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Some synthetic applications of vinylphosphane oxides

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ABSTRACT

Vinylphosphane oxides have been used as Michael acceptors for the diastereoselective synthesis of *anti* α-functionalized-β-silylated phosphane oxides and β-stannyl-, β-phenylthio- or β-phosphanyl phosphane oxides. Although the utility of these substrates as dipolarophiles was more limited, we have obtained a mixture of 3- and 4-phosphanylpyrazoles in which the latter is the major regioisomer, by 1,3-cycloaddition with *N*-phenylsydnone. Moreover, vinylphosphane oxides reacted with aldehydes in the presence of LDA by a Baylis–Hillman type reaction, leading to (*E*)-β-hydroxyphosphane oxides, which were readily converted in allenes. It is noteworthy that the application of this methodology to silylated substrates has permitted us to synthesize an interesting and more versatile silylallene.

1. Introduction

Organophosphorus compounds are of great chemical and biological interest.[1] They have also found much utility as ligands in asymmetric catalysis.[2] These hemilabile ligands have also encountered success with applications in small-molecule activation, small-molecule sensing and stabilization of transition complexes.[3] Owing to the multiple ways in which they can be employed, the synthesis of small molecules containing phosphorus has garnered significant attention.[4] More importantly, the ability to generate phosphorus compounds with chiral centers at or near phosphorus in an asymmetric fashion is particularly attractive.

Previously, we have synthesised vinylphosphane oxides by regio- and stereo-specific cleavage of epoxysilanes[5] with lithium diphenylphosphide. In this paper, we describe some synthetic applications of vinylphosphane oxides as Michael acceptors, 1,3-dipolarophiles and precursors in the synthesis of allenes.

The use of vinylphosphane oxides as Michael acceptors has been previously proved.[6] We have studied the conjugate addition of heteroatomic nucleophiles at stereodefined vinylphosphane oxides attaining a diastereospecific useful route to synthesise highly functionalized phosphane oxides containing two or three chiral centers.

The reactivity of these substrates in 1,3-dipolar cycloadditions is low and has been practically limited to β-unsubstituted vinylphosphane oxides. They react with nitrile oxides or nitrones to give mixtures of 4- and 5-phosphanyl-2-isoxazolines or isoxazolidines, respectively.[7] We have prepared for the first time, 3- and 4-phosphanyl-*N*-phenylpyrazoles by reaction of vinylphosphane oxides with *N*-phenylsydnone.

On the other hand, we have synthesised silylallenes through a methodology,[8] which involves Horner–Wittig elimination of silylated β-hydroxyalkenylphosphane oxides obtained, in turn, by reaction of silyl alkenylphosphane oxides with aldehydes in the presence of lithium amides.

2. Results and discussion

We have studied the behavior of stereodefined vinylphosphane oxides, which were obtained by us previously,[5] as electrophilic acceptors toward a variety of heteroatomic nucleophiles, such as silyl- and stannyl-metals, sulfur, and phosphorus compounds.

2.1. Reaction of vinylphosphane oxides with silylcuprates and silyllithium reagents

Although the reaction of vinylphosphane oxides with lithium dialkylcuprates[6b,c,9] has been previously studied, the behavior of these substrates with lithium silylcuprates has received little attention. Fleming et al.[10] described the addition of lithium bis-dimethylphenylsilyl and bis-trimethylsilylcuprate at *E*-1-propenyldiphenylphosphane oxide to give a mixture of two and four diastereoisomers of the corresponding β-silylated alkylphosphane oxide, respectively. Later, Warren et al.[6b,c] prepared diastereoselectively β-silyl phosphane oxides by reaction of γ-oxygenated chiral vinylphosphane oxides with lithium bis-dimethylphenylsilylcuprate.

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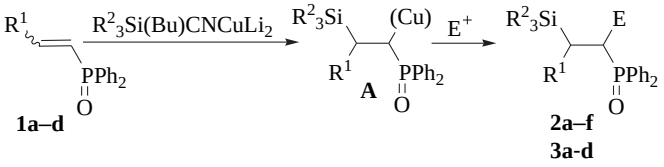
The known stability and versatility of the silyl groups confer on theses phosphane oxides an additional interest. Therefore, we decided to study the behavior of vinylphosphane oxides with different substitution patterns toward higher-order lithium silylcuprates. We have used mixed cuprates of carbon and silicon—butylsilylcuprates—which transfer selectively the silyl group but they are more advantageous than the bis-silylcuprates because they cheapen the synthesis and simplify the isolation process. Moreover, with the aim of increasing the functionalization of theses compounds we have tried to capture the intermediates of the silylcupration with various electrophiles such as allyl bromide, ethyl chloroformate, benzoyl chloride, iodine, and some aldehydes.

The vinylphosphane oxides **1a**–**d** reacted with lithium butyl (dimethylphenylsilyl) and butyl(*tert*-butyldiphenylsilyl)cuprate to give a phosphorylated intermediate **A**, which afforded the β-silylated phosphane oxides **2a**–**f** by hydrolysis. Moreover, this intermediate **A** could be captured 'in situ' by ethyl chloroformate and allyl bromide yielding **3a**–**d**. Nevertheless, **A** was shown to be unreactive toward other electrophiles, such as benzaldehyde, isobutyraldehyde, benzoyl chloride, and iodine.

The α-functionalized β-silylated phosphane oxides **3a**,**b**,**d** were isolated as a mixture of *syn*-*anti* diastereomers, in which the *anti* isomer was the major product. The results are collected in Scheme 1 and Table 1.



Scheme 1.

Table 1
Silylcupration of vinylphosphane oxides and reaction with electrophiles

Vinylphosphane oxide	Silylcuprate	Electrophile	Products
1a; R^1=Me (*Z*)	$R^2{}_3$=Me_2Ph	H^+	**2a** (74%)
1a	$R^2{}_3$=$Ph_2{}^tBu$	H^+	**2b** (70%)
1b; R^1=Bu (*Z*)	$R^2{}_3$=Me_2Ph	H^+	**2c** (67%)
1c; R^1=$SiMe_2Ph$ (*E*)	$R^2{}_3$=Me_2Ph	H^+	**2d** (59%)
1d; R^1=Ph (*E*)	$R^2{}_3$=Me_2Ph	H^+	**2e** (52%)
1d	$R^2{}_3$=$Ph_2{}^tBu$	H^+	**2f** (43%)
1a	$R^2{}_3$=Me_2Ph	$ClCO_2Et$	*anti*-**3a** (36%)+*syn*-**3a** (11%)
1a	$R^2{}_3$=Me_2Ph	$BrCH_2CH{=}CH_2$	*anti*-**3b** (39%)+*syn*-**3b** (12%)
1c	$R^2{}_3$=Me_2Ph	$BrCH_2CH{=}CH_2$	**3c** (50%)
1d	$R^2{}_3$=Me_2Ph	$BrCH_2CH{=}CH_2$	*anti*-**3d** (35%)+*syn*-**3d** (10%)

The *syn* or *anti* silylcuprate addition of *Z* or *E* vinylphosphane oxides afforded two possible diastereoisomers in a conformation stabilized by Si—O interactions. Probably the *anti* isomer is, in all cases, the major product because it is the more stable. In the *anti* isomer the most bulky groups are more distant as can be seen in the Newman projections (Fig. 1).

The configurational assignation of the *syn* and *anti* isomers of **3a**–**d** was possible by ^{1}H NMR spectroscopy and NOESY experiments. The coupling constants between *vic*-protons are those expected according to the dihedral angle, φ=60° in the *syn* isomer and φ=180° in the *anti* isomer. Thus, the *syn*-**3a**, which in the quelated conformation has a φ=60° showed a $J_{H/H}$=1.7 Hz, while the *anti*-**3a** isomer with φ=180° has a $J_{H/H}$=12.4 Hz. Moreover, the minor diastereoisomer of **3b** showed a positive NOE between the protons attached to the chiral carbons while no NOE effect was observed between these hydrogens in the major product. It confirms that in

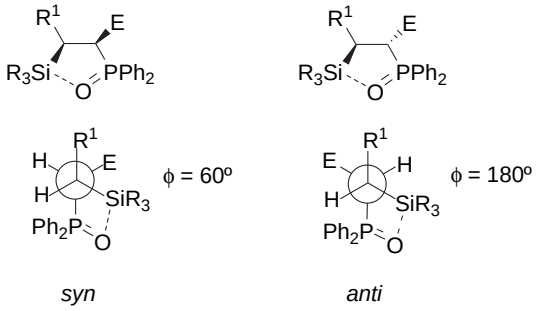
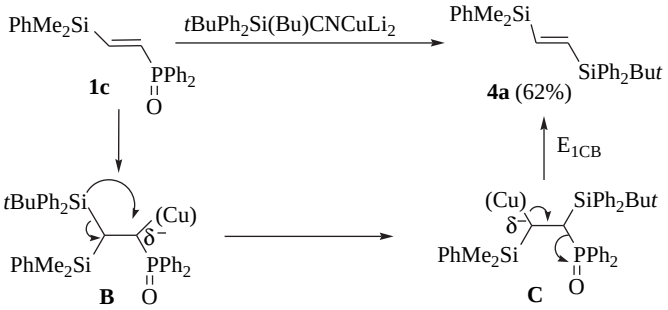


Fig. 1. Newman projections of *syn* and *anti* isomers.

the minor *syn*-**3b** the two hydrogen atoms are in close spatial proximity, whereas in the major *anti*-**3b** they are far away in space.

The only exception to this outcome is that observed in the reaction of **1c** with the *tert*-butyldiphenylsilylcuprate. Instead of the expected addition product, we isolated the *E*-vinyldisilane **4a**. This anomalous behavior could be due to the rearrangement of *tert*-butyldiphenylsilyl group, which has more migratory aptitude than the dimethylphenylsilyl group,[11] from the *gem*-disilylated carbon to the α-C. This would decrease the steric impedance of intermediate **B**, giving the intermediate **C** in which the *quasi*-carbanion is stabilized by the α-silyl group. The E_{1CB} elimination of the phosphanyl group afforded the *E*-disilylalkene **4a** (Scheme 2).



Scheme 2.

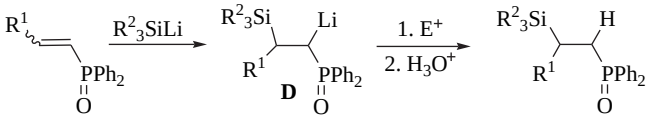
Given the limited reactivity of the silylcuprate intermediate **A** toward electrophiles, we tested the behavior of these vinylphosphane oxides with silyllithium reagents with the aim of increasing the reactivity of the resulting silyllithium intermediate **D** with electrophiles, which were shown to be unreactive toward the silylcuprate intermediate **A** resulting from the silylcupration.

We have studied the reaction of the vinylphosphane oxides **1a**,**1c**, **1e**, and **1f** with dimethylphenyl- and *tert*-butyldiphenylsilyllithium reagents and capture of the corresponding intermediate **D** with allyl bromide, ethyl chloroformiate, benzoyl chloride, benzaldehyde, and iodine. Unfortunately, the lithium intermediate was shown to be unreactive toward the electrophiles tested. In all cases, the product resulting from its hydrolysis was isolated. The yield for **2a**, **2b**, and **2d** was worse than that obtained by silylcupration (Scheme 3).

When the β-silyl vinylphosphane oxide **1c** reacted with *tert*-butyldiphenylsilyllithium gave, as occurred in its reaction with the *tert*-butyldiphenylsilylcuprate, the vinylsilane **4a**. On the other hand, the treatment of the β-phenyl vinylphosphane oxide **1d** with dimethylphenyl- and *tert*-butyldiphenylsilyllithium also afforded the vinylsilanes **4b** and **4c**, respectively (Scheme 4).

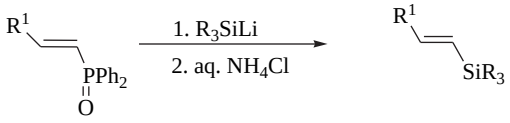
Probably in this case, the 1,2-rearrangement of the silyl group is favored due to the major carbanionic character of the lithiated intermediate regarding the cuprate intermediate and the formation of a new carbanion stabilized by the phenyl group (Scheme 5).

This outcome provides a simple and direct access to vinylsilanes from vinylphosphane oxides.



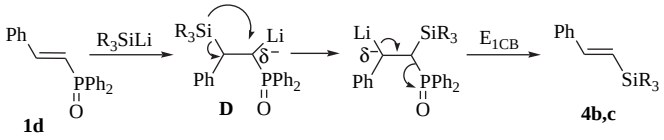
1a; R^1 = Me (*Z*)	$R^2{}_3$ = Me_2Ph	**2a** (49%)
1a	$R^2{}_3$ = Ph_2But	**2b** (63%)
1c; R^1 = $SiMe_2Ph$ (*E*)	$R^2{}_3$ = Me_2Ph	**2d** (57%)
1e; R^1 = H	$R^2{}_3$ = Me_2Ph	**2g** (65%)
1f; R^1 = $SiMe_3$ (*E*)	$R^2{}_3$ = Me_2Ph	**2h** (45%)

Scheme 3.



1c; R^1 = $SiMe_2Ph$	**4a** (63%); R_3 = Ph_2But
1d; R^1 = Ph	**4b** (77%); R_3 = Me_2Ph
1d	**4c** (68%); R_3 = Ph_2But

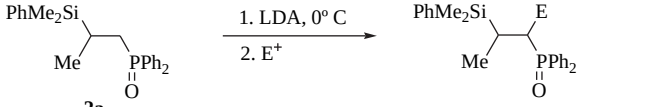
Scheme 4.



Scheme 5.

Owing to the scarce or null reactivity of the intermediates **A** and **D**, resulting from the silylcupration or silyllithiation toward electrophiles we have opted for an alternative methodology used by Fleming,[10] consisting of the α-deprotonation of the β-silylated phosphane oxides, resulting from hydrolysis of the silylcuprate intermediate **A** and subsequent capture with electrophiles.

The results depend on the nature of the group attached at β-position. The lithiated intermediate of the β-methyl phosphane oxide **2a** was shown to be reactive toward electrophiles such as allyl bromide, benzoyl chloride, iodine, benzaldehyde, and isobutyraldehyde (Scheme 6).

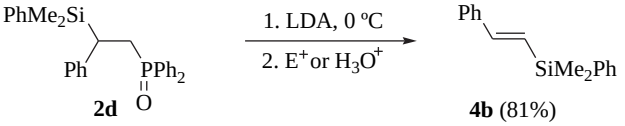


E^+ = $BrCH_2CH{=}CH_2$	***anti*-3b** (38%) ***syn*-3b** (20%) E = $CH_2CH{=}CH_2$
E^+ = ClCOPh	***anti*-3e** (41%) ***syn*-3e** (15%) E = COPh
E^+ = I_2	***anti*-3f** (45%); E = I
E^+ = PhCHO	**3g** (44%); E = CH(OH)Ph
E^+ = $(CH_3)_2CHCHO$	**3h** (53%); E = CH(OH)*i*Pr

Scheme 6.

Nevertheless, the lithium intermediate, resulting from deprotonation with LDA of the β-phenyl phosphane oxide **1d**, in the presence or absence of electrophiles, was converted in the same vinylsilane **4b** obtained by silyllithiation (Scheme 7).

The diastereoselectivity observed in the reactions of **2a** with electrophiles in the presence of LDA depend on the nature of the



Scheme 7.

electrophile. The reaction occurred with total diastereoselectivity[12] when iodine, benzaldehyde, and isobutyraldehyde were used, while mixtures of the two possible diastereoisomers were obtained in the reactions with allyl bromide and benzoyl chloride. The mixture of *syn*-**3b** and *anti*-**3b** was separated by chromatography and their configurations were assigned as previously mentioned. Although the two diastereoisomers of **3e** were impossible to separate, the configurational determination of the *syn* and *anti* isomer was possible by ^{1}H NMR spectroscopy and NOESY experiments. The coupling constants $J_{H/H}$=2.5 Hz and $J_{H/H}$=11.7 Hz, together with the presence or absence of the NOE effect between these protons, permit us the unequivocal assignation of *syn*-**3e** and *anti*-**3e**, respectively (Fig. 2). Probably, the exclusive formation of the *anti* diastereoisomer when iodine was utilised as an electrophile would be due to the steric requirement of the bulky iodine atom. In the *anti* isomer the iodine atom is *anti* to the silyl group in the quelated Newman projection (Fig. 2).

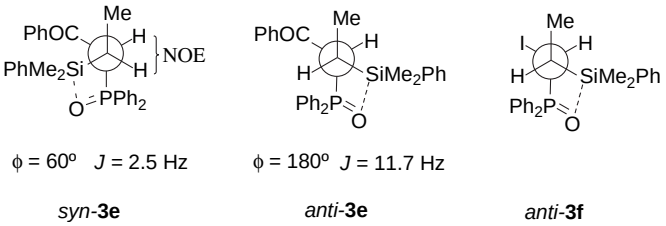


Fig. 2. Newman projections of *syn*-**3e** and *anti*-**3e**.

When benzaldehyde and isobutyraldehyde were used as electrophiles two new chiral carbons were created and, consequently, four diastereoisomers could be obtained. Nevertheless, the reaction took place with total diastereoselectivity to give **3g** and **3h** as sole isomers. The stereochemical assignation of the β-hydroxyphosphane oxides **3g** and **3h** was difficult. Intramolecular hydrogen bond between the hydroxy and phosphanyl groups was confirmed by comparative IR spectroscopy of the compounds in the solid state and at different dilutions in CH_2Cl_2. The frequency and shape of the ν OH band did not change. Starting from this fact and on the assumption that the major products in the reactions of the lithiated phosphane oxide **2a** with all electrophiles tested were those that have the *anti* relationship between the silyl group and the electrophile, we assigned the relative configurations in the C-2 and C-3. Therefore, **3g** and **3h** could have one of the two structures collected in Fig. 3.

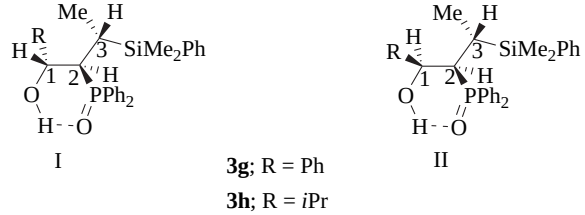


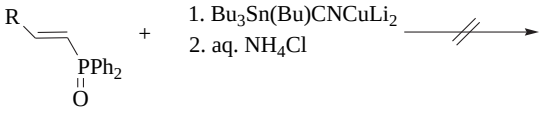
Fig. 3. Possible structures for **3g** and **3h**.

The spatial arrangement of the hydrogens attached at C-1 and C-2 could be determined by the magnitude of the coupling constants and NOESY spectra. The $J_{H/H}$=7.8 Hz for **3g** and $J_{H/H}$=9.1 Hz for **3h** would indicate a dihedral angle of approximately 180°. Moreover, in the NOESY spectra no positive NOE was observed between both hydrogens. Therefore, we have assigned the structure I (1*RS*,2*SR*,3*SR*) for **3g** and **3h**.

2.2. Reaction of vinylphosphane oxides with stannylcuprates and stannyllithium reagents

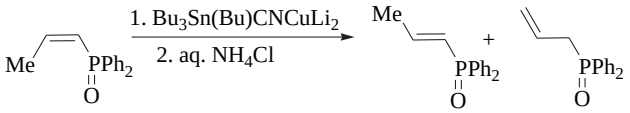
We also looked at the behavior of vinylphosphane oxides toward stannylcuprates with the objective of synthesising β-stannylated phosphane oxides.

In the same reaction conditions used for the reactions with silylcuprates, the conjugated addition of the mixed higher-order lithium butyl(tributylstannyl)cuprate at methyl-, phenyl- or silyl-phosphane oxides was not possible. The silyl and phenyl substituted phosphane oxides **1c** and **1d** were shown to be unreactive toward the stannyl cuprate and the *Z*-methyl derivative **1a** underwent isomerisation giving a mixture of the *E* isomer **1g** and the allylphosphane oxide **5** (Scheme 8).



1c; R = $SiMe_2Ph$

1d; R = Ph

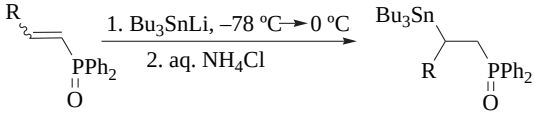


1a **1e** (66%) **5** (32%)

Scheme 8.

With the aim of achieving the conjugate addition to vinylphosphane oxides of the stannyl group, we tested their reactions with the more nucleophilic tributylstannyllithium reagent.

The *Z*-methyl and unsubstituted vinylphosphane oxides **1a** and **1e** reacted with the tributylstannyllithium affording the corresponding β-stannyl compounds **6a** and **6b**. However, the β-silyl and β-phenyl vinylphosphane oxides **1c** and **1d** did not experience the β-addition of the stannyl group. Probably, the β-silyl or β-phenyl substituent increases the steric impedance and consequently prevents the addition in the β-position (Scheme 9).



1a; R = Me (*Z*) **6a** (68%)

1c; R = $SiMe_2Ph$ (*E*) —

1d; R = Ph (*E*) —

1e; R = H **6b** (42%)

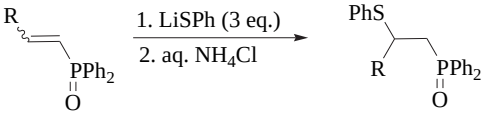
Scheme 9.

2.3. Reaction of vinylphosphane oxides with lithium sulphides and phosphides

An interesting application of the vinylphosphane oxides is their use as Michael acceptors toward sulfur and phosphorus nucleophiles to synthesise precursors of the useful bidentate 1,2-donor ligands for transition–metal catalysed synthesis.

Z or *E* β-Substituted alkenylphosphane oxides **1a**, **1c**, and **1d** reacted with 3 equiv of the lithium phenylsulfide yielding the β-phenylthio phosphane oxides **7a**–**c** (Scheme 10).

When the lithium diphenylphosphide was used as a nucleophile the conjugate addition took place exclusively on the β-methyl phosphane oxide **1a** to give the 1,2-diphosphanyl derivative **8a** with an excellent yield. The more hindered β-silyl and β-phenyl



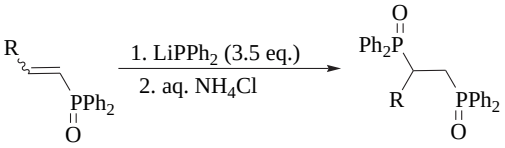
1a; R = Me (*Z*) **7a** (77%)

1c; R = $SiMe_2Ph$ (*E*) **7b** (63%)

1d; R = Ph (*E*) **7c** (75%)

Scheme 10.

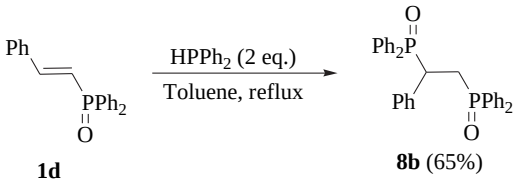
phosphane oxides **1c** and **1d** did not add this reagent. Nevertheless, it is noteworthy that the conjugate addition of the phosphanyl group on the β-phenyl phosphane oxide **1d** was possible by heating with 2 equiv of diphenylphosphine in toluene at reflux giving **8b** with an acceptable yield (Scheme 11).



1a; R = Me (*Z*) **8a** (95%)

1c; R = $SiMe_2Ph$ (*E*) —

1d; R = Ph (*E*) —



1d **8b** (65%)

Scheme 11.

2.4. 1,3-Dipolar cycloadditions of alkenylphosphane oxides

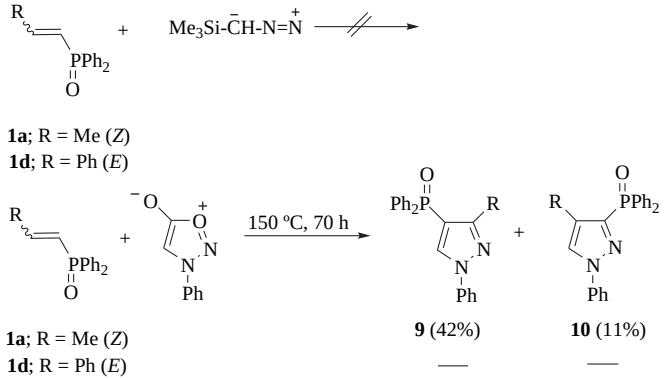
The reactivity of these substrates as dipolarophiles is low and practically is limited to β-unsubstituted alkenylphosphane oxides. They have been used in cycloaddition reactions with nitrile oxides and nitrones to provide phosphanyl isoxazolines and isoxazolidines, respectively.

We have tried to synthesize phosphanylpyrazoles by the 1,3-dipolar cycloaddition of the vinylphosphane oxides **1a** and **1d** with trimethylsilyldiazomethane and *N*-phenylsydnone. In the reactions with trimethylsilyldiazomethane the starting products were recovered. On the other hand, the cycloaddition reactions with *N*-phenylsydnone proceeded with difficulty. High temperature and long reactions times (150 °C for 70 h) were necessary for the cycloaddition with **1a** to take place. In these conditions, we predominantly obtained[13] the 3-methyl-1-phenyl-4-phosphanyl pyrazole **9** together with the 4-methyl-1-phenyl-3-phosphanyl pyrazole **10**. The *E* β-phenyl alkenylphosphane oxide **1d** was shown to be unreactive (Scheme 12).

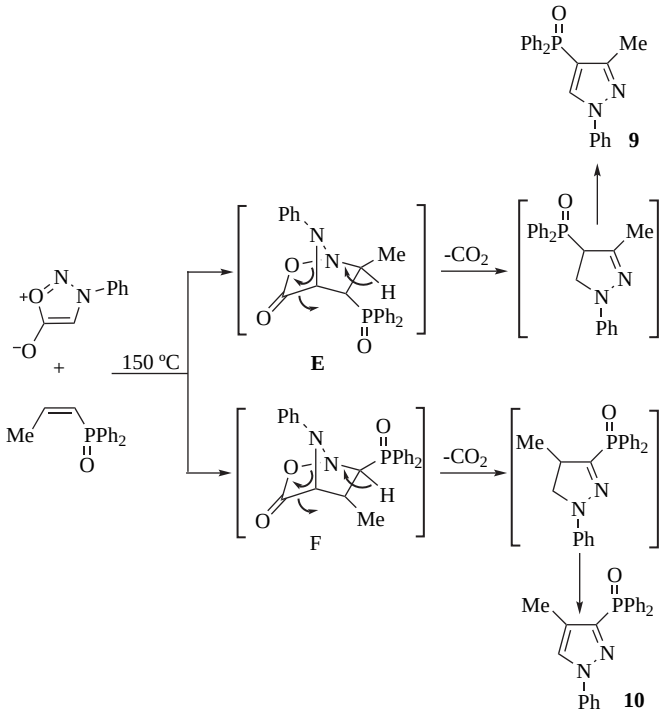
It can be postulated that the formation of phosphanylpyrazoles **9** and **10** arises by way of two possible **E** and **F** cycloadducts. The major product **9** should result from the orientation in which the carbon terminus of *N*-phenylsydnone is bonded at the α-C of the vinylphosphane oxide. The pyrazoles **9** and **10** should be formed by spontaneous aromatization of the corresponding 2-pyrazolines resulting from loss of CO_2 in the intermediate **E** and **F** adducts, respectively (Scheme 13).

These heteroaryldiphenylphosphane oxides, easily converted in the corresponding phosphanes,[14] can be used as building blocks for the linkage of the desirable features of the organic π-conjugated unit (e.g., semiconductivity, luminescence, flexibility) with some

electronically interesting functional properties of metal complexes (e.g., optical, magnetic).[15]



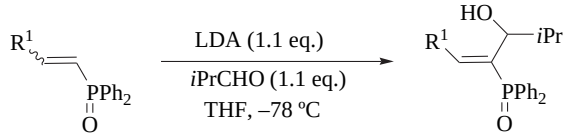
Scheme 12.



Scheme 13.

2.5. Reactions of vinylphosphane oxides with aldehydes in the presence of LDA. Synthesis of allenes

The alkenylphosphane oxides **1a**, **1c**, and **1d** reacted with isobutyraldehyde and lithium diisopropylamide by a Baylis–Hillman type reaction[8] leading to the (*E*)-β-hydroxyphosphane oxides **11a**–**c** (Scheme 14).



1a; R^1 = Me (*Z*) — **11a** (47%)

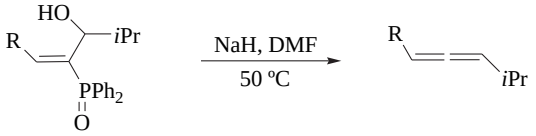
1c; R^1 = $SiMe_2Ph$ (*E*) — **11b** (58%)

1d; R^1 = Ph (*E*) — **11c** (64%)

Scheme 14.

It could also be proved that the β-hydroxyalkenylphosphane oxides **11b**,**c** are readily converted in versatile allenes[16] **12a**,**b** by basic treatment under Horner–Wittig elimination conditions (Scheme 15).

Although this methodology had been previously used,[8] it is noteworthy that its application to silylated substrates has permitted us the synthesis of the interesting and more versatile silyl allene[17] **12a**.



11b; R = $SiMe_2Ph$ — **12a** (57%)

11c; R = Ph — **12b** (65%)

Scheme 15.

3. Conclusions

In summary, we have explored the conjugate addition of heteroatomic nucleophiles (silyl- and stannyl-lithium and cuprates, or lithium phenylsulfide and diphenylphosphide) at stereodefined vinylphosphane oxides previously prepared by regio- and stereospecific cleavage of silyloxiranes with lithium diphenylphosphide. The most interesting results were obtained by α-deprotonation of the β-silylated phosphane oxide resulting from silylcupration and subsequent reaction with electrophiles. The reaction, which occurred with total or partial diastereoselectivity has turned out to be a useful stereoselective route to synthesise α-functionalized β-silylated phosphane oxides containing two or three chiral carbons. On the other hand, the Michael addition of sulfur or phosphorus nucleophiles afforded precursors of bidentate 1,2-donord ligands used in homogeneous catalysis. Moreover, the formation of a sulfur–C bond constitutes a key reaction in biosynthesis as well as in the chemical synthesis of biologically potent compounds[18] and the introduction of a second phosphane group gives rise to P,P-chelate metal complexes, in which their electronic properties could be improved. Likewise, the heteroarylphosphanes due to the ability of P-centers to coordinate to transition metals offer manifold opportunities to build supramolecular architectures in which the π-systems can be organized in a well-defined manner. Finally, the availability of cumulative double bonds in silylallenes makes these compounds valuable precursors of versatile allyl- or vinyl-silanes.

4. Experimental

4.1. General

THF was distilled from sodium benzophenone ketyl in a recycling still. All chromatographic and work-up solvents were distilled prior to use. Copper(I)cyanide was dried in vacuo over P_2O_5. The mixed butyl(dimethylphenylsilyl)- and butyl(*tert*-butyldiphenylsilyl)-cuprate reagents were prepared mixing 1 equiv of the corresponding silyllithium, 1 equiv of butyllithium and 1 equiv of copper(I) cyanide.[19] The mixed butyl(tributylstannyl)cuprate was prepared in the same way.[20] The trimethylsilyldiazomethane is commercial (Aldrich) and the *N*-phenylsydnone was synthesised starting from *N*-phenylglicine.[21] All reactions involving organometallic reagents were carried out under nitrogen atmosphere. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded at 300, 75 and 121 MHz, respectively, in $CDCl_3$ as an internal standard. Carbon multiplicities were assigned by DEPT experiments. Reactions were monitored by TLC on a pre-coated plate of silica gel 60 (nano-SIL-20, Macherey–Nagel). Flash chromatography was performed on silica gel 60 (230–400 mesh, M-N). The starting alkenylphosphane oxides were

previously prepared by us[5] from epoxysilanes by regio- and stereospecific cleavage with lithium diphenylphosphide.

4.2. Silylcupration of alkenylphosphane oxides and trapping with electrophiles. General procedure

A THF solution of the lithium butyl(dimethylphenylsilyl)cuprate or butyl(*tert*-butyldiphenylsilyl)cuprate (2 mmol) was added at −78 °C under N_2 to a stirred solution of the alkenylphosphane oxides **1a**–**d** (1 mmol) in THF (5 mL). The mixture was stirred for 1 h and then the electrophile (3 mmol) was added at −78 °C. The mixture was slowly allowed to warm to 0 °C and stirred at this temperature until TLC indicated complete reaction. The reaction mixture was then quenched at 0 °C with aqueous ammonium chloride, extracted with ether and the organic layer dried ($MgSO_4$). The ethereal solvents were evaporated and the residue chromatographed to give the following compounds.

*4.2.1. [2-(Dimethylphenylsilyl)propyl]diphenylphosphane oxide (**2a**).* Yield: 279 mg (74%); R_f (AcOEt) 0.40; mp 95–98 °C (from Et_2O/hexane); IR ($CHCl_3$) 1258, 1183, 1117 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.26 (s, 3H), 0.28 (s, 3H), 1.13 (d, J=7.3 Hz, 3H), 1.40 (m, 1H), 2.00 (dt, J=15.2, 11.8 Hz, 1H), 2.29 (ddd, J=1.2, 8.3, 15.2 Hz, 1H), 7.33–7.77 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −6.3, −5.0, 13.3 (d, J=6.6 Hz), 15.3, 30.7 (d, J=67.8 Hz), 127.8, 128.4 (d, J=11.2 Hz), 129.1, 130.3 (d, J=9.1 Hz), 130.8 (d, J=8.8 Hz), 131.3, 132.6 (d, J=96.6 Hz), 133.9, 134.6 (d, J=95.1 Hz), 136.9; ^{31}P NMR (121 MHz, $CDCl_3$) δ 33.96; [found: C, 73.36; H, 6. 98. $C_{23}H_{27}OPSi$ (378.16) requires C, 72.98; H, 7.19%].

*4.2.2. [2-(tert-Butyldiphenylsilyl)propyl]diphenylphosphane oxide (**2b**).* Yield: 337 mg (70%); R_f (AcOEt) 0.38; IR ($CHCl_3$) 1180, 1120 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ1.08 (s, 9H), 1.40 (d, J=6.7 Hz, 3H), 2.12 (m, 2H), 2.53 (dd, J=9.2, 13.4 Hz, 1H), 7.27–7.78 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ11.2 (d, J=6.4 Hz), 17.0, 18.9, 29,1, 32.0 (d, J=67.0 Hz), 127.3, 127.7, 128.5 (d, J=12.7 Hz), 128.6 (d, J=10.2 Hz), 129.2, 129.3, 130.5 (d, J=8.7 Hz), 130.8 (d, J=8.9 Hz), 131.4 (d, J=2.2 Hz), 133.0 (d, J=96.5 Hz), 133.3, 134.1, 134.5 (d, J=94.2 Hz), 136.4; ^{31}P NMR (121 MHz, $CDCl_3$) δ 33.44; [found: C, 76.89; H, 7.60. $C_{31}H_{35}OPSi$ (482.22) requires C, 77.14; H, 7.31%].

*4.2.3. [2-(Dimethylphenylsilyl)hexyl]diphenylphosphane oxide (**2c**).* Yield: 281 mg (67%); R_f (AcOEt) 0.41; IR ($CHCl_3$) 1255, 1180, 1110 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.29 (s, 3H), 0.31 (s, 3H), 0.72 (t, J=7.1 Hz, 3H), 1.08 (m, 4H), 1.37 (m, 1H), 1.55 (m, 2H), 2.14 (dt, J=15.3, 11.0 Hz, 1H), 2.27 (ddd, J=2.7, 9.9, 15.3 Hz, 1H), 7.32–7.69 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.7, −3.6, 13.8, 18,8 (d, J=6.0 Hz), 22.8, 29.3 (d, J=67.9 Hz), 30.3, 30.9, 127.8, 128.4 (d, J=11.4 Hz), 129.0, 130.5 (d, J=8.9 Hz), 130.8 (d, J=8.9 Hz), 131.3, 133.1 (d, J=96.7 Hz), 133.9, 134.5 (d, J=97.5 Hz), 137.9; ^{31}P NMR (121 MHz, $CDCl_3$) δ 32.97; [found: C, 73.96; H, 6. 77. $C_{26}H_{33}OPSi$ (420.20) requires C, 74.25; H, 7.91%].

*4.2.4. [2,2-Bis(dimethylphenylsilyl)ethyl]diphenylphosphane oxide (**2d**).* Yield: 293 mg (59%); R_f (AcOEt) 0.46; IR ($CHCl_3$) 1266, 1187, 1112 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 6H), 0.26 (s, 6H), 0.83 (dt, J=21., 5.8 Hz, 1H), 2.40 (dd J=5..8, 12.5 Hz, 2H), 7.15–7.57 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.8, −1.5, 4.4 (d, J=6.6 Hz), 26.3 (d, J=66.9 Hz), 127.6, 128.4 (d, J=11.0 Hz), 128.8, 130.8 (d, J=8.8 Hz), 131.2, 133.5 (d, J=94.9 Hz), 134.2, 139.3; ^{31}P NMR (121 MHz, $CDCl_3$) δ 31.85; [found: C, 72.52; H, 6. 81. $C_{30}H_{35}OPSi_2$ (498.20) requires C, 72.25; H, 7.07%].

*4.2.5. [2-(Dimethylphenylsilyl)-2-phenylethyl]diphenylphosphane oxide (**2e**).* Yield: 228 mg (52%); R_f (AcOEt) 0.45; mp 189–191 °C (from Et_2O/hexane); IR ($CHCl_3$) 1262, 1180, 1118 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.22 (s, 3H), 0.27 (s, 3H), 2.65 (ddd, J=2.3, 15.9, 28.5 Hz, 1H), 2.72 (dt, J=7.2, 15.9 Hz, 1H), 2.88 (ddd, J=2.3, 10.9, 15.9 Hz, 1H), 6.73–7.60 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.5, −4.1, 28.6 (d, J=5.8 Hz), 30.1 (d, J=67.3 Hz), 124.7, 127.7, 127.9, 128.0, 128.4 (d, J=11.3 Hz), 129.3, 130.6 (d, J=8.9 Hz), 130.8 (d, J=9.3 Hz), 131.4, 1325 (d, J=103.6 Hz), 133.9 (d, J=96.6 Hz), 134.3, 136.3, 140.9; ^{31}P NMR (121 MHz, $CDCl_3$) δ 32.28; [found: C, 76.57; H, 6. 46. $C_{28}H_{29}OPSi$ (440.17) requires C, 76.33; H, 6.63%].

*4.2.6. [2-(tert-Butydiphenylsilyl)-2-phenylethyl]diphenylphosphane oxide (**2f**).* Yield: 234 mg (43%); R_f (AcOEt) 0.36; IR ($CHCl_3$) 1190, 1118 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.79 (s, 9H), 2.49 (ddd, J=4.7, 12.1, 15.1 Hz, 1H), 2.82 (t, J=15.1 Hz, 1H), 3.81 (dd, J=12.1, 16.0 Hz, 1H), 6.72–7.74 (m, 25H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.1, 23.0, 27.8, 33.0 (d, J=66.8 Hz), 125.3, 127.4, 127.5, 127.6, 127.8, 128.4 (d, J=11.2 Hz), 129.3, 129.5, 130.3 (d, J=9.5 Hz), 130.5 (d, J=2.3 Hz), 130.8 (d, J=9.7 Hz), 131.3 (d, J=2.2 Hz), 132.0 (d, J=96.4 Hz), 133.4, 133.7, 134.9 (d, J=95.0 Hz), 137.1, 141.2; ^{31}P NMR (121 MHz, $CDCl_3$) δ 31.42; [found: C, 79. 61; H, 6.62. $C_{36}H_{37}OPSi$ (544.24) requires C, 79.37; H, 6.85%].

*4.2.7. Ethyl (2RS,3SR)-2-(diphenylphosphany)l-3-(dimethylphenyl silyl)butanoate (syn-**3a**).* Yield: 49 mg (11%); R_f (AcOEt/CH_2Cl_2 9:1) 0.73; IR ($CHCl_3$) 1725, 1258, 1183, 1117 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.25 (s, 3H), 0.28 (s, 3H), 0.89 (t, J=7.1 Hz, 3H), 1. 36 (d, J=7.5 Hz, 3H), 1.58 (m, 1H), 3.50 (dd, J=1.7, 9.2 Hz, 1H), 3.84 (q, J=7.1 Hz, 2H), 7.19–8.06 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.5, −4.5, 11.5, 13.5, 18.4, 46.6 (d, J=61.0 Hz), 60.8, 127.5, 128.4 (d, J=11.2 Hz), 129.1, 130.3 (d, J=9.1 Hz), 130.8 (d, J=8.8 Hz), 131.3, 132.6 (d, J=96.6 Hz), 133.9, 134.6 (d, J=95.1 Hz), 136.8, 168.9; ^{31}P NMR (121 MHz, $CDCl_3$) δ 29.83; [found: C, 69.63; H, 7.25. $C_{26}H_{31}O_3PSi$ (450.18) requires C, 69.31; H, 6.93%].

*4.2.8. Ethyl (2RS,3RS)-2-(diphenylphosphanyl)-3-(dimethylphenyl silyl)butanoate (anti-**3a**).* Yield: 162 mg (36%); R_f (AcOEt/CH_2Cl_2 9:1) 0.71; mp 120–122 °C (from Et_2O/hexane); IR ($CHCl_3$) 1725, 1258, 1183, 1117 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.26 (s, 3H), 0.29 (s, 3H), 0.69 (t, J=7.3 Hz, 3H), 0.99 (d, J=7.5 Hz, 3H), 2.04 (m, 1H), 3.03 (m, 1H), 3.34 (m, 1H), 3.44 (dd, J=12.3, 13.0 Hz, 1H), 7.26–8.16 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.6, −4.2, 13.1, 14.2 (d, J=5.7 Hz), 19.2 (d, J=4.9 Hz), 52.5 (d, J=54.8 Hz), 60.8, 127.5, 128.4 (d, J=11.2 Hz), 129.1, 130.3 (d, J=9.1 Hz), 130.8 (d, J=8.8 Hz), 131.3, 132.6 (d, J=96.6 Hz), 133.9, 134.6 (d, J=95.1 Hz), 136.8, 170.3; ^{31}P NMR (121 MHz, $CDCl_3$) δ 28.98; [found: C, 69.11; H, 6. 75. $C_{26}H_{31}O_3PSi$ (450.18) requires C, 69.31; H, 6.93%].

*4.2.9. (2RS,3SR)-[2-(Dimethylphenylsilyl)hex-5-en-3-yl]diphenyl phosphane oxide (syn-**3b**).* Yield: 50 mg (12%); R_f (AcOEt) 0.75; IR ($CHCl_3$) 1638, 1258, 1182, 1120 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.35 (s, 3H), 0.36 (s, 3H), 1.01 (d, J=7.7 Hz, 3H), 1.57 (m, 1H), 2.24 (m, 1H), 2.44 (m, 1H), 2.60 (m, 1H), 4.79 (dd, J=1.6, 17.0 Hz, 1H), 4.89 (dd, J=1.6, 10.0 Hz, 1H), 5.55 (ddt, J=10.0, 17.0, 6.9 Hz, 1H), 7.29–7.80 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −3.1, −3.0, 14.0 (d, J=8.5 Hz), 20.0, 33.5, 40.8 (d, J=69.5 Hz), 116.8, 127.6, 128.3 (d, J=11.1 Hz), 128.5 (d, J=11.2 Hz), 128.7, 130.7 (d, J=8.6 Hz), 130.8, 131.3 (d, J=10.1 Hz), 131.5, 133.5 (d, J=94.7 Hz), 134.0, 134.3 (d, J=93.7 Hz), 136.4 (d, J=10.9 Hz), 139.2; ^{31}P NMR (121 MHz, $CDCl_3$) δ 35.12; [found: C, 74.43; H, 7. 22. $C_{26}H_{31}OPSi$ (418.19) requires C, 74.60; H, 7.46%].

*4.2.10. (2RS,3RS)-[2-(Dimethylphenylsilyl)hex-5-en-3-yl]diphenyl phosphane oxide (anti-**3b**).* Yield: 163 mg (39%); R_f (AcOEt) 0.81; IR ($CHCl_3$) 1638, 1250, 1183, 1122 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.26 (s, 3H), 0.34 (s, 3H), 1.22 (d, J=7.7 Hz, 3H), 1.41 (m, 1H), 2.35 (m, 2H), 2.63 (m, 1H), 4.60 (dd, J=1.4, 10.0 Hz, 1H), 4.72 (dd, J=1.4, 17.0 Hz, 1H), 5.26 (ddt, J=10.0, 17.0, 7.0 Hz, 1H), 7.32–7.67 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.2, −3.9, 10.3, 19.7, 29.1, 37.0 (d, J=66.4 Hz), 115.8, 127.8, 128.2 (d, J=10.9 Hz), 128.5 (d, J=11.1 Hz), 129.3, 130.8 (d, J=8.3 Hz), 131.1, 132.9 (d, J=94.4 Hz), 133.6, 134.1 (d, J=89.2 Hz), 136.9 (d, J=93.7 Hz),

136.4 (d, J=5.4 Hz), 137.6; ^{31}P NMR (121 MHz, $CDCl_3$) δ 37.57; [found: C, 74.86; H, 7. 63. $C_{26}H_{31}OPSi$ (418.19) requires C, 74.60; H, 7.46%].

*4.2.11. [1,1-Bis(dimethylphenylsilyl)pent-4-en-2-yl]diphenylphosphane oxide (**3c**).* Yield: 269 mg (50%); R_f (AcOEt) 0.75; IR ($CHCl_3$) 1640, 1255, 1187, 1123 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.36 (s, 3H), 0.38 (s, 3H), 0.55 (s, 3H), 0.57 (s, 3H), 1.45 (m, 1H), 2.54 (m, 2H), 2.84 (m, 1H), 4.63 (dd, J=1.6, 9.9 Hz, 1H), 4. 95 (dd, J=1.6, 17.0 Hz, 1H), 5.35 (ddt, J=9.9, 17.0, 7.1 Hz, 1H), 7.19–7.70 (m, 20H); ^{31}P NMR (121 MHz, $CDCl_3$) δ 34.68; [found: C, 73.81; H, 7.52. $C_{33}H_{39}OPSi_2$ (538.23) requires C, 73.56; H, 7.30%].

*4.2.12. (1RS,2SR)-[1-(Dimethylphenylsilyl)-1-phenylpent-4-en-2-yl] diphenylphosphane oxide (syn-**3d**).* Yield: 48 mg (10%); R_f (AcOEt/CH_2Cl_2 9:1) 0.64; IR ($CHCl_3$) 1634, 1250, 1185, 1120 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.15 (s, 3H), 0.45 (s, 3H), 2.52 (m, 1H), 2.61 (m, 2H), 3.07 (m, 1H), 4.64 (dd, J=1.6, 10.3 Hz, 1H), 4. 77 (dd, J=1.6, 17.0 Hz, 1H), 5.32 (m, 1H), 7.08–7.74 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.8, −3.8, 31.9, 35.6, 39.8 (d, J=68.3 Hz), 116.2, 124.3, 127.5, 127.9, 128.0, 128.4 (d, J=11.3 Hz), 129.6, 130.9 (d, J=8.9 Hz), 131.8 (d, J=9.3 Hz), 132.4, 132.7 (d, J=93.6 Hz), 134.8 (d, J=92.6 Hz), 134.3, 136.3, 142.4; ^{31}P NMR (121 MHz, $CDCl_3$) δ 35.93; [found: C, 77.71; H, 7.15. $C_{31}H_{33}OPSi$ (480.20) requires C, 77.46; H, 6.92%].

*4.2.13. (1RS,2RS)-[1-(Dimethylphenylsilyl)-1-phenylpent-4-en-2-yl] diphenylphosphane oxide (anti-**3d**).* Yield: 168 mg (35%); R_f (AcOEt/CH_2Cl_2 9:1) 0.62; IR ($CHCl_3$) 1636, 1250, 1180, 1120 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.42 (s, 6H), 1.09 (s, 9H), 6.77 (d, J=22.6 Hz, 1H), 7.08 (m, 2H), 3.15 (m, 1H), 4.57 (dd, J=1.6, 17.0 Hz, 1H), 4. 68 (dd, J=1.6, 10.4 Hz, 1H), 5.46 (m, 1H), 7.10–7.61 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.5, −1.8, 33.3, 36.4, 46.7 (d, J=66.9 Hz), 116.3, 124.9, 127.8, 127.9, 128.1, 128.4 (d, J=11.3 Hz), 129.6, 130.9 (d, J=8.9 Hz), 131.8 (d, J=9.3 Hz), 132.4, 132.7 (d, J=85.3 Hz), 134.2 (d, J=96.8 Hz), 133.7, 135.8, 143.6; ^{31}P NMR (121 MHz, $CDCl_3$) δ 35.35; [found: C, 77.23; H, 6. 77. $C_{31}H_{33}OPSi$ (480,20) requires C, 77.46; H, 6.92%].

*4.2.14. E-1-(tert-Butyldiphenylsilyl)-2-(dimethylphenylsilyl)ethene (**4a**).* Yield: 248 mg (62%); R_f (hexane) 0.36; IR ($CHCl_3$) 1590, 1250, 1112, 1010 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.42 (s, 6H), 1.09 (s, 9H), 6.77 (d, J=22.5 Hz, 1H), 7.08 (d, J=22.5 Hz, 1H), 7.20–7.41 (m, 9H), 7.53–7.60 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.6, 18.3, 27.9, 127.6, 129.0, 134.1, 135.8, 138.7, 152.2, 157.5; [found: C, 77.68; H, 7.86. $C_{26}H_{32}Si_2$ (400,20) requires C, 77.93; H, 8.05%].

4.3. Silyllithiation of alkenylphosphane oxides. Typical procedure

Dimethylphenyl- or *tert*-butyldiphenylsilyllithium (2 mmol) was added at 0 °C under N_2 to a stirred solution of the vinylphosphane oxides **1a**, **1c**, **1e** or **1f** (1 mmol) in dry THF (3 mL). The mixture was stirred at 0 °C until TLC indicated complete reaction. Quenching at that temperature with aqueous ammonium chloride, aqueous work-up with diethyl ether, drying ($MgSO_4$), and chromatography gave the following products.

*4.3.1. [2-(Dimethylphenylsilyl)propyl]diphenylphosphane oxide (**2a**).* Yield: 185 mg (49%).

*4.3.2. [2-(tert-Butyldiphenylsilyl)propyl]diphenylphosphane oxide (**2b**).* Yield: 303 mg (63%).

*4.3.3. [2,2-Bis(dimethylphenylsilyl)ethyl]diphenylphosphane oxide (**2d**).* Yield: 283 mg (57%).

*4.3.4. [2-(Dimethylphenylsilyl)ethyl]diphenylphosphane oxide (**2g**).* Yield: 236 mg (65%); R_f (AcOEt) 0.35; mp 142–144 °C (from Et_2O/hexane); IR ($CHCl_3$) 1258, 1184, 1120 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.27 (s, 6H), 0.98 (dd, J=7.1, 17.7 Hz, 2H), 2.13 (dt, J=7.1, 9.7 Hz, 2H), 7.28–7.81 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −3.5, 6.0 (d, J=7.1 Hz), 23.5 (d, J=69.6 Hz), 127.9, 128.4 (d, J=11.2 Hz), 129.1, 130.3 (d, J=9.1 Hz), 130.8 (d, J=8.8 Hz), 131.3, 132.6 (d, J=96.6 Hz), 133.9, 134.3 (d, J=95.1 Hz), 137.5; ^{31}P NMR (121 MHz, $CDCl_3$) δ 35.72; [found: C, 72.23; H, 7 18. $C_{22}H_{25}OPSi$ (364.14) requires C, 72.49; H, 6.91%].

*4.3.5. [2-(Dimethylphenylsilyl)-2-(trimethylsilyl)ethyl]diphenyl phosphane oxide (**2h**).* Yield: 196 mg (45%); R_f (AcOEt) 0.45; IR ($CHCl_3$) 1251, 1190, 1112 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ −0.06 (s, 9H), 0.28 (s, 6H), 0.31 (s, 6H), 0.60 (ddd, J=4.4, 7.2, 22.3 Hz, 1H), 2.30 (ddd, J=7.2, 12.7, 15.4 Hz, 1H), 2.43 (ddd, J=4.4, 10.8, 15.4 Hz, 1H), 7.33–7.53 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.2, −1.5, 0.2, 4.1 (d, J=6.3 Hz), 26.1 (d, J=67.0 Hz), 128.1, 128.4 (d, J=11.8 Hz), 128.9, 130.8 (d, J=9.6 Hz), 131.0 (d, J=10.3 Hz), 131.5, 133.2 (d, J=97.1 Hz), 134.0, 134.1(d, J=95.9 Hz), 139.4; ^{31}P NMR (121 MHz, $CDCl_3$) δ 31.61; [found: C, 69.01; H, 7. 80. $C_{25}H_{33}OPSi_2$ (436.18) requires C, 68.76; H, 7.62%].

*4.3.6. E-1-(tert-Butyldiphenylsilyl)-2-(dimethylphenylsilyl)ethene (**4a**).* Yield: 236 mg (59%).

*4.3.7. E-1-(Dimethylphenylsilyl)-2-phenylethene (**4b**).* Yield: 183 mg (77%)[22]

*4.3.8. E-1-(tert-Butyldiphenylsilyl)-2-phenylethene (**4c**).* Yield: 232 mg (68%)[23]

4.4. α-Deprotonation of the β-silylated phosphane oxides and capture with electrophiles. General procedure

A solution of the β-silyl phosphane oxides **2a** or **2d** (1 mmol) in dry THF (3 mL) was added to a stirred THF solution of lithium diisopropylamide (2 mmol) [prepared from diisopropylamine (0.28 mL, 2 mmol) and BuLi (1.25 mL, 1.6 M solution in hexane, 2 mmol) in dry THF (3 mL) at −20 °C under N_2 for 15 min]. The mixture was stirred at 0 °C for 30 min and then was added the electrophile (3 mmol) and the system was stirred at this temperature and then warmed to room temperature until TLC indicated complete reaction (reaction time=1–10 h). The mixture was hydrolysed with a saturated aqueous NH_4Cl solution and extracted with diethyl ether, and the organic layer was dried ($MgSO_4$). The residue obtained after evaporation of ether was purified by flash chromatography on silica gel using AcOEt/CH_2Cl_2 or hexane as eluents to give the compounds characterized below.

*4.4.1. (2RS,3SR)-[2-(Dimethylphenylsilyl)hex-5-en-3-yl]diphenyl phosphane oxide (syn-**3b**).* Yield: 83 mg (20%).

*4.4.2. (2RS,3RS)-[2-(Dimethylphenylsilyl)hex-5-en-3-yl]diphenyl phosphane oxide (anti-**3b**).* Yield: 158 mg (38%).

*4.4.3. (1RS,2SR)-1-Benzoyl-[2-(dimethylphenylsilyl)propyl]diphenyl phosphane oxide (syn-**3e**).* Yield: 72 mg (15%); R_f (AcOEt/CH_2Cl_2 1:1) 0.39; IR ($CHCl_3$) 1682, 1258, 1182, 1120 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 3H), 0.15 (s, 3H), 1.38 (d, J=7.5 Hz, 3H), 2.05 (m, 1H), 4.59 (dd, J=2.5, 13.3 Hz, 1H), 7.09–8.25 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.3, −3.3, 12.0, 21.0, 49.0 (d, J=57.0 Hz), 125.5, 127.6, 128.7(d, J=11.9 Hz), 129.3, 130.7 (d, J=9.6 Hz), 131.5, 131.8, 132.3 (d, J=99.5 Hz), 136.5, 136.8 138.7, 197.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ 31.02; [found: C, 74.82; H, 6.28. $C_{30}H_{31}O_2PSi$ (482.18) requires C, 74.66; H, 6.47%].

*4.4.4. (1RS,2RS)-1-Benzoyl-[2-(dimethylphenylsilyl)propyl]diphenyl phosphane oxide (anti-**3e**).* Yield: 197 mg (41%); R_f (AcOEt/CH_2Cl_2

1:1) 0.37; IR ($CHCl_3$) 1680, 1252, 1180, 1118 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.14 (s, 3H), 0.20 (s, 3H), 1.18 (d, J=7.5 Hz, 3H), 2.30 (m, 1H), 4.79 (dd, J=11.7, 18.5 Hz, 1H), 7.09–8.25 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −3.9, −2.7, 14.2, 20.7, 54.1 (d, J=49.4 Hz), 124.7, 127.3, 128.1(d, J=13.1Hz), 129.1, 130.5 (d, J=9.7 Hz), 131.5, 132.1, 133.3 (d, J=101.5 Hz), 135.2, 137.0, 138.3, 198.4; ^{31}P NMR (121 MHz, $CDCl_3$) δ 30.23; [found: C, 74.42; H, 6. 61. $C_{30}H_{31}O_2PSi$ (482.18) requires C, 74.66; H, 6.47%].

*4.4.5. (1RS,2RS)-1-Iodo-[2-(dimethylphenylsilyl)propyl]diphenyl phosphane oxide (anti-**3f**).* Yield: 226 mg (45%); R_f (AcOEt) 0.63; IR ($CHCl_3$) 1250, 1180, 1118 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.25 (s, 3H), 0.46 (s, 3H), 1.14 (q, J=6.7 Hz, 1H), 1.29 (d, J=6.7 Hz, 3H), 4.42 (s, 1H), 7.28–7.68 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.1, −4.1, 14.7, 21.8, 29.3 (d, J=63.2 Hz), 128.0, 128.7 (d, J=11.6 Hz), 129.6, 130.9 (d, J=8.4 Hz), 131.7, 132.9 (d, J=94.1 Hz), 133.9, 136.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ 32.21; [found: C, 54.55; H, 5.43. $C_{23}H_{26}IOPSi$ (504.05) requires C, 54.77; H, 5.20%].

*4.4.6. (1RS,2SR,3SR)-3-(Dimethylphenylsilyl)-1-phenyl-2-(diphenyl phosphanyl)butan-1-ol (**3g**).* Yield 212 mg (44%); R_f ($AcOEt/CH_2Cl_2$ 1:1) 0.51; mp 158–160 °C (from Et_2O/hexane); IR ($CHCl_3$) 3200, 1252, 1185, 1110 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.04 (s, 3H), 0.19 (s, 3H), 1.35 (m, 1H), 1.38 (s, 3H), 2.90 (t, J=7.8 Hz, 1H), 3.15 (br, s, 1H), 5.27 (dd, J=6.3, 7.8 Hz, 1H), 6.94–7.87 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −3.9, −3.8, 13.6, 18.9, 44.8 (d, J=65.7 Hz), 71.5, 126.4, 127.2, 128.5 (d, J=11.8 Hz), 129.6, 131.3 (d, J=8.8 Hz), 131.7, 132.9 (d, J=94.1 Hz), 134.2, 139.4, 142.4; ^{31}P NMR (121 MHz, $CDCl_3$) δ 38.68; [found: C, 74.59; H, 6.63. $C_{30}H_{33}O_2PSi$ (484.20) requires C, 74.35; H, 6.86%].

*4.4.7. (3RS,4SR,5SR)-2-Methyl-5-(dimethylphenylsilyl)-4-(diphenyl phosphanyl)hexan-3-ol (**3h**).* Yield 238 mg (53%); R_f ($AcOEt/CH_2Cl_2$ 1:1) 0.38; mp 141–143 °C (from Et_2O/hexane); IR ($CHCl_3$) 3300, 1250, 1185, 1110 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.23 (s, 3H), 0.38 (s, 3H), 0.44 (d, J=6.5 Hz, 3H), 0.84 (d, J=6.5 Hz, 3H), 1.33 (s, 3H), 1.35 (m, 2H), 2.75 (d, J=9.0 Hz, 1H), 3.52 (dt, J=25.8, 9.0 Hz, 1H), 5.26 (d, J=9.0 Hz, 1H), 7.30–7.72 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.5, −3.3, 11.8, 19.7, 19.9, 21.9, 34.0, 37.9 (d, J=61.9 Hz), 80.2 (d, J=4.1 Hz), 127.9, 128.4 (d, J=11.2 Hz), 129.4, 130.3 (d, J=8.5 Hz), 131.5, 132.7 (d, J=96.2 Hz), 134.0, 135.0 (d, J=89.4 Hz), 137.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ 43.12; [found: C, 71.72; H, 7.98. $C_{27}H_{35}O_2PSi$ (450.21) requires C, 71.96; H, 7.83%].

*4.4.8. E-1-(Dimethylphenylsilyl)-2-phenylethene (**4b**).* Yield: 192 mg (81%).[22]

4.5. Stannylcupration of alkenylphosphane oxides. General procedure

A solution of a vinylphosphane oxide **1a**,**c**,**d** (1 mmol) in THF dry (2 mL) was added to a stirred solution of lithium butyl(tributylstannyl)cuprate (2 mmol) in THF (2 mL) at −78 °C under N_2. The reaction mixture was stirred at that temperature for 1 h and then was gradually warmed to 0 °C over 3 h. The mixture was then hydrolysed with a saturated aqueous NH_4Cl solution and extracted with ether, and the organic layer was dried ($MgSO_4$). The solvent was evaporated and the residue was chromatographed to give the compounds characterized below.

*4.5.1. (E)-1-Propenyldiphenylphosphane oxide (**1g**).* Yield 159 mg (66%)[5b]

*4.5.2. Allyldiphenylphosphane oxide (**5**).* Yield 77 mg (32%); R_f (AcOEt) 0.22; IR ($CHCl_3$) 1636, 1178, 925 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.15 (dd, J=7.5, 15.6 Hz, 2H), 5.15 (m, 2H), 5.67 (m, 1H), 7.40–7.56 (m, 6H), 7.69–7.78 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.0 (d, J=68.7 Hz), 121.0 (d, J=11.8 Hz), 128.5 (d, J=9.3 Hz), 129.1 (d, J=11.7 Hz), 131.0 (d, J=9.1 Hz), 131.8, 133.2 (d, J=99.1 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 30.70; [found: C, 74.10; H, 6.42. $C_{15}H_{15}OP$ (242.09) requires C, 74.37; H, 6.24%].

4.6. Stannyllithiation of alkenylphosphane oxides. General procedure

Tributylstannyllithium (2 mmol) was added at −78 °C under N_2 to a stirred solution of the vinylphosphane oxides **1a**, **1c**, **1d** or **1e** (1 mmol) in dry THF (3 mL). The mixture was stirred at this temperature for 2 h and then was allowed to warm to 0 °C and stirred until TLC indicated complete reaction. Quenching at that temperature with aqueous ammonium chloride, aqueous work-up with diethyl ether, drying ($MgSO_4$), and chromatography gave the following products.

4.6.1. Diphenyl-[2-(tributylstannyl)propyl]phosphane oxide (6a). Yield 363 mg (68%); R_f ($AcOEt/CH_2Cl_2$ 3:1) 0.34; ^1H NMR (300 MHz, $CDCl_3$) δ 0.92 (m, 15H), 1.25 (d, J=7.3 Hz, 3H), 1.20–150 (m, 12H), 1.66 (m, 1H), 2.47 (m, 2H), 7.42–7.53 (m, 6H), 7.70–7.79 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.4, 11.2, 13.7, 20.1 (d, $J_{C,P}$=5.4 Hz), 27.5 (d, $J_{C,Sn}$=53.4 Hz), 29.2 (d, $J_{C,Sn}$=19.3 Hz), 35.3 (d, $J_{C,P}$=64.8 Hz), 128.5 (d, $J_{C,P}$=11.3 Hz), 130.5 (d, $J_{C,P}$=9.0 Hz), 131.4, 133.6 (d, $J_{C,P}$=95.4 Hz); ^{31}P NMR (121 MHz, CDCl3) δ 32.73 ($J_{P,Sn}$=177.0 Hz); [found: C, 61.01; H, 7.98. $C_{27}H_{43}OPSn$ (534.21) requires C, 60.81; H, 8.13%].

*4.6.2. Diphenyl-[2-(tributylstannyl)ethyl]phosphane oxide (**6b**).* Yield 218 mg (42%); R_f ($AcOEt/CH_2Cl_2$ 3:1) 0.32; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (m, 15H), 1.20–150 (m, 12H), 1.74 (m, 2H), 2.34 (m, 2H), 7.44–7.55 (m, 6H), 7.70–7.80 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.8, 13.7, 17.6, 27.3 (d, $J_{C,Sn}$=52.8 Hz), 27.6 (d, $J_{C,P}$=74.6 Hz), 29.0 (d, $J_{C,Sn}$=19.8 Hz), 128.5 (d, $J_{C,P}$=11.2 Hz), 130.9 (d, $J_{C,P}$=8.8 Hz), 131.5, 132.8 (d, $J_{C,P}$=95.5 Hz); ^{31}P NMR (121 MHz, CDCl3) δ 34.90 (JP,Sn=198.0 Hz); [found: C, 59.72; H, 8.28. $C_{26}H_{41}OPSn$ (520.19) requires C, 60.14; H, 7.96%].

4.7. Reactions of the alkenylphosphane oxides with lithium sulphides and phosphides. General procedure

A solution of a vinylphosphane oxide **1a**, **1c** or **1d** (1 mmol) in dry THF (3 mL) was added dropwise to a stirred THF solution of lithium phenylsulphide (3 mmol) [prepared from benzenethiol (0.3 mL, 3 mmol) and butyllithium (1.875 mL, 1.6 M solution in hexane, 3 mmol) in THF (5 mL) at −78 °C under N_2 for 10 min] or lithium diphenylphosphide (3.5 mmol) [prepared from diphenylphosphane (0.602 mL, 3.5 mmol) and BuLi (2.184 mL, 1.6 M solution in hexane, 3.5 mmol) in THF (5 mL) at 0 °C under N_2 for 30 min]. In the reactions of **1c** with lithium phenylsulphide the mixture was allowed to warm to room temperature and stirred at that temperature for 24 h. With **1a** and **1d** the reaction mixture was heated at reflux of THF till the full consumption of starting materials was observed by TLC (reaction time for **1a**: 20 h; **1d**: 22 h). In the reactions with lithium diphenylphosphide the mixture was allowed to warm to room temperature and stirred for 5 days. Quenching with aqueous ammonium chloride, aqueous work-up with ether, drying ($MgSO_4$), and chromatography gave the products characterized below.

*4.7.1. [2-(Phenylthio)propyl]diphenylphosphane oxide (**7a**).* Yield 271 mg (77%); R_f (AcOEt) 0.31; IR ($CHCl_3$) 1190 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.46 (d, J=6.7 Hz, 3H), 2.44 (dt, J=15.0, 11.5 Hz, 1H), 2.69 (ddd, J=2.6, 9.6, 15.0 Hz, 1H), 3.58 (m, 1H), 7.24–7.70 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7, 36.9 (d, J=65.2 Hz), 38.2, 127.4, 128.6 (d, J=11.5 Hz), 128.9, 129.0. 130.4 (d, J=9.2 Hz), 131.7,

132.2 (d, J=98.4 Hz), 134.0; ^{31}P NMR (121 MHz, CDCl3) δ 30.21; [found: C, 71.32; H, 5. 88. $C_{21}H_{21}OPS$ (352.11) requires C, 71.57; H, 6.01%].

*4.7.2. [2-(Dimethylphenylsilyl)-2-(phenylthio)ethyl]diphenylphosphane oxide (**7b**).* Yield 297 mg (63%); R_f (AcOEt) 0.51; IR ($CHCl_3$) 1262, 1190, 1116 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.45 (s, 3H), 0.46 (s, 3H), 2.57 (m, 2H), 3.09 (ddd, J=5.6, 7.6, 15.4 Hz, 1H), 7.09–7.62 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.2, −3.7, 26.7, 32.4 (d, J=66.5 Hz), 126.1, 127.4, 128.2 (d, J=11.2 Hz), 128.3, 129.2. 130.1 (d, J=9.5 Hz), 131.7, 133.5 (d, J=99.5 Hz), 134.3, 136.2, 136.6; ^{31}P NMR (121 MHz, CDCl3) δ 30.13; [found: C, 71.46; H, 6. 44. $C_{28}H_{29}OPSSi$ (472.14) requires C, 71.15; H, 6.18%].

*4.7.3. [2-Phenyl-2-(phenylthio)ethyl]diphenylphosphane oxide (**7c**).* Yield 310 mg (75%); R_f(AcOEt) 0.33; IR ($CHCl_3$) 1192 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.02 (m, 2H), 4.79 (dt, J=5.5, 9.1 Hz, 1H), 6.92–7.82 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.6 (d, J=67.0 Hz), 46.9, 127.3, 127.5, 127.9, 128.1 (d, J=11.8 Hz), 128.6, 128.8, 130.5 (d, J=8.6 Hz), 131.7, 132.0 (d, J=93.8 Hz), 132.6, 134.0, 140.1; ^{31}P NMR (121 MHz, CDCl3) δ 28.72; [found: C, 75.56; H, 5. 33. $C_{26}H_{23}OPS$ (414.12) requires C, 75.34; H, 5.59%].

*4.7.4. 1,2-Bis(diphenylphosphanyl)propane (**8a**).* Yield 421 mg (95%); R_f (AcOEt) 0.30; IR ($CHCl_3$) 1188 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (dd, J=7.0, 16.9 Hz, 3H), 2.35 (m, 2H), 2.80 (m, 1H), 7.16–7.57 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4, 26.7 (d, J=70.2 Hz), 28.5 (d, J=69.3 Hz), 128.4 (d, J=9.9 Hz), 130.4 (d, J=9.6 Hz), 131.7, 133.2 (d, J=98.9 Hz), 133.1 (d, J=98.2 Hz); ^{31}P NMR (121 MHz, CDCl3) δ 31.64 (d, $J_{P,P}$=49.8 Hz), 37.91 (d, $J_{P,P}$=49.8 Hz); [found: C, 73.26; H, 6.19. $C_{27}H_{26}O_2P_2$ (444.14) requires C, 72.97; H, 5.90%].

4.8. Reaction of the alkenylphosphane oxide 1d with diphenylphosphane

Diphenylphosphane (2 mmol) was added to a stirred solution of the **1d** (1 mmol) in toluene (5 mL). The mixture was heated to reflux of toluene until the full consumption of starting materials was observed by TLC (reaction time: 30 h). The solvent was evaporated, and the residue was chromatographed to give the compound characterized below.

*4.8.1. 1,2-Bis(diphenylphosphanyl)-1-phenylethane (**8b**).* Yield 329 mg (65%); R_f (AcOEt) 0.15; IR ($CHCl_3$) 1175 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.83 (dq, J=1.5, 11.8 Hz, 1H), 3.17 (ddd, J=4.7, 6.8, 11.8 Hz, 1H), 4.28 (dt, J=11.8, 6.8 Hz, 1H), 6.78–8.08 (m, 25H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.9 (d, J=69.3 Hz), 39.1 (d, J=68.2 Hz), 126.8, 127.4 (d, J=9.6 Hz), 128.7, 130.9 (d, J=9.9 Hz), 131.7, 132.4, 133.7 (d, J=99.8 Hz), 133.9 (d, J=98.5 Hz), 134.5 (d, J=15.6 Hz); ^{31}P NMR (121 MHz, CDCl3) δ 30.80 (d, $J_{P,P}$=46.8 Hz), 36.02 (d, $J_{P,P}$=46.8 Hz); [found: C, 75.51; H, 5.32. $C_{32}H_{28}O_2P_2$ (506.16) requires C, 75.88; H, 5.57%].

4.9. 1,3-Dipolar cycloaddition of alkenylphosphane oxides with *N*-phenylsydnone

A mixture of *N*-phenylsydnone (3 mmol) and the vinylphosphane oxides **1a** or **1d** (1 mmol) in dry xylene (5 mL) was stirred at reflux for 70 h. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography giving the following products.

*4.9.1. 3-Methyl-1-phenyl-4-(diphenylphosphanyl)pyrazole (**9**).* Yield 146 mg (42%); R_f (AcOEt) 0.57; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3H), 7.25–7.82 (m, 16H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.8, 112.5 (d, J=123.5 Hz), 119.4, 127.3, 128.2 (d, J=9.6 Hz), 129.1, 130.7, 132.4, 133.6 (d, J=99.6Hz), 134.2, 139.1, 153.2; ^{31}P NMR (121 MHz, CDCl3) δ 19.74; [found: C, 73.48; H, 5.55; N 7.82. $C_{22}H_{19}N_2OP$ (358.12) requires C, 73.73; H, 5.34; N 8.03%].

*4.9.2. 4-Methyl-1-phenyl-3-(diphenylphosphanyl)pyrazole (**10**).* Yield 39 mg (11%); R_f (AcOEt) 0.57; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.05 (d, J=1.2 Hz, 3H), 7.25–7. 82 (m, 16H); ^{31}P NMR (121 MHz, CDCl3) δ 19.82; [found: C, 73.95; H, 5.13; .N, 7.66. $C_{22}H_{19}N_2OP$ (358.12) requires C, 73.73; H, 5.34; N, 7.82%].

4.10. Synthesis of (*E*)-β-hydroxyalkenylphosphane oxides by Baylis–Hillman type reactions from vinylphosphane oxides. General procedure

A THF solution of LDA (5.5 mmol) [freshly prepared from diisopropylamine (0.77 mL, 5.5 mmol) and BuLi (3.43 mL, 1.6 M solution in hexane, 5.5 mmol) in dry THF (6 mL) at −20 °C under N_2 for 15 min] was added to a stirred solution of the vinylphosphane oxide **1a**,**c**,**d** (5 mmol) and isobutyraldehyde (5.5 mmol) in dry THF (5 mL) at −78 °C for 1 h. The reaction mixture was allowed to warm to room temperature and quenched by addition of saturated aqueous ammonium chloride solution, extracted with ethyl acetate, and dried ($MgSO_4$). The crude product was chromatographed (SiO_2, AcOEt) to give the following products.

*4.10.1. (E)-5-Methyl-3-(diphenylphosphanyl)hex-2-en-4-ol (**11a**).* Yield 737 mg (47%); R_f (AcOEt) 0.62; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.59 (d, J=6.7 Hz, 3H), 1.16 (d, J=6.7 Hz, 3H), 1.90 (m, 4H), 4.10 (dt, J=23.7, 10.5 Hz, 1H), 4.97 (d, J=10.5 Hz, 1H), 6.06 (m, 1H), 7.29–7.59 (m, 6H), 7.65–7.90 (m, 4H); ^{31}P NMR (121 MHz, CDCl3) δ 38.21; [found: C, 72.75; H, 7.18. $C_{19}H_{23}O_2P$ (314.14) requires C, 72.59; H, 7.37%].

*4.10.2. (E)-1-(Dimethylphenylsilyl)-2-(diphenylphosphanyl)pent-1-en-3-ol (**11b**).* Yield 1.26 g (58%); R_f (AcOEt) 0.60; IR ($CHCl_3$) 3390, 1438, 1252, 1158, 1115 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.39 (d, J=6.5Hz, 3H), 0.44 (s, 3H), 0.46 (s, 3H), 0.95 (d, J=6.5 Hz, 3H), 2.01 (m, 1H), 4.09 (dt, J=22.6, 10.7 Hz, 1H), 4. 53 (d, J=10.7 Hz, 1H), 6.24 (d, J=31.1 Hz, 1H), 7.29–7.83 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −1.2, −0.7, 19.4, 19.5, 33.3, 81.9 (d, J=9.7 Hz), 128.0, 128.4 (d, J=11.7 Hz), 129.4, 131.6 (d, J=9.3 Hz), 131.9, 133.6 (d, J=103.0 Hz), 133.7, 137.3, 146.7, 153.5 (d, J=80.7 Hz); ^{31}P NMR (121 MHz, CDCl3) δ 37.57; [found: C, 72.03; H, 6.89. $C_{26}H_{31}O_2PSi$ (434.18) requires C, 71.86; H, 7.19%].

*4.10.3. (E)-1-Phenyl-2-(diphenylphosphanyl)pent-1-en-3-ol (**11c**).* Yield 1.20 g (64%); R_f (AcOEt) 0.50; IR ($CHCl_3$) 3390, 1438, 1160 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.47 (d, J=6.5Hz, 3H), 0.99 (d, J=6.5 Hz, 3H), 2.04 (m, 1H), 4.48 (dt, J=23.0, 10.9 Hz, 1H), 4. 47 (d, J=10.9 Hz, 1H), 6.84 (d, J=22.8 Hz, 1H), 7.26–7.95 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.4, 19.5, 33.5 (d, J=2.3 Hz), 77.5 (d, J=6.3 Hz), 128.5 (d, J=10.5 Hz), 132.0 (d, J=9.7 Hz), 132.2 (d, J=2.5 Hz), 133.3 (d, J=103.9 Hz), 135.0 (d, J=19.7 Hz), 137.5 (d, J=92.0 Hz), 144.1 (d, J=12.4 Hz); ^{31}P NMR (121 MHz, CDCl3) δ 38.36; [found: C, 76.83; H, 6.82. $C_{24}H_{25}O_2P$ (376.16) requires C, 76.58; H, 6.69%].

4.11. Synthesis of allenes. General procedure

A solution of the hydroxyphosphane oxide **11b** or **11c** (3 mmol) in dry DMF (15 mL) was added to a stirred suspension of sodium hydride (6 mmol) in dry DMF (10 mL). The reaction mixture was stirred at 50 °C for 1 h and then hydrolysed with a saturated aqueous solution of ammonium chloride. The aqueous layer was extracted with methylene chloride and dried ($MgSO_4$). Solvents were evaporated under reduced pressure and the crude allenes

were purified by flash chromatography (SiO_2, hexane) to afford the following products.

*4.11.1. 1-(Dimethylphenylsilyl)-4-methylpenta-1,2-diene (**12a**).* Yield 396 mg (57%); R_f (hexane) 0.61; IR ($CHCl_3$) 1958, 1252, 1115 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.09 (s, 3H), 0.33 (s, 3H), 1.55 (d, J=4.0 Hz, 6H), 2.15 (m, 1H), 5.76 (d, J=17.9, 1H), 6.15 (dd, J=17.9, 6.6 Hz, 1H), 7.20–7.68 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.2, 22.4, 22.5, 28.5, 83.2, 101.8, 127.5, 129.3, 134.0, 138.6, 210.7; [found: C, 77.69; H, 10.27. $C_{15}H_{24}Si$ (232.16) requires C, 77.51; H, 10.41%].

*4.11.2. 4-Methyl-l-phenylpenta-1,2-diene (**12b**).* Yield 339 mg (65%).[24]

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.10.016.

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