Reaction of *in-situ* generated α-silylated allylic phosphonate carbanions with aldehydes. An unexpected cyclization reaction†

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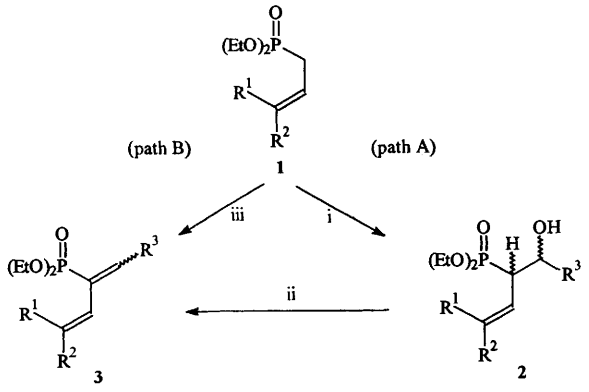
Lithiated α-trimethylsilyl cinnamyl-, prenyl- and crotyl-phosphonate carbanions 4 were generated quantitatively *in situ* from corresponding phosphonates 1, and their reactions with aldehydes were studied. When reacted at 0 °C with aromatic or aliphatic aldehydes, the cinnamyl derivative 4a gave phosphonodienes 7 in high yield and with high stereoselectivity. In contrast, the prenyl derivative 4b showed strict γ-regioselectivity in its reactions with aromatic aldehydes, leading to cyclic organophosphorus compounds 11; with aliphatic aldehydes, a mixture of corresponding heterocyclic compound 11 as major product, and of phosphonodiene 9, as minor product, was obtained. Reactions of crotyl derivative 4c with aromatic or aliphatic aldehydes were highly γ-regioselective too, and phosphonoalcohols 13 could be isolated upon hydrolysis at −70 °C. When warmed near 50 °C, alkoxides 12 underwent cyclization reaction to give heterocyclic compounds 14.

We recently studied the reactivity of allylic and α-silylated allylic phosphonate carbanions towards various electrophilic reagents.[1,2] In the first paper,[1] we proposed a convenient synthesis of new 2-diethylphosphonyl-1,3-dienes **3**, in two steps, from allylic phosphonates **1**, *via* isolated intermediate alcohols **2** (Scheme 1, path A).

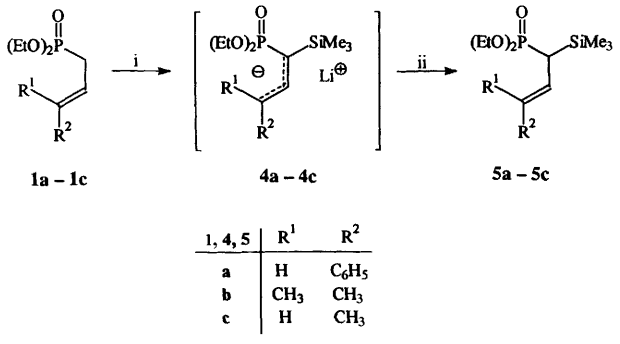


Scheme 1 *Reagents and conditions:* i, LDA, THF, −70 °C/R^3CHO/H_3O^+, −70 °C; ii, DCC, $CuCl_2$ (catalytic); iii, LDA, THF, −70 °C/Me_3SiCl, −70 °C/R^3CHO, 0 °C

Pursuing this study, we decided to investigate an alternative one-step route to these phosphonodienes **3** *via* an α-silylated allylic phosphonate carbanion, generated *in situ*, acting as Peterson reagent towards carbonyl compounds (Scheme 1, path B).

Results and discussion

On the basis of this concept, we first examined the silylation reaction of cinnamyl- and prenyl-phosphonate **1a** and **1b**, according to the procedure described for crotylphosphonate **1c**.[2] As expected, we found that all these phosphonates were α-regioselectively silylated, when treated with an excess of lithium diisopropylamide (LDA), at −70 °C, in the presence of chlorotrimethylsilane. Corresponding α-trimethylsilylated phosphonates **5** were quantitatively obtained from the lithiated intermediates **4**, upon acidic hydrolysis at the same temperature (Scheme 2). Phosphonates **5** were purified by distillation and



1, 4, 5	R^1	R^2
a	H	C_6H_5
b	CH_3	CH_3
c	H	CH_3

Scheme 2 *Reagents and conditions:* i, LDA (1.2 mol equiv.), THF, −70 °C/Me_3SiCl (1.1 mol equiv.), −70 °C; ii, H_3O^+, −70 °C

isolated in high yield. Their structures were unequivocally established by NMR spectroscopy (see Experimental section).

In contrast to the known γ-regioselective silylation reaction of lithiated allylphosphonate ($R^1 = R^2 = H$),[3] the strict α-regioselective reactivity of the lithiated derivatives of cinnamyl-, prenyl- and crotyl-phosphonates is likely to result from the difficulty encountered by the bulky chlorotrimethylsilane approaching the crowded γ site of the reagent. It is noteworthy that not a trace of the α,β-unsaturated isomers of phosphonates **5** was detected in the crude mixtures resulting from protonation of **4**. Moreover, when prepared as described above, lithiated reagents **4** were stable even at room temperature and their formation could be monitored by ^{31}P NMR spectroscopy [δ (THF) ~45, ~44 and ~48 for **4a**, **4b** and **4c**, respectively]. The large downfield shift in the ^{31}P NMR spectra of species **4**, compared with their parent compounds, is in agreement with a delocalization of their negative charge, in a salt-like structure as depicted in Scheme 2.[4,5]

Next, we studied the reactivity of lithiated derivatives **4** towards aldehydes. The results significantly depend upon the structure of **4**.

Reaction of lithiated α-trimethylsilyl cinnamylphosphonate derivative 4a

Reagent **4a**, quantitatively obtained by treating cinnamylphosphonate **1a** with 2.2 equiv. of LDA in THF at −70 °C,

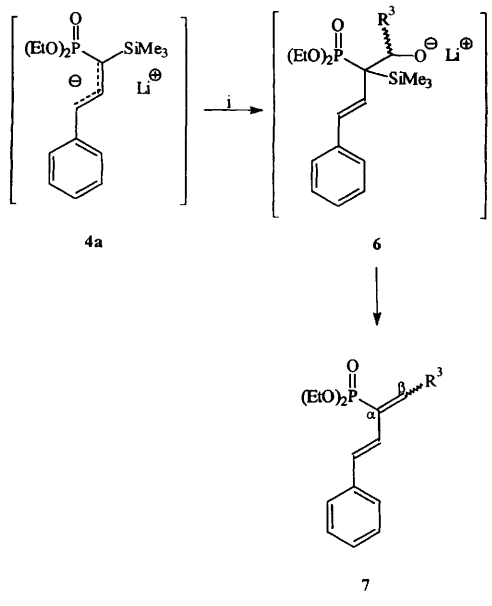
† Preliminary report of this work was presented as a poster at the XIIIth International Conference on Phosphorus Chemistry, Jerusalem, July 1995.

Table 1 Physical and analytical data of phosphonodienes 7

Product	R^3	$E:Z$ Ratio[a]	$^{31}P(CDCl_3)$, δ(ppm) E; Z	Yield (%)[b]
7a	C_6H_5	96:4	17.9; 16.7	91
7b	4-$CH_3OC_6H_4$	100:0	17.8	84
7c	4-$CF_3C_6H_4$	100:0	16.3	88
7d	$(CH_3)_2CH$	15:85	17.7; 15.4	92[c]
7e	$CH_3CH_2(CH_3)CH$	12:88	17.4; 15.9	93[c]

[a] Determined on crude mixture, by ^{31}P NMR integration measurements. [b] Yield of purified oily products. Purification by flash chromatography (eluent: ether). [c] The E and Z isomers were separated with good yields by column chromatography [eluent: ether–hexane (4/1)].

followed by addition of 1.1 equiv. of Me_3SiCl at the same temperature, was subsequently reacted with 1.1 equiv. of an aromatic or aliphatic aldehyde. The expected Peterson olefination reaction started off very slowly at −70 °C, but was fast and complete near 0 °C, giving the desired phosphonodiene **7**, isolated in excellent yield after usual work-up (Scheme 3,



Scheme 3 *Reagents and conditions:* i, R^3CHO/−70 °C to 0 °C; sat. aq. NH_4Cl/20 °C

Table 1). Unexpectedly, this Peterson olefination reaction exhibited very high stereoselectivity, as shown in Table 1. The geometry of the newly formed double bond depends on the nature of the aldehyde used: almost stereomerically pure (*E*,*E*)-phosphonodienes (**7a–7c**) were obtained with aromatic aldehydes, whereas predominantly (*Z*,*E*)phosphonodienes (**7d–7e**) resulted from reaction with aliphatic aldehydes. Steric requirements might be responsible for the selective formation of one of the two diastereomeric intermediate alkoxy adducts **6**, which gives one of the two stereomeric dienes **7**, upon *syn*-elimination of lithium trimethylsilyloxide. The (*E*)- or (*Z*)-geometry of the C_α=C_β double bond in dienes **7** was assigned by $^3J_{PH_\beta}$ coupling constant measurements (~22 or ~46 Hz, respectively), in ^1H NMR spectra.[6,7] In some examples, we succeeded in separating individual (*E*,*E*)- and (*Z*,*E*)-isomers **7** by column chromatography over silica gel.

Reaction of lithiated α-trimethylsilyl prenylphosphonate derivative 4b

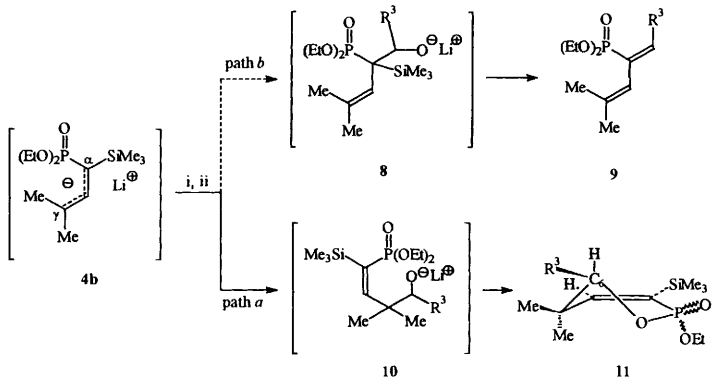
When treated with aromatic aldehydes at −70 °C, reagent **4b** (prepared quantitatively *in situ* from prenylphosphonate **1b**, by a procedure analogous to the one described above for reagent **4a**) surprisingly led to heterocyclic compounds **11**, phosphorus analogues of α,β-unsaturated δ-lactones (Scheme 4, path *a*). These phosphonolactones, whose structures were unambiguously established by ^1H, ^{13}C and ^{31}P NMR spectroscopy, were obtained with good diastereoselectivity, as determined by ^{31}P NMR measurements on the crude mixtures (Table 2). In the six-membered ring systems of various substituted 2-oxo-1,3,2-dioxaphosphorinanes, the dihedral dependence of the $^3J_{PH}$ coupling constants ($^3J_{PH_{eq}}$ ~ 20 Hz ≫ $^3J_{PH_{ax}}$ ~ 3 Hz) has proved to be useful in conformational analyses of these compounds, although the NMR data do not permit a decision of whether the preferred conformer has an axial or an equatorial P=O bond.[8] By analogy, in compounds **11**, the relatively low $^3J_{POC_6H}$ values (in the order of 5–6 Hz), which are similar in the two diastereoisomers, could be in agreement with an axial disposition of the C_6-H bond in the preferred pseudo-chair conformation of each diastereoisomer, as depicted in Scheme 4. Moreover, in $^{31}P\{^1H\}$ NMR spectra of products **11**, in addition to their main singlet, each diastereoisomer exhibits one symetrical doublet ($^2J_{P-Si}$ ~ 15 Hz), resulting from coupling between the ^{31}P nucleus and the non-zero-spin ^{29}Si isotope (4.7% of natural abundance).

In contrast to the reagent **4a**, which reacted exclusively as a Peterson reagent in spite of the presence of a bulky substituent at the reaction site, lithiated derivative **4b**, having the same steric requirements at the α position, showed strict γ-regioselectivity in its reactions with aromatic aldehydes. The presence of two electron-donating methyl groups, very likely reinforces the nucleophilicity of the γ site in **4b**, which easily reacts with electrophilic aromatic aldehydes, to give intermediate alkoxides **10**. In the second step, the stability of the leaving ethoxide anion and the reformation of the strong P–O bond in a six-membered stable structure, probably make up the driving force of the process. Few examples of such six-membered phosphonolactones, were previously reported.[9–11]

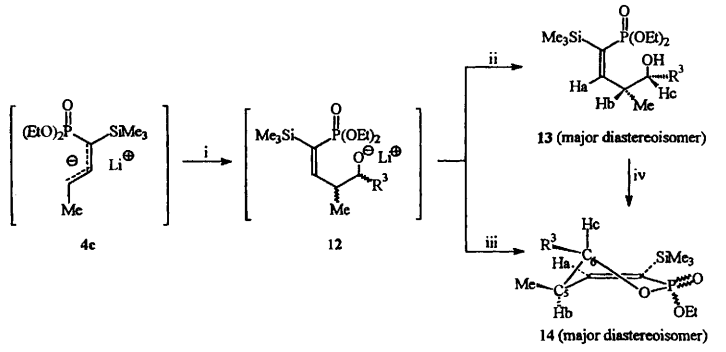
Except for pivalaldehyde, which behaved like its aromatic counterparts, extension of the reaction to other aliphatic aldehydes led to a mixture of the corresponding phosphonolactone (products **11e–i**, Table 2) as the major product (>70%) and of the stereomerically pure (*Z*,*E*)-phosphonodiene **9** as the minor product. Separation of these dienes **9**, which are the result of the decomposition of the corresponding Peterson adducts **8**, was easily achieved by fractional distillation under reduced pressure (see Experimental section). Some modifications have been attempted in order to make the reaction more regioselective with aliphatic aldehydes. Replacing ethoxy groups by the larger isopropoxy ones at the phosphorus atom, using potassium hexamethyldisilazane as base instead of LDA, in toluene or in THF, raising the reaction temperature near 20 °C, as well as increasing the reaction time or changing reactant ratios, were unable to significantly alter the course of the reaction.

Reaction of lithiated α-trimethylsilyl crotylphosphonate derivative 4c

Reagent **4c**, generated under similar conditions as that described above for **4a** and **4b**, reacted efficiently at −70 °C, with both aromatic or aliphatic aldehydes to give the intermediate lithium alkoxide **12** [^{31}P NMR (THF), δ ~32], confirming the same γ-regioselective reactivity of reagent **4c** towards aldehydes, as that observed in its reactions with



Scheme 4 *Reagents and conditions:* i, R^3CHO/THF/−70 °C; ii, H_3O^+/−70 °C



Scheme 5 *Reagents and conditions:* i, R^3CHO/THF/−70 °C; ii, 2 mol dm^{-3} HCl, −70 °C; iii, heat ~50 °C; iv, NaH/THF/0 °C to 50 °C

Table 2 Physical and analytical data of heterocyclic compounds **11**

Product	R^3	$^{31}P(CDCl_3)$ δ(ppm) (Diastereomeric ratio)[a]	Mp °C (bp °C/mmHg)	Yield (%)[b]	Percentage of diene **9**[c]
11a	C_6H_5	14.8; 15.8 (72:28)	—[e]	92	0
11b	4-$CH_3OC_6H_4$	15.1; 16.0 (82:18)	108	89	0
11c	2-$CF_3C_6H_4$	14.9; 15.3 (43:57)[d]	—[e]	86	0
11d	2,4-$Cl_2C_6H_3$	15.2; 15.7 (28:72)	101	80	0
11e	CH_3	13.8; 14.4 (66:34)	(105/0.3)	65	28
11f	$CH_3CH_2CH_2$	13.9; 14.6 (81:19)	(125/0.3)	76	7
11g	$(CH_3)_2CH$	15.0; 15.5 (85:15)	(122/0.3)	56	30
11h	cyclopropyl	14.3; 14.4 (60:40)	(130/0.25)	60	25
11i	$(CH_3)_3C$	15.2; 16.2 (93:7)	—[e]	82	0

[a] Determined on the crude mixtures, by ^{31}P NMR integration measurements. [b] Yield of purified products. [c] Determined on the crude mixtures, by ^{31}P and ^1H NMR integration measurements. [d] Pure diastereomer (δ 14.9) was separated as a solid (mp 115–117 °C) in 25% yield by column chromatography over silica gel [eluent: ether–hexane (9/1)]. [e] Oily products purified by flash chromatography over silica gel (eluent: ether).

ethyl formate or ethyl chloroformate.[2] Acidic hydrolysis of **12**, at −70 °C, afforded corresponding phosphonoalcohols **13** in very good yield (Scheme 5, Table 3). The stereoselectivity of this reaction was uniformly high. On the one hand, the geometry of the double bond in **13** is strictly of (*Z*)-configuration, as confirmed by $^3J_{PH_a}$ coupling constant measurements in ^1H NMR spectra (see Experimental section); on the other hand, ^{31}P as well as ^1H NMR spectra revealed a large diastereoselectivity in favour of the *erythro* diastereoisomer, of which one enantiomer is represented in Scheme 5. *Threo* and *erythro* isomers were assigned according to the $^3J_{H_bH_c}$ coupling constant measurements in ^1H NMR spectra, using the well-accepted J^{threo} (7–9 Hz) > $J^{erythro}$ (2–3 Hz) relationship[1,12] (see Experimental section).

When the reaction mixture containing lithium alkoxide **12** was warmed to *ca.* 50 °C for a few minutes before hydrolysis, heterocyclic compounds **14** were immediately obtained. Moreover, treatment of alcohols **13** with NaH in THF at 0 °C, then warming to 50 °C, proceeded smoothly to give the corresponding phosphonolactones **14**. Whatever the process used for their formation, compounds **14** were obtained in the same diastereoisomeric ratio and were isolated in very good yield (Table 4). In spite of the presence of three stereogenic centres in **14**, only two diastereoisomers were detected. In two examples (**14a** and **14b**), the ^1H NMR signal of the proton H_c could be resolved (see Experimental section). For the major isomer, the smaller coupling constant value (4.5 Hz for **14a**; 5.2 Hz for **14b**) was attributed to $^3J_{POC_6H_c}$ as a result of decoupling experiments, and the higher one (10.6 Hz for **14a**; 11.6 Hz for **14b**) was consequently assigned to $^3J_{H_bH_c}$. These results might

Table 3 Physical and analytical data of phosphonoalcohols **13**

Product	R^3	^{31}P ($CDCl_3$) δ(ppm) (*erythro*:*threo*)[a]	Yield (%)[b]	Bp °C/mmHg[c]
13a	C_6H_5	21.7; 21.9 (70:30)	92	155/0.3
13b	4-$CH_3OC_6H_4$	21.8; 21.9 (70:30)	90	162/0.2
13c	$CH_3CH_2CH_2$	20.9; 21.6 (85:15)	87	128/0.15
13d	$(CH_3)_2CH$	20.0; 22.0 (90:10)	88	120/0.2
13e	CH_3	21.2; 21.3 (87:13)	88	116/0.25
13f	$(CH_3)_3C$	19.7; 20.4 (85:15)	94	—

[a] Determined on crude mixtures by ^{31}P NMR and/or ^1H NMR integration measurements. [b] Yield of purified products. Purification by flash chromatography over SiO_2 (eluent: ether). [c] Most of these products could be distilled, but with some decomposition.

Table 4 Physical and analytical data of heterocyclic compounds **14**

Product	R^3	^{31}P ($CDCl_3$) δ(ppm) (Diastereomeric ratio)[a]	Bp °C/mmHg	Yield (%)[b]
14a	C_6H_5	15.2; 14.4 (28:72)	—[c]	81
14b	4-$CH_3OC_6H_4$	15.4; 14.8 (42:58)	—[c]	73
14c	$CH_3CH_2CH_2$	15.3; 14.7 (80:20)	122/0.25	74
14d	$(CH_3)_2CH$	15.1; 14.7 (81:19)	128/0.2	71

[a] Determined on crude mixtures, by ^{31}P NMR and ^1H NMR integration measurements. [b] Yield of purified products. Purification by flash chromatography over SiO_2 (eluent: ether). [c] Oily products which decomposed during distillation.

suggest, for the major diastereoisomers of compounds **14**, a preferred conformation with axially disposed C_5-H_b and C_6-H_c bonds, as depicted in Scheme 5. Therefore, it appears that a partial configurational isomerisation likely occurs at the allylic carbon C_5, under the strong basic conditions of the cyclization process, favouring the formation of the less sterically constrained diastereoisomer.

In conclusion, the chemical course of the reaction of the lithiated derivative of an α-silylated allylic phosphonate towards aldehydes depends on the structure of the starting phosphonate. Thus, in the cinnamyl series, the reaction is α-regioselective leading to the target phosphonodienes **7**, *via* a Peterson olefination reaction. In contrast, in the prenyl and crotyl series, the reaction, which is widely γ-regioselective, gives access to interesting heterocyclic compounds **11** and **14**. It is noteworthy that phosphorus analogues of unsaturated lactones have recently received attention because of their significant biological activity.[13,14] Chemical applications of these compounds are currently under investigation in our laboratory.

Experimental

General

All experiments were performed under an atmosphere of dry argon. THF was dried over CaH_2 and distilled from solutions of sodium–benzophenone ketyl before use. TLC was performed on Merck 60 F-254 silica gel plates and column chromatography over silica gel (230–400 mesh). Gas chromatography (GC) was performed on a Girdel chromatograph equipped with a 2 m OV17 column. Mass spectra were obtained with a GC-MS Hewlett Packard 5970 Spectrometer. Elemental microanalyses were carried out on a Carlo Erba 1106 analyser. Mps were taken on a Kofler apparatus and are uncorrected. NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 200 MHz for proton, 50.3 MHz for carbon and at 81.01 MHz for phosphorus. ^{31}P downfield shifts (δ) are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4 in H_2O. ^1H and ^{13}C chemical shifts (δ) are reported in ppm relative to TMS as internal standard and coupling constants (J) are given in Hz.

General procedure for the synthesis of α-silylated allylic phosphonates

A mixture of BuLi in hexane (7 cm^3, 11 mmol) and THF (20 cm^3) under argon was cooled to −70 °C. Diisopropyl amine (1.1 g, 11 mmol) in THF (8 cm^3) was added dropwise. The reaction mixture was then stirred at −70 °C for 30 min. Allylic phosphonate (10 mmol) in THF (10 cm^3) was added dropwise with stirring for about 15 min, after which a solution of trimethylchlorosilane (1.2 g, 11 mmol) in THF (10 cm^3) was added. The temperature was not allowed to exceed −70 °C during the additions. The reaction was quenched using 2 mol dm^{-3} HCl solution (~20 cm^3) and was stirred at room temperature for 5 min. Diethyl ether (20 cm^3) was then added and the organic phase was separated. The aqueous phase was extracted with ether (2 × 15 cm^3). The organic phases were then dried ($MgSO_4$) and concentrated under reduced pressure. The crude material was purified by fractional distillation under reduced pressure to yield the title compounds.

Diethyl (*E*)-3-phenyl-1-trimethylsilylprop-2-enylphosphonate 5a. Oily product (2.73 g, 84%), bp 132 °C/0.25 mmHg (Found: C, 59.12; H, 8.31. $C_{16}H_{27}O_3PSi$ requires C, 58.89; H, 8.28%); δ_P 27.3; δ_H 0.15 [9 H, s, $(CH_3)_3Si$], 1.2–1.4 (6 H, m, CH_3CH_2O), 2.4 (1 H, dd, J_{HP} 21.4, J_{HH} 10.4, HC_1), 3.9–4.2 (4 H, m, CH_3CH_2O), 6.2 (1 H, ddd, J_{HP} 26.3, J_{HH} 15.7, J_{HH} 10.5, HC_2), 6.35 (1 H, dd, J_{HH} 15.7, J_{HH} 3.9, HC_3), 7.2–7.4 (5 H, m, H_{arom}); δ_C −1.0 [s, $(CH_3)_3Si$], 16.0 (d, J 6.1, CH_3CH_2O), 34.3 (d, J

128.6, C_1), 61.0 and 62.0 (2 d, *J* 6.7 and 7.1, CH_3CH_2O), 121.8 (d, *J* 10.8, C_2), 125.3–128.0 (*o,m,p*-C_{arom}), 131.4 (d, *J* 16.0, C_3), 136.5 (d, *J* 2.7, *i*-C_{arom}).

Diethyl 3-methyl-1-trimethylsilylbut-2-enylphosphonate 5b. Oily product (2.4 g, 87%), bp 95 °C/0.5 mmHg (Found: C, 51.76; H, 9.47. $C_{12}H_{27}O_3PSi$ requires C, 51.79; H, 9.71%); δ_P 28.6; δ_H 0.05 [9 H, s, $(CH_3)_3Si$], 1.25 and 1.28 (6 H, 2 t, *J* 7.0, CH_3CH_2O), 1.58 and 1.76 [6 H, 2 d, *J* 5.0, $(CH_3)_2C_3$], 2.35 (1 H, dd, J_{HP} 23.2, J_{HH} 11.8, HC_1), 4.0–4.2 (4 H, m, CH_3CH_2O), 5.0–5.15 (1 H, m, HC_2); δ_C −2.0 [s, $(CH_3)_3Si$], 16.2 and 16.3 (2 d, *J* 6.4 and 6.3, CH_3CH_2O), 18.0 and 25.8 [2 d, *J* 2.4 and 2.9, $(CH_3)_2C_3$], 29.2 (d, *J* 127.8, C_1), 60.5 and 61.5 (2 d, *J* 6.7 and 7.1, CH_3CH_2O), 115.5 (d, *J* 10.5, C_2), 133.0 (d, *J* 15.4, C_3).

Diethyl (*E*)-1-trimethylsilylbut-2-enylphosphonate 5c. All data were previously described.[2]

General procedure for the synthesis of phosphonodienes 7

To a stirred solution of lithium diisopropylamide (LDA) (22 mmol) in THF (25 cm^3) at −70 °C (prepared as previously described), cinnamylphosphonate (2.54 g, 10 mmol) in THF (10 cm^3) was added dropwise. The resulting solution was stirred at the same temperature for 5 min, after which a solution of trimethylchlorosilane (1.3 g, 12 mmol) in THF (10 cm^3) was added, followed by the addition of the aldehyde (12 mmol) in THF (10 cm^3). The resulting solution was then stirred at 0 °C for 60 min. Diethyl ether (20 cm^3) was added and the resulting solution was hydrolysed with saturated aq. ammonium chloride solution (~20 cm^3). The organic phase was separated and the aqueous phase was then extracted with diethyl ether (3 × 15 cm^3). The organic phases were dried ($MgSO_4$), and concentrated under reduced pressure to give the crude product which was purified by column chromatography and elution with (4:1) ether–hexane. The physical and analytical data of phosphonodienes **7** are recorded in Table 1.

(1*E*,3*E*)-2-Diethoxyphosphonyl-1,4-diphenylbuta-1,3-diene 7a. Oily product (3.11 g, 91%), purified by flash chromatography over silica gel and elution with ether (Found: C, 70.49; H, 6.62. $C_{20}H_{23}O_3P$ requires C, 70.17; H, 6.72%); δ_P 17.9; δ_H 1.3 (6 H, t, *J* 7.0, CH_3CH_2O), 4.0–4.3 (4 H, m, CH_3CH_2O), 6.9–7.2 (2 H, m, HC_3 and HC_4), 7.2–7.5 (10 H, m, H_{arom}), 7.7 (1 H, d, *J* 21.9, HC_1); δ_C 16.3 (d, *J* 7.0, CH_3CH_2O), 62.05 (d, *J* 5.3, CH_3CH_2O), 122.0 (d, *J* 9.2, C_4), 126.6–130.0 (m, *o,m,p*-C_{arom}), 128.7 (d, *J* 174.6, C_2), 134.3 (d, *J* 4.3, C_3), 135.3 (d, *J* 21.3, *i*-C_{arom}-C_1), 137.1 (d, *J* 1.6, *i*-C_{arom}-C_4), 144.2 (d, *J* 9.1, C_1); *m/z* 342 (M), 285 (M − 56), 204, 77, 29.

(1*E*,3*E*)-2-Diethoxyphosphonyl-1-(4-methoxyphenyl)-4-phenylbuta-1,3-diene 7b. Oily product (3.12 g, 84%), purified by flash chromatography over silica gel and elution with ether (Found: C, 68.01; H, 6.66. $C_{21}H_{25}O_4P$ requires C, 67.74; H, 6.72%); δ_P 17.8; δ_H 1.4 (6 H, t, *J* 7.0, CH_3CH_2O), 3.9 (3 H, s, OCH_3), 4.0–4.3 (4 H, m, CH_3CH_2O), 6.9–7.2 (2 H, m, HC_3 and HC_4), 7.2–7.5 (9 H, m, H_{arom}), 7.6 (1 H, d, *J* 22.4, HC_1); δ_C 16.2 (d, *J* 6.4, CH_3CH_2O), 55.6 (s, OCH_3), 62.1 (d, *J* 5.2, CH_3CH_2O), 122.2 (d, *J* 9.1, C_4), 125.0 (d, *J* 170.3, C_2), 126.4–132.0 (m, *o,m,p*-C_{arom}-C_1 and -C_4), 128.6 (d, *J* 21.7, *i*-C_{arom}-C_1), 134.0 (d, *J* 4.5, C_3), 136.0 (s, *i*-C_{arom}-C_4), 144.5 (d, *J* 10.4, C_1); *m/z* 372 (M), 315 (M − 56), 234, 191, 77, 28.

(1*E*,3*E*)-2-Diethoxyphosphonyl-1-(4-trifluoromethylphenyl)-4-phenylbuta-1,3-diene 7c. Oily product (3.6 g, 88%), purified by flash chromatography over silica gel and elution with ether (Found: C, 61.30; H, 5.21. $C_{21}H_{22}F_3O_3P$ requires C, 61.46; H, 5.36%); δ_P 16.3; δ_H 1.4 (6 H, t, *J* 7.0, CH_3CH_2O), 4.0–4.3 (4 H, m, CH_3CH_2O), 7.1 (1 H, dd, J_{HP} 28.8, J_{HH} 16.7, HC_3), 7.2–7.7 (11 H, m, H_{arom} and HC_4 and HC_1); δ_C 16.2 (d, *J* 6.3, CH_3CH_2O), 62.3 (d, *J* 5.5, CH_3CH_2O), 121.0 (d, *J* 8.8, C_4), 125.0–131.0 (m, *o,m,p*-C_{arom} and CF_3), 128.0 (d, *J* 180.8, C_2), 136.1 (d, *J* 4.3, C_3), 137.0 (s, *i*-C_{arom}-C_4), 139.1 (d, *J* 21.5, *i*-C_{arom}-C_1), 142.2 (d, *J* 10.2, C_1); *m/z* 410 (M), 381 (M − 29), 353 (M − 56), 333, 272, 202, 77, 29.

(1*E*,3*E*)-3-Diethoxyphosphonyl-5-methyl-1-phenylhexa-1,3-diene 7d. All data were previously described.[1]

(1*E*,3*Z*)-3-Diethoxyphosphonyl-5-methyl-1-phenylhexa-1,3-diene 7d. Oily product (2.4 g, 78%), separated by column chromatography over silica gel and elution with (4:1) ether–hexane (Found: C, 66.33; H, 8.33. $C_{17}H_{25}O_3P$ requires C, 66.23; H, 8.11%); δ_P 15.4; δ_H 1.15 [6 H, d, *J* 7.0, $(CH_3)_2C_5$], 1.3 (6 H, t, *J* 7.0, CH_3CH_2O), 3.1 (1 H, m, HC_5), 4.0–4.2 (4 H, m, CH_3CH_2O), 6.4 (1 H, dd, J_{HP} 47.5, J_{HH} 10.6, HC_4), 6.6 (1 H, d, *J* 16.2, HC_1), 6.7 (1 H, dd, J_{HP} 30.1, J_{HH} 16.2, HC_2); 7.2–7.5 (5 H, m, H_{arom}); δ_C 16.0 (d, *J* 6.5, CH_3CH_2O), 23.0 (d, *J* 2.2), (CH_3-C_5 and C_6), 29.0 (d, *J* 5.3, C_5), 62.0 (d, *J* 5.3, CH_3CH_2O), 125.0 (d, *J* 173.9, C_3), 126.0–129.0 (m, *o,m,p*-C_{arom}), 128.0 (d, *J* 13.1, C_1), 130.5 (d, *J* 6.7, C_2), 137.0 (s, *i*-C_{arom}), 157.0 (d, *J* 12.0, C_4); *m/z* 308 (M), 293 (M − 15), 169, 91, 77, 29.

(1*E*,3*E*)-3-Diethoxyphosphonyl-5-methyl-1-phenylhepta-1,3-diene (1*E*,3*E*)-7e. Oily product (0.22 g, 7%), separated by column chromatography over silica gel and elution with (4:1) ether–hexane (Found: C, 67.2; H, 8.08. $C_{18}H_{27}O_3P$ requires C, 67.08; H, 8.38%); δ_P 17.4; δ_H 0.9 (3 H, d, *J* 7.0, H_3C-C_5), 1.1 (3 H, t, *J* 7.0, CH_3-C_6), 1.35 (6 H, t, *J* 7.0, CH_3CH_2O), 1.4 (2 H, m, CH_2-C_7), 2.8 (1 H, m, HC_5), 4.0–4.2 (4 H, m, CH_3CH_2O), 6.8 (1 H, dd, J_{HP} 22.6, J_{HH} 10.5, HC_4), 6.85–7.1 (2 H, m, HC_1 and HC_2), 7.2–7.5 (5 H, m, H_{arom}); δ_C 12.1 (s, C_7), 16.2 (d, *J* 6.4, CH_3CH_2O), 20.0 (s, C_6), 30.0 (s, H_3C-C_5), 35.0 (d, *J* 16.2, C_5), 62.0 (d, *J* 5.1, CH_3CH_2O), 121.0 (d, *J* 11.3, C_1), 125.0 (d, *J* 173.4, C_3), 126.0–128.0 (m, *o,m,p*-C_{arom}), 133.3 (d, *J* 4.2, C_2), 137.3 (s, *i*-C_{arom}), 155.0 (d, *J* 7.4, C_4).

(1*E*,3*Z*)-3-Diethoxyphosphonyl-5-methyl-1-phenylhepta-1,3-diene (1*E*,3*Z*)-7e. Oily product (2.47 g, 77%), separated by column chromatography over silica gel and elution with (4:1) ether–hexane (Found: C, 67.10; H, 8.45. $C_{18}H_{27}O_3P$ requires C, 67.08; H, 8.38%); δ_P 15.9; δ_H 0.98 (3 H, d, *J* 7.0, CH_3-C_5), 1.1 (3 H, t, *J* 7.0, CH_3-C_6), 1.38 (6 H, t, *J* 7.0, CH_3CH_2O), 1.5 (2 H, m, CH_2-C_7), 3.22–3.42 (1 H, m, HC_5), 4.0–4.24 (4 H, m, CH_3CH_2O), 6.35 (1 H, dd, J_{HP} 48.0, J_{HH} 10.7, HC_4), 6.7 (1 H, d, *J* 16.2, HC_1), 6.9 (1 H, dd, *J* 23.8, *J* 16.2, HC_2), 7.2–7.5 (5 H, m, H_{arom}); δ_C 12.0 (s, C_7), 16.2 (d, *J* 6.5, CH_3CH_2O), 21.0 (s, CH_2), 30.0 (s, H_3C-C_5), 35.1 (d, *J* 5.0, C_5), 61.0 (d, *J* 5.2, CH_3CH_2O), 125.7 (d, *J* 173.8, C_3), 125.8–127.8 (m, *o,m,p*-C_{arom}), 127.5 (d, *J* 12.0, C_1), 129.6 (d, *J* 6.6, C_2), 137.7 (s, *i*-C_{arom}), 157.0 (d, *J* 12.2, C_4); *m/z* 322 (M), 293 (M − 29), 231, 155, 91, 77, 29.

General procedure for the synthesis of dihydrooxaphosphorine oxides 11a–i, phosphonoalcohols 13a–f and dihydrooxaphosphorine oxides 14a–d

Lithium derivative **4b** or **4c** was generated as previously described for **4a** using LDA (26 mmol), after which a solution of the aldehyde (15 mmol) in THF (10 cm^3) was added at −70 °C. The reaction mixture was stirred for 30 min and then quenched at the same temperature with 4 mol dm^{-3} HCl solution until pH ≈ 2 and was stirred at room temperature for 5 min. Diethyl ether (20 cm^3) was added and the organic phase was separated. The aqueous phase was then extracted with diethyl ether (3 × 15 cm^3). The organic phases were dried ($MgSO_4$), and concentrated under reduced pressure to give the crude product **11** or **13**. However, in the crotyl series, raising the temperature of the reaction mixture, before acidic hydrolysis, to about 50 °C afforded the corresponding cyclic organophosphorus compound **14**. The crude products were then purified by column chromatography over silica gel or distillation under reduced pressure. The physical and analytical data of cyclic compounds **11a–i**, phosphonoalcohols **13a–e** and cyclic compounds **14a–d** are recorded in Tables 2, 3 and 4, respectively.

2-Ethoxy-5,5-dimethyl-6-phenyl-3-trimethylsilyl-5*H*-1,2-oxaphosphorine-2-oxide 11a. Oily product (3.1 g, 92%), purified by flash chromatography over silica gel and elution with ether (Found: C, 58.99; H, 7.97. $C_{17}H_{27}O_3PSi$ requires C, 60.35; H, 7.98%); δ_H 0.25 [9 H, s, $(CH_3)_3Si$], 0.9$_{min}$, 1.1$_{min}$ and 0.95$_{maj}$,

1.0_{maj} [6 H, 4s, $(CH_3)_2C_5$], 1.3_{maj} and 1.4_{min} (3 H, 2 t, *J* 7.0, CH_3CH_2O), 4.0–4.3 (2 H, m, CH_3CH_2O), 5.2_{maj} and 5.42_{min} (1 H, 2 d, *J* 5.4, HC_6), 6.6_{maj} and 6.62_{min} (1 H, 2 d, J_{HP} 56.2, J_{HP} 55.4, HC_4), 7.2–7.4 (5 H, m, H_{arom}); δ_C −1.0 [s, $(CH_3)_3Si$], 16.4 (d, *J* 5.9, CH_3CH_2O), 20.1 and 24.7 [2 s, $(CH_3)_2C_5$] 40.1 (d, *J* 11.8, C_5), 60.6_{maj} and 62.1_{min} (2 d, *J* 6.9, CH_3CH_2O), 83.0_{min} and 84.2_{maj} (2 d, *J* 3.7, *J* 5.5, C_6), 127.8_{maj} and 128.0_{min} (2 d, *J* 127.5 and 125.2, C_3), 127.0–128.8 (m, *o*,*m*,*p*-C_{arom}), 136.7 (d, *J* 7.4, *i*-C_{arom}), 165.5 (d, *J* 3.5, C_4); *m*/*z* 338 (M), 323 (M − 15), 232, 163, 77, 29.

2-Ethoxy-6-(4-methoxyphenyl)-5,5-dimethyl-3-trimethylsilyl-5*H*-1,2-oxaphosphorine-2-oxide 11b. Yellow solid (3.27 g, 89%), purified by recrystallization from ether (Found: C, 58.90; H, 8.19. $C_{18}H_{29}O_4PSi$ requires C, 58.69; H, 7.88%); δ_H 0.3 [9 H, s, $(CH_3)_3Si$], 0.9_{min}, 0.98_{min} and 0.93_{maj}, 0.96_{maj} [6 H, 4 s, $(CH_3)_2C_5$], 1.3_{maj} and 1.4_{min} (3 H, 2 t, *J* 7.0, CH_3CH_2O), 3.8 (3 H, s, OCH_3), 4.0–4.3 (2 H, m, CH_3CH_2O), 5.1_{maj} and 5.4_{min} (1 H, 2 d, *J* 5.8, HC_6), 6.6_{maj} and 6.7_{min} (1 H, 2 d, J_{HP} 56.1, J_{HP} 55.5, HC_4), 6.9 and 7.3 (4 H, 2 d, *J* 8.6, H_{arom}); δ_C −1.0 [s, $(CH_3)_3Si$], 16.2 (d, *J* 5.9, CH_3CH_2O), 20.0 and 25.0 [2 s, $(CH_3)_2C_5$], 40.2 (d, *J* 11.8, C_5), 55.0 (s, OCH_3), 60.1_{maj} and 62.2_{min} (2 d, *J* 6.9, CH_3CH_2O), 82.8_{min} and 84.0_{maj} (2 d, *J* 3.7, *J* 5.5, C_6), 113.0–129.0 (m, *o*,*m*-C_{arom}), 127.0_{maj} (d, *J* 127.5, C_3), 129.1 (d, *J* 5.3, *i*-C_{arom}), 159.0 (s, *p*-C_{arom}), 165.7 (d, *J* 3.7, C_4); *m*/*z* 368 (M), 353 (M − 15), 339 (M − 29), 136, 121, 77, 29.

2-Ethoxy-6-(2-trifluoromethylphenyl)-5,5-dimethyl-3-trimethylsilyl-5*H*-1,2-oxaphosphorine-2-oxide 11c. Oily product (3.49 g, 86%), purified by flash chromatography over silica gel and elution with ether (Found: C, 53.29; H, 7.05. $C_{18}H_{26}F_3O_3PSi$ requires C, 53.20; H, 6.40%); δ_H 0.25 [9 H, s, $(CH_3)_3Si$], 0.9_{maj}, 1.18_{maj} and 0.95_{min}, 1.1_{min} [6 H, 4 s, $(CH_3)_2C_5$], 1.3_{maj} and 1.37_{min} (3 H, 2 t, *J* 7.0, CH_3CH_2O), 4.0–4.3 (2 H, m, CH_3CH_2O), 5.72_{maj} and 5.9_{min} (1 H, 2 d, *J* 5.5, *J* 6.0, HC_6), 6.6_{maj} and 6.65_{min} (1 H, 2 d, J_{HP} 57.0 and J_{HP} 56.1, HC_4), 7.18–7.82 (4 H, m, H_{arom}); δ_C −1.0 [s, $(CH_3)_3Si$], 16.1 (d, *J* 5.8, CH_3CH_2O), 21.1 and 24.7 [2 d, *J* 2.4, *J* 2.2, $(CH_3)_2C_5$], 40.1 (d, *J* 12.4, C_5), 60.6_{min} and 62.0_{maj} (2 d, *J* 6.9, CH_3CH_2O), 77.6 (d, *J* 5.4, C_6), 124.0 (q, *J* 272.2, F_3CAr), 126.0 (q, *J* 272.2, F_3CC), 127.1 (d, *J* 123.9, C_3), 128.4–131.0 (m, *o*,*m*,*p*-C_{arom}), 135.0 (d, *J* 5.9, *i*-C_{arom}), 165.2 (d, *J* 3.6, C_4); *m*/*z* 406 (M), 391 (M − 15), 232, 121, 73, 29. The minor diastereoisomer δ_P = 14.9 was separated pure, as crystals (mp 115–117 °C) in 25% yield by column chromatography over silica gel and elution with (9 : 1) ether–hexane

2-Ethoxy-6-(2,4-dichlorophenyl)-5,5-dimethyl-3-trimethylsilyl-5*H*-1,2-oxaphosphorine-2-oxide 11d. Yellow solid (3.25 g, 80%), purified by flash chromatography over silica gel and elution with ether (Found: C, 50.28; H, 6.19. $C_{17}H_{25}Cl_2O_3PSi$ requires C, 50.12; H, 6.14%); δ_H 0.25 [9 H, s, $(CH_3)_3Si$], 0.95_{maj}, 1.05_{maj} and 1.01_{min}, 1.03_{min} [6 H, 4 s, $(CH_3)_2C_5$], 1.27_{min} and 1.37_{maj} (3 H, 2 t, *J* 7.0, CH_3CH_2O), 4.0–4.25 (2 H, m, CH_3CH_2O), 5.75_{min} and 5.9_{maj} (1 H, 2 d, *J* 5.7, *J* 5.2, HC_6), 6.6_{min} and 6.65_{maj} (1 H, 2 d, J_{HP} 56.9 and J_{HP} 54.6, HC_4), 7.2–7.6 (3 H, m, H_{arom}); δ_C −1.0 [s, $(CH_3)_3Si$], 16.1 (d, *J* 6.6, CH_3CH_2O), 21.0. and 25.0 [2 s, $(CH_3)_2C_5$], 40.1_{min} and 41.2_{maj} (2 d, *J* 11.7, *J* 11.3, C_5), 60.7_{min} and 62.4_{maj} (2 d, *J* 5.7, *J* 6.9, CH_3CH_2O), 77.8_{maj} and 78.3_{min} (2 d, *J* 3.3, *J* 4.9, C_6), 126.0–134.6 (m, *o*,*m*,*p*-C_{arom} and C_3), 164.8_{min} and 165.0_{min} (2 d, *J* 3.8, *J* 3.5, C_4).

2-Ethoxy-5,5,6-trimethyl-3-trimethylsilyl-5*H*-1,2-oxaphosphorine-2-oxide 11e. Oily product (1.8 g, 65%), separated and purified by fractional distillation under reduced pressure (Found: C, 51.67; H, 9.03. $C_{12}H_{25}O_3PSi$ requires C, 52.17; H, 9.05%); δ_H 0.22 [9 H, s, $(CH_3)_3Si$], 0.97_{min}, 1.03_{min} and 1.02_{maj}, 1.1_{maj} [6 H, 4 s, $(CH_3)_2C_5$], 1.2–1.4 (3 H, m, CH_3CH_2O), 3.95–4.25 (2 H, m, CH_3CH_2O), 4.28–4.52 (1 H, m, HC_6), 6.5_{maj} and 6.53_{min} (1 H, 2 d, J_{HP} 55.6 and J_{HP} 54.8, HC_4); δ_C −1.0 [s, $(CH_3)_3Si$], 16.1–16.3 (m, *C*-C_6), 16.4 (d, *J* 6.9, CH_3CH_2O), 19.5 and 25.0 [2 s, $(CH_3)_2C_5$], 39.1_{maj} and 39.5_{min} (2 d, *J* 12.8, *J* 10.9, C_5), 60.8_{maj} and 62.4_{min} (2 d, *J* 6.8, CH_3CH_2O), 78.5_{min} and 79.0_{maj} (2 d, *J* 4.5, *J* 6.0, C_6), 127.0_{maj} and 127.2_{min} (2 d, *J* 127.9, *J* 124.0, C_3), 166.0 (d, *J* 3.8, C_4).

2-Ethoxy-5,5-dimethyl-6-(propyl)-3-trimethylsilyl-5*H*-1,2-oxaphosphorine-2-oxide 11f. Oily product (2.3 g, 76%), separated and purified by fractional distillation under reduced pressure (Found: C, 55.25; H, 9.02. $C_{14}H_{29}O_3PSi$ requires C, 55.26; H, 9.35%); δ_H 0.18 [9 H, s, $(CH_3)_3Si$], 0.86 (3 H, t, *J* 6.9, CH_3), 0.91_{min} and 0.96_{maj}, 0.98_{maj} [6 H, 3 s, $(CH_3)_2C_5$], 1.18–1.32 (3 H, m, CH_3CH_2O), 1.33–1.7 (4 H, m, CH_2-CH_2), 3.9–4.25 (3 H, m, CH_3CH_2O and HC_6), 6.42_{maj} and 6.43_{min} (1 H, 2 d, J_{HP} 55.3 and J_{HP} 54.7, HC_4); δ_C −0.02 [s, $(CH_3)_3Si$], 13.5 (s, CH_3), 16.1 (d, *J* 6.2, CH_3CH_2O), 19.0 (s, $CH_3CH_2CH_2$), 20.1 and 24.2 [2 s, $(CH_3)_2C_5$], 32.0 (d, *J* 7.1, $CH_3CH_2CH_2$), 39.0 (2 d, *J* 12.5, C_5), 60.0_{maj} and 62.0_{min} (2 d, *J* 6.8, CH_3CH_2O), 80.0_{min} and 83.0_{maj} (2 d, *J* 4.8, *J* 6.3, C_6), 127.5_{maj} and 128.0_{min} (2 d, *J* 128.4, *J* 124.3, C_3), 165.6_{min} and 165.75_{maj} (2 d, *J* 4.0, *J* 4.2, C_4).

2-Ethoxy-5,5-dimethyl-6-(isopropyl)-3-trimethylsilyl-5*H*-1,2-oxaphosphorine-2-oxide 11g. Oily product (1.54 g, 56%), separated and purified by fractional distillation under reduced pressure (Found: C, 55.35; H, 9.52. $C_{14}H_{29}O_3PSi$ requires C, 55.26; H, 9.35%); δ_H 0.24 [9 H, s, $(CH_3)_3Si$], 1.0–1.17 [12 H, m, $(CH_3)_2C_5$ and $(CH_3)_2CH$-C_6], 1.34 (3 H, t, *J* 7.0, CH_3CH_2O), 1.73–2.08 [1 H, m, $(CH_3)_2CH$-C_6], 3.98 (1 H, dd, *J* 6.3 and 3.1, HC_6), 4.0–4.3 (2 H, m, CH_3CH_2O), 6.42_{maj} and 6.43_{min} (1 H, 2 d, J_{HP} 56.3 and J_{HP} 55.2, H-C_4); δ_C -0.1_{maj} and 0.1_{min} [2 s, $(CH_3)_3Si$], 16.2_{min} and 16.3_{maj} (2 d, *J* 6.6 and 6.3, CH_3CH_2O), 17.5 and 23.0 [2 s, $(CH_3)_2CH$-C_6], 20.7 and 25.5 [2 d, *J* 2.7 and 1.7, $(CH_3)_2$-C_5], 29.1_{maj} and 29.2_{min} (2 d, *J* 6.2, *C*-C_6), 40.0 (d, *J* 11.5, C_5), 61.0_{maj} and 62.5_{min} (2 d, *J* 6.9, CH_3CH_2O), 85.7_{min} and 87.0_{maj} (2 d, *J* 5.2 and 6.8, C_6), 127.0_{maj} and 127.2_{min} (2 d, *J* 128.6 and 124.9, C_3), 166.2_{min} and 166.4_{maj} (2 d, *J* 3.9 and 4.2, C_4).

2-Ethoxy-6-(cyclopropyl)-5,5-dimethyl-3-trimethylsilyl-5*H*-1,2-oxaphosphorine-2-oxide 11h. Oily product (1.8 g, 60%), separated and purified by fractional distillation under reduced pressure (Found: C, 55.49; H, 8.84. $C_{14}H_{27}O_3PSi$ requires C, 55.62; H, 8.94%); δ_H 0.15 [9 H, s, $(CH_3)_3Si$], 0.2–0.6 and 0.9–1.0 (5 H, m, H-Pr[c]), 1.04, 1.06 and 1.1 [6 H, 3 s, $(CH_3)_2C_5$], 1.25 (3 H, t, *J* 7.0, CH_3CH_2O), 3.38_{maj} (1 H, dd, *J* 8.2 and 5.2, HC_6), 3.5_{min} (1 H, dd, *J* 8.6 and 6.7, HC_6), 4.0–4.23 (2 H, m, CH_3CH_2O), 6.42_{maj} and 6.46_{min} (1 H, 2 d, J_{HP} 55.9 and J_{HP} 55.1, H-C_4); δ_C −0.1 [2 s, $(CH_3)_3Si$], 2.1_{min} and 4.25_{min} (2 s, C-Pr[c]), 2.3_{maj} and 3.9_{maj} (2 s, C-Pr[c]), 11.2_{maj} and 11.4_{min} (2 d, *J* 8.6 and 7.1, *C*-C_6), 16.2_{min} and 16.5_{maj} (2 d, *J* 7.2 and 6.0, CH_3CH_2O), 20.2_{maj} and 25.0_{maj} [2 d, *J* 2.7 and 1.6, $(CH_3)_2C_5$], 20.4_{min} and 25.2_{min} [2 d, *J* 2.6 and 1.9, $(CH_3)_2C_5$], 40.1 (d, *J* 12.1, C_5), 60.2_{maj} and 61.8_{min} (2 d, *J* 6.9 and 6.8, CH_3CH_2O), 87.0_{min} and 87.15_{maj} (2 d, *J* 4.6 and 5.9, C_6), 127.0_{maj} and 127.5_{min} (2 d, *J* 127.6 and 123.7, C_3), 165.7_{min} and 166.0_{maj} (2 d, *J* 3.6 and 3.8, C_4) *m*/*z* 302 (M), 287 (M − 15), 273 (M − 29), 189, 121, 29.

2-Ethoxy-6-(*tert*-butyl)-5,5-dimethyl-3-trimethylsilyl-5*H*-1,2-oxaphosphorine-2-oxide 11i. Oily product (2.6 g, 82%), purified by flash chromatography over silica gel and elution with ether (Found: C, 56.45; H, 9.51. $C_{15}H_{31}O_3PSi$ requires C, 56.60; H, 9.74%); δ_H 0.2 [9 H, s, $(CH_3)_3Si$], 0.9_{min} and 1.17_{maj}, 1.23_{maj} [6 H, 3 s, $(CH_3)_2C_5$], 1.12 [9 H, s, $(CH_3)_3CC_6$], 1.35 (3 H, t, *J* 7.0, CH_3CH_2O), 3.9 (1 H, d, *J* 6.6, HC_6), 4.0–4.3 (2 H, m, CH_3CH_2O), 6.3 (1 H, d, J_{HP} 56.6, H-C_4); δ_C 0.1 [s, $(CH_3)_3Si$], 16.5 (d, *J* 6.5, CH_3CH_2O), 21.4 and 27.5 [d and s, *J* 2.5, $(CH_3)_2C_5$], 37.5 [2 s, $(CH_3)_3CC_6$], 37.5 (d, *J* 5.8, C-C_6), 42.0 (d, *J* 10.5, C_5), 61.0 (d, *J* 6.9, CH_3CH_2O), 89.0 (d, *J* 7.6, C_6), 126.0 (d, *J* 128.8, C_3), 168.5 (d, *J* 4.5, C_4); *m*/*z* 318 (M), 261 (M − 57), 232, 121, 29.

(4*Z*)-4-Diethoxyphosphonyl-2-methyl-hexa-2,4-diene 9e. All data were previously described.[1]

(4*Z*)-4-Diethoxyphosphonyl-2-methylocta-2,4-diene 9f. Liquid (0.08 g, 3%), separated by fractional distillation under reduced pressure (Found: C, 59.95; H, 9.76. $C_{13}H_{25}O_3P$ requires C, 59.98; H, 9.68%), bp 105 °C/0.3 mmHg; δ_P 16.5; δ_H 1.0

(3 H, t, J 6.9, CH_3CH_2), 1.3 (6 H, t, J 7.0, CH_3CH_2O), 1.35–1.6 (2 H, m, CH_2CH_3), 1.7–1.83 [6 H, m, $(CH_3)_2C{=}C$], 2.6 (2 H, dq, J 7.7, $H_2C\text{-}C_5$), 4.08 (4 H, quint, J 7.0, CH_3CH_2O), 5.7–5.8 (1 H, m, HC_3), 6.1 (1 H, dt, J_{HP} 51.5, J_{HH} 7.7, HC_5); δ_C 13.8 (s, C_8), 16.2 (d, J 6.5, CH_3CH_2O), 18.9 and 25.9 [2 s, $(CH_3)_2C{=}C$], 22.5 (d, J 2.2, C_7), 32.0 (d, J 6.4, C_6), 61.3 (d, J 5.6, CH_3CH_2O), 123.0 (d, J 10.3, C_3), 127.1 (d, J 173.7, C_4), 136.3 (d, J 11.6, C_2), 150.5 (d, J 11.4, C_5).

(4*Z*)-4-Diethoxyphosphonyl-2,6-dimethylhepta-2,4-diene 9g. Liquid (0.45 g, 17%), separated by fractional distillation under reduced pressure (Found: C, 60.08; H, 9.70. $C_{13}H_{25}O_3P$ requires C, 59.98; H, 9.68%), bp 90 °C/0.3 mmHg; δ_P 16.0; δ_H 1.04 [3 H, d, J 6.8, $(CH_3)_2CH$], 1.37 (6 H, t, J 7.1, CH_3CH_2O), 1.68–1.82 [6 H, m, $(CH_3)_2C{=}C$], 3.26–3.48 (1 H, m, HC_6), 4.1 (4 H, quint, J 7.1, CH_3CH_2O), 5.67–5.77 (1 H, m, HC_3), 5.9 (1 H, dd, J_{HP} 50.9, J_{HH} 10.6, HC_5); δ_C 16.25 (d, J 6.7, CH_3CH_2O), 18.8 and 26.1 [d and s, J 2.1, $(CH_3)_2C{=}C$], 19.0 and 22.5 [2 d, J 7.0 and 2.4, $(CH_3)_2C_6$], 29.2 (d, J 6.3, C_6), 61.8 (d, J 5.5, CH_3CH_2O), 123.0 (d, J 10.3, C_3), 124.1 (d, J 174.0, C_4), 136.2 (d, J 11.6, C_2), 157.4 (d, J 12.0, C_5).

(1*Z*)-1-cyclopropyl-2-diethoxyphosphonyl-4-methylpenta-1,3-diene 9h. Liquid (0.39 g, 15%), separated by fractional distillation under reduced pressure (Found: C, 59.95; H, 8.73. $C_{13}H_{23}O_3P$ requires C, 60.46; H, 8.91%), bp 100 °C/0.25 mmHg; δ_P 16.9; δ_H 0.5–1.0 (4 H, m, H-Pr^c), 1.3 (6 H, t, J 7.0, CH_3CH_2O), 1.62–1.83 [6 H, m, $(CH_3)_2C{=}C$], 2.48–2.7 (1 H, m, HC-C_1), 4.1 (4 H, quint, J 7.0, CH_3CH_2O), 5.4 (1 H, dd, J_{HP} 49.2, J_{HH} 10.7, HC_1), 5.65–5.77 (1 H, m, HC_3); δ_C 2.1 and 4.3 (2 s, C-Pr^c), 12.2 (d, J 6.7, $HC\text{-}C_1$), 16.2 (d, J 6.2, CH_3CH_2O), 18.6 and 25.9 [d and s, J 2.1, $(CH_3)_2C{=}C$], 61.2 (d, J 5.2, CH_3CH_2O), 122.7 (d, J 9.3, C_3), 124.0 (d, J 174.7, C_2), 135.7 (d, J 12.2, C_4), 155.1 (d, J 11.2, C_1).

Diethyl (1*Z*)-4-hydroxy-3-methyl-1-trimethylsilyl-4-phenylbut-1-enylphosphonate 13a. The crude product was purified by flash chromatography and elution with ether (Found: C, 58.42; H, 8.51. $C_{18}H_{31}O_4PSi$ requires C, 58.37; H, 8.37%); δ_H 0.2_{er} and 0.25_{th} [9 H, 2 s, $(CH_3)_3Si$], 0.82_{th} and 0.95_{er} (3 H, 2 d, J 5.7, $H_3C\text{-}C_3$), 1.2–1.4 (6 H, m, CH_3CH_2O), 3.45–3.9 (1 H, m, HC_3), 3.9–4.1 (5 H, m, CH_3CH_2O and OH), 4.25_{th} and 4.78_{er} (1 H, 2 d, J 9.1 and 3.9, HC_4), 6.2_{er} and 6.6_{th} (1 H, 2 dd, J_{HP} 62.6, J_{HH} 10.8 and J_{HP} 60.8, J_{HH} 10.4, HC_2), 7.1–7.4 (5 H, m, H_{arom}); δ_C -0.9_{th} and 0.0_{er} [2 s, $(CH_3)_3Si$], 16.0_{er} and 17.0_{th} (2 s, $H_3C\text{-}C_3$), 16.0_{er} and 16.1_{th} (2 d, J 6.2 and 6.0, CH_3CH_2O), 43.0_{er} and 45.4_{th} (2 d, J 11.6 and 12.3, C_3), 61.3_{er} and 61.8_{th} (2 d, J 6.5, CH_3CH_2O), 77.6_{th} and 77.75_{er} (2 d, J 2.1 and 1.8, C_4), 126.8–128.1 (m, *o*,*m*,*p*-C_{arom}), 128.2_{th} and 128.25_{er} (2 d, J 136.0 and 136.5, C_1), 143.6_{th} and 144.4_{er} (2 s, *i*-C_{arom}), 164.0_{er} and 164.8_{th} (2 s, C_2); m/z 355 (M − 15), 264, 192, 121, 73, 45, 29, 15.

Diethyl (1*Z*)-4-hydroxy-3-methyl-1-trimethylsilyl-4-(*p*-methoxyphenyl)but-1-enylphosphonate 13b. The crude product was purified by flash chromatography and elution with ether (Found: C, 56.77; H, 8.39. $C_{19}H_{33}O_5PSi$ requires C, 57.00; H, 8.25%); δ_H 0.13_{er} and 0.2_{th} [9 H, 2 s, $(CH_3)_3Si$], 0.8_{th} and 0.95_{er} (3 H, 2 d, J 5.7 and 6.7, $H_3C\text{-}C_3$), 1.28_{er}, 1.32_{er} and 1.3_{th}, 1.34_{th} (6 H, 4 t, J 7.0, CH_3CH_2O), 3.64–3.75 (1 H, m, H-C_3), 3.78_{er} and 3.85_{th} (2 s, $H_3C\text{-OAr}$), 3.9–4.16 (5 H, m, CH_3CH_2O and OH), 4.2_{th} and 4.67_{er} (1 H, 2 d, J 9.0 and 3.9, HC_4), 6.2_{er} and 6.6_{th} (1 H, 2 dd, J_{HP} 62.8, J_{HH} 10.4 and J_{HP} 61.7, J_{HH} 10.3, HC_2), 6.8_{er}, 7.2_{er} and 6.88_{th}, 7.26_{th} (4 H, 4 d, J 8.7, H_{arom}); δ_C -0.9_{th} and 0.0_{er} [2 s, $(CH_3)_3Si$], 15.8_{er} and 16.0_{th} (2 s, $H_3C\text{-}C_3$), 16.0_{er} and 16.1_{th} (2 d, J 6.2 and 6.0, CH_3CH_2O), 43.0_{er} and 45.4_{th} (2 d, J 11.6 and 12.3, C_3), 61.3_{er} and 61.8_{th} (2 d, J 6.5, CH_3CH_2O), 77.6_{th} and 77.75_{er} (2 d, J 2.1 and 1.8, C_4), 126.8–128.1 (m, *o*,*m*,*p*-C_{arom}), 128.2_{th} and 128.25_{er} (2 d, J 136.0 and 136.5, C_1), 143.6_{th} and 144.4_{er} (2 s, *i*-C_{arom}), 164.0_{er} and 164.8_{th} (2 s, C_2).

Diethyl (1*Z*)-4-hydroxy-3-methyl-1-trimethylsilylhept-1-enylphosphonate 13c. The crude product was purified by flash chromatography and elution with ether (Found: C, 53.54; H, 9.56. $C_{15}H_{33}O_4PSi$ requires C, 53.57; H, 9.82%); δ_H 0.0_{th} and 0.1_{er} [9 H, 2 s, $(CH_3)_3Si$], 0.83_{er} and 0.85_{th} (3 H, 2 t, J 6.7 and 6.4, $CH_3\text{-}C_6$), 0.9_{th} and 0.95_{er} (3 H, 2 d, J 6.1 and 6.6, CH_3C_3), 1.25_{er}, 1.28_{er} and 1.3_{th} (6 H, 3 t, J 7.0, CH_3CH_2O), 1.35–1.61 (4 H, m, H_2C_5 and H_2C_6), 3.2–3.4 (1 H, m, HC_4), 3.43–3.59 (1 H, m, HC_3), 3.85–4.1 (5 H, m, 2 × CH_3CH_2O and OH), 6.5_{er} and 6.55_{th} (1 H, 2 dd, J_{HP} 62.3, J_{HH} 10.4 and J_{HP} 62.1, J_{HH} 9.9, HC_2); δ_C 0.0_{er} and 0.5_{th} [2 s, $(CH_3)_3Si$], 13.85_{th} and 13.9_{er} (2 s, C_7), 15.2_{er} and 16.3_{th} (2 d, J 1.9, $H_3C\text{-}C_3$), 16.0 (d, J 6.7, CH_3CH_2O), 18.3_{th} and 19.2_{er} (2 s, C_6), 34.5_{er} and 35.0_{th} (2 s, C_5), 42.5_{er} and 43.2_{th} (2 d, J 11.4 and 11.8, C_3), 60.6_{er} and 60.9_{th} (2 d, J 5.8, CH_3CH_2O), 73.8_{th} and 74.4_{er} (s, d, J 1.4, C_4), 130.0_{th} and 130.2_{er} (2 d, J 137.0 and 137.2, C_1), 164.8_{er} and 165.1_{th} (2 s, C_2).

Diethyl (1*Z*)-4-hydroxy-3,5-dimethyl-1-trimethylsilylhex-1-enylphosphonate 13d. The crude product was purified by flash chromatography and elution with ether to yield the title compound as an oil (Found: C, 53.78; H, 10.14. $C_{15}H_{33}O_4PSi$ requires C, 53.57; H, 9.82%).

Diethyl *erythro*-(1*Z*)-4-hydroxy-3,5-dimethyl-1-trimethylsilylhex-1-enylphosphonate *er*-13d. Oily product separated as pure diastereoisomer by bulb-to-bulb distillation under reduced pressure; δ_P 20.0; δ_H 0.18 [9 H, s, $(CH_3)_3Si$], 0.95 [6 H, d, J 6.8, $(CH_3)_2C_5$], 1.02 (3 H, d, J 6.6, $H_3C\text{-}C_3$), 1.3 (6 H, t, J 7.0, CH_3CH_2O), 1.59–1.79 (1 H, m, HC_5), 2.8 (1 H, bs, OH), 3.22 (1 H, t, J 4.9, HC_4), 3.32–3.52 (1 H, m, HC_3), 4.0 (4 H, quint, J 7.0, CH_3CH_2O), 6.6 (1 H, dd, J_{HP} 62.4, J_{HH} 10.2, HC_2); δ_C 0.0 [s, $(CH_3)_3Si$], 14.2 (d, J 2.4, $H_3C\text{-}C_3$), 16.3 (d, J 6.6, CH_3CH_2O), 17.4 and 19.9 [2 s, $(CH_3)_2C_5$], 31.2 (s, C_5), 40.0 (d, J 11.1, C_3), 60.4 and 60.6 (2 d, J 5.8, CH_3CH_2O), 79.5 (d, J 1.8, C_4), 129.0 (d, J 137.6, C_1), 165.2 (s, C_2); m/z 321 (M − 15), 264, 192, 121, 75, 73, 43, 15.

Diethyl *threo*-(1*Z*)-4-hydroxy-3,5-dimethyl-1-trimethylsilylhex-1-enylphosphonate *th*-13d. The NMR data were determined on the crude mixture, δ_H 0.17 [s, $(CH_3)_3Si$], 0.93 [d, J 6.8, $(CH_3)_2C_5$], 1.2 (d, J 6.6, $H_3C\text{-}C_3$), 1.35 (t, J 7.0, CH_3CH_2O), 1.4–1.57 (m, HC_5), 3.05–3.15 (m, HC_4), 3.9–4.1 (m, CH_3CH_2O), 4.1–4.15 (m, HC_3), 6.58 (dd, J_{HP} 61.8, J_{HH} 10.0, HC_2); δ_C −0.7 [s, $(CH_3)_3Si$], 14.05 (s, $H_3C\text{-}C_3$), 16.4 (d, J 5.8, CH_3CH_2O), 16.5 and 20.4 [2 s, $(CH_3)_2C_5$], 29.6 (s, C_5), 41.0 (d, J 12.1, C_3), 61.0 and 61.2 (2 d, J 6.0, CH_3CH_2O), 77.9 (d, J 2.0, C_4), 130.0 (d, J 136.3, C_1), 165.6 (s, C_2).

Diethyl (1*Z*)-4-hydroxy-3-methyl-1-trimethylsilylpent-1-enylphosphonate 13e. The crude product was purified by flash chromatography and elution with ether (Found: C, 50.89; H, 9.05. $C_{13}H_{29}O_4PSi$ requires C, 50.64; H, 9.41%); δ_H 0.2 [9 H, s, $(CH_3)_3Si$], 1.01_{th} and 1.03_{er} (3 H, 2 d, J 6.5 and 6.7, $CH_3\text{-}C_4$), 1.1_{th} and 1.13_{er} (3 H, 2 d, J 6.0 and 6.4, $H_3C\text{-}C_3$), 1.36 and 1.38 (6 H, 2 t, J 7.0, CH_3CH_2O), 3.37–3.5 (1 H, m, HC_4), 3.58 (1 H, bs, OH), 3.7–3.85 (1 H, m, HC_3), 3.9–4.2 (4 H, m, CH_3CH_2O), 6.52 (1 H, dd, J_{HP} 62.4, J_{HH} 10.4, HC_2); δ_C 0.0 [s, $(CH_3)_3Si$], 15.9_{er} and 16.2_{th} (2 d, J 1.8 and 2.2, $CH_3\text{-}C_3$), 16.0 (d, J 6.9, CH_3CH_2O), 18.2_{er} and 20.9_{th} (2 s, C_5), 41.0_{er} and 44.3_{th} (2 d, J 11.5 and 11.7, C_3), 60.8_{er} and 61.0_{th} (2 d, J 5.8 and 5.4, CH_3CH_2O), 70.2_{th} and 70.7_{er} (2 d, J 1.0 and 1.8, C_4), 130.2_{th} and 131.0_{er} (2 d, J 136.4 and 136.9, C_1), 163.9_{er} and 165.0_{th} (2 s, C_2); m/z 293 (M − 15), 264, 192, 121, 75, 73, 45, 29.

Diethyl (1*Z*)-4-hydroxy-3,5,5-trimethyl-1-trimethylsilylhex-1-enylphosphonate 13f. The crude product was purified by flash chromatography and elution with ether (Found: C, 55.20; H, 10.02. $C_{16}H_{35}O_4PSi$ requires C, 54.85; H, 10.00%); δ_H: 0.3_{th} and 0.5_{er} [9 H, 2 s, $(CH_3)_3Si$], 0.84_{th} and 0.9_{er} [9 H, 2 s, $(CH_3)_3C_5$], 1.01_{er} and 1.04_{th} (3 H, 2 d, J 6.7 and 6.8, $CH_3\text{-}C_3$), 1.28 (6 H, 2 t, J 7.0, CH_3CH_2O), 3.18_{er} and 3.2_{th} (1 H, 2 d, J 5.0 and 13.0, HC_4), 3.85 (1 H, bs, OH), 3.36–3.6 (1 H, m, HC_3), 3.9–4.2 (4 H, m, CH_3CH_2O), 6.68_{er} and 6.98_{th} (1 H, dd, J_{HP} 62.3, J_{HH} 10.3 and J_{HP} 62.8, J_{HH} 10.4, HC_2); δ_C −1.0 [s, $(CH_3)_3Si$], 15.2–16.2 (m, CH_3CH_2O and $CH_3\text{-}C_3$), 26.5_{er} and 27.0_{th} [2 s, $(H_3C)_3C_5$], 35.9_{th} and 36.2_{er} (2 s, C_5), 38.4_{th} and 39.2_{er} (2 d, J 11.3 and 11.1, C_3), 60.6_{er}, 60.8_{er} and 61.3_{th} (3 d, J 6.2 and 6.3, CH_3CH_2O), 83.1_{er} and 82.4_{th} (d and s, J 1.5, C_4), 125.5_{er} and 126.2_{th} (2 d, J 139.0 and 139.7, C_1), 165.2_{th} and 166.0_{er} (2 s, C_2).

2-Ethoxy-5-methyl-6-phenyl-3-trimethysilyl-5*H*-1,2-oxaphosphorine-2-oxide 14a. Oily product (2.6 g, 81%), purified by flash chromatography over silica gel and elution with ether (Found: C, 59.17; H, 8.08. $C_{16}H_{25}O_3PSi$ requires C, 59.25; H, 7.71%); δ_H 0.24_{min} and 0.25_{maj} [9 H, 2 s, $(CH_3)_3Si$], 0.82_{min} and 0.93_{maj} (3 H, 2 d, *J* 7.1 and 7.4, CH_3-C_5), 1.3_{min} and 1.35_{maj} (3 H, 2 t, *J* 7.1, CH_3CH_2O), 2.65–2.80 (1 H, m, HC_5), 3.82–4.28 (2 H, m, CH_3CH_2O), 5.15_{maj} and 5.6_{min} (1 H, 2 dd, *J* 10.6, 4.5 and 5.3, 3.0, HC_6), 6.75_{maj} and 7.05_{min} (1 H, 2 dd, J_{HP} 55.5, J_{HH} 1.5 and J_{HP} 56.0, J_{HH} 5.9, HC_4), 7.2–7.4 (5 H, m, H_{arom}); δ_C 0.0_{maj} and 0.08_{min} [2 s, $(CH_3)_3Si$], 16.0–18.1 (m, CH_3CH_2O and CH_3-C_5), 39.0_{min} and 41.0_{maj} (2 d, *J* 12.3 and 9.0, C_5), 61.0–62.6 (m, CH_3CH_2O), 79.1_{min} and 83.0_{maj} (2 d, *J* 6.2 and 4.1, C_6), 125.0–133.0 (m, *o*,*m*,*p*-C_{arom} and C_3), 138.6 (d, *J* 7.2, *i*-C_{arom}), 160.3–161.1 (m, C_4).

2-Ethoxy-5-methyl-6-(4-methoxyphenyl)-3-trimethylsilyl-5*H*-1,2-oxaphosphorine-2-oxide 14b. Oily product (2.6 g, 73%), purified by flash chromatography over silica gel and elution with ether (Found: C, 57.99; H, 7.16. $C_{17}H_{27}O_4PSi$ requires C, 57.62; H, 7.62%); δ_H 0.24 [9 H, s, $(CH_3)_3Si$], 0.82_{min} and 0.92_{maj} (3 H, 2 d, *J* 7.0, CH_3-C_5), 1.2–1.4 (3 H, m, CH_3CH_2O), 3.82_{maj} and 3.84_{min} (3 H, 2 s, H_3C-OAr), 2.6–2.75 (1 H, m, HC_5), 3.9–4.23 (2 H, m, CH_3CH_2O), 5.07_{maj} and 5.6_{min} (1 H, 2 dd, *J* 11.6, 5.2 and 7.0, 3.5, HC_6), 6.8–7.38 (5 H, m, H_{arom} and HC_4); δ_C −0.1 [s, $(CH_3)_3Si$], 12.0 (d, *J* 3.0, CH_3-C_5), 15.8–16.3 (m, CH_3CH_2O), 39.2_{min} and 40.0_{maj} (2 d, *J* 13.4 and 12.6, C_5), 55.6 (s, H_3C-OAr), 60.8_{min} and 62.1_{maj} (2 d, *J* 6.9 and 6.8, CH_3CH_2O), 78.7_{min} and 82.4_{maj} (2 d, *J* 5.3 and 4.5, C_6), 113.0_{min} and 114.0_{maj} (2 s, *o*-C_{arom}), 128.3_{min} and 129.1_{maj} (2 d, *J* 130.3 and 132.0, C_3), 129.0_{maj} and 133.0_{min} (2 s, m-C_{arom}), 130.4_{min} and 130.45_{maj} (2 d, *J* 7.8 and 7.5, *i*-C_{arom}), 158.5_{min} and 159.2_{maj} (2 s, *p*-C_{arom}), 160.0_{min} and 160.6_{maj} (2 d, *J* 4.0 and 3.8, C_4).

2-Ethoxy-5-methyl-6-(propyl)-3-trimethysilyl-5*H*-1,2-oxaphosphorine-2-oxide 14c. Oily product (2.15 g, 74%), purified by flash chromatography over silica gel elution with ether (Found: C, 53.92; H, 9.18. $C_{13}H_{27}O_3PSi$ requires C, 53.79; H, 9.31%); δ_H 0.18 [9 H, s, $(CH_3)_3Si$], 0.9 (3 H, t, *J* 6.6, CH_3CH_2), 1.0 (3 H, d, *J* 8.6, CH_3-C_5), 1.3 (3 H, t, *J* 7.0, CH_3CH_2O), 1.37–1.7 (4 H, m, $CH_3CH_2CH_2$), 2.1–2.3 (1 H, m, HC_5), 3.97–4.2 (2 H, m, CH_3CH_2O), 4.3–4.42 (1 H, m, HC_6), 6.9_{maj} and 6.92_{min} (1 H, 2 dd, J_{HP} 55.5, J_{HH} 5.6, HC_4); δ_C −0.1 [s, $(CH_3)_3Si$], 11.3 (d, *J* 3.0, CH_3-C_5), 13.6_{maj} and 13.7_{maj} (2 s, CH_3CH_2), 16.1_{min} and 16.3_{maj} (2 d, *J* 6.1, CH_3CH_2O), 18.5_{maj} and 18.7_{min} (2 s, CH_3CH_2), 35.1 (d, *J* 6.8, C-C_6), 37.0 (d, *J* 13.8, C_5), 60.15_{maj} and 60.3_{min} (2 d, *J* 7.0, CH_3CH_2O), 78.5 (d, *J* 6.2, C_6), 129.1 (d, *J* 128.3, C_3), 160.5_{maj} and 163.0_{min} (2 d, *J* 4.1 and 4.2, C_4); *m*/*z* 275 (M − 15), 247 (M − 28), 190 (M − 57), 163, 121, 73, 29.

2-Ethoxy-5-methyl-6-(isopropyl)-3-trimethysilyl-5*H*-1,2-oxaphosphorine-2-oxide 14d. Oily product (2.05 g, 71%), purified by flash chromatography over silica gel and elution with ether (Found: C, 53.41; H, 9.71. $C_{13}H_{27}O_3PSi$ requires C, 53.79; H, 9.31%); δ_H 0.22 [9 H, s, $(CH_3)_3Si$], 0.84_{maj} and 0.95_{min} (3 H, 2 d, *J* 7.1 and 7.9, CH_3-C_5), 1.05_{min} and 1.1_{maj} [6 H, 2 d, *J* 7.0, $(CH_3)_2CH$], 1.3 (3 H, t, *J* 7.0, CH_3CH_2O), 1.8–2.0 (1 H, m, HC-C_6), 2.1–2.3 (1 H, m, HC_5), 3.83–4.0 (1 H, m, HC_6), 4.05–4.3 (2 H, m, CH_3CH_2O), 6.9 (1 H, dd, J_{HP} 55.6, J_{HH} 5.8, HC_4); δ_C −0.18 [s, $(CH_3)_3Si$], 10.8 (d, *J* 3.0, CH_3-C_5), 16.1 (d, *J* 6.2, CH_3CH_2O), 19.2 [s, $(CH_3)_2CH$], 29.0_{min} and 29.8_{maj} (d, *J* 5.8 and 6.7, C-C_6), 34.4_{maj} and 35.5_{min} (2 d, *J* 13.5, C_5), 60.0_{maj} and 60.05_{min} (2 d, *J* 6.9, CH_3CH_2O), 83.8_{maj} and 84.5_{min} (2 d, *J* 6.6 and 5.7, C_6), 128.5_{maj} and 130.0_{min} (2 d, *J* 128.0 and 128.5, C_3), 160.02_{maj} and 161.5_{min} (2 d, *J* 4.3 and 4.5, C_4).

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