

Reactivity of lithium diphenylphosphonium diylides towards phosphorus electrophiles: Synthesis of α,β -unsaturated phosphorus compounds

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Dedicated to Professor Jean F. Normant on the occasion of his 65th birthday

Abstract

The study of the reactivity of non-stabilized, semi-stabilized and stabilized lithium diphenylphosphonium diylides **1–4** towards Ph_2PCl , allowed the synthesis of various α,β -unsaturated phosphines **13–14**, via the intermediate formation of the corresponding functionalized monoylides **9–10** and their in situ reaction with carbonyl compounds. In many cases, the reaction is *Z*-stereoselective and the created double bond can be di- or also trisubstituted. The precise $^1\text{H-NMR}$ study of the phosphines **13a–d** and the X-ray analysis of **13a** (*Z* isomer) allowed us to assign without ambiguity the stereochemistry of these compounds and to solve a $^1\text{H-NMR}$ question. Contrary to reported results in the literature for **13a**, we have shown that for the double bond of this phosphine, there is no exception to the general rule $^3J_{\text{HH}}(\text{trans}) > ^3J_{\text{HH}}(\text{cis})$. The extension of this reactivity study to other phosphorus electrophiles such as $\text{Ph}_2\text{P}(\text{O})\text{Cl}$, $\text{Ph}_2\text{P}(\text{S})\text{Cl}$ and $(\text{EtO})_2\text{P}(\text{O})\text{Cl}$ allowed, as preliminary results, the *E*-stereoselective synthesis of styrylphosphine oxide and sulfide and diethyl styrylphosphonate. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Phosphonium diylide; Metallated ylide; Wittig reaction; α,β -Unsaturated phosphine; Phosphine X-ray structure; $^1\text{H-NMR}$

1. Introduction

Lithium phosphonium diylides, whose first example was discovered by G. Wittig in 1949 [1], were until the recent past mainly studied as ligands in coordination chemistry [2]. In order to test the potential of these compounds in synthesis, we have developed a general synthetic route to their direct precursors, the dialkylphosphonium salts [3], thus allowing an easy access to all types of diylides whatever their non-stabilized (**1**, **2**), semi-stabilized (**3**) or stabilized (**4**) character (Scheme 1). We have then studied the reactivity of these diylides, and shown that these reagents thanks to a strong nucleophilic character, are excellent tools in organic synthesis. Indeed, they offer a general method for the synthesis of various α,β -unsaturated compounds

(sulfoxides, amides, esters, acids, amidines, phosphines), the double bond being di- or trisubstituted [4]. Recently, in a preliminary note we have shown that the non-stabilized and unsubstituted lithium diylide **1** ($\text{R}=\text{H}$) reacts with phosphorus electrophiles such as Ph_2PCl , $\text{Ph}_2\text{P}(\text{O})\text{Cl}$ and $\text{Ph}_2\text{P}(\text{S})\text{Cl}$, allowing the synthesis of the styrylphosphine and the corresponding oxide and sulfide [4e].

We report here more general results dealing with the study of the reactivity of various types of diylides (**1–4**) regardless of their stabilization degree, towards phosphorus electrophiles. A general method for the synthesis of α,β -unsaturated phosphines as well as other phosphorus compounds has been developed. In addition, this article deals with an NMR question concerning an apparent peculiarity of the styrylphosphine **13a** for which it has been reported that the $^3J_{\text{HH}}$ corresponding to the double bond is larger for the *Z* isomer than for the *E* one. In fact, this apparent inversion does not exist, as we will demonstrate in this article.

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2. Results

The results presented here are based on the proposed sequence below (Scheme 1). In a first step, phosphonium diylides **1–4** in the presence of a phosphorus electrophile such as diphenylchlorophosphine, lead via a nucleophilic substitution to the formation of monoylides **5–8** which are transformed instantaneously, via an intramolecular prototropy, into the functionalized monoylides **9–12**. In a second step, the in situ addition of a carbonyl compound, mainly an aldehyde, allows the formation of the corresponding α,β -unsaturated phosphines **13–16**, by a Wittig reaction. The formations of **9–12** (two doublets: $^2J_{PP}$ coupling constant), of the two possible isomers (*E* and/or *Z*) of the vinylphosphines **13–16**, as well as of $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{R}$ (resulting from a Wittig reaction), are monitored by ^{31}P -NMR.

Starting from a non-stabilized and non-substituted diylide **1** ($\text{R}=\text{H}$) and in presence of aromatic, heteroaromatic or enolisable aldehydes, the synthesis of the corresponding α,β -unsaturated phosphines **13a–f** is performed in very good yields (Table 1; entries 1–6). This one pot synthetic method proceeds in very mild conditions (addition of $\text{Ph}_2\text{P}\text{Cl}$ and of the aldehyde at 20°C), the two reactions with the phosphorus electrophile and then with aldehyde being instantaneous. However, in the presence of phenylcyclohexanone, the carbonyl compound reacts only with the intermediate monoylide **5**, affording the (4-methylenecyclohex-1-yl)benzene **17h** (Table 1; entry 8).

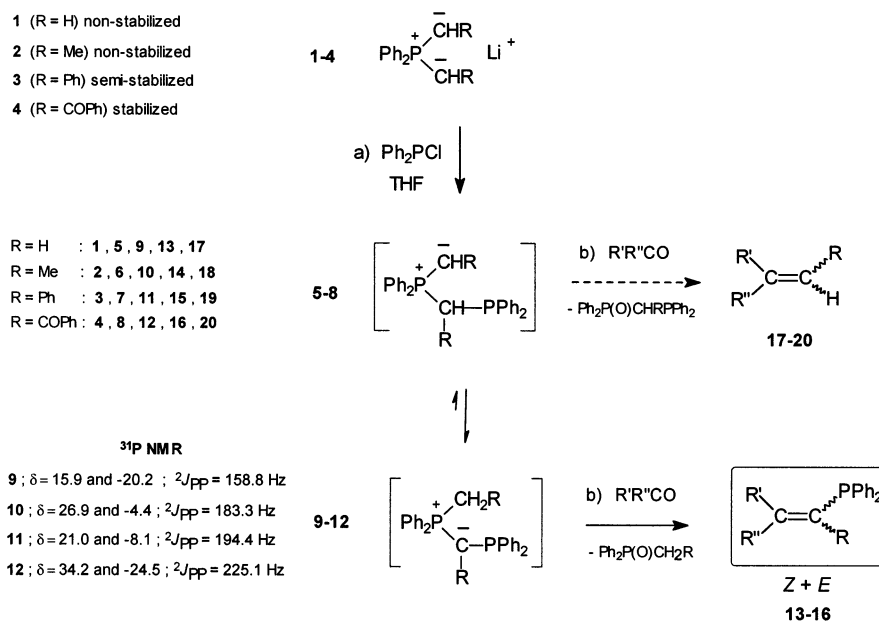
Starting from a non-stabilised and substituted diylide **2** ($\text{R}=\text{Me}$), the first step with $\text{Ph}_2\text{P}\text{Cl}$ proceeds very quickly but, in presence of benzaldehyde, the alkene

18a (entry 9) is obtained as the main product of the reaction. The expected trisubstituted vinylic phosphine **14a** is also generated, but in a low yield around 10%. However, using the activated *p*-nitrobenzaldehyde, the corresponding trisubstituted α,β -unsaturated phosphine **14c** is synthesized in an acceptable yield (entry 10). The corresponding alkene **18c** was not obtained in this case.

The configuration of the created double bond of **13–14** corresponds to a Wittig reaction from reactive monoylides **9** and **10** of non-stabilized type (the carbanion is substituted by H or Me and by Ph_2P , which are not electron-withdrawing substituents). This type of ylides normally affords predominantly *Z*-alkenes, although the reaction conditions may have an important effect on the stereochemistry [5]. Indeed, in most cases, the major α,β -unsaturated phosphine formed is the *Z* one, although a ratio *Z/E* of about 50/50 has been observed for the 2-pyridylcarboxaldehyde (with **1**; entry 4) and for the nitrobenzaldehyde (with **2**; entry 10).

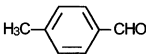
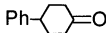
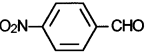
The semi-stabilized **3** ($\text{R}=\text{Ph}$) and stabilized **4** ($\text{R}=\text{COPh}$) diylides, react also quantitatively with the diphenylchlorophosphine, but only the corresponding alkene **19a** (*E/Z*: 75/25) and **20a** (*E/Z*: 90/10) are generated in the reaction mixture (yields: 65–70%), using in the second addition step benzaldehyde as carbonyl compound (entries 11 and 12).

The method allows then the one pot synthesis, usually *Z* stereoselective, of various α,β -unsaturated phosphines. The yields are good and the double bond can be di- or trisubstituted. This method is interesting in comparison with those of the literature which present some disadvantages. The limitations encountered, are for example low yields and oxidation problems [6], the necessity to work in presence of AIBN or under UV



Scheme 1. Synthesis of α,β -unsaturated phosphines **13–16**.

Table 1
Synthesis of α,β -unsaturated phosphines **13–16** and alkenes **17–20**

R'R"CO	entry	R	time ^a (mn)	13-16		17-20		13-16 : $\delta^{31}\text{P}$ (THF)		
					yield ^{b,c} (%)		yield ^b (%)	<i>E</i> ^d	<i>Z</i> ^d	<i>E</i> / <i>Z</i> ^e
PhCHO	1	H	1	13a	95			-10.8	-24.2	10 / 90
	2	H	1	13b	80			-11.1	-24.2	30 / 70
	3	H	1	13c	90			-9.5	-23.3	15 / 85
	4	H	10	13d	70			-12.2	-15.5	55 / 45
	5	H	10	13e	80			-11.2	-19.7	22 / 78
PhCH(Me)CH ₂ -CHO	6	H	1	13f	85			-13.1	-31.3	30 / 70
H ₂ CO	7	H	1	13g	100 ^g			-10.96		
	8	H	48 ^f	13h	0		17h 40			
PhCHO	9	Me	72 ^f	14a	<10		18a 50	8.3	-11.8	15 / 85
	10	Me	12 ^f	14c	50		18c 0	7.8	-12.4	50 / 50
PhCHO	11	Ph	48 ^f	15a	0		19a 70			
PhCHO	12	COPh	48 ^f	16a	0		20a 65			

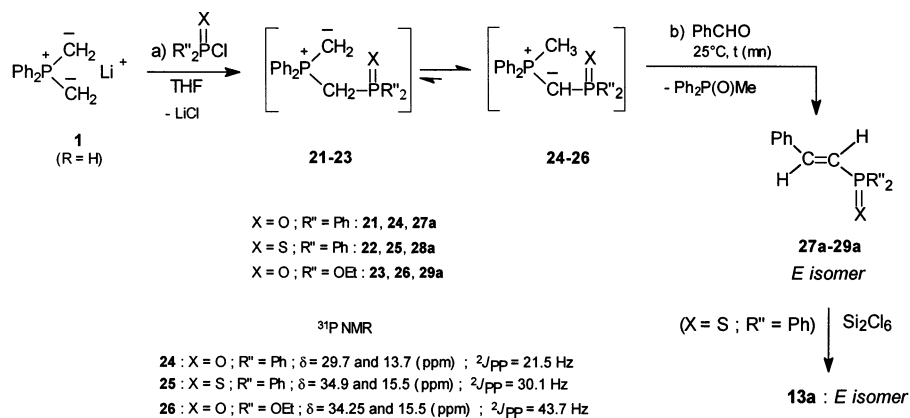
^a Reaction time after addition of the aldehyde ; reaction temperature : 20°C. ^b Isolated yield after separation by column chromatography. ^c The formation rate, determined by ³¹P-NMR, is quantitative for **13a–g**. ^d Chemical shifts (ppm) of **13–16** (*E* and *Z* isomers) in the reaction mixture (THF). ^e Ratio determined by ³¹P-NMR. ^f Reaction time after addition of the aldehyde, in hours. Reaction temperature : 65°C. ^g Value corresponding to the formation rate of **13g** *in situ*. Only the corresponding phosphine oxide is isolated after the work-up of the reaction mixture.

irradiation [7], isomerisation problems for the product [8] or even the preliminary isolation of diphosphorus precursors (in this last case, only melting points and micro-analyses are given for the identification of the phosphines [9]).

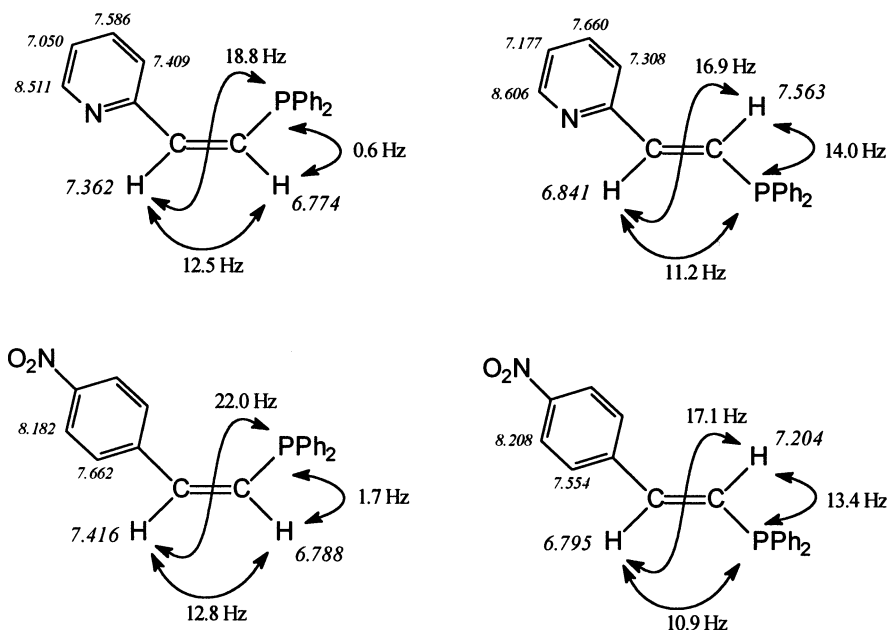
Concerning the styryl phosphine **13a**, it has been reported in the literature [10,11] that for this phosphine, and another one with R = propyl, ³J_{HH}(*trans*) could be less than ³J_{HH}(*cis*). However this unique result to our knowledge, is not clearly linked to the geometry of the molecule, no apparent inversion being established when R is a methyl or a *tert*-butyl group. Additionally the two numerical values attributed to the coupling constants of **13a** (10.8 and 12.8 Hz) were too small to correspond to ³J_{HH}(*trans*). Confronted to these results, a doubt was present for the phosphines **13–14**: Were

the observed ³J_{HH}(*cis*) and ³J_{HH}(*trans*), in every case assigned to the real isomers, respectively *Z* and *E*.

Indeed, in the literature this assignment is based on synthetic methods. For example in the case of **13a** the identification is based on the reaction of Ph₂PCl with the Grignard reagent of *E* and *Z* bromostyrene, which afforded a mixture of the styrylphosphine *E* and *Z* isomers [10]. This identification method being in our opinion not totally unambiguous, we have, still in the case of **13a**, confirmed the correct assignment by reducing the P=S bond of the well identified *E* isomer of the corresponding styrylphosphine sulfide **28a** (Scheme 2). However, a total inversion of configuration during the reduction, although unlikely, being not wholly excluded, we have definitively resolve the question of the correct identification of the isomers *Z* and *E*, by a



Scheme 2.

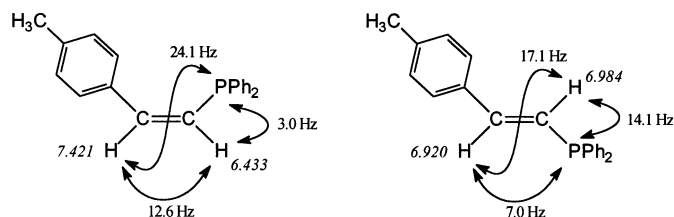
Fig. 1. ^1H -NMR parameters of the *Z* and *E* ethylenic phosphines **13d** ($\text{R}'\text{R}''\text{CO} : \text{C}_5\text{H}_4\text{N-CHO}$) and **13c** ($\text{R}'\text{R}''\text{CO} : \text{O}_2\text{N-C}_6\text{H}_4\text{-CHO}$) in CDCl_3 .

reinvestigation of the ^1H -NMR spectra of some phosphines **13–14**.

The comparison of the ^1H -NMR spectra of four of our phosphines, **13a–d** allowed us to assign without ambiguity the chemical shifts and coupling constants of the three spin system given by the two hydrogens of the double bond and the phosphorus atom of their *Z* and *E* isomers.

Among these four compounds, **13c** and **13d** present the most easily analysed spectra: the three nuclei form an AMX spin system in which $\Delta\nu_{\text{AM}}$ is so large that one-half of the AM part is located under or very close to the large signals of the $\text{P}(\text{phenyl})_2$ group. *gs*-COSY experiments using a high digital resolution (0.2 Hz/pt) allow the detection of the hidden signal with a good precision and identify at the same time which signal belongs to the hydrogen close to the pyridyl group in **13d**: the analyses of the 4-spin system of the pyridine

are straightforward and show that the signal of H-6 is correlated with the high-frequency olefinic hydrogen in the *Z* isomer and with the low-frequency one in the *E* isomer. Similar long-range correlations are observed in **13c** where the $\text{AA}'\text{XX}'$ system of the *p*-nitrophenyl group is obviously identified in 2D spectra. The results are collected in Fig. 1.

Fig. 2. ^1H -NMR parameters of *Z* and *E* ethylenic phosphines **13b** ($\text{R}'\text{R}''\text{CO} : \text{Me-C}_6\text{H}_4\text{-CHO}$) in CDCl_3 .

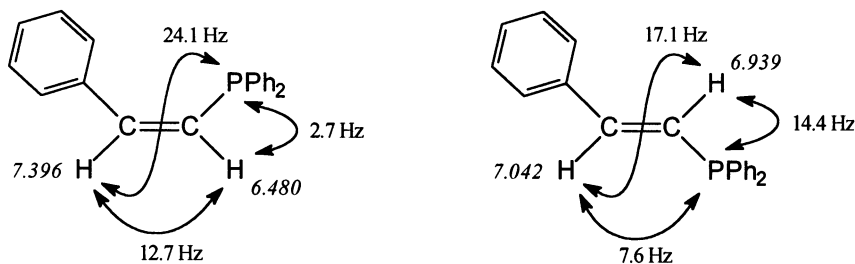


Fig. 3. ^1H -NMR parameters of *Z* and *E* ethylenic phosphines **13a** (R'R''CO: PhCHO) in $[\text{}^2\text{H}]_6$ -acetone/ CDCl_3 80/20.

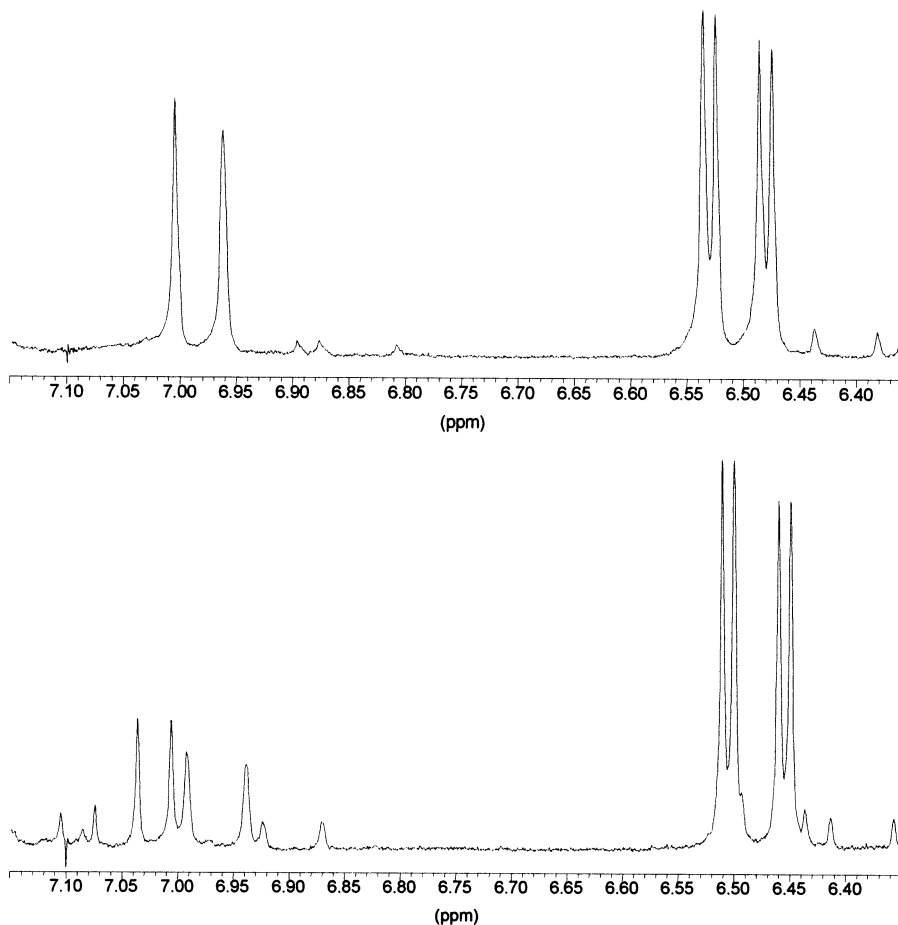


Fig. 4. (top) ^1H -NMR spectrum of the *E* isomer of **13a** in CDCl_3 . (bottom) ^1H NMR spectrum of the *E* isomer of **13a** in a mixture 80/20 of $[\text{}^2\text{H}]_6$ -acetone and CDCl_3 .

Compounds **13a** and **13b** differ from the preceding ones in the sense that the signals of the aryl groups coming from the carbonyl compounds (phenyl and *p*-methylphenyl respectively), are strongly mixed with those of the $\text{P}(\text{phenyl})_2$ groups, keeping off any detection of long-range correlations with one hydrogen of the double-bond. However, chemical shifts and coupling constants of the *Z* isomers leave no doubt about the assignments if they are compared to **13c** and **13d** (Figs. 2 and 3). The same holds for the *E* isomer of **13b**, even if the two signals of the olefinic hydrogens are very close and require the 3-spin system to be analysed as ABX to obtain the coupling constants (Fig. 2).

The spectrum of the *E* isomer of **13a** in CDCl_3 shows a simple doublet at 6.984 ppm with a splitting of 11 Hz (Fig. 4(top)) already described first by Aguiar in 1966 [6] then by Duncan [10] and Mitchell [11]. Actually, this doublet is due to a degeneracy of the ABX system where $\Delta\nu_{\text{AB}}$ is close to zero and the observed splitting is not a coupling constant. By addition of successive amounts of $[\text{}^2\text{H}]_6$ -acetone to the CDCl_3 solution, the anisochrony of the two hydrogens is increased, leading the eight transitions of the AB part to appear (Fig. 4(bottom)) and allowing the calculation of the chemical shifts and coupling constants reported in Fig. 3.

Our results, besides the fact that they prove the

identification of the isomers of the phosphines **13**, indicate then that for **13a**, the apparent inversion in the coupling constants was the result of an inadequate interpretation of the ^1H -NMR spectra.

Thus, the four phosphines we studied do not present any exception to the rule $^3J_{\text{HH}}(\text{trans}) > ^3J_{\text{HH}}(\text{cis})$, and this classic rule applies also for $^3J_{\text{PH}}$. Another point to notice is the large $^2J_{\text{PH}}$ in *E* isomers compared to the *Z* ones, a point which disagrees with the results quoted by Mitchell [11].

Additionally, in the case of **13a**, we checked the correct isomeric assignment from a crystal of the corresponding postulated *Z* isomer [mp = 89°C: δ ^{31}P = –24.2 (THF)] and confirmed this configuration by X-Ray analysis (Fig. 5 and Table 2).

A preliminary study of the reactivity of **1** has also allowed the synthesis of the oxides **27a** and sulfides **28a** corresponding to the styrylphosphine **13a**, as well as the synthesis of the diethyl styrylphosphonate **29a**, using respectively $\text{Ph}_2\text{P}(\text{O})\text{Cl}$, $\text{Ph}_2\text{P}(\text{S})\text{Cl}$ and $(\text{EtO})_2\text{P}(\text{O})\text{Cl}$ as phosphorus electrophiles and the benzaldehyde as a

carbonyl compound. The postulated mechanism is of the same type as described for the synthesis of the phosphines **13**–**16**. The yields are good and the reaction is *E*-stereoselective, according to the stabilized character of the intermediate monoylide **24**–**26**, substituted by the electron-withdrawing group $\text{Ph}_2\text{P}(\text{S})$, $\text{Ph}_2\text{P}(\text{O})$ or $(\text{EtO})_2\text{P}(\text{O})$ [5]. Work is in progress to generalise, as for $\text{Ph}_2\text{P}(\text{O})\text{Cl}$, the synthesis to other α,β -unsaturated phosphorus compounds, by variation of the carbonyl substrate.

3. Conclusions

The study of the reactivity of non-stabilized, semi-stabilized and stabilized lithium diphenylphosphonium diylides **1**–**4** towards $\text{Ph}_2\text{P}(\text{O})\text{Cl}$, $\text{Ph}_2\text{P}(\text{S})\text{Cl}$ and $(\text{EtO})_2\text{P}(\text{O})\text{Cl}$, allowed us to develop, in the case of non-stabilized diylides, a general and one-pot synthetic method to synthesize various α,β -unsaturated phosphorus compounds (phosphines **13**–**14**, phosphine oxide **27a**, phosphine sulfide **28a**, phosphonate **29a**), via the intermediate formation of the corresponding functionalized monoylides **9**–**10** or **24**–**26** and their in situ reaction with carbonyl compounds. Depending on the stabilisation degree of the intermediate monoylide the reaction is *Z* or *E* stereoselective and the created double bond can be di- or trisubstituted. Additionally, we have shown that for the double bond of phosphines **13**, the classic rule $^3J_{\text{HH}}(\text{trans}) > ^3J_{\text{HH}}(\text{cis})$ is still valid. These results show once again the interest of diylides **1**–**4** as synthetic tools. Further developments will be undertaken in order to enlarge the field of application of this reaction with the synthesis of other α,β -unsaturated phosphorus compounds, as for example the butadienyl phosphines and analogues.

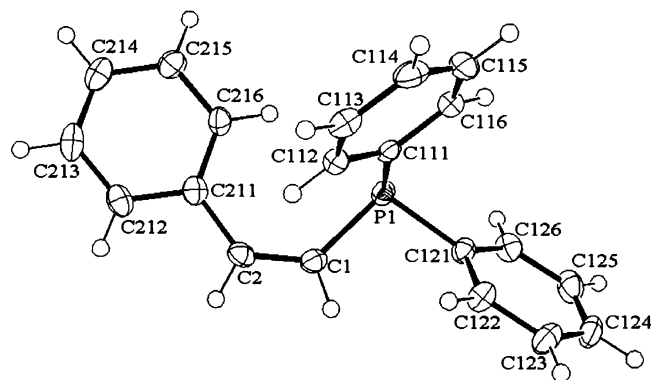


Fig. 5. Molecular structure of the *Z* isomer of **13a**.

Table 2

Selected bond distances (Å) and bond angles (°) with e.s.d.s. in parentheses for **13a**

Bonds lengths	
C(2)–C(211)	1.467(2)
C(1)–C(2)	1.339(2)
P(1)–C(121)	1.8385(14)
P(1)–C(111)	1.8412(15)
P(1)–C(1)	1.8140(16)
Bond angles	
C(1)–P(1)–C(111)	102.77(7)
C(1)–P(1)–C(121)	99.78(7)
C(111)–P(1)–C(121)	98.57(6)
P(1)–C(1)–C(2)	130.62(12)
C(1)–C(2)–C(211)	131.14(15)
P(1)–C(111)–C(112)	125.28(11)
P(1)–C(111)–C(116)	115.93(12)
P(1)–C(121)–C(122)	122.09(12)
P(1)–C(121)–C(126)	119.01(12)
C(2)–C(211)–C(212)	117.76(14)
C(2)–C(211)–C(216)	124.34(14)

4. Experimental

Melting points were determined using a Wild Leitz 350 and are given uncorrected. ^1H and ^{31}P -NMR spectra were recorded on a Bruker AC-200 spectrometer at 200.1 MHz and 81.0 MHz respectively. ^1H -2D experiments were performed on a Bruker DRX-250 with a *z*-gradients unit. ^1H and ^{31}P chemical shifts are in ppm from TMS and external 85% H_3PO_4 respectively. ^{31}P quantitative measurements on reaction mixtures (THF) were made using a relaxation delay of 20 sec with no ^1H irradiation and an external $[\text{H}_2]_6$ -DMSO lock. The program gNMR was used for the calculations of ^1H spectra [12]. IR spectra were obtained with a Perkin–Elmer 377. Mass spectra were measured with a Jeol JMS DX-300 spectrometer. All solvents were distilled from drying agents prior to use. Tetrahydrofuran (THF) was distilled under nitrogen atmosphere over

Table 3
Synthesis of vinylic phosphorus compounds **27a–29a**

Entry	Time ^a (min)	X	R''	27a–29a			27a–29a δ ³¹ P (THF)		
					FR ^b (%)	Yield ^c (%)	<i>E</i> ^d	<i>Z</i> ^d	<i>E/Z</i> ^e
1	1	O	Ph	27a	100	90	25.47	^g	100/0
2	1	S	Ph	28a	100	86	37.76	29.36	95/5
3	40 ^f	O	OEt	29a		50	19.66		100/0

^a Reaction time after addition of the aldehyde. Reaction temperature: 20°C.

^b Formation rate determined by ³¹P-NMR.

^c Isolated yield after column chromatography.

^d Chemical shifts (ppm) of **27a–29a** (*E* and *Z* isomers) in the reaction mixture (THF).

^e Ratio determined by ³¹P-NMR.

^f Reaction time in hours. Reaction temperature: 65°C.

^g The *Z* isomer has been obtained by the quantitative oxidation of *Z*-**13a** with H₂O₂: δ ³¹P = 20.0 ppm.

Table 4
Characterisation of α,β -unsaturated phosphines **13–14** ^a

Compound	¹ H NMR (CDCl ₃) δ (ppm), <i>J</i> (Hz)		MS (EI) <i>m/z</i>
13a	<i>Z</i> : 89°C (hexane) Lit. 93–95°C [10]	Figs 3, 4a, 4b	288
13b	<i>Z</i> : 102°C (hexane)	Fig. 2	302
13c	<i>Z</i> and <i>E</i> mixture (83/17): 83°C (hexane)	Fig. 1	333
14c	<i>Z</i> and <i>E</i> mixture (50/50): 104°C	<i>Z</i> isomer: 1.87 (dd, ³ <i>J</i> _{PH} = 3, ⁴ <i>J</i> _{HH} = 1.5, 3 H, CH ₃) 7.34–7.39 (m, 11 H, 2 C ₆ H ₅ and =CH) 7.5 (d, ³ <i>J</i> _{HH} = 8.5, 2 H, C ₆ H ₄) 8.15 (d ³ <i>J</i> _{HH} = 8.5, 2 H, C ₆ H ₄) <i>E</i> isomer: 2.06 (dd, ³ <i>J</i> _{PH} = 10, ⁴ <i>J</i> _{HH} = 1.4, 3 H, CH ₃) 6.55 (d, ³ <i>J</i> _{PH} = 11, 1H, =CH) 7.34–7.44 (m, 10 H, 2 C ₆ H ₅) 7.48 (d, ³ <i>J</i> _{HH} = 8.8, 2 H, C ₆ H ₄) 8.22 (d ³ <i>J</i> _{HH} = 8.8, 2 H, C ₆ H ₄)	347
13d	<i>Z</i> : 116°C (hexane)	Fig. 1	289
13e	Isomer mixture: oil	<i>Z</i> isomer: 6.31 (dd, ² <i>J</i> _{PH} = 1.5, ³ <i>J</i> _{HH} = 13, 1 H, P–CH) 6.37 (dd, 1H, OCH=CH) 6.55 (d, 1H, OCH=CH–CH) 7.12 (dd, ³ <i>J</i> _{HH} = 13, ³ <i>J</i> _{PH} = 23.7, 1H, H–C=C–P) 7.31–7.50 (m, 11H, 2 C ₆ H ₅ and O–CH) <i>E</i> isomer: 6.31 (d, 1H, OCH=CH–CH) 6.41 (dd, 1H, OCH=CH) 6.64 (dd, ² <i>J</i> _{PH} = 12.4, ³ <i>J</i> _{HH} = 17, 1 H, P–CH) 6.88 (dd, ³ <i>J</i> _{HH} = 17, ³ <i>J</i> _{PH} = 9.7, 1H, H–C=C–P) 7.30–7.48 (m, 11H, 2 C ₆ H ₅ and O–CH)	278
13f	Isomer mixture: oil	1.26–1.37 (m, 3H, CH ₃) 2.59–2.63 (m, 1H, CH–Me) 2.84–3.0 (m, 2H, CH ₂) 5.96–6.82 (m, 2H, CH=CH) 7.12–7.84 (m, 15H, ArH)	330

^a Satisfactory elemental analyses were obtained for the *Z* pure or the *Z/E* mixtures of **13** or **14**.

sodium/benzophenone and stored over sodium. The reactions were performed under nitrogen using Schlenk techniques. *n*-Butyllithium commercial solutions in hexane (Aldrich) were titrated before use [13]. Commercial aldehydes and ketones (Aldrich) were used without purification. Phosphorus electrophiles, Ph₂P(OR)Cl, Ph₂P(O)Cl, Ph₂P(S)Cl and (EtO)₂P(O)Cl, were distilled under vacuum and stored under nitrogen prior use.

4.1. Reactivity of **1–4** towards Ph₂P(OR)Cl, Ph₂P(O)Cl, Ph₂P(S)Cl and (EtO)₂P(O)Cl. Synthesis of the α,β -unsaturated phosphorus compounds **13–14**, **27a–29a**: General procedure

The diphenyldialkylphosphonium salt corresponding to the diylide **1–4** [3] (5.6 mmol) is introduced in THF (200 ml). To the heterogeneous mixture, cooled at

– 50°C, a solution of *n*-BuLi (7 ml of 1.6 M solution in hexane; 11.2 mmol) is added dropwise. At the end of the addition, the mixture is allowed to warm up in one hour to 20°C (yellow solution). The phosphorus electrophile Ph₂P(OR)Cl, Ph₂P(O)Cl, Ph₂P(S)Cl or (EtO)₂P(O)Cl (5.6 mmol), is then directly added (without additional solvent) to the solution. After 15 minutes at 20°C, the carbonyl compound (5.6 mmol) is quickly and directly added. The reaction times and temperatures, are indicated, depending on the carbonyl compounds, in Tables 1 and 3.

Work-up: At the end of the reaction (monitored by ³¹P-NMR), the solution is concentrated and the resulting oils are dissolved into dichloromethane. After washing of the organic layer with water (3 × 50 ml) and drying over MgSO₄, the mixture is filtered and concentrated, at a temperature below 25°C. The resulting

Table 5
Crystal data and details of the structure determination for **13a**

Formula	C ₂₀ H ₁₇ P
Formula weight (g)	288.33
Shape (color)	Box (colorless)
Size (mm)	0.75 × 0.28 × 0.12
Crystal system	Monoclinic
Space group	P2 ₁ /c
a (Å)	16.352(3)
b (Å)	5.9197(9)
c (Å)	16.582(4)
β (°)	109.33(2)
V (Å ³)	1514.6
Z	4
F(000)	608
ρ (calc), (g cm ⁻³)	1.264
μ (Mo–Kα) (cm ⁻¹)	1.661
Diffractometer	Stoe IPDS
Radiation (Mo–Kα) (λ)	0.71073
Temperature (K)	160(2)
Detector distance (mm)	70
Scan mode	φ (rotation)
φ range (°)	0.0 < φ < 199.5
φ increment (°)	1.5
Exposure time (min)	3
2θ range (°)	4.3 < 2θ < 52.1
Absorption method	None
Number of reflections collected	11984
Number of unique reflections	2843
Merging factor R _{int}	0.0394
Reflections used (I > 2σ(I))	2075
R	0.0305
R _w	0.0363
Weighting scheme	Chebyshev
Coefficient Ar	1.28, 0.237, 0.970
(Δ/σ) _{max}	0.011
Δρ _{min} /Δρ _{max}	–0.250/0.306
GOF	1.070
Variable parameters	191

crude oils are purified by chromatography on alumina (solvents: hexane–dichloromethane, 90:10) to give the corresponding α,β-unsaturated phosphorus compounds. The characterisation of the phosphines **13**–**14** is presented Table 1 (³¹P-NMR), Table 4 (¹H-NMR, Mass, elemental analyses and melting point when available), in the NMR discussion and in Section 4.2.

4.2. X-ray crystal structure determination of **13a**

The data were collected on a STOE IPDS diffractometer equipped with a graphite oriented monochromator utilising Mo–Kα radiation (λ = 0.71073). The final unit cell parameters were obtained by the least-squares refinement of 5000 reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collections.

The structure was solved by direct methods (SIR97) [14] and refined by least-squares procedures on *F*. All H atoms attached to carbon were introduced in calcula-

tion in idealised positions (*d*(CH) = 0.96 Å) and their atomic coordinates were recalculated after each cycle. They were given isotropic thermal parameters 20% higher than those of the carbon to which they are attached. Least-squares refinements were carried out by minimising the function $\Sigma w(|F_o| - |F_c|)$, where *F*_o and *F*_c are the observed and calculated structure factors. The weighting scheme used in the last refinement cycles was $w = w'[1 - \{\Delta F/6\sigma(F_o)\}^2]$ where $w' = 1/\Sigma A_r T_r(x)$ with three coefficients *A_r* for the Chebyshev polynomial *A_rT_r(x)* where *x* was *F_c/F_c(max)* [15]. Models reached convergence with $R = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$, having values listed in Table 5.

The calculations were carried out with the CRYSTALS package programs [16] and the molecular view was realised with the help of ORTEP [17].

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 150786. Copies of these data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk.

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