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Radical Addition Reactions of Phosphorus Hydrides: Tuning the Reactivity of Phosphorus Hydrides, the Use of Microwaves and Horner–Wadsworth–Emmons-Type Reactions

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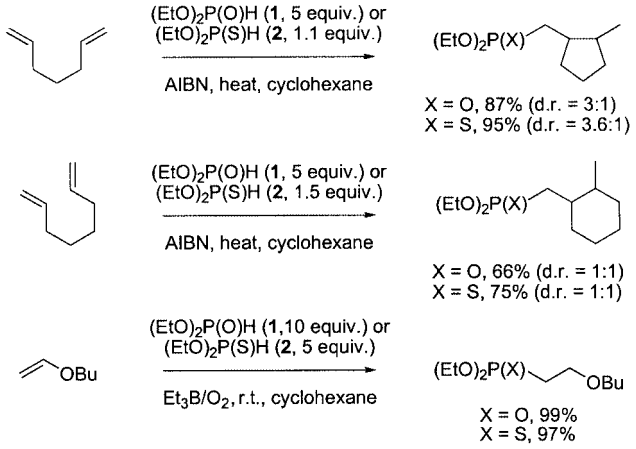
The reactivity of phosphorus hydrides in radical addition reactions are compared, and the substituents on phosphorus are shown to affect the efficiency of the reactions. The change in reactivity is attributed to the different bond dissociation energies of the P–H bonds, which have been calculated. Phosphorus hydrides with particularly weak P–H bonds are shown to undergo radical additions by microwave irradiation, in the absence of conventional initiators. These radical addition reactions produce phosphonothioates, phosphinothioates and phosphane sulfides, which react in HWE-type reactions, to afford substituted alkenes.

Introduction

An important area of modern research is the development of synthetic radical reactions that use non-metal hydrides.[1] This research is partly driven by the need to move away from toxic metal hydrides, chiefly tributyltin hydride. Tributyltin hydride is still used extensively in small-scale synthesis, but the problems of toxicity and product purification have limited its use, particularly on a large scale in the chemical industry.[2]

In recent years, the use of phosphorus hydrides as replacements for tributyltin hydride in radical reductions has been investigated. Of particular interest has been the use of phosphorus hydrides to reduce organohalides and xanthates. Following Barton's seminal work on reductions using dialkyl phosphites [$(RO)_2P(O)H$],[3] the use of other phosphorus hydrides,[4] most notably hypophosphorous acid (and its salts),[5] have been reported. The mechanisms of these reactions involve intermediate phosphorus-centred radicals that, for example, abstract halogen atoms from organohalides.

Phosphorus-centred radicals also add to C=C bonds. Examples of addition of phosphanes,[6] diphenylphosphane oxide [$Ph_2P(O)H$],[7] hypophosphites,[8] diethyl phosphite [$(EtO)_2P(O)H$, **1**][9] and diethyl thiophosphite [$(EtO)_2P(S)H$, **2**][9] to various alkenes have been reported. Work within our own group[10] included the investigation of the addition of **1** and **2** to various electron-rich alkenes and dienes using AIBN or Et_3B/O_2 as the initiator. As shown from the examples in Scheme 1, $(EtO)_2P(S)H$ (**2**) is significantly more reactive than $(EtO)_2P(O)H$ (**1**). The use of 1.1 to 5 equiv. of $(EtO)_2P(S)H$ (**2**) gives addition products in excellent yields, whereas typically at least 5 equiv. of $(EtO)_2P(O)H$ (**1**) are required to achieve similar yields of addition products. This effect has been observed by other groups[9] and is attributed to $(EtO)_2P(S)H$ (**2**) having a weaker P–H bond than $(EtO)_2P(O)H$ (**1**).



Scheme 1. Comparison of $(EtO)_2P(O)H$ (**1**) with $(EtO)_2P(S)H$ (**2**) in radical additions.

Although the pronounced difference in reactivity between phosphites [$(RO)_2P(O)H$] and thiophosphites [$(RO)_2P(S)H$] is known, the importance of the two alkoxy substituents on the reactivity of the phosphorus hydrides in radical additions has not been well investigated.[6] Initially, this paper describes how the reactivity of the phosphorus hy-

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drides can be tuned by varying the substituents on phosphorus. This is followed by an investigation to develop a new method for initiating radical additions of phosphorus hydrides, which uses microwaves. Finally, the reactivity of the organophosphorus adducts (from the radical reactions) in Horner–Wadsworth–Emmons-type reactions (HWE) are compared for the first time.

Results and Discussion

Comparing the Reactivity of Different Phosphorus Hydrides in Radical Additions

The influence of the phosphorus substituents in radical additions was investigated using the phosphorus hydrides **1**–**5** (Figure 1). The hydrides **1** and **4** are commercially available, **2** was prepared (in 95% yield) by heating **1** with Lawesson's reagent,[9b] **3**[11] was prepared (in 95% yield) by a sequence of reactions including a DCC-mediated coupling between phenylphosphinic acid and ethanol, then treatment with Lawesson's reagent; and **5** was obtained (in 61% yield) by heating diphenylphosphane with sulfur.[6a] A series of experiments were carried out investigating the reactions of equimolar mixtures of two of the phosphorus hydrides with 1-octene and Et_3B/O_2 (at room temp. in toluene) (Table 1). The ratio of the addition products **6**–**10** was then determined from the ^1H NMR spectra of the crude reaction mixtures (each of the addition products **6**–**10** were prepared independently by reaction of 1-octene with each of the five hydrides **1**–**5**). These results show that *O*-ethyl phenylphosphinothioate (**3**) adds more rapidly to 1-octene than diethyl thiophosphite (**2**) and particularly, diethyl phosphite (**1**) (Table 1, Entries 1–2). Diphenylphosphane oxide (**4**) is more reactive than diethyl phosphite (**1**), but less reactive than diethyl thiophosphite (**2**) (Entries 3–4). However, this may not be a true reflection of the reactivity of **4** because it is only partially soluble in toluene at room temp. – related reactions at higher temperatures (using AIBN as the initiator) produced similar yields of adducts derived from **4** and **2**. Finally, diphenylphosphane sulfide (**5**)[10c] adds more rapidly to 1-octene than *O*-ethyl phenylphosphinothioate (**3**) (Entry 5).

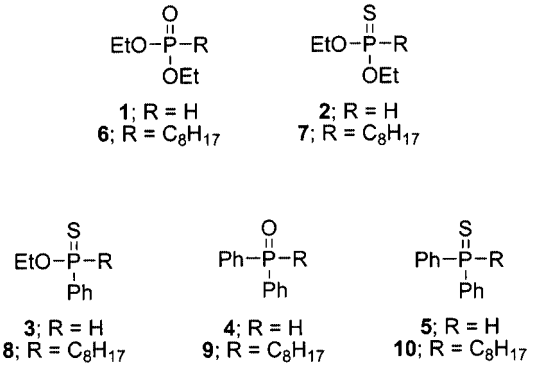


Figure 1. Phosphorus hydrides and the adducts from addition to 1-octene.

Table 1. Results from the competitive addition reactions.

Entry	Phosphorus hydrides	Adducts (ratios[a])
1	**1** + **2**	**6/7** (0:100)[b]
2	**2** + **3**	**7/8** (33:66)
3	**1** + **4**[c]	**6/9** (0:100)
4	**2** + **4**[c]	**7/9** (65:35)
5	**3** + **5**	**8/10** (21:79)

[a] Determined from the ^1H NMR spectra (octyl adducts **6**–**10** were prepared independently to verify analysis of the mixtures by ^1H NMR spectroscopy). [b] A similar result has been reported by Piettre.[9c] [c] Diphenylphosphane oxide (**4**) is only partially soluble in toluene at room temp.

These investigations show that the replacement of EtO with Ph groups, on phosphorus, increases the rate of addition of the phosphorus hydride to the C=C bond of 1-octene. Also, phosphorus hydrides with P=S bonds are considerably more reactive than those with P=O bonds. These results are summarised by the order of reactivity shown in Figure 2.

The order of reactivity of phosphorus hydrides **1**–**5** (to 1-octene) can be explained by the theoretical bond dissociation energies (BDE) of the P–H bonds, calculated using density functional theory (DFT) (Figure 2). The substituents on phosphorus affect the BDEs of the P–H bonds, and it is seen that phosphorus hydrides with the weakest P–H bonds add fastest to the C=C bond of 1-octene. In these chain reactions, addition of the phosphorus radical to the C=C bond forms an intermediate carbon-centred radical that abstracts a hydrogen atom from the phosphorus hydride. The weaker the P–H bond in the phosphorus hydride, the faster the rate of hydrogen-atom abstraction and formation of the organophosphorus product **6**–**10**.

The different BDEs of P–H bonds also explain the contrasting products from the reaction of the unsaturated phosphorus hydrides **11**–**14** with Et_3B/O_2 (Scheme 2). The thiophosphites **11** and **13** were prepared (in 44–48% yield) from the reaction of diphenyl phosphite[12,13] with 1-octanol in pyridine, followed by the reaction with triethylamine, then allyl alcohol or 3-buten-1-ol (and pivaloyl chloride in pyridine) and finally, heating with Lawesson's reagent. The *O*-alkenyl phenylphosphinothioates **12** and **14** were formed

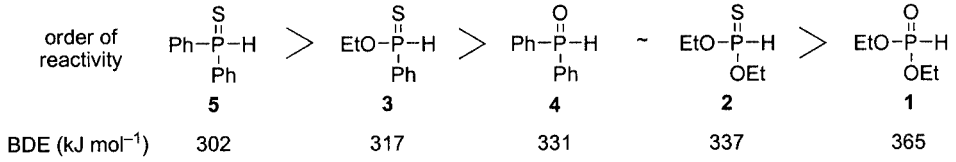
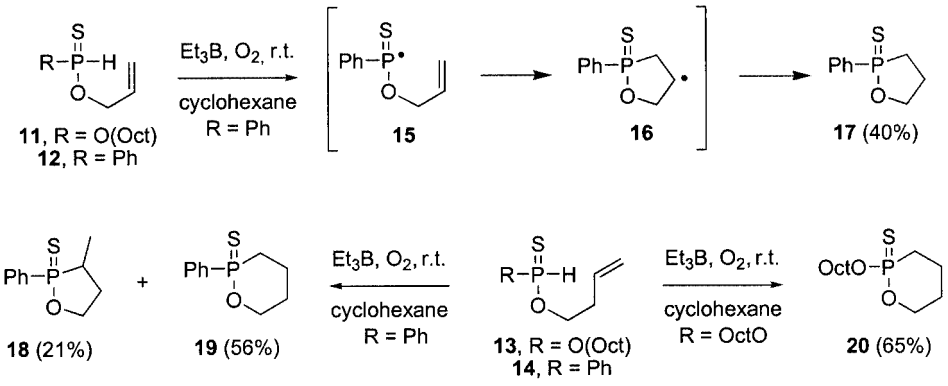


Figure 2. Order of reactivity of phosphorus hydrides to 1-octene.



Scheme 2. Reactions of unsaturated phosphinothioates with triethylborane.

(in 31–41% yield) by a DCC-promoted coupling of phenylphosphinic acid with allyl alcohol or 3-buten-1-ol followed by thionation using Lawesson's reagent.

When *O*-allyl *O*-octyl thiophosphite (**11**) was stirred overnight in cyclohexane with triethylborane (0.6 equiv.), no cyclic product was isolated, only recovered starting material in 50% yield. (The low recovery of starting material may be attributed to the formation of oligomers and/or polymers). In contrast, the reaction of *O*-allyl phenylphosphinothioate (**12**) with triethylborane (under the same conditions) gave the oxaphospholane **17** in 40% yield – the formation of **17** is explained by 5-*endo*-*trig* cyclisation[14] of the phosphorus-centred radical **15** to give **16**. These results are explained by considering how the P–H BDEs of **11** and **12** affects the two hydrogen-atom abstraction steps leading to the oxaphospholane products. Firstly, because the phosphinothioate **12** contains a weaker P–H bond than **11**, the phosphorus-centred radical **15** is formed faster than the corresponding phosphorus-centred radical from **11**. Secondly, the hydrogen-atom abstraction reaction of the carbon-centred radical **16** with phosphinothioate **12** (to form **17**) is expected to be faster than the corresponding reaction starting from **11**.

The hydrides **13** and **14** also react differently with Et_3B/O_2. Whereas hydride **13** undergoes a 6-*endo*-*trig* radical cyclisation to form the oxaphosphinane **20** (only a trace amount of a 5-ring product was observed in the ^{13}C NMR spectrum), the hydride **14** produces a mixture of the oxaphospholane **18** (as a single isomer) and oxaphosphinane **19**, by 5-*exo*-*trig* and 6-*endo*-*trig* radical cyclisation, respectively. It is possible that the phosphorus-centred radicals derived from **13** and **14** undergo reversible cyclisation on to the C=C bond to produce the 6-ring products (via the thermodynamically more stable secondary carbon radicals). Alternatively, the primary radicals derived from 5-*exo*-*trig* cyclisation of **13** and **14** may undergo a neophyl rearrangement (by addition to the P=S bond followed by fragmentation) to form the 6-*endo* products. However, the 5-ring product (**18**) is also formed from **14**, because the P–H bond in **14** is relatively weak. Hence, the primary carbon radical produced on 5-*exo*-*trig* cyclisation is able to abstract a hydrogen atom from **14** at a sufficiently fast rate to compete with radical fragmentation/rearrangement of the five-membered ring.

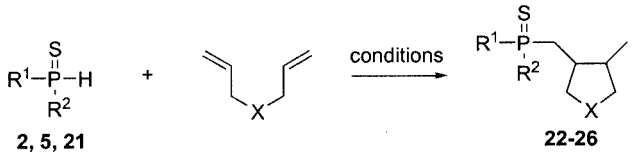
Microwave-Assisted Reactions

Although common initiators (including AIBN or Et_3B) promote radical addition reactions of the phosphorus hydrides **1**–**5**, it was of interest to investigate whether radical reactions of hydrides with particularly weak P–H bonds could be initiated simply by heating. Initially, 1.2 equiv. of phosphinothioate **21** (prepared in 53% yield by a DCC-promoted coupling of phenylphosphinic acid with 1-octanol, followed by reaction with Lawessons reagent) was heated to reflux with diallyl ether (1 equiv.) in cyclohexane, but this gave the tetrahydrofuran **22** in only 39% yield (as a 2:2:1:1 mixture of inseparable diastereoisomers) after 60 h (Table 2, Entry 1). Perhaps, the intermediate phosphorus-centred radical is produced by the reaction of **21** with the dissolved oxygen in the cyclohexane. The corresponding cyclisation of diallyl ether, with Et_3B (0.3 equiv.) as the initiator, gave **22** in 67% yield after 1 h (Table 2, Entry 2). In both reactions, mixtures of four diastereoisomers of **22** were formed – the two major isomers presumably have the C-3/C-4 substituents in a *cis* configuration (as predicted by a chair-like transition state for the radical cyclisation).

Because cyclisation by conventional heating was so slow and gave only a modest yield of product, our attention turned to the use of microwave irradiation. Remarkable decreases in reaction times and, in some cases, cleaner reactions and higher yields have been reported by the use of microwaves, although there are few examples of microwave-assisted radical reactions.[15] Initially, the phosphinothioate **21** (1.2 equiv.) was treated with diallyl ether, in a sealed tube in dioxane at 150 °C, using microwave irradiation for 1 h. This afforded the desired tetrahydrofuran **22** in 70% yield (Table 2, Entry 3). Pleasingly, the yield of **22** obtained by the use of microwave irradiation is considerably higher than by the use of conventional heating, and the reaction time is considerably shorter.

A number of solvents were tested for the cyclisation of diallyl ether using **21**, including toluene and DMF, with the

Table 2. Microwave-assisted cyclisations of 1,6-dienes.



Entry	P-Hydride	R^1	R^2	X	Conditions	Product (%)/*dr*[a]
1	**21**	OctO	Ph	O	heat, cyclohexane, 60 h	**22** (39/2:2:1:1)
2	**21**	OctO	Ph	O	Et_3B, room temp., cyclohexane, 1 h	**22** (67/3.7:3.7:1:1)
3	**21**	OctO	Ph	O	microwave, 150 °C, dioxane, 1 h	**22** (70/2:2:1:1)
4	**21**	OctO	Ph	O	microwave, 150 °C, toluene, 1 h	**22** (93/2:2:1:1)
5	**21**	OctO	Ph	NBoc	microwave, 150 °C, toluene, 1 h	**23** (60[b])
6	**5**	Ph	Ph	O	microwave, 150 °C, toluene, 1 h	**24** (59/2:1[c])
7	**5**	Ph	Ph	NBoc	microwave, 150 °C, toluene, 1 h	**25** (70/1.9:1[c])
8	**2**	EtO	EtO	O	microwave, 150 °C, toluene, 1 h	**26** (19/2:1[c])

[a] Diastereoisomer ratio determined from the ^1H NMR spectrum. [b] The diastereoisomer ratio could not be determined due to the presence of conformers. [c] *cis*/*trans* ratio.

former being eventually shown to be the most effective one, and tetrahydrofuran **22** was isolated in 93% yield after 1 h (Table 2, Entry 4). Pyrrolidines can also be efficiently prepared. Reaction of **21** with *tert*-butyl diallylcarbamate, at 150 °C (by microwave heating) in toluene for 1 h, afforded the pyrrolidine **23** in 60% yield (Table 2, Entry 5).

Diphenylphosphane sulfide (**5**) also reacts with 1,6-dienes under the same conditions. The reaction of **5** with diallyl ether produced the tetrahydrofuran **24** in 59% yield, whereas the reaction with *tert*-butyl diallylcarbamate gave the pyrrolidine **25** in 70% yield (Table 2, Entries 6–7).

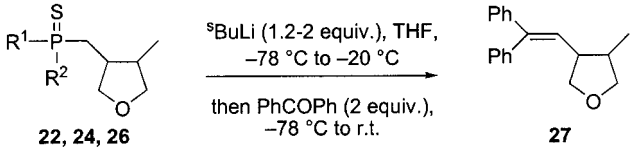
Interestingly, the reaction of diethyl thiophosphite (**2**) with diallyl ether in the microwave afforded the tetrahydrofuran **26** in only 19% yield (Table 2, Entry 8). The modest yield is consistent with the results reported earlier, which showed that phosphorus hydrides bearing Ph (rather than OEt) substituents are more reactive because of the weaker P–H bonds.

Horner–Wadsworth–Emmons-Type Reactions

Corey first investigated the use of non-stabilised phosphonothioates in Horner–Wadsworth–Emmons-type (HWE) reactions.[16] Previous studies within our own group have since shown that organophosphorus adducts, produced from radical additions of diethyl thiophosphite (**2**) to alkenes, can undergo HWE-type reactions.[17] This offers a general approach to tri- and tetrasubstituted alkenes. For example, heating diallyl ether with **2** and AIBN forms the phosphonothioate **26**, which on immediate deprotonation, followed by the reaction with benzophenone affords the trisubstituted alkene **27** in excellent yield (Table 3, Entry 1).

Although HWE-type reactions of phosphonothioates (such as **26**) have been investigated, we were not aware of the corresponding reactions using phosphinothioates or phosphane sulfides. To investigate if non-stabilised phosphinothioates and phosphane sulfides could also undergo HWE-type reactions, the compounds **22** and **24** were deprotonated and reacted with benzophenone (Table 3, Entries 2 and 3). It is pleasing to see that both compounds react to produce the desired trisubstituted alkene **27**. Interestingly, for **24**, it appears that the *cis* isomer reacts faster than the *trans* isomer (unreacted **24** was recovered as a 1:1 mixture of diastereoisomers in 42% yield).

Table 3. HWE-type reactions.



Entry	Precursor (*dr*)	R^1	R^2	Yield of **27** (*cis*:*trans*) [a]
1	**26**[b]	EtO	EtO	92% (3.0:1)[17]
2	**22** (3.7:3.7:1:1)	OctO	Ph	72% (3.7:1)
3	**24** (2.1:1)[c]	Ph	Ph	43% (22.0:1)

[a] Determined from the ^1H NMR spectrum. [b] Not isolated, prepared in-situ from the reaction of **2** with diallyl ether. [c] *cis*/*trans* ratio.

Conclusions

This work has shown that phosphorus hydrides add to various C=C bonds, and this offers a mild, efficient and general approach to organophosphorus derivatives including phosphonothioates, phosphinothioates and phosphane sulfides. These radical additions can be initiated using conventional initiators or, in some cases, by microwaves. The use of microwaves is particularly attractive because much shorter reaction times are required to form products, when compared to conventional heating or use of initiators. It has also been shown that the substituents on the phosphorus hydrides affects the rate of addition of these compounds to C=C bonds. The experimental results are explained by the different energies of the P–H bonds, which are calculated using density functional theory. Finally, the importance of the development of a concise approach to phospho-

nothioates, phosphinothioates and phosphane sulfides is demonstrated by the use of these compounds in HWE-type reactions.

Experimental Section

General Remarks: IR spectra were recorded with an ATI Mattson Genesis FTIR spectrometer. NMR spectra were recorded with a Joel EX 270, a Bruker DMX 300, a Jeol ECX 400 or a Bruker AMX 500 MHz spectrometer. The carbon spectra were assigned with DEPT experiments. Coupling constants (*J*) were recorded in Hertz to the nearest 0.5 Hz in the ^{1}H NMR spectra and to the nearest 1 Hz in the ^{13}C NMR spectra. Mass spectra were recorded with a Fisons Instruments VG Analytical Autospec Spectrometer system. Microwave reactions were performed in a CEM Focused Microwave Synthesis System. Thin layer chromatography was performed on Merck aluminium-backed silica gel plates. Compounds were visualised under a UV lamp, using alkaline potassium permanganate solution, cerium(IV) sulphate/molybdic acid solution and/or iodine.

Density functional theory calculations employed the hybrid B3LYP functional[18] as implemented in Gaussian03.[19] Singly polarized 6-31G(d,p) basis sets were used on all atoms.[20] Fully unconstrained geometry optimisations on the parent molecules and the radicals were followed by computation of analytic Hessians in order to identify the species as minima and to obtain the zero-point and thermal corrections to enthalpies (at 298.15 K and 1 atm). Gas-phase bond dissociation energies (BDEs) were then determined as enthalpy changes for the homolytic cleavage of the P–H bond: BDE = *H*(radical) + *H*(hydrogen) – *H*(parent). Density functional theory calculations of the Si–H bond dissociation energies in $(Me_3Si)_3SiH$ and Et_3SiH compare well with those reported previously[21] (i.e. 331 vs. 343 kJ·mol^{-1} and 377 vs. 386 kJ·mol^{-1}).

A Typical Competition Reaction: Competition Between Diethyl Phosphite (1) and Diethyl Thiophosphite (2): To a stirred solution of diethyl thiophosphite (**2**) (0.137 g, 0.89 mmol), diethyl phosphite (**1**) (0.123 g, 0.89 mmol) and 1-octene (0.100 g, 0.140 cm^3, 0.89 mmol) in toluene (15 cm^3) at room temp. under nitrogen was added a 1 M solution of triethylborane in hexanes (0.27 cm^3, 0.27 mmol). The solution was stirred for 1.5 h. Further triethylborane (0.27 cm^3, 0.27 mmol, 1 M solution in hexanes) was added and the solution was stirred for 12 h. The solution was concentrated in vacuo. Kugelrohr distillation (75 °C, 2 Torr) removed the remaining phosphorus hydrides from the mixture affording the crude product. Water (50 cm^3) and EtOAc (50 cm^3) were added to the crude mixture, the layers were separated and the aqueous layer was extracted with EtOAc (2 × 50 cm^3). The organic layer was dried ($MgSO_4$), filtered and concentrated in vacuo affording *O*,*O*-diethyl octylphosphonothioate (**7**) (0.234 g, 99%) as a colourless oil. R_f = 0.4 (light petroleum/EtOAc, 9:1). IR ($CDCl_3$): $\tilde{\nu}$ = 2954 (s), 2856 (s), 1051 (s, P–O), 1026 (s, P–O), 956 (s, P=S) cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 4.13–3.90 (m, 4 H, 2 × POC*H*$_2$CH$_3$), 1.92–1.82 (m, 2 H, PC*H*$_2$), 1.63–1.55 (m, 2 H, PCH$_2$C*H*$_2$), 1.30–1.00 (m, 12 H, 6 × C*H*$_2$), 1.23 (t, *J* = 7.0 Hz, 6 H, 2 × POCH$_2$C*H*$_3$), 0.81 (t, *J* = 7.0 Hz, 3 H, C*H*$_3$) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 62.1 (d, $^2J_{CP}$ = 7 Hz, 2 × PO*C*H$_2$CH$_3$), 34.5 (d, $^1J_{CP}$ = 111 Hz, P*C*H$_2$), 31.7 (*C*H$_2$CH$_2$CH$_3$), 30.2 (d, $^3J_{CP}$ = 18 Hz, PCH$_2$CH$_2$*C*H$_2$), 29.0, 28.9 (2 × *C*H$_2$), 22.6 (d, $^2J_{CP}$ = 2 Hz, PCH$_2$*C*H$_2$CH$_2$), 22.5 (*C*H$_2$), 16.1 (d, $^3J_{CP}$ = 7 Hz, 2 × POCH$_2$*C*H$_3$), 14.0 (*C*H$_3$) ppm. ^{31}P NMR (109.3 MHz, $CDCl_3$): δ = 100.5 ppm. MS (CI, NH_3): *m*/*z* (%) = 267 (100) [M + H$^+$]. HRMS: found: [M + H$^+$], 267.1542, $C_{12}H_{28}O_2PS$ requires 267.1548.

***O*-Ethyl Octyl(phenyl)phosphinothioate (8):** Colourless oil. R_f = 0.3 (light petroleum/EtOAc, 9:1). IR ($CDCl_3$): $\tilde{\nu}$ = 3054 (s), 2954 (s), 2929 (s), 2856 (s), 1437 (s, P–C$_{ipso}$), 1034 (s, P–O), 949 (s, P=S) cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.88–7.77 (m, 2 H, C*H*, aromatic), 7.50–7.34 (m, 3 H, C*H*, aromatic), 4.13–3.94 (m, 1 H, POC*H*$_A$H$_B$), 3.79–3.61 (m, 1 H, POCH$_A$*H*$_B$), 2.17–1.87 (m, 2 H, PC*H*$_2$), 1.30–1.00 (m, 12 H, 6 × C*H*$_2$), 1.18 (t, *J* = 7.0 Hz, 6 H, 2 × POCH$_2$C*H*$_3$), 0.78 (t, *J* = 7.0 Hz, 3 H, CH$_2$CH$_2$C*H*$_3$) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 133.3 (d, $^1J_{CP}$ = 95 Hz, *C*$_{ipso}$, aromatic), 131.8 (d, $^4J_{CP}$ = 3 Hz, *C*H, aromatic), 131.0 (d, $^2J_{CP}$ = 10 Hz, 2 × *C*H, aromatic), 128.3 (d, $^3J_{CP}$ = 12 Hz, 2 × *C*H, aromatic), 60.6 (d, $^2J_{CP}$ = 6 Hz, PO*C*H$_2$CH$_3$), 36.2 (d, $^1J_{CP}$ = 80 Hz, P*C*H$_2$), 31.6 (*C*H$_2$CH$_2$CH$_3$), 30.2 (d, $^3J_{CP}$ = 18 Hz, PCH$_2$CH$_2$*C*H$_2$), 29.0, 22.5 (3 × *C*H$_2$), 22.3 (d, $^2J_{CP}$ = 2 Hz, PCH$_2$*C*H$_2$CH$_2$), 16.1 (d, $^3J_{CP}$ = 7 Hz, POCH$_2$*C*H$_3$), 14.0 (*C*H$_3$) ppm. ^{31}P NMR (109.3 MHz, $CDCl_3$): δ = 94.1 ppm. MS (CI, NH_3): *m*/*z* (%) = 299 (100) [M + H$^+$]. HRMS: found: [M + H$^+$] 299.1590, $C_{16}H_{28}OPS$ requires 299.1599.

Octyl(diphenyl)phosphane Oxide (9): Colourless oil. R_f = 0.4 (EtOAc/MeOH, 20:1). IR ($CDCl_3$): $\tilde{\nu}$ = 3053 (s), 2955 (s), 2929 (s), 2856 (s), 1437 (s, P–C$_{ipso}$), 1271 (s, P–O), 1182 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68–7.60 (m, 4 H, 4 × C*H*, aromatic), 7.44–7.32 (m, 6 H, 6 × C*H*, aromatic), 2.21–2.12 (m, 2 H, PC*H*$_2$), 1.55–1.47 (m, 2 H, C*H*$_2$), 1.35–1.24 (m, 2 H, C*H*$_2$), 1.20–1.08 (m, 8 H, 4 × C*H*$_2$), 0.76 (t, *J* = 7.0 Hz, 3 H, C*H*$_3$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 132.8 (d, $^1J_{CP}$ 98, 2 × *C*$_{ipso}$, aromatic), 131.5 (d, $^4J_{CP}$ 2, 2 × *C*H, aromatic), 130.6 (d, $^2J_{CP}$ 9, 4 × *C*H, aromatic), 128.5 (d, $^3J_{CP}$ 11, 4 × *C*H, aromatic), 31.6 (*C*H$_2$CH$_2$CH$_3$), 30.2 (d, $^3J_{CP}$ 15, PCH$_2$*C*H$_2$), 29.5 (d, $^1J_{CP}$ 72, P*C*H$_2$), 28.9, 22.4 (3 × *C*H$_2$), 21.2 (d, $^2J_{CP}$ 4, PCH$_2$*C*H$_2$CH$_2$), 13.9 (*C*H$_3$) ppm. ^{31}P NMR (109.3 MHz, $CDCl_3$): δ = 33.7 ppm. MS (CI, NH_3): *m*/*z* (%) = 315 (100) [M + H$^+$]. HRMS: found: [M + H$^+$], 315.1869. $C_{20}H_{28}OP$ requires 315.1878.

Octyl(diphenyl)phosphane Sulfide (10): Colourless oil. R_f = 0.4 (light petroleum/EtOAc, 3:2). IR ($CDCl_3$): $\tilde{\nu}$ = 2929 (s), 1438 (s, P–C$_{ipso}$), 934 (s, P=S) cm^{-1}. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.87–7.73 (m, 4 H, 4 × C*H*, aromatic), 7.50–7.43 (m, 6 H, 6 × C*H*, aromatic), 2.50–2.38 (m, 2 H, PC*H*$_2$), 1.70–1.47 (m, 2 H, C*H*$_2$), 1.45–1.24 (m, 2 H, C*H*$_2$), 1.25–1.16 (m, 8 H, 4 × C*H*$_2$), 0.85 (t, *J* = 7.0 Hz, 3 H, C*H*$_3$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 132.8 (d, $^1J_{CP}$ = 80 Hz, 2 × *C*$_{ipso}$, aromatic), 131.3 (d, $^4J_{CP}$ = 3 Hz, 2 × *C*H, aromatic), 131.0 (d, $^2J_{CP}$ = 10 Hz, 4 × *C*H, aromatic), 128.5 (d, $^3J_{CP}$ = 12 Hz, 4 × *C*H, aromatic), 32.5 (d, $^1J_{CP}$ = 56 Hz, P*C*H$_2$), 31.6 (*C*H$_2$CH$_2$CH$_3$), 30.6 (d, $^3J_{CP}$ = 17 Hz, PCH$_2$CH$_2$*C*H$_2$), 29.0, 22.5 (3 × *C*H$_2$), 22.1 (d, $^2J_{CP}$ = 3 Hz, PCH$_2$*C*H$_2$CH$_2$), 14.0 (*C*H$_3$) ppm. ^{31}P NMR (109.3 MHz, $CDCl_3$): δ = 43.4 ppm. MS (CI, NH_3): *m*/*z* (%) = 331 (100) [M + H$^+$]. HRMS: found: [M + H$^+$], 331.1641. $C_{20}H_{28}PS$ requires 331.1649.

2-Phenyl-1,2λ^5-oxaphospholane-2-thione (17): To a stirred solution of *O*-allyl phenylphosphinothioate (**12**) (0.100 g, 0.51 mmol) in cyclohexane (30 cm^3) at room temp. under nitrogen was added a 1 M solution of triethylborane in hexanes (0.15 cm^3, 0.15 mmol). The solution was stirred for 1 h, then further triethylborane (0.15 cm^3, 0.15 mmol) was added and the solution was stirred for 12 h. The solution was concentrated in vacuo and purification with column chromatography (silica; light petroleum/EtOAc, 4:1) afforded the title compound **17**[22] (0.040 g, 40%) as a colourless liquid. R_f = 0.3 (light petroleum/EtOAc, 4:1). IR ($CDCl_3$): $\tilde{\nu}$ = 2957 (s), 1437 (s, P–C), 1022 (s, P–O), 945 (s, P=S) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98–7.86 (m, 2 H, 2 × C*H*, aromatic), 7.59–7.46 (m, 3 H, 3 × C*H*, aromatic), 4.55–4.30 (m, 1 H, OC*H*$_A$H$_B$), 3.97–3.90 (m, 1 H, OCH$_A$*H*$_B$), 2.62–2.40 (m, 1 H, OCH$_2$CH$_2$C*H*$_E$H$_F$P), 2.33–2.20

(m, 2 H, $OCH_2CH_2CH_EH_FP$ and $OCH_2CH_CH_DCH_2P$), 2.17–1.90 (m, 1 H, $OCH_2CH_CH_DCH_2P$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 133.8 (d, $^1J_{CP}$ = 103 Hz, C_{ipso}, aromatic), 132.0 (d, $^4J_{CP}$ = 3 Hz, *C*H, aromatic), 130.7 (d, $^2J_{CP}$ = 11 Hz, *C*H, aromatic), 128.5 (d, $^3J_{CP}$ = 13 Hz, 2×*C*H, aromatic), 63.5 (d, $^2J_{CP}$ = 7 Hz, $POCH_2CH_2CH_2$), 32.2 (d, $^1J_{CP}$ = 75 Hz, PCH_2), 23.6 (d, $^3J_{CP}$ = 6 Hz, $POCH_2CH_2$) ppm. MS (CI, NH_3) *m*/*z* (%) = 199 (100) [M + H^+]. HRMS: found: [M + H^+], 199.0345. $C_9H_{12}OPS$ requires 199.0347.

3-Methyl-2-phenyl-1,2λ^5-oxaphospholane-2-thione (18) and 2-Phenyl-1,2λ^5-oxaphosphinane-2-thione (19): To a stirred solution of *O*-(3-butenyl) phenylphosphinothioate (**14**) (0.200 g, 0.94 mmol) in cyclohexane (30 cm^3) at room temp. under nitrogen was added a 1 M solution of triethylborane in hexanes (0.28 cm^3, 0.28 mmol). The solution was stirred for 1 h. Further triethylborane (0.28 cm^3, 0.28 mmol, 1 M solution in hexanes) was added and the solution was stirred for 12 h. The solution was concentrated *in vacuo*. Purification with column chromatography (silica; 7:3, light petroleum/EtOAc) afforded thiones **19** (0.112 g, 56%) and **18** (0.042 g, 21%) as colourless oils.

2-Phenyl-1,2λ^5-oxaphosphinane-2-thione (19): R_f = 0.4 (light petroleum/EtOAc, 7:3). IR ($CDCl_3$) $\tilde{\nu}$ = 2948 (s), 1437 (s, P–C_{ipso}), 1022 (s, P–O), 958 (s, P=S) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.00–7.94 (m, 2 H, 2×C*H*, aromatic), 7.58–7.46 (m, 3 H, 3×C*H*, aromatic), 4.62 (tdd, *J* = 11.5, 6.5 and 3.0 Hz, 1 H, $OCH_AH_BCH_2CH_2P$), 4.22–4.10 (m, 1 H, $OCH_AH_BCH_2CH_2P$), 2.50–2.35 (m, 1 H, $OCH_2CH_2CH_CH_DP$), 2.35–2.25 (m, 1 H, $OCH_2CH_2CH_CH_DP$), 2.15–2.00 (m, 2 H, CH_2), 1.93–1.75 (m, 2 H, CH_2) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 133.2 (d, $^1J_{CP}$ = 108 Hz, C_{ipso}, aromatic), 132.2 (d, $^4J_{CP}$ = 3 Hz, *C*H, aromatic), 130.7 (d, $^2J_{CP}$ = 11 Hz, *C*H, aromatic), 128.5 (d, $^3J_{CP}$ = 18 Hz, *C*H, aromatic), 65.8 (d, $^2J_{CP}$ = 6 Hz, $POCH_2CH_2CH_2$), 33.4 (d, $^1J_{CP}$ = 67 Hz, PCH_2), 26.6 (d, $^2J_{CP}$ = 6 Hz, PCH_2CH_2), 20.1 (d, $^3J_{CP}$ = 7 Hz, $PCH_2CH_2CH_2$) ppm. MS (CI, NH_3): *m*/*z* (%) = 213 (100) [M + H^+]. HRMS: found: [M + H^+], 213.0504. $C_{10}H_{14}OPS$ requires 213.0503.

3-Methyl-2-phenyl-1,2λ^5-oxaphospholane-2-thione (18): (isolated as a single diastereoisomer). R_f = 0.2 (light petroleum/EtOAc, 7:3). IR ($CDCl_3$) $\tilde{\nu}$ = 2948 (s), 1437 (s, P–C_{ipso}), 1022 (s, P–O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.70 (m, 2 H, 2×C*H*, aromatic), 7.58–7.40 (m, 3 H, 3×C*H*, aromatic), 4.57–4.42 (m, 2 H, OCH_2), 2.70–2.55 (m, 1 H, PC*H*), 2.50–2.25 (m, 2 H, OCH_2CH_2CHP), 0.92 (dd, *J* = 19.5 and 7.5 Hz, 3 H, $PCHCH_3$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 132.2 (d, $^4J_{CP}$ = 3 Hz, *C*H, aromatic), 131.9 (d, $^2J_{CP}$ = 11 Hz, 2×*C*H, aromatic), 131.5 (d, $^1J_{CP}$ = 112 Hz, C_{ipso}, aromatic), 128.3 (d, $^3J_{CP}$ = 12 Hz, 2×*C*H, aromatic), 70.0 (d, $^2J_{CP}$ = 2 Hz, $POCH_2$), 41.7 (d, $^1J_{CP}$ = 62 Hz, PCH), 33.1 (d, $^3J_{CP}$ = 4 Hz, OCH_2CH_2), 13.0 (CH_3) ppm. MS (CI, NH_3) *m*/*z* (%) = 213 (100) [M + H^+]. HRMS: found: [M + H^+], 213.0504. $C_{10}H_{14}OPS$ requires 213.0503.

2-(Octyloxy)-1,2λ^5-oxaphosphinane-2-thione (20): To a stirred solution of *O*-(3-butenyl) *O*-octyl thiophosphite (**13**) (0.100 g, 0.38 mmol) in cyclohexane (20 cm^3) under nitrogen was added a 1 M solution of triethylborane in hexanes (0.11 cm^3, 0.11 mmol). The solution was stirred for 1 h. Further triethylborane (0.11 cm^3, 0.11 mmol, 1 M solution in hexanes) was added and the solution was stirred for 12 h. The solution was concentrated in vacuo. Purification with column chromatography (silica; 19:1, light petroleum/EtOAc) afforded the thione **20** (0.065 g, 65%) as a colourless liquid. R_f = 0.2 (light petroleum/EtOAc, 19:1). IR ($CDCl_3$): $\tilde{\nu}$ = 2928 (s), 2856 (s), 1013 (br. m, P–O), 931 (s, P=S) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = (major 6-*endo* product) 4.34–4.22 (m, 1 H, OCH_AH_B), 4.20–4.00 [m, 3 H, $POCH_2$ (chain) and OCH_AH_B], 2.20–1.60 [8 H, m, PCH_2, $POCH_2CH_2$ (ring), $POCH_2CH_2$ (chain) and PCH_2CH_2], 1.43–1.20 (m, 10 H, 5×CH_2), 0.88 (t, *J* = 7.0 Hz, 3 H, $CH_2CH_2CH_3$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): (major 6-*endo* product) 69.2 [d, $^2J_{CP}$ = 8 Hz, $POCH_2$ (ring)], 65.6 [d, $^2J_{CP}$ = 9 Hz, $POCH_2$ (chain)], 31.9 (d, $^1J_{CP}$ = 98 Hz, PCH_2), 31.7 [CH_2 (chain)], 30.2 [d, $^3J_{CP}$ = 7 Hz, $POCH_2CH_2$ (chain)], 29.1, 29.0, [2×CH_2 (chain)], 25.9 [d, $^2J_{CP}$ = 7 Hz, PCH_2CH_2 (ring)], 25.6 [d, $^3J_{CP}$ = 14 Hz, $POCH_2CH_2$ (ring)], 22.6 [2×CH_2 (chain)], 21.4 [d, $^3J_{CP}$ = 9 Hz, $PCH_2CH_2CH_2$ (ring)], 14.0 ($CH_2CH_2CH_3$) ppm. MS (CI, NH_3): *m*/*z* (%) = 265 (100) [M + H^+]. HRMS: found: [M + H^+], 265.1393. $C_{12}H_{26}O_2PS$ requires 265.1391.

The presence of trace quantities of the minor 5-*exo* product in the crude material was indicated by the ^{13}C NMR spectrum: δ = 36.9 (d, $^1J_{CP}$ = 95 Hz, PCH), 11.7 (d, $^2J_{CP}$ = 3 Hz, $PCHCH_3$) ppm.

Typical Procedure for a Microwave-Assisted Reaction: Synthesis of *O*-Octyl (4-Methyltetrahydrofuran-3-yl)methyl(phenyl)phosphinothioate (22): To a stirred solution of *O*-octyl phenylphosphinothioate (**21**) (0.100 g, 0.37 mmol) in dioxane (5 cm^3) was added diallyl ether (0.029 g, 0.036 cm^3, 0.31 mmol). The solution was heated to 150 °C in a sealed tube in a microwave and stirred for 1 h at this temperature. The solution was concentrated in vacuo. Purification with column chromatography (silica; light petroleum/EtOAc, 4:1) afforded the (phenyl)phosphinothioate **22** (0.080 g, 70%) as a colourless oil, as a 2:2:1:1 mixture of inseparable (3*R**,4*S**,8*R**)/(3*R**,4*S**,8*S**)/(3*R**,4*R**,8*R**)/(3*R**,4*R**,8*S**) diastereoisomers from the ^1H NMR spectrum. R_f = 0.2 (light petroleum/EtOAc, 4:1). IR ($CDCl_3$); $\tilde{\nu}$ = 2928 (s), 2856 (s), 1437 (s, P–C_{ipso}), 1095 (s, P–O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = (major 3*R**,4*S**,8*R** and 3*R**,4*S**,8*S** diastereoisomers) 7.95–7.84 (m, 2 H, 2×C*H*, aromatic), 7.57–7.45 (m, 3 H, 3×C*H*, aromatic), 4.10–3.86 (m, 2 H, $POCH_AH_B$ and OC*H*H), 3.88 and 3.71 (dd and t, *J* = 8.0, 6.0 and 8.0 Hz, 1 H, OC*H*H), 3.65–3.19 (m, 2 H, $POCH_AH_B$ and 2×OCH*H*), 2.81–2.59 (m, 1 H, PCH_2CH), 2.39–2.25 (m, 1 H, $CHCH_3$), 2.20–2.00 (m, 2 H, PCH_2), 1.65–1.55 (m, 2 H, $POCH_2CH_2$), 1.37–1.19 (m, 10 H, 5×CH_2), 0.96 and 0.86 (2×d, *J* = 7.0 and 7.0 Hz, 3 H, $CHCH_3$), 0.88 (t, *J* = 6.5 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = (major 3*R**,4*S**,8*R** and 3*R**,4*S**,8*S** diastereoisomers) 133.4, 133.2 (2×d, $^1J_{CP}$ = 96 and 96 Hz, C_{ipso}, aromatic), 132.2, 132.1 (2×d, $^4J_{CP}$ = 3 and 3 Hz, *C*H, aromatic), 131.4, 131.3 (2×d, $^2J_{CP}$ = 12 and 11 Hz, 2×*C*H, aromatic), 2×128.5 (2×d, $^3J_{CP}$ = 12 and 12 Hz, 2×*C*H, aromatic), 74.7, 74.6 (OCH_2CHCH_3), 71.7, 71.4 (2×d, $^3J_{CP}$ = 5 and 7 Hz, OCH_2CHCH_2), 2×64.8 (2×d, $^2J_{CP}$ = 7 and 7 Hz, 2×$POCH_2CH_2$), 37.0, 36.8 (2×d, $^2J_{CP}$ = 2 and 3 Hz, PCH_2CH), 36.5, 36.3 (2×d, $^3J_{CP}$ = 17 and 15 Hz, $CHCH_3$), 35.0, 34.9 (2×d, $^1J_{CP}$ = 81 and 81 Hz, PCH_2), 31.7 (CH_2), 30.2 (d, $^3J_{CP}$ = 8 Hz, $POCH_2CH_2$), 29.1, 29.0, 25.6, 22.6 (4×CH_2), 14.0 (CH_2CH_3), 13.4, 13.3 ($CHCH_3$) ppm. MS (CI, NH_3): *m*/*z* (%) = 369 (100) [M + H^+]. HRMS: found: [M + H^+], 369.2016. $C_{20}H_{34}O_2PS$ requires 369.2017.

The presence two minor (3*R**,4*R**,8*R**) and (3*R**,4*R**,8*S**) diastereoisomers were indicated by ^1H and ^{13}C NMR spectroscopy. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.10–3.93 (m, 2 H, POC*H* and OC*H*), 3.93 and 3.80 (2×dd, *J* = 8.0, 6.0 and 8.0, 6.0 Hz, 1 H, OC*H*), 3.65–3.12 (m, 2 H, POC*H* and 2×OC*H*), 2.50–2.30 (m, 1 H, PCH_2CH), 2.00–1.83 (m, 1 H, $CHCH_3$), 1.02 and 0.95 (2×d, *J* = 6.5 and 6.5 Hz, 3 H, $CHCH_3$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 2×74.1 (OCH_2CHCH_3), 73.5, 73.4 (2×d, $^3J_{CP}$ = 6 and 8 Hz, OCH_2CHCH_2), 41.6, 41.3 (2×d, $^2J_{CP}$ = 2 and 3 Hz, PCH_2CH), 41.1, 41.0 (2×d, $^3J_{CP}$ = 15 and 15 Hz, $CHCH_3$), 39.5, 39.3 (2×d, $^1J_{CP}$ = 81 and 81 Hz, PCH_2), 15.6, 15.4 ($CHCH_3$) ppm.

***tert*-Butyl 3-Methyl-4-{[(octyloxy)(phenyl)phosphonothioyl]methyl}-1-pyrrolidinecarboxylate (23):** Colourless oil (60%). R_f = 0.4 (light petroleum/EtOAc, 4:1). IR (CH_2Cl_2): $\tilde{\nu}$ = 3055 (s), 2929 (s), 2858 (s), 2361 (s), 1695 (s, C=O), 1437 (s, P–C_{ipso}), 1110 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): (major peaks): δ = 7.98–7.86 (m, 2 H, 2×C*H*, aromatic), 7.55–7.45 (m, 3 H, 3×C*H*, aromatic), 4.12–3.99 (m, 2 H, OCH_2), 3.69–2.73 (m, 5 H, 2×NCH_2 and C*H*CHCH$_3$), 2.37–1.59 (m, 5 H, PCH_2, C*H*CH$_3$ and OCH$_2$CH_2), 1.45 [9 H, s, C(CH_3)$_3$], 1.42–1.19 (m, 10 H, 5×CH_2), 0.86 and 0.83 (2×d, 2×*J* = 7.0 Hz, 3 H, 2×CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): (major peaks): δ = 152.1 (*C*O$_2$), 132.0 (d, $^1J_{CP}$ = 81, C_{ipso}, aromatic), 130.3–126.5 (m, 5×*C*H, aromatic), 78.5 [O*C*(CH$_3$)$_3$], 62.8 (O*C*H$_2$), 51.1, 50.2 (N*C*H$_2$), 47.3, 47.0, 33.8, 30.0 (*C*HCH$_2$N, *C*HCH$_3$, PCH$_2$ and OCH$_2$*C*H$_2$), 29.2 [OC(*C*H$_3$)$_3$], 27.1, 26.5, 23.7, 20.7 (*C*H$_2$), 13.3, 12.2 (*C*H$_3$) ppm. ^{31}P NMR (109.3 MHz, $CDCl_3$): (major peak): δ = 92.5 ppm. MS (CI, NH_3): *m*/*z* (%) = 468 (28) [M + H$^+$], 368 (100). HRMS: found: M + H$^+$, 468.2704. $C_{25}H_{42}NO_3PS$ requires 468.2726.

(4-Methyltetrahydrofuran-3-yl)methyl(diphenyl)phosphane Sulfide (24): Colourless oil (59%, 2:1 *cis*/*trans* mixture of inseparable diastereoisomers from the ^1H NMR spectrum). R_f = 0.4 (light petroleum/EtOAc, 1:1). IR (CH_2Cl_2): $\tilde{\nu}$ = 3050 (s), 2960 (s), 2875 (s), 1437 (s, P–C_{ipso}), 1103 (s) cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ = (major *cis* diastereoisomer) 7.92–7.79 (m, 4 H, 4×C*H*, aromatic), 7.51–7.38 (m, 6 H, 6×C*H*, aromatic), 3.82 (dd, *J* = 8.0 and 6.0 Hz, 1 H, OC*H*H), 3.67 (dd, *J* = 8.0 and 7.5 Hz, 1 H, OC*H*H), 3.41 (dd, *J* = 8.0 and 4.0 Hz, 1 H, OCH*H*), 3.27 (dd, *J* = 8.0 and 4.0 Hz, 1 H, OCH*H*), 2.80–2.20 (m, 4 H, PCH_2, PCH$_2$C*H* and C*H*CH$_3$), 0.93 (d, *J* = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = (major *cis* diastereoisomer) 133.0 (d, $^1J_{CP}$ = 81 Hz, C_{ipso}, aromatic), 132.3 (d, $^1J_{CP}$ = 80 Hz, C_{ipso}, aromatic), 131.4 (d, $^4J_{CP}$ = 3 Hz, 2×*C*H, aromatic), 131.0–130.7 (m, 4×*C*H, aromatic), 128.4 (d, $^3J_{CP}$ = 12 Hz, 2×*C*H, aromatic), 128.3 (d, $^3J_{CP}$ = 12 Hz, 2×*C*H, aromatic), 74.2 (O*C*H$_2$CHCH$_3$), 71.1 (d, $^3J_{CP}$ = 5 Hz, O*C*H$_2$CHCH$_2$), 36.7 (d, $^2J_{CP}$ = 2 Hz, PCH$_2$*C*H), 36.6 (d, $^3J_{CP}$ = 8 Hz, *C*HCH$_3$), 30.8 (d, $^1J_{CP}$ = 57 Hz, P*C*H$_2$), 13.3 (*C*H$_3$) ppm. MS (CI, NH_3): *m*/*z* (%) = 317 (100) [M + H$^+$], 100%). HRMS: found: [M + H$^+$], 317.1120. $C_{18}H_{22}OPS$ requires 317.1129.

The presence of the minor *trans* diastereoisomer was indicated by ^1H and ^{13}C NMR spectroscopy. ^1H NMR (270 MHz, $CDCl_3$): δ = 3.89 (t, *J* = 7.8 Hz, 1 H, OC*H*H), 3.66 (dd, *J* = 8.0 and 7.5 Hz, 1 H, OC*H*H), 3.22 (dd, *J* = 8.0 and 8.5 Hz, 1 H, OCH*H*), 3.20 (t, *J* = 8.0 Hz, 1 H, OCH*H*), 0.96 (d, *J* = 6.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 132.8 (d, $^1J_{CP}$ = 80 Hz, C_{ipso}, aromatic), 132.6 (d, $^1J_{CP}$ = 80 Hz, C_{ipso}, aromatic), 73.7 (O*C*H$_2$CHCH$_3$), 73.2 (d, $^3J_{CP}$ = 3 Hz, O*C*H$_2$CHCH$_2$), 41.2 (d, $^2J_{CP}$ = 2 Hz, PCH$_2$*C*H), 41.1 (d, $^3J_{CP}$ = 13 Hz, *C*HCH$_3$), 35.4 (d, $^1J_{CP}$ = 57 Hz, P*C*H$_2$), 15.3 (*C*H$_3$) ppm.

***tert*-Butyl 3-[(Diphenylphosphinothioyl)methyl]-4-methyl-1-pyrrolidinecarboxylate (25):** Colourless oil (70%, 1.9:1 *cis*/*trans* mixture of inseparable diastereoisomers from the ^1H NMR spectrum). R_f = 0.5 (light petroleum/EtOAc, 1:1). IR (CH_2Cl_2): $\tilde{\nu}$ = 2975 (s), 2932 (s), 1685 (s, C=O), 1409 (s, P–C_{ipso}), 1103 (w) cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ = (major *cis* diastereoisomer, mixture of conformers) 7.95–7.78 (m, 4 H, 4×C*H*, aromatic), 7.55–7.40 (m, 6 H, 6×C*H*, aromatic), 3.60–2.70 (m, 4 H, 2×NCH_2), 2.60–2.10 (m, 4 H, PCH_2, PCH$_2$C*H* and C*H*CH$_3$), 1.36 [br. s, 9 H, C(CH_3)$_3$], 0.90 (d, *J* = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = (major *cis* diastereoisomer, mixture of conformers) 154.3, 153.9 [N*C*(O)O], 133.0 (br. d, $^1J_{CP}$ = 81 Hz, 2 × C_{ipso}, aromatic), 131.7–131.0 (m, 2×*C*H, aromatic), 130.8–130.5 (m, 4×*C*H, aromatic), 128.7–128.3 (m, 4×*C*H, aromatic), 78.8, 78.7 [O*C*(CH$_3$)$_3$], 52.5–51.4 (br. m, N*C*H$_2$), 49.0–48.5 (br. m, N*C*H$_2$), 40.3–39.2 (br. m, *C*H), 36.4–34.3 (br. m, *C*H), 31.4 (d, $^1J_{CP}$ = 57 Hz, P*C*H$_2$), 28.3 [C(*C*H$_3$)$_3$], 13.6 (CH*C*H$_3$) ppm. MS (CI, NH_3): *m*/*z* (%) = 416 (20) [M + H$^+$], 316 (100), 360 (40). HRMS: found: [M + H$^+$], 416.1811. $C_{23}H_{31}NO_2PS$ requires 416.1813.

The presence of the minor *trans* diastereoisomer was indicated by ^1H and ^{13}C NMR spectroscopy. ^1H NMR (270 MHz, $CDCl_3$): δ = 1.00 (d, *J* = 6.5 Hz, 3 H, CHCH_3) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 35.0 (d, $^1J_{CP}$ = 56 Hz, P*C*H$_2$), 15.2 (CH*C*H$_3$) ppm.

***O*,*O*-Diethyl (4-Methyltetrahydrofuran-3-yl)methylphosphonothioate (26):** Colourless oil (19%, 2:1 *cis*/*trans* mixture of inseparable diastereoisomers from the ^1H NMR spectrum). R_f = 0.2 (light petroleum/EtOAc, 4:1). IR ($CHCl_3$): $\tilde{\nu}$ = 2990 cm^{-1} (s), 2976 (s), 2862 (s), 1059 (s, P–O), 1030 (s, P–O), 955 (s, P=S) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = (major *cis* isomer) 4.15–3.98 (m, 4 H, 2×POCH_2CH$_3$), 3.94 (t, *J* = 8.5 Hz, 1 H, OCH_AH$_B$), 3.92 (dd, *J* = 8.5 and 6.0 Hz, 1 H, OCH_CH$_D$), 3.56 (t, *J* = 8.5 Hz, 1 H, OCH$_A$-H_B), 3.47 (dd, *J* = 8.5 and 4.0 Hz, 1 H, OCH$_C$$H_D$), 2.65–2.53 (m, 1 H, PCH$_2$C*H*), 2.35–2.25 (m, 1 H, C*H*CH$_3$), 2.08–1.58 (m, 2 H, CH_2P), 1.23 (t, *J* = 7.0 Hz, 6 H, 2×POCH$_2$CH_3), 0.88 (d, *J* = 7.5 Hz, 3 H, CHCH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = (major *cis* isomer) 74.7 (O*C*H$_2$CHCH$_3$), 71.5 (d, $^3J_{CP}$ = 8 Hz, O*C*H$_2$CHCH$_2$), 62.4 (d, $^2J_{CP}$ = 7 Hz, PO*C*H$_2$CH$_3$), 62.2 (d, $^2J_{CP}$ = 7 Hz, PO*C*H$_2$CH$_3$), 37.0 (d, $^2J_{CP}$ = 3 Hz, PCH$_2$*C*H), 36.3 (d, $^3J_{CP}$ = 13 Hz, *C*HCH$_3$), 33.0 (d, $^1J_{CP}$ = 112 Hz, *C*H$_2$P), 2×16.1 (2×d, $^3J_{CP}$ = 7 and 7 Hz, 2×POCH$_2$CH_3), 13.3 (CH*C*H$_3$) ppm. MS (CI, NH_3): *m*/*z* (%) = 253 (100) [M + H$^+$]. HRMS: found: [M + H$^+$], 253.1030. $C_{10}H_{22}O_3PS$ requires 253.1027.

The presence of the minor *trans* diastereoisomer was indicated by ^1H and ^{13}C NMR spectroscopy. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.98 (d, *J* = 6.5 Hz, 3 H, CHCH_3) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 74.3 (O*C*H$_2$CHCH$_3$), 73.6 (d, $^3J_{CP}$ = 5 Hz, O*C*H$_2$CHCH$_2$), 41.7 (d, $^2J_{CP}$ = 4 Hz, PCH$_2$*C*H), 40.8 (d, $^3J_{CP}$ = 17 Hz, *C*HCH$_3$), 37.2 (d, $^1J_{CP}$ = 113 Hz, P*C*H$_2$), 15.6 (CH*C*H$_3$) ppm.

Typical Procedure for the HWE-type Reaction: Synthesis of 3-(2,2-Diphenylvinyl)-4-methyltetrahydrofuran (27) From *O*-Octyl (4-Methyltetrahydrofuran-3-yl)methyl(phenyl)phosphinothioate (22): To a stirred solution of the phosphinothioate **22** (0.130 g, 0.35 mmol) (as a 3.7:3.7:1:1:1 mixture of diastereoisomers from the ^1H NMR spectrum) in dry THF (4 cm^3) at –78 °C under nitrogen was added a 1.23 M solution of *s*BuLi in THF (0.57 cm^3, 0.71 mmol) dropwise. The solution was warmed to –20 °C within 0.75 h and then cooled to –78 °C. A THF solution (2 cm^3) of benzophenone (0.129 g, 0.71 mmol) was added. The solution was warmed to room temp. and then stirred for 12 h. Water (50 cm^3) and EtOAc (50 cm^3) were added to the crude mixture, the layers were separated and the aqueous layer was extracted with EtOAc (2×50 cm^3). The organic layer was dried ($MgSO_4$), filtered and concentrated in vacuo. Purification with column chromatography (silica; light petroleum/EtOAc, 9:1) afforded the tetrahydrofuran **27** (0.057 g, 72%) as a colourless oil, as a 3.7:1 *cis*/*trans* mixture of inseparable diastereoisomers from the ^1H NMR spectrum. R_f = 0.3 (light petroleum/EtOAc, 9:1). IR ($CDCl_3$): $\tilde{\nu}$ = 3059 (s), 3023 (s), 2964 (s), 2869 (s), 1657 (m, C=C) cm^{-1}. ^1H NMR (270 MHz, $CDCl_3$): δ = (major *cis* diastereoisomer) 7.40–7.15 (m, 5 H, 5×C*H*, aromatic), 6.04 (d, *J* = 10.5 Hz, 1 H, C=C*H*), 3.92 (dd, *J* = 7.5 and 8.0 Hz, 1 H, OCH_CH$_D$), 3.89 (dd, *J* = 6.5 and 8.0 Hz, 1 H, OCH_AH$_B$), 3.69 (dd, *J* = 8.0 and 6.5 Hz, 1 H, OCH$_A$$H_B$), 3.53 (dd, *J* = 8.0 and 5.5 Hz, 1 H, OCH$_C$$H_D$), 2.97 (dq, *J* = 10.5 and 6.5 Hz, 1 H, OCH$_2$C*H*CH), 2.35–2.26 (m, 1 H, OCH$_2$C*H*CH$_3$), 1.08 (d, *J* = 7.0 Hz, 3 H, CHCH_3) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = (major *cis* diastereoisomer) 143.7 (C_{ipso},

aromatic), 142.9 (CH=*C*), 140.0 (C_{ipso}, aromatic), 129.8 (4×*C*H, aromatic), 128.1 (4×*C*H, aromatic), 127.2 (2×*C*H, aromatic), 127.0 (C=*C*H), 75.0 (O*C*H$_2$CHCH$_3$), 72.9 (O*C*H$_2$CHCH), 43.0 (OCH$_2$*C*HCH), 38.2 (OCH$_2$*C*HCH$_3$), 13.9 (*C*H$_3$) ppm. MS (EI): *m*/*z* (%) = 264 (100) [M$^+$], 205 (100), 180 (65). HRMS: found: [M$^+$], 264.1512. $C_{19}H_{20}O$ requires 264.1515.

The presence of the minor *trans* diastereoisomer was indicated by ^{1}H and ^{13}C NMR spectroscopy. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 5.92 (d, J = 10.0 Hz, 1 H, C=C*H*), 4.03 (t, J = 8.0 Hz, 1 H, OCH_CH$_D$), 3.96–3.85 (m, 1 H, OCH_AH$_B$), 3.60 (t, J = 8.5 Hz, 1 H, OCH$_A$$H_B$), 3.27 (dd, J = 8.5 and 8.0 Hz, 1 H, OCH$_C$$H_D$), 3.40–2.90 (m, 1 H, OCH$_2$C*H*CH), 2.59–2.43 (m, 1 H, OCH$_2$C*H*CH$_3$), 0.93 (d, J = 7.0 Hz, 3 H, CH$_3$) ppm. ^{13}C NMR (67.9 MHz, $CDCl_3$): δ = 144.2 (C_{ipso}, aromatic), 141.9 (CH=*C*), 139.9 (C_{ipso}, aromatic), 129.8 (4×*C*H, aromatic), 128.1 (4×*C*H, aromatic), 127.1 (2×*C*H, aromatic), 126.8 (C=*C*H), 75.2 (O*C*H$_2$CHCH$_3$), 73.4 (O*C*H$_2$CHCH), 49.4 (OCH$_2$*C*HCH), 41.7 (OCH$_2$*C*HCH$_3$), 15.1 (*C*H$_3$) ppm.

Supporting Information (see footnote on the first page of this article). Experimental procedures and spectroscopic data for **11**, **12** and **21**. Compounds **13** and **14** were prepared using the same approach as outlined for **11** and **12**, respectively.

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