Russian Chemical Reviews **72** (8) 705 – 713 (2003) © 2003 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2003v072n08ABEH000800

Reactions of phosphorus ylides with acyl chlorides: pathways and preparative potential

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Abstract. Data concerning the reactions of phosphorus ylides with acyl chlorides that occur by different pathways depending on the nature of the ylide or acyl chloride and on the reaction conditions are summarised and systematised. The products of these reactions are of interest as building blocks for the synthesis of other classes of compounds. The bibliography includes 131 references.

I. Introduction

Phosphorus ylides (or alkylidenephosphoranes, phosphonium methylides) [1,2] are compounds with a P=C bond. They possess great synthetic potential and are used to obtain other classes of compounds. It is mostly triphenylphosphine derivatives, such as methylidenetriphenylphosphorane (**1**) and substituted alkylidenephosphoranes **2** and **3**, that find practical use. The P=C bond in these compounds is polarised considerably in such a way that the electron density is shifted from the prosphorus atom to the carbon atom (structure **A**).

$$\underset{\mathbf{1}}{Ph_3P{=}CH_2} \qquad \underset{\mathbf{2}}{Ph_3P{=}CHR^1} \longleftrightarrow \underset{\mathbf{A}}{Ph_3\overset{+}{P}{-}\overset{-}{C}HR^1} \qquad \underset{\mathbf{3}}{Ph_3P{=}CR^1R^2}$$

R^1, R^2 = Alk, Ar, COAlk, COAr, CO_2Alk, CN.

The presence of partial negative charge on the ylide carbon atom makes these compounds highly reactive, primarily with respect to electrophilic reagents.

Prosphorus ylides **2** and **3** containing alkyl or aryl substituents at the ylide carbon atom are the most reactive. They are sensitive to moisture and atmospheric oxygen; therefore, they are not isolated in pure form but are obtained in anhydrous solvents, usually in an inert atmosphere, just prior to the reaction. If electron-withdrawing groups (COR, CO_2R, CN) are present as substituents at the ylide carbon atom and the negative charge is partially shifted to them, the reactivity of the ylides decreases. Such compounds can be isolated in a free state and stored under ordinary conditions. Some of them are available commercially, *e.g.*, acetylmethylidenetriphenylphosphorane (**2**, R^1 = COMe), benzoylmethylidenetriphenylphosphorane (**2**, R^1 = COPh), ethoxycarbonylmethylidenetriphenylphosphorane (**2**, R^1 = CO_2Et), *etc*.

The reaction of phosphorus ylides with aldehydes (the Wittig reaction) is the most famous; it is widely employed in syntheses of unsaturated compounds. The Wittig reaction has been described in detail in a number of reviews and monographs,[3–12] including one recent review [13] dedicated to the 100th anniversary of this reaction's creator.

Wide circles of chemists are less aware of reactions of alkylidenephosphoranes with other electrophilic reagents, *inter alia*, acyl halides. Depending on the nature of the starting compounds and sometimes on the reaction conditions, the reactions of phosphorus ylides with acyl halides occur by different pathways and give different products. In the future, some of these transformations affording interesting organic products [1,2,14] may become preparative methods for their synthesis. As of now, several examples of reactions of phosphorus ylides with acyl chlorides for possible preparative use are known: the formation of acylated ylides followed by their thermolysis into acetylene compounds or oxidation to give polycarbonyl derivatives; synthesis of allene compounds; synthesis of enol esters, *etc*.

Since the publication of the review by Bestmann and Zimmermann [1] and the monograph by Kolodyazhnyi [2] which cover the literature on reactions of phosphorus ylides with acyl chlorides reported before 1990, a lot of new publications have appeared that require generalisation and systematisation. Therefore, it seems expedient to cover this aspect of the chemistry of alkylidenephosphoranes in a separate review. The authors of this review tried to cover, as thoroughly as possible, the literature on reactions of phosphorus ylides with acyl chlorides for the period from 1990 to 2002. Moreover, the review considers the most significant publications of the preceding years.

II. Acylation of phosphorus ylides. Transylidation

Acylation occurs most readily with acyl chlorides and alkylidenephosphoranes **3**, which contain no hydrogen atoms at the ylide carbon atom: the acyl residue adds to the ylide carbon atom to give *C*-acylated phosphonium salts **4**.[15–17] Alkaline hydrolysis of the latter results in ketones.

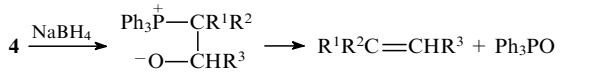
$$\underset{\mathbf{3}}{Ph_3P{=}CR^1R^2} + R^3{-}C(=O){-}Cl \longrightarrow \underset{\mathbf{4}}{\left[Ph_3\overset{+}{P}{-}\underset{\displaystyle COR^3}{\underset{|}{C}}R^1R^2\right]Cl^-} \xrightarrow{OH^-} R^3C(O)CHR^1R^2 + Ph_3PO$$

R^1, $R^2 \neq$ H.

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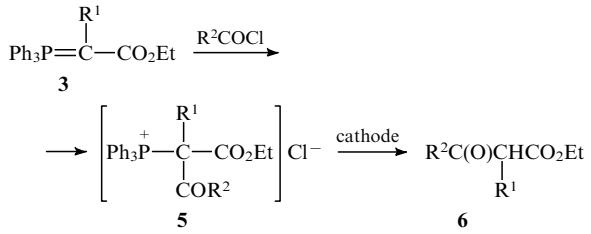
Received 9 December 2002
Uspekhi Khimii **72** (8) 787 – 796 (2003); translated by S S Veselyi

Reduction of *C*-acylated phosphonium salts **4** with sodium borohydride occurs *via* intermediate betaines, which quickly eliminate triphenylphosphine oxide to give alkenes.[16]



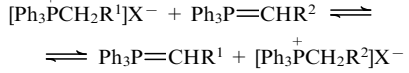
R^1 = Me; R^2 = Me, Ph; R^3 = Ph, MeC_6H_4.

A similar reaction of acyl chlorides with phosphoranes **3** containing the ester group, followed by cathodic reduction of acylated phosphonium chlorides **5**, provides a method to obtain esters of α-substituted β-oxo acids **6**.[17]



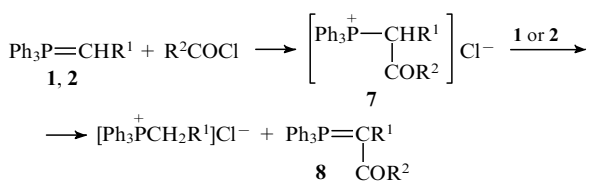
R^1 = Me, Pr, C_5H_{11}, $(CH_2)_2CO_2Me$, Ph, CH=CHPh, $(CH_2)_2Ph$;
R^2 = Et, Bu.

Monosubstituted alkylidenephosphoranes **2** containing a hydrogen atom at the ylide carbon are conjugated bases, whereas the corresponding phosphonium salts are acids. The position of equilibrium depends on the nature of substituents R^1 and R^2



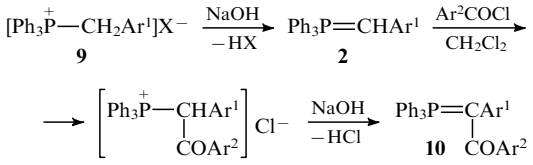
and is strongly (often, almost completely) shifted to the right if R^1 is a much stronger electron-withdrawing group than R^2; in fact, this is the case in acylation reactions.

The phosphonium salts **7** initially formed upon acylation of phosphoranes **1** and **2** are rather strong acids due to the effect of the acyl group. They eliminate HCl under the action of the initial phosphorane molecules to give acylated ylides **8** (weaker bases than the original phosphoranes). Thus, transylidation occurs:[18–21] the phosphonium salt and the ylide react to give a new phosphonium salt and a new ylide. This principle is widely employed in the synthesis of α-acylated ylides **8**.[22–29]



R^1 = H, Me, Et, Pr^n, Pr^i, Bu^n, C_5H_{11}, Ph, CO_2Et; R^2 = Me, Et, Pr^n, Pr^i, Bu^n, Bu^t, C_5H_{11}, C_6H_{13}, cyclo-C_4H_7, cyclo-C_6H_{11}, CH=CHMe, Ph, 2-$MeOC_6H_4$, 2-$MeSC_6H_4$, $CH_2P(O)(OEt)_2$.

The usual procedure for the acylation of unstable alkylidene- and arylmethylidenephosphoranes **1**–**3** (R^1, R^2 = Alk, Ar) involves the addition of phenyl- or butyllithium to a solution of the appropriate phosphonium salt in an anhydrous solvent, followed by treatment of the resulting phosphorane with the acylating agent in an inert atmosphere. The process can be simplified considerably by using the two-phase system CH_2Cl_2 – 50% aqueous NaOH. These conditions were used to acylate benzylidenetriphenylphosphorane and other arylmethylidenephosphoranes (**2**, R^1 = Ar)[30–32] formed upon treatment of the corresponding phosphonium salts **9** with NaOH.†



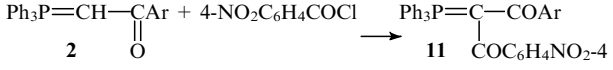
Ar^1 = Ph, 4-PhC_6H_4, 2,4-$Cl_2C_6H_3$, 3-FC_6H_4, 4-$NO_2C_6H_4$, 4-$MeO_2CC_6H_4$, 2,3,5,6-Cl_4-4-MeC_6, 4-$PhCOC_6H_4$, 4-(4-MeC_6H_4N=N)C_6H_4, 1-naphthyl, 2-naphthyl, 4-methyl-1-naphthyl, 9-phenanthryl;
Ar^2 = Ph, 4-ClC_6H_4, 3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 2-furyl.

The reaction is carried out under conditions of phase-transfer catalysis; the phosphonium salt serves as the carrier of ions from the aqueous phase to the organic phase. This procedure makes acylphosphoranes **10** accessible; the latter are used in syntheses of diarylacetylenes.

This two-phase system can also be used to acylate stable ylides; in this case, there is no need to isolate the free ylide beforehand.[32]

The optimum phosphorane-to-acyl chloride ratio in transylidation is 2 : 1. Otherwise, the excess acyl chloride can further react with the acylated ylide to give side products.

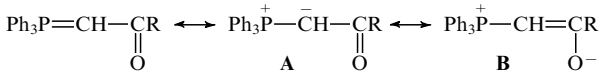
The reactions of aroylmethylidenetriphenylphosphoranes (**2**, R^1 = COAr) with *p*-nitrobenzoyl chloride in the ratio 2 : 1 resulted in *C*-acylated phosphoranes **11**, which are crystalline products with sharp melting points.[34]



Ar = Ph, 4-ClC_6H_4, 4-MeC_6H_4, 4-$NO_2C_6H_4$, 2-thienyl.

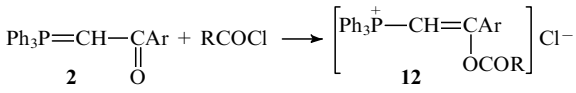
Later, the *C*-acylation of other ylides with similar structures with *p*-nitrobenzoyl chloride as well as cinnamoyl chloride, furoyl chloride and phenylacetyl chloride was described.[35,36] However, Nesmeyanov *et al.*[37] doubted that it was possible to obtain *C*-acylated products from 2-oxoalkylidenephosphoranes; they believed that *O*-acylation was most probable.

In phosphorane molecules containing a carbonyl group bound to the ylide carbon atom, the electron density is shifted from the ylide carbon atom (structure **A**) to the oxygen atom of the carbonyl group to give structure **B**, as confirmed by spectral methods.[25,38–40]



R = Alk, Ar, OAlk.

In such a case, the reaction centre of the 2-oxoylide molecule is transferred to the carbonyl oxygen; this is actually observed in acylation and alkylation reactions. For example, it was shown[34] that aroylmethylidenetriphenylphosphoranes (**2**, R^1 = COAr) react with acetyl chloride and benzoyl chloride in accordance with structure **B** to give *O*-acylated salts **12**.

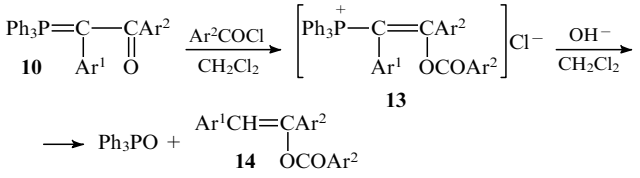


Ar = Ph, 4-BrC_6H_4, 4-ClC_6H_4, 4-MeC_6H_4; R = Me, Ph.

† Simultaneously, the concentrated alkaline solution acts as a desiccant for dichloromethane.[33]

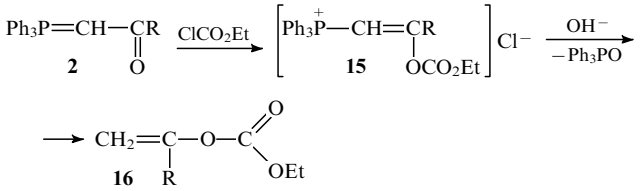
O-Acylation of phosphoranes was also observed in some other studies.[35, 41–44]

Treatment of phosphorus ylides with a 2.5–3-fold excess of an acyl chloride under conditions of phase-transfer catalysis results in secondary acylation of the initially formed ylide **10**; this is accompanied by the transfer of the reaction centre to the carbonyl oxygen atom. Subsequently, the *O*-acylated phosphonium salt **13** is cleaved by an alkali to give enol esters **14**.[45, 46]



Ar^1 = Ph, 4-MeC_6H_4, 4-PhC_6H_4, 1-naphthyl, 2-naphthyl, 4-methyl-1-naphthyl; Ar^2 = Ph, 2-ClC_6H_4, 4-ClC_6H_4, 2-MeC_6H_4, 4-MeC_6H_4.

Chloroformates react with 2-oxoalkylidenephosphoranes with the attack also on the oxygen atom under conditions of phase-transfer catalysis giving *O*-acylated phosphonium salts **15**; the latter are cleaved by an alkali into enol carbonates **16**.[47]

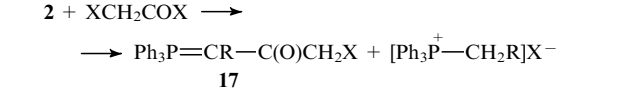


O-Acylated phosphonium salts can be isolated and stored under ordinary conditions, but they are very unstable at elevated temperatures. Probably, *O*-acylated phosphonium salts can serve as acylating agents, with respect to the original phosphorane molecules in particular.

It was shown[48] that heating of *O*-acylation products results in their slow rearrangement with migration of the acyl residue to the carbon atom, *i.e.*, with formation of *C*-acylation products.

Preparation of *C*-acylated derivatives from 2-oxoalkylidenephosphoranes is only possible with acyl chlorides activated by electron-withdrawing groups. In addition to *p*-nitrobenzoyl chlorides, this reaction can be carried out with ethoxalyl chloride, 2-oxoacyl chlorides, 2-furoyl chloride, *etc.*

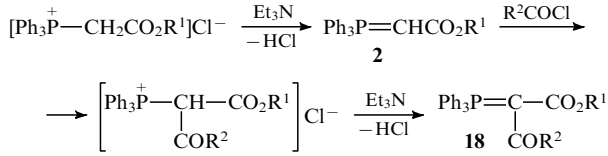
Halogen-substituted acyl halides (chloroacetyl chloride, bromoacetyl bromide, trichloroacetyl chloride) behave as acylating agents[49] with respect to alkoxycarbonyl- and cyanomethylidenetriphenylphosphoranes. The reaction is accompanied by transylidation to give *C*-acylated phosphoranes **17**.



R = CO_2Me, CO_2Et, CN; X = Cl, Br.

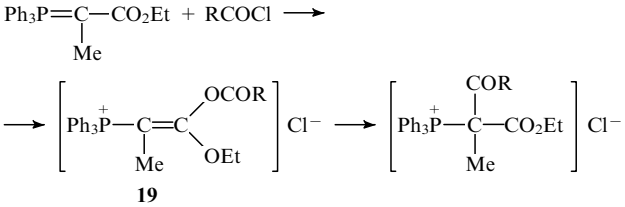
The halogen atoms of the α-halogenoketone moiety of the ylides **17** can undergo nucleophilic substitution, although the effect of the phosphoranylidenemethyl group makes them less reactive than in ordinary halogenoketones.

Upon transylidation, half of the starting ylide is present in the reaction mixture as a phosphonium salt. This drawback can be avoided if another base, for example triethylamine, is used to bind the hydrogen halide.[50–53] Yet another advantage of this method is that preliminary isolation of the starting phosphorane in a free state is unnecessary. One can perform the reaction using an appropriate phosphonium salt and a twofold excess of triethylamine.[54, 55] Successive transformations of a phosphonium salt gave *C*-acylated ylides **18**.



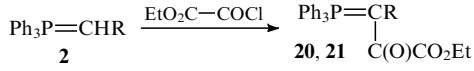
R^1 = Me, Et, Bu, Bn; R^2 = $CHCl_2$, CCl_3, $CClF_2$, CHF_2, CF_3, C_2F_5, CCl_2Me, Ph, 2-MeC_6H_4, 4-MeC_6H_4, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$, 4-ClC_6H_4, 2-$MeSC_6H_4$, C≡CBu, C≡CPh, 2-furyl, 2-thienyl.

It was found[56] that alkoxycarbonyl-substituted ylides give unstable *O*-acylated salts **19** at low temperatures, which then undergo spontaneous rearrangement into *C*-acylated phosphonium salts.



R = Me, $(CH_2)_2CO_2Me$, $(CH_2)_2CO_2Bn$.

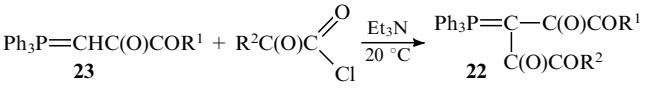
The reaction of acetylmethylidenetriphenylphosphorane (**2**, R = COMe) with ethoxalyl chloride gave ylide **20** with two carbonyl groups and one ester group, whereas the reaction of methoxycarbonylmethylidenetriphenylphosphorane (**2**, R = CO_2Me) gave trioxo ylide **21**, which contains one carbonyl group and two ester groups.[57]



R = COMe (**20**), CO_2Me (**21**).

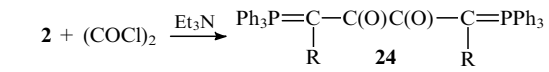
The low yields of phosphoranes **20** and **21** (9% and 33%, respectively) can be explained by the fact that Koz'minykh *et al.*[57] used an equimolar phosphorane : acyl chloride ratio. Better results were achieved with triethylamine.[58, 59]

Tetraoxoylides **22** are formed in reactions of dicarbonyl phosphoranes **23** with 2-oxoacyl chlorides.[60–62]



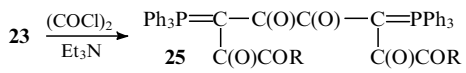
R^1, R^2 = Me, Ph, OMe, OEt.

The reactions of alkylidenephosphoranes with dicarboxylic acid chlorides result in bisylides. In certain studies,[61, 63, 64] oxalyl chloride was used for acylation. For example, bisylides **24** were obtained by treatment of phosphoranes **2** with oxalyl chloride in the presence of triethylamine.[63] Reactions of alkylidenephosphoranes **2** with other dicarboxylic acid chlorides, as well as reactions of monoacyl chlorides with bisylides containing hydrogen atoms at the ylide carbon atoms, result in similar products.[64]



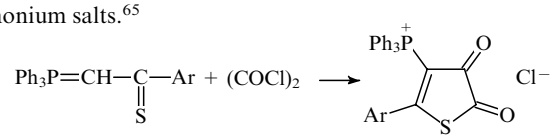
R = Ph, 4-ClC_6H_4, 4-BrC_6H_4, CO_2Me, CO_2Et, COPh.

Furthermore, Aitken and Karodia[61] obtained hexacarbonyl bisylides **25** using the reaction of dicarbonyl phosphoranes **23** with oxalyl chloride.



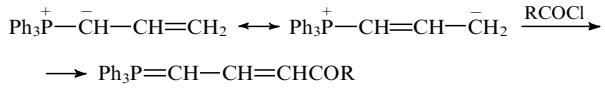
R = Ph, OMe, OEt.

The reactions of oxalyl chloride with alkylidenephosphoranes containing the thiocarbonyl group resulted in heterocyclic phosphonium salts.[65]



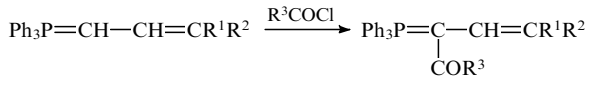
Ar = Ph, 4-MeC$_6$H$_4$.

Vinylmethylidenetriphenylphosphorane is acylated at the γ-position; this is accompanied by transylidation.[66, 67]



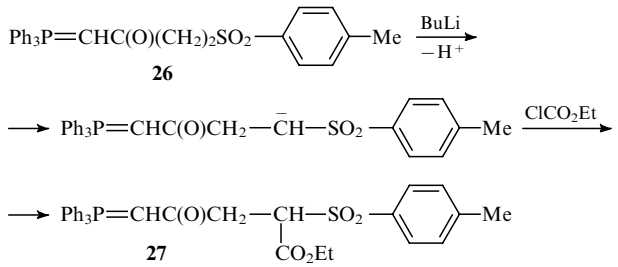
R = Me, Pr^n, Pr^i, Bu^n, OMe.

However, vinylmethylidenephosphoranes containing two γ-substituents only undergo α-acylation.[68]



R^1 = Ph, R^2 = H; R^1 = R^2 = Me; R^3 = Ph, 4-ClC$_6$H$_4$, 4-MeC$_6$H$_4$, CH=CHPh.

An unusual example of the acylation of phosphorane **26** containing a sulfonyl group was reported.[69] Its treatment with butyllithium results in deprotonation from the α-position with respect to the sulfonyl group, giving a carbanionic centre which is stronger than the ylide carbon atom. Subsequent acylation with ethyl chloroformate results in the new phosphorane **27**, which can subsequently be used in the Wittig reaction.

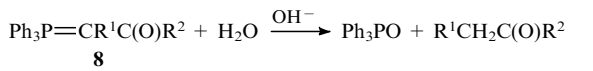


Acylated ylides possess biological activity; in particular, they were found to have antimicrobial properties. A short survey of results of studies on the biological action of acylmethylidenephosphoranes and the corresponding phosphonium salts has been published.[57]

III. Reactions and preparative value of acylated ylides

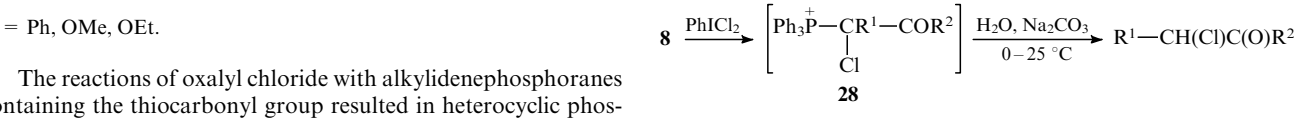
1. Hydrolysis and reduction. Synthesis of ketones and carboxylic acids

Acylphosphoranes **8** can serve as intermediates in the syntheses of other classes of compounds, *e.g.*, ketones, using alkaline hydrolysis,[15, 18, 70] reductive cleavage in the presence of zinc in acetic acid [18, 20, 68, 71] or other methods.[18, 26, 69, 72]



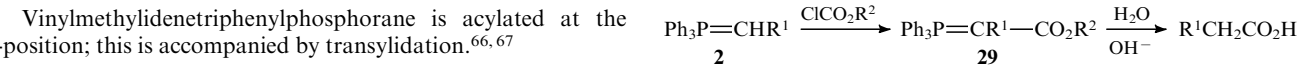
R^1 = H, Me, Pr, Ph; R^2 = Me, Pr, C$_5$H$_{11}$, Ph, CH=CHPh, (CH$_2$)$_2$Ph.

Chlorination of phosphoranes **8** with dichloroiodobenzene followed by hydrolysis of salts **28** results in α-chloro ketones.[26]



R^1 = Et, Pr^n, C$_5$H$_{11}$, Bn; R^2 = Me, Pr^i, cyclo-C$_3$H$_5$, cyclo-C$_6$H$_{11}$.

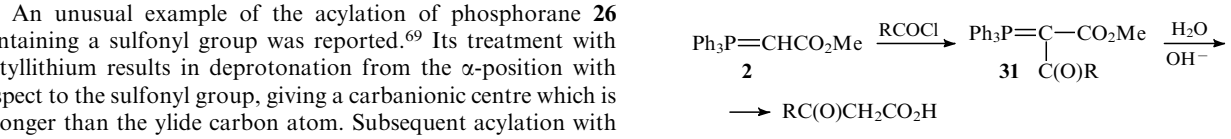
The ester group is introduced in alkylidenephosphorane molecules using alkyl chloroformates as acylating agents;[66, 69, 73] subsequent hydrolysis of the resulting phosphoranes **29** gives carboxylic acids.



R^1 = H, Me, Et, Pr, cyclo-C$_3$H$_5$, cyclo-C$_6$H$_{11}$, Ph; R^2 = Me, Et.

Cyclopropanecarboxylic acid **30** was obtained in 84% yield using this method.[73]

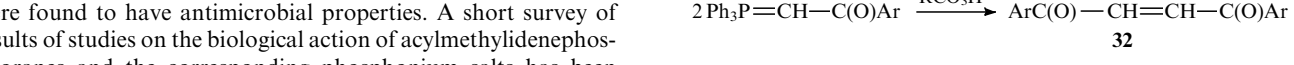
Alkaline hydrolysis of acylated phosphoranes **31** yielded β-oxo acids, while their acid hydrolysis yielded their esters.[74]



R = Me, Pr, C$_5$H$_{11}$, C$_{13}$H$_{27}$, Ph, 2-furyl.

2. Oxidation of acylmethylidenephosphoranes

The oxidation of acylated ylides is yet another example of their preparative usage. Different products are obtained depending on the oxidant. It was shown [75, 76] that oxidation of stabilised acylylides with peroxy acids gives diacyl-substituted ethylenes. The best results were achieved in the synthesis of diaroylethylenes **32**. Presumably, the original phosphorane is partly oxidised into arylglyoxal during the reaction; the latter then undergoes the Wittig reaction with other ylide molecules to give diaroylethylenes.



Ar = Ph, 4-BrC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-NO$_2$C$_6$H$_4$, 4-MeCONHC$_6$H$_4$; R = Me, C$_7$H$_{15}$.

Similar compounds were obtained upon the oxidation of aroylmethylidenetriphenylphosphoranes with selenous acid in dioxane.[77, 78] Treatment of acyl- and alkoxycarbonylmethylidenephosphoranes with alkene ozonides [79, 80] results in symmetrical alkenes containing ketone or ester groups. The reaction occurs probably *via* intermediate glyoxals, as was proved [81] by analysing the products obtained upon treatment of aroylmethylidenephosphoranes with ozone at −70 °C. Under these conditions, phenylglyoxal (**33**) was obtained from benzoylmethylidenetriphenylphosphorane (**2**, R = COPh) and diketone **34** was obtained from the substituted ylide **8** (R^1 = R^2 = Ph).

$$Ph_3P{=}CH{-}C(O)Ph \xrightarrow[-70\ ^\circ C]{O_3} PhC(O){-}CHO$$
2 **33**

$$Ph_3P{=}CPh{-}C(O)Ph \xrightarrow[-70\ ^\circ C]{O_3} PhC(O){-}C(O)Ph$$
8 **34**

Later, Bestmann *et al.*[82] showed that it is better to use the ozone–triphenylphosphite adduct for the preparation of diketones from phosphoranes **8**.

$$Ph_3P{=}CR^1C(O)R^2 \xrightarrow[-78\ ^\circ C]{O_3,\ (PhO)_3P} R^1C(O){-}C(O)R^2$$
8

R^1 = Me, Bu; R^2 = Bu, C_5H_{11}, C_6H_{13}, $(CH_2)_8CH{=}CH_2$.

Similar α-diketones were obtained using $NaIO_4$,[83] OsO_4 and $KMnO_4$[84] as oxidants. Potassium permanganate was found to be the most suitable for the oxidation of compounds **10** with aromatic substituents into the corresponding non-symmetrical diketones **35** in a two-phase system.[85]

$$Ph_3P{=}C(Ar^1)C(O)Ar^2 \xrightarrow{KMnO_4} Ar^1C(O){-}C(O)Ar^2$$
10 **35**

Ar^1 = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 2-$NO_2C_6H_4$; Ar^2 = Ph, 2-$MeOC_6H_4$, 4-$MeOC_6H_4$, 2-$MeSC_6H_4$, 4-ClC_6H_4, 2-$NO_2C_6H_4$, 2-furyl, 2-thienyl.

Acylation of methoxymethylidenetriphenylphosphorane **36** with acyl chlorides involving transylidation followed by oxidation of the products **37** with lead dioxide or lead tetraacetate was recommended[86] as a method for the synthesis of α-oxo acid esters. The same esters were obtained by oxidation of phosphoranes **38** with atmospheric oxygen.[87]

$$Ph_3P{=}CHOMe \quad \textbf{36}$$
$$\downarrow RCOCl$$
$$Ph_3P{=}C(COMe)C(O)R \quad \textbf{37} \qquad \xrightarrow[(\text{or } PbO_2)]{Pb(OAc)_4} RC(O){-}CO_2Me$$
$$Ph_3P{=}CR{-}CO_2Me \quad \textbf{38} \qquad \xrightarrow{O_2}$$

R = Me, Pr^i, Bu, cyclo-C_3H_5, cyclo-C_4H_7, Ph, CH=CHPh, C≡CPh, 3-pyridyl, 2-(2-furyl)vinyl.

An original method was proposed for the synthesis of esters and amides of α-oxo acids by oxidative cleavage of acyl(cyano)methylidenetriphenylphosphoranes **39** with ozone[88] or dimethyldioxirane[89] in the presence of nucleophiles. Thus the oxidation in the presence of alcohols affords esters **40**, whereas in the presence of amines α-oxo amides **41** are formed, including peptides that are active as inhibitors of hydrolytic enzymes.[88]

$$Ph_3P{=}CH{-}CN \quad \textbf{2}$$
$$\downarrow R^1COCl$$
$$Ph_3P{=}C(CN)C(O)R^1 \quad \textbf{39} \qquad \xrightarrow{O_3,\ R^2OH} R^1C(O){-}CO_2R^2 \quad \textbf{40}$$
$$\xrightarrow{O_3,\ R^3NH_2} R^1C(O){-}C(=O)NHR^3 \quad \textbf{41}$$

R^1 = Ph, amino acid and peptide residues;
R^2 = H, Me, Bn; R^3 = Bn, $CH(CH_2Ph)CO_2Et$.

Tricarbonyl compounds, *viz.*, esters of 2,3-dioxo carboxylic acids **42**, were obtained by oxidation of acylated alkylidenephosphoranes **18** with ozone,[90] magnesium monoperoxyphthalate[91] or dimethyldioxirane.[92]

$$Ph_3P{=}C(CO_2R^1)COR^2 \quad \textbf{18} \xrightarrow{[O]} R^2C(O){-}C(O){-}CO_2R^1 \quad \textbf{42}$$

R^1 = Me, Bu^t, Bn; R^2 = Me, $(CH_2)_2Cl$, CH=CMe_2, CH=CHOMe, $(CH_2)_2CH{=}CH_2$, $(CH_2)_2CH{=}CMe_2$, $CH_2CH(Me)CH_2CH{=}CMe_2$, Ph, CH=CHPh, 2-furyl, 2-thienyl.

It is unlikely that nitrogen dioxide tested as an oxidant for alkylidenephosphoranes[93,94] will find preparative use because even small variations in the phosphorane structure result in different product mixtures.

3. Thermolysis. Synthesis of functionalised acetylenes

Of other transformations involving acylated ylides, the Wittig reaction occurring at high temperatures is used most widely. In this reaction, the phosphoranylidene group reacts with the carbonyl group of the same molecule in a α-position with respect to the ylide carbon atom so that the phosphorus atom is bound with the oxygen atom of the oxo group, resulting in elimination of triphenylphosphine oxide and formation of a triple C≡C bond. If the carbonyl group is more remote from the ylide carbon atom, ring closure through the C=C bond can occur. The first examples of this reaction were known back in the 1960s.[41,50,95] The process was carried out at 200–280 °C at reduced pressure with distillation of the resulting products. In the past decade, Aitken *et al.*[51,52,58,61–64] developed a higher-temperature version of this reaction (500 and even 700 °C), *i.e.*, vacuum flash pyrolysis.

If the phosphorane molecule contains one carbonyl group, the reaction gives alkyl(aryl)acetylenes.[28,29,41,52]

$$Ph_3P{=}C(R^1)C(=O)R^2 \xrightarrow{\text{thermolysis}} R^1C{\equiv}CR^2 + Ph_3PO$$

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

Selenium-substituted acetylenes **43** were obtained using the following scheme:[96]

$$Ph_3P{=}CHC(O)R^1 + R^2SeBr \xrightarrow[N_2]{20\ ^\circ C} Ph_3P{=}C(SeR^2)C(O)R^1 \xrightarrow{200-220\ ^\circ C} R^1C{\equiv}CSeR^2 \quad \textbf{43}$$

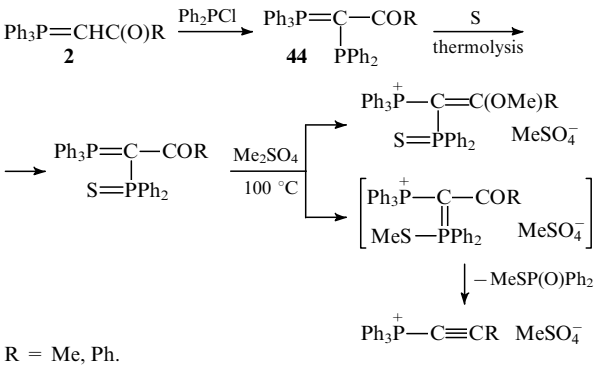
R^1 = Me, CF_3, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-$NO_2C_6H_4$, 2-thienyl; R^2 = Ph, 4-ClC_6H_4, 4-Cl-2-$NO_2C_6H_3$, 3-$CF_3C_6H_4$.

Thermolysis of aryl(trifluoroacetyl)methylidenephosphoranes obtained upon acylation of arylmethylidenetriphenylphosphoranes with trifluoroacetic anhydride results in aryl(trifluoromethyl)acetylenes.[97]

$$Ph_3P{=}CHAr \xrightarrow{(CF_3CO)_2O} Ph_3P{=}C(Ar)C(O)CF_3 \xrightarrow{\text{thermolysis}} ArC{\equiv}CCF_3$$

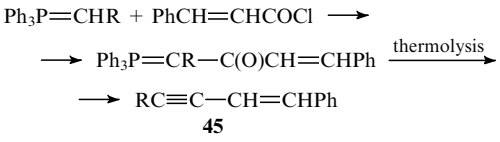
Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-$NO_2C_6H_4$.

Reactions of diphenylchlorophosphine with alkylidenephosphoranes **2**,[98] including those containing an oxo group,[99,100] give ylides **44**. Heating of these compounds with sulfur yields diphenylthiophosphoryl-substituted alkylidenephosphoranes. Methylation of the resulting ylides with dimethyl sulfate occurs both at the oxygen and the sulfur atoms. However, *S*-methylation products are so unstable that they undergo *in situ* thermolysis in mild conditions giving salts of phosphorus-containing acetylene derivatives.[100]

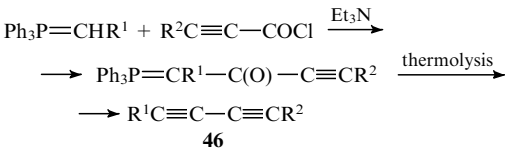


R = Me, Ph.

Acylation of phosphoranes with cinnamoyl chloride followed by thermolysis of the resulting acylylides gave conjugated enynes **45**;[101] the use of alkynoyl chlorides as acylating agents followed by thermolysis resulted in diacetylenes **46**.[50, 63]



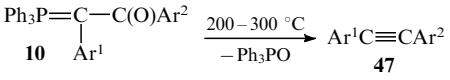
R = H, Me, Et, Pr^n, Pr^i, Bu, Ph, 2-MeOC$_6$H$_4$, 4-NO$_2$C$_6$H$_4$, 2-thienyl, CO$_2$Et.



R^1 = Ph, CN, CO$_2$Et; R^2 = Bu, Ph.

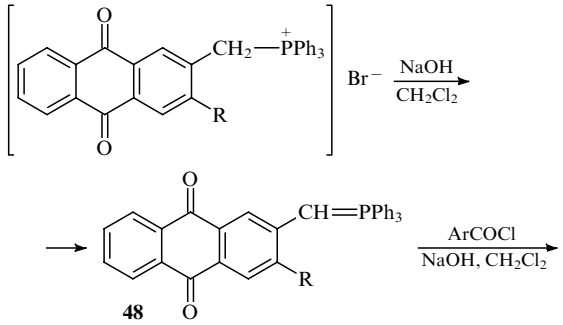
Derivatives **46** were also obtained by high-temperature vacuum flash-pyrolysis of dicarbonyl bisylides **24** containing aromatic substituents. If bisylides **24** incorporate aliphatic substituents, this method fails.[63]

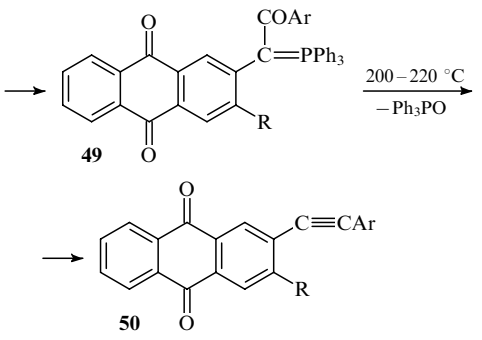
The thermolysis of phosphoranes is successfully used to synthesise diarylacetylenes. For example, diarylacetylenes **47** with perfluorobenzene rings[102] and with anthracene, phenanthrene, pyrene and chrysene fragments[103] were obtained by thermolysis of phosphoranes **10** used in the reaction without special purification.



Ar^1, Ar^2 = Ph, C$_6$F$_5$, 1-anthryl, 9-anthryl, 2-phenanthryl, 3-phenanthryl, 9-phenanthryl, 1-pyrenyl, 2-pyrenyl, 6-chrysenyl.

Acylation of anthraquinonylmethylidenephosphoranes **48** in a two-phase system followed by thermolysis of the resulting acylylides **49** gave diarylacetylenes **50** containing an anthraquinone fragment.[104]

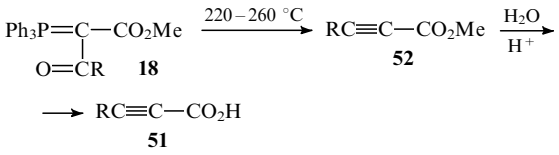




R = H, Me, F; Ar = Ph, 4-ClC$_6$H$_4$, 4-MeC$_6$H$_4$, 3-NO$_2$C$_6$H$_4$, 4-NO$_2$C$_6$H$_4$, 2-furyl.

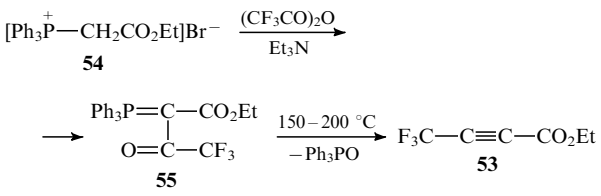
Diarylacetylenes form a considerable group of organic luminophores, although it is not as abundant as that of diarylethylenes.[103, 105–107]

The thermolysis of acylated phosphoranes is often used to obtain functionalised alkynes: alkynyl ketones,[42, 50] alkynonitriles,[41, 50] esters and amides of acetylenecarboxylic acids.[51, 53, 74, 108–110] A method was suggested[95] for the synthesis of alkynoic acids **51** by vacuum thermolysis of acylated ylides **18** followed by hydrolysis of the resulting esters **52**.



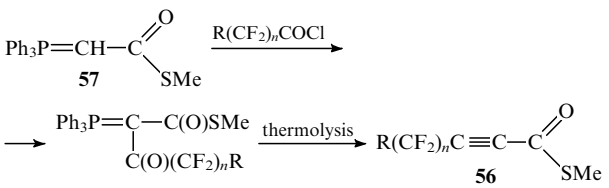
R = Me, Ph, 2-ClC$_6$H$_4$, 4-ClC$_6$H$_4$, 4-MeC$_6$H$_4$, 2-MeOC$_6$H$_4$, 3-MeOC$_6$H$_4$, 3-NO$_2$C$_6$H$_4$, Bn, CH=CHPh, 1-naphthyl, 2-furyl.

A preparative method for the synthesis of ethyl 4,4,4-trifluorobutynoate **53** from ethoxycarbonylmethyltriphenylphosphonium bromide **54** was developed.[55] Trifluoroacetic anhydride in the presence of triethylamine was used as the acylating agent. The key step of this reaction involves thermolysis of acylated phosphorane **55** to give compound **53** containing a triple C≡C bond.



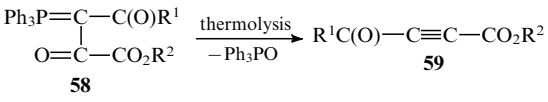
Later, this method was used to obtain esters of other acetylenecarboxylic acids from phosphonium salt **54** and carboxylic acid chlorides.

Thioesters of polyfluorinated carboxylic acids **56** were synthesised by acylation of ylide **57** containing a methylthiocarbonyl group with polyfluorinated acid chlorides followed by heating of the resulting acylylides to 190–220 °C *in vacuo*.[111]



R = CF$_3$: n = 1, 2, 6; R = Cl: n = 3, 5.

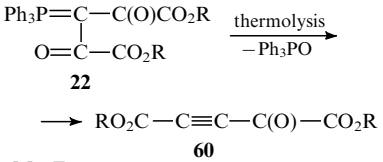
Acetylenedi- and -tricarbonyl compounds were obtained by vacuum flash-pyrolysis. On heating to 500 °C *in vacuo*, phosphoranes **58** give esters of 4-oxoalk-2-ynoic acids **59**.[58, 59]



58 **59**

R^1 = Me, Ph, 4-BrC_6H_4, 4-ClC_6H_4, 4-$NO_2C_6H_4$, OMe, OEt;
R^2 = Me, Et.

Thermolysis of tetracarbonylylides **22** resulted in esters of 2-oxopentynedioic acid **60**.[60, 61]



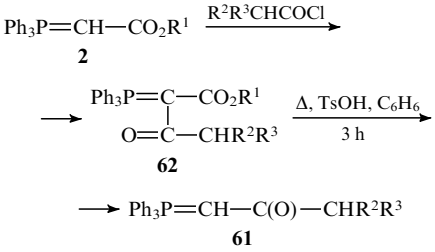
22 **60**

R = Me, Et.

However, vacuum flash-pyrolysis of polycarbonyl bisphosphoranes, such as tetraoxobisylides **24** (R = COPh, CO_2Alk) and hexaoxobisylides **25**, result in deeper destruction of the molecules of these compounds.[61, 63, 64, 112]

If the carbonyl group in the phosphorane molecule is remote from the ylide carbon atom, its thermolysis results in cyclisation and sometimes in heterocyclisation. Some examples of these reactions are documented.[113–121]

The thermal decomposition of acylated alkoxycarbonylmethylidenephosphoranes **43** or the respective phosphonium salts in acidic media, which involves the loss of the alkoxycarbonyl group and results in acylphosphoranes, can be of value as a preparative method.[27, 70, 122] The reaction can be used for the synthesis of acylphosphoranes if the corresponding α-halogenoketones are difficult to access. For example, chiral 2-oxoalkylidenephosphoranes **61** were synthesised by acylation of ylides **2** containing an alkoxycarbonyl group with chiral α-substituted acid chlorides followed by decomposition of intermediates **62** by refluxing in benzene in the presence of *p*-toluenesulfonic acid.[27]

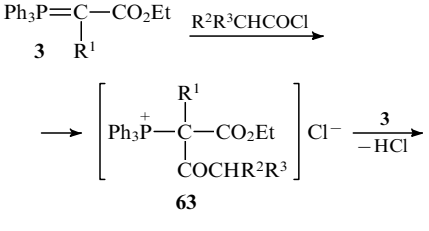


2 **62** **61**

R^1 = Me, Bu^t; R^2, R^3 = F, Me, Bu, cyclo-$C_6H_{11}CH_2$.

4. Synthesis of allenic compounds

The synthesis of allenic compounds is yet another interesting and promising example of reactions of alkylidenephosphoranes with acyl chlorides. Bestmann *et al.*[123, 124] found that the reaction of acyl chlorides with stable phosphorus ylides **3** containing the α-ethoxycarbonyl group results in esters of allenecarboxylic acids. This involves *C*-acylation of the ylide, the reaction of the resulting phosphonium salts **63** with a second molecule of the original phosphorane **3** with γ-elimination of a proton and simultaneous elimination of triphenylphosphine oxide to give allenecarboxylic esters **64**.



3 **63** **64**

R^1 = Me, Pr, $(CH_2)_2$Ph; R^2, R^3 = H, Me, Et, Pr, Bu, C_5H_{11}, Ph, Bn, CH_2CO_2Me.

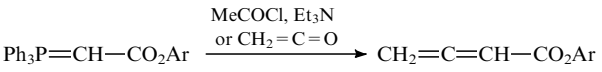
Esters of other allenecarboxylic acids were obtained under the same conditions.[125] If phosphorane molecules contain hydrogen atoms at the ylide carbon atoms, acylation involves transylidation and allenecarboxylic esters are not formed.

Lang and Hansen [126, 127] proposed that the reaction be performed in the presence of triethylamine. This also made it possible to obtain allenic derivatives from phosphoranes containing α-hydrogen atoms. In addition, this method allows one to use the corresponding phosphonium salts instead of phosphoranes. The reaction mechanism changes in the presence of triethylamine. Acyl chlorides no longer behave as acylating agents. In the presence of triethylamine, they eliminate HCl to give ketenes, which subsequently undergo the Wittig reaction with phosphoranes.



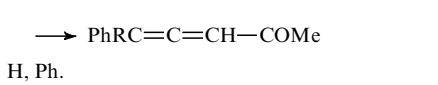
R^1, R^2 = H, Me, Et, Bu^t, C_5H_{11}, Ph, CO_2Me, Cl.

This approach was used to synthesise other ethyl [128] and aryl [129] allenecarboxylates; the latter were also obtained by independent syntheses from ketene.



Ar = Ph, 4-MeC_6H_4, 4-$Bu^nC_6H_4$, 4-$Bu^tC_6H_4$, 3-MeC_6H_4, 2-MeC_6H_4, 2-$Bu^nC_6H_4$, 3,5-$Me_2C_6H_3$, 2,4-$Me_2C_6H_3$, 2,3-$Me_2C_6H_3$, 2,5-$Me_2C_6H_3$, 2,6-$Me_2C_6H_3$, 2,3,5-$Me_3C_6H_2$, 2,4,6-$Me_3C_6H_2$, 2,3,6-$Me_3C_6H_2$.

Phenylacetyl and diphenylacetyl chlorides react with acetylmethylidenephosphorane in the presence of triethylamine to give allenyl ketones.[130]



R = H, Ph.

Silicon-substituted allenes were obtained [131] from phosphoranes and silicon-containing ketenes.

* * *

It should be noted in conclusion that the reaction of phosphorus ylides with acyl chlorides is not the only example of the chemistry of these compounds. Reactions of phosphorus ylides with acyl chlorides are not solely of theoretical interest; they also open new prospects for the synthesis of other classes of compounds that cannot be synthesised by other methods. In particular, it seems promising to synthesise allenic compounds from alkylidenephosphoranes, although this direction has been developed insufficiently yet and there are few publications in this field. Thus, the practical value of alkylidenephosphoranes is not limited to their use as components of the Wittig reaction.

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