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Epoxysilanes as substrates in regio- and stereo-specific synthesis of silylated γ-hydroxyphosphane oxides, precursors of stereodefined allylphosphane oxides

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ABSTRACT

Epoxysilanes experienced *trans* stereospecific α- or β-cleavage by the lithium derivative of methyldiphenylphosphane oxide leading to different compounds. The behaviour of the epoxysilanes towards this nucleophilic reagent depends on the nature of the silyl group, the position of the substituents and the configuration of the epoxysilane. Unsubstituted and *cis* β-substituted dimethylphenylsilylepoxides underwent α-nucleophilic attack of lithium methyldiphenylphosphane oxide giving stereodefined γ-phosphanyl-β-silylalcohols **2**. Nevertheless, in the same conditions the intermediate β-hydroxysilane, formed by α-opening from *trans* β-substituted dimethylphenylsilylepoxides, experienced Peterson elimination to give stereodefined allylphosphane oxides **3**. The steric requirements for the nucleophilic attack determined the regiochemistry of the reaction. α-Substituted phenyldimethylsilyl and *tert*-butyldiphenylsilylepoxides were exclusively attacked at the β-position affording γ-hydroxy-γ-silylphosphane oxides **4** and γ-phosphanyl silyl ethers **5**, resulting from Brook rearrangement.
On the other hand, the allylphosphane oxides **3** resulting from *syn*- or *anti*-eliminación of β-dimethylphenylsilyl-γ-hydroxyphosphane oxides **2**, are of interest in the synthesis of phosphorylated and functionalised building blocks.

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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 centres at or near phosphorus in an asymmetric fashion is particularly attractive. Furthermore, it is known that phosphorus substituents regulate important biological functions[5], and that the introduction of organophosphorus functionalities in simple synthons may afford useful substrates for the preparation of biologically active compounds.

Previously, we have synthesised various organophosphorus compounds from silyl and stannylepoxides by cleavage with lithium diphenylphosphide. The *anti* stereospecific nucleophilic opening from silyl and disilylepoxides[6] took place regioselectively in α or β depending of the substrate structure. Using unsubstituted or α- and β-C-substituted silylepoxides, we have synthesised vinylphosphonium iodides or vinylphosphane oxides by α-opening and silyl enol ethers, vinylsilanes or α-hydroxysilanes by β-opening. On the other hand, α,β- or α,α-disilylepoxides afforded β-silyl vinylphosphane oxides or α-silylated silyl enol ethers by α- and β-cleavage, respectively. In view of the different behaviour of silyl- and stannyloxiranes towards the nucleophilic attack and with the aim of increasing the synthetic possibilities of the cleavage of metallated epoxides by lithium diphenylphosphide, we extended this methodology to stannylated epoxides[7]. Unsubstituted or C-substituted stannyloxiranes reacted stereospecifically with lithium diphenylphosphide to give either β-hydroxyphosphane oxides resulting from α-opening or β-phosphanyl ketones by β-opening. Furthermore, the reactivities of distannyloxiranes depend on their configurations. The *cis* isomers afforded the corresponding α,β-diphosphanyl alcohols, while the *trans* isomers were shown to be unreactive. On the other hand, the regiochemistry of the ring-opening from β-silylated stannyloxiranes is controlled by the tin group and, depending on the nature of the silyl group, led either to

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stereodefined β-silyl vinylphosphane oxides or to β-stannyl silyl enol ethers. Finally, the *gem*-silyl-stannyloxiranes underwent β-opening to give mixtures of β-phosphanyl acylsilanes and silyl enol ethers. All compounds are interesting synthons of great versatility in organic chemistry.

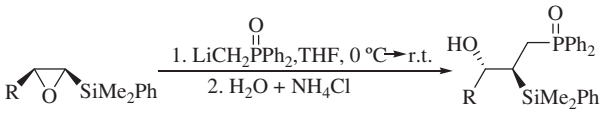
Recently we have reported[8] some synthetic applications of the vinylphosphane oxides as Michael acceptors, 1,3-dipolarophiles and precursors in the synthesis of allenes.

Following on with our current research in the synthesis of organophosphorus compounds from silylepoxides, in this occasion we have studied the regio- and stereo-specific cleavage of epoxysilanes with the lithium derivative of the methyldiphenylphosphane oxide with the aim of synthesising stereodefined allylphosphane oxides. Allylic phosphorous compounds are attractive electrophiles in organic synthesis, because an allylic fragment in the molecule provides possibilities for further functionalisation.

2. Results and discussion

2.1. Cleavage of silylepoxides with lithium methyldiphenylphosphane oxide

The behaviour of silylepoxides towards the lithium derivative of the methyldiphenylphosphane oxide depends on the nature of the silyl group, the position of the substituents and configuration of the epoxysilane. Unsubstituted **1a** and *cis* β-methyl dimethylphenylsilylepoxide **1b** underwent α-nucleophilic attack of lithium methyldiphenylphosphane oxide giving stereodefined γ-hydroxy-β-silyl phosphane oxides **2a**,**b** (Scheme 1).

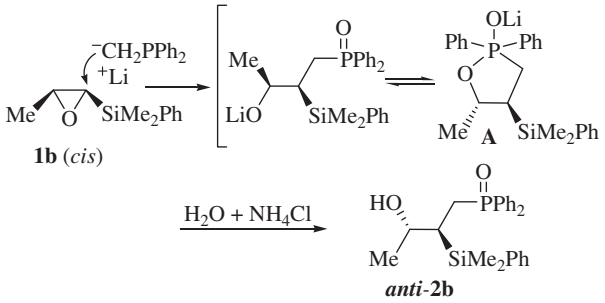


1a; R = H — **2a** (94%); R = H

1b; R= Me — ***anti*-2b** (73%); R = Me

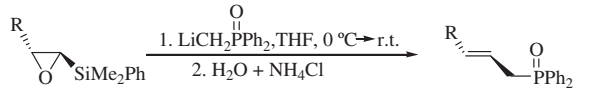
Scheme 1.

The outcome is different to the observed by us in the cleavage of silylepoxides towards other nucleophiles, such as: lithium diphenylphosphide[6], or lithium phenylsulfide[9]. In this case the γ-alkoxy-β-silyl phosphane oxide intermediate **A**, resulting from the α-opening, does not experience Peterson elimination due to its stabilisation by coordination of the alkoxyl group with the phosphorus leading to regio- and stereospecific γ-hydroxy-β-silyl phosphane oxides **2** in the final hydrolysis (Scheme 2).



Scheme 2.

Nevertheless, in the same conditions the α-opening of *trans* β-phenyl- **1c** and β-silyl dimethylphenylsilylepoxide **1d** was followed by Peterson-elimination affording the *trans* allylphosphane oxides **3a** and **3b**, respectively (Scheme 3).

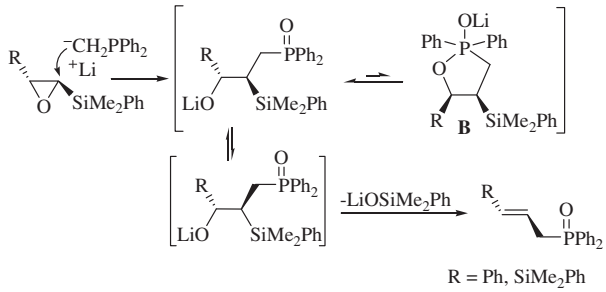


1c; R = Ph — **3a** (68%); R = Ph

1d; R= $SiMe_2Ph$ — **3b** (61%); R = $SiMe_2Ph$

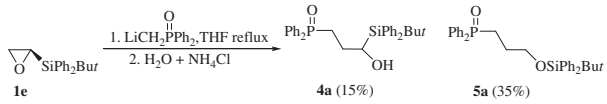
Scheme 3.

Probably in this case, the Peterson elimination took place because the stability of the necessary conformation for the O–P interactions in the corresponding intermediate **B** is minor than the intermediate **A.** In the intermediate **B** the R group (phenyl or dimethylphenylsilyl) should be eclipsed with the dimethylphenylsilyl group (Scheme 4), whereas in the intermediate **A** the methyl and silicon group are staggered (Scheme 2).



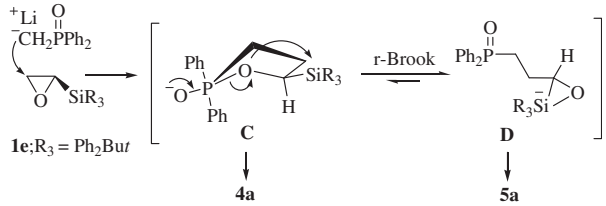
Scheme 4.

On the other hand, the bulky *tert*-butyldiphenylsilyl group changes the regioselectivity and supplies useful differences in the chemistry of silylepoxides. Unsubstituted *tert*-butyldiphenylsilylepoxide **1e** was exclusively attacked by nucleophile at the β-position to give a mixture of the γ-hydroxy-γ-silylphosphane oxide **4a** and the γ-phosphanyl silyl ether **5a**, in which the latter was the major product (Scheme 5).



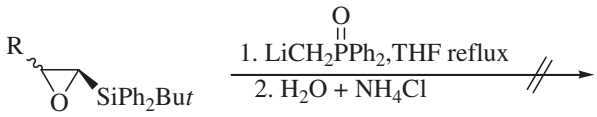
Scheme 5.

The formation of **4a** and **5a** should occur by hydrolysis of the intermediate **C** formed from β-opening (**4a**) and the intermediate **D**, resulting Brook rearrangement (**5a**). This latter is the major product due to the high migratory aptitude of the *tert*-butyldiphenylsilyl group[6b] (Scheme 6).



Scheme 6.

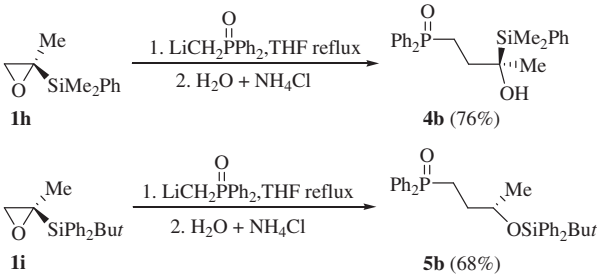
When the β-position bears an alkyl or phenyl group the reaction did not take place. β-Substituted *tert*-butyldiphenylsilylepoxides **1f**,**g** were recovered even after prolonged heating with lithium methyldiphenylphosphane oxide in THF at reflux (Scheme 7).



1f; R = Me (*cis*)
1g; R = Ph (*trans*)

Scheme 7.

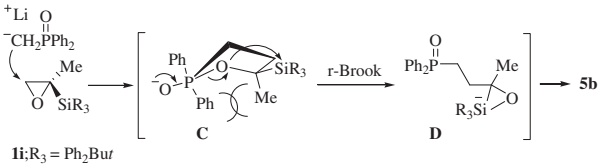
The steric requirements for the nucleophilic attack determined the regiochemistry of the reaction. If the α-position is substituted, even starting from dimethylphenylsilylepoxides, only β-cleavage took place. The 1-methyl-1-dimethyl phenylsilylepoxide **1h** and the 1-methyl-1-*tert*-butyl diphenylepoxide **1i** underwent β-opening affording the γ-hydroxy-γ-silyl phosphane oxide **4b** and the γ-phosphanyl silyl ether **5b**, respectively (Scheme 8).



Scheme 8.

Again the higher migratory aptitude of the *tert*-butyldiphenylsilyl than the dimethylphenylsilyl group was made plain (phenyl groups on silicon have been shown to accelerate the Brook rearrangement)[10].

It is known that alkyl-substitution at the carbon atom on which a carbanion is generated slows down the rate of a Brook rearrangement. Nevertheless, α-methylepoxysilane **1i** produced solely Brook-rearrangement product **5b**, in contrast to the result with α-unsubstituted **1e** in which a mixture of unrearranged product **4a** and rearranged product **5a** was formed. The absence of unrearranged product starting from **1i** could be explained considering the high instability of initial intermediate **C**, resulting from β-opening, due to the steric interaction between the methyl and phenyl group in the more favourable folded conformation. In this case, the reaction evolved exclusively through the rearranged intermediate **D** leading to the γ-phosphanyl silyl ether **5b** (Scheme 9).

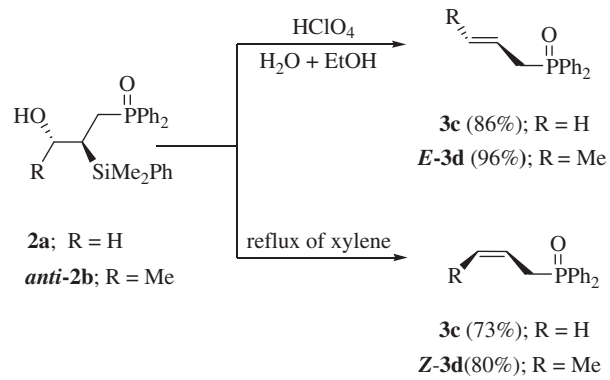


Scheme 9.

2-Silyl-3-hydroxyphosphane oxides **2** resulting from α-opening and 3-silyl-3-hydroxy phosphane oxides **4** formed by β-opening are interesting precursors of chiral 1,3-hydroxyphosphines, a class of versatile mixed bidentate 1,3-donor ligands for transition-metal-catalysed asymmetric synthesis[11]. Moreover, silylated hydroxyphosphane oxides **2** or **4** can undergo a wide range of reactions. It includes transformations of the hydroxyl group or those of the phosphanyl functionality or both. We have used the γ-hydroxy-β-silyl phosphane oxides **2** in the synthesis of allyl phosphane oxides and β-phosphanyl-α-silylketones.

2.2. Synthesis of allylphosphane oxides

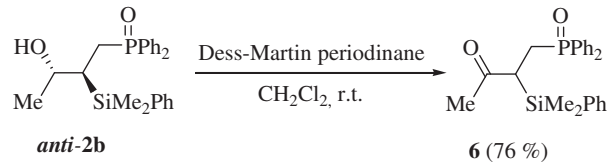
2-Dimethylphenylsilyl-3-hydroxyphosphane oxides **2** have proven to be of great utility in the synthesis of stereodefined allyl phosphane oxides. They experience acid-catalysed *anti*-elimination of $HOSiMe_2Ph$ affording allylphosphane oxides, which are stereoisomers of those we have obtained by thermal *syn*-elimination (Scheme 10).



Scheme 10.

2.3. Synthesis of β-phosphanyl-α-silylketones

Oxidation of 2-dimethylphenylsilyl-3-hydroxyphosphane oxide **2b** with PCC/Py in methylene chloride at room temperature led to the desilylated ketone. Fortunately, the β-phosphanyl-α-silylketone **6** was isolated using Dess–Martin oxidation (Scheme 11).



Scheme 11.

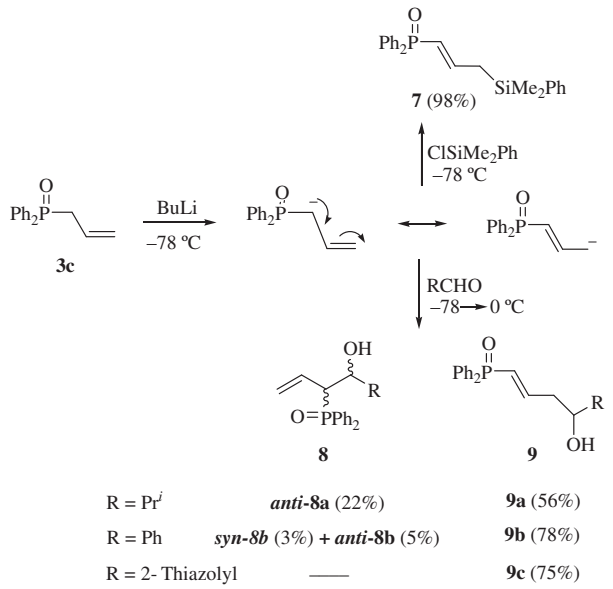
2.4. Synthetic applications of allylphosphane oxides

Allylphosphane oxides are attractive reagents in organic synthesis. They can be of great interest as substrates in carbanion-stabilised reactions[12]. Likewise, as occur with allylic phosphates and allylic phosphinates[13], they could be used as electrophiles for the introduction of an allylic fragment in the molecule through copper-mediated coupling reaction with organometallic reagents.

We have used allylphosphane oxides as stabilised carbanions in addition and substitution process with the aim of synthesising versatile functionalised synthons. Now we described some initial results starting from the unsubstituted allylphosphane oxide **3c**.

The allylic phosphane oxide **3c** when treated with *n*-butyllithium delivers an allylphosphanyl anion. This phosphorus-stabilised allyl anion is an ambident nucleophile capable to react with a variety of electrophiles at two sites (α- or γ-position) to give versatile allyl or vinylphosphane oxides, respectively.

Although a number of factors have been identified as important influences on site selectivity, there is as yet no comprehensive basis for predicting the observed regiochemistry. We have proved total γ-regioselectivity in the reaction with chlorodimethyl phenylsilane, in agreement with earlier reports using chlorotrimethylsilane as an electrophile[14]. Nevertheless, the stabilised carbanion derivated from **3c** reacted with some aldehydes, such as isobutyraldehyde, benzaldehyde and thiazole-2-carbaldehyde giving predominantly or exclusively the γ-product, in contrast to the α-regioselectivity observed by other authors[14b,15] (Scheme 12).



Scheme 12.

From the stereochemical viewpoint, the reaction took place with high diastereoselectivity. In all cases, the formation of γ-adducts proceeds with total *E* stereoselectivity. On the other hand, in the α-adduct two chiral carbons are created and, consequently, two diastereoisomers could be obtained. The reactions with isobutyraldehyde took place with total diastereoselectivity to give ***anti*-8a** as sole isomer. However, with benzaldehyde a mixture of ***syn*-8b** and ***anti*-8b** was isolated, in which the *anti* is the major diastereoisomer.

The configurational assignation of the *syn* and *anti* isomers was possible by IR and ^{1}H NMR spectroscopy. Intramolecular hydrogen bond between the hydroxy and phosphanyl groups was confirmed by comparative IR spectroscopy of the compounds in film and at different dilutions in CH_2Cl_2. The frequency and shape of the ν OH band did not change. Starting from this fact, the coupling constants between *vic*-protons are those expected according to the dihedral angle, ϕ=180° in the *syn* isomer and ϕ=60° in the *anti* isomer. Thus, the ***syn*-8b**, which in the chelated conformation has a ϕ=180° showed a $J_{H/H}$=9.6 Hz, while the ***anti*-8a** or ***anti*-8b**, with ϕ=60° has a $J_{H/H}$=2.1 Hz (Fig. 1).

The scope of this methodology is being object of research by our group using *Z* or *E* differently substituted allylphosphane oxides. The experimental results and theoretical study to explain the

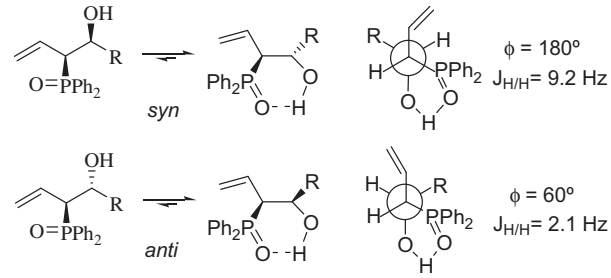
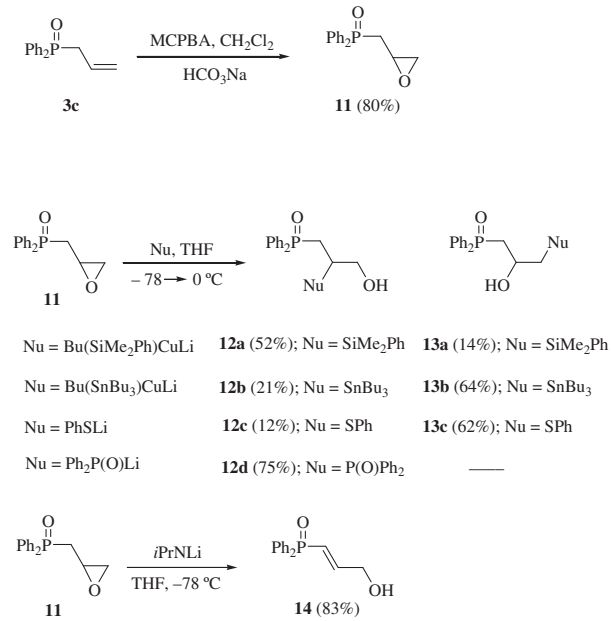


Fig. 1. Newman projections of *syn* and *anti* isomers.

observed regioselectivity will be published by us as soon as possible.

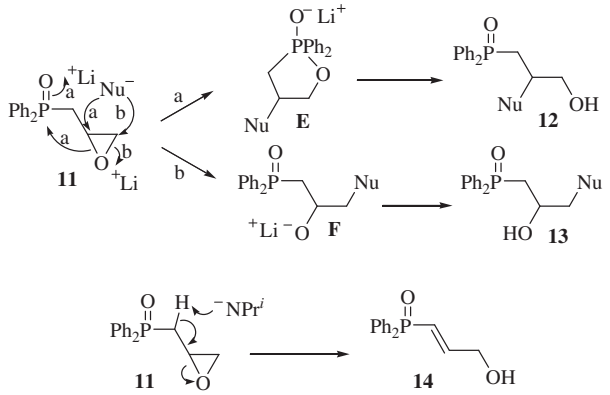
On the other hand, the double bond of allyl phosphane oxides provides possibilities for further functionalisation (hydroxylation [16], epoxidation, halogenation, etc.).

We have proved the easy epoxidation of allylphosphane oxides **3** and subsequent cleavage by different nucleophiles. Thus, the unsubstituted allylphosphane oxide **3c** was converted with excellent yield into the β-phosphanyl epoxide **10**, which was cleavage by heteroatomic nucleophiles (silyl- and stannyl-cuprates, lithium phenylsulfide, lithium diphenylphosphide and lithium diisopropylamide) giving versatile trifunctionalised synthons (Scheme 13).



Scheme 13.

Except for the phosphorus nucleophile, the reaction was not regioselective leading to a mixture of regioisomers **12** and **13**. Probably the initial complexation of the metal species to the phosphanyl group favours the nucleophilic attack at the β-position giving the chelation-controlled product **12** via the intermediate **E** stabilized by P–O coordination (pathway a). Soft and bulky stannyl and sulfur nucleophiles preferred the attack at the unsubstituted carbon atom to give the stereo-controlled product **13** across the less hindered intermediate **F** (pathway b). On the other hand, LDA behaves as a base, extracting a proton from the adjacent methylene to the phosphanyl group. The resulting phosphorus-stabilised carbanion led to the allylic alcohol **14** by ring cleavage (Scheme 14).



Scheme 14.

With the aim of knowing and explaining the regiochemistry and diastereoselectivity of this opening we are studying the reaction of *Z* or *E* substituted β-phosphanylepoxides towards the same heteronucleophiles. The results will be published as soon as possible.

3. Conclusions

We have developed an efficient stereoselective synthesis of 2- and 3-silylated 3-hydroxyphosphane oxides **2** and **4** by α- or β-opening of silylepoxides with the lithium derivative of the methyldiphenylphosphane oxide. Moreover, we have proved that γ-phosphanyl-β-silyl alcohols **2** can be oxidized, under extremely mild condition by the use of the Dess–Martin reagent, to give β-phosphanyl α-silylketones. α-Silyl aldehydes[17] or ketones[18] can serve not only for the stereoselective synthesis of biologically important primary or secondary α-vinylcarbonyl compounds but also for the preparation of synthetic intermediates, e.g., substrates for Cope and Claisen rearrangements. Moreover, the presence in all compounds of a phosphanyl group increases their biological and synthetic interest.

Finally, we have shown some synthetic applications of the allylphosphane oxides, resulting from α-opening from epoxysilanes or subsequent *syn* or *anti* elimination.

4. Experimental section

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. All reactions involving organometallic reagents were carried out under nitrogen atmosphere. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in $CDCl_3$ as an internal standard. Carbon multiplicities were assigned by DEPT experiments. Reactions were monitored by TLC on pre-coated plates (Silicagel 60, nano-SIL-20, Macherey–Nagel). Flash chromatography was performed on silica gel 60 (230–400 mesh, M–N). Silylepoxides **1a**–**c**, **1e**–**i** were prepared by epoxidation [19,20] of the corresponding vinylsilanes obtained by reaction with electrophiles of the intermediates from dimethylphenylsilyl- or *tert*-butyldiphenylsilyl cupration of alkynes [20,21] (**1a**–**c**, **1e**–**g**) or allene [22,23] (**1h** and **1i**). The synthesis of the 1,2-disilylepoxide **1d** was previously described by us[6b]. In the reactions with silyl or stannylcuprates we have used mixed higher order cuprates of carbon and silicon or tin–lithium butylsilyl or butylstannylcuprates, which selectively transfer the silyl or stannyl group but they are more advantageous than lithium bis-silyl or bis-stannylcuprates because they cheapen the synthesis and simplify the isolation process. The Dess–Martin periodinane was bought (Aldrich).

4.2. Cleavage of epoxysilanes with lithium methyldiphenyl phosphane oxide. Typical procedure

To a stirred THF solution of lithium methyldiphenyl phosphane oxide [prepared from methyldiphenylphosphane oxide (1 mmol) and butyllithium (0.625 mL, 1.6 M solution in hexane, 1 mmol) in THF (5 mL) at 0 °C under an N_2 atmosphere for 30 m] was added dropwise a solution of the silyloxirane **1a**–**i** (1 mmol) in THF (5 mL). Depending on the reactivity of the silylepoxide, the resulting solution was allowed to warm up to room temperature for **1a**–**d**, or heated at reflux for **1e**–**i**. The reaction mixture was stirred at this temperature until TLC indicated complete reaction. Ammonium chloride aqueous solution was added and the mixture was extracted with ether and dried ($MgSO_4$). The ethereal solvents were evaporated and the residue chromatographed to give the following compounds.

*4.2.1. 2-(Dimethylphenylsilyl)-3-(diphenylphosphanyl) propan-1-ol (**2a**).* Yield 370 mg (94%); R_f (AcOEt) 0.38; IR ($CHCl_3$) 3296, 1437, 1254, 1158, 1110 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.28 (s, 3H), 0.29 (s, 3H), 1.37 (m, 1H), 2.19 (dt, *J*=11.6, 15.4 Hz, 1H), 2.45 (dd, *J*=5.6, 15.4 Hz, 1H), 3.64 (dt, *J*=2.1, 9.9 Hz, 1H), 3.91 (dt, *J*=2.1, 9.9 Hz, 1H), 5.75 (dd, *J*=2.1, 9.9 Hz, 1H), 7.35–7.64 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −6.0, −4.2, 25.3, 30.5 (d, *J*=65.6 Hz), 64.0, 128.3, 128.7, 129.5, 130.0 (d, *J*=98.6 Hz), 130.4 (d, *J*=9.4 Hz), 131.8, 133.8, 136.2; ^{31}P NMR (121 MHz, $CDCl_3$) δ 37.29; [Found: C, 70.39; H, 6.73. $C_{33}H_{37}O_2PSi$ (394.15) requires C, 70.02; H, 6.90%].

*4.2.2. (2SR,3SR)-3-(Dimethylphenylsilyl)-4-(diphenylphosphanyl)butan-2-ol (**anti-2b**).* Yield 297 mg (73%); R_f (AcOEt) 0.40; IR ($CHCl_3$) 3297, 1437, 1250, 1158, 1110 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.28 (s, 3H), 0.29 (s, 3H), 1.23 (d, *J*=6.2 Hz, 3H), 1.25 (m, 1H), 2.27 (ddd, *J*=1.1, 6.1, 15.4 Hz, 1H), 2.46 (dt, *J*=10.6, 15.4 Hz, 1H), 3.84 (dq, *J*=8.1, 6.2 Hz, 1H), 7.33–7.62 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.3, −2.7, 25.9, 27.8 (d, *J*=66.2 Hz), 28.5 (d, *J*=6.2 Hz), 67.9, 128.0, 128.6 (d, *J*=11.6 Hz), 129.3, 130.5 (d, *J*=9.2 Hz), 131.8, 133.3 (d, *J*=97.7 Hz), 133.8, 137.4; ^{31}P NMR (121 MHz, $CDCl_3$) δ 37.49; [Found: C, 70.79; H, 6.98. $C_{24}H_{29}O_2PSi$ (408.17) requires C, 70.56; H, 7.15%].

*4.2.3. (E)-3-(Diphenylphosphanyl)-1-phenylprop-1-ene (**3a**).* Yield 216 mg (68%); R_f (AcOEt) 0.42; IR ($CHCl_3$) 1641, 1437, 1184, 896 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.30 (ddd, *J*=0.6, 7,5, 15.0 Hz, 2H), 6.18 (ddt, *J*=13.5, 15.8, 7.5 Hz, 1H), 6.43 (ddt, *J*=4.4, 15.8, 0.6 Hz, 1H), 7.17–7.80 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.6 (d, *J*=68.7 Hz), 118.3 (d, *J*=9.7 Hz), 126.2, 127.5, 128.4, 128.6 (d, *J*=11.5 Hz), 131.0 (d, *J*=9.0 Hz), 131.9, 132.3 (d, *J*=98.7 Hz), 135.6 (d, *J*=12.1 Hz), 137.0; ^{31}P NMR (121 MHz, $CDCl_3$) δ 30.86; [Found: C, 79.59; H, 5.88. $C_{21}H_{19}OP$ (318.12) requires C, 79.23; H, 6.02%].

*4.2.4. (E)-1-(Dimethylphenylsilyl)-3-(diphenylphosphanyl)prop-1-ene (**3b**).* Yield 229 mg (61%); R_f (AcOEt) 0.41; IR ($CHCl_3$) 1590, 1443, 1250, 1187, 1112, 990 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.42 (s, 6H), 3.15 (ddd, *J*=1.1, 6.5, 15.2 Hz, 2H), 5.76 (ddt, *J*=4.5, 19.8, 1.1 Hz, 1H), 6.28 (ddt, *J*=19.8, 6.5, 1.1 Hz, 1H), 7.26–7.78 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −2.7, 34.9 (d, *J*=66.3 Hz), 122.3 (d, *J*=10.3 Hz), 127.8, 128.6, 129.0, 131.2 (d, *J*=9.3 Hz), 132.6, 133.9, 134.6 (d, *J*=96.8 Hz), 138.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ 30.73; [Found: C, 72.98; H, 6.93. $C_{23}H_{25}OPSi$ (376.14) requires C, 73.37; H, 6.69%].

*4.2.5. 1-(tert-Butyldiphenylsilyl)-3-(diphenylphosphanyl)propan-1-ol (**4a**).* Yield 75 mg (15%); R_f (AcOEt) 0.35; IR ($CHCl_3$) 3395, 1437, 1184, 1110 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.09 (s, 9H), 1.88 (m,

2H), 2.49 (m, 2H), 3.84 (dd, J=4.1, 9.5 Hz, 1H), 7.27–7.74 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.4, 26.9, 28.2, 28.8 (d, J=72.9 Hz), 63.5, 127.5, 128.6 (d, J=11.3 Hz), 129.1, 130.7 (d, J=9.4 Hz), 131.7, 133.0, 133.5 (d, J=92.8 Hz), 136.0; ^{31}P NMR (121 MHz, $CDCl_3$) δ 35.87; [Found: C, 74.39; H, 6.94. $C_{31}H_{35}O_2PSi$ (498.21) requires C, 74.67; H, 7.07%].

*4.2.6. 2-(Dimethylphenylsilyl)-4-(diphenylphosphanyl)butan-2-ol (**4b**).* Yield 310 mg (76%); R_f (AcOEt) 0.24; IR (film) 3344, 1437, 1173, 1248, 1119 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.31 (s, 3H), 0.32 (s, 3H), 1.19 (s, 3H), 1.81 (m, 2H), 2.35 (m, 2H), 7.29–7.75 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.9, 18.4, 22.8 (d, J=72.4 Hz), 23.4, 30.4, 64.6 (d, J=9.8 Hz), 127.8, 128.6 (d, J=10.9 Hz), 129.2, 130.8 (d, J=9.8 Hz), 131.7, 132.5 (d, J=98.7 Hz), 134.4, 136.3; ^{31}P NMR (121 MHz, $CDCl_3$) δ 35.81; [Found: C, 70.39; H, 6.95. $C_{24}H_{29}O_2PSi$ (408.12) requires C, 70.56; H, 7.15%].

*4.2.7. Diphenyl-[3-(tert-butyldiphenylsilyloxy)propyl]phosphane oxide (**5a**).* Yield 174 mg (35%); R_f (AcOEt) 0.38; IR ($CHCl_3$) 1434, 1106, 1100 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05 (s, 9H), 1.85 (m, 2H), 2.42 (dt, J=4.7, 11.6 Hz, 2H), 3.71 (t, J=5.8 Hz, 2H), 7.27–7.76 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2, 26.1 (d, J=63.5 Hz), 26.9, 29.7, 63.8 (d, J=16.0 Hz), 127.7, 128.7 (d, J=11.4 Hz), 129.7, 130.8 (d, J=9.2 Hz), 131.7, 132.9 (d, J=96.6 Hz), 133.5, 135.5; ^{31}P NMR (121 MHz, $CDCl_3$) δ 33.81; [Found: C, 74. 91; H, 7.19. $C_{31}H_{35}O_2PSi$ (498.21) requires C, 74.67; H, 7.07%].

*4.2.8. Diphenyl-[3-(tert-butyldiphenylsilyloxy)butyl]phosphane oxide (**5b**).* Yield 348 mg (68%); R_f (AcOEt) 0.40; IR ($CHCl_3$) 1437, 1188, 1111 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (s, 9H), 1.07 (d, J=6.2 Hz, 3H), 1.72 (m, 2H) 2.15 (m, 1H), 2.41 (m, 1H), 3.95 (m, 1H), 7.30–7.72 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.2, 22.8, 25.1 (d, J=73.3 Hz), 27.0, 29.6, 69.3 (d, J=16.1 Hz), 127.4, 127.5, 128.5 (d, J=10.5 Hz), 129.6, 130.7 (d, J=9.1 Hz), 131.5, 133.0 (d, J=98.4 Hz), 134.0, 134.2, 135.7, 135.8; ^{31}P NMR (121 MHz, $CDCl_3$) δ 34.00; [Found: C, 75. 11; H, 7.41. $C_{32}H_{37}O_2PSi$ (512.23) requires C, 74.97; H, 7.27%].

4.3. Elimination of β-hydroxysilanes. Stereospecific synthesis of allylphosphane oxides

Method A. To a solution of the β-hydroxysilane **2a** or **2b** (1 mmol) in MeOH/H_2O=20:1 (10 mL) was added perchloric acid (1 mL). The mixture was stirred at room temperature for 3 h. Quenching with ice/H_2O, aqueous work-up with diethyl ether, drying ($MgSO_4$) and flash chromatography gave the following products.

*4.3.1. 3-(Diphenylphosphanyl)prop-1-ene (**3c**).* Yield 208 mg (86%); R_f (AcOEt) 0.48; IR ($CHCl_3$) 1636, 1437, 1178, 997, 924 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.15 (dd, J=7.5, 15.6 Hz, 2H), 5.15 (m, 2H), 5.67 (m, 1H), 7.40–7.78 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 36.0 (d, J=68.7 Hz), 121.0 (d, J=11.8 Hz), 127.5 (d, J=9.3 Hz), 128.3 (d, J=11.7 Hz), 131.0 (d, J=9.1 Hz), 131.8, 132.2 (d, J=99.1 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 30.69; [Found: C, 74.52; H, 6.08. $C_{15}H_{15}OP$ (242.09) requires C, 74.37; H, 6.24%].

*4.3.2. (E)-4-(Diphenylphosphanyl)but-2-ene (**E-3d**).* Yield 245 mg (96%); R_f (AcOEt) 0.43; IR ($CHCl_3$) 1652, 1436, 1182, 972 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.62 (dd, J=1.6, 6.4 Hz, 3H), 3.09 (ddd, J=0.9, 7.1, 14.0 Hz, 2H), 5.43 (dq, J=15.0, 6.4 Hz, 1H), 5.51 (dt, J=15.0, 7.1 Hz, 1H), 7.30–7.78 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.1, 34.7 (d, J=69.8 Hz), 118.9 (d, J=9.4 Hz), 128.5 (d, J=11.7 Hz), 131.0 (d, J=8.9 Hz), 131.7, 131.9 (d, J=11.8 Hz), 132.7 (d, J=97.5 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 30.97; [Found: C, 75.21; H, 6.52. $C_{16}H_{17}OP$ (256.10) requires C, 74.99; H, 6.69%].

Method B. A solution of the β-hydroxysilane **2a** or **2b** (1 mmol) in xylene (5 mL) was heated to reflux of xylene until the full consumption of starting material was observed by TLC (reaction time: 5 h). The solvent was evaporated and the residue was chromatographed to give the following compounds.

*4.3.3. 3-(Diphenylphosphanyl)prop-1-ene (**3c**).* Yield: 176 mg (73%).

*4.3.4. (Z)-4-(Diphenylphosphanyl)but-2-ene (**Z-3d**).* Yield 204 mg (80%); R_f (AcOEt) 0.41; IR ($CHCl_3$) 1612, 1437, 1184, 701 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48 (dd, J=2.2, 4.3 Hz, 3H), 3.15 (dd, J=7.4, 14.8 Hz, 2H), 5.48 (m, 1H), 5.67 (m, 1H), 7.43–7.78 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.0, 29.7 (d, J=70.3 Hz), 118.3 (d, J=8.6 Hz), 128.5 (d, J=11.7 Hz), 129.5 (d, J=11.7 Hz), 131.0 (d, J=9.2 Hz), 131.7, 132.6 (d, J=98.6 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 31.24; [Found: C, 74.73; H, 6.81. $C_{16}H_{17}OP$ (256.10) requires C, 74.99; H, 6.69%].

4.4. Oxidation of 2-dimethylphenylsilyl-3-hydroxy phosphane oxide 2b. Synthesis of the β-phosphanyl-α-silylketone 6

To a solution of **2b** (0.40 g, 1 mmol) in methylene chloride (10 mL) was added Dess–Martin periodinane (0.51 g, 1.2 mmol) under a nitrogen atmosphere at room temperature. The reaction mixture was stirred at the same temperature until starting alcohol was consumed, as determined by TLC analysis. Et_2O (20 mL) and aq 1% $Na_2S_2O_3$ solution (5 mL) were added followed by satd aq $NaHCO_3$ (5 mL) and the resulting mixture was stirred for 15 min. The organic phase was separated, dried ($MgSO_4$), and concentrated. Purification by chromatography provided the α-silylketone **6** (308 mg, 76%) as a colourless oil; R_f (hexane/AcOEt=10:1) 0.36; IR (CH_2Cl_2) 1712, 1438, 1252, 1195, 1100 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.14 (s, 3H), 0.20 (s, 3H), 2.13 (s, 3H), 2.57 (m, 2H), 2.78 (m, 1H), 7.35–7.78 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −3.9, −2.1, 23.2 (d, J=66.7 Hz), 29.7, 32.2, 127.3, 128.7 (d, J=11.9 Hz), 129.6, 130.7 (d, J=9.5 Hz), 131.9, 134.2 (d, J=98.7 Hz), 133.0, 136.8, 201.3; ^{31}P NMR (121 MHz, $CDCl_3$) δ 32.89; [Found: C, 71.16; H, 6.81. $C_{24}H_{27}O_2PSi$ (406.15) requires C, 70.91; H, 6.69%].

4.5. Reaction of lithiated allylphosphane oxides with electrophiles. Typical procedure

To a solution of the allyldiphenylphosphane oxide **3c** (1.5 mmol) in dry THF (3 mL) was added a solution of BuLi (0.94 mL, 1.6 M solution in hexane, 1.5 mmol) in dry THF (3 mL) at −78 °C under N_2. The resulting mixture was stirred at this temperature for 10 min and then was added the chlorodimethylphenylsilane (3 mmol), isobutyraldehyde (4.5 mmol), benzaldehyde (2.2 mmol) or thiazole-2-carbaldehyde (2.5 mmol). For the silylation the system was stirred at −78 °C and for the reaction with aldehydes the mixture was allowed to warm at 0 °C until TLC indicated complete reaction (reaction time=1–2 h). The mixture was hydrolysed with methanol (silylation) or with a satd aq NH_4Cl soln and extracted with diethyl ether, and the organic layer was dried ($MgSO_4$). The residue obtained after evaporation of solvents was purified by flash chromatography on silica gel using AcOEt as eluent to give the compounds characterized below.

*4.5.1. (E)-3-(Dimethylphenylsilyl)-1-(diphenylphosphanyl)prop-1-ene (**7**).* Yield 368 mg (98%); R_f (AcOEt) 0.62; IR ($CHCl_3$) 1606, 1437, 1257, 1112, 970 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.45 (s, 3H), 2.05 (dd, J=7.8, 2.1 Hz, 2H), 5.95 (ddt, J=22.8, 15.6, 2.1 Hz, 1H), 6.71 (ddt, J=19.2, 15.6, 7.8 Hz, 1H), 7.40–7.70 (m, 15H); ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.96; [Found: C, 73.15; H, 6.51. $C_{23}H_{25}OPSi$ (376.14) requires C, 73.37; H, 6.69%].

*4.5.2. (3RS,4SR)-2-Methyl-4-(diphenylphosphanyl)hex-5-en-3-ol (**anti-8a**).* Yield 69 mg (22%); R_f (AcOEt) 0.40; IR (film) 3300, 1440, 1150, 997, 924 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (d, J=5.1 Hz,

3H), 0.95 (d, J=5.1 Hz, 3H), 1.82 (m, 1H), 3.25 (dt, J=2.1, 7.2 Hz, 1H), 3.62 (dt, J=2.1, 7.5 Hz, 1H), 5.05 (dd, J=16.3, 2.1 Hz, 1H), 5.23 (dd, J=10.4, 3.0 Hz, 1H), 6.10 (ddt, J=16.3, 10.4, 7.5 Hz, 1H), 7.30–7.92 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.5, 19.5, 32.2, 47.5 (d, J=67.0 Hz), 75.1, 122.1 (d, J=12.1 Hz), 128.5 (d, J=16.2 Hz), 129.4 (d, J=9.5 Hz), 130.1 (d, J=98 Hz), 131.5 (d, J=8.2 Hz), 132.7, 143.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ 38.45; [Found: C, 72.81; H, 7.18. $C_{19}H_{23}O_2P$ (314.14) requires C, 72.59; H, 7. 37%].

*4.5.3. (E)-2-Methyl-6-(diphenylphosphanyl)hex-5-en-3-ol (**9a**).* Yield 176 mg (56%); R_f (AcOEt) 0.22; IR (film) 3250, 1443, 1125, 920 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.95 (d, J=6.1 Hz, 6H), 1.72 (m, 1H), 2.43 (m, 1H), 2.53 (m, 1H), 3.55 (m, 1H), 6.35 (dd, J=18.2, 24.0 Hz, 1H), 6.82 (m, 1H), 7.43–7.82 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.3, 19.6, 34.2, 39.3 (d, J=8.2 Hz), 74.1, 124.4 (d, J=73.2 Hz), 129.5, 130.7, 131.7, 132.5, 133.7 (d, J=90.2 Hz), 151; ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.22; [Found: C, 72.98; H, 7.51$C_{19}H_{23}O_2P$ (314.14) requires C, 72.59; H, 7. 37%].

*4.5.4. (1RS,2RS)-1-phenyl-2-(diphenylphosphanyl)but-3-en-1-ol (**syn-8b**).* Yield 10.5 mg (3%); R_f (AcOEt) 0.45; IR (film) 3300, 1445, 1147, 990, 930 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.55 (ddd, J=21.8, 9.6, 2.5 Hz, 1H), 4.75 (dd, J=17.1, 2.3 Hz, 1H), 4.90 (dd, J=10.2, 2.3 Hz, 1H), 5.05 (t, J=9.6 Hz, 1H), 5.22 (dtd, J=17.1, 10.2, 2.5 Hz, 1H), 7.20–7.95 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.5 (d, J=100 Hz), 72.2, 121.6 (d, J=9.1 Hz), 126.4, 127.5 (d, J=10.2 Hz), 128.2, 129.1, 129.6, 131.7 (d, J=10.1 Hz), 133.1 (d, J=90 Hz), 142.1 (d, J=8.3 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 37.33; [Found: C, 75.61; H, 5.91. $C_{22}H_{21}O_2P$ (348.13) requires C, 75.85; H, 6. 08%].

*4.5.5. (1RS,2SR)-1-phenyl-2-(diphenylphosphanyl)but-3-en-1-ol (**anti-8b**).* Yield 17.5 mg (5%); R_f (AcOEt) 0.33; IR (film) 3300, 1445, 1147, 990, 930 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.25 (dt, J=2.1, 6.2 Hz, 1H), 4.71 (dd, J=8.7, 2.1 Hz, 1H), 5.12 (dd, J=10.9, 3.5 Hz, 1H), 5.42 (dd, J=9.6 Hz, 1H), 6.12 (dtd, J=17.2, 10.9, 6.0 Hz, 1H), 7.20–7.95 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.2 (d, J=66.2 Hz), 71.6, 122.7 (d, J=11.7 Hz), 126.2, 127.1, 128.5, 129.6 (d, J=9.5 Hz), 130.9 (d, J=97.2 Hz), 131.5 (d, J=8.3 Hz), 132.0, 133.4, 141.6 (d, J=8.3 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 37.55; [Found: C, 76.03; H, 6.2.0. $C_{22}H_{21}O_2P$ (348.13) requires C, 75.85; H, 6. 08%].

*4.5.6. (E)-1-phenyl-4-(diphenylphosphanyl)but-3-en-1-ol (**9b**).* Yield 272 mg (78%); R_f (AcOEt) 0.18; IR (film) 3250, 1445, 1120, 925 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.65 (m, 2H), 4.76 (t, J=6.2 Hz, 1H), 6.05 (dd, J=17.3, 24.1 Hz, 1H), 6.65 (m, 1H), 7.24–7.52 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 44.3 (d, J=17.1 Hz), 72.3, 125.2 (d, J=92.2 Hz), 126.4, 127.6, 128.8, 129.6 (d, J=9.5 Hz), 130.9 (d, J=8.6 Hz), 132.3, 133.1 (d, J=100 Hz), 143.9, 148.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ 24.54; [Found: C, 75.68; H, 5.97 $C_{22}H_{21}O_2P$ (348.13) requires C, 75.85; H, 7. 08%].

*4.5.7. (E)-4-(Diphenylphosphanyl)-1-(2-thiazolyl)but-3-en-1-ol (**9c**).* Yield 266 mg (75%); R_f (AcOEt) 0.12; IR (film) 3250, 1445, 1120, 925 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.85 (m, 1H), 3.04 (m, 1H), 5.20 (dd, J=6.2, 5.6 Hz, 1H), 6.38 (dd, J=18.6, 16.9 Hz, 1H), 6.84 (tt, J=16.9, 6.2 Hz, 1H), 7.30–7.70 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.5 (d, J=12.1 Hz), 61.5, 119.3, 124.2 (d, J=89.1 Hz), 125.6 (d, J=100 Hz), 128.5 (d, J=11.3 Hz), 132.5 (d, J=8.6 Hz), 133.3, 142.9, 148.5, 176.6; ^{31}P NMR (121 MHz, $CDCl_3$) δ 25.62; [Found: C, 64.42; H, 5.27 $C_{19}H_{18}NO_2PS$ (348.13) requires C, 64.21; H, 5.11%].

4.6. Epoxidation of allylphosphane oxide 3c

MCPBA (3 mmol) and NaHCO3 (4 mmol) were added to a solution of **3c** (2 mmol) in CH_2Cl_2 (6 mL). The reaction mixture was stirred at room temperature until TLC indicated complete reaction. The mixture was washed several times with an aqueous solution of $NaHSO_3$, $NaHCO_3$, and NaCl. The organic layer was dried ($MgSO_4$), the solvent removed and the residue was purified by chromatography (Silicagel, AcOEt) to give the β-phosphanylepoxide **11** (413 mg, 80%) as a colourless oil; R_f (AcOEt) 0.23; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33 (dt, J=6.7, 12.2 Hz, 1H), 2.50 (dd, J=4.5, 2.6 Hz, 1H), 2.75 (t, J=4.5 Hz, 1H), 2.81 (ddd, J=5.4, 10.6, 12.2 Hz, 1H), 3.25 (m, 1H), 7.45–7.81 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.1 (d, J=68.5 Hz), 46.6, 47.4 (d, J=5.1 Hz), 128.7 (d, J=11.9 Hz), 130.6 (d, J=10.1 Hz), 132.0, 133.2 (d, J=88.9 Hz); ^{31}P NMR (121 MHz, $CDCl_3$) δ 29.75; [Found: C, 69.58; H, 6.01. $C_{15}H_{15}O_2P$ (258.08) requires C, 69.76; H, 5.85%].

4.7. Cleavage of the β-phosphanylepoxide 11 with heteronucl eophiles. General procedure

A solution of **11** (1 mmol) in dry THF (5 mL) was added dropwise to a stirred THF solution of nucleophile (1.5 mol) in THF (5 mL) at −78 °C under N_2. As nucleophiles were used: lithium butyl(dimethylphenylsilyl)cuprate[24], lithium butyl (tributylstannyl)cuprate[25], lithium phenylsulfide [prepared from benzenethiol (0.15 mL, 1.5 mmol) and butyllithium (0.936 mL, 1.6 M solution in hexane, 1.5 mmol) in THF (5 mL) at −78 °C under N_2 for 10 min], lithium diphenylphosphide [prepared from diphenylphosphine (0.258 mL, 1.5 mmol) and BuLi (0.936 mL, 1.6 M solution in hexane, 1.5 mmol) in THF (5 mL) at 0 °C under N_2 for 30 min] or lithium diisopropylamide [prepared from diisopropyl amine (0.21 mL, 1.5 mmol) and BuLi (0.936 mL, 1.6 M solution in hexane, 1.5 mmol) in dry THF (5 mL) at −20 °C under N_2 for 15 min]. The mixture was slowly allowed to warm to 0 °C and stirred at this temperature, except for the reaction with LDA (−78 °C) until TLC indicated complete reaction (30–60 min). When the reaction was carried out at 0 °C, the mixture was quenched with aqueous NH_4Cl, and with methanol in the reactions at −78 °C. The organic layer was extracted with Et_2O and dried with $MgSO_4$, the ethereal solvents were removed under reduced pressure and the residue chromatographed to give the following compounds.

*4.7.1. 2-(Dimethylphenylsilyl)-3-(diphenylphosphanyl)propan-1-ol (**12a**)=(**2a**).* Yield 205 mg (52%).

*4.7.2. 1-(Dimethylphenylsilyl)-3-(diphenylphosphanyl)propan-2-ol (**13a**).* Yield 55 mg (14%); R_f (AcOEt) 0.39; IR (film) 3200, 1445, 1252, 1185, 1110 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.31 (s, 6H), 1.25 (m, 2H), 2.45 (ddd, J=15.2, 12.4, 1.5 Hz, 1H), 2.55 (ddd, J=5.4, 15.2, 12.4 Hz, 1H), 4.41 (m, 1H), 7.40–7.70 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −3.6, 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), 142.4; ^{31}P NMR (121 MHz, $CDCl_3$) δ 35.20; [Found: C, 70.22; H, 6.78$C_{23}H_{27}O_2PSi$ (394.15) requires C, 70.02; H, 6.90%].

*4.7.3. 2-(Tributylstannyl)-3-(diphenylphosphanyl)propan-1-ol (**12b**).* Yield 115 mg (21%); R_f (AcOEt) 0.42; IR (film) 3250, 1445, 1185 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (m, 15H), 1.30 (m, 6H), 1.37 (m, 1H), 1.50 (m, 6H), 2.45 (dt, J=5.6, 15.4 Hz, 1H), 2.54 (dt, J=2.2, 5.4 Hz, 1H), 3.75 (m, 2H), 5.65 (sbr, 1H), 7.40–7.54 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.7, 13.5, 18.6, 27.3 (d, $J_{C,Sn}$=52.8 Hz), 29.2 (d, $J_{C,Sn}$=19.8 Hz), 30.5 (d, $J_{C,P}$=94.6 Hz), 66.0, 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, $CDCl_3$) δ 36.43 ($J_{P,Sn}$=198.0 Hz); [Found: C, 59.32; H, 8.08. $C_{27}H_{43}O_2PSn$ (550.20) requires C, 59.04; H, 7.89%].

*4.7.4. 1-(Tributylstannyl)-3-(diphenylphosphanyl)propan-2-ol (**13b**).* Yield 352 mg (64%); R_f (AcOEt) 0.44; IR (film) 3350, 1445, 1185 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (m, 15H), 1.25 (m, 6H), 1.53 (m, 6H), 1.90 (m, 1H), 2.05 (m, 1H), 2.45 (dt, J=1.6, 12.4 Hz, 1H),

2.54 (dt, J=5.4, 12.4 Hz, 1H), 4,4 (m, 1H), 5.50 (sbr, 1H), 7.35–7.64 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.4, 11.2, 13.7, 27.5 (d, $J_{C,Sn}$=53.4 Hz), 29.2 (d, $J_{C,Sn}$=19.3 Hz), 34.2 (d, $J_{C,P}$=110 Hz), 69.4, 128.7 (d, $J_{C,P}$=11.6 Hz), 130.5 (d, $J_{C,P}$=98.6 Hz), 132.4 (d, $J_{C,P}$=9.4 Hz), 132.6; ^{31}P NMR (121 MHz, CDCl3) δ 34.23 ($J_{P,Sn}$=177.0 Hz); [Found: C, 58.71; H, 7.63. $C_{27}H_{43}O_2PSn$ (550.20) requires C, 59.04; H, 7.89%].

*4.7.5. 3-(Diphenylphosphanyl)-2-(phenylthio)propan-1-ol (**12c**).* Yield 44 mg (12%); R_f (AcOEt) 0.31; IR ($CHCl_3$) 3300, 1440, 1180 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.15 (m, 2H), 3.95 (m, 1H), 4.25 (dd, J=2.5, 9.9 Hz, 1H), 4.34 (dd, J=5.5, 9.9 Hz, 1H), 5.3 (s br, 1H), 7.25–7.82 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.3 (d, J=65.6 Hz), 68.8, 69.1, 126.0, 128.7 (d, J=11.6 Hz), 129.5, 130.0 (d, J=98.6 Hz), 130.4 (d, J=9.4 Hz), 131.9, 133.8, 135.2; ^{31}P NMR (121 MHz, CDCl3) δ 36.62; [Found: C, 68.66; H, 5. 53. $C_{21}H_{21}O_2PS$ (368.10) requires C, 68.46; H, 5.75%].

*4.7.6. 1-(Diphenylphosphanyl)-3-(phenylthio)propan-2-ol (**13c**).* Yield 228 mg (62%); R_f (AcOEt) 0.33; IR (film) 3350, 1440, 1180 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.51 (m, 1H), 2.83 (m, 1H), 3.00 (dd, J=6.0, 14.5 Hz 1H), 3.25 (dd, J=6.0, 14.5 Hz, 1H), 4.15 (m, 1H), 4.78 (s br, 1H), 7.35–7.80 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.5 (d, J=71.3 Hz), 41.5, 66.5, 69.1, 126.0 (d, J=14.1 Hz), 128.9 (d, J=11.6 Hz), 129.5, 1310 (d, J=96.1 Hz), 132.4 (d, J=11.4 Hz), 132.9, 133.6, 137.6; ^{31}P NMR (121 MHz, CDCl3) δ 35.37; [Found: C, 68.26; H, 5. 98. $C_{21}H_{21}O_2PS$ (368.10) requires C, 68.46; H, 5.75%].

*4.7.7. 2,3-Bis(diphenylphosphanyl)propan-1-ol (**12d**).* Yield 345 mg (75%); R_f (AcOEt) 0.13; IR (film) 3300, 1445, 1188 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.65 (m, 1H), 2.73 (m, 1H), 3.15 (m, 2H), 3.55 (m, 1H), 7.36–7.87 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.1 (d, J=22.3 Hz), 28.3 (d, J=26.1 Hz), 61.1, 128.7 (d, J=11.6 Hz), 130.0 (d, J=98.6 Hz), 131.4 (d, J=9.4 Hz), 133.7; ^{31}P NMR (121 MHz, CDCl3) δ 31.64 (d, $J_{P,P}$=49.8 Hz), 36.19 (d, $J_{P,P}$=49.8 Hz); [Found: C, 70.26; H, 5.45. $C_{27}H_{26}O_3P_2$ (460.14) requires C, 70.43; H, 5.69%].

*4.7.8. (E)-3-(Diphenylphosphanyl)prop-2-en-1-ol (**14**).* Yield 214 mg (83%); R_f (AcOEt) 0.25; IR (film) 3300, 1445, 1188 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.45 (m, 2H), 6.65 (ddd, J=26.3, 15.7, 4.1 Hz), 6.92 (dt, J=15.7, 2.2 Hz), 7.44–7.75 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 62.2 (d, J=17.1 Hz), 119.7 (d, J=105.1 Hz), 128.7 (d, J=12.2 Hz), 130.9 (d, J=9.9 Hz), 131.8, 132.3 (d, J=106.8 Hz), 152.5; ^{31}P NMR (121 MHz, CDCl3) δ 24.54; [Found: C, 69.16; H, 5.64. $C_{15}H_{15}O_3P$ (258.08) requires C, 69.76; H, 5.85%].

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.06.039. These data include MOL files and InChiKeys of the most important compounds described in this article.

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