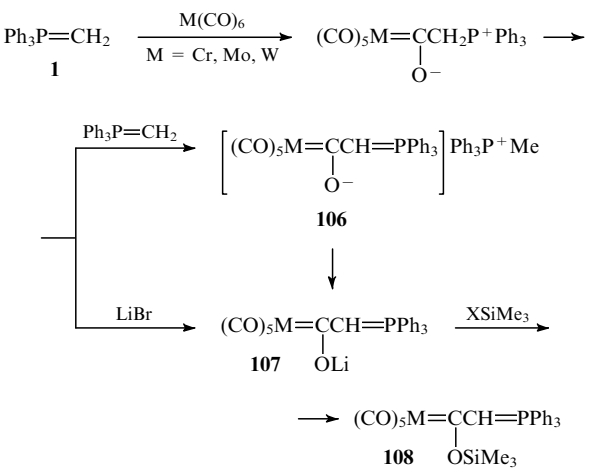


The phosphorus ylides react with the ligands of transition metal complexes to give *C*-metal-substituted phosphorus ylides.[184–187] For instance, when chromium, molybdenum and tungsten hexacarbonyls were heated with ylides **104** at 50–60 °C in light petroleum or were subjected to UV irradiation, complexes **105** were obtained.[188–191]

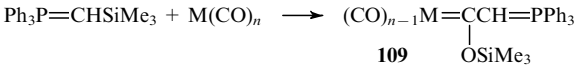


R = Ph, CH=CH2, CH2CH=CH2, CH2CMe=CH2, CH=CHMe, CH=CHPh; M = Mo, W.

A large number of phosphorus ylides that contain fragments of transition-metal complexes at the α-carbon atom separated from the ylide carbanion by one or two atoms have been prepared. Some of these ylides readily enter into the Wittig reaction.[171] The reaction of the phosphorus ylides with the polycarbonyls of the Group VI–VIII metals may occur either by the addition of the ylide carbon atom to one of the C=O groups of the metal carbonyl or by the substitution of the C=O group. The direction of the reaction and its products depend on the reaction conditions. Thus triphenylphosphonium methylide adds to a C=O group of chromium, tungsten, and iron polycarbonyls with the formation of the stable anionic phosphorus ylides **106** with the mesomeric structure.[192–193.] In the presence of lithium bromide, the phosphorus ylides **107** with the lithium atom at the enolic oxygen are formed;[194–196] they are converted into the ylides **108** in the reactions with trimethylsilyl triflate or fluorosulfonate.[194]

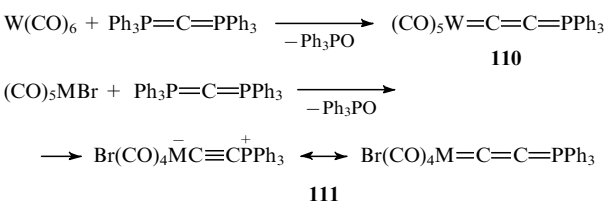


The ylides **109** are also formed in the reactions of metal carbonyls with the *C*-silylated phosphorus ylides.[197, 198]



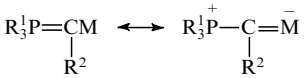
M = Cr, Mo, W, Fe; n = 5, 6.

Hexaphenylcarbodiphosphorane reacts with metal carbonyl complexes with the formation of the stable and low-reactive cumulene ylides **110** and **111**.[183, 196, 199, 200]

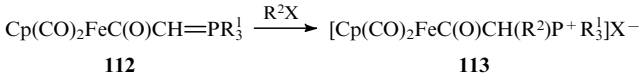


M = Mn, Re.

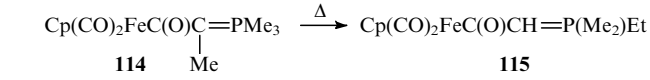
The ^{13}C and ^{31}P NMR spectra and the X-ray structural analysis of ylides containing the Group VI–VIII transition metal atoms attest to the high extent of the delocalisation of the ylide carbon atom negative charge by the transition metals, which act as strong acceptors of electrons by a $p_\pi - d_\pi$ mechanism. These results also indicate the considerable contribution of the resonance form with a double metal–carbon bond.[168, 169, 197–205]



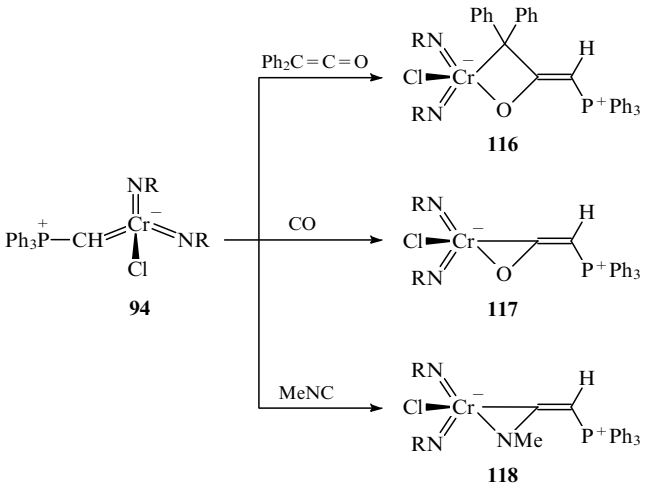
Consequently, the nucleophilicity of ylides containing transition metal atoms of the Group VI–VIII transition metal atoms is moderate, and thus they react only with strong electrophiles. X-Ray structural analysis of the compound **112** demonstrated the high extent of the delocalisation of the ylide carbon atom negative charge over the system of conjugated multiple bonds and iron atom; **112** reacts at the α-carbon atom with hydrogen chloride, trimethylchlorosilane, and alkyl halides with the formation of the phosphonium salts **113**.[198]



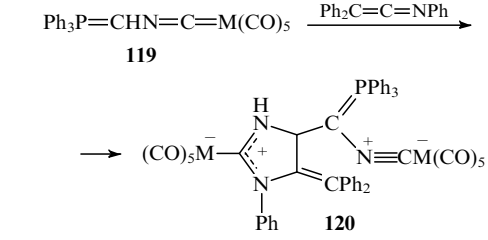
The phosphorus ylides **114** rearrange on heating with the formation of new phosphorus ylides **115**.



The reactions of insertion into the metal-carbon bond are characteristic of ylides containing the Group VI–VIII transition metals. For instance, the chromium complex **94** enters into unusual cycloaddition reactions with diphenylketene, carbon monoxide, and isocyanides with formation of vinylphosphonium salts **116–118**.[170]



The metallonitrile ylides **119**, M = Cr, W, add to ketene imine with the formation of the cyclic ylides **120**.[145, 206] The reaction of metallonitrile ylides with isocyanates and carbon disulfide proceeds similarly.[207, 208]

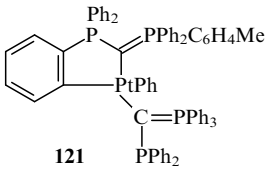


M = Cr, W.

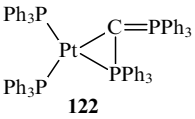
5. Ylides containing the platinum subgroup metal atoms

A variety of cyclic and acyclic platinum metal complexes with phosphorus ylide ligands have been synthesiszed. However, compounds with the double P=C bond are rare among them, since the metal-containing phosphorus ylides formed readily dimerise.[37, 203–206, 209–212]

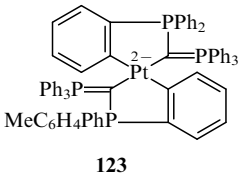
The compounds **121–123** were obtained from hexaphenylcarbodiphosphorane and the corresponding cationic platinum complexes and represent a few examples of the phosphorus ylides with platinum at the α-carbon atom.[3, 167, 213]



121



122



123

* * *

It follows from the above material that transition metals effectively stabilise the ylide carbanion lowering its nucleophilicity. Nevertheless, in some cases such ylides exhibit a relatively high reactivity. The phosphorus ylides containing transition metals have not yet found extensive application in synthesis. Certain prerequisites allow one to anticipate considerable extension of their practical application. For instance, the metal complexes of phosphorus ylides are reported to be used as catalysts for the polymerisation of alkenes and as medicinals.[214–216]

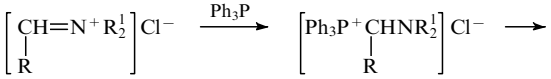
IV. Phosphorus ylides substituted at the α-carbon atom by atoms of elements of Groups VA – VIIA of the Periodic Table

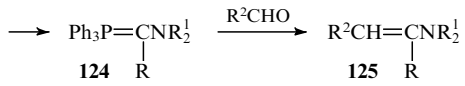
The phosphorus ylides substituted by Group VA – VIIA elements at the α-carbon atom are of both theoretical and synthetical interest. They are widely used in the synthesis of biologically active compounds.[9, 217–220]

1. Ylides containing the Group VA elements

The structures of the phosphorus ylides stabilised by nitrogen, phosphorus, and arsenic atoms are highly diversified due to the varying valence and different coordination states of these elements. The chemical properties of such phosphorus ylides are also characterised by considerable peculiarities. All this promoted the development of the chemistry of this class of phosphorus ylides and elaboration on their basis of new preparative methods for the synthesis of various valuable organic compounds.

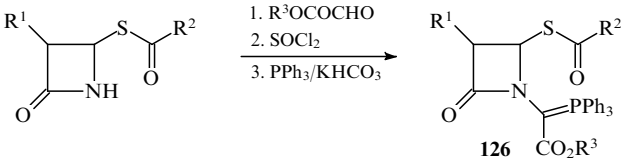
Quantum-chemical *ab initio* calculations[116] show that the trivalent nitrogen atom destabilises the ylide carbanion. Therefore, the *C*-amino-substituted phosphorus ylides are stable only if the second substituent at the α-carbon atom exhibits electron-accepting properties, which compensate the electron-donating effect of the amino group. For this reason, the transylidation reaction cannot be used for the synthesis of *C*-amino-substituted ylides. The C – N-ylides are usually synthesised by the dehydrohalogenation of the corresponding phosphonium salts. The Wittig reaction of the C – N-ylides **124** generated from the *C*-aminophosphonium salts leads to the enamines **125**. Attempts to synthesise the non-stabilised C – N-ylides have failed.[221]





124 **125**

The reactions developed by Woodward[222] for the synthesis of the ylides **126** containing the 4-acylthioazetidin-2-one group at the α-carbon atom, which are used for the preparation of the β-lactame antibiotics, are of considerable preparative value.



126

A method of generation of the phosphorus ylides based on the reaction of azetidine derivatives with an excess of a phosphite, phosphinite, or tertiary phosphine gained industrial significance.[218, 219] The reaction is carried out at room temperature under mild conditions.[220]

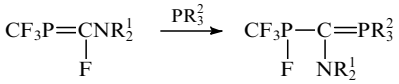


127

PR^3_3 = $P(OEt)_3$, $P(OEt)_2Me$, PPh_3.

The phosphorus ylides **127**, that are formed with high yield readily enter into the Wittig reaction.

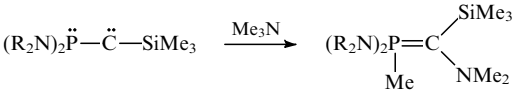
The reaction of the compounds of two-coordinate phosphorus with lower trialkylphosphines leads to the phosphorus ylides **128**, which contain a phosphorus atom and a dialkylamino group at the α-carbon atom. This reaction is accompanied by the substitution of the fluorine atom at the sp^2-hybridised carbon atom with the phosphonium group and substituent migration of the fluorine atom to the trivalent phosphorus atom.[223]



128

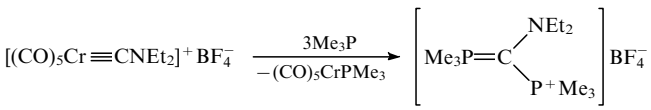
R^1 = Me, Et; R^2 = Me, Et.

Cowley *et al.*[224] have synthesised the C – N-phosphorus ylide **129** by adding trimethylamine to a phosphinocarbene.



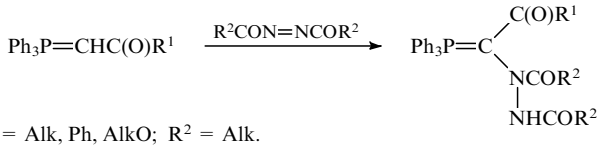
129

Kreissl *et al.*[225] have synthesised the ylide-phosphonium salt **130** by the reaction of trimethylphosphine with a carbene–chromium complex.



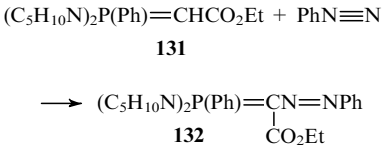
130

The Michael addition of phosphorus acyl ylides to cyclic and acyclic compounds with a multiple N=N bond activated by carbonyl groups is a convenient way for the synthesis of C–N-ylides.[226–228]



R^1 = Alk, Ph, AlkO; R^2 = Alk.

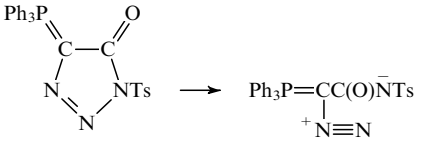
Triphenylphospine and phosphorous acid amides react with *C*-ethoxycarbonyl- and *C*-acetyl-*N*-nitrile imines to give stable azomethylenephosphonium ylides $R_3{}^1P=C(R^2)N=NPh$ [R^1 = Ph, $C_5H_{10}N$; R^2 = CO_2Et, C(O)Me].[229, 230] The ylide **132** has been obtained by the reaction of the ylide **131** with diazonium salt followed by the treatment with sodium ethoxide.[231]



131 **132**

The ylide $Ph_3P=C(N=NPh)_2$ with the two azogroups at the α-carbon atom has been prepared by reaction of bisphenylazomethane with triphenyldichlorophosphorane in the presence of triethylamine.[232]

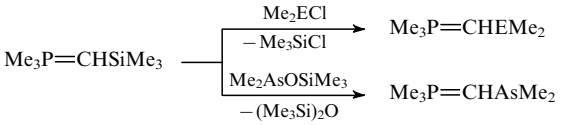
The 1,3-dipolar cycloaddition of triphenylphosphonium ketene ylides to toluenesulfonyl azide leads to the ylides **133** containing a triazoline ring, which may produce ylides **134** with a diazo group at the α-carbon atom.[233]



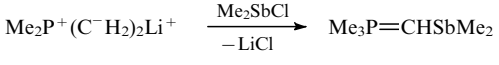
133 **134**

In contrast to the nitrogen atom, the atoms of trivalent phosphorus, arsenic, and antimony efficiently stabilise the ylide carbanion, thus making the transylidation reaction the main route to the synthesis of *C*-phosphino-, *C*-arsino-, and *C*-stibino-substituted phosphorus ylides.[79, 80]

These ylides are obtained by the reaction of *C*-silyl- and *C*-lithium-substituted phosphorus ylides with chlorophosphines, -arsines, and -stibines.

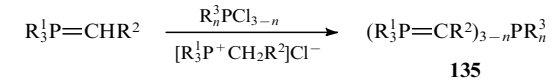


E = P, As, Sb.



Trimethylsilyl arsinic acid may be used instead of chloroarsines.[79, 80, 154]

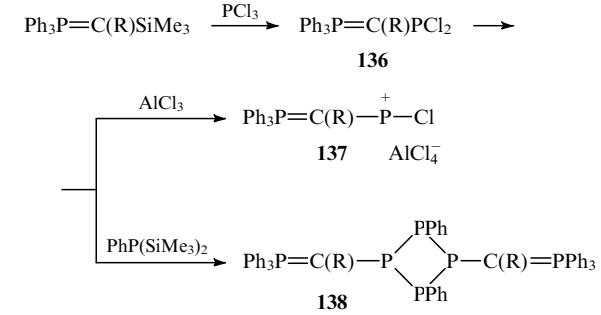
Diaryl- and dialkyl-chlorophosphines, alkyl- and aryl-chlorophosphines, aminochlorophosphines, and phosphorus trichloride react with non-stabilised phosphorus ylides to give the compounds **135** with one, two, or three phosphorus ylide groups at the trivalent phosphorus atom.[156, 234–238]



135

R^1 = Ph, Alk_2N; R^2 = H, Alk; R^3 = Alk, Ar, Alk_2N, Cl; n = 0–2.

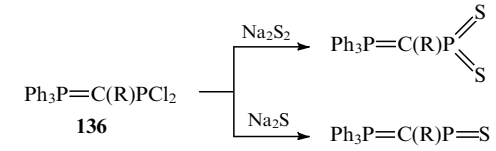
Schmidbaur *et al.*[239, 240] have synthesised the dichlorophosphinoylide **136**, which is an interesting initial compound for preparation of phosphorus ylides of unusual structure. In the reaction with aluminium chloride, it gives the ylidylphosphenium cation **137** and with bis(trimethylsilyl)phenylphosphine it gives 1,3-bis(triphenylphosphoniumylidyl)cyclotetraphosphine **138**. X-Ray structural analysis of the compound **138** demonstrated *trans*-orientation of all the substituents of the four-membered ring.[241]



136 **137** **138**

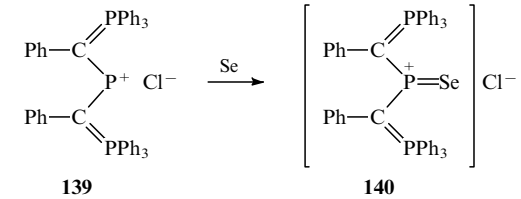
R = Alk, Ar, $SiMe_3$.

Dichlorophosphinoylide **136** was used by Schmidpeter *et al.* for the synthesis of the first stable phosphorus ylides with the phosphorus sulfide and phosphorus disulfide groups at the ylide carbon atom.[242–244]



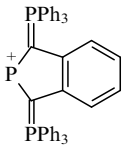
136

In the last few years, considerable attention has been paid to the synthesis of phosphorus ylides substituted at the ylide carbanion with phosphorus atoms with unusual coordination.[242–248] Phosphorus ylides, which contain two-coordinate trivalent[242, 248] and three-coordinate pentavalent phosphorus atoms[243, 244] at the ylide carbon atom have been synthesised. Schmidpeter[244, 245] has shown that bisylide-substituted monochlorophosphine **139** with the phosphenium structure adds selenium with the formation of bisylide-substituted selenoxophosphonium chloride **140**. The compound **140** was the first chalcogen-phosphonium ion with a trigonal planar phosphorus atom isolated in the individual form.[244, 245]



139 **140**

Diphosphoniumisophosphindol **141** containing a two-coordinate phosphorus atom at the ylide carbon atom has been synthesised by the reaction of the corresponding bisphosphorane with phosphorus trichloride and triethylamine.[243, 245, 246] The crystal and molecular structure of the phosphorus ylide **141** was described.[245, 249]



141

Grobe *et al.*[247] have prepared phosphorus ylides substituted with the trivalent phosphorus atom at the ylide carbon atom by adding trimethylphosphine to fluorinated phosphaalkenes. The formation of the ylides was explained by the electrophilic character of the two-coordinate phosphorus atom.

$$Me_3P + F_3CP{=}C(F)X \xrightarrow[CH_2Cl_2]{-196 \text{ to } -80\ ^\circ C} Me_3P{=}\underset{X}{\overset{}{C}}{-}PCF_3 \quad (F)$$

X = F, OMe, OEt.

The four-coordinate phosphorus atom efficiently stabilises the ylide carbanion, which makes the reaction of transylidation the general technique for the preparation of various *C*-phosphorus-substituted ylides containing phosphoryl or thiophosphoryl groups at the α-carbon atom.[117,209,250] This method has also been used for the synthesis of ylides containing one, two, or three P=C groups at the four-coordinate phosphorus atom.[154,238,251]

$$Ph_3P{=}CHR \xrightarrow{Ph_nP(S)Cl_{3-n}} (Ph_3P{=}CR)_{3-n}P(S)Ph_n$$

$n = 0-2$.

The salt method has also been used, although not so often, for the preparation of the *C*-phosphorus-substituted ylides. Thus triphenylphosphonium diphenylphosphonomethylide can be obtained by the quaternization of triphenylphosphine with diphenyl chloromethylphosphonate on heating to 175 °C.[252]

$$(PhO)_2P(O)CH_2Cl \xrightarrow{Ph_3P} [(PhO)_2P(O)CH_2P^+Ph_3]Cl^- \longrightarrow (PhO)_2P(O)CH{=}PPh_3$$

The bis- and tris(diorganylphosphino)methanes are alkylated by alkyl halides with the formation of the methylenephosphonium salts, which give carbodiphosphoranes[253] on dehydrohalogenation. Similarly, tris(diorganylphosphino)methanes give ylide-bisphosphonium salts **142**.[253–259]

$$CH(PMe_2)_3 \xrightarrow{MeI} [CH(P^+Me_3)_3]3I^- \xrightarrow[-HI]{} [Me_3P{=}C(P^+Me_3)_2]2I^-$$

142

The ylide **143** (for the synthesis of the ylide **143** see Refs 255–264) easily undergoes recombination with trimethylphosphonium dimethylphosphinomethylide to give the bisphosphino-substituted ylide **144**.[74,151,254,255]

$$\underset{CH_2PMe_2}{\overset{}{Me_2P{=}C(PMe_2)_2}} \xrightarrow{Me_3P{=}CHPMe_2} 2Me_3P{=}C(PMe_2)_2$$

143 **144**

The phosphorus ylides stabilised by phosphorus, arsenic or antimony atoms are thermally stable. Tri- and penta-valent phosphorus atoms at the ylide carbon atom efficiently delocalise its electron density, which is confirmed by physicochemical studies.[251,265] Thus the effect of the phosphorus-containing groups X on the CH-acidity of the ylides $Ph_3P{=}CHX$ forms the following series:

$$P(O)(OR)_2 > P(O)Ph_2 = P(S)Ph_2 > PPh_2$$

X-Ray structural studies of the element-substituted phosphorus ylides reveal the shortening of the P=C bond (in Å): $Ph_3P{=}C(R)EPh_2$: 1.720 (E = P),[266] 1.698 (E = As),[267] and 1.692 (E = Sb).[268] Two or three phosphonium groups at the ylide carbon atom decrease even more the basicity of the compounds.[269,270] For instance, tris(triphenylphosphonium) methylide cannot be protonated even by strong acids. Bis(triphenylphosphonium) diphenylphosphinomethylide **145** ($R = P^+Ph_3$) is protonated at the trivalent phosphorus atom,[215,216] while triphenylphosphonium diphenylphospino(ethoxycarbonyl)methylide ($R = CO_2Et$) is protonated both at the α-carbon atom and at the trivalent phosphorus atom.[271] Mastryukova *et al.*[272] have shown by NMR the existence of a tautomeric equilibrium between the **A** and **B** forms of the compound **145**.

$$\underset{R}{\overset{}{Ph_2P{-}C{=}PPh_3}} \quad \textbf{145} \xrightarrow{HCl} \left[\underset{R}{\overset{}{Ph_2P{-}CHP^+Ph_3}}\right]Cl^- \rightleftharpoons \left[\underset{R}{\overset{}{Ph_2PH{=}C{-}P^+Ph_3}}\right]Cl^-$$

A **B**

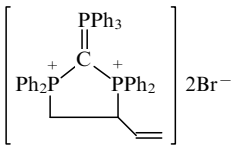
$R = CO_2Et$.

The protonation of the phenylphosphinoyl methylide **146** leads to CH- (**C**), or OH-protonated (**D**) forms depending on the properties of the substituents R. Protonation at the carbon atom takes place in the case of $R = SO_2C_6H_4Me\text{-}4$ and PPh_3. If R = CO_2Et the OH- and CH-protonated forms coexist in solution in a tautomeric equilibrium.[273]

$$\underset{O\ \ R}{\overset{\|}{Ph_2P{-}C{=}PPh_3}} \quad \textbf{146} \xrightarrow{HCl} \left[\underset{O\ \ R}{\overset{\|}{Ph_2P{-}CHP^+Ph_3}}\right]Cl^- \rightleftharpoons \left[\underset{HO\ \ R}{\overset{|}{Ph_2P{=}C{-}P^+Ph_3}}\right]Cl^-$$

C **D**

The alkylation of the phosphine-phosphonium ylides occurs at the trivalent phosphorus atom with the formation of P-alkylated phosphonium salts, while the alkylation of the phosphoryl- or thiophosphoryl-substituted phosphorus ylides gives the *C*-substituted phosphonium salts.[251,265,274] The reaction of triphenylphosphonium bis(diphenylphosphino)methylide with 1,4-dibromobut-2-ene is a convenient method for the preparation of the ylide-phosphonium salts **147** containing the 1,3-diphospholane ring.[275,276]

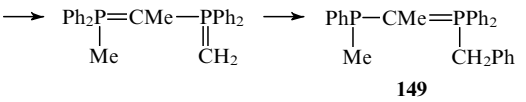


147

Some *C*-phosphorus-containing phosphorus ylides undergo skeletal rearrangements. Under the action of the trimethylphosphonium methylide, the phenyl group migrates from the phosphorus atom to the ylide carbon atom, and the phosphonium salt **148** is converted into the phosphorus ylide **149**.[277]

$$\left[\underset{Me}{\overset{}{Ph_2P{=}CMe{-}}}\underset{Me}{\overset{}{P^+Ph_2}}\right]I^- \xrightarrow[-Me_4P^+I^-]{Me_3P{=}CH_2}$$

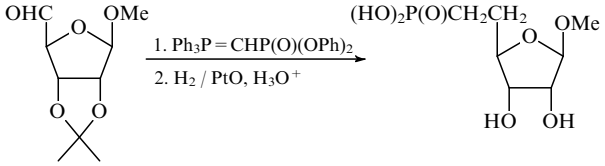
148



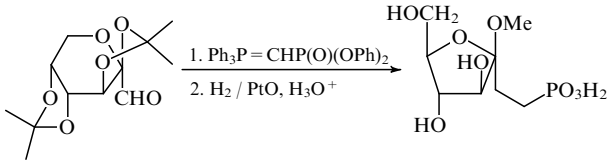
149

Despite the relatively low nucleophilicity of ylides stabilised by the four-coordinate phosphorus atom, they enter into the Wittig reaction with aldehydes on heating to form phosphorus-containing alkenes. The use of *C*-phosphorus-substituted ylides as alkenating agents is especially important for the synthesis of natural substances. In particular, the *C*-phosphorus-substituted ylides are used to prepare isosteric analogues of phosphates of natural origin.[278–280]

Carbohydrates with protected hydroxy groups are easily alkenated by triphenylphosphonium diphenoxyphosphorylmethylide. The vinylphosphonates formed as a result of the alkenation are hydrogenated over platinum or palladium oxide and hydrolysed to form the phosphonic acids.[281]

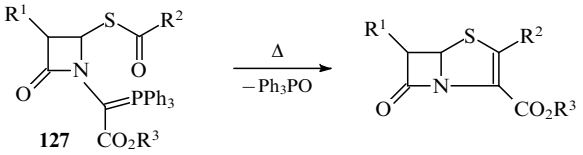


Using the same triphenylphosphonium diphenoxyphosphorylmethylide, the synthesis of the phosphonate analogue of fructose-1-phosphate has been performed;this manifested the properties of bioregulator of hexose-phosphate transport systems.[282]



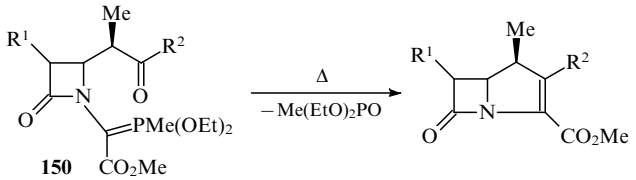
Similarly, isosteric analogues of a series of phospholipids and sugar phosphates have been prepared.[283–285] Huang *et al.*[286] have synthesised phosphorus-containing pyrethroids using *C*-phosphorus-substituted ylides.

The phosphorus ylides **127** undergo an intramolecular Wittig reaction on heating and give penemates in high yields.They have found an important practical application in the synthesis of β-lactam antibiotics.[287] Syntheses of a series of other β-lactam antibiotics, which are derivatives of penemic and cefemic acids, have been described.[287–295]



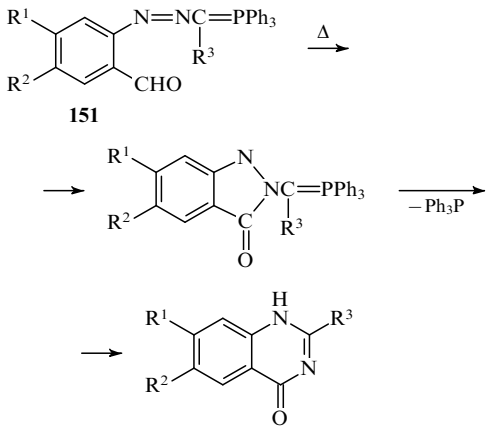
127

Japanese workers have prepared carbopeneme derivatives in high yields by refluxing the phosphorus ylide **150** in xylene. This technique has been proposed for industrial applicaion.[218,219]



150

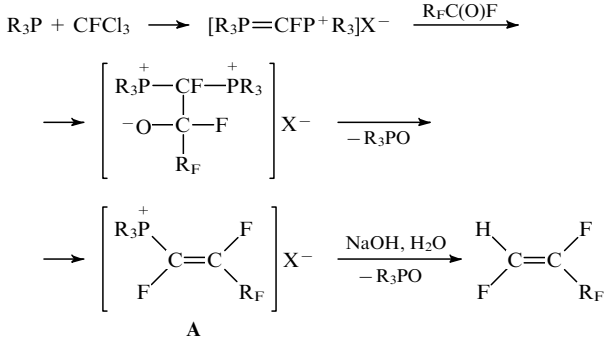
The thermolysis of triphenylphosphonium azomethylide gives the ylides **151** which are converted into 4-oxo-1,4-dihydroquinazolines on further heating.[227,296,297]



151

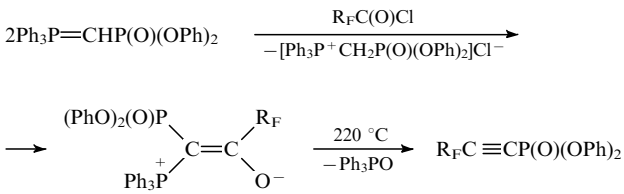
R^3 = CO_2Me, C(O)Me, SO_2Ph, $SO_2C_6H_4Me$-4, C(S)SMe.

Burton *et al.* have developed a method for the synthesis of fluoroalkenes based on *C*-phosphorus-substituted ylides. The reaction presumably proceeds *via* a mechanism similar to that of the Wittig reaction and involves the formation of a betaine, which decomposes to give phosphine oxide and vinylphosphonium salt **A**. The phosphonium salt **A** readily decomposes with the cleavage of the C–P bond under the action of dilute alkali. The yields of fluoroalkenes do not exceed 45%–62%.[298,299]



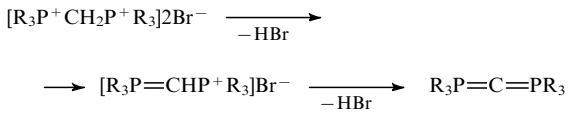
A

Perfluoroalk-1-ynylphosphonates are obtained by pyrolysis of 2-hydroxyalkenyltriphenylphosphonium ylides, which follows the intramolecular Wittig-type reaction.[300]

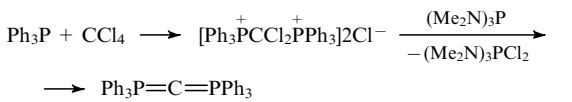


C-Phosphine-substituted phosphorus ylides are used as ligands in transition metal complexes.[226,260–264] Thus substitution of the ligands in the chromium carbonyl complexes $Cr(CO)_5L$, where L = THF, C_7H_8, $Me_2S(O)CH_2$ by *C*-phosphine-substituted phosphorus ylides leads to cyclic and acyclic phosphorus ylides with a metal–phosphorus(III) bond. These complexes are diamagnetic substances stable in air and soluble in organic solvents.[184,301]

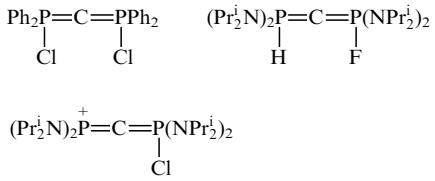
Carbodiphosphorane dicarbanions stabilised by two phosphonium groups provide an example of *C*-phosphorus-substituted ylides important for synthesis.[302] Carbodiphosphoranes are obtained by dehydrohalogenation of the ylide-phosphonium salts with sodium amide, butyllithium, potassium in dimethoxyethane, sodium hydride, triethylphosphonium ethylide.[303–308]



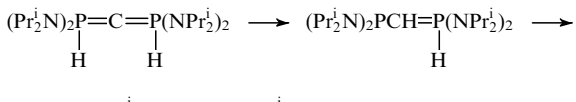
The ylide-phosphonium salts formed upon the treatment of triphenylphosphine with carbon tetrachloride are dehydrochlorinated by tris-(dimethylamino)phosphine to give carbodiphosphoranes in good yields.[305]



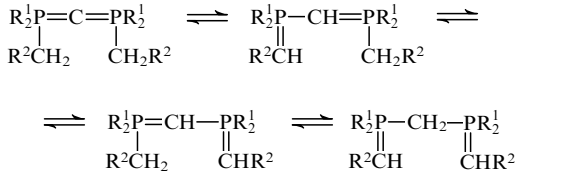
In the last few years, carbodiphosphoranes of unusual structure with fluorine, chlorine or even hydrogen atoms at the phosphorus atom have been obtained.[309–313]



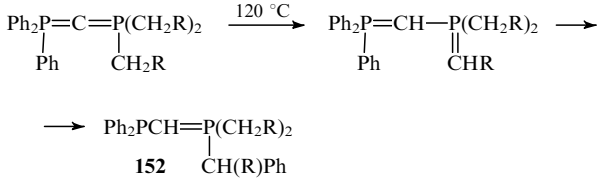
Carbodiphosphoranes $(Pr^i_2N)_2HP=C=PH(NPr^i_2)_2$ with the P–H bond are unstable and are converted into aminophosphines as a result of a prototropic shift.[10, 271, 313]



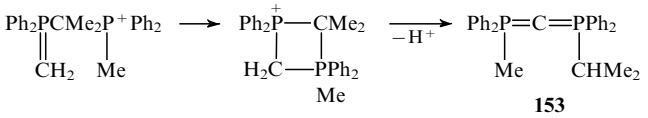
A close chemical interrelation exists between the carbodiphosphoranes and the *C*-phosphorus-substituted ylides. For instance, the carbodiphosphoranes with alkyl groups at the phosphorus atom exist as prototropic tautomers.[314, 315] The tautomeric equilibrium depends on the electronic effect of the substituents. Electron-accepting and electron-donating substituents shift the equilibrium towards the bis-ylide or the carbodiphosphorane form, respectively. It is believed that the prototropic exchange between the tautomers is intramolecular.[308, 314–318]



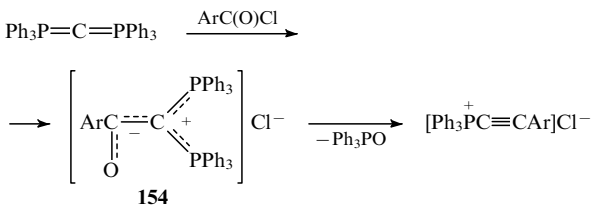
The asymmetric alkyl-containing carbodiphosphoranes are converted into phosphino-substituted ylides **152** on heating to 120 °C. The reaction occurs *via* intermediate formation of the bis-ylide as a result of phenyl group migration from the phosphorus atom to the ylide carbon atom.[222, 319]



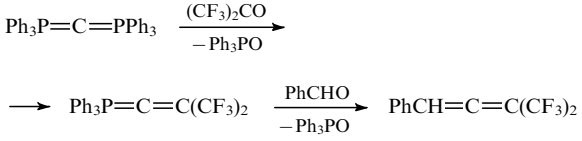
The ylide-phosphonium salts with a dimethylmethylene group between two phosphorus atoms undergo isomerisation *via* the four-membered intermediate state into the carbodiphosphoranes **153**.[320]



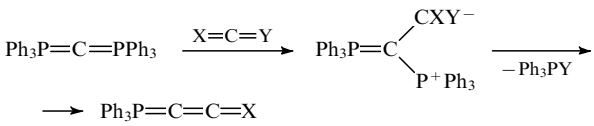
The reaction of carbodiphosphoranes with electrophiles results in substitution at the central carbon atom or in the side chain. For instance, hexamethylcarbodiphosphorane reacts with chlorotrimethylsilane to give the ylide containing a trimethylsilyl group at the side carbon atom. In contrast, reaction of carbodiphosphoranes with alkyl halides, chlorophosphines, and acid chlorides usually occurs at the ylide carbon atom with the formation of the corresponding ylide-phosphonium salts.[259] In the reaction with aromatic acid chlorides, hexaphenylcarbodiphosphorane gives *C*-acylated ylide-phosphonium salts **154**, which are converted on heating into (arylethynyl)phosphonium salts as a result of an intramolecular Wittig reaction.[321]



The carbodiphosphoranes are valuable reagents in organic synthesis. They exhibit high nucleophilicity and therefore readily react with aldehydes and ketones. The allenylides thus formed enter into the Wittig reaction with aldehydes and ketones to give allenes.[262]

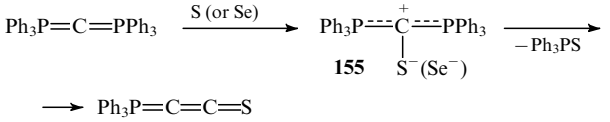


The reaction of carbodiphosphoranes with heterocumulenes (carbon dioxide, carbon disulfide, isocyanates, ketenes) yields betaines stable at room temperature, which are converted into phosphonium ketenylides, thioketenylides, keteniminylides, allenylides.[304, 322–326]

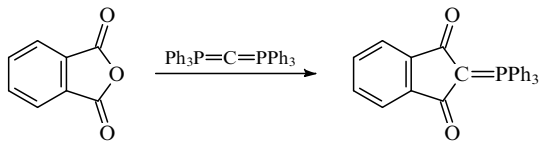


X = O, S, NAr, CPh_2; Y = O, S.

Hexaphenylcarbodiphosphorane when treated with sulfur or selenium first yields the betaines **155,** which are stable at low temperature; at room temperature, they are converted into the triphenylphosphonium ketenylides.[327]



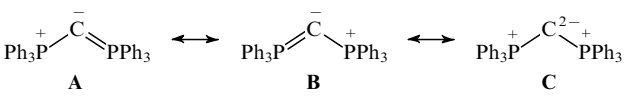
The reaction of hexaphenylcarbodiphosphorane with phthalic anhydride occurs with the substitution of the anhydride oxygen atom by the ylide function.[321, 328]



In the reaction with salicyl aldehyde, hexaphenylcarbodiphosphorane gives a six-membered cyclic oxaphosphorane.[329]

Carbodiphosphoranes are used as ligands in ylide complexes of transition metals.[135, 187, 330–335]

X-ray structural analysis and electron diffraction data proved carbodiphosphoranes to be dicarbanions. The central carbon atom of the carbodiphosphoranes has a hybridisation close to sp^2, and the ground state of the carbodiphosphoranes may be described by the canonical structures **A**, **B**, and **C**.[330–340]



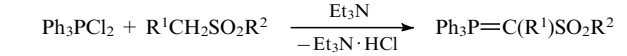
A **B** **C**

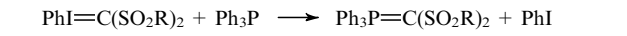
Structural investigations of hexaphenylcarbodiphophorane with triboluminescent properties, *i.e.* the ability to generate light on mechanical treatment, are of special interest.[340–343] Hexaphenylcarbodiphosphorane forms several crystalline modifications: orthorhombic crystals do not have triboluminescent properties, whereas monoclinic crystals do possess such properties. The molecules in monoclinic and orthorhombic modifications have different P=C=P bond angles and Ph–P.....P–Ph dihedral angles.[344, 345] The dipole moment of hexaphenylcarbodiphosphorane in benzene is 4.69±0.05 D.[337, 338]

2. Phosphorus ylides containing Group VIA elements

The phosphorus ylides stabilised by oxygen, sulfur, selenium or tellurium atoms possess diversified structures and properties. The chemistry of these ylides is being rapidly developed. Convenient procedures for their preparation are elaborated, and chemical properties are studied. The ylides stabilised by the Group VIA elements are used in the synthesis of natural substances and biologically active compounds.

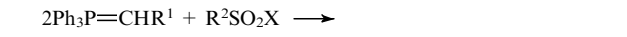
The very stable *C*-sulfonyl-substituted ylides are the most readily available phosphorus ylides of this group. They can be prepared by simple methods, such as the direct phosphorylation of sulfonylalkanes by polyhalophosphoranes in the presence of triethylamine,[346] the salt method in the presence of organic bases, or by the reaction of diphenyldialkylaminophosphines with bis(sulfonyl)methanes and alkyl halides.[347–349] Heating of phenyliodonium ylides with triphenylphosphine in benzene in the presence of copper acetylacetonate as a catalyst gives phosphonium ylides in high yield.[350, 351]





R^1 = Me, Ph, SO_2R^2.

The sulfonyl ylides **157** can be obtained by the transylidation of phosphorus ylides **156** with sulfonyl fluorides or sulfonic anhydrides.[348, 349] At the same time, the reaction of phosphorus ylides with arenesulfonyl chlorides results in the chloro-substituted phosphorus ylides **158** rather than the sulfonyl-substituted ylides.[348]

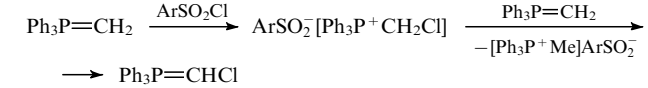


156



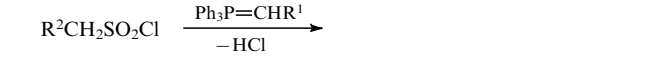
157

X = F, R^3SO_3;



158

The reactions of phosphorus ylides with alkenesulfonyl halides are also accompanied by rearrangements, which result in migration of the substituent R^1 from the ylide carbon atom to the carbon atom of the SO_2CH_2 group sulfur atom and the substituent R^2 migrates to the ylide carbon atom. The ratio of the isomers of *C*-sulfony-lsubstituted phosphorus ylides **159**, and **160** thus formed depends on the nature of the substituents R^1 and R^2.[350, 351]

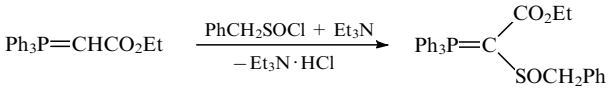


159 **160**

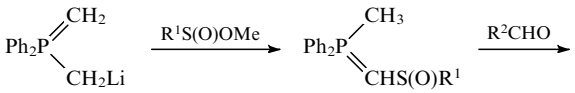
The reaction presumably proceeds *via* the formation of sulfenes $R^2CH=SO_2$, which give unstable four-membered cyclic intermediates **161** as a result of the addition to phosphoranes, and are subsequently converted into the isomers **159**, and **160**.

161

In order to introduce the sulfinyl group to the phosphorus atom, the reaction of the stabilised ylides with the sulfinyl chlorides in the presence of triethylamine is used. This reaction presumably proceeds *via* the intermediate formation of sulfines.[352–354]



The reaction of diylides **20** (R=H) with sulfinates gives *C*-sulfinyl ylides **162**. The Wittig reaction of the latter with aldehydes proceeds with excellent stereoselectivity ($E:Z > 91:9$).

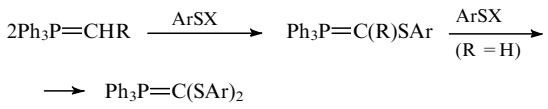


20 (R = H) **162**



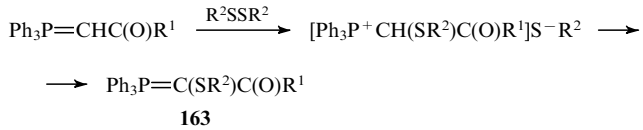
The same reaction with the chiral sulfinate yields chiral *E*-vinylsulfoxides ($E:Z > 99:1$) and is accompanied by the >96% inversion of configuration at the sulfur atom.[50]

There exist convenient procedures for the preparation of the phosphorus ylides containing a bivalent sulfur atom at the α-carbon atom. The reactions of the stabiliszed and non-stabilised phosphorus ylides with sulfenyl chlorides in benzene or THF at 20 °C and the ratio of the reagents 2 : 1 or 3 : 1 are used most often. As a result of the transylidation reaction, the ylides containing one or two thio groups at the α-carbon atom are formed.[354–358] Tolylthio *p*-toluenesulfonate, *N*-methyl-*N*-phenylthioacetamide,[162] dimethylsuccinimidosulfonium chloride [354, 355, 359] are used as thioarylating reagents.



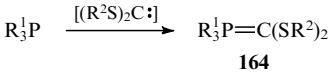
X = Cl, $ArSO_2$, MeC(O)NMe.

The reaction of phosphorus ylides with disulfides in benzene gives the ylides **163** in a yield of about 90%.[354, 355, 360]



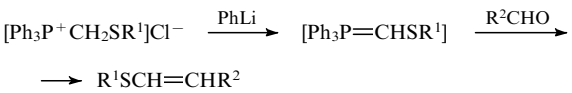
R^1 = Me, MeO; R^2 = $R_2NC(S)$, EtO_2C.

The synthesis of the ylides **164** with two thioether groups at the carbon atom by the reaction of tertiary phosphines with bisalkyl(aryl)thiocarbenes has been reported.[361, 362] Dithiocarbenes were generated by the action of sodium hydride on the corresponding tosylhydrazone[361] or by the decomposition of tris(phenylthio)-methyllithium.[362]

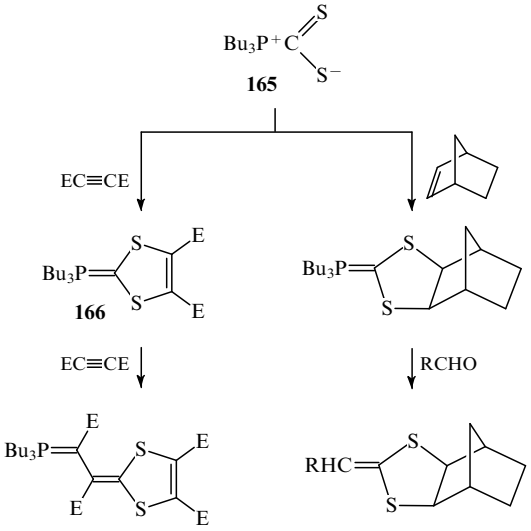


R^1 = Bu, Ph; R^2 = Et, Ph.

The most important method of synthesis of ylides containing alkylthio groups at the α-carbon atom is the dehydrohalogenation of the phosphonium salts by organolithium derivatives. The ylides synthesised by this method have been used in the Wittig reaction without isolation from the reaction solutions.[8, 9]

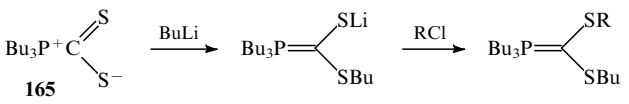


The adduct of tributylphosphine with carbon disulfide **165**, which was isolated more than a hundred years ago by Hoffmann,[363] has been recently intensely studied. The ability of the adduct to enter into cycloaddition reactions with the formation of phosphorus ylides containing the dithiolane ring is not the least reason for such an interest.[364, 365]



E = CO_2Et.

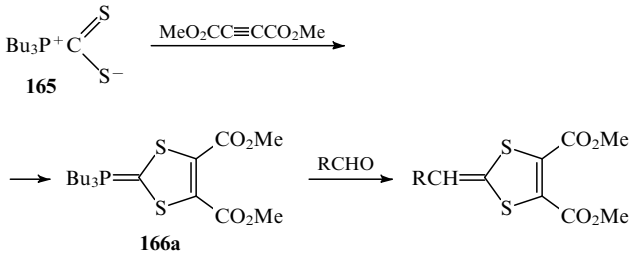
Polezhayeva *et al.* have introduced the adduct **165** into reactions with various dipolarophiles to prepare *C*-dithio-substituted phosphorus ylides of both cyclic and acyclic structure.[366]



R = Me_3Si, $PhCH_2$, Ph_2P.

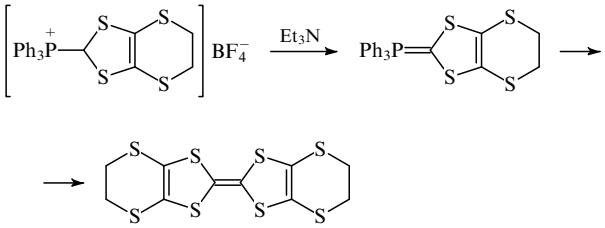
The ability of dithia- and tetrathiafulvenes to generate the electroconducting salts stimulated a great interest in phosphorus ylides containing thiafulvene groups.[367–371] Thus 2-thioxo- and 2-oxo-1,3-dithiol-4-ylmethylides have been proposed as reagents for the synthesis of 1,3-dithia- and tetrathiafulvenes.[372]

The addition of dimethyl acetylenedicarboxylate to the adduct **165** has led to the highly reactive cyclic ylide **166a,** which enters into the Wittig reaction and yields dithiafulvenes with π-donating properties.[370]

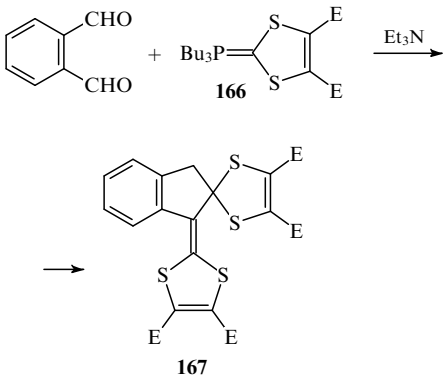


The 1,3-dithiol-2-ylides have been generated from the corresponding phosphonium salts with the dithiolane ring even under the action of triethylamine or diisopropylamine.[367]

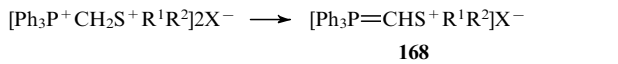
The ylides containing the 1,3-dithiol-2-ylide fragment have been used for the preparation of the corresponding polyformyltetrathiafulvalenes with a strong π-donating capacity.[330, 369]



The derivatives of tetrathiafulvene **167** have been synthesised by the condensation of ylide **166** with phthalic aldehyde.[368]

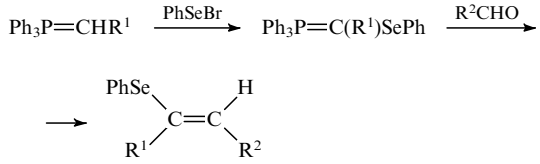


By the reaction of triphenylphosphonium methoxycarbonylmethylide with thiocyanogen, triphenylphosphonium 2-oxo-1-thiocyanopropylide, $Ph_3P=C(SCN)C(O)Me$, has been synthesised in 65% yield.[295] The alkylation of the alkylthiomethyltriphenylphosphonium salt gives the phosphonium sulfonium salt, which yields the ylide-sulfonium salt **168** upon dehydrohalogenation.[373]

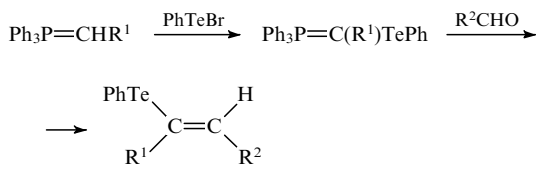


168

It was proposed to prepare *C*-selenium-substituted ylides by the reaction of phosphorus ylides with phenylselenyl bromide.[374] The *C*-selenium substituted phosphorus ylides enter into the Wittig reaction with aldehydes to yield various phenylselenoalkenes.[374–378]

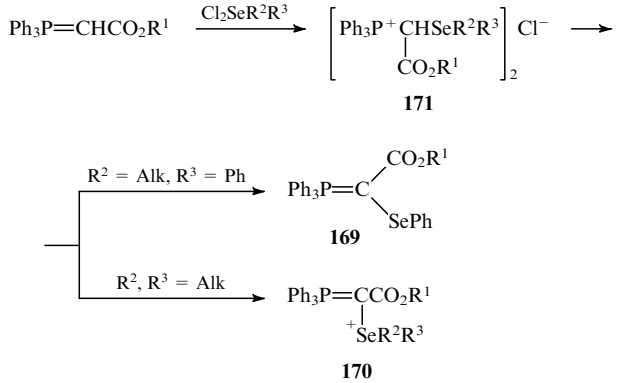


The *C*-tellurium-substituted phosphorus ylides have been synthesised similarly and used for the preparation of tellurium-substituted alkenes.[379]



R^1, R^2 = Alk, Ar.

The reaction of dichloroselenides with triphenylphosphonium alkoxycarbonylmethylides results in the *C*-selenium-substituted ylides **169** or phosphonium selenonium ylides **170**. If the intermediate salts **171** contain two alkyl groups, they are dehydrochlorinated by the excess of phosphorus ylide with the formation of ylide-selenonium salts **170**. If there are a phenyl and an alkyl group at the selenium atom, the ylide **169** is formed.[380, 381]

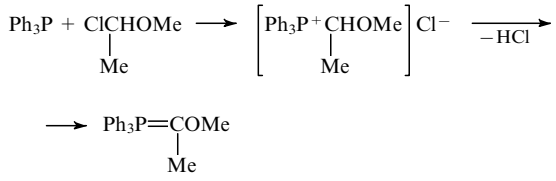


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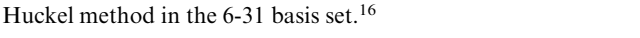
169

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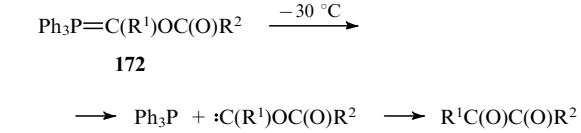
The phosphorus ylides with alkoxyl and aroxyl groups at the α-carbon atom are usually obtained by the salt method.[383, 384] Thus the treatment of a suspension of a finely-ground phosphonium salt by phenyllithium in ether gives a bright-red solution of *C*-alkoxymethylide, which readily reacts with aldehydes and ketones to give alkyl vinyl ethers.[365, 383] Triphenylphosphonium α-methoxyethylide is prepared by the reaction of triphenylphosphine with α-chloroethy lmethyl ether in benzene. The phosphonium salt is then treated with potassium *tert*-butoxide in dimethoxyethane at −40 °C for a few minutes. The red solution of the highly active ylide is formed which easily alkenates aldehydes and ketones.[385]



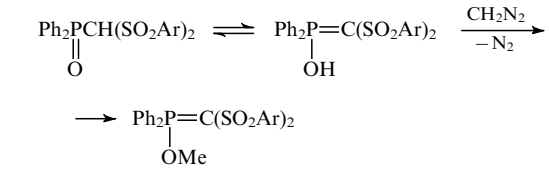
The ylides with oxygen or bivalent sulfur atoms at the α-carbon atom are unstable. They are normally used for the further one-pot chemical transformation. *ab initio* Calculations show that although the presence of the oxygen atom at the negatively charged carbon atom should in general stabilise the carbanion, it is not the case for the phosphorus ylides. *C*-Oxygen-substituted phosphorus ylides exhibit an enhanced tendency to dissociate into carbenes and tertiary phosphine, which allows one to regard them as the carbene complexes of tertiary phosphines. The formation of carbenes at the intermediate stage of the reaction is confirmed by *ab initio* calculations by the extended Huckel method in the 6-31 basis set.[16]



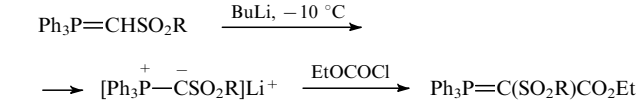
The ylides **172** also decompose readily with the formation of carbenes, which give 1,2-diketones as a result of intramolecular rearrangement.[386]



The *C*-Sulfonyl-substituted ylides are characterised by high thermal stability due to efficient delocalisation of the negative charge of the ylide carbon atom by the hexavalent sulfur atom, which has been confirmed by physicochemical studies,[387–392] in particular by X-ray structural analysis.[348, 393] The IR- spectra of ylides containing sulfonyl or sulfinyl groups at the carbon atom show considerable shift of the S=O and SO_2 frequencies towards the longwave region due to the efficient delocalization of the carbanion negative charge by these groups.[349, 387–390] The triad prototropic tautomerism is typical of bis(arylsulfon-yl)methylphosphine oxides, which exist in the CH-phosphine oxide form in crystals and as tautomeric mixtures of the OH-ylide and CH-phosphine oxide forms in solutions; these forms can be easily indicated by spectroscopy.[391] Diphenylbis(arylsulfonyl)methylphosphine oxides resemble in their chemical properties the OH-acids of tetracoordinated phosphorus. Thus, they are *O*-methylated by diazomethane [391, 392]

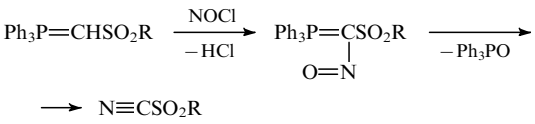


Hydrogen at the α-carbon atom in the *C*-sulfonyl-substituted ylides is active and can be readily substituted by various groups. The treatment of the ylides by butyllithium results in the substitution of the hydrogen atom by lithium with the formation of the dicarbanion **173**, which reacts with chlorine-containing electrophiles.[348]

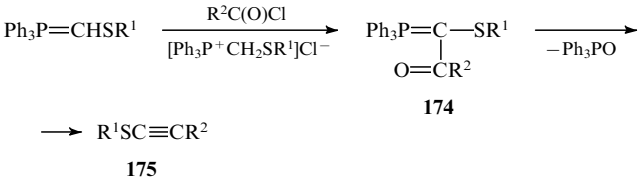


173

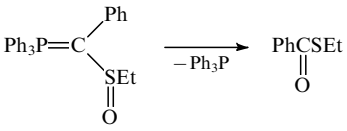
The reaction of *C*-sulfonyl-substituted ylides with nitrosyl chloride in pyridine leads to the substitution of the hydrogen atom at the α-carbon atom by a nitroso group. The ylide thus formed is converted into sulfonyl cyanide in a Wittig-type intramolecular reaction.[348, 394]



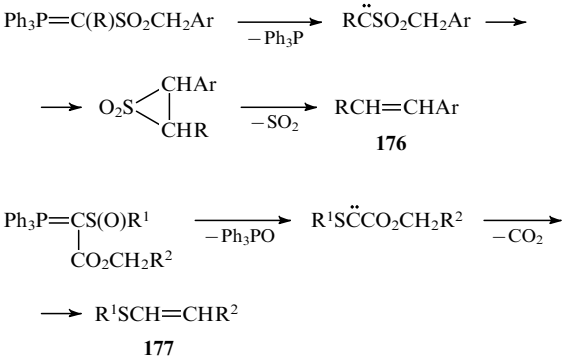
Flash-vacuum pyrolysis of the acylmethylides **174** obtained by the reaction of the *C*-alkylthio-substituted ylides with acid chlorides produces the alkyl(aryl) thioacetylenes **175** in good yields.[348, 358, 394, 395]



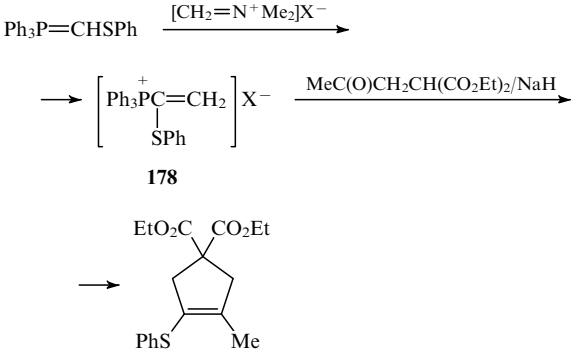
Flash-vacuum pyrolysis of sulfinyl-stabilised ylides gives thioesters in satisfactory yield.[397]



Flash-vacuum pyrolysis of sulfonyl- and sulfinyl-stabilised phosphorus ylides is accompanied by the elimination of phosphine or phosphine oxide with the formation of thio-, sulfinyl-, or sulfonylcarbenes, which give the alkenes **176** and **177** as a result of rearrangements and insertion reactions.[396, 397]

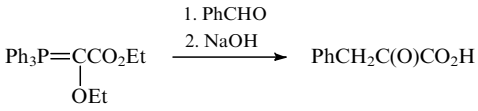


The substituted vinylphosphonium salts **178** are obtained by the reaction of phenylthiomethylides with iminium salts; they are used in the synthesis of cyclopentadienes.[398]

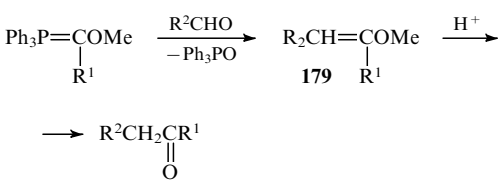


The *C*-sulfonyl-substituted ylides are characterised by weak basicity and nucleophilicity, which accounts for their low activity in the Wittig reaction. The monosubstituted ylides react only with aldehydes and do not react with ketones. Triphenylphosphonium bis-sulfonylmethylides also do not react with carbonyl compounds. On the contrary, phosphorus ylides with alkylthio, alkoxyl, or aryloxyl groups at the α-carbon atom readily enter into the Wittig reaction with various carbonyl compounds.[399–410]

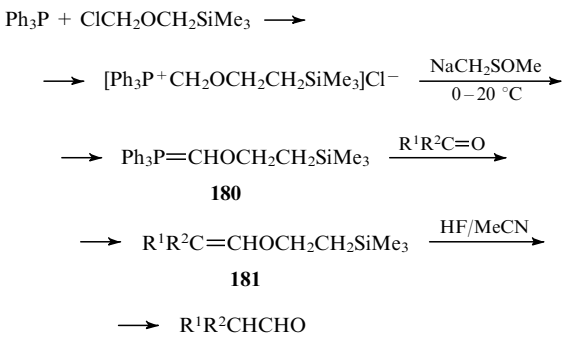
The reaction of ethoxy(ethoxycarbonyl)methylides with aldehydes and the subsequent hydrolysis of the vinyl ethers formed is a convenient way for the preparation of oxo carboxylic acids.[403]



The ylides with the alkoxyl groups at the ylide carbon atom alkenate both aldehydes and ketones with the formation of the vinyl ethers **179**, which give on hydrolysis the corresponding aldehydes ($R^1 = H$) or ketones ($R^1 = Me$), the latter may be again introduced into the Wittig reaction with triphenylphosphonium methoxymethylide thereby extending the carbon chain.[399–401]

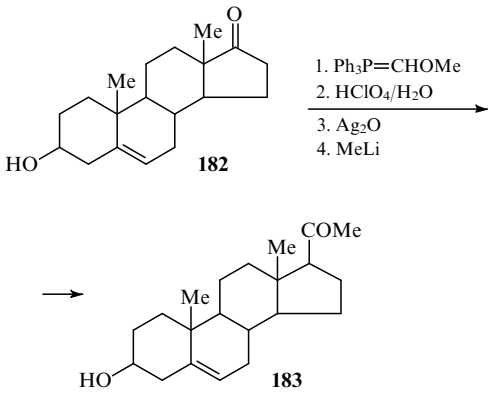


The silicon-containing α-alkoxymethylides **180** are especially convenient for this purpose. Vinyl ethers **181** that are formed in the reaction of the ylide **180** with aldehydes and ketones give aldehydes on treatment with 5% hydrogen fluoride in acetonitrile or with perchloric acid.



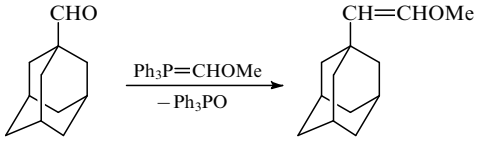
This method has been used for the preparation of various steroid aldehydes.[401–410]

Danishefski *et al.* have developed a simple method for the preparation of pregnenolone **183** by the reaction of the androstenolone **182** with the *C*-oxygen-substituted ylide, prepared by dehydrohalogenation of the methoxymethyltriphenylphosphonium salt with sodium hydride in dimethyl sulfoxide.[411, 412]

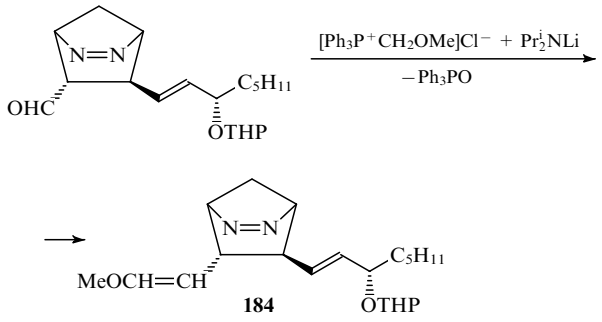


Triphenylphosphonium methoxymethylide enters into the Wittig reaction with sterically hindered carbonyl compounds.

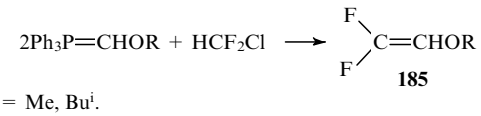
For instance, it easily alkenates adamantane-1-carbaldehyde in ether at −40 °C.[413]



Corey *et al.*[415] have shown that the dehydrochlorination of the α-methoxyalkylphosphonium salts proceeds smoothly under the action of lithium diisopropylamide. The ylides thus obtained have been used for the synthesis of the 9,11-aza-analogues of prostaglandin endoperoxide PGH2 **184**.

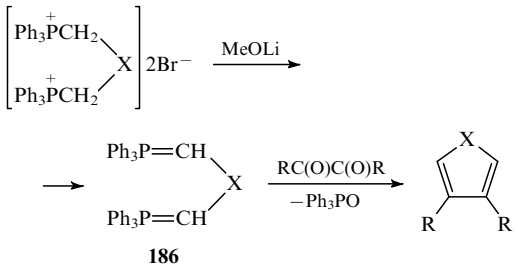


The Wittig-type reactions of triphenylphosphonium alkoxymethylides with chlorodifluoromethane present a synthetic route to the *gem*-difluoroolefins **185**.[414]



R = Me, Bu^i.

Bis(triphenylphosphoniomethyl)oxide and -sulfide are converted under the action of lithium methoxide into bis-ylides. The latter are introduced into the Wittig reaction with dialdehydes or diketones for the synthesis of various heterocycles including macrocycles.[416] For instance, the reaction of the ylides **186** with β-diketones gives furan and thiophene derivatives,



X = O, S,

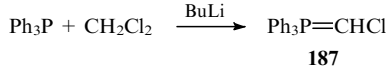
with cycloheptatriene-1,6-dicarbaldehyde and biphenyl-2,2′-dialdehyde 4,9-methanooxa[22]-annulenes[417] or nine-membered rings are formed, respectively.[418,419] [13]-Annulenes with conjugated double and triple bonds have also been synthesised.[420]

3. *C*-Halogen-substituted phosphorus ylides

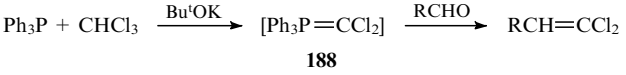
The interest in the *C*-halogen-substituted phosphorus ylides is caused by the possibility of their application for the preparation of haloalkenes, which are valuable reagents for synthesis.[421]

The *C*-halogen-substituted phosphorus ylides are usually formed in the reaction of tertiary phosphines with any source of mono- or di-halomethylene species.

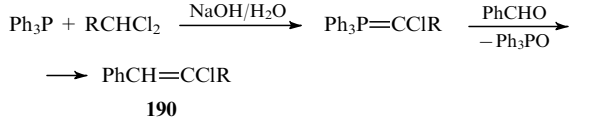
One of the most common methods for the synthesis of the phosphorus ylides with one or two halogen atoms at the α-carbon atom involves the addition of the halocarbenes and carbenoids to tertiary phosphines. They are most often prepared by the treatment of polyhalogenmethanes with strong bases in the presence of tertiary phosphine.[422–427] This method has been used by Seyferth *et al.*[425], and Wittig and Schlosser[426] for the preparation of triphenylphosphonium chloromethylide **187** from dichloromethane, butyllithium, and triphenylphosphine.



Dichlorocarbene generated from chloroform under the action of potassium *tert*-butoxide reacts with triphenylphosphine to give a suspension of triphenylphosphonium dichloromethylide **188** which is used in the Wittig reaction without isolation from the reaction mixture. The ylide $Ph_3P=CFCl$ (**189**) containing chlorine and fluorine atoms at the α-carbon atom has been prepared in the same way.[422]

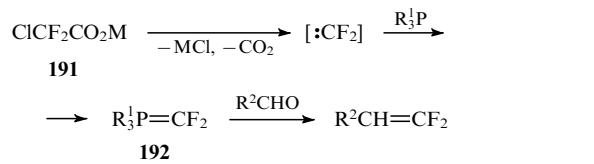


Triphenylphosphonium dichloromethylide **188** has been also synthesised in a heterogeneous medium, dichlorocarbene being generated from chloroform under the action of 50% alkali in the presence of the phase transfer catalyst (TEBA) and triphenylphosphine. In this case ylide in the nascent state enters the Wittig reaction.[428] When a benzene solution of chloroform (or dichloromethylthioether), triphenylphosphine, benzaldehyde and a catalytic amount of TEBA was vigorously stirred at room temperature for 1.5 h with 40% aqueous sodium hydroxide, β-chlorostyrenes **190** were prepared in yields of about 40% – 50%. This reaction has been used for the preparation of pyrethroids.[429,430]

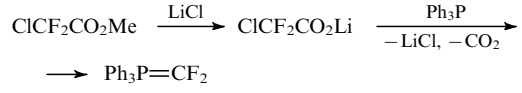


R = Cl, R′S.

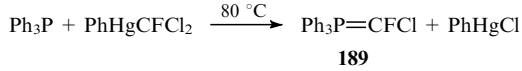
The decarboxylation of the trishalogenacetic acid salts **191** is accompanied by the formation of dihalocarbenes, which, in the presence of tertiary phosphines, give phosphorus ylides **192;** the latter enter into the Wittig reaction with carbonyl compounds.[431–435] An improvement of this method involves the reaction of triphenylphosphine with methyl chlorodifluoroacetate acid in the presence of lithium chloride, which presumably proceeds *via* the formation of difluorocarbene.[436–439]



M = Li, Na, K, $SnMe_3$, R^2 = Bu, Ph;



Heating of triphenylphosphine with dichlorofluoromethyl(phenyl)mercury, which is the source of chlorofluorocarbene, yields triphenylphosphonium chlorofluoromethylide **189**.[440]



In some cases the reaction occurs without the formation of dihalocarbene. For instance, sodium dichlorofluoroacetate in a reaction with a tertiary phosphine gives a betaine, which is converted on decarboxylation into triphenylphosphonium chlorofluoromethylide **189**.[424, 425, 432]

$$Ph_3P + Cl_2CFCO_2Na \xrightarrow[-NaCl]{} [Ph_3P^+CFClCO_2^-] \xrightarrow[-CO_2]{} \mathbf{189}$$

The *C*-halogen-substituted phosphorus ylides **194** have been obtained by the dehydrohalogenation of halomethyltriphenylphosphonium salts **193** by butyl- and phenyllithium, lithium diisopropylamide, and potassium *tert*-butoxide.[399, 441–452]

$$Ph_3P + CH_2FI \longrightarrow \underset{\mathbf{193}}{[Ph_3P^+CH_2F]I^-} \xrightarrow{RM} \underset{\mathbf{194}}{Ph_3P{=}CHF}$$

R = Bu, Ph, Pr^i_2N, Bu^t; M = Li, K.

Butyl- and phenyllithium not only deprotonate the phosphonium salt, but can also exchange the halogen atoms at the α-carbon for lithium[441–452] or a butyl group[142] giving rise to a mixture of ylides **194** and **195**. A mixture of alkenes was formed in the subsequent reaction with carbonyl compounds. The ability of the triphenylphosphonium halomethylides to react with organolithium compounds increases in the series Cl < Br < I.[449–452]

$$[Ph_3P^+CH_2X]X^- \xrightarrow{PhLi} Ph_3P{=}CHX + Ph_3P{=}CH_2$$

X = Br, Cl, I;

$$[Ph_3P^+CH_2F]I^- \xrightarrow{BuLi} \underset{\mathbf{194}}{Ph_3P{=}CHF} + \underset{\mathbf{195}}{Ph_3P{=}CHBu} \xrightarrow{R_2C{=}O} R_2C{=}CHF + R_2C{=}CHBu$$

The substitution of butyl- or phenyllithium by a sterically hindered sodium bis(trimethylsilyl)amide allows one to eliminate the side processes.[443, 444] The dehydrohalogenation of chloromethyltriphenylphosphonium chloride by the unstabilised phosphorus ylides, *e.g.* triphenylphosphonium methylide, occurs very smoothly without side processes and gives a pure triphenylphosphonium chloromethylide **187** in the form of orange crystals with high yields.[443] The dehydrochlorination of dichloromethyltriphenylphosphonium chloride by hexaphenylcarbodiphosphorane in aprotic solvents gave dichloromethylide **188** exclusively.[443, 445]

$$[Ph_3P^+CH_2Cl]Cl^- \xrightarrow[-[Ph_3P^+Me]Cl^-]{Ph_3P{=}CH_2} \mathbf{187}$$

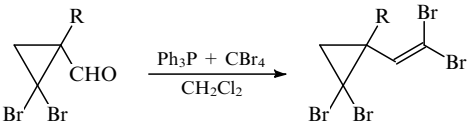
$$[Ph_3P^+CHCl_2]Cl^- \xrightarrow[-[Ph_3P{=}CHP^+Ph_3]Cl^-]{Ph_3P{=}C{=}PPh_3} \mathbf{188}$$

The dehydrohalogenation of trihalomethylphosphonium salts **196**,[446, 453–467] which are obtained by the reaction of tertiary phosphines with tetrahalomethanes, is an important route for the synthesis of *C*-halogen-substituted phosphorus ylides.[449–451, 453] The polyhalomethylphosphonium salts are dehalogenated by tertiary phosphines such as triphenylphosphine or tris(dimethylamino)phosphine.[458–461]

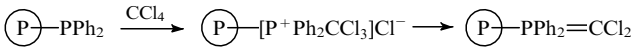
$$2R^1_3P + CX_4 \longrightarrow \underset{\mathbf{196}}{[R^1_3P^+CX_3]X^-} \xrightarrow[-R^2_3PX_2]{R^2_3P} \underset{\mathbf{197}}{R^1_3P{=}CX_2}$$

CX_4 = CCl_4, CBr_4, CBr_2Cl_2, CCl_2F_2, $CBrCl_3$; R^2 = Ph, Me_2N.

This method has been successfully used in the synthesis of some natural and biologically active compounds, *e.g.* for the preparation of dibromovinyl dibromocyclopropanes.[446, 461]



This method has also been used for the preparation of the phosphonium dichloromethylides immobilised on a polymer carrier.[468]



The reaction of triphenylphosphine with tetrahalomethanes may be accompanied by the formation of ylide-phosphonium salts **198** (X = Cl, F), which are used for preparation of haloketones.[462–465]

$$2Ph_3P \xrightarrow[-Ph_3PCl_2]{CXCl_3} Ph_3P{=}CXCl \xrightarrow{Ph_3P} \underset{\mathbf{198}}{[Ph_3P{=}CXP^+Ph_3]Cl^-}$$

X = Cl, F.

Burton and Van Hamme have proposed to perform dehalogenation of polyhalomethylphosphonium salts by the Group II metals (zinc, cadmium, or mercury).[456] This procedure gives an organometallic phosphonium salt, which dissociated to a metal chloride and the phosphorus ylide **189**; the latter readily enters into the Wittig reaction with aldehydes and ketones.[451] Heating of triphenylphosphine with chlorotrifluoromethane in the presence of zinc results in the formation of quasi-complex organometallic compounds, which were isolated in the individual form. Analogously, triphenylphosphine reacts with fluorodiiodomethane to give a stable fluoroiodomethyltriphenylphosphonium iodide, which is converted into triphenylphosphonium fluoromethylide **194** under the action of a zinc-copper couple.[142, 447]

$$Ph_3P + CFCl_3 + Zn \xrightarrow{60\ ^\circ C} \left[\begin{array}{c} Ph_3P^+CFCl \\ | \\ ZnCl \end{array}\right] Cl^- \rightleftharpoons[-ZnCl_2]$$

$$\underset{\mathbf{199}}{}$$

$$\rightleftharpoons \underset{\mathbf{189}}{Ph_3P{=}CFCl} \xrightarrow{RCHO} RCH{=}CFCl$$

$$Ph_3P + CHFI_2 \longrightarrow [Ph_3P^+CHFI]I^- \xrightarrow{Zn/Cu,\ 0\ ^\circ C} \underset{\mathbf{194}}{Ph_3P{=}CHF}$$

NMR Studies have demonstrated that the reaction of a trihalomethylphosphonium salt with zinc gives the organozinc complex **200,** which dissociates to $ZnCl_2$ and the phosphorus ylide **201**.[383] The equilibrium is strongly shifted towards the complex **200.** Nevertheless,the Wittig reaction occurs in the presence of a carbonyl compound, which is evidence for the formation of the ylide **201**.[414, 446]

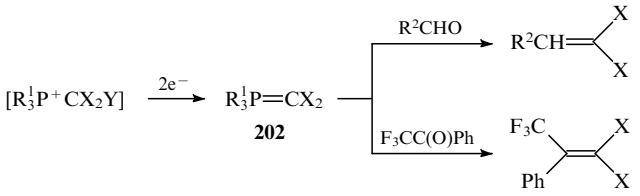
$$[(Me_2N)_3P^+CFCl_2]Cl^- \xrightarrow{Zn}$$

$$\longrightarrow \underset{\mathbf{200}}{[(Me_2N)_3P^+CFCl(ZnCl)]Cl^-} \rightleftharpoons[-ZnCl_2]$$

$$\rightleftharpoons \underset{\mathbf{201}}{(Me_2N)_3P{=}CFCl} \xrightarrow[-(Me_2N)_3PO]{R_2CO} R_2C{=}CFCl$$

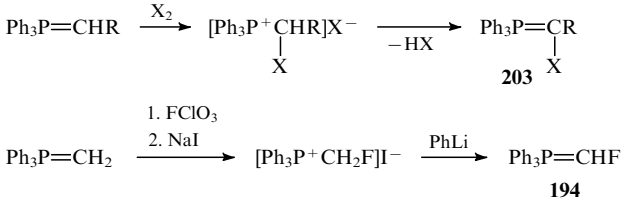
Collignon *et al.* have applied an electrochemical technique for the synthesis of *C*-halogen-substituted phosphorus ylides. The two-electron electrochemical reduction of dihalo- and trihalomethylphosphonium salts in acetonitrile led to the phosphorus ylides **202,** which enter into the Wittig reaction with aldehydes and

reactive ketones in aprotic medium (DMF or acetonitrile) to yield the corresponding haloalkenes.[463]

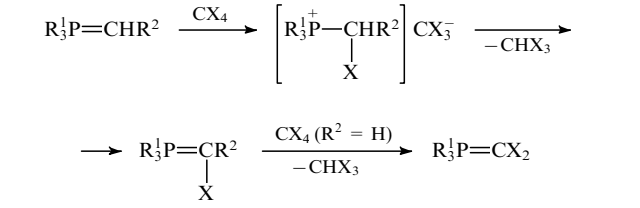


X = Y = Cl; X = F, Y = Br.

The *C*-halogen-substituted phosphorus ylides **203** have been synthesised by the halogenation of the phosphorus ylides with hydrogen atoms at the ylide carbon atom. In the case of ylides containing strong electron acceptors at the α-carbon atom (R = CO_2Alk, C(O)Alk, C(O)Ar), the dehydrochlorination of the intermediate phosphonium salt is performed in the presence of triethylamine.[467] Chlorine, bromine,[467] phenyliododichloride,[468] and chloramine T [469,470] have been used as halogenating agents. The unstabilised phosphorus ylides are halogenated by perhalofluoroalkanes. The reaction occurs regioselectively and high yields of α-haloalkylphosphonium salts are achieved.[471] The fluorination of triphenylphosphonium methylide by $FClO_3$ followed by NaI gives the fluoromethylphosphonium salt. On its dehydroiodination, triphenylphosphonium fluoromethylide **194** has been obtained in high yield, it enters into the Wittig reaction with aldehydes to form vinylfluorides.[472]

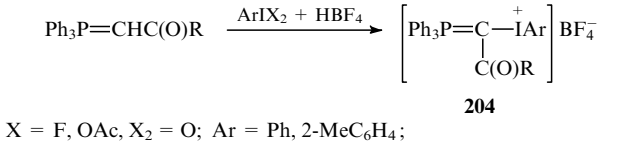


The exchange of a hydrogen atom at the ylide carbon atom for chlorine or bromine occurs on the interaction of phosphorus ylides with carbon tetrachloride and carbon terabromide.[473,474]



X = Br, Cl.

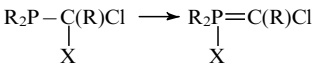
The phosphonium-iodonium ylides **204** have been prepared by the reaction of the stabilised phosphorus ylides with derivatives of trivalent iodine.[475]



X = F, OAc, X_2 = O; Ar = Ph, 2-MeC_6H_4;

R = EtO, Ph, 4-MeC_6H_4.

The halogen atom at the α-carbon atom of the tertiary alkylphosphines is highly mobile, which determines its migration towards the phosphorus atom, the 1,2(C → P)-halogenotropic shift.

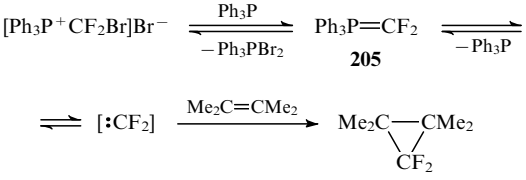


α-Haloalkylphosphines containing electron-accepting substituents at the α-carbon atom rearrange rather easily into phosphorus ylides, and the halogen atom in such ylides may be substituted by various substituents. Numerous examples of the preparation of phosphorus ylides by this method have been described.[12,476–483]

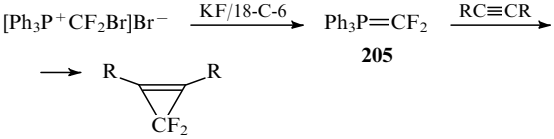
The *C*-halosubstituted phosphorus ylides have been studied in detail using quantum-chemical calculations and physicochemical methods. The *ab initio* quantum-chemical calculations performed by Dixon [484] and Bestmann [16] have shown that the *C*-fluorine-containing ylide $H_3P{=}CHF$ has a non-planar P=CHF group with an inversion barrier of about 2.8 kcal mol^{-1}. Francl *et al.*[485] have assumed, in accordance with Dixon's results, that the zwitter-ionic character of the P=C bond in the $H_3P{=}CF_2$ molecule is minimal. On the basis of the differences in electron densities it has been concluded that the introduction of a fluorine atom at the α-atom enhances the π-character of the P=C bond.

The alkoxycarbonyl- and acylfluoromethylides exist as mixtures of two geometrical isomers. This is a result of hindered rotation about the P=C bond, caused by partial enolisation of the compounds with considerable shift of the negative charge to the carbonyl oxygen atom.[441]

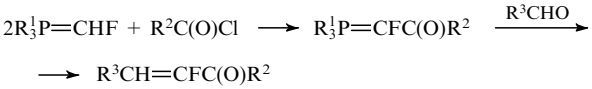
The stability of the *C*-halogen-containing phosphorus ylides depends on the electron-accepting properties of the second substituent at the ylide carbon atom. The *C*-halogenoylides stabilised by strong electron-accepting substituents can be isolated and purified, while non-stabilised ylides with one or two halogen atoms at the α-carbon atom are unstable and thus they are usually introduced in subsequent reactions without isolation and purification.[443,445] Only triphenylphosphonium chloromethylide [443] and -dichloromethylide [446] have been isolated in pure state. Triphenylphosphonium difluoromethylide **205**, which has been prepared by the reaction of bromodifluoromethyltriphenylphosphonium bromide with tertiary phosphines or with potassium fluoride in the presence of 18-crown-6 dissociates readily into difluorocarbene and triphenylphosphine. Difluorocarbene has been captured by tetramethylethylene. The formation of 1,1-difluoro-2,2,3,3-tetramethylcyclopropane in solution indicated the presence of difluorocarbene.[486]



Schlosser *et al.*[487] have recently demonstrated that difluoromethylide **205** adds to mono- and disubstituted acetylenes to give difluorocyclopropenes in good yield.



The alkylation, acylation, and arylation of simple fluoromethylides leads directly to *C*-substituted fluoromethylides as a result of transylidation and presents a convenient synthetic route to various fluoroalkenes.[467]



The acylation of *C*-fluoro-substituted ylides **206** obtained by the reaction of tributylphosphine with trichlorofluoromethane followed by bromination is a convenient way for the preparation of haloalkyl ketones.[465]

$$Bu_3P + CFCl_3 \longrightarrow$$

$$\longrightarrow \left[Bu_3P{=}C(F){-}\overset{+}{P}Bu_3 \right] Cl^- \xrightarrow{RC(O)Cl/Br_2} RC(O)CFBr_2$$

206 **207**

The reactions of *C*-bromo-substituted ylides with potassium iodide or thiocyanate result in the substitution of the bromine atom at the ylide carbon atom by iodine or a thiocyano group.[467, 489]

$$Ph_3P{=}C(Br)COR \xrightarrow{KX} Ph_3P{=}C(X)COR$$

X = I, SCN.

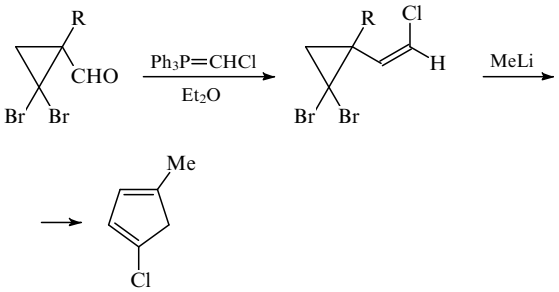
The α-haloalkylphosphines exist in a tautomeric equilibrium with ylides containing the halogen at the phosphorus atom, therefore, they manifest the chemical properties characteristic of both trivalent phosphorus and ylides. The ratio of the tautomers depends on the electron-accepting properties of the substituents at the α-carbon atom: electron-accepting substituents shift the equilibrium towards the ylides, while electron-donating substituents, on the contrary, increase the equilibrium concentration of α-haloalkylphosphines.[489–492]

$$R^1_2PCH(R^2)Cl \rightleftharpoons R^1_2P(Cl){=}CHR^2$$

R^2 = Cl, Br, Alk, Ar.

The *C*-halogen-substituted phosphorus ylides are valuable reagents in the synthesis of haloalkenes. Electron-accepting halogen atoms at the ylide carbon atom decrease the nucleophilicity of the phosphorus ylides. Therefore, triphenylphosphonium halogenylides readily alkenate aldehydes and activated ketones, and do not alkenate non-activated ketones and carboxylic esters. The reactivity of halogenylides may be enhanced by introducing electron-donating substituents at the phosphorus atom, *e.g.*, dimethylamino groups, which decrease the electrophilicity of the phosphonium group. Tris(dialkylamino)phosphonium ylides demonstrate definite advantages as haloalkenating reagents over the triphenylphosphonium ylides. For instance, tris(dimethylamino)phosphonium dichloromethylide converts ethyl-*cis-trans*-caronaldehyde into chrysanthemic acid in high yield, which could not be achieved with triphenylphosphonium ylide **187**.[453, 457–459]

The halovinylsubstituted dibromocyclopropanes, the initial compounds for the synthesis of cyclopentadienes, and alkenes, have been obtained using triphenylphosphonium chloromethylide.[461]

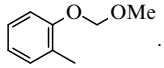


Schlosser has proposed a highly stereoselective method for the synthesis of haloalkenes, which involves 2-methoxymethoxyphenylphosphonium ylides **208** instead of triphenylphosphonium ylides. In this case, the ratio of *cis-trans* isomers of alkenes **209** was 98 : 2 – 99 : 1.[427]

$$Mmp_3P \xrightarrow{ICH_2X} [Mmp_3P^+CH_2X]I^- \xrightarrow{NaNH_2/THF}$$

$$\longrightarrow Mmp_3P{=}CHX \xrightarrow{RCHO} RCH{=}CHX$$

208 **209**

X = Cl, Br, I; Mmp = 

The reaction of aldehydes with the ylide **210** containing a fluorine atom at the phosphorus atom yielded the four-membered cycloadducts of the Wittig reaction, **211**, which have been isolated in the individual form; their structure was studied by NMR. On heating to 60 – 80 °C, the adducts decomposed into 1,1-dihaloalkenes and bis(diethylamino)phosphoryl fluoride.[493]

$$(Et_2N)_2P(F){=}CX_2 \xrightarrow{Pr^iCHO}$$

210

$$\longrightarrow (Et_2N)_2P(F)(O{-}CHPr^i){-}CX_2 \xrightarrow[-(Et_2N)_2P(O)F]{} X_2C{=}CHPr^i$$

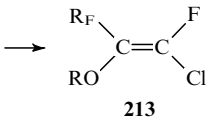
211

X = Cl, Br.

The interaction of tris(dimethylamino)phosphonium chlorofluoromethylide **201** with fluoroalkylcarboxylic esters is stereoselective and occurs with the predominant formation of *Z*-isomers of alkyl polyfluoroalkenyl ethers **213**.

$$[(Me_2N)_3P^+CFCl_2]Cl^- \longrightarrow (Me_2N)_3P{=}CFCl \xrightarrow{R_FC(O)OR}$$

212 **201**



213

However, monofluoro-, fluorochloro-, and bromofluoromethylides usually react with aldehydes and asymmetrical ketones to give mixtures of *Z*- and *E*-alkenes.[383, 384] The yields and the stereochemistry of the Wittig reaction in the case of tris(dimethylamino)phosphonium halogenylides depend on the method of dechlorination of the phosphonium salt. A high yield of (*Z*)-1-chloro-2-propoxyperfluoropropene is achieved in the case of dechlorination of the salt **212** with tris(dimethylamino)phosphine in the presence of isopropyl trifluoroacetate.[446, 453–456] The zinc – copper couple dehalogenates exothermally the phosphonium salts **212** in the presence of carbonyl compounds $R^1R^2C{=}O$ (R^1 = Ph, C_6H_{13}, CF_3; R^2 = H, Ph, CF_3, Me, AlkO), with the formation of 1-chloro-1-fluoroalkenes. In the case of aldehydes and activated ketones, the yields of alkenes are almost quantitative, while with ketones of the acetophenone type the yields are about 70%.

The difluoromethylide **214**, which is generated from tris(dimethylamino)phosphine and dibromofluoromethane, is a convenient source of the difluoromethylene group; **214** enters into the Wittig reaction with cyclohexanone, acetophenone, and propiophenone.[453, 455, 456]

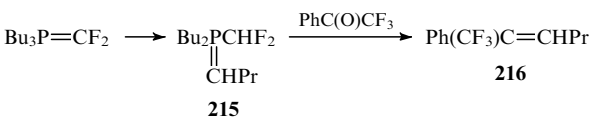
$$(Me_2N)_3P{=}CF_2 + R^1R^2C{=}O \xrightarrow{20\ ^\circ C}$$

214

$$\longrightarrow R^1R^2C{=}CF_2 + (Me_2N)_3PO$$

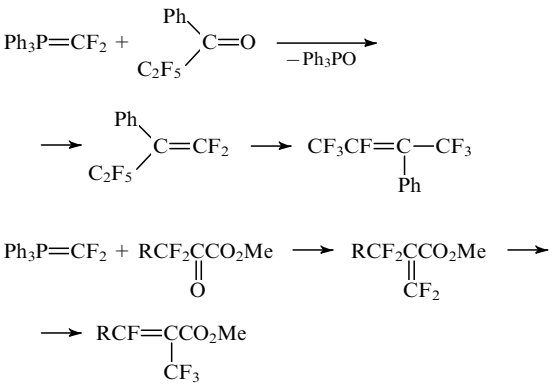
Triphenylphosphonium fluoromethylide **194** alkenates aliphatic and aromatic aldehydes, and activated and non-activated ketones.[142, 448] Triphenylphosphonium fluorochloromethylide **189** generated in the reaction of triphenylphosphine with sodium

dichlorofluoroacetate acid enters into the Wittig reaction with aldehydes and activated ketones to yield 1 : 1 mixtures of *Z*- and *E*-alkenes in 1 : 1 ratio,[142,448] and alkenates aromatic α-oxocarboxylic esters with formation of α-aryl chlorofluoroacrylic acids.[423,424,436,437,494–496] Triphenylphosphonium difluoromethylide **205** converts aldehydes and activated ketones into α,α-difluoroolefins in high yields; however, it does not alkenate cyclohexanone and acetophenone because of their insufficient electrophilicity. Tributylphosphonium difluoromethylide has high reactivity owing to the electron-donating effect of the butyl groups. This ylide, generated by the haloacetate method, alkenates *in situ* such non-activated ketones as benzophenone, cyclohexanone, methylketones RC(O)Me, where R = C_5H_{11}, Ph, 2-furyl, 2-thienyl, *etc*.[436,437] Examples of anomaly in the course of the Wittig reaction with tributylphosphonium difluoromethylide are known. For instance, in the reaction of tributylphosphonium difluoromethylide with trifluoroacetophenone, a prototropic rearrangement of the difluoromethylide into the butylide **215** yields the alkene **216**.[431,436]

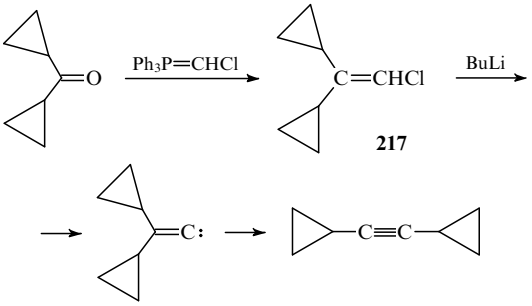


215 **216**

The Wittig reaction of *C*-fluoro-substituted ylides with ketones containing perfluoroalkyl groups is sometimes accompanied by isomerisation associated with the migration of the fluorine atom from the perfluoroalkyl to difluoromethylene group.[432] The isomerisation of fluoroalkenes is suppressed when the reaction is performed in the absence of strong bases or dehalogenating agents.[431]

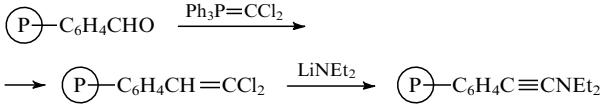


The reaction of triphenylphosphonium chloromethylide with dicyclopropyl ketone gives the chloroalkene **217** in 81% yield; it is transformed into dicyclopropylacetylene, which is formed *via* a carbenoid.[497]



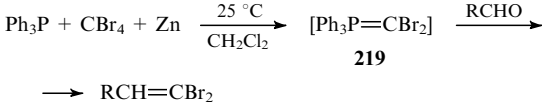
217

Triphenylphosphonium dichloromethylide was used for the modification of polymeric reagents, for instance, for the preparation of polymeric ynamines **218**.[498]



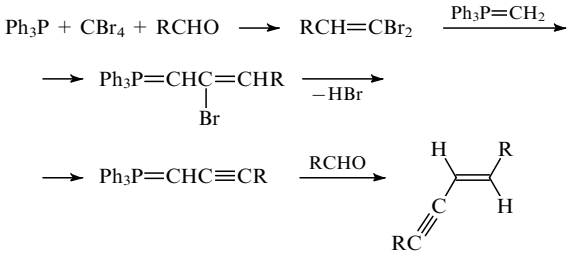
218

Corey has proposed a convenient method for the synthesis of haloalkenes by the reaction of triphenylphosphine with carbon tetrabromide in the presence of zinc dust.[497] The dibromomethylide **219** reacts *in situ* with aldehydes to form dibromoalkenes[494] that have been used in the synthesis of retinoids,[494] alkynes,[497] and alkynecarboxylic acids.[359,446]

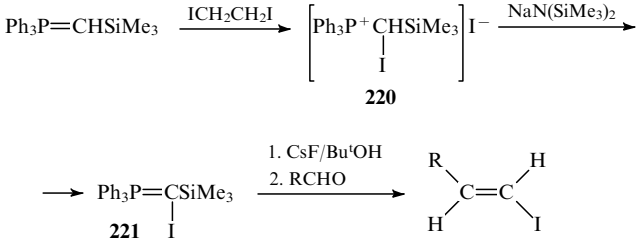


219

Bestmann has prepared synthons of pheromones based on the *C*-halogen-substituted ylides.[499]

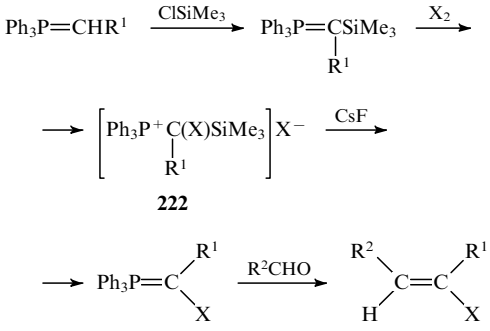


Methods for the preparation of α-haloalkenes on the basis of *C*-silicon-substituted ylides have been developed. The mild iodination of triphenylphosphonium trimethylsilylmethylide with 1,2-diiodoethane gives the iodoalkylphosphonium salt **220** in high yield. The dehydroiodination of the salt **220** by sodium bis(trimethylsilyl)amide results in the formation of the trimethylsilyliodomethylide **221**, which is stereoselectively transformed into α-iodoalkenes on treatment with cesium fluoride in *tert*-butyl alcohol in the presence of carbonyl compounds.[500]



220 **221**

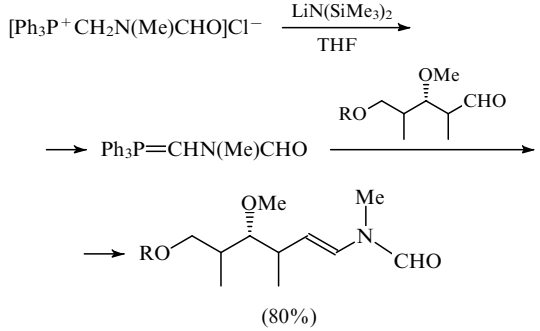
The successive treatment of non-stabilised phosphorus ylides by chlorotrimethylsilane and halogen yields α-haloalkylα-trimethylsilyl-triphenylphosphonium salts **222**, their desilylation by cesium fluoride in the presence of aldehydes results in haloalkenes.[501]



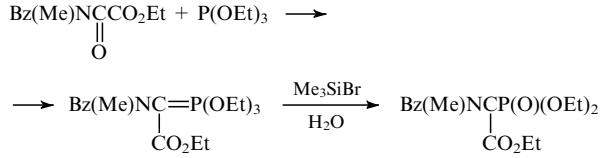
222

V. Conclusion

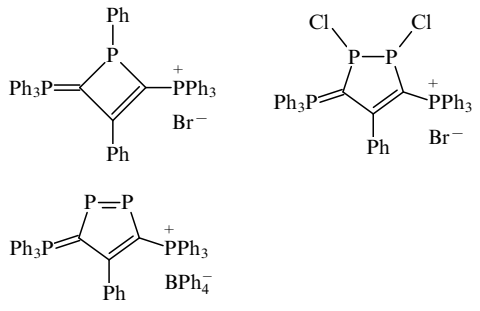
Heteroatoms at the ylide carbon atom thus considerably affect the chemical properties and the reactivity of the phosphorus ylides. Certain heteroatoms, such as the atoms of the main Group I and II, nitrogen, tin, and lead atoms increase the electron density at the carbon atom and the reactivity of ylides, while on the contrary, other heteroatoms such as silicon and germanium atoms, Group V – VII atoms and transition elements stabilise the ylide carbanion, thus lowering its nucleophilicity. As a result, *C*-substituted phosphorus ylides acquire new remarkable chemical properties and offer new synthetic opportunities. This determines the deep interest of chemists in the *C*-hetero-substituted phosphorus ylides as exceptionally promising reagents in organic synthesis.[502] Thus after the present review has been completed, new data on the chemistry of the *C*-element-substituted phosphorus ylides, especially ylides containing Group V main elements at the α-carbon atom appeared. Paterson *et al.*[503] have synthesised *N*-methylformamido-substituted phosphorus ylide by the action of lithium bis(trimethylsilyl)amide on the phosphonium salt. This ylide was shown to be an effective reagent for the transformation of aldehydes into the corresponding *N*-alkenyl-*N*-methylformamides.



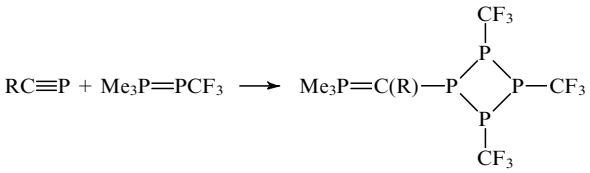
Japanese chemists have synthesised trialkoxyphosphonium ylides with a nitrogen atom at the ylide carbon atom and converted them into the α-alkylaminophosphonates.[504]



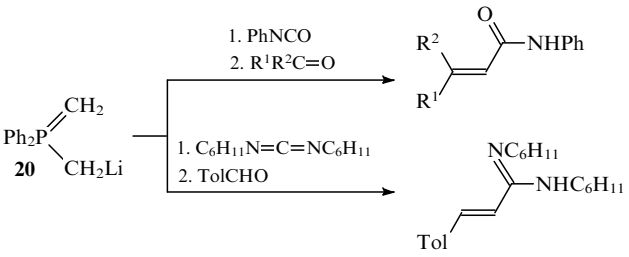
C-Phosphino-substituted phosphorus ylides have been also intensely studied. Schmidpeter *et al.*[505] have synthesised four- and five-membered heterocycles with an exocyclic ylide group including heterocycles with a double P = P bond.



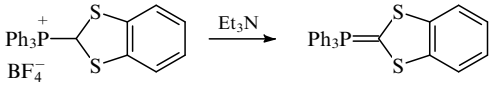
Grobe[506] has performed a very interesting synthesis of a phosphorus ylide with a tetraphosphetene ring at the α-carbon atom starting from the derivatives of mono- or two-coordinate phosphorus.



Cristau *et al.*[507] have studied the reactivity of ylide-anions **20** towards carbodiimides and isocyanates. The reaction is performed in two steps: at first heterocumulene is treated with the ylide-anion, and then the ylide adduct is introduced in the reaction with an aldehyde or ketone. As a result, α,β-unsaturated amides and amidines are formed in high yields and stereoselectivity.



Clausen and Becher[508] have described a new synthetic route to tetrathiafulvenes from cyclic dithiosubstituted phosphorus ylides, which were generated from the corresponding phosphonium salts by the action of triethylamine.



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