The Synthesis of δ-Hydroxy Allylic Phosphine Oxides by Palladium(II)-catalysed Allylic Acetate Transposition

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Palladium(II)-catalysed allylic acetate transposition, when driven by the diphenylphosphinoyl (Ph_2PO) group, is regiospecific (acetate moves away from the Ph_2PO group), stereoselective (the new double bond is *E*), and stereospecific (the acetate moves *supra*facially across the allyl system). The rearranged acetates can be hydrolysed to δ-hydroxy allylic phosphine oxides which are useful intermediates in a variety of synthetic methods.

We have used allylic phosphine oxides in the stereocontrolled synthesis of allylic[1] and homoallylic[2] alcohols, allylic sulfides[1] and homoallylic amines.[3] Stereocontrolled syntheses of dienols,[4,5] alkenyl β-hydroxy sulfides,[6] unsaturated α-amino acids,[7] and alkenyl oxazolidinones[8] have made use of allylic phosphine oxides bearing an allylic hydroxy group (δ-hydroxy allylic phosphine oxides). This paper describes the synthesis of δ-hydroxy allylic phosphine oxides by stereospecific, *E*-stereoselective palladium(II)-catalysed transposition of allylic acetates, driven by the diphenylphosphinoyl group.[9]

Our published route to the title compounds makes use of either an acid-catalysed allylic rearrangement and acetylation[4] of an allylic alcohol or a thermal rearrangement of an allylic nitrobenzoate ester.[10] Because of the cationic transition states of these reactions, some important substitution patterns do not rearrange even under the vigorous conditions of the reaction, which generally produce large amounts of eliminated by-products. In contrast, Overman's palladium(II)-catalysed method[11] for the rearrangement of allylic acetates has allowed us to make a broader range of the title compounds under mild conditions (at room temperature or in refluxing THF) in a matter of minutes to hours, and requiring less than 10 mol% catalyst.

Lithiated methyldiphenylphosphine oxide **1** (R^1 = H) was added to unsaturated aldehydes **2a–f**, to give the allylic alcohols **3a–f**. These were acetylated (acetic anhydride, pyridine) and the allylic acetates **4a–f** stirred at room temperature with 5–10 mol% bis(acetonitrile) palladium(II) chloride in dry THF.[11,12]† **Table 1** presents the results of these reactions.

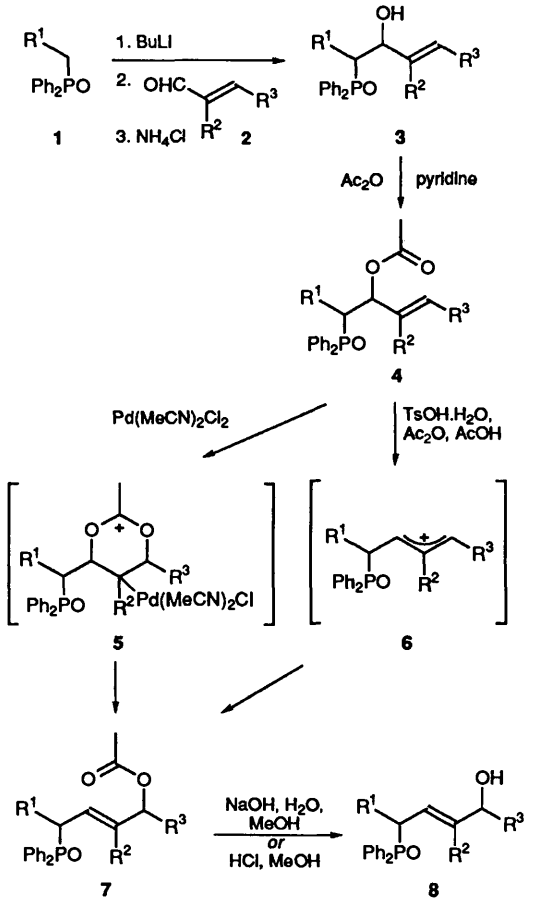
Rearrangements of the acetates **4a–c**, which all have R^2 = H, proceeded in high yield, with the completely unsubstituted **7a** being formed somewhat more slowly than monosubstituted **7b** or **7c**.‡ Acetates **4d–f**, which have an alkyl substituent R^2 on the central carbon atom of the allyl group, did not rearrange under these conditions, however. For comparison with these palladium(II)-catalysed rearrangements, allylic transposition of the allylic alcohols **3a–f** was also attempted by acid-catalysed acetylation.[4,14] The results of treating allylic alcohols **3a–f** with toluene-*p*-sulfonic acid and acetic anhydride in acetic acid are shown in Table 2.[15]

For the palladium(II)-catalysed rearrangements to be successful, the only requirement is that R^2 = H. The unreactivity of **4d–f** can be ascribed (as the unreactivity of similarly medially-substituted allylic esters has been)[16–18] to the instability of the σ-complex **5**, which, when $R^2 \neq$ H, is a tertiary alkylpalladium species. Importantly, the palladium-catalysed reaction allows rearrangement of unsubstituted, unbranched allylic acetates like **4a**. The acid-catalysed acetylation, on the other hand, is not a

Table 1 Synthesis and rearrangement of allylic acetates **4** with Pd^{II}

Entry	R^1	R^2	R^3	Yield **3** (%)	Yield **4** (%)	Yield **7** (%)
a	H	H	H	60	80	76
b	H	H	Me	76	98	87
c	H	H	Pr	71	98	75
d	H	Me	Me	81	88	7[a]
e	H	Me	H	78	94	0[a]
f	H	Bu	H	45	85	0[a]

[a] By NMR. Remainder was unrearranged acetate **4**.



† For a review on Pd^{II}-catalysed allylic transpositions, see ref. 12.

‡ We suggest that this surprising observation is due to the greater stability of the terminal alkene's palladium(II) complex. Mercury(II) salts have been used to favour the contrathermodynamic product in alkene equilibrations by preferentially complexing with the less hindered terminal isomer.

Table 2 Acid-catalysed acetylation of allylic alcohols **3**

Entry	R^1	R^2	R^3	Yield **7** (%)
a	H	H	H	12[a,b]
b	H	H	Me	83[c]
c	H	H	Pr	68
d	H	Me	Me	74
e	H	Me	H	9[a]
f	H	Bu	H	9[a]

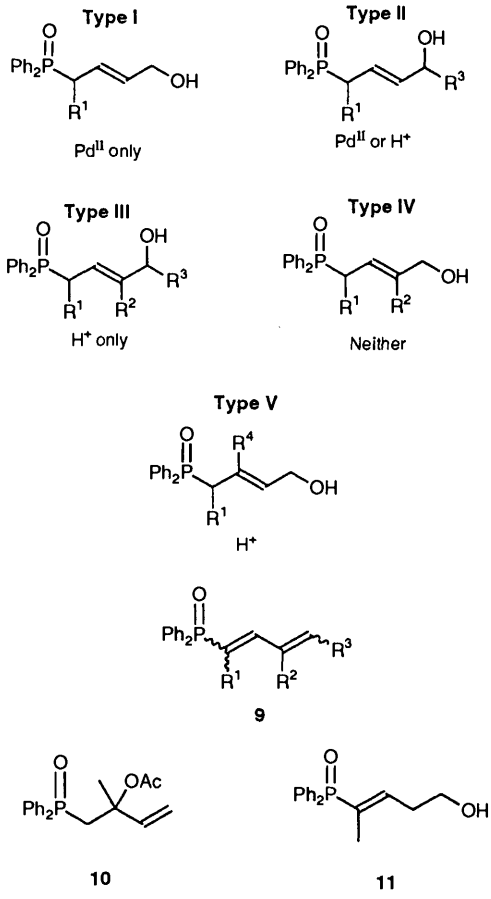
[a] By ^{1}H NMR. Remainder unrearranged acetylated starting material **4**. [b] TsOH (1.1 equiv.), 60 °C, 24 h. [c] From ref. 5.

Table 3 Hydrolysis of rearranged allylic acetates **7**

Entry	Starting material **7**	R^1	R^2	R^3	Method	Yield **8** (%)
1	**a**	H	H	H	A	85
2	**b**	H	H	Me	A	71[a]
3	**b**	H	H	Me	B	64[a]
4	**b**	H	H	Me	C	71[a]
5	**b**	H	H	Me	D	0[b]
6	**b**	H	H	Me	E	50[a]
7	**b**	H	H	Me	F	99[c]
8	**c**	H	H	Pr	A	69
9	**d**	H	Me	Me	A	81

[a] Diene **9b** detected by TLC. [b] Diene **9b** only product by NMR. [c] None of diene **9b** could be detected by TLC.

Methods: A, NaOH, H_2O, MeOH; B, K_2CO_3, MeOH; C, K_2CO_3, H_2O, MeOH; D, LiOH, H_2O, THF; E, LiO_2H, H_2O, THF; F, HCl, MeOH



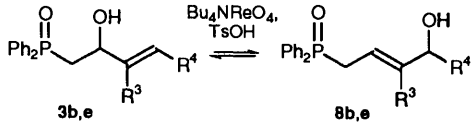
successful route to rearranged acetate **7a**, nor to **7e** or **7f**. With this method, only compounds with $R^3 \neq H$ rearrange. When $R^3 = H$, the rearrangement is very slow because the allyl cation intermediate[19] **6** is insufficiently stabilised by electron-donating alkyl groups. Alkyl groups at R^2 (Table 2, entries **e** and **f**) cannot stabilise the allyl cation **6** because they are too close to the node of its LUMO.

Allylic alcohol or ester rearrangements are usually successful only when driven by an increase in the number of substituents on the double bond or by a shift into conjugation.[12,17] In this case neither of these forces is acting, and it must be the diphenylphosphinoyl group which is driving the rearrangements, since **4b** and **7b**, and **4c** and **7c**, both have the same number of substituents on their double bonds. This is probably a steric effect. Palladium(II)-catalysed rearrangements of allylic acetates are known[20] with only very small differences in steric crowding between the two allylic regioisomers.

The rearranged allylic acetates **7a–f** were readily hydrolysed under basic conditions (K_2CO_3, MeOH or NaOH, H_2O, MeOH) to the allylic alcohols **8a–f**, which are the title δ-hydroxy allylic phosphine oxides (Table 3). In most cases, an appreciable amount of the dienes **9** was also formed by base-catalysed elimination. We therefore now prefer an acid-catalysed method (conc. HCl, MeOH) for the hydrolysis of these esters. The yield of alcohol **8b** was substantially improved, and the by-products **9** were not formed, when this method was used to hydrolyse the acetate **7b** (Table 3, entry 7).

Our two routes to δ-hydroxy allylic phosphine oxides **8a–f**, palladium(II)-catalysed rearrangement or acid-catalysed acetylation, are usefully complementary. We can divide the substitution patterns of the product δ-hydroxy allylic phosphine oxides **8** into 5 types, illustrated as Type I–Type V. Type I (the unsubstituted series, which has proved the most valuable in further synthetic applications)[7,8] is available only by palladium(II)-catalysed rearrangement, and Type III only by acid-catalysed acetylation. Type II is available by either method, and Type IV by neither. Type V has been made by acid-catalysed acetylation, but our attempts to make similar compounds by palladium(II)-catalysed rearrangement were thwarted by difficulties in making the hindered tertiary acetate **10** under basic conditions.

It was also possible (Table 4) to transpose alcohol **3b** to **8b** using Bu_4NReO_4[21] (entry 1) or a palladium-catalysed allylic Mitsunobu displacement (entry 2).[22] Allylic alcohol **3e** did not rearrange using either of these methods (entries 3 and 4).



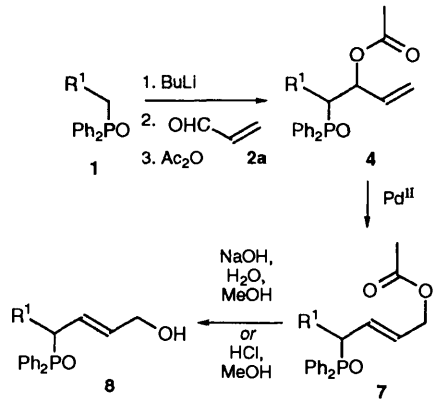
Several alkyldiphenylphosphine oxides **1** were lithiated and added to acrolein **2a** in the first step of the synthesis of some chiral δ-hydroxy allylic phosphine oxides. The product lithium alkoxides were quenched *in situ* with acetic anhydride to give the allylic acetates **4g–l** as mixtures of diastereoisomers. The dependence of the stereoselectivity in similar additions on the size of the R^1 group has been described:[23] the selectivity is lower with larger R^1. Treatment of each diastereoisomeric mixture of allylic acetates **4g–l** with $Pd(MeCN)_2Cl_2$ gave a single rearranged compound **7g–k** or a mixture of two diastereoisomers **7l**. These were hydrolysed, sometimes without further purification, to give allylic alcohols **8g–l**. The two diastereoisomers of **8l** were separated by HPLC. The results of these reactions are presented in Table 5.

As with the rearrangement of **4a**, rearrangement of these Type I allylic acetates was rather slow. Reactions carried out

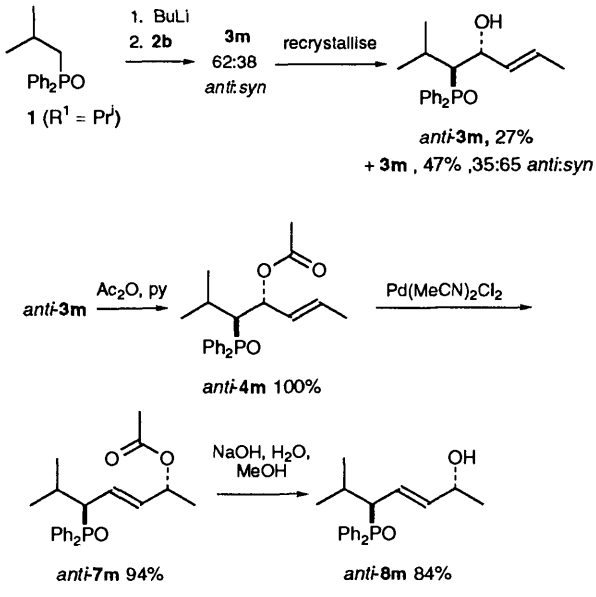
Table 4 Alternative methods for allylic transposition

Entry	Starting material 3	Method[a]	Ratio 8:3[b]
1	**b**	A	76:24
2	**b**	B	66:34
3	**e**	A	0:100
4	**e**	B	0:100

[a] A, Bu_4NReO_4, TsOH; B, (1) Ph_3P, DEAD, $Pd(MeCN)_2Cl_2$, AcOH; (2) HCl, MeOH. [b] By NMR analysis of the crude product mixture.



in refluxing THF were complete in hours rather than days, but at some cost to yield (entries 2 and 8). Hydrolysis of the rearranged acetates was most reliably accomplished with HCl in MeOH (entries 2 and 8). Base-catalysed hydrolyses of the unbranched allylic acetates **7g–i** were low-yielding because of a competing base-catalysed double-bond migration: **11** was a major by-product in the base-catalysed hydrolysis of **7g**. This was not a problem with the more hindered allylic acetates **7j**, **7k** and **7l**. The diastereoisomeric mixture of the acetates **7l** was



hydrolysed without separation and the alcohols *anti*-**8l** and *syn*-**8l** were separated by HPLC. The stereochemistry of the two diastereoisomers of **8l** was assigned from the crystal structure of an epoxide derivative.[8]

The stereospecificity of the rearrangement was exploited in the synthesis of *anti*-**8m**. 2-Methylpropyldiphenylphosphine oxide **1** (R^1 = Pr^i) was lithiated and added to crotonaldehyde to give a 62:38 mixture of diastereoisomers **3m**. Repeated fractional recrystallisation of this mixture eventually gave a sample of pure *anti*-**3m**. This was acetylated (acetic anhydride, pyridine), and the allylic acetate *anti*-**4m** treated with Pd $(MeCN)_2Cl_2$. In a matter of minutes at room temperature, only one diastereoisomer of rearranged product *anti*-**7m** was formed in high yield. Hydrolysis gave *anti*-**8m**. This stereospecific route to δ-hydroxy allylic phosphine oxides bearing 1,4-related chiral centres with an *anti* relationship is usefully complementary to the highly stereoselective route to such compounds bearing a *syn* relationship that we have already reported.[10] Other similar examples[9,24] have shown this palladium(II)-catalysed rearrangement to be completely stereospecific.

Experimental

General methods have been described.[3] Flash chromatography was carried out according to the method of Still, Kahn and Mitra.[25] ^{13}C NMR were assigned using the attached proton test which gives normal (marked +) or inverted (marked −) signals.

General Procedure for the Addition of Lithiated Alkyldiphenylphosphine Oxides **1** *to Aldehydes and Ketones* **2**.—Butyllithium (1.5–1.6 mol dm^{-3} solution in hexane) was added dropwise to a stirred solution of the alkyldiphenylphosphine oxide in dry THF (0.2 mol dm^{-3} in phosphine oxide) under nitrogen at a temperature between 0 °C and −70 °C until a persistent orange colour was obtained (generally after only a few drops). Further butyllithium (1.1 equiv.) was added dropwise, either by syringe or dropping funnel. The orange solution was cooled to −70 °C for 5–15 min. The aldehyde or ketone was added dropwise by syringe, or by distillation directly into the reaction flask. At the end of the addition, the colour faded or changed (to yellow, blue or green), and occasionally a fine precipitate formed. A slight excess of aldehyde, ketone or ester was added (a total of about 1.1 equiv. if added by syringe). The temperature was maintained at −70 °C for a further 10 min before the mixture was allowed to warm to 0 °C. Saturated aqueous ammonium chloride was added, the precipitate dissolved with a small amount of water, and most of the THF removed under reduced pressure. The aqueous suspension was extracted into dichloromethane (× 3), and the combined organic extracts were washed with saturated brine, dried (Na_2SO_4), and evaporated under reduced pressure to yield the crude product.

1-*Diphenylphosphinoylbut*-3-*en*-2-*ol* **3a**.—By the general method, methyldiphenylphosphine oxide **1** (R^1 = H) (10.64 g, 50 mmol) and acrolein distilled into the flask gave a crude product as an oil. Flash chromatography of this, eluting with EtOAc, gave the alcohol[4] **3a** (4.26 g, 52%) as a waxy solid which could not be recrystallised (Found: M^+, 272.0970. $C_{16}H_{17}O_2P$ requires *M*, 272.0966); R_f (EtOAc) 0.28; $\nu_{max}(CHCl_3)/cm^{-1}$ 3380 (OH), 1640 (C=C), 1440 (PPh) and 1140 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.3 (10 H, m, Ph_2PO), 5.82 (1 H, ddd, *J* 16.0, 10.4 and 5.5, C*H*=CH_2), 5.19 (1 H, dd, *J* 16.0 and 1.1, CH=CH_AH_B), 4.99 (1 H, dd, *J* 10.4 and 1.1, CH=CH_AH_B), 4.8 (1 H, br s, OH), 4.55 (1 H, m, C*H*OH) and 2.61–2.36 (2 H, ABXP, m, PCH_2); δ_C(100 MHz; $CDCl_3$) 140.1$^+$ ($^3J_{PC}$ 13.2, *C*H–CH_2), 134–128 (Ph_2PO), 114.6$^-$ (CH=CH_2), 67.7$^+$ ($^2J_{PC}$ 3.9, CHOH) and 36.6$^-$ ($^1J_{PC}$ 70.0, PCH_2); *m*/*z* 272 (13%, M^+), 216 (71, Ph_2POMe), 215 (100, Ph_2POCH_2), 202 (35, Ph_2POH) and 201 (54, Ph_2PO).

(E)-1-*Diphenylphosphinoylpent*-3-*en*-2-*ol* **3b**.—In the same way, methyldiphenylphosphine oxide **1** (R^1 = H) (10.64 g, 49 mmol) and crotonaldehyde gave a crude product as an oil. Flash chromatography, eluting with EtOAc, gave the alcohol[4]

Table 5 Synthesis of some δ-hydroxy allylic phosphine oxides

Entry	Product 8	R^1	Yield 4 (%)	Ratio of diastereoisomers of 4[a]	Yield 7 (%)	Yield 8 (%)	Yield 4→8 (%)
1	**g**	Me	70	85:15[b]			18[c]
2	**g**				65[d]	64[e]	42
3	**h**	Et	79	81:19[b]			31[c]
4	**i**	Pentyl	86	71:29[b]			18[c]
5	**j**	Pr^i	58	65:35[b]			55[c]
6	**j**				84	91	76
7	**k**	Cyclohexyl	89	68:32[b]			77[c]
8	**k**				42[d]	76[e]	32
9	**l**	Bu^i	73	51:31:10:8[f]	68	25 + 23[g]	17 + 16[g]

[a] By NMR. [b] *anti*:*syn*. [c] Intermediate **7** not isolated or purified. [d] Rearrangement carried out in refluxing THF. [e] Hydrolysed with HCl, MeOH. [f] *anti,anti*:*anti*, *syn*:*syn*, *anti*:*syn*. [g] *anti*-**8l** and *syn*-**8l** respectively.

3b (10.86 g, 76%) as prisms, m.p. 99.5–100.5 °C (from EtOAc) (lit.,[4] 102–103 °C), with spectroscopic data as previously reported.[4]

(E)-1-*Diphenylphosphinoylhept*-3-*en*-2-*ol* **3c**.—In the same way, methyldiphenylphosphine oxide **1** (R^1 = H) (8.68 g, 40 mmol) and hex-2-enal (5.2 cm^3, 45 mmol) gave a crude product as an oil. Chromatography on silica, eluting with 5:1 EtOAc–hexane, gave the *alcohol* **3c** (8.93 g, 71%) as a waxy solid which could not be recrystallised (Found: M^+, 314.1428. $C_{19}H_{23}O_2P$ requires *M*, 314.1435); R_F (EtOAc) 0.34; $\nu_{max}(CHCl_3)/cm^{-1}$ 3360 (OH), 1660 (C=C), 1435 (PPh) and 1140 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 5.60 (1 H, dt, *J* 15.4 and 6.5, CH=C*H*CH_2), 5.43 (1 H, dd, *J* 15.4 and 6.2, C*H*=CHCH_2), 4.53 (1 H, m, C*H*OH), 4.1 (1 H, br s, OH), 2.56 (1 H, ddd, *J* 14.6, 11.1 and 9.5, PCH_AH_B), 2.41 (1 H, ddd, *J* 14.9, 7.8 and 3.0, PCH_AH_B), 1.88 (2 H, q, *J* 7.2, CH=CHCH_2), 1.29 (2 H, sextet, *J* 7.3, CH_2Me) and 0.81 (3 H, t, *J* 7.3, Me); δ_C(100 MHz; $CDCl_3$) 134–128 (Ph_2PO and C=C), 67.8$^+$ ($^2J_{PC}$ 4.1, CHOH), 37.0$^-$ ($^1J_{PC}$ 68.8, PCH_2), 34.1$^-$ (*C*H_2CH$_2$Me), 22.0$^-$ (*C*H_2Me) and 13.7$^+$ (Me); *m*/*z* 314 (6%, M^+), 296 (20, M − H_2O), 216 (62, Ph_2POMe), 215 (100, Ph_2POCH_2), 202 (47, Ph_2POH) and 201 (57, Ph_2PO).

(E)-1-*Diphenylphosphinoyl*-3-*methylpent*-3-*en*-2-*ol* **3d**.—In the same way, methyldiphenylphosphine oxide **1** (R^1 = H) (8.65 g, 40 mmol) and 2-methylbut-2-enal (4.4 cm^3, 46 mmol) gave a crude product as a solid. Recrystallisation from EtOAc gave the *alcohol* **3d** (9.77 g, 81%) as plates, m.p. 146–148 °C (from EtOAc) (Found: C, 72.0 H, 7.0; P. 10.5%; M^+, 300.1284. $C_{18}H_{21}O_2P$ requires C, 72.2; H, 7.1; P, 10.7%; *M*, 300.1288); R_F (EtOAc) 0.30; $\nu_{max}(CHCl_3)/cm^{-1}$ 3370 (OH), 1440 (PPh) and 1140 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 5.48 (1 H, dq, *J* 1 and 6.7, C*H*Me), 4.45 (1 H, dt, *J* 2.3 and 10.2, C*H*OH), 4.0 (1 H, br s, OH), 2.59 (1 H, ddd, *J* 14.9, 11.9 and 10.2, PCH_AH_B), 2.38 (1 H, ddd, *J* 14.9, 7.4 and 2.3, PCH_AH_B), 1.58 (3 H, d, *J* 1.0, CH=C*Me*) and 1.53 (3 H, d, *J* 6.7, CH*Me*); δ_C(100 MHz; $CDCl_3$) 136.8$^-$ ($^3J_{PC}$ 12.0, CH=*C*), 134–128 (Ph_2PO), 120.9$^+$ (*C*HMe), 72.2$^+$ ($^2J_{PC}$ 4.0, CHOH), 35$^-$ ($^1J_{PC}$ 69.0, PCH_2), 12.9$^+$ and 11.3$^+$ (Me × 2); *m*/*z* 300 (9%, M^+), 282 (16, M − H_2O), 216 (48, Ph_2POMe), 215 (100, Ph_2POCH_2), 202 (63, Ph_2POH) and 201 (63, Ph_2PO).

1-*Diphenylphosphinoyl*-3-*methylbut*-3-*en*-2-*ol* **3e**.—In the same way, methyldiphenylphosphine oxide **1** (R^1 = H) (12.93 g, 60 mmol) and methacrolein (5.9 cm^3, 71 mmol) gave a crude product as a solid. Recrystallisation from EtOAc gave the *alcohol* **3e** as minute prisms, m.p. 107–108 °C (from EtOAc) (Found: C, 71.2; H, 67.5; P, 10.7%; M^+, 286.1109. $C_{17}H_{19}O_2P$ requires C, 71.3; H, 6.6; P, 10.8%; *M*, 286.1122); R_F(EtOAc) 0.29; $\nu_{max}(CHCl_3)/cm^{-1}$ 3400 (OH), 1630 (C=C), 1430 (PPh) and 1140 (P=O); δ_H(400 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 4.98 (1 H, s, C=CH_AH_B), 4.80 (1 H, s, C=CH$_A$$H_B$), 4.48 (1 H, t, *J* 10.2, C*H*OH), 4.0 (1 H, br s, OH), 2.55 (1 H, dt, *J* 14.9 and 10.7, PCH_AH_B), 2.43 (1 H, ddd, *J* 14.9, 7.7 and 1.8, PCH$_A$$H_B$) and 1.71 (3 H, s, Me); δ_C(100 MHz; $CDCl_3$) 146.2$^-$ ($^3J_{PC}$ 13.0, C=*C*Me), 134–128 (Ph_2PO), 111.2$^-$ (C=*C*H_2), 70.4$^+$ ($^2J_{PC}$ 4.5, CHOH), 35.2$^-$ ($^1J_{PC}$ 69.6, PCH_2) and 17.7$^+$ (Me); *m*/*z* 286 (M^+, 9%), 245 (19, Ph_2POCH_2CHOH), 216 (79, Ph_2POMe), 215 (100, Ph_2POCH_2), 202 (33, Ph_2POH) and 201 (49, Ph_2PO).

3-*Butyl*-1-*diphenylphosphinoylbut*-3-*en*-2-*ol* **3f**.—In the same way, methyldiphenylphosphine oxide **1** (R^1 = H) (10.76 g, 50 mmol) and 2-butylacrolein (6.35 g, 57 mmol) gave a crude product as an oil. Flash chromatography of this on silica, eluting with 10:1 EtOAc–hexane, gave the *alcohol* **3f** (7.45 g, 45%) as prisms, m.p. 65–66 °C (from EtOAc) (Found: C, 73.3; H, 7.8; P, 9.4%; M^+, 328.1597. $C_{20}H_{25}O_2P$ requires C, 73.15; H, 7.7; P, 9.4; *M*, 328.1602); R_F (EtOAc) 0.39; $\nu_{max}(CHCl_3)/cm^{-1}$ 3380 (OH), 1640 (C=C), 1430 (PPh) and 1140 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 5.08 (1 H, s, C=CH_AH_B), 4.82 (1 H, s, C=CH$_A$$H_B$), 4.49 (1 H, dt, *J* 2.8, 10.1, C*H*OH), 4.1 (1 H, br s, OH), 2.6–2.4 (2 H, ABXP m, PCH_2), 2.1–1.8 (2 H, m, CH_2=CCH_2), 1.4–1.2 (4 H, m, CH_2CH_2Me) and 0.84 (3 H, t, *J* 7.0, Me); δ_C(100 MHz; $CDCl_3$) 150.7$^-$ ($^3J_{PC}$ 12.2, *C*=CH_2), 134–128 (Ph_2PO), 109.6$^-$ (C=*C*H_2), 69.6$^+$ ($^2J_{PC}$ 4.3, CHOH), 35.8$^-$ ($^1J_{PC}$ 69.3, PCH_2), 31.1$^-$ (CH_2=*C*CH_2), 29.9$^-$ (*C*H_2CH$_2$-Me), 22.5$^-$ (*C*H_2Me) and 14.0$^+$ (Me); *m*/*z* 328 (19%, M^+), 310 (9, M − H_2O), 285 (25, M − C_3H_8), 245 (35, Ph_2POCH_2CHOH), 216 (62, Ph_2POMe), 215 (100, Ph_2POCH_2), 202 (55, Ph_2POH) and 201 (76, Ph_2PO).

(4RS,5SR)-(E)-5-*Diphenylphosphinoyl*-6-*methylhept*-2-*en*-4-*ol* anti-**3m**.—In the same way, (2-methylpropyl)diphenylphosphine oxide **1** (R^1 = Pr^i) (12.97 g, 50.2 mmol) and freshly distilled crotonaldehyde gave a crude product as a solid (16.82 g, quantitative). This was a 62:38 mixture (by ^{1}H NMR) of diastereoisomers *anti*-**3m** and *syn*-**3m**, which could not be separated by HPLC (eluting with 3:2 EtOAc–hexane). Repeated recrystallisation from ethyl acetate eventually gave the pure *alcohol anti*-**3m** (4.420 g, 27%) as prisms, m.p. 146.5–147.5 °C (from EtOAc) (Found: C, 73.2; H, 7.75; P, 9.5%; M^+, 328.1615. $C_{20}H_{25}O_2P$ requires C, 73.15; H, 7.7; P, 9.4%; *M*, 328.1638); R_F (EtOAc) 0.42; $\nu_{max}(CHCl_3)/cm^{-1}$ 3400 (OH), 1430 (PPh) and 1165 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 5.66 (1 H, ddq, *J* 15.3, 1.4 and 6.3, C=C*H*Me), 5.48 (1 H, ddd, *J* 15.3, 5.1 and 1.2, C*H*=CHMe), 4.65 (1 H, dddd, *J* 9.7, 5.1, 2.3 and 1.5, C*H*OH), 4.0 (1 H, br s, OH), 2.37 (1 H, dt, *J* 9.3 and 2.5, PCH), 2.3 (1 H, m, C*H*Me$_2$), 1.61 (3 H, d × fine m, *J* 6.2, C=CH*Me*), 1.12 (3 H, d, *J* 7.0, CH*Me*$_A$Me$_B$) and 0.98

(3 H, d, *J* 7.0, $CHMe_AMe_B$); δ_C(100 MHz; $CDCl_3$) 135–126 (Ph_2PO and C=C), 71.6$^+$ (CHOH), 48.6$^+$ ($^1J_{PC}$ 66.4, PCH), 26.2$^+$ ($CHMe_2$), 23.4$^+$ ($^3J_{PC}$ 9.7, $CHMe_AMe_B$), 23.1$^+$ (C=CH*Me*) and 17.6$^+$ ($CHMe_AMe_B$); *m/z* 328 (1%, M$^+$), 311 (2, M − OH), 285 (2.5, M − C_3H_7), 258 (29, $Ph_2POCH_2CHMe_2$), 243 (100, Ph_2POCH_2CO), 202 (19, Ph_2POH) and 201 (25, Ph_2PO).

General Procedure for the Acetylation of Allylic Alcohols **3**.—The alcohol (1 mmol) was dissolved in pyridine (2.5 cm^3) and acetic anhydride (2.5 cm^3) and the solution stirred under nitrogen for 2 h. The reaction mixture was then diluted with ethyl acetate (25 cm^3) and washed with 2 mol dm^{-3} hydrochloric acid (20 cm^3 × 3), saturated aqueous sodium hydrogen carbonate, 20% aqueous copper sulfate and brine. The organic fractions were dried ($MgSO_4$) and evaporated under reduced pressure to yield a crude product.

1-*Diphenylphosphinoylbut*-3-*en*-2-*yl Acetate* **4a**.—By the general method, the alcohol **3a** (1.090 g, 4.0 mmol) gave a crude product which was purified by flash chromatography, eluting with 4:1 EtOAc–hexane, to yield the acetate[4] **4a** (1.004 g, 80%), as needles, m.p. 124–127 °C (from EtOAc) (lit.,[4] 121–122 °C), with spectroscopic data as previously reported.[4]

(E)-1-*Diphenylphosphinoylpent*-3-*en*-2-*yl Acetate* **4b**.—In the same way, the alcohol **3b** (507.6 mg, 1.02 mmol) gave the *acetate* **4b** (570 mg, 98%) as needles, m.p. 112–114 °C (from EtOAc) (Found: C, 69.55; H, 6.4; P, 9.2%; M$^+$, 328.1200. $C_{19}H_{21}O_3P$ requires C, 69.5; H, 6.45; P. 9.4%; *M*, 328.1228); R_F(EtOAc) 0.31; $\nu_{max}(CHCl_3)/cm^{-1}$ 1710 (C=O), 1430 (PPh) and 1150 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.3 (10 H, m, Ph_2PO), 5.7–5.4 (3 H, m, OCHCH=CH), 2.79 (1 H, ddd, *J* 15.2, 7.6 and 6.1, PCH_AH_B), 2.58 (1 H, ddd, *J* 14.9, 12.7 and 5.4, PCH_AH_B), 1.63 (3 H, s, Ac) and 1.56 (3 H, dd, *J* 6.3 and 1, CH*Me*); δ_C(100 MHz; $CDCl_3$) 169.6$^-$ (C=O), 134–128 (Ph_2PO and C=C), 69.6$^+$ (*C*HOAc), 35.2$^-$ ($^1J_{PC}$ 69.3, PCH_2), 20.7$^+$ (O=C*Me*) and 17.6$^+$ (C=C*Me*); *m/z* 328 (4%, M$^+$), 285 (12, M − Ac), 269 (93, M − OAc), 215 (22, Ph_2POCH_2), 202 (43, Ph_2POH) and 201 (100, Ph_2PO).

(E)-1-*Diphenylphosphinoylhept*-3-*en*-2-*yl Acetate* **4c**.—In the same way, the alcohol **3c** (626.3 mg, 2.0 mmol) gave the *acetate* **4c** (695.7 mg, 98%) as needles, m.p. 95–96 °C (from EtOAc) (Found: C, 70.6; H, 7.2; P. 8.6%; M$^+$, 356.1561. $C_{21}H_{25}O_3P$ requires C, 70.8; H, 7.05; P, 8.7%; *M*, 356.1541); R_F (EtOAc) 0.49; $\nu_{max}(CHCl_3)/cm^{-1}$ 1715 (C=O), 1665 (C=C), 1430 (PPh) and 1150 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 5.7–5.4 (3 H, m, OCHCH=CH), 2.83 (1 H, dd, *J* 15.2 and 8.3, PCH_AH_B), 2.61 (1 H, ddd, *J* 15.2, 13.2 and 5.2, PCH_AH_B), 1.88 (2 H, q, *J* 7.0, C=CHCH_2), 1.63 (3 H, s, Ac), 1.29 (2 H, sextet, *J* 7.5, CH_2Me) and 0.82 (3 H, t, *J* 7.3, CH_2Me); δ_C(100 MHz; $CDCl_3$) 169.5$^-$ (C=O), 135.1$^+$ (CH=*C*HCH$_2$), 134–128 (Ph_2PO), 127.6$^+$ ($^3J_{PC}$ 8.1, *C*H=CHCH$_2$), 69.8$^+$ (*C*HOAc), 35.2$^-$ ($^1J_{PC}$ 69.6, PCH_2), 34.0$^-$ (CH=CH*C*H$_2$), 21.7$^-$ (CH_2Me), 20.6$^+$ (O=C*Me*) and 13.5$^+$ (CH_2Me); *m/z* 356 (5%, M$^+$), 313 (17, M − Ac), 297 (100, M − OAc), 296 (19, M − AcOH), 215 (18, Ph_2POCH_2), 202 (57, Ph_2POH) and 201 (95, Ph_2PO).

(E)-1-*Diphenylphosphinoyl*-3-*methylpent*-3-*en*-2-*yl Acetate* **4d**.—In the same way, the alcohol **3d** (347.8 mg, 1.16 mmol) gave the *acetate* **4d** (350.2 mg, 88%) as prisms, m.p. 112–117 °C (from EtOAc) (Found: C, 70.3; H, 6.65; P, 9.3%; M$^+$, 342.1362. $C_{20}H_{23}O_3P$ requires C, 70.2; H, 6.75; P, 9.05%; *M*, 342.1385); R_F(EtOAc) 0.31; $\nu_{max}(CHCl_3)/cm^{-1}$ 1720 (C=O), 1440 (PPh) and 1150 (P=O); δ_H(400 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 5.59 (1 H, dt, *J* 5.1 and 8.5, C*H*OAc), 5.49 (1 H, q, *J* 6.6, C*H*Me), 2.80 (1 H, dt, *J* 15.1, 8.8, PCH_AH_B), 2.50 (1 H, ddd, *J* 15.1, 13.3 and 4.9, PCH_AH_B), 1.66 (3 H, s, Ac), 1.53 (3 H, s, CH=C*Me*) and 1.47 (3 H, d, *J* 6.6, CH*Me*); δ_C(100 MHz; $CDCl_3$) 169.4$^-$ (C=O), 134–128 (Ph_2PO and *C*=CHMe), 124.2$^+$ (C=*C*HMe), 73.6$^+$ (*C*HOAc), 33.9$^-$ ($^1J_{PC}$ 69.4, PCH_2), 20.7$^+$ (O=C*Me*), 13.0$^+$ and 11.2$^+$ (*Me*C=CH*Me*); *m/z* 342 (11%, M$^+$), 299 (5, M − Ac), 283 (48, M − OAc), 282 (30, M − AcOH), 215 (13, Ph_2POCH_2), 202 (71, Ph_2POH) and 201 (100, Ph_2PO).

1-*Diphenylphosphinoyl*-3-*methylbut*-3-*en*-2-*yl Acetate* **4e**.—In the same way, the alcohol **3e** (296.6 mg, 1.04 mmol) gave the *acetate* **4e** (318 mg, 94%) as prisms, m.p. 121–122 °C (from EtOAc) (Found: C, 69.7; H, 6.45; P. 9.4%; M$^+$, 328.1225. $C_{19}H_{21}O_3P$ requires C, 69.5; H, 6.45; P. 9.4%; *M*, 328.1229); R_F (EtOAc) 0.32; $\nu_{max}(CHCl_3)/cm^{-1}$ 1720 (C=O), 1645 (C=C), 1440 (PPh) and 1150 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 5.60 (1 H, dd, *J* 9.2 and 3.8, C*H*OAc), 4.93 (1 H, s, $C=CH_AH_B$), 4.85 (1 H, s, $C=CH_AH_B$), 2.79 (1 H, ddd, *J* 15.1, 9.5 and 7.5, PCH_AH_B), 2.53 (1 H, ddd, *J* 15.2, 14.1 and 3.9, PCH_AH_B), 1.72 (3 H, s, CH_2=C*Me*) and 1.62 (3 H, s, Ac); δ_C(100 MHz; $CDCl_3$) 169.3$^-$ (C=O), 142.7$^-$ ($^3J_{PC}$ 9.4, *C*=CH$_2$), 134–128 (Ph_2PO), 113.4$^-$ (C=*C*H$_2$), 71.4$^+$ (*C*HOAc), 34.1$^-$ ($^1J_{PC}$ 69.2, PCH_2), 20.5$^+$ (O=C*Me*) and 17.8$^+$ (CH_2=C*Me*); *m/z* 328 (2.5%, M$^+$), 285 (3.5 M − Ac), 269 (100, M − OAc), 215 (16, Ph_2POCH_2), 202 (35, Ph_2POH) and 201 (88, Ph_2PO).

3-*Butyl*-1-*diphenylphosphinoylbut*-3-*en*-2-*yl Acetate* **4f**.—In the same way, the alcohol **3f** (325.0 mg, 1.0 mmol) gave the *acetate* **4f** (315 mg, 85%) as needles, m.p. 125–125.5 °C (from EtOAc) (Found: C, 71.55; H, 7.55; P. 8.5%; M$^+$, 370.1694. $C_{22}H_{27}O_3P$ requires C, 71.35; H, 7.35; P. 8.35%; *M*, 370.1698); R_F (EtOAc) 0.39; $\nu_{max}(CHCl_3)/cm^{-1}$ 1720 (C=O), 1640 (C=C), 1430 (PPh) and 1150 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 5.59 (1 H, dt, *J* 3.2 and 9.6, C*H*OAc), 4.98 (1 H, s, $C=CH_AH_B$), 4.83 (1 H, s, $C=CH_AH_B$), 2.75 (1 H, ddd, *J* 15.9, 9.7 and 7.4, PCH_AH_B), 2.52 (1 H, dt, *J* 3.4 and 14.6, PCH_AH_B), 1.98 (2 H, t, CH_2=CCH_2), 1.58 (3 H, s, Ac), 1.4–1.2 (4 H, m, CH_2CH_2Me) and 0.85 (3 H, t, *J* 7.0, Me); δ_C(100 MHz; $CDCl_3$) 169.2$^-$ (C=O), 147.8$^-$ ($^3J_{PC}$ 9.4, *C*=CH$_2$), 134–128 (Ph_2PO), 111.3$^-$ (C=*C*H$_2$), 70.8$^+$ ($^2J_{PC}$ 3.3, *C*HOAc), 34.6$^-$ ($^1J_{PC}$ 68.9, PCH_2), 31.3$^-$ (CH_2=C*C*H$_2$), 29.6$^-$ (CH_2CH_2Me), 22.4$^-$ (CH_2Me), 20.5$^+$ (O=C*Me*) and 13.9$^+$ (Me); *m/z* 370 (5%, M$^+$), 311 (100, M − OAc), 215 (11, Ph_2POCH_2), 202 (59, Ph_2POH) and 201 (97, Ph_2PO).

(4RS,5SR)-(E)-5-*Diphenylphosphinoyl*-6-*methylhept*-2-*en*-4-*yl Acetate* anti **4m**.—In the same way, the alcohol *anti*-**3m** (2.92 g, 8.9 mmol) gave, after 22 h, and without further purification, the *acetate anti*-**4m** (3.34 g, 101%) as an unrecrystallisable glass (Found: M$^+$, 370.1686. $C_{22}H_{27}O_3P$ requires *M*, 370.1698); R_F (EtOAc) 0.50; $\nu_{max}(CDCl_3)/cm^{-1}$ 1725 (C=O), 1440 (PPh) and 1165 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 5.6–5.4 (3 H, m, C*H*=CH and C*H*OAc), 2.71 (1 H, m, PCH), 2.15 (1 H, m, C*H*Me$_2$), 1.62 (3 H, s, Ac), 1.41 (3 H, d, *J* 5.6, C=CH*Me*), 1.04 (3 H, d, *J* 7.0, $CHMe_AMe_B$), and 0.96 (3 H, d, *J* 7.1, $CHMe_AMe_B$); δ_C(100 MHz; $CDCl_3$) 169.5$^-$ (C=O), 136–128 (Ph_2PO and C=C), 73.4$^+$ (*C*HOAc), 46.6$^+$ ($^1J_{PC}$ 69.2, PCH), 27.4$^+$ (*C*HMe$_2$), 23.2$^+$ ($^3J_{PC}$ 12.2, $CHMe_AMe_B$), 21.0$^+$ (O=C*Me*), 19.7$^+$ (C=CH*Me*) and 17.5$^+$ ($CHMe_AMe_B$); *m/z* 370 (0.8%, M$^+$), 327 (2, M − Ac), 311 (42, M − OAc), 243 (27, Ph_2POCH_2CO), 202 (55, Ph_2POH) and 201 (100, Ph_2PO).

General Procedure for the Direct Synthesis of β-*Acetoxy Phosphine Oxides* **4** *from Alkyldiphenylphosphine Oxides* **1**.—Butyllithium (1.5–1.6 mol dm^{-3} solution in hexane; 36.5 cm^3, 55 mmol, 1.1 equiv.) was added, *via* a dropping funnel, to a stirred solution of the alkyldiphenylphosphine oxide (50 mmol) in dry

THF (250 cm^3) under nitrogen at −70 °C. The orange or red solution was stirred at −70 °C for 5–15 min. Acrolein was then distilled directly into the reaction flask until the colour of the solution had faded to pale yellow. The temperature was maintained at −70 °C for 30 min before addition of acetic anhydride (9.5 cm^3, 100 mmol, 2 equiv.) *via* the dropping funnel. After being stirred at −70 °C for a further 30 min, the mixture was allowed to warm to room temperature, often, a gelatinous white precipitate being formed. Water (100–250 cm^3) was added, and most of the THF removed under reduced pressure. The aqueous suspension was extracted into dichloromethane (×3), and the combined organic extracts were washed with saturated aqueous sodium hydrogencarbonate and saturated brine, dried (Na_2SO_4), and evaporated under reduced pressure to yield the crude product, which was purified by flash chromatography.

(3RS,4SR)-*and*(3RS,4RS)-4-*Diphenylphosphinoylbut*-1-*en*-3-*yl Acetate* anti- *and* syn-**4g**.—In this way, ethyldiphenylphosphine oxide **1** (R^1 = Me) (11.48 g, 49.9 mmol) gave, after flash chromatography, eluting with EtOAc, a mixture of the *acetates* **4g** (11.46 g, 70%; 85:15 *anti*:*syn* by ^{1}H NMR) as an oil (Found: M^+, 328.1201. $C_{19}H_{21}O_3P$ requires *M*, 328.1228); R_F (EtOAc) 0.33; δ_H(250 MHz; $CDCl_3$) 8.0–7.4 (10 $H^{anti+syn}$, m, Ph_2PO), 6.00 (1 H^{syn}, m, C*H*=CH_2), 5.93 (1 H^{anti}, ddd, *J* 16.9, 10.6 and 6.2, C*H*=CH_2), 5.6 (1 $H^{anti+syn}$, m, CHOAc), 5.3–5.1 (2 $H^{anti+syn}$, m, CH=CH_2), 2.92 (1 H^{syn}, m, CHP), 2.73 (1 H^{anti}, ddq, *J* 9.4, 3.2 and 7.3, CHP), 1.78 (3 H^{syn}, s, OAc), 1.69 (3 H^{anti}, s, OAc), 1.19 (3 H^{anti}, dd, *J* 16.0 and 7.4, CH*Me*) and 1.10 (3 H^{syn}, dd, *J* 15.9 and 7.2, CH*Me*); *m*/*z* 328 (0.8%, M^+), 269 (89, M − OAc), 230 (25, Ph_2POCH_2Me), 229 (20, $Ph_2POCHMe$), 219 (26, $Ph_2PO_2H_2$), 202 (52, Ph_2POH) and 201 (100, Ph_2PO).

(3RS,4SR)- *and* (3RS,4RS)-4-*Diphenylphosphinoylpent*-1-*en*-3-*yl Acetate* anti- *and* syn-**4h**.—In the same way, propyldiphenylphosphine oxide **1** (R^1 = Et) (9.009 g, 37.2 mmol) gave, after flash chromatography, eluting with EtOAc, a mixture of the *acetates* **4h** (10.01 g, 79%; 81:19 *anti*:*syn* by ^{1}H NMR) as an oil; R_F (EtOAc) 0.33 and 0.39; δ_H(250 MHz; $CDCl_3$) 8.0–7.4 (10 $H^{anti+syn}$, m, Ph_2PO), 6.20 (1 H^{anti}, ddd, *J* 17.5, 10.5 and 7.0, C*H*=CH_2), 6.09 (1 H^{syn}, m, C*H*=CH_2), 5.64 (1H^{anti}, d × fine m, *J* 19, C*H*OAc), 5.55 (1 H^{syn}, m, C*H*OAc), 5.3–5.15 (2 $H^{anti+syn}$, m, CH=CH_2), 2.75 (1 H^{syn}, m, CHP), 2.63 (1 H^{anti}, m, CHP), 2.2–1.7 (2 $H^{anti+syn}$, m, CH_2Me), 1.88 (3 H^{syn}, s, OAc), 1.59 (3 H^{anti}, s, OAc), 0.97 (3 H^{anti}, t, *J* 7.0, CH_2*Me*) and 0.86 (3 H^{syn}, t, *J* 7.0, $3H_2$*Me*).

(3RS,4SR)-*and*(3RS,4RS)-4-*Diphenylphosphinoyldec*-1-*en*-3-*yl Acetate* anti- *and* syn-**4i**.—In the same way, hexyldiphenylphosphine oxide **1** (R^1 = Pentyl) (12.44 g, 43.4 mmol) gave, after flash chromatography, eluting with 4:1 EtOAc–cyclohexane, a mixture of the *acetates* **4i** (14.29 g, 86%; 71:29 *anti*:*syn* by ^{1}H NMR) as an oil; R_F (EtOAc) 0.43 and 0.53; δ_H(250 MHz; $CDCl_3$) 8.0–7.4 (10 $H^{anti+syn}$, m, Ph_2PO), 6.20 (1 H^{anti}, ddd, *J* 17.0, 10.5 and 7.0, C*H*=CH_2), 6.08 (1 H^{syn}, m, C*H*=CH_2), 5.61 (1 H^{anti}, d × fine m, *J* 20, C*H*OAc), 5.6 (1 H^{syn}, m, C*H*OAc), 5.3–5.15 (2 $H^{anti+syn}$, m, CH=CH_2), 2.80 (1 H^{syn}, m, CHP), 2.68 (1 H^{anti}, m, CHP), 2.2–0.7 [11 $H^{anti+syn}$, m, $(CH_2)_2$Me], 1.89 (3 H^{syn}, s, OAc) and 1.58 (3 H^{anti}, s, OAc).

(3RS,4SR)- *and* (3RS,4RS)-4-*Diphenylphosphinoyl*-5-*methylhex*-1-*en*-3-*yl Acetate* anti- *and* syn-**4j**.—In the same way, (2-methylpropyl)diphenylphosphine oxide **1** (R^1 = Pr^i) (25.85 g, 100.0 mmol) gave, after recrystallisation from ethyl acetate, a mixture of the *acetates* **4j** (20.76 g, 58%; 65:35 *anti*:*syn* by ^{1}H NMR) as a waxy solid (Found: M^+, 356.1508. $C_{21}H_{25}O_3P$ requires *M*, 356.3542); R_F(EtOAc) 0.44 and 0.50; δ_H(250 MHz; $CDCl_3$) 8.0–7.4 (10 $H^{anti+syn}$, m, Ph_2PO), 6.21 (1 H^{anri}, ddd, *J* 17.1, 10.1 and 6.8, C*H*=CH_2), 5.96 (1 H^{syn}, ddd, *J* 16.6, 10.5 and 5.9, C*H*=CH_2), 5.71 (1 H^{anti}, d × fine m, *J* 18, C*H*OAc), 5.7 (1 H^{syn}, m, C*H*OAc), 5.2–5.05 (2 $H^{anti+syn}$, m, CH=CH_2), 2.80 (1 H^{syn}, m, CHP), 2.73 (1 H^{anti}, m, CHP), 2.3–2.0 (1 $H^{anti+syn}$, m, C*H*Me_2), 1.84 (3 H^{syn}, s, OAc), 1.72 (3 H^{anti}, s, OAc), 1.15 (3 H^{anti}, d, *J* 7, CH$Me_A$$Me_B$), 1.10 (3 H^{anti}, d, *J* 7, CH$Me_A$$Me_B$) and 1.04 (6 H^{syn}, d, *J* 7, CHMe_2); *m*/*z* 356 (6%, M^+), 355 (9, M − H), 297 (86, M − OAc), 255 (27, $Ph_2POC_4H_6$), 219 (20, $Ph_2PO_2H_2$), 202 (90, Ph_2POH) and 201 (100, Ph_2PO).

(3RS,4SR)- *and* (3RS,4RS)-4-*Cyclohexyl*-4-*diphenylphosphinoylbut*-1-*en*-3-*yl Acetate* anti- *and* syn-**4k**.—In the same way, (cyclohexylmethyl)diphenylphosphine oxide **1** (R^1 = cyclohexyl) (3.04 g, 10.0 mmol) gave, after flash chromatography, eluting with 3:1 EtOAc–hexane, a mixture of the *acetates* **4k** (3.51 g, 89%; 68:32 *anti*:*syn* by ^{1}H NMR) as an oil (Found: M^+, 396.1838. $C_{24}H_{29}O_3P$ requires *M*, 396.1854); R_F (EtOAc) 0.50; δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 $H^{anti+syn}$, m, Ph_2PO), 6.17 (1 H^{anti}, ddd, *J* 17.0, 10.6 and 6.7, C*H*=CH_2), 5.96 (1 H^{syn}, ddd, *J* 16.7, 10.5 and 5.7, C*H*=CH_2), 5.66 (1 H^{anti}, d × fine m, *J* 18.2, C*H*OAc), 5.6 (1 H^{syn}, m, C*H*OAc), 5.2–5.0 (2 $H^{anti+syn}$, m, CH=CH_2), 2.73 (1 H^{syn}, ddd, *J* 11.1, 4.7 and 3.0, CHP), 2.64 (1 H^{anti}, ddd, *J* 9.1, 3.7 and 3.0, CHP), 2.2–0.9 [11 $H^{anti+syn}$, m, $CH(CH_2)_5$], 1.83 (3 H^{syn}, s, OAc) and 1.72 (3 H^{anti}, s, OAc); *m*/*z* 396 (3%, M^+), 395 (3, M − H), 337 (92, M − OAc), 255 (85, $Ph_2POC_4H_6$), 202 (100, Ph_2POH) and 201 (82, Ph_2PO).

(3RS,4RS,5RS)-, (3RS,4RS,5SR)-, (3RS,4SR,5RS)- *and* (3RS,4SR,5SR)-4-*Diphenylphosphinoyl*-5-*methylhept*-1-*en*-3-*yl Acetate* **4l**.—In the same way, (2-methylbutyl)diphenylphosphine oxide **1** (R^1 = Bu^i) (1.5502 g, 5.69 mmol) gave, after flash chromatography, eluting with 3:1 EtOAc–hexane, a 51:31:10:8 (by ^{1}H NMR) mixture of the *acetates* **4l** (1.5396 g, 73%) as an oil (Found: M^+, 370.1685. $C_{22}H_{27}O_3P$ requires *M*, 370.1698); R_F (EtOAc) 0.54; *m*/*z* 370 (2%, M^+), 311 (25, M − AcO), 243 (21, Ph_2POCH_2CHO), 202 (40, Ph_2POH), 201 (50, Ph_2PO) and 69 (100).

General Procedure for the Rearrangement of Allylic Acetates **4** *under Palladium*(II) *Catalysis*.—Bis(acetonitrile)palladium(II) chloride (Aldrich Chemical Co.; 5–10 mol%) was added to a stirred solution of the acetate in dry THF (*ca.* 0.1 mol dm^{-3} in acetate) at room temperature under nitrogen. The red–brown mixture was stirred under nitrogen for between 1 h and 6 days, or refluxed under nitrogen for 3–5 h, until TLC showed near completion. Evaporation of the THF under reduced pressure yielded a crude brown product. Purified compounds could be freed from traces of yellow or brown colouration by passing them through a short column of alumina, type UG1.

(E)-4-*Diphenylphosphinoylbut*-2-*en*-1-*yl Acetate* **7a**.—In this way, the acetate **4a** (4.4961 g, 14.3 mmol) and $Pd(MeCN)_2Cl_2$ (187 mg, 0.72 mmol, 5.0 mol%) in THF (200 cm^3) gave, after being stirred at room temperature for 46 h, a crude product, which was purified by flash chromatography, eluting with EtOAc–5% hexane and then EtOAc, to yield the *acetate* **7a** (3.4035, g, 76%) as needles, m.p. 56–57 °C (from EtOAc) (Found: C, 68.6; H, 6.05; P. 9.8%; M^+, 314.1068. $C_{18}H_{19}O_3P$ requires C, 68.8; H, 6.1; P, 9.85%; *M*, 314.1072); R_F(EtOAc) 0.29; $\nu_{max}(CHCl_3)/cm^{-1}$ 1715 (C=O), 1660 (C=C), 1430 (PPh) and 1140 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.3 (10 H, m, Ph_2PO), 5.65 (2 H, m, CH=CH), 4.37 (2 H, t, *J* 4.5, CH_2OAc), 3.08 (2 H, dd, *J* 14.1 and 6.7) and 1.92 (3 H, s, Me); δ_C(100 MHz; $CDCl_3$) 170.5$^-$ (C=O), 133–128 (Ph_2PO), 130.2$^+$ ($^3J_{PC}$ 11.5, C=*C*CH_2-OAc), 123.8$^+$ ($^2J_{PC}$ 8.8, PCH_2*C*H=C), 64.2$^-$ (*C*H_2OAc), 34.7$^-$ ($^1J_{PC}$ 68.1, PCH_2) and 20.8$^+$ (Me); *m*/*z* 314 (20%, M^+), 254 (63, M − AcOH), 219 (41, $Ph_2PO_2H_2$), 202 (51, Ph_2POH) and 201 (100, Ph_2PO).

(E)-5-*Diphenylphosphinoylpent*-3-*en*-2-*yl Acetate* **7b**.—In the same way, the acetate **4b** (600.0 mg, 1.83 mmol) and $Pd(MeCN)_2Cl_2$ (40.0 mg, 0.154 mmol, 8.4 mol%) in THF (20 cm^3) gave, after being stirred at room temperature for 1 h, a crude product which was purified by flash chromatography, eluting with EtOAc, to yield the acetate[4] **7b** (520 g, 87%) as needles, m.p. 91–92 °C (from EtOAc) (Found: C, 69.6; H, 6.4; P. 9.65%; M^+, 328.1224. $C_{19}H_{21}O_3P$ requires C, 69.5; H, 6.45; P. 9.45%; *M*, 328.1228); R_F (EtOAc) 0.30; $\nu_{max}(CHCl_3)/cm^{-1}$ 1720 (C=O), 1660 (C=C), 1430 (PPh) and 1150 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 5.68 (1 H, dq, *J* 15.6 and 5.9, PCH_2CH=C), 5.48 (1 H, ddd, *J* 15.6, 6.1 and 4.5, C=C*H*CHOAc), 5.19 (1 H, d × quintet, *J* 2.2 and 6.3, C*H*OAc), 3.09 (2 H, ABXP m, PCH_2), 1.96 (3 H, s, Ac) and 1.13 (3 H, d, *J* 6.5, CH*Me*); δ_C(100 MHz; $CDCl_3$) 170.1$^-$ (C=O), 135.8$^+$ ($^3J_{PC}$ 11.5, *C*HCHO), 133–128 (Ph_2PO), 121.0$^+$ ($^2J_{PC}$ 8.9, PCH_2CH), 70.2$^+$ (*C*HOAc), 34.6$^-$ ($^1J_{PC}$ 68.0, PCH_2), 21.2$^+$ (O=C*Me*) and 19.9$^+$ (CH*Me*); *m*/*z* 328 (24%, M^+), 285 (15, M − Ac), 269 (28, M − OAc), 268 (19, M − AcOH), 219 (73, $Ph_2PO_2H_2$', 202 (45, Ph_2POH) and 201 (100, Ph_2PO).

(E)-1-*Diphenylphosphinoylhept*-2-*en*-4-*yl Acetate* **7c**.—In the same way, the acetate **4c** (424.8 mg, 1.20 mmol) and $Pd(MeCN)_2Cl_2$ (18.0 mg, 0.069 mmol, 5.8 mol%) in THF (9 cm^3) gave, after being stirred at room temperature for 2 h 40 min, a crude product which was purified by flash chromatography, eluting with 5:1 EtOAc–hexane and then EtOAc, to yield the *acetate* **7c** (316.6 mg, 75%) as needles, m.p. 84.5–85.5 °C (from EtOAc) (Found: C, 70.65; H, 7.25; P, 8.6%; M^+, 356.1525. $C_{21}H_{25}O_3P$ requires C, 70.75; H, 7.05; P. 8.7%; *M*, 356.1541); R_F (EtOAc) 0.44; $\nu_{max}(CHCl_3)/cm^{-1}$ 1715 (C=O), 1665 (C=C), 1440 (PPh) and 1145 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 5.63 (1 H, dq, *J* 15.5 and 7.0, PCH_2CH=C), 5.42 (1 H, ddd, *J* 15.5, 6.8 and 5.6, C=C*H*CHOAc), 5.07 (1 H, 6, *J* 6.5, C*H*OAc), 3.08 (2 H, ABXP m, PCH_2), 1.95 (3 H, s, Ac), 1.5–1.25 (2 H, m, CH_2CH_2Me), 1.1–1.0 (2 H, m, CH_2Me) and 0.78 (3 H, t, *J* 7.1, CH_2Me); δ_C(100 MHz; $CDCl_3$) 170.1$^-$ (C=O), 135.0$^+$ ($^3J_{PC}$ 11.6, C=*C*HCHOAc), 133–128 (Ph_2PO), 121.8$^+$ ($^2J_{PC}$ 8.9, PCH_2CH=C), 73.9$^+$ (*C*HOAc), 36.2$^-$ (CH_2CH_2Me), 34.7$^-$ ($^1J_{PC}$ 67.9, PCH_2), 21.2$^+$ (O=C*Me*), 18.0$^-$ (CH_2Me) and 13.7$^+$ (CH_2Me); *m*/*z* 356 (16%, M^+), 313 (13, M − Ac), 297 (34, M − OAc), 219 (47, Ph_2PO_2H), 202 (56, Ph_2POH) and 201 (100, Ph_2PO).

Attempted Rearrangement of the Acetate **4d**.—In the same way, the acetate **4d** (483.2 mg, 1.41 mmol) and $Pd(MeCN)_2Cl_2$ (27.6 mg, 0.106 mmol, 7.5 mol%) in THF (15 cm^3) gave, after being stirred at room temperature for 26 h, a crude product which was shown by ^1H NMR, to contain a 93:7 mixture of the unrearranged and rearranged acetates **4d** and **7d**.

Attempted Rearrangement of the Acetate **4e**.—In the same way, the acetate **4e** (252 mg, 0.768 mmol) and $Pd(MeCN)_2Cl_2$ (16.2 mg, 0.0624 mmol, 8.1 mol%) in THF (8 cm^3) gave, after being stirred at room temperature for 2 days, a crude product which was shown, by ^1H NMR, to consist solely of the unrearranged acetate **4e**.

Attempted Rearrangement of the Acetate **4f**.—In the same way, the acetate **4f** (150.1 mg, 0.406 mmol) and $Pd(MeCN)_2Cl_2$ (7.6 mg, 0.029 mmol, 7.2 mol%) in THF (4 cm^3) gave, after being stirred at room temperature for 24 h, a crude product which was shown, by ^1H NMR, to consist solely of the unrearranged acetate **4f**.

(E)-4-*Diphenylphosphinoylpent*-2-*en*-1-*yl Acetate* **7g**.—In the same way, the mixture of the acetates *anti*- and *syn*-**4g** (337 mg, 1.03 mmol) and $Pd(MeCN)_2Cl_2$ (22 mg, 0.085 mmol, 8.5 mol%) gave, after refluxing for 3 h, a crude product. Purification by flash chromatography, eluting with EtOAc, gave the *acetate* **7g** (217.9 mg, 65%) as an oil (Found: M^+, 328.1210. $C_{19}H_{21}O_3P$ requires *M*, 328.1228); R_F (EtOAc) 0.17; ν_{max}(film)/cm^{-1} 1730 (C=O), 1440 (PPh) and 1180 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 5.83 (1 H, ddd, *J* 15.5, 7.8 and 6.5, PCHC*H*=C), 5.59 (1 H, dq, *J* 16.2 and 5.3, C=C*H*CH_2O), 4.48 (2 H, ABX m, CH_2O), 3.26 (1 H, dqn, *J* 11.6 and 7.0, PCH), 2.06 (3 H, s, Ac) and 1.36 (3 H, dd, *J* 16.0 and 7.1, CH*Me*); δ_C(100 MHz; $CDCl_3$) 170.6$^-$ (C=O), 132–127 (Ph_2PO and C=C), 64.4$^-$ (CH_2O), 37.5$^+$ ($^1J_{PC}$ 68.1, PCH), 20.9$^+$ (O=C*Me*) and 12.7$^+$ ($^1J_{PC}$ 3.3, CH*Me*); *m*/*z* 328 (2%, M^+), 268 (10, M − AcOH), 219 (98, $Ph_2PO_2H_2$), 202 (32, Ph_2POH) and 201 (100, Ph_2PO).

In another experiment, the mixture of acetates *anti*- and *syn*-**4g** (5.31 g, 16.17 mmol) and $Pd(MeCN)_2Cl_2$ (360.9 mg, 1.39 mmol, 8.6 mol%) gave, after being stirred at room temperature for 18 h, a crude product which was hydrolysed without purification.

(E)-4-*Diphenylphosphinoylhex*-2-*en*-1-*yl Acetate* **7h**.—In the same way, the mixture of acetates *anti*- and *syn*-**4h** (10.01 g, 29.2 mmol) and $Pd(MeCN)_2Cl_2$ (598.7 mg, 2.31 mmol, 7.9 mol%) gave, after being stirred at room temperature for 66 h, a crude product which was partially purified by passage through a short column of silica (eluting with EtOAc) to remove polar impurities and remaining starting material. The resulting brown oil was hydrolysed without further purification; R_F (EtOAc) 0.23.

(E)-4-*Diphenylphosphinoylnon*-2-*en*-1-*yl Acetate* **7i**.—In the same way, the mixture of acetates *anti*- and *syn*-**4i** (14.29 g, 37.2 mmol) and $Pd(MeCN)_2Cl_2$ (708.4 mg, 2.73 mmol, 7.3 mol%) gave, after being stirred at room temperature for 66 h, a crude product which was partially purified by passage through a short column of silica (eluting with 2:1 EtOAc–cyclohexane) to remove polar impurities. The resulting brown oil was hydrolysed without further purification; R_F (EtOAc) 0.34.

(E)-4-*Diphenylphosphinoyl*-5-*methylhex*-2-*en*-1-*yl Acetate* **7j**.—In the same way, the mixture of acetates *anti*- and *syn*-**4j** (11.57 g, 32.6 mmol) and $Pd(MeCN)_2Cl_2$ (422.2 mg, 1.63 mmol, 5 mol%) gave, after being stirred at room temperature for 78 h, a crude product, which was purified by flash chromatography, eluting with EtOAc, to yield the *acetate* **7j** (9.76 g, 84%) as needles, m.p. 110–111 °C (from EtOAc) (Found: C, 70.8; H, 7.1; P, 8.7%; M^+, 356.1533. $C_{21}H_{25}O_3P$ requires C, 70.8; H, 7.05; P. 8.7%; *M*, 356.1542); R_F(EtOAc) 0.37; $\nu_{max}(CHCl_3)/cm^{-1}$ 1730 (C=O), 1440 (PPh) and 1180 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 5.88 (1 H, ddd, *J* 16.7, 10.6 and 6.3, PCHC*H*=C), 5.47 (1 H, ddt, *J* 16.1, 4.1 and 6.2, C=C*H*CH_2O), 4.48 (2 H, ABX m, CH_2O), 2.91 (1 H, ddd, *J* 10.6, 8.8 and 3.2, PCH), 2.20 (1 H, d × septet, *J* 3.4 and 6.9, C*H*Me_2), 1.93 (3 H, s, Ac), 1.04 (3 H, d, *J* 6.9, CH*Me*$_A$Me$_B$) and 0.89 (3 H, d, *J* 6.7, CHMe$_A$*Me*$_B$); δ_C(100 MHz; $CDCl_3$) 170.2$^-$ (C=O), 133–126 (Ph_2PO and C=C), 64.0$^-$ (CH_2O), 49.5$^+$ ($^1J_{PC}$ 67.8, PCH), 27.4$^+$ (*C*HMe_2), 22.8$^+$ ($^3J_{PC}$ 11.7, CH*Me*$_A$Me$_B$), 20.7$^+$ (O=C*Me*) and 18.6$^+$ (CHMe$_A$*Me*$_B$); *m*/*z* 356 (2%, M^+), 313 (10, M − Ac), 297 (10, M − OAc), 219 (97, $Ph_2PO_2H_2$), 202 (50, Ph_2POH) and 201 (100, Ph_2PO).

In another experiment, the mixture of acetates *anti*- and *syn*-**4j** (20.76 g, 58 mmol) and $Pd(MeCN)_2Cl_2$ (1.31 g, 5.04 mmol, 7.5 mol%) were stirred for 3 days at room temperature. TLC showed incomplete reaction, so further $Pd(MeCN)_2Cl_2$ (495 mg, 1.9 mmol, 2.9 mol%) was added, and stirring was continued for a further 3 days. After evaporation, the residue was passed through a short column of silica (eluting with EtOAc) to give a crude product which was hydrolysed without further purification.

(E)-4-*Cyclohexyl*-4-*diphenylphosphinoylbut*-2-*en*-1-*yl Acetate* **7k**.—In the same way, the mixture of acetates *anti*- and *syn*-**4k** (602 mg, 1.54 mmol) and $Pd(MeCN)_2Cl_2$ (36 mg, 0.139 mmol, 9 mol%) gave, after refluxing for 5 h, a crude product which was purified by flash chromatography, eluting with 4:1 EtOAc–hexane, to give the *acetate* **7k** (360.0 mg, 60%) as needles, m.p. 128–130 °C (from EtOAc) (Found: C, 72.8; H, 7.45; P, 7.9%; M + H, 397.1900. $C_{24}H_{29}O_3P$ requires C, 72.2; H, 7.35; P. 7.8%; *M* + H, 397.1932); R_F (EtOAc) 0.40; $\nu_{max}(CDCl_3)/cm^{-1}$ 1730 (C=O), 1435 (PPh) and 1140 (P=O); δ_H(250 MHz; $CDCl_3$) 8.0–7.4 (10 H, m, Ph_2PO), 5.93 (1 H, ddd, *J* 15.5, 10.7 and 6.2, PCHC*H*=C), 5.44 (1 H, ddq, *J* 15.6, 2.0 and 6.1, C=C*H*CH_2O), 4.40 (2 H, ABX m, CH_2O), 2.92 (1 H, ddd, *J* 9.5, 9.3 and 3.4, PCH), 2.2–1.0 [11 H, m, $CH(CH_2)_5$] and 2.03 (3 H, s, Ac); δ_C(100 MHz; $CDCl_3$) 170.6$^-$ (C=O), 134–127 (Ph_2PO and C=C), 64.3$^-$ (CH_2O), 49.9$^+$ ($^1J_{PC}$ 68.3, PCH), 37.6$^+$ [PCH*C*H$(CH_2)_2$], 33.1$^-$ [$^3J_{PC}$ 10.5, $CH(CH_2)_A(CH_2)_B$], 29.6$^-$ [$^3J_{PC}$ 3.0, $CH(CH_2)_A(CH_2)_B$], 26.4$^-$, 26.2$^-$, 25.9$^-$ [$(CH_2)_3$] and 20.9$^+$ (OC*Me*); *m*/*z* 397 (18%, M + H), 396 (12, M^+), 336 (20, M – AcOH), 314 [51, M – $CH(CH_2)_5$], 255 (55, $Ph_2POC_4H_6$), 219 (65, $Ph_2PO_2H_2$), 202 (60, Ph_2POH) and 201 (100, Ph_2PO).

In another experiment, the mixture of acetates *anti*- and *syn*-**4k** (3.78 g, 9.54 mmol) and $Pd(MeCN)_2Cl_2$ (212.5 mg, 0.819 mmol, 8.6 mol%) gave, after being stirred at room temperature for 25 h, a crude product which was hydrolysed without further purification.

(4RS,5RS)- *and* (4RS,5SR)-(E)-4-*Diphenylphosphinoyl*-5-*methylhept*-2-*en*-1-*yl Acetate* anti- *and* syn-**7l**.—In the same way, the diastereoisomeric mixture of acetates **4l** (3.70 g, 10.0 mmol) and $Pd(MeCN)_2Cl_2$ (217 mg, 0.836 mmol, 8.4 mol%) gave, after refluxing for 3 h, a crude product which was purified by flash chromatography, eluting with 2:1 EtOAc–hexane, to yield a 50:50 (by ^1H NMR) mixture of the *acetates anti*-**7l** and *syn*-**7l** (2.52 g, 68%) as an oil (Found: M^+, 370.1693. $C_{22}H_{27}O_3P$ requires *M*, 370.1698); R_F (EtOAc) 0.49; δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 5.85 (1 $H^{anti+syn}$, m, PCHCH=CH), 5.4 (1 $H^{anti+syn}$, m, CH=C*H*CH_2OAc), 4.37 (2 $H^{anti+syn}$, m, CH_2OAc), 3.01 (1 H^{syn}, dt, *J* 11.0 and 2.3, CHP), 2.89 (1 H^{syn}, ddd, *J* 11.8, 8.7 and 3.3, CHP), 1.93 (3 $H^{anti+syn}$, s, OAc), 2.1–1.8 (2 $H^{anti+syn}$, m, CH_2Me) and 1.1–0.6 (6 $H^{anti+syn}$, m, Me × 2); *m*/*z* 370 (40%, M^+, 311 (50, M – AcO), 219 (98, $Ph_2PO_2H_2$), 202 (85, Ph_2POH) and 201 (100, Ph_2PO).

(2RS,5SR)-E(-5-*Diphenylphosphinoyl*-6-*methylhept*-3-*en*-2-*yl Acetate* anti-**7m**.—In the same way, the acetate *anti*-**4m** (2.81 g, 7.59 mmol) and Pd $(MeCN)_2Cl_2$ (137 mg, 0.53 mmol, 7.0 mol%) gave, after being stirred at room temperature for 1 h, a crude product which was purified by flash chromatography, eluting with EtOAc, to yield the *acetate anti*-**7m** (2.63 g, 94%) as minute needles, m.p. 130–135 °C (from EtOAc) (Found: C, 71.35; H, 7.4; P, 8.4%; M^+, 370.1714. $C_{22}H_{27}O_3P$ requires C, 71.35; H, 7.35; P, 8.35%; *M*, 370.1698); R_F (EtOAc) 0.39; $\nu_{max}(CDCl_3)/cm^{-1}$ 1735 (C=O), 1440 (PPh) and 1180 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 5.77 (1 H, ddd, *J* 15.6, 10.5 and 6.1, PCHC*H*=C), 5.29 (1 H, ddd, *J* 15.3, 7.0 and 4.2, C=C*H*CHOAc), 5.14 (d × quintet, *J* 1.0 and 6.8, C*H*OAc), 2.81 (1 H, ddd, *J* 10.8, 8.8 and 3.3, PCH), 2.23 (1 H, d × septet, *J* 3.5 and 7.0, C*H*Me_2), 1.93 (3 H, s, Ac), 1.02 (3 H, d, *J* 6.9, CHMe_AMe_B), 0.95 (3 H, d, *J* 6.4, OCH*Me*) and 0.88 (3 H, d, *J* 6.8, CHMe_AMe_B); irradiation of the multiplet at δ 5.14 reduced the doublet at δ 0.95 to a singlet, δ_C(100 MHz; $CDCl_3$) 170.0$^-$ (C=O), 136.6$^+$ ($^3J_{PC}$ 12.4, C=*C*HCHO), 134–128 (Ph_2PO), 124.0$^+$ ($^2J_{PC}$ 6.5, PCH*C*H=C), 70.5$^+$ (*C*HOAc), 49.9$^+$ ($^1J_{PC}$ 68.1, PCH), 27.5$^+$ (*C*Me_2), 23.0$^+$ ($^3J_{PC}$ 12.6, CHMe_AMe_B), 21.2$^+$ (O=C*Me*), 20.0$^+$ (OCH*Me*) and 18.8$^+$ ($^3J_{PC}$ 1.9, CHMe_AMe_B); *m*/*z* 370 (0.1%, M^+), 327 (6, M – Ac), 311 (3, M – OAc), 283 (3, M – MeCHOAc), 219 (68, $Ph_2PO_2H_2$), 202 (35, Ph_2POH) and 201 (100, Ph_2PO).

General Procedure for Acid-catalysed Rearrangements of the Allylic Alcohols **3**.—A solution of the allylic alcohol (1 mmol) in glacial acetic acid (2.5 cm^3) was added in one portion to a solution of toluene-*p*-sulfonic acid monohydrate (0.5 mmol) in acetic anhydride (1.25 cm^3) and glacial acetic acid (2.5 cm^3). The mixture was stirred under nitrogen for 1–48 h, before being poured into water (50 cm^3) and extracted with CH_2Cl_2 (10 cm^3 × 5). The combined organic fractions were washed with dilute aqueous ammonia and saturated brine, dried ($MgSO_4$) and evaporated. The crude product was either purified by flash chromatography or hydrolysed directly without purification.

Attempted Rearrangement of the Alcohol **3a**.—In this way, the alcohol **3a** (116.3 mg, 0.428 mmol), with toluene-*p*-sulfonic acid monohydrate (100 mg, 0.53 mmol, 1.2 equiv.), after being stirred for 43 h at 60 °C, gave a crude product (112.6 mg) which was (by ^1H NMR) shown to be 88:12 mixture of the unrearranged and rearranged acetates **4a** and **7a**.

(E)-1-*Diphenylphosphinoylhept*-2-*en*-4-*yl Acetate* **7c**.—In the same way, the alcohol **3c** (902 mg, 2.87 mmol) gave, after 24 h, a crude product which was purified by flash chromatography, eluting with 5:1 EtOAc–hexane, to give the acetate **7c** (613.4 mg, 68%).

(E)-1-*Diphenylphosphinoyl*-3-*methylpent*-3-*en*-2-*yl Acetate* **7d**.—In the same way, the alcohol **3d** (476.7 mg, 1.58 mmol) gave, after 26.5 h, a crude product which was purified by flash chromatography, eluting with EtOAc, to give the *acetate* **7d** (400 mg, 74%) as needles, m.p. 148–150 °C (from EtOAc) (Found: C, 70.4; H, 6.9; P, 9.3%; M^+, 342.1368. $C_{20}H_{23}O_3P$ requires C, 70.2; H, 6.75; P, 9.05%; *M*, 328.1385); R_F (EtOAc) 0.25; $\nu_{max}(CHCl_3)/cm^{-1}$ 1720 (C=O), 1440 (PPh) and 1150 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 5.51 (1 H, q, *J* 7.1, CH=C), 5.14 (1 H, q, *J* 6.8, C*H*OAc), 3.08 (2 H, dd, *J* 15.4 and 7.8, PCH_2), 1.96 (3 H, s, Ac), 1.40 (3 H, d, *J* 2.8, CH=C*Me*) and 1.15 (3 H, d, *J* 6.6, CH*Me*); δ_C(100 MHz; $CDCl_3$) 170.1$^-$ (C=O), 140.1$^-$ ($^3J_{PC}$ 11.7, CH=C), 133–128 (Ph_2PO), 114.9$^+$ ($^2J_{PC}$ 8.3, *C*H=C), 74.5$^+$ (*C*HOAc), 30.7$^-$ ($^1J_{PC}$ 68.9, PCH_2), 21.2$^+$ (O=C*Me*), 19.0$^+$ (CH=C*Me*) and 12.5$^+$ (OCH*Me*); *m*/*z* 342 (14%, M^+), 283 (12, M – AcO), 282 (35, M – AcOH), 219 (18, $Ph_2PO_2H_2$), 202 (100, Ph_2POH) and 201 (62, Ph_2PO).

Attempted Rearrangement of the Alcohol **3e**.—In the same way, the alcohol **3e** (457.1 mg, 1.60 mmol) gave, after 48 h, a crude product (520 mg) which was shown (by ^1H NMR) to be a 91:9 mixture of the unrearranged acetate **4e** and a compound presumed to be rearranged acetate **7e**. Purification by flash chromatography, eluting with EtOAc, gave the unrearranged acetate **4e** (367.1 mg, 70%).

Attempted Rearrangement of the Alcohol **3f**.—In the same way, the alcohol **3f** (625.8 mg, 1.91 mmol) gave, after 46 h, a crude product which was showh (by ^1H NMR) to be a 91:9 mixture of the unrearranged acetate **4f** and a compound presumed to be the rearranged acetate **7f**.

Rearrangement of the Alcohol **3b** *under Perrhenate Catalysis*.—A solution of tetrabutylammonium perrhenate (29.1 mg, 0.059 mmol, 10 mol%) and toluene-*p*-sulfonic acid monohydrate (9 mg, 0.047 mmol, 8 mol%) in dry dichloromethane (3 cm^3) was added to a stirred solution of the alcohol **3b** (170.1 mg, 0.59 mmol) in dry dichloromethane (4.6 cm^3) at room temperature under nitrogen. Stirring was continued for 48 h.

The solvent was evaporated and the residue was shown (by ^{1}H NMR) to be a 76:24 mixture of rearranged and unrearranged allylic alcohols **8b** and **3b**.

Attempted Rearrangement of the Alcohol **3e** *under Perrhenate Catalysis.*—In a similar manner, tetrabutylammonium perrhenate (15 mg, 0.030 mmol, 13 mol%), toluene-*p*-sulfonic acid monohydrate (*ca.* 5 mg) and the alcohol **3e** (69.5 mg, 0.242 mmol) gave a product which was shown to contain, by ^{1}H NMR, only starting material **3e** and catalysts.

Rearrangement of the Alcohol **3b** *by Palladium-catalysed Allylic Mitsunobu Reaction.*—Acetic acid (40 mm^3, 0.70 mmol, 1.6 equiv.) and diethyl azodicarboxylate (DEAD) (0.11 cm^3, 0.70 mmol, 1.6 equiv.) were added to a stirred solution of **3b** (124.8 mg, 0.434 mmol), triphenylphosphine (170 mg, 0.649 mmol, 1.5 equiv.) and bisacetonitrilepalladium(II) chloride [$Pd(MeCN)_2Cl_2$] (12 mg, 0.046 mmol, 11 mol%) in dry THF (4 cm^3) at room temperature under nitrogen. After being stirred for 30 min, the solvent was removed, and the residue taken up in dry methanol (5 cm^3). Concentrated hydrochloric acid (0.5 cm^3) was added, and the mixture was stirred for 24 h. It was then poured into 50% saturated aqueous sodium hydrogencarbonate (25 cm^3) and extracted with dichloromethane (×3). The combined organic fractions were washed with saturated brine, dried (Na_2SO_4) and evaporated under reduced pressure to give a crude product. ^{1}H NMR analysis of this material showed it to contain a 66:34 mixture of the rearranged and unrearranged alcohols **8b** and **3b**.

Attempted Rearrangement of **3e** *by a Palladium-catalysed Allylic Mitsunobu Reaction.*—In a similar way, **3e** gave a crude product shown to contain, by ^{1}H NMR, only starting material **3e**, DEAD and triphenylphosphine oxide.

General Procedure for the Base-catalysed Hydrolysis of the Acetates **7**. Aqueous sodium hydroxide (2 mol dm^{-3}; 2 cm^3) was added to a stirred solution of the acetate (1 mmol) in methanol (8 cm^3). Heat was generated and the mixture was stirred at the resulting raised temperature for 5–60 min; it was then diluted with water (100 cm^3). Much of the methanol was removed under reduced pressure and the residue was extracted with dichloromethane (×3). The combined organic fractions were washed with saturated brine, dried (Na_2SO_4) and evaporated to yield a crude product which was purified by flash chromatography or by recrystallisation.

(E)-4-*Diphenylphosphinoylbut*-2-*en*-1-*ol* **8a**.—In this way, the acetate **7a** (1.15 g, 3.66 mmol) gave, after purification by flash chromatography, eluting with EtOAc and then EtOAc–75% MeOH, the alcohol[5] **8a** as needles (851.4 mg, 85%), m.p. 88–89 °C (from EtOAc) (lit.,[5] 74.5–75.5 °C) (Found: C, 70.7; H, 6.3; P, 11.4%; M$^+$, 272.0960. $C_{16}H_{17}O_2P$ requires C, 70.6; H, 6.3; P, 11.4%; *M*, 272.0966); R_F (EtOAc) 0.10; $\nu_{max}(CHCl_3)/cm^{-1}$ 3325 (OH), 1440 (PPh) and 1140 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.3 (10 H, m, Ph_2PO), 5.8–5.55 (2 H, m, CH=CH), 4.00 (2 H, t, *J* 4.5, C*H*$_2$OH), 3.10 (2 H, dd, *J* 14.3 and 6.8, PCH_2) and 3.0 (1 H, br s, OH); δ_C(100 MHz; $CDCl_3$) 136.2$^+$ ($^3J_{PC}$ 11.3, C=*C*HCH$_2$OH), 133–128 (Ph_2PO), 119.7$^+$ ($^2J_{PC}$ 9.1, PCH$_2$*C*H=C), 62.9$^-$ (CH_2OH) and 34.4$^-$ ($^1J_{PC}$ 68.1, PCH_2); *m*/*z* 272 (20%, M$^+$), 254 (8, M − H_2O), 219 (15, $Ph_2PO_2H_2$), 217 (15), 202 (41, Ph_2POH) and 201 (100, Ph_2PO).

(E)-5-*Diphenylphosphinoylpent*-3-*en*-2-*ol* **8b**.—In the same way, the acetate **7b** (89.3 mg, 0.27 mmol) gave, after purification by flash chromatography, eluting with EtOAc–5% MeOH, the alcohol[4] **8b** as an oil (54.7 mg, 71%). ^{1}H NMR of the early fractions from the column [R_F (EtOAc) 0.38] showed signals characteristic of a vinyl phosphine oxide, tentatively identified as the diene **9** (R^1,R^2 = H; R^3 = Me).

Similarly, impure acetate **7b** derived from the acid-catalysed rearrangement (23.7 mmol maximum), gave, after purification by flash chromatography, eluting with EtOAc–2% MeOH and then EtOAc–15% MeOH, the alcohol **8b** (3.61 g, 53% from the alcohol **3b**).

(E)-1-*Diphenylphosphinoylhept*-2-*en*-4-*ol* **8c**.—In the same way, the acetate **7c** (203.2 mg, 0.59 mmol) gave, after purification by flash chromatography, eluting with EtOAc and then EtOAc–10% MeOH, the *alcohol* **8c** (143.3 mg, 81%) as prisms, m.p. 90–92.5 °C (from EtOAc–MeOH) (Found: C, 72.4; H, 7.3; P, 9.7%; M$^+$, 314.1432. $C_{19}H_{23}O_2P$ requires C, 72.6; H, 7.35; P, 9.85%; *M*, 314.1436); R_F (EtOAc) 0.11; ν_{max} ($CHCl_3$)/cm^{-1} 3340 (OH), 1420 (PPh) and 1140 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 5.65–5.43 (2 H, m, CH=CH), 3.95 (1 H, dq, *J* 1.8 and 6.4, C*H*OH), 3.1 (1 H, br s, OH), 3.05 (2 H, dd, *J* 14.4 and 6.7, PCH_2), 1.45–1.0 [4 H, m, (C*H*$_2$)$_2$Me] and 0.76 (3 H, t, *J* 7.2, Me); δ_C(100 MHz; $CDCl_3$) 140.1$^+$ ($^3J_{PC}$ 11.3, HOCH*C*H=C), 133–128 (Ph_2PO), 118.8$^+$ ($^2J_{PC}$ 9.1, PCH$_2$*C*H), 71.9$^+$ (CHOH), 39.0$^-$ (HOCH*C*H$_2$), 34.3$^-$ ($^1J_{PC}$ 68.5, PCH_2), 18.3$^-$ (*C*H$_2$Me) and 13.9$^+$ (Me); *m*/*z* 314 (6%, M$^+$), 296 (5, M − H_2O), 271 (51, *M* − C_3H_7), 202 (45, Ph_2POH) and 201 (100, Ph_2PO).

(E)-5-*Diphenylphosphinoyl*-3-*methylpent*-3-*en*-2-*ol* **8d**.—In the same way, the acetate **7d** (103 mg, 0.29 mmol) gave, after purification by flash chromatography, eluting with EtOAc and then EtOAc–12% MeOH, the *alcohol* **8d** (69.2 mg, 69%), as prisms, m.p. 148–148.5 °C (from MeOAc–MeOH) (Found: C, 72.05; H, 7.1; P, 10.4%; M$^+$, 300.1263. $C_{18}H_{21}O_2P$ requires C, 72.2; H, 7.05; P, 10.7%; *M*, 300.1279); R_F (EtOAc) 0.17; $\nu_{max}(CHCl_3)/cm^{-1}$ 3320 (OH), 1430 (PPh) and 1145 (P=O); δ_H(400 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 5.48 (1 H, q, *J* 7.5, CH=C), 4.13 (1 H, q, *J* 6.2, C*H*OH), 3.07 (2 H, dd, *J* 14.7 and 7.7, PCH_2), 2.5 (1 H, br s, OH), 1.42 (3 H, d, *J* 2.6, CH=C*Me*) and 1.10 (3 H, d, *J*. 6.4, CH*Me*); δ_C(100 MHz; $CDCl_3$) 144.7$^-$ ($^3J_{PC}$ 11.4, CH=*C*), 134–128 (Ph_2PO), 112.5$^+$ ($^2J_{PC}$ 8.7, *C*H=C), 72.9$^+$ (CHOH), 30.4$^-$ ($^1J_{PC}$ 67.1, PCH_2), 21.3$^+$ (CH=C*Me*) and 11.8$^+$ (HOCH*Me*); *m*/*z* 300 (10%, M$^+$), 282 (27, M − H_2O), 202 (100, Ph_2POH) and 201 (69, Ph_2PO).

(E)-4-*Diphenylphosphinoylpent*-2-*en*-1-*ol* **8g**.—In the same way, the crude acetate **7g** (16.17 mmol) gave a residue which was purified by flash chromatography, eluting with EtOAc and then EtOAc–15% MeOH, to yield a crude product (2.223 g, 48%). ^{1}H NMR showed this to consist of a 40:60 mixture of the desired *alcohol* **8g** and a compound identified as (E)-4-*diphenylphosphinoylpent*-3-*en*-1-*ol* **11** from the ^{1}H NMR spectrum of the mixture: R_F (EtOAc–10% MeOH) 0.30; δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 6.33 (1 H, ddt, *J* 21, 7 and 2, PC=CH), 3.72 (2 H, t, *J* 7, C*H*$_2$OH), 2.52 (2 H, dq, *J* 3 and 7, C*H*$_2$CH$_2$OH) and 1.86 (3 H, d, *J* 13, PCMe). Further purification by HPLC, eluting with $CHCl_3$–7% MeOH, gave the *alcohol* **8g** (836.8 mg, 18% from acetates **4g**) as an oil (Found: M$^+$, 286.1120. $C_{17}H_{19}O_2P$ requires *M*, 286.1123); R_F (EtOAc–10% MeOH) 0.30; ν_{max}(neat)/cm^{-1} 3320 (OH), 1440 (PPh), 1170 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 5.9–5.5 (2 H, m, CH=CH), 4.01 (2 H, ABX m, C*H*$_2$OH), 3.22 (1 H, dq, *J* 17 and 7, PCH), 1.9 (1 H, br s, OH) and 1.31 (3 H, dd, *J* 16 and 7, Me); δ_C(100 MHz; $CDCl_3$) 133.4$^+$ ($^3J_{PC}$ 10.2, C=*C*HCH$_2$OH), 133–128 (Ph_2PO), 127.3$^+$ ($^2J_{PC}$ 7.3, PCH*C*H=C), 63.1$^-$ ($^4J_{PC}$ 2.2, CH_2OH), 37.2$^+$ ($^1J_{PC}$ 68.5, PCH) and 12.9$^+$ ($^2J_{PC}$ 3.6, Me); *m*/*z* 286 (9%, M$^+$), 219 (40, $Ph_2PO_2H_2$), 202 (50, Ph_2POH' and 201 (100, Ph_2PO).

(E)-4-*Diphenylphosphinoylhex*-2-*en*-1-*ol* **8h**.—In the same way, crude acetate **7h** (29.2 mmol) gave, after 5 min, a crude product which was purified by flash chromatography, eluting with $CHCl_3$–2.5% MeOH and then $CHCl_3$–5% MeOH, to give the *alcohol* **8h** (2.73 g, 31%) as minute plates, m.p. 110–111 °C (from EtOAc) (Found: C, 72.1; H, 7.1; P, 10.05%; M^+, 300.1292. $C_{18}H_{21}O_2P$ requires C, 72.0; H, 7.05; P, 10.3%; *M*, 300.1279); R_F (EtOAc) 0.13; ν_{max}(Nujol)/cm^{-1} 3260 (OH), 1440 (PPh) and 1175 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 5.59 (2 H, m, CH=CH), 3.98 (2 H, ABX m, CH_2OH), 2.91 (1 H, ddq, *J* 3, 2 and 8, PCH), 2.4 (1 H, br s, OH), 1.8–1.6 (2 H, m, CH_2Me) and 0.92 (3 H, t, *J* 7, Me); δ_C(100 MHz; $CDCl_3$) 135.3$^+$ ($^3J_{PC}$ 10.8, C=*C*HCH$_2$OH), 133–128 (Ph_2PO), 125.8$^+$ ($^2J_{PC}$ 2.2, PCH*C*H=C), 63.1$^-$ ($^4J_{PC}$ 1.2, CH_2OH), 45.5$^+$ ($^1J_{PC}$ 66.0, PCH), 20.7$^-$ ($^2J_{PC}$ 2.2, *C*H$_2$Me) and 12.6$^+$ ($^3J_{PC}$ 13.2, Me); *m*/*z* 300 (3%, M^+), 219 (20, $Ph_2PO_2H_2$), 202 (30, Ph_2POH), 201 (59, Ph_2PO) and 84 (100).

(E)-4-*Diphenylphosphinoylnon*-2-*en*-1-*ol* **8i**.—In the same way, crude acetate **7i** (37.2 mmol) gave, after 5 min, a crude product which was purified by flash chromatography, eluting with $CHCl_3$–2.5% MeOH, to give the *alcohol* **8i** (2.33 g, 18%) as an unrecrystallisable waxy solid (Found: M^+, 342.1737. $C_{21}H_{27}O_2P$ requires *M*, 342.1748); R_F (EtOAc) 0.13; ν_{max} (Nujol)/cm^{-1} 3300 (OH), 1440 (PPh) and 1180 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 5.56 (2 H, m, CH=CH), 3.98 (2 H, ABX, m, CH_2OH), 3.00 (1 H, quintet, *J* 7, PCH), 2.3 (1 H, br s, OH), 1.8–1.0 [8 H, m, $(CH_2)_4Me$] and 0.82 (3 H, t, *J* 6.5, Me); δ_C(100 MHz; $CDCl_3$) 135.0$^+$ ($^3J_{PC}$ 11.6, C=*C*HCH$_2$OH), 133–128 (Ph_2PO), 126.4$^+$ ($^2J_{PC}$ 7.3, PCH*C*=C), 63.1$^-$ ($^4J_{PC}$ 2.2, CH_2OH), 43.6$^+$ ($^1J_{PC}$ 68.2, PCH), 31.3$^-$ (PCH*C*H$_2$), 27.4$^-$ ($^3J_{PC}$ 2.2, PCHCH$_2$*C*H$_2$), 27.1$^-$ (*C*H$_2$CH$_2$-Me), 22.2$^-$ (*C*H$_2$Me) and 13.9$^+$ (Me); *m*/*z* 342 (8%, M^+), 219 (31, $Ph_2PO_2H_2$), 202 (67, Ph_2POH) and 201 (100, Ph_2PO).

(E)-4-*Diphenylphosphinoyl*-5-*methylhex*-2-*en*-1-*ol* **8j**.—In the same way, pure acetate **7j** (245.45 mg, 0.689 mmol) gave a crude product which was purified by flash chromatography, eluting with EtOAc–4% MeOH, to yield the *alcohol* **8j** (197.24 mg, 91%) as prisms, m.p. 158.5–160 °C (from EtOAc) (Found: C, 72.45; H, 7.4; P, 9.85%; M^+, 314.1456. $C_{19}H_{23}O_2P$ requires C, 72.6; H, 7.35; P, 9.85%; *M*, 314.1435); R_F (EtOAc) 0.12; ν_{max}($CHCl_3$)/ cm^{-1} 3330 (OH), 1440 (PPh) and 1140 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 5.76 (1 H, ddd, *J* 15.5, 10.4 and 6.0, PCH*C*H=C), 5.46 (1 H, dq, *J* 14.9 and 5.2, C=C*H*CH$_2$OH), 3.92 (2 H, ABX m, CH_2OH), 3.6 (1 H, br s, OH), 2.86 (1 H, ddd, *J* 10.6, 8.8 and 3.1, PCH), 2.13 (1 H, d × septet, *J* 3.7 and 6.8, C*H*Me$_2$), 0.97 (3 H, d, *J* 6.8, CH*Me*$_A$Me$_B$) and 0.86 (3 H, d, *J* 6.7, CHMe$_A$*Me*$_B$); δ_C(100 MHz; $CDCl_3$) 137.1$^+$ ($^3J_{PC}$ 11.9, C=*C*HCH$_2$OH), 134–128 (Ph_2PO), 121.8$^+$ ($^2J_{PC}$ 6.6, PCH*C*H=C), 62.7$^-$ (CH_2OH), 49.4$^+$ ($^1J_{PC}$ 68.0, PCH), 27.5$^+$ (*C*HMe$_2$), 22.8$^+$ (J_{PC} 13.1, CH*Me*$_A$Me$_B$) and 18.7$^+$ (CHMe$_A$*Me*$_B$); *m*/*z* 314 (2.4%, M^+), 296 (2, M – H_2O), 271 (13, M – C_3H_7), 219 (42, $Ph_2PO_2H_2$), 202 (66, Ph_2POH) and 201 (100, Ph_2PO).

(E)-4-*Cyclohexyl*-4-*diphenylphosphinoylbut*-2-*en*-1-*ol* **8k**.—In the same way, the crude acetate **7k** (0.54 mmol) gave, after purification by flash chromatography, eluting with EtOAc–1% MeOH, the *alcohol* **8k** (2.61 g, 77%) as prisms, m.p. 155–161 °C (from EtOAc) (Found: C, 74.55; H, 7.9; P, 8.9%; M^+, 354.1734. $C_{22}H_{27}O_2P$ requires C, 74.55; H, 7.7; P, 8.75%; *M*, 354.1748); R_F (EtOAc) 0.15; ν_{max}($CHCl_3$)/cm^{-1} 3360 (OH), 1450 (PPh) and 1150 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 5.81 (1 H, dddt, *J* 15.4, 10.4, 6.2 and 1, PCHC*H*=C), 5.46 (1 H, ddt, *J* 15.6, 4.5 and 6.0, C=C*H*CH$_2$OH), 3.94 (2 H, ABX m, CH_2OH), 2.88 (1 H, ddd, *J* 11.0, 8.5 and 3.6, PCH) and 2.2–1.0 (11 H, m, ring); δ_C(100 MHz; $CDCl_3$) 135.9$^+$ ($^3J_{PC}$ 12.5, C=*C*HCH$_2$OH), 134–128 (Ph_2PO), 124.3$^+$ ($^2J_{PC}$ 7.4, PCH*C*H=C), 63.1$^-$ ($^4J_{PC}$ 1.4, CH_2OH), 49.6$^+$ ($^1J_{PC}$ 67.0, PCH), 37.6$^+$ [$^2J_{PC}$ 2.2, PCH*C*H(CH$_2$)$_2$], 33.1$^-$ [$^3J_{PC}$ 11.3, CH(*C*H$_2$)$_A$-(CH$_2$)$_B$], 29.5$^-$ [$^3J_{PC}$ 3.0, CH(CH$_2$)$_A$(*C*H$_2$)$_B$], 26.4$^-$, 26.2$^-$ and 25.8$^-$ [(CH$_2$)$_3$]; *m*/*z* 354 (1.5%, M^+), 336 (5, M – H_2O), 272 (40, Ph_2POCH_2CH=CHCH$_2$OH), 219 (33, $Ph_2PO_2H_2$), 202 (100, Ph_2POH) and 201 (91, Ph_2PO).

(4RS,5SR)- *and* (4RS,5RS)-(E)-4-*Diphenylphosphinoyl*-5-*methylhept*-2-*en*-1-*ol* anti- *and syn*-**8l**.—In the same way, the 50:50 mixture of acetates *anti*-**7l** and *syn*-**7l** (2.50 g, 6.75 mmol) gave, after purification by flash chromatography, eluting with EgOAc and then EtOAc–4% MeOH, a mixture of the *alcohols* **8l** (1.14 g, 51%). Further purification by HPLC, eluting with $CHCl_3$–2.5% MeOH, gave the *anti diastereoisomer anti*-**8l** (505 mg, 23%) as prisms, m.p. 165–166 °C (from EtOAc–MeOH), retention time 23 min (Found: C, 73.0; H, 7.75; P, 9.4%; M + H, 329.1645. $C_{20}H_{15}O_2P$ requires C, 73.15; H, 7.65; P, 9.45%; *M* + H, 329.1670); R_F (EtOAc) 0.20; ν_{max}($CDCl_3$)/cm^{-1} 3300 (OH), 1660 (C=C, 1440 PPh) and 1170 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 5.77 (1 H, ddd, *J* 15.4, 10.5 and 5.9, PCHC*H*=CH), 5.47 (1 H, dq, *J* 15.4 and 5.1, CH=C*H*CH$_2$OH), 3.92 (2 H, ABX m, CH_2OH), 2.91 (1 H, ddd, *J* 11.7, 8.4 and 3.5, CHP), 2.02 (1 H, m, C*H*Me), 1.86 (1 H, m, CH_AH_BMe), 1.10 (1 H, m, CH_AH_BMe), 0.88 (3 H, d, *J* 6.6, CH*Me*) and 0.74 (3 H, t, *J* 7.4, CH_2Me); δ_C(62.9 MHz; $CDCl_3$) 136.4$^+$ ($^3J_{PC}$ 12.0, CH=*C*H$_2$OH), 136–128 (Ph_2PO), 123.7$^+$ ($^2J_{PC}$ 6.9, PCH*C*H=CH), 63.0$^-$ ($^4J_{PC}$ 1.6, CH_2OH), 50.1$^+$ ($^1J_{PC}$ 68.1, CHP), 34.6$^+$ ($^2J_{PC}$ 1.8, *C*HMe), 25.5$^-$ ($^3J_{PC}$ 2.8, *C*H$_2$Me), 12.6$^+$ ($^3J_{PC}$ 12.6, CH*Me*) and 11.9$^+$ (CH_2Me); *m*/*z* (+FAB) 329 (90%, M + H) and 201 (100, Ph_2PO).

Also obtained was the *syn diastereoisomer* syn-**8l** (565 mg, 25%) as prisms, m.p. 110–111 °C (from EtOAc), retention time 25 min (Found: C, 73.05; H, 7.85; P, 9.45%; M + H, 329.1639. $C_{20}H_{15}O_2P$ requires C, 73.15; H, 7.65; P, 9.45%; *M* + H, 329.1670); R_F (EtOAc) 0.20; ν_{max}($CDCl_3$)/cm^{-1} 3300 (OH), 1650 (C=C), 1430 (PPh) and 1170 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 5.83 (1 H, ddd, *J* 15.4, 10.5 and 5.9, PCHC*H*=CH), 5.46 (1 H, dq, *J* 15.4 and 5.1, CH=C*H*CH$_2$OH), 3.95 (2 H, ABX m, CH_2OH), 3.06 (1 H, ddd, *J* 11.4, 10.2 and 2.4, CHP), 1.85 (1 H, m, C*H*Me), 1.26 (2 H, m, CH_2Me), 1.07 (3 H, d, *J* 6.9, CH*Me*) and 0.81 (3 H, t, *J* 7.4, CH_2Me); δ_C(62.9 MHz; $CDCl_3$) 136.5$^+$ ($^3J_{PC}$ 11.9, CH=*C*HCH$_2$OH), 136–128 (Ph_2PO), 122.5$^+$ ($^2J_{PC}$ 7.0, PCH*C*H=CH), 63.0$^-$ ($^4J_{PC}$ 2.4, CH_2OH), 46.5$^+$ ($^1J_{PC}$ 68.6, CHP), 34.0$^+$ ($^2J_{PC}$ 2.1, *C*HMe), 29.2$^-$ ($^3J_{PC}$ 13.3, *C*H$_2$Me), 16.3$^+$ (CH*Me*) and 11.7$^+$ (CH_2Me); *m*/*z* (+FAB) 329 (100%, M + H) and 201 (90, Ph_2PO).

(2RS,5SR)-(E)-5-*Diphenylphosphinoyl*-6-*methylhept*-3-*en*-2-*ol* anti-**8m**.—In the same way, pure acetate *anti*-**7m** (2.60 g, 7.02 mmol) gave, after 45 min, a crude solid, which was purified by recrystallisation from ethyl acetate to yield the *alcohol anti*-**8m** (1.9292 g, 84%) as needles, m.p. 156.5–157.5 °C (from EtOAc) (Found: C, 73.35; H, 7.55; P, 9.5%; M – Me, 313.1381. $C_{20}H_{25}O_2P$ requires C, 73.15; H, 7.65; P, 9.45%; *M* – Me, 313.1357); R_F(EtOAc) 0.13; ν_{max}($CHCl_3$)/cm^{-1} 3380 (OH), 1440 (PPh) and 1150 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 5.68 (1 H, ddd, *J* 15.7, 10.4 and 5.9, PCHC*H*=C), 5.33 (1 H, ddd, *J* 15.4, 6.7 and 4.2, C=C*H*CHOH), 4.12 (d × quintet, *J* 1.4 and 6.4, C*H*OH), 2.81 (1 H, ddd, *J* 10.9, 8.3 and 3.2, PCH), 2.75 (1 H, s, OH), 2.16 (1 H, d × septet, *J* 3.5 and 7.0, C*H*Me$_2$), 1.02 (3 H, d, *J* 6.9, CH*Me*$_A$Me$_B$), 0.89 (3 H, d, *J* 6.3, CHOH*Me*) and 0.88 (3 H, d, *J* 6.7, CHMe$_A$*Me*$_B$); δ_C(100 MHz; $CDCl_3$) 142.0$^+$ ($^3J_{PC}$ 11.9, C=*C*HCHOH), 134–128 (Ph_2PO), 120.4$^+$ ($^2J_{PC}$ 6.9, PCH*C*H=C), 68.2$^+$ (CHOH), 49.5$^+$ ($^1J_{PC}$ 67.8, PCH), 27.5$^+$ (*C*HMe$_2$), 23.1$^+$ (CHOH*Me*), 23.0$^+$ ($^3J_{PC}$ 12.6, CH*Me*$_A$Me$_B$) and 18.8$^+$ ($^3J_{PC}$ 1.7, CH-

Me_AMe_B); *m/z* 313 (1.5%, M − Me), 310 (4, M − H_2O), 285 (16, M − C_3H_7), 219 (27, $Ph_2PO_2H_2$), 202 (76, Ph_2POH) and 201 (100, Ph_2PO).

General Procedure for the Acid-catalysed Methanolysis of the Acetates **7**.—Concentrated hydrochloric acid (1 cm^3) was added to a stirred solution of the acetate (1 mmol) in methanol (20 cm^3). Stirring was continued overnight. The reaction mixture was then poured into 1:1 saturated aqueous sodium hydrogencarbonate–water (50 cm^3) and extracted with dichloromethane (×3). The combined organic fractions were washed with brine, dried (K_2CO_3–$MgSO_4$) and evaporated under reduced pressure to yield a crude product, which was purified by flash chromatography.

(E)-5-*Diphenylphosphinoylpent*-3-*en*-2-*ol* **8b**.—In this way, the acetate **51b** (62.8 mg, 0.191 mmol) gave, after 25 h, and after purification by flash chromatography, eluting with EtOAc–7% MeOH, the *alcohol* **64b** (53.8 mg, 99%). TLC of the crude reaction mixture showed none of the less polar impurities.

(E)-4-*Diphenylphosphinoylpent*-2-*en*-1-*ol* **8g**.—In the same way, the acetate **7g** (167 mg, 0.509 mmol) gave, after 17 h, a crude product which was purified by flash chromatography, eluting with EtOAc–5% MeOH, to give the *alcohol* **8b** (93 mg, 64%).

(E)-4-*Cyclohexyl*-4-*diphenylphosphinoylbut*-2-*en*-1-*ol* **8k**.—In the same way, the acetate **7k** (130 mg, 0.328 mmol) gave, after 17 h, a crude product. This was purified by flash chromatography, eluting with EtOAc–2% and then EtOAc–4% MeOH, to give the *alcohol* **8k** (88.7 mg, 76%).

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