Stereochemical Control (*E*/*Z* and *syn*/*anti*) by the Diphenylphosphinoyl Group in the Synthesis of Allylic Alcohols by Allylic Rearrangement and by 1,4-Diastereoselective Reduction of Enones

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Allylic rearrangement of substitued 2-hydroxyalk-3-en-1-yl(diphenyl)phosphine oxides to 4-hydroxyalk-2-en-1-yl(diphenyl)phosphine oxides can be performed with total regio- and reasonable stereochemical control. Alternatively, the reduction of substituted 4-diphenylphosphinoylbut-2-en-1-ones shows remarkable 1,4-diastereoselectivity. All these reactions are directed by the diphenylphosphinoyl (Ph_2PO) group.

Rearrangements of allylic alcohols are widely used in synthesis,[1] and we have described[2] the use of phosphine oxides derived by such rearrangements in the synthesis of alkadienols by the Horner–Wittig reaction. This paper[3] describes aspects of stereochemical control in the rearrangement of single diastereoisomers of allylic alcohols. The simplest rearrangement,[2] of the adduct **2** from methyldiphenylphosphine oxide **1**, butyllithium and butenone, gives a mixture of *E* and *Z* isomers of the transposed allylic alcohol **3** in excellent yield under Babler's conditions of acid-catalysed acetylation.[4] When adducts of longer chain alkyldiphenylphosphine oxides and enals or enones, *e.g.* **5**, are rearranged, only the *E* isomer is formed, but the question of diastereoselectivity arises. We report on the stereospecificity of the reaction, *i.e.* that single diastereoisomers of **6** can be made from single diastereoisomers of **5**, and on its inherent stereoselctivity, *i.e.* that intermediates such as allyl cations can show a 1,4-diastereoselectivity. All the rearrangements reported in this paper are driven by the diphenylphosphinoyl (Ph_2PO) group, which is always attached to one of the chiral centres, and all are totally *E* selective for the reasons we have already discussed.[2]

Addition of hexyldiphenylphosphine oxide **4** to butenone gave a 60:40 mixture of diastereoisomers **5** with *anti*-**5** predominating. Rearrangement of the mixture in aqueous acid[5] gave a 67:33 mixture of *anti*:*syn* alcohols **6** with some elimination products. Loss of product by elimination can be much more serious: attempted rearrangement of either **7** or **9**, adducts of **1** and the appropriate enone, gave only the *E*,*E* dienes **8** and **10**. These compounds behaved like tertiary non-allylic alcohols.[6]

Rearrangement of each diastereoisomer of **5** under acid-catalysed acetylation conditions[4] gave a mixture of *anti* and *syn* acetates **11** again favouring the *anti* compound. There is a small match/mismatch effect: the *anti* alcohol **5** gives rather more of the rearranged *anti* acetate **11** than does the *syn* alcohol **5**. The 67:33 mixture of alcohols **5** from the preparation gave the expected weighted mean (63:37). Neither these acetates, nor the alcohols derived from them by hydrolysis, could be separated but enough pure *anti*-**11** was separated by HPLC for characterisation. The stereochemistry was confirmed by an X-ray crystal structure analysis[7] of the epoxide[8] made from *anti*-**11**.

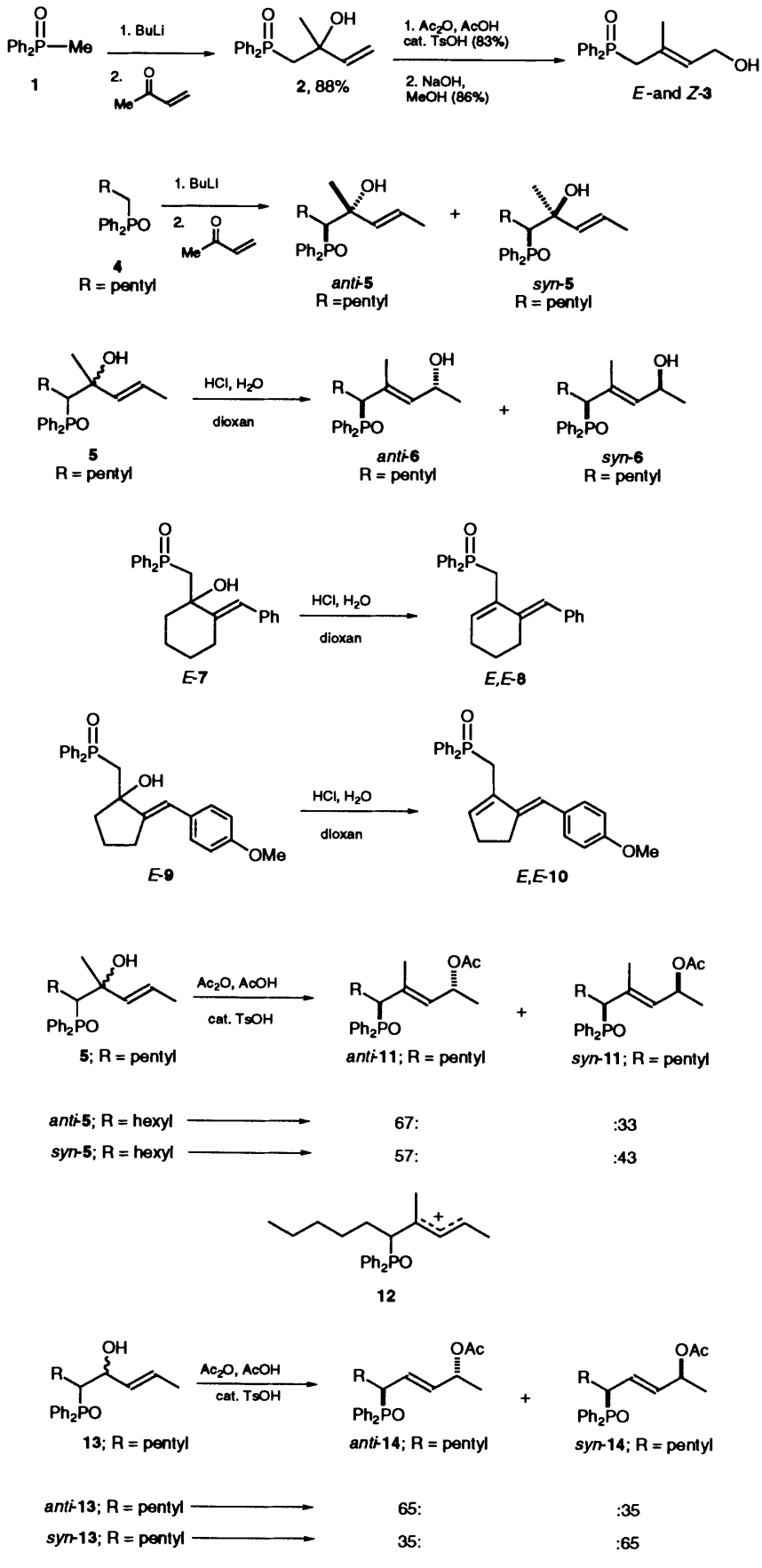
Both the acid-catalysed rearrangement and the rearrangement under conditions of acid-catalysed acetylation have the allyl cation **12** as an intermediate. A possible explanation for the rather weak stereoselectivities in these rearrangements and the small match/mismatch effect is that this cation prefers the *E*,*E* conformation **12** and that the molecule of water or acetic acid prefers to add from the face of the cation opposite to the large Ph_2PO group.

The crotonaldehyde adducts **13** of **4** were easily separated by fractional crystallisation on a 20 g scale in yields of 57% (*anti*-**13**) and 29% (*syn*-**13**) so that it was possible to study their rearrangements under a variety of conditions. This is a more interesting case as the double bonds in **13** and **14** have the same number of substituents.[2] Acid-catalysed acetylation showed a more marked stereospecificity: each isomer of **13** gave predominantly rearranged acetate **14** of the same configuration in a 65:35 ratio. Presumably, the molecule of acetic acid already present as the leaving group migrates suprafacially across an allylic cation of the same configuration as **12**. The rearranged acetates could not be separated, but hydrolysis gave a mixture of rearranged alcohols which could be partly separated by chromatography and crystallisation. Nevertheless, a method of stereospecific rearrangement is clearly preferable.

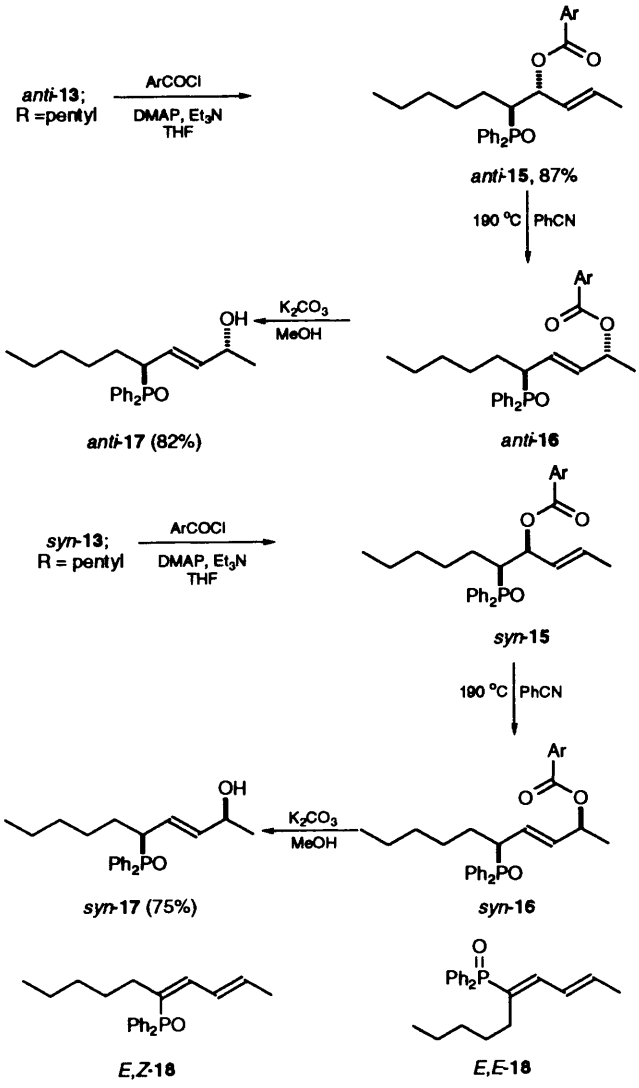
The two reactions used so far are not stereospecific because the allyl cation intermediates are only weakly solvated by neutral species (water or acetic acid) in the presence of more molecules of the same nucleophiles. Solvation by an anionic nucleophile would be tighter and studies by Goering[9] revealed that rearrangement of allylic *p*-nitrobenzoates in non-nucleophilic polar solvents offered the best hope. We prepared the *p*-nitrobenzoates *syn* and *anti*-**15** of each of the allylic alcohols **13** and rearranged them in benzonitrile at 190 °C. Each ester gave a totally rearranged ester **16** (Scheme 1) with some elimination product **18**. (In contrast, various attempted rearrangements of the acetate derived from *anti*-**5** led only to decomposition.) The rearranged esters **16** could be isolated by crystallisation of this mixture but it was more convenient to hydrolyse them to the rearranged alcohols **17** which could easily be separated and purified. The ester *anti*-**15** gave 93:7 *anti*:*syn* **17** while the *syn* ester was slightly less stereospecific (90:10). The rearranged alcohols from the acid-catalysed acetylation route were identified by comparison with these diastereoisomers given the known[9] suprafacial nature of the rearrangement.

The by-products were dienes **18**: pure *E*,*E*-**18** from *syn*-**15**, and a 71:29 *E*,*Z*:*E*,*E*-**18** mixture from *anti*-**15**. A concerted thermal ester elimination from *syn*-**15** would indeed give *E*,*E*-**18** while the loss of stereospecificity in elimination from *anti*-**15** presumably reflects the crowded transition state leading to the *E*,*Z*-diene. Elimination cannot be avoided in this stereospecific rearrangement but we have since developed an alternative method which avoids it altogether.[10]

The other main limitation to this approach to alcohols such



as **17** is that the stereoselectivity of the original coupling of the lithium derivative of the phosphine oxide to the enal or enone determines the maximum material conversion into any single isomer. This coupling is normally *anti* (*i.e.*, erythro)[11] selective, but only weakly so with enals and enones.[10,12] One alternative approach involves the reduction of enones such as **19**, **20** or **21**. In general, such reactions requiring the 1,4 transmission of stereochemical information over a rigid *E*-alkene give very poor

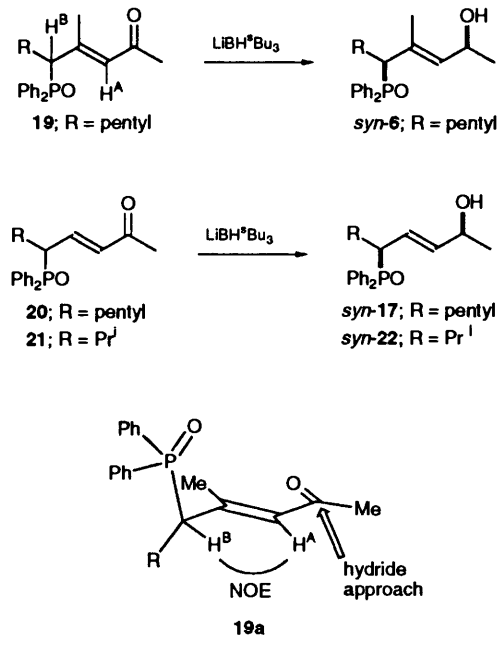


Scheme 1 Rearrangement of allylic esters **15**; Ar = *p*-nitrophenyl

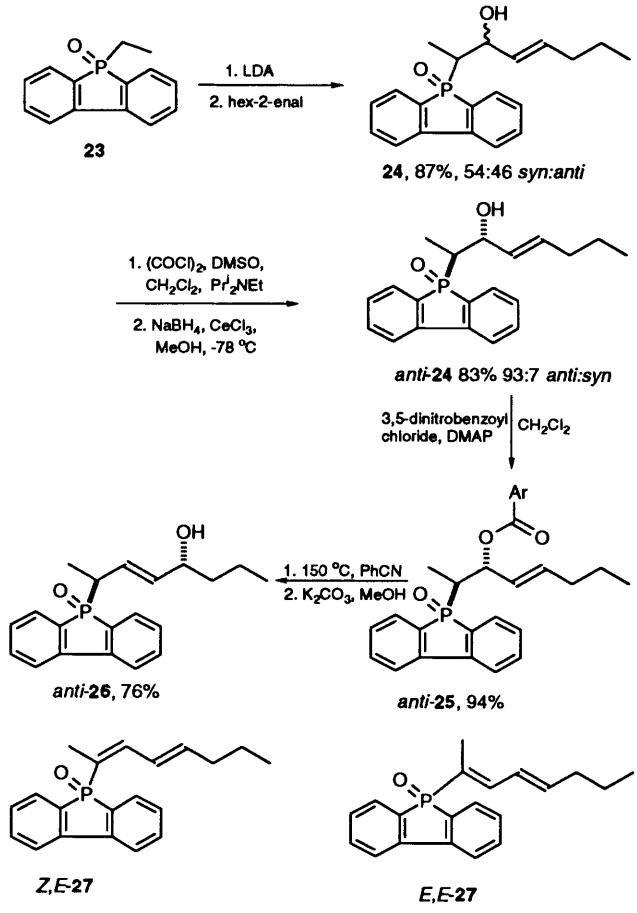
selectivity,[13] but we have found that the Ph_2PO group is exceptionally good at directing this type of remote stereochemical induction.

The enone **19** was made[2] by oxidative rearrangement of the mixture of alcohols **5**, and enones **20** and **21** by oxidation of the mixture of alcohols from the acid-catalysed acetylation route. Reduction of the enone **19** with $NaBH_4$ gave a 67:33 mixture of alcohols **6** favouring the *syn* isomer. The more hindered reducing agent lithium tri-*sec*-butylborohydride (L-Selectride) gave good stereoselectivity (> 80:20) in favour of *syn*-**6** which could be isolated in 69% yield. A strong NOE effect in the NMR spectrum[2] of **19** between H^A and H^B suggests an approach of the hydride from the face opposite the Ph_2PO group to conformation **19a** of the enone. This conformation resembles the proposed conformation of the allyl cation **12** or an extended Felkin conformation[11] with the C–P bond parallel to the p-orbitals of the enone. Reduction of the enones **20** and **21** with L-Selectride again gave selectivity in favour of the *syn* alcohols **17** and **22**, 72:28 when R is linear (hexyl), but 87:13 when R is branched (Pr^i). It is particularly useful that the major alcohol from the reduction has the *syn* stereochemistry of the minor product of the Horner–Wittig reaction.

An alternative approach to the *anti* isomers is based on our work with the bisbenzophosphole group.[14] Though there was almost no stereoselectivity in the initial coupling of **23** with LDA and hexenal, Swern[15] oxidation to the unstable enone and immediate reduction under the Luche[16] conditions gave



nearly pure *anti*-**24**. Recrystallisation gave pure *anti*-**24**; column chromatography of the original mixture gave pure *syn*-**24** in 45% yield. Each diastereoisomer was converted into its 3,5-dinitrobenzoate ester **25** and rearranged in benzonitrile at 150 °C to give the alcohol *anti*-**26** in 76% yield. The lower temperature is possible because the second nitro group accelerates the reaction. Rearrangement was complete and



Scheme 2 Rearrangement of dibenzophosphole analogues; Ar = 3,5-dinitrophenyl

nearly stereospecific (93:7 for *anti*-**22** and 90:10 for *syn*-**22**) with considerably less elimination: 6% of *Z,E*-**27** from *anti*-**24** and 6% of *E,E*-**27** from *syn*-**24**.

This is probably the best that one can do by these methods and pure alcohols such as **6** and **17** were used to make epoxides and hence unsaturated compounds with control over both the chiral centres and the geometry of the double bond.[8,17] For later and more demanding applications we prefer a Pd^{II} catalysed rearrangement.[10]

Experimental

(E)-5-*Diphenylphosphinoyl*-4-*methyldec*-2-*en*-4-*ol* E-**5**.—Butyllithium (1.5 mol dm^{-3} solution in hexane) was added dropwise to a stirred solution of hexyldiphenylphosphine oxide[18] (1.44 g, 5 mmol) in dry ether (50 cm^3) under nitrogen at 0 °C until a permanent red colour formed and then further butyllithium (3.5 cm^3, 5 mmol) was added dropwise and the solution stirred for 10 min. A solution of pent-3-en-2-one (0.43 g, 5 mmol) in dry ether (10 cm^3) was added over 5 min and the solution was stirred for a further 10 min, after which saturated aqueous ammonium chloride (20 cm^3) was added, the layers were separated, and the aqueous layer was extracted with ether (3 × 20 cm^3). The combined organic fractions were dried and evaporated under reduced pressure to give an oil which was purified by flash chromatography on silica, eluting with dichloromethane–ether (3:1) to give the *allylic alcohol* (1.2 g, 65%) as a colourless oil containing a 3:2 mixture of diastereoisomers. In a separate experiment the crude product (0.9 g) was purified on a short fat column of SiO_2 eluting with EtOAc and by HPLC (EtOAc–70% hexane; 14 cm^3 min^{-1}) to give the two separate diastereoisomers. The major *diastereoisomer* (0.22 g, 23%) formed white crystals, m.p. 97–98 °C (from hexane) (Found: C, 74.5; H, 8.55. $C_{23}H_{31}O_2P$ requires C, 74.6; H, 8.45%), R_F (EtOAc) 0.40, HPLC retention time 13.5 min, ν_{max}/cm^{-1} 3350 (OH), 1440 (PPh) and 1175 (P=O); $\delta_H(CDCl_3)$ 0.70 (3 H, t, *J* 5, *Me*CH_2) 0.8–1.8 [8 H, m, $(CH_2)_4$] 1.26 (3 H, s, *Me*COH), 1.53 (3 H, d, *J* 6, *Me*CH), 2.30 (1 H, m, PCH) 5.37 (1 H, br d, *J* 15 and < 1, C*H*=CHMe), 5.3 (1 H, br s, OH), 5.75 (1 H, dq, *J* 15 and 6, CH=C*H*Me) and 7.3–8.0 (10 H, m, Ph_2PO); *m/z* 355 (18%, M − Me) 286 (45, M − C_5H_8O) and 202 (100, Ph_2POH). The minor *diastereoisomer* (0.25 g, 26%) formed white crystals, m.p. 107–108 °C (from hexane) (Found: C, 74.3; H, 8.5. $C_{23}H_{31}O_2P$ requires C, 74.6; H, 8.45%), R_F (EtOAc) 0.42, HPLC retention time 12.5 min, ν_{max}/cm^{-1} 3350 (OH), 1440 (PPh) and 1163 (P=O); $\delta_H(CDCl_3)$ 0.70 (3 H, t, *J* 5.5, *Me*CH_2), 0.8–1.8 [8 H, m, $(CH_2)_4$], 1.11 (3 H, dd, *J* 6 and < 1, *Me*CH), 1.30 (3 H, s, *Me*COH), 2.2 (1 H, m, PCH), 5.15 (1 H, br d, *J* 15 and < 1, C*H*=CHMe), 5.1 (1 H, s, OH), 5.63 (1 H, dq, *J* 15 and 6, CH=C*H*Me) and 7.3–8.0 (10 H, m, Ph_2PO); *m/z* 355 (1%, M − Me), 286 (45, M − C_5H_8O) and 202 (100, Ph_2POH).

Allylic Rearrangement of E-**5** *in Mineral Acid by the method of Braude and Stern.*[5]—Dilute hydrochloric acid (20 cm^3) was added to a solution of *E*-**5** (2.5 g, 6.8 mmol) in dioxane (50 cm^3) at room temperature. The solution was stirred for 10 min and extracted with dichloromethane (3 × 25 cm^3). The combined organic fractions were dried ($NaSO_4$) and evaporated under reduced pressure to give an oil. TLC and ^1H NMR of this crude product showed that it was a *ca.* 2:1 mixture of diastereoisomers of the rearranged alcohols **6**, and *ca.* 20% of dehydration products. The major diastereoisomer could be separated by flash chromatography on silica, eluting with MeOH in EtOAc, to give (2RS,5SR; E)-5-*diphenylphosphinoyl*-4-*methyldec*-3-*en*-2-*ol* (anti-**6**), (0.4 g, 16%) as white crystals, m.p. 131.5–132.5 °C (from hexane:25% EtOAc), R_F(EtOAc) 0.37. For full characterisation see the minor diastereoisomer obtained on reduction of the enone **19**. The relative stereochemistry of *anti*-**6** was determined by an X-ray crystal study.[7]

(E)-2-*Benzylidene*-1-(*diphenylphosphinoylmethyl*)*cyclohexanol* E-**7**.—Benzylidenecyclohexanone was prepared by the method of Walton[19] and identified on the basis of spectroscopic evidence.[20] Methyldiphenylphosphine oxide (2.16 g) in ether (100 cm^3) was treated with butyllithium in hexane (7 cm^3) and the enone (1.86 g) was treated in the usual way[6] to give, after recrystallisation from ethyl acetate–hexane, the *alcohol* E-**7** (2.37 g, 59%), m.p. 142–144 °C, R_F (EtOAc) 0.5; ν_{max}/cm^{-1} 3300 (OH) and 1190 (P=O); $\delta_H(CDCl_3)$ 7.2–7.9 (10 H, m, Ph_2PO), 6.5–7.2 (6 H, m, Ph and C=C*H*Ph), 5.85 (1 H, s, OH), 3.05 (1 H, dd, *J* 8, 15, PCH^ACH^B), 2.55 (1 H, dd, *J* 12, 15, PCH^ACH^B), 2.5 (1 H, br d, *J* 12, C=CCH) and 0.9–2.1 (7 H, m, remaining CHs) (Found: M^+, 402.1752. $C_{26}H_{27}O_2P$ requires *M*, 402.1749); *m/z* 402 (6%, M^+), 384 (87), 383 (58), 215 (91, Ph_2POCH_2), 202 (100, Ph_2POH) and 201 (66, Ph_2PO).

(E)-1-(*Diphenylphosphinoylmethyl*)-2-p-*methoxybenzylidenecyclopentanol* E-**9**.—In a similar way to that described above, methyldiphenylphosphine oxide (2.16 g), butyllithium in hexane (7 cm^3) and 2-*p*-methoxybenzylidenecyclopentanone[19] (2.02 g) gave, after recrystallisation from ethanol, the alcohol *E*-**9** (52%), m.p. 141–143 °C, R_F (EtOAc) 0.34; ν_{max}/cm^{-1} 3340 (OH), 1605 (C=C) and 1168 (P=O); $\delta_H(CDCl_3)$ 7.3–7.9 (10 H, m, Ph_2PO), 7.10 (2 H, d, *J* 9, Ar), 6.80 (2 H, d, *J* 9, Ar), 6.51 (1 H, t, *J* 2.5, ArC*H*=C), 5.46 (1 H, s, OH), 3.74 (3 H, s, OMe), 3.0 (1 H, dd, *J* 10, 15, PCH^ACH^B), 2.4 (1 H, dd, *J* 8, 15, PCH^{A}CH^B), 2.5 (2 H, m, C=CCH_2) and 1.5–2.0 (4 H, m, remaining CH_2s); *m/z* 418 (1%, M^+), 400 (100), 215 (15, Ph_2POCH_2), 201 (44, Ph_2PO) and 198 (100, M − H_2O and Ph_2POH).

(E,E)-6-*Benzylidene*-1-(*diphenylphosphinoylmethyl*)*cyclohexene* E,E-**8**.—The alcohol *E*-**7** (0.5 g) was treated with HCl in dioxane to give, after recrystallisation from ethanol, the diene *E,E*-**8** (220 mg, 46%), m.p. 108–111 °C, R_F(EtOAc) 0.25; ν_{max}/cm^{-1} 1210 (P=O); $\delta_H(CDCl_3)$ 7.2–8.0 (10 H, m, Ph_2PO), 6.9–7.2 (5 H, m, Ph), 6.35 (1 H, s, PhC*H*=), 5.9 (1 H, q, *J* 4, C=C*H*CH_2), 3.3 (2 H, d, J_{PH} 15, PCH_2) and 1.2–2.5 (6 H, m, remaining CH_2s); *m/z* 384 (100%, M^+), 383 (57), 202 (92, Ph_2POH) and 201 (40, Ph_2PO).

(E)-1-(*Diphenylphosphinoylmethyl*)-5-p-*methoxybenzylidenecyclopentene* E-**10**.—The alcohol *E*-**9** (1 g) in methanol (170 cm^3) was treated with conc. HCl (1 cm^3) for 10 min at room temperature. Water (100 cm^3) and dichloromethane (100 cm^3) were added to the mixture and the layers separated; the aqueous layer was then extracted with dichloromethane (2 × 40 cm^3). The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Recrystallisation from ethyl acetate gave the diene *E,E*-**10** (53%), m.p. 107–110 °C, R_F (EtOAc) 0.25; ν_{max}/cm^{-1} 1620, 1605 (diene) and 1197 (P=O); λ_{max}/nm (EtOH) 302 (13 100), 314 (8900), 293 (12 000) and 221 (12 400); $\delta_H(CDCl_3)$ 7.3–7.9 (10 H, m, Ph_2PO), 7.24 (2 H, d, *J* 9, Ar), 6.82 (2 H, d, *J* 9, Ar), 6.13, 6.24 (each 1 H, br s, C=CHs), 3.78 (3 H, s, OMe), 3.30 (2 H, d, J_{PH} 14, PCH_2) and 2.3–2.8 (4 H, m, CH_2s); *m/z* 400 (18%, M^+), 215 (14, Ph_2POCH_2), 201 (22, Ph_2PO) and 198 (31, M − H_2O and Ph_2POH) and 94 (100).

(E)-2-*Acetoxy*-5-*diphenylphosphinoyl*-4-*methyldec*-3-*ene* E-**11** *by the Method of Babler.*[4]—A diastereoisomeric mixture of *E*-**5** (0.75 g, 2 mmol) was dissolved in glacial acetic acid (4 cm^3) and the solution added rapidly to a stirred solution of toluene-*p*-sulfonic acid monohydrate (180 mg) and acetic anhydride (4 cm^3) in glacial acetic acid (8 cm^3) at room temperature. Stirring was continued for 1.5 h under nitrogen. The solution was

poured into water (100 cm^3) and extracted with dichloromethane (3 × 30 cm^3) and the combined organic layers were washed with 2 mol dm^{-3} aqueous NaOH (40 cm^3), saturated aqueous sodium hydrogen carbonate (40 cm^3), and water (40 cm^3), dried (Na_2SO_4) and evaporated under reduced pressure to give an oil which was purified by flash chromatography; this afforded a 1.7:1 mixture (by ^1H NMR) of the diastereoisomers (0.49 g, 60%) as a white crystalline solid. This mixture could not be separated, but a slightly higher running fraction from the above column was purified further by HPLC on silica, eluting with 3:2 EtOAc–hexane, to give the major (2*RS*, 5*SR*) diastereoisomer of the *allylic acetate* (*anti*-**11**) (50 mg, 6%) as an oil, R_F 0.52, ν_{max}/cm^{-1} 1732 (C=O), 1440 (PPh) and 1192 (P=O); $\delta_H(CDCl_3)$ 0.7–1.0 (6 H, m, *Me*CH_2 and *Me*CH), 1.0–2.0 [8 H, m, $(CH_2)_4$], 1.71 (3 H, m, J_{HP} and J_{HH} < 1, *Me*C=CH), 1.94 (3 H, s, MeCO), 2.90 (1 H, m, PCH), 5.0–5.6 (2 H, m, =C*H*CHOAc) and 7.3–8.0 (10 H, m, Ph_2PO) (Found: M^+, 412.2169. $C_{23}H_{33}O_3P$ requires *M*, 412.2167); *m*/*z* 412 (5%, M^+), 352 (88, M − AcOH) and 201 (100, Ph_2PO). The minor diastereoisomer showed peaks at $\delta_H(CDCl_3)$ 1.20 (3 H, d, *J* 6, *Me*CH) and 1.90 (3 H, s, MeCO). The relative stereochemistry was determined by hydrolysis to the allylic alcohol **6**. The reaction was repeated under the same conditions on the separate diastereoisomers of **5**. The major diastereoisomer gave a 2:1 ratio (*anti*:*syn*) while the minor diastereoisomer gave a 1.3:1 ratio.

Hydrolysis of the Rearranged Allylic Ester E-anti-**11**.—A solution of *E-anti*-**11** (50 mg, 0.12 mmol) in a mixture of MeOH (4 cm^3) and 10% aqueous NaOH (1 cm^3) was stirred at room temperature for 30 min and extracted with ether (3 × 5 cm^3). The combined organic fractions were washed with water (2 × 5 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give a crude oil (one spot on TLC). ^1H NMR spectroscopy showed this product was pure *anti*-**6**. When the reaction was repeated using a *ca.* 1.7:1 diastereoisomeric mixture a clean reaction occurred to give a *ca.* 2:1 mixture of *anti*:*syn*-**6**

(E)-5-*Diphenylphosphinoyldec*-2-*en*-4-*ol* **13**.—Butyllithium (1.5 mol dm^{-3} solution in hexane) was added dropwise to a stirred solution of hexyldiphenylphosphine oxide (42.9 g, 150 mmol) in THF (550 cm^3) at 0 °C under nitrogen followed by further butyllithium (105 cm^3, 160 mmol) added between 0 °C and −10 °C. A solution of freshly distilled crotonaldehyde (11.0 g, 12.8 cm^3, 158 mmol) in THF (150 cm^3) was added dropwise over 20 min with cooling at −60 °C to the mixture which was then warmed to 0 °C over 15 min and quenched with saturated aqueous ammonium chloride (50 cm^3). The THF was evaporated under reduced pressure and water (400 cm^3) was added to the residue, which was extracted with dichloromethane (3 × 200 cm^3). The combined organic extracts were dried (Na_2SO_4) and evaporated under reduced pressure to give a white crystalline solid (53.0 g, 98%). Fractional recrystallisation of 35 g of this product followed by flash chromatography on silica, eluting with EtOAc–hexane (1:1) followed by EtOAc, gave the separate diastereoisomers. The less soluble 4RS,5RS-*diastereoisomer syn*-**13** (10.28 g, 29%), had m.p. 171.5–172 °C (from EtOAc–25% hexane) (Found: C, 73.9; H, 8.3. $C_{22}H_{29}O_2P$ requires C, 74.1; H, 8.15%), R_F (EtOAc:33% hexane) 0.21; ν_{max}/cm^{-1} 3350 (OH), 1440 (PPh) and 1160 (P=O); $\delta_H(CDCl_3)$ 0.76 (3 H, t, *J* 7, *Me*CH_2), 1.0–2.0 [8 H, m, $(CH_2)_4$], 1.43 (3 H, d, *J* 6, *Me*CH), 2.2–2.7 (1 H, m, PCH), 4.48 (1 H, dt, J_{PH} 18.5 and J_{HH} 5.5, C*H*OH), 4.70 (1 H, br s, OH), 5.35 (1 H, dd, *J* 16 and 6, MeCH=C*H*), 5.65 (1 H, dq, *J* 16 and 6, MeC*H*=CH), and 7.3–8.0 (10 H, m, Ph_2PO); *m*/*z* 356 (2%, M^+), 338 (4, M − H_2O), 286 [44, $Ph_2P(OH)CH(CH_2)_4Me$], 229 (100, $Ph_2POCH{=}CH_2$), 202 (93, Ph_2POH) and 201 (38, Ph_2PO). The more soluble 4RS,5SR-*diastereoisomer anti*-**13** (20.3 g, 57%) had m.p. 108–109 °C (from EtOAc–75% hexane) (Found: C, 74.2; H, 8.2%; M^+, 356.1904. $C_{22}H_{29}O_2P$ requires C, 74.1; H, 8.15%; *M*, 356.1905); R_F (EtOAc–33% hexane) 0.27; ν_{max}/cm^{-1} 3400 (OH), 1440 (PPh) and 1160 (P=O); $\delta_H(CDCl_3)$, 0.72 (3 H, t, *J* 7, *Me*CH_2), 0.9–2.0 [8 H, m, $(CH_2)_4$], 1.63 (3 H, d, *J* 6, *Me*CH), 2.2–2.5 (1 H, m, PCH), 4.57 (1 H, br ddd, J_{PH} 13, J_{HH} 4 and 2, C*H*OH), 4.80 (1 H, br s, OH), 5.46 (1 H, dd, *J* 16 and 6, MeCH=C*H*), 5.70 (1 H, dq, *J* 16 and 6, MeC*H*=CH) and 7.3–8.0 (10 H, m, Ph_2PO); $\delta_C(CDCl_3)$, 13.7 (q, *Me*CH_2), 17.48 (q, *Me*CH), 21.97 and 22.18 (2 × t, Me*C*H_2CH_2), 29.57 (dt, J_{PC} 6.9, PCHCH_2CH_2CH_2), 31.55 (t, PC*H*CH_2), 43.19 (dd, J_{PC} 68.0, PCH), 70.52 (d, CHOH), 126.51 (d, CH=*C*H) and 128.34–133.0 (11 C, m, Ph_2PO and *C*H=CH); *m*/*z* 356 (2%, M^+), 338 (5, M − H_2O), 286 [53, $Ph_2P(OH)CH(CH_2)_4Me$], 229 (98, $Ph_2POCH{:}CH_2$), 202 (100, Ph_2POH) and 201 (55, Ph_2PO). The *syn* and *anti* stereochemistries were assigned by comparison of the coupling constant between phosphorus and the proton adjacent to the hydroxy group for the two diastereoisomers.[21]

(E)-2-*Acetoxy*-4-*diphenylphosphinoyldec*-3-*ene* **14** *by the Method of Babler*.[4]—A solution of the diastereoisomeric mixture of **13** (17.6 g, 50 mmol) in glacial acetic acid (100 cm^3) was added in one portion to a stirred solution of toluene-*p*-sulfonic acid (3.0 g) in acetic acid (200 cm^3) and acetic anhydride (100 cm^3) at 0 °C under nitrogen. The reaction mixture was allowed to warm to room temperature over 2 h and stirring was continued for 16 h. Sodium carbonate (3 g) was then added to the mixture and the solvent evaporated under reduced pressure to give an oil. A portion of this crude product was purified by flash chromatography on silica, eluting with EtOAc–hexane (7:3) to give a *ca.* 1:1 mixture of the *acetates* [0.30 g, 68% overall yield from **4**] as a colourless oil, R_F (EtOAc–66% hexane) 0.21; ν_{max}/cm^{-1} 1725 (C=O) and 1442 (PPh); $\delta_H(CDCl_3)$ 0.81 (3 H, t, *J* 7, *Me*CH_2), 1.00 and 1.05 (3 H, 2 × t, *J* 6.4, *Me*CH), 1.0–2.1 [8 H, m, $(CH_2)_4$], 1.93 and 1.94 (3 H, 2 × s, MeCO), 2.8–3.0 (1 H, m, PCH), 5.0–5.6 (3 H, m, CH=CHCHOAc) and 7.3–7.9 (10 H, m, Ph_2PO) (Found: M^+, 398.2020. $C_{24}H_{31}O_3P$ requires *M*, 398.2011); *m*/*z* 398 (11%, M^+), 339 (5, M − AcO), 338 (5, M − AcOH), 219 (66), 202 (40, Ph_2POH) and 201 (100, Ph_2PO). The diastereoisomeric ratio was determined from the relative intensity of the signals at δ 1.00 and 1.05 and also from those at δ 1.93 and 1.94. The signals at δ 1.05 and 1.93 were shown to be due to the (2*RS*,4*RS*) isomer *syn*-**14** by unambiguous synthesis. Treatment of the major diastereoisomer of the unrearranged alcohol **13** under the same conditions gave a 98% yield of a 65:35 mixture of *anti*:*syn*-**14** as a colourless oil (^1H NMR and TLC). The minor diastereoisomer gave a 98% yield of a 35:65 mixture of *anti*:*syn*-**14** as a white solid. When the reaction was performed with a shorter reaction time (6 h) the crude product showed extra peaks in the ^1H NMR at $\delta_H(CDCl_3)$ 1.50 and 1.85 due to the unrearranged acetate and its diastereoisomer.

(2RS,4RS; E)-2-*Acetoxy*-5-*diphenylphospinoyldec*-3-*ene* syn-**14**.—A solution of *syn*-**13** (1.78 g, 5 mmol), DMAP[22] (100 mg) and acetic anhydride (0.75 g, 7.5 mmol) in a mixture of triethylamine (40 cm^3) and THF (40 cm^3) was stirred at room temperature under nitrogen for 6 h. The solution was evaporated under reduced pressure and the oil dissolved in ether (150 cm^3). The solution was washed with saturated aqueous $CuSO_4$ (2 × 50 cm^3), 5% ammonia (50 cm^3) and water (2 × 50 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give an oil. Purification of this by flash chromatography (SiO_2/EtOAc–25% hexane followed by EtOAc) gave the *acetate syn*-**14** (0.087 g, 44%) as a crystalline solid, m.p. 92–93 °C (from hexane–15% EtOAc) (Found: C, 72.1; H, 7.9; P. 7.75. $C_{24}H_{31}O_3P$ requires C, 72.4; H, 7.8; P. 7.8%); R_F (EtOAc–66% hexane) 0.21; ν_{max}/cm^{-1} 1730 (C=O);

$\delta_H(CDCl_3)$ 0.75 (3 H, t, *J* 7, *Me*CH_2), 1.05 (3 H, d, *J* 6, *Me*CH), 0.9–2.0 [8 H, m, $(CH_2)_4$], 1.93 (3 H, s, MeCO), 2.8–3.2 (1 H, m, PCH), 5.1–5.9 (3 H, m, CH=CHCHOAc) and 7.3–8.0 (10 H, m, Ph_2PO).

(4RS,5SR; E)-4-*Acetoxy*-5-*diphenylphosphinoyldec*-2-*ene*.—In a similar way, *anti*-**13** gave, without chromatography, the *acetate* (1.32 g, 74%) as a white crystalline solid, m.p. 112–112.5 °C; ν_{max}/cm^{-1} 1720 (C=O); $\delta_H(CDCl_3)$ 0.73 (3 H, t, *Me*CH_2), 0.9–1.8 [8 H, m, $(CH_2)_4$], 1.50 (3 H, s, MeCO), 1.60 (3 H, d, *J* 6, *Me*CH), 2.5–2.8 (1 H, m, PCH), 5.4–6.2 (3 H, m, CH=CHCHO) and 7.5–8.0 (10 H, m, Ph_2PO) (Found: M^+, 398, 1990. $C_{24}H_{31}O_3P$ requires *M*, 398.2011); *m*/*z* 398 (2.5%, M^+), 339 (65, M – AcO), [5%, $Ph_2P(OH)CH(CH_2)_4Me$], 269 (14), 242 (9), 229 (26, $Ph_2POCH{:}CH_2$), 202 (87, Ph_2POH) and 201 (100, Ph_2PO). Attempted rearrangement of this acetate by heating in $[^2H_8]$toluene at 110 °C for 24 h in an NMR tube alone or with toluene-*p*-sulfonic acid led to slow dehydration without rearrangement. The acetate when heated in a saturated solution[22] of $Cu(OAc)_2$ in either $[^2H_8]$toluene or $[^2H_3]$acetonitrile for several days at 60 °C gave no reaction.

(E)-5-*Diphenylphosphinoyldec*-3-*en*-2-*ol* **17** *by Hydrolysis of the Rearranged Acetates* **14**.—A solution of the crude mixture of rearranged acetates (20 mmol) and potassium carbonate (9 g) in methanol (150 cm^3) was stirred at room temperature for 6 h. The mixture was then diluted with water (300 cm^3) and extracted with dichloromethane (3 × 100 cm^3). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure to give a solid. Higher running impurities were separated on silica eluting with EtOAc–60% hexane followed by EtOAc to give a *ca.* 1:1 mixture of alcohols *syn* and *anti*-**13** (6.12 g, 86%). Recrystallisation from EtOAc–60% hexane gave the (2RS,5SR) *diastereoisomer anti*-**13** (2.6 g, 41%) as a white crystalline solid, m.p. 127.5–128.5 °C; R_F (EtOAc) 0.11; ν_{max}/cm^{-1} 3300 (OH); $\delta_H(CDCl_3)$ 0.81 (3 H, t, *J* 6.5, *Me*CH_2), 0.95 (3 H, d, *J* 6.5, *Me*CH), 1.0–1.8 [8 H, m, $(CH_2)_4$], 1.9 (1 H, br s, OH), 2.93 (1 H, ddt, J_{HP} 9, J_{HH} 5 and 9, PCH), 4.13 (1 H, d quintet, *J* 2 and 6.5, C*H*OH), 5.36 (1 H, ddd, J_{HP} 4, J_{HH} 16 and 6.5, CH=C*H*CHOH), 5.51 (1 H, ddd, J_{HP} 10, J_{HH} 16 and 5, C*H*=CHCHOH) and 7.4–7.9 (10 H, m, Ph_2PO) (Found: M^+, 356.1905. $C_{22}H_{29}O_2P$ requires *M*, 356.1905); *m*/*z* 356 (11%, M^+), 219 (30, $Ph_2PO_2H_2$), 202 (89, Ph_2POH) and 201 (100, Ph_2PO). Evaporation of the mother liquors gave a *ca.* 7:1 mixture of diastereoisomers *syn*- and *anti*-**13** as an oil (2.9 g, 47%) with the (2RS,5RS) *diastereoisomer syn*-**13** predominating; R_F (EtOAc) 0.11; ν_{max}/cm^{-1} 3300 (OH), 1440 (P–Ph), 1250 (C–O) and 1180 (P=O); $\delta_H(CDCl_3)$ 0.75 (3 H, t, *J* 7, *Me*CH_2), 1.03 (3 H, d, *J* 7, *Me*CH), 1.0–2.1 [8 H, m, $(CH_2)_4$], 2.8–3.2 (2 H, m, PCH and OH), 4.0–4.35 (1 H, m, C*H*OH), 5.1–5.8 (2 H, m, CH=CH) and 7.3–8.1 (10 H, m, Ph_2PO) (Found: M^+, 356.1904. $C_{22}H_{29}O_2P$ requires *M*, 356.1904); *m*/*z* 356 (0.72%, M^+) 253 (27), 227 (52), 219 (100, $Ph_2PO_2H_2$), 202 (80, Ph_2POH) and 201 (98, Ph_2PO). The diastereoisomeric ratio of *syn* to *anti*-**13** was determined by comparison of the relative intensities of the signals at δ 1.03 and 0.95 in the ^1H NMR spectrum.

(4RS,5SR; E)-5-*Diphenylphosphinoyldec*-2-*en*-4-*yl Nitrobenzoate* anti-**15**.—A solution of the alcohol *anti*-**13** (6.4 g, 19 mmol), 4-nitrobenzoyl anhydride[24] (7.66 g, 27 mmol) and DMAP[22] (350 mg) in a mixture of triethylamine (50 cm^3) and THF (150 cm^3) was stirred at room temperature under nitrogen for 2.5 h before evaporation under reduced pressure. The residual oil was dissolved in ethyl acetate (200 cm^3) and the solution was washed with 2 mol dm^{-3} aqueous NaOH (2 × 50 cm^3), 1 mol dm^{-3} aqueous HCl (50 cm^3) and saturated aqueous $NaHCO_3$ (50 cm^3), dried (Na_2SO_4) and evaporated under reduced pressure to give an oil. Purification of this on a short fat column (SiO_2/EtOAc–50% hexane) gave the *ester* (7.85 g, 87%) as a white crystalline solid, m.p. 134–134.5 °C (from EtOAc–hexane) (Found: C, 68.7; H, 5.9; N, 2.8; P, 6.0%; M^+, 505.2034. $C_{29}H_{32}NO_5P$ requires C, 68.9; H, 6.35; N, 2.9; P, 6.4%; *M*, 505.2018); R_F (EtOAc) 0.60; ν_{max}(Nujol)/cm^{-1} 1729 (C=O), 1538 and 1281 (NO_2), 1446 (P–Ph) and 1191 (P=O); δ_H ($CDCl_3$) 0.80 (3 H, t, *J* 7, *Me*CH_2) 1.0–2.0 [8 H, m, $(CH_2)_4$], 1.70 (3 H, d, *J* 6, *Me*CH), 2.7–3.1 (1 H, m, PCH), 5.5–6.2 (3 H, m, CH=CHCHO), 7.3–8.1 (10 H, m, Ph_2PO) and 7.88 and 8.21 (4 H, two distorted doublets, *J* 8, $NO_2C_6H_4CO_2$); *m*/*z* 505 (0.6%, M^+), 339 (38, M – $NO_2C_6H_4CO_2$), 202 (51, Ph_2POH) and 201 (100, Ph_2PO).

(4RS,5RS; E)-5-*Diphenylphosphinoyldec*-2-*en*-4-*yl Nitrobenzoate* syn-**15**.—This compound, prepared in a similar way to that described above from *syn*-**13**, was a white crystalline solid (8.24 g, 91%), m.p. 137–137 °C (from EtOAc–hexane) (Found: C, 68.7; H, 6.45; N, 3.0; P, 6.7, M^+, 505.2017. $C_{29}H_{32}NO_5P$ requires C, 68.9; H, 6.34; N, 2.9; P, 6.4%; *M*, 505.2018); R_F (EtOAc) 0.52; ν_{max}(Nujol)/cm^{-1} 1729 (C=O), 1529 and 1278 (NO_2), 1442 (P–Ph) and 1182 (P=O); $\delta(CDCl_3)$ 0.66 (3 H, t, *J* 7, *Me*CH_2), 0.8–2.0 [8 H, m, $(CH_2)_4$], 1.63 (3 H, d, *J* 5, *Me*CH), 2.90 (1 H, m, PCH), 5.6–6.1 (3 H, m, CH=CHCHO), 7.3–8.1 (10 H, m, Ph_2PO) and 7.99 and 8.22 (4 H, two distorted doublets, *J* 9, $NO_2C_6H_4CO_2$); *m*/*z* 505 (4%, M^+), 339 (29, M – NO_2PhCO_2), 338 (16, M – $NO_2C_6H_4CO_2$), 254 (30) and 201 (100, Ph_2PO).

(2RS,5SR; E)-5-*Diphenylphosphinoyldec*-2-*en*-2-*yl* 4-*Nitrobenzoate* anti-**16**.—A solution of the ester *anti*-**15** (7.07 g, 14 mmol) in benzonitrile (220 cm^3; deoxygenated by nitrogen for 10 min) was heated at reflux (190 °C) under nitrogen for 1 h. The solution was cooled and the benzonitrile evaporated under reduced pressure to give a white solid. A small portion (100 mg) of this crude product was recrystallised to give the rearranged *ester* (72 mg, 72%) as a white crystalline solid, m.p. 162–163 °C (from EtOAc–hexane) (Found: C, 68.8; H, 6.15; N, 3.1; P, 6.3%; M^+ 505.2004. $C_{29}H_{32}NO_5P$ requires C, 68.9; H, 6.35; N, 2.9; P, 6.4%; *M*, 505.2018); R_F(EtOAc) 0.32; ν_{max}(Nujol)/cm^{-1} 1728 (C=O), 1534 and 1288 (NO_2), 1445 (P–Ph) and 1190 (P=O); $\delta(CDCl_3)$ 0.83 (3 H, t, *J* 7, *Me*CH_2), 1.0–2.0 [8 H, m, $(CH_2)_4$], 1.27 (3 H, d, *J* 6, *Me*CH), 3.09 (1 H, m, PCH) 5.3–6.1 (3 H, m, CH=CHCHO), 7.3–8.1 (10 H, m, Ph_2PO) and 8.19 and 8.39 (4 H, two distorted doublets, *J* 9, $NO_2C_6H_4CO_2$); *m*/*z* 505 (M^+, 6%), 448 (40), 368 (8), 338 (10, M – $NO_2C_6H_4CO_2H$) and 201 (100, Ph_2PO).

(2RS,5SR; E)-5-*Diphenylphosphinoyldec*-3-4-*yl* 4-*Nitrobenzoate* syn-**16**.—This compound was prepared in a similar way from *syn*-**15**. Recrystallisation of a small portion of the crude product (100 mg) gave the *ester* (72 mg, 72%) as a white crystalline solid, m.p. 176–177 °C (from EtOAc–hexane) (Found: C, 68.6; H, 6.1; N, 2.9; P, 6.3%; M^+, 505.2000. $C_{29}H_{32}NO_5P$ requires C, 68.9; H, 6.35; N, 2.9; P, 6.4%; *M*, 505.2018); R_F (EtOAc) 0.33; ν_{max}(Nujol)/cm^{-1} 1728 (C=O), 1529 and 1280 (NO_2), 1441 (P–Ph) and 1180 (P=O); δ_H ($CDCl_3$) 0.78 (3 H, t, *J* 7, *Me*CH_2), 1.0–2.0 [8 H, m, $(CH_2)_4$], 2.8–3.2 (1 H, m, PCH), 5.3–6.0 (3 H, m, CH=CHCHO), 7.3–8.0 (10 H, m, Ph_2PO) and 8.18 and 8.34 (4 H, two distorted doublets, *J* 9, $NO_2C_6H_4CO_2$); *m*/*z* 505 (M^+, 13%), 368 (27), 339 (28, M – $NO_2C_6H_4CO_2$), 338 (36, M – $NO_2C_6H_4CO_2H$) and 201 (100, Ph_2PO).

(2RS,5SR; E)-5-*Diphenylphosphinoyldec*-3-*en*-2-*ol* anti-**17** *from the Rearranged* 4-*Nitrobenzoate*.—A solution of the crude rearranged 4-nitrobenzoate *anti*-**16** (6.97 g, 13.8 mmol) and potassium carbonate (10.0 g) in methanol (200 cm^3) was stirred at room temperature under nitrogen for 24 h before evaporation

under reduced pressure and addition of ethyl acetate (200 cm^3). The resulting solution was washed with saturated aqueous $NaHCO_3$ (2 × 50 cm^3) and water (50 cm^3), dried (Na_2SO_4) and evaporated under reduced pressure to give a white solid. The higher running impurities were removed on a short fat column (SiO_2/EtOAc followed by EtOAc–5% MeOH) to give the *alcohol* (4.10 g, 82% from *anti*-**15**) as a white crystalline solid, m.p. 127.5–128.5 °C; R_F(EtOAc) 0.11, identical by ^1H NMR to the less soluble diastereoisomer obtained by hydrolysis of the rearranged acetates. Comparison of the relative intensities of the signals at δ 1.00 and 1.05 (both doublets) in the ^1H NMR spectrum of the crude product showed it to be a 14:1 mixture of the diastereoisomers *anti*-and *syn*-**17**. Concentration of the higher running fractions from the column gave an oil (1.6 g) which was tentatively assigned as a 1.5:1 mixture of the (2*E*,4*Z*)- and (2*E*,4*E*)-isomers of 5-*diphenylphosphinoyldeca*-2,4-*diene* **18** (1.6 g, 16%); R_F (EtOAc) 0.36; δ($CDCl_3$) 0.72 (3 H, m, *Me*CH_2), 0.9–1.3 [6 H, m, Me(CH_2)$_3$], 1.77$^{(major)}$ and 1.82$^{(minor)}$ (3 H, two doublets, *J* 7, *Me*CH), 1.9–2.4 (2 H, m, CH_2C=CH), 5.7–7.0 (3 H, m, CH=CH–CH=C) and 7.3–7.9 (10 H, m, Ph_2PO).

(2RS,5SR; E)-5-*Diphenylphosphinoyldec*-3-*en*-2-*ol* syn-**17**.—This compound was obtained in a similar way from the rearranged 4-nitrobenzoate *syn*-**16**. The *alcohol* (4.3 g, 75%) was an oil which was identical, on the basis of ^1H NMR, MS and TLC evidence, with the more soluble diastereoisomer obtained by hydrolysis of the rearranged acetates. Comparison of the signals at δ1.05 in the ^1H NMR spectrum showed the product to be a 9:1 mixture of diastereoisomers of *syn*- and *anti*-**17**. The higher running fractions from the short fat column were concentrated to give (2E,4E)-5-*diphosphinoyldeca*-2,4-*diene* **18** (2.25 g, 23%) as colourless oil, R_F(EtOAc) 0.36; δ($CDCl_3$) 0.77 (3 H, t, *J* 7, *Me*CH_2), 1.0–1.5 [6 H, m, (CH_2)$_3$], 1.82 (3 H, d, *J* 7, *Me*CH_2), 1.0–1.5 [5 H, m, (CH_2)$_3$], 1.82 (3 H, d, *J* 7, *Me*CH), 2.1–2.5 (2 H, m, CH_2C=C), 5.98 (1 H, dq, *J* 15 and 7, MeC*H*), 6.4–7.0 (2 H, m, PC=C*H*–C*H*=CH) and 7.4–8.1 (10 H, m, Ph_2PO) (Found: M^+, 338.1823. $C_{22}H_{27}OP$ requires *M*, 338.1800); *m*/*z* 338 (M^+, 28%), 202 (95, Ph_2POH) and 201 (100, Ph_2PO).

(E)-5-*Diphenylphosphinoyl*-4-*methyldec*-3-*en*-2-*one* **19** (R = pentyl).—A solution of the alcohol **6** (0.7 g, 2.0 mmol) in dichloromethane (2 cm^3) was added in one portion to a stirred suspension of pyridinum chlorochromate[25] (0.41 g, 2.0 mmol) in dichloromethane (3 cm^3) at room temperature and stirring continued for 2 h. Ether (5 cm^3) was added to the mixture, the supernatant solution was decanted and the black resinous residue washed with ether (3 × 2 cm^3). The combined organic fractions were washed with 2 mol dm^{-3} aqueous NaOH (10 cm^3), 2 mol dm^{-3} aqueous HCl (10 cm^3) and saturated aqueous $NaHCO_3$ (2 × 5 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give an oil. The oil was purified by column chromatography (SiO_2/EtOAc–25% hexane) to give the *enone* (0.42 g, 60%) as white crystals, m.p. 138–140 °C (from EtOAc–hexane) (Found: C, 75.2; H, 7.95%; M^+ 368.1915. $C_{23}H_{29}O_2P$ requires C, 75.0; H, 7.9%; *M*, 368.1905), R_F 0.46; ν_{max}(Nujol)/cm^{-1} 1685 and 1612 (C=C–C=O), 1439 (P–Ph) and 1191 (P=O); δ_H($CDCl_3$) 0.80 (3 H, t, *J* 6, *Me*CH_2), 1.0–2.0 [8 H, m, (CH_2)$_4$], 2.00 (3 H, s, MeCO), 2.06 (3 H, dd, J_{HP} 2.5, J_{HH} < 1, MeC=C), 2.95 (1 H, m, PCH), 6.13 (1 H, br d, J_{HP} br d, J_{HP} 4, CHCO) and 7.3–8.1 (10 H, m, Ph_2PO). Irradiation of the signal at δ 6.13 caused an 11% enhancement of the signal at δ 2.95; δ_C($CDCl_3$), 13.95 (q, *Me*CH_2), 19.79 (q, *Me*C=C), 22.38 (t, Me*C*H_2), 27.50 (t, MeCH_2*C*H_2), 27.77 (dt, J_{CP} 13.0, PCHCH_2-*C*H_2), 31.41 (t, PCH*C*H_2), 31.81 (q, *Me*CO), 51.80 (dd, J_{CP} 64.4, PCH), 128.34–131.97 (11 C, m, Ph_2PO and MeC=*C*), 152.38 (s, Me*C*=C) and 197.98 (s, CO) (Found: M^+, 368.1915. $C_{23}H_{29}O_2P$ requires *M*, 368.1905); *m*/*z* 368 (10.4% M), 325 (45, M – MeCO), 219 (100, $Ph_2PO_2H_2$) and 201 (80, Ph_2PO); λ_{max}(EtOH)/nm 205, 226 and 248 (ε 24 700, 20 700 and 12 600).

(E)-5-*Diphenylphosphinoyldec*-3-*en*-2-*one* **20**.—(a) *By Collins oxidation.*[26] Chromium trioxide (18 g, 0.18 mol, flakes pre-dried over P_2O_5), was added in one portion to a well stirred solution of pyridine (28.5 g, 0.37 mmol, pre-dried on UG 1 alumina) in dry dichloromethane (500 cm^3) and stirring continued for 20 min under a dry atmosphere. A solution of the crude mixture of alcohols *syn*- and *anti*-**17** from hydrolysis of the rearranged acetates (8.72 g, 24.5 mmol) in dichloromethane (20 cm^3) was added in one portion and stirring continued at room temperature for 30 min. Silica (100 g) was added to the mixture and stirring continued for a further 10 min. Filtration, thorough washing of the silica with ethyl acetate and evaporation of the combined organic fractions under reduced pressure gave an oil which was dissolved in ether (200 cm^3). The solution was washed with 2 mol dm^{-3} aqueous NaOH (2 × 100 cm^3), 1 mol dm^{-3} aqueous HCl (100 cm^3) and brine (50 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give an oil. Purification of this by flash chromatography (SiO_2–EtOAc) gave the *enone* (6.0 g, 68%) as a white crystalline solid, m.p. 137–138 °C (from EtOAc–hexane); R_F (EtOAc) 2.24; ν_{max}(Nujol)/cm^{-1} 1678 and 1621 (C=C–C=O), 1442 (P–Ph) and 1188 (P=O); δ_H($CDCl_3$) 0.81 (3 H, t, *J* 7, *Me*CH_2), 1.0–2.0 [8 H, m, (CH_2)$_4$], 2.14 (3 H, s, MeCO), 3.0–3.4 (1 H, m, PCH), 6.01 (1 H, dd, *J* 16 and 4, CH=C*H*CO), 6.75 (1 H, ddd, *J* 16, 10 and 6, C*H*=CHCO) and 7.4–7.8 (10 H, m, Ph_2PO); δ_C($CDCl_3$) 13.80 (q, *Me*CH_2), 22.20 (t, Me*C*H_2), 26.64 (q, *Me*CO), 27.05 (t, MeCH_2*C*H_2), 27.59 (dt, J_{PC} 11.9, PCHCH_2*C*H_2), 31.09 (t, PCH*C*H_2), 44.71 (dd, J_{PC} 65.6, PCH), 128.4–131.93 (10 C, m, Ph_2PO), 135.05 (dd, J_{PC} 11.1, CH=*C*HCO), 142.49 (dd, J_{PC} 6.3, *C*H=CHCO) and 197.36 (s, C=O) (Found: M^+, 354. 1753. $C_{22}H_{27}O_2P$ required *M*, 354. 1749); *m*/*z* 354 (2.5%, M^+), 311 (5, M – MeCO), 297 [2.5 M – (CH_2)$_4$Me], 219 (100, $Ph_2PO_2H_2$), 202 (30, Ph_2POH) and 201 (55, Ph_2PO).

(b) *By pyridinium chlorochromate oxidation.* A suspension of the crude mixture of alcohols (0.5 g, 1.4 mmol) pyridinium chlorochromate[25] (0.6 g, 2.8 mmol) and flash silica (1.2 g) in dichloromethane (10 cm^3) was stirred at room temperature under nitrogen for 2 h. The suspension was filtered and the silica thoroughly washed with ethyl acetate (100 cm^3). The combined organic fractions were washed with 2 mol dm^{-3} aqueous NaOH (2 × 50 cm^3), 1 mol dm^{-3} aqueous HCl (50 cm^3) and brine (50 cm^3), dried (Na_2SO_4) and evaporated under reduced pressure to give the *enone* (0.34 g, 68%) as a white solid which was pure by TLC and identical (on the basis of ^1H NMR evidence) with the recrystallised product of Collins oxidation. This second method of oxidation is much cleaner.

Reduction of Compound **19** *with Sodium Borohydride.*—Sodium borohydride (12 mg, 0.3 mmol) was dissolved in a mixture of methanol (3 cm^3) and 10% aqueous NaOH (0.2 cm^3) and added in one portion to a solution of the enone **19** (111 mg, 0.3 mmol) in methanol (3 cm^3). Stirring of the mixture was continued for 15 min after which 2 mol dm^{-3} aqueous HCl (10 cm^3) was carefully added dropwise to it. The solution was extracted with Et_2O (3 × 5 cm^3) and the combined organic fractions were washed with saturated aqueous $NaHCO_3$ (10 cm^3) and water (10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The crude oil was purified on a short fat column (SiO_2–EtOAc) and by HPLC (EtOAc–10% hexane, 14 cm^3 min^{-1}) which give two major products: (2RS,5SR)-5-*diphenylphosphinoyl*-4-*methyldec*-3-*en*-2-*ol* (*anti*-**6**) (37 mg, 34%) as an oil, R_F (EtOAc) 0.37; HPLC retention time 11.5 min; ν_{max}(film)/cm^{-1} 3570 and 3300br (OH), 1440 (P–Ph) and 1178 (P=O); δ_H($CDCl_3$) 0.80 (3 H, t, *J* 7, *Me*CH_2), 0.84 (3 H, d, *J* 6, *Me*CH), 0.9–1.9 [8 H, m, (CH_2)$_4$], 1.66 (3 H, m, *J* < 1, MeC=C),

2.70 (1 H, br s, OH), 2.86 (1 H, m, PCH), 4.40 (1 H, quintet, *J* 6, C*H*OH), 5.20 (1 H, dd, J_{HP} 4, J_{HH} 6, C=CH) and 7.3–8.0 (10 H, m, Ph_2PO) (Found: M^+, 370.2074. $C_{23}H_{31}O_2P$ requires *M*, 370.2062); *m/z* 370 (1.5% M), 202 (96, Ph_2POH) and 201 (100 Ph_2PO); and (2RS, 5SR)-5-*diphenylphosphinoyl*-4-*methyldec*-3-*en*-2-*ol* (*syn*-**6**) (59 mg, 54%) as an oil; R_F (EtOAc) 0.33; HPLC retention time 15.5 min; ν_{max}(film)/cm^{-1} 3550 and 3300br (OH), 1438 (P–Ph) and 1178 (P=O); δ_H($CDCl_3$) 0.80 (3 H, t, *J* 5 *Me*CH_2), 1.10 (3 H, d, *J* 6.5, *Me*CH), 1.0–2.2 [8 H, m, $(CH_2)_4$], 1.68 (3 H, m, *J* < 1, MeC=C), 2.50 (1 H, br s, OH), 2.90 (1 H, m, PCH), 4.40 (1 H, br quintet, *J* 8 and < 1, C*H*OH), 5.21 (1 H, br dd, *J* < 1, 8 and 5, C=CH) and 7.3–8.0 (10 H, m, Ph_2PO) (Found: M − H_2O, 252.1962. $C_{23}H_{29}OP$ requires *M*, 252.1956); *m/z* 252 (21%, M − H_2O), 202 (100, Ph_2POH) and 201 (100, Ph_2PO).

L-Selectride Reductions.—The enone **19**. Lithium tri-*sec*-butylborohydride (L-Selectride) (1 mol dm^{-3} solution in THF; 12 cm^3, 12 mmol) was added dropwise over 5 min to a stirred solution of the enone (3.68 g, 10 mmol) in dry THF (200 cm^3) at −65 °C under nitrogen and stirring continued for 30 min. Further L-Selectride (2 cm^3, 2 mmol) was added to the mixture and stirring continued for a further 30 min. After this, acetone (15 cm^3) was added to the solution which was then warmed to −30 °C. After 10 min, a mixture of 2 mol dm^{-3} aqueous NaOH (20 cm^3) and hydrogen peroxide (100 volume equivalent solution; 20 cm^3) was added to the mixture over 5 min with cooling (exothermic reaction). The solution was stirred at 10 °C for 20 min, after which water (200 cm^3) was added to it and the pH adjusted to 6 with 2 mol dm^{-3} aqueous HCl. The THF was removed under reduced pressure and the aqueous solution extracted with dichloromethane (3 × 120 cm^3). The combined organic fractions were dried (Na_2SO_4) and evaporated under reduced pressure to give a colourless oil. All traces of butan-2-ol were removed under high vacuum. Flash chromatography (SiO_2/EtOAc–2% MeOH) gave recovered enone (0.7 g, 19%) and the (2RS, 5RS)-*allylic alcohol syn*-**6** (2.38 g, 65%, 81% based on recovered starting material) as an oil, identical [on the basis of TLC (EtOAc), IR and ^1H NMR evidence] to the major diastereoisomer obtained on sodium borohydride reduction of **19**. None of the other diastereoisomer *anti*-**6** was observed in the ^1H NMR spectrum of the crude reduction product (> 6:1 stereoselectivity).

The enone **20**. This reaction was carried out in a similar way at −65 °C but with an extended reaction time of 3 h. The crude product was separated from baseline material by PLC (SiO_2–EtOAc) to give a colourless oil (130 mg, 74%). Comparison of the methyl doublets at δ 1.03 and 0.94 in the ^1H NMR spectrum showed that this product was a 2.6:1 mixture of the *allylic alcohol* diastereoisomers *syn*-**17** and *anti*-**17** respectively.

Attempted Reduction of the Enone **19** *with REDAL.*—Reduction of the enone (0.55 g, 1.5 mmol) in dry THF (50 cm^3) at 0 °C under nitrogen with sodium bis(2-methoxyethoxy)-lithium aluminium hydride (REDAL)[27] (3.5 mol dm^{-3} solution; 0.95 cm^3, 3.4 mmol) gave a mixture purified by flash chromatography (SiO_2/EtOAc–10% hexane) to give diphenylphosphine oxide[28] (230 mg, 72%) and a *ca.* 2:1 mixture of geometric isomers of 4-*methyldec*-4-*en*-2-*ol* (45 mg, 18%); δ_H($CDCl_3$) 0.90 (3 H, t, *J* 7, *Me*CH_2), 1.19$^{(major)}$ and 1.21$^{(minor)}$ (3 H, two doublets, *J* 7, C*H*CH), 1.1–1.5 [6 H, m, Me(CH_2)$_3$], 1.63$^{(major)}$ and 1.73$^{(minor)}$ (3 H, 2 × br s, CH_3C=C), 1.8–2.3 (4 H, m, CH_2C=CCH_2), 3.7–4.1 (1 H, m, C*H*OH) and 5.30$^{(major)}$ and 5.38$^{(minor)}$ (1 H, 2 × br t, *J* 7, CH=C). Irradiation at δ 3.9 causes the signals at δ 1.19 and 1.21 to collapse to a broad singlet. Irradiation at δ 1.20 causes the signal at δ 3.7–4.1 to simplify to two double doublets the major one of which has *J* 8 and 5 (Found: M^+ − H, 169.1502. $C_{11}H_{21}O$ requires *M* − H, 169.1513); *m/z* 169.9 (15%, M − H), 152 (4, M − OH), 153 (4, M − H_2O), 125 (20, M − MeCHOH) and 85 (100). The slower running component was a single geometric isomer of 4-*methyldec*-3-*en*-2-*ol*, δ_H($CDCl_3$) 0.90 (3 H, t, *J* 7, *Me*CH_2), 1.0–2.3 (15 H, m), 4.62 (1 H, dq, *J* 8 and 6, C*H*OH) and 5.29 (1 H, br d, *J* 8, CH=C) (Found: M^+ − H_2, 168.1517. $C_{11}H_{20}O$ requires *M* − H_2 168.1520); *m/z* 169 (16%, M − H), 168 (34, M − H_2), 153 (32, M − OH) 129 (40) and 69 (100, C_4H_9).

(2RS,5SR; E)- *and* (2RS,5RS; E)-*Diphenylphosphinoyl*-6-*methylhept*-3-*en*-2-*yl Acetates.*—A solution of a 65:35 mixture[10] of (4RS,5SR; E)- and (4RS,5RS; E)-5-diphenylphosphinoyl-6-methylhept-2-en-4-ol (1.97 g, 6.0 mmol) in glacial acetic acid (15 cm^3) was added in one portion to a solution of toluene-*p*-sulfonic acid monohydrate (3 mmol) in acetic anhydride (7.5 cm^3) and glacial acetic acid (7.5 cm^3). The mixture was stirred under nitrogen for 24 h, 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, R_F (EtOAc) 0.40, was hydrolysed directly without purification.

(2RS,5RS; (E)-5-*Diphenylphosphinoyl*-6-*methylhept*-3-*en*-2-*ol* syn-**22**.—Aqueous sodium hydroxide (2 mol dm^{-3}, 12 cm^3) was added to a stirred solution of above mixture of rearranged acetates (6.0 mmol) in methanol (50 cm^3); heat was generated. The mixture was stirred at the resulting raised temperature for 60 min and 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, eluting with EtOAc and with EtOAc–10% MeOH, to yield a white solid (1.837 g, 93% from the unrearranged alcohols). HPLC showed that this was a 53:47 mixture of *anti*-**22** and *syn*-**22**. Further purification by HPLC, eluting with CH_2Cl_2–6% MeOH, gave the *alcohol syn*-**22** (0.624 g, 32%) as prisms, m.p. 178–179 °C (from EtOAc), R_t 21 min (Found: C, 72.95; H, 7.55; P. 9.49%; M − Me, 313.1372. $C_{20}H_{25}O_2P$ requires C, 73.15; H, 7.67; P. 9.43%; *M* − Me, 313.1357); R_F (EtOAc) 0.13; ν_{max}($CHCl_3$)/cm^{-1} 3360 (OH), 1450 (PPh) and 1150 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 5.73 (1 H, dddd, *J* 15.0, 10.6, 6.0 and 0.5, PCHC*H*=C), 5.36 (1 H, ddd, *J* 16.0, 6.3 and 4.1, C=C*H*CHOH), 4.14 (d × quintet, *J* 0.5 and 5.9, C*H*OH), 2.83 (1 H, ddd, *J* 11.1, 8.3 and 3.3, PCH), 2.19 (1 H, d × septet, *J* 3.3 and 7.0, C*H*Me_2), 1.8 (1 H, br s, OH), 1.05 (3 H, d, *J* 6.7, CH*Me*$_A$Me$_B$), 1.03 (3 H, d, *J* 6.8, CHMe$_A$*Me*$_B$) and 0.88 (3 H, d, *J* 6.3, CHOH*Me*); δ_C(100 MHz; $CDCl_3$) 141.8 ($^3J_{PC}$ 12.0, C=*C*HCHOH), 134–128 (Ph_2PO), 120.7 ($^2J_{PC}$ 6.4, PCH*C*H=C), 67.9 (CHOH), 49.5 ($^1J_{PC}$ 68.0, PCH), 27.5 (*C*HMe_2), 23.0 (CHOH*Me*), 22.9 ($^3J_{PC}$ 12.6, CH*Me*$_A$Me$_B$) and 18.9 ($^3J_{PC}$ 2.2, CHMe$_A$*Me*$_B$); *m/z* 313 (1%, M − Me), 310 (2, M − H_2O), 285 (13, M − C_3H_7), 219 (23, $Ph_2PO_2H_2$), 202 (81, Ph_2POH) and 201 (100, Ph_2PO). Also obtained was *anti*-**22** (0.919 g, 47%), R_t 22.5 min.

(E)-5-*Diphenylphosphinoyl*-6-*methylhept*-3-*en*-2-*one* **21**.—Oxalyl chloride (1.5 cm^3, 17.2 mmol) was added to a stirred solution of DMSO (1.45 cm^3, 20.4 mmol) in dry dichloromethane (75 cm^3) at −70 °C under nitrogen. After 10 min, a solution of the mixed alcohols **22** (3.1816 g, 9.69 mmol) in dry dichloromethane (50 cm^3) was added to it, and then, after a further 5 min, triethylamine (7 cm^3, 50 mmol). Stirring was continued at −70 °C for 10 min, before the mixture was allowed to warm to 10 °C over 30 min. Water (100 cm^3) was added to the mixture and the layers were separated; the aqueous fraction was extracted with dichloromethane (×2). The combined

organic fractions were washed with saturated brine, dried ($MgSO_4$) and evaporated under reduced pressure to yield a crude product. Purification of this by flash chromatography, eluting with 8:1 EtOAc–hexane, gave the *enone* **21** (2.85, g 90%) as fine needles, m.p. 121–122 °C (from EtOAc) (Found: M^+, 326.1432. $C_{20}H_{23}O_2P$ requires *M*, 326.1436); R_F (EtOAc) 0.32; $\nu_{max}(CHCl_3)/cm^{-1}$ 1677, 1655 (C=O), 1620 (C=C), 1445 (PPh) and 1160 (P=O); δ_H(250 MHz; $CDCl_3$) 8.0–7.5 (10 H, m, Ph_2PO), 6.95 (1 H, ddd, *J* 16.1, 10.9 and 6.7, PCHC*H*=CH), 5.95 (1 H, dd, *J* 16.0 and 3.7, CH=C*H*CO), 3.11 (1 H, ddd, *J* 11.0, 7.8 and 3.3, CHP), 2.40 (1 H, m, C*H*Me_2), 2.23 (3 H, s, Ac), 1.21 (3 H, d, *J* 6.9, CH*Me*$_A$$Me_B$) and 1.04 (3 H, d, *J* 6.8, CHMe_A*Me*$_B$); δ_C(100 MHz; $CDCl_3$) 197.4 ($^4J_{PC}$ 1.7, C=O), 140.0 ($^2J_{PC}$ 6.0, PCH*C*H–CH), 136.5 ($^3J_{PC}$ 11.0, CH=*CH*CO), 133–128 (Ph_2PO), 50.4 ($^1J_{PC}$ 65.4, CHP), 28.1 ($^5J_{PC}$ 2.9, *Me*CO), 26.4 (*C*HMe_2), 23.1 ($^3J_{PC}$ 12.0, CH*Me*$_A$$Me_B$) and 18.9 ($^3J_{PC}$ 2.6, CHMe_A*Me*$_B$); *m/z* 326 (12%, M^+), 283 (16, M – Ac), 219 (95, $Ph_2PO_2H_2$), 202 (58, Ph_2POH), 201 (82, Ph_2PO) and 77 (100, Ph).

L-Selectride Reduction of the Enone **21**.—L-Selectride (1 mol dm^{-3} solution; 14 cm^3, 14 mmol, 1.9 equiv.) was added to a stirred solution of the enone **21** (2.37 g, 7.26 mmol) in dry THF (150 cm^3) at −70 °C under nitrogen. Stirring was continued at −70 °C for 20 min, after which the reaction mixture was allowed to warm to 0 °C. Acetone (10 cm^3) was added to it followed by 2 mol dm^{-3} aqueous sodium hydroxide (20 cm^3) and aqueous hydrogen peroxide [26% (100 volumes); 20 cm^3]. After a few minutes, the mixture was poured into water (200 cm^3) and neutralised with 2 mol dm^{-3} hydrochloric acid. Most of the THF was removed under reduced pressure and the aqueous residue was extracted into dichloromethane (×4). The combined organic fractions were dried (Na_2SO_4) and evaporated under reduced pressure to yield a crude solid, which HPLC showed to consist of an 87:13 mixture of *syn*-**22** and *anti*-**22** (eluting with chloroform–5% MeOH; R_f's 45 and 50 min). One recrystallisation from ethyl acetate gave the pure (by HPLC and ^1H NMR) *alcohol syn*-**22** (1.665 g, 70%).

(E)-2-(5-*Oxodibenzophosphol*-5-*yl*)*oct*-4-*en*-3-*ol* **24**.—5-Ethyl-5*H*-dibenzophosphole 5-oxide[14,29] **23** (2.0 g, 8.77 mmol) in THF (80 cm^3) was added dropwise to a solution of LDA [from butyllithium (1.5 mol dm^{-3} solution in hexane; 8.2 cm^3) and diisopropylamine (1.42 g, 14.0 mmol)] in THF (40 cm^3) at 0 °C. The deep red solution was cooled to −78 °C and (*E*)-hex-2-enal (1.21 g, 12.3 mmol) was added dropwise to it so that the temperature remained < −75 °C. The mixture was stirred at −78 °C for 30 min and then diluted with water (20 cm^3). The mixture was allowed to warm to room temperature and the THF was evaporated under reduced pressure. Brine (40 cm^3) was added to the mixture which was then extracted with dichloromethane (4 × 50 cm^3). The combined organic fractions were dried ($MgSO_4$) and evaporated under reduced pressure to give a foam. ^1H NMR analysis (250 MHz, $CDCl_3$) of the double doublets at δ 0.81 and 0.51, and analytical HPLC (eluting with EtOAc–3% MeOH) showed that this was a 46:54 mixture of *diastereoisomers syn* and *anti*-**24** (HRF:LRF). These were separated by flash column chromatography on silica gel (6 cm), eluting with ethyl acetate–3% methanol. The first *diastereoisomer* to be eluted from the column was the (2*RS*,3SR)-adduct *anti*-**24** (1.11 g, 39%) as plates [from EtOAc–light petroleum (b.p. 40–60 °C)], m.p. 192–194 °C (Found: C, 73.3; H, 7.1; P. 9.6%; M^+, 326.1456. $C_{20}H_{23}O_2P$ requires C, 73.6; H, 7.1; P. 9.5%; *M*, 326.1346), R_F (EtOAc) 0.37; ν_{max}(Nujol)/cm^{-1} ($CHCl_3$) 3380br OH), 3000–2840 (CH), 1665 (C=C), 1600 (Ph), 1440 (P–Ph) and 1155 (P=O); δ_H(250 MHz, $CDCl_3$) 7.99–7.36 (8 H, m, dibenzo-H), 5.78 [1 H, dt, J_d 15.2, J_t 6.5, CH(OH)-CH=C*H*], 5.60 (1 H, ddd, *J* 15.2, 5.6, 1.0, CH(OH)C*H*=CH), 4.98 (1 H, m, CHO), 2.45 (1 H, ddq, J_{PH} 13.1, J_d 2.6, J_q 7.3, PCH), 1.7 (1 H, br s, exchanges with D_2O, OH), 2.05 (2 H, br q, *J ca.* 7, CH=CHCH_2), 1.37 (2 H, sextet, *J* 7.3, CH_2Me), 0.89 (3 H, t, *J* 7.3, CH_2*Me*) and 0.81 (3 H, dd, J_{PH} 18.7, J_{HH} 7.3, PCH*Me*); *m/z* 326 (3%, M^+), 228 (100, Ar_2POEt), 200 (64, Ar_2POH), 199 (61, Ar_2PO) and 152 (28, Ar_2). Next to be eluted was a mixture of diastereoisomers (85 mg, 3%). The second *diastereoisomer* to be eluted from the column was the (2*RS*,3*RS*)- adduct *syn*-**24** (1.28 g, 45%) as microcrystals [from EtOAc–light petroleum (b.p. 40–60 °C)], m.p. 192–194 °C (Found: C, 73.8; H, 7.25; P, 9.5%; M^+, 326.1434. $C_{20}H_{23}O_2P$ requires C, 73.6; H, 7.1; P. 9.5%; *M*, 326.1436); R_F (EtOAc) 0.30; ν_{max}(Nujol)/cm^{-1} ($CHCl_3$) 3380br (OH), 3000–2830 (CH), 1670 (C=C), 1600 (Ph), 1440 (P–Ph), and 1155 (P=O); δ_H(250 MHz, $CDCl_3$) 7.95–7.40 (8 H, m, dibenzo-H), 5.70 (1 H, dt, J_d 15.2, J_t 7.2, OCHCH=C*H*), 5.46 (1 H, dd, *J* 15.2, 7.7, OCHC*H*=CH), 4.49 (1 H, br q, *J* ca. 8, OCH), 2.43 (1 H, m, PCH), 2.01 (2 H, m, CH=CHCH_2), 1.38 (2 H, sextet, *J* 7.3, CH_2Me), 1.2 (1 H, br s, exchanges with D_2O, OH), 0.86 (3 H, t, *J* 7.3, CH_2*Me*) and 0.51 (3 H, dd, J_{PH} 19.2, J_{HH} 7.3, PCH*Me*); *m/z* 326 (5%, M^+), 228 (100, Ar_2POEt), 200 (57, Ar_2POH), 199 (56, Ar_2PO) and 152 (16, Ar_2).

(E)-2-(5-*Oxodibenzophosphol*-5-*yl*)*oct*-4-*en*-3-*one*.—Dimethyl sulfoxide (53 mg, 0.68 mmol) in dichloromethane (0.45 cm^3) was added dropwise to a stirred solution of oxalyl chloride (43 mg, 0.34 mmol) in dichloromethane (2.4 cm^3) at −60 °C. The mixture was stirred at −60 °C for 2 min after which the enol **24** (46:54 mixture of diastereoisomers; 100 mg, 0.31 mmol) in dichloromethane (0.9 cm^3) was added to it. The mixture was stirred at −60 °C for 15 min and then *N*,*N*-diisopropylethylamine (0.2 cm^3) was added to it. The mixture was stirred at −60 °C for 5 min and was then allowed to warm to room temperature over 20 min when it was diluted with water (20 cm^3) and extracted with dichloromethane (3 × 10 cm^3). The combined organic fractions were dried ($MgSO_4$) and evaporated under reduced pressure to give a brown oil which was purified by flash column chromatography on a short (8 × 1 cm) column of silica gel, eluting with ethyl acetate to give the *enone* (90 mg, 90%) as an unstable oil; this decomposed over *ca.* 24 h at 0 °C, R_F (EtOAc) 0.33; ν_{max}/cm^{-1} ($CHCl_3$) 2960–2840 (CH), 1680 (C=O), 1620 (C=C) and 1600 (Ph); δ_H(250 MHz, $CDCl_3$) 7.86–7.38 (8 H, m, dibenzo-H), 6.91 (1 H, dt, J_d 15.4, J_t 7.0, COCH=C*H*), 6.34 (1 H, d, *J* 15.4 COC*H*=CH), 3.88 (1 H, dq, J_{PH} 18.4, J_{HH} 7.0, PCH), 2.16 (2 H, br q, *J ca.* 7, CH=CHCH_2), 1.46 (2 H, sextet, *J* 7.3, CH_2Me), 1.05 (3 H, dd, J_{PH} 17.7, J_{HH} 7.0, PCH*Me*) and 0.91 (3 H, t, *J* 7.3, CH_2*Me*) (Found: M^+, 324.1267. $C_{20}H_{21}O_2P$ requires *M*, 324.1279); *m/z* 324 (30%, M^+), 228 (43, Ar_2POEt), 217 (38, $Ar_2PO_2H_2$), 200 (74, Ar_2POH), 199 (100, Ar_2PO) and 152 (48, Ar_2).

Reduction of (E)-2-(5-*Oxodibenzophosphol*-5-*yl*)*oct*-4-*en*-3-*one*.—Sodium borohydride (5.6 mg, 0.148 mmol) in ethanol (1 cm^3) was added over 10 min to a stirred solution of cerium chloride heptahydrate (55 mg, 0.148 mmol) and the enone (48 mg, 98%) in methanol (1 cm^3) at −78 °C. The mixture was stored at this temperature for 1 h after which HCl (1 mol dm^{-3}, 1 cm^3) was added to it. Solvents were evporated from the mixture under reduced pressure and water (10 cm^3) was added to the residue which was then extracted with dichloromethane (3 × 10 cm^3). The combined organic fractions were dried ($MgSO_4$) and evaporated under reduced pressure. The product was purified by chromatography on a short (2 cm) column of silica, eluting with ethyl acetate to give the alcohol **24** as a white solid. ^1H NMR analysis (250 MHz, $CDCl_3$) of the double doublets at δ 0.81 and 0.51 showed that this was a *ca.* 95:5 mixture of the (2*RS*,3*SR*)-*anti*-**24** and (2*RS*,3*RS*)-*syn* **24** adducts.

Oxidation and Immediate Reduction of the Alcohols **24**.—Dimethyl sulfoxide (53 mg, 0.68 mmol) in dichloromethane (0.45 cm^3) was added dropwise to a stirred solution of oxalyl chloride (43 mg, 0.34 mmol) in dichloromethane (2.4 cm^3) at −60 °C. The mixture was stirred at −60 °C for 2 min after which the enol **24** (46:54 mixture of diastereoisomers, 100 mg, 0.31 mmol) in dichloromethane (0.9 cm^3) was added to it. The mixture was stirred at −60 °C for 15 min and then *N*,*N*-diisopropylethylamine (0.2 cm^3) was added to it. The mixture was stirred at −60 °C for 5 min and then was allowed to warm to room temperature over 20 min. Solvent was evaporated from the mixture under reduced pressure (high vacuum, 0 °C) and the residue was reduced by sodium borohydride (126 mg, 0.31 mmol) and cerium chloride heptahydrate (115 mg, 0.31 mmol) to give (*E*)-2-(5-oxodibenzophosphol-5-yl)oct-4-en-3-ol **24** (83 mg, 83%) as a white solid. ^1H NMR analysis (250 MHz, $CDCl_3$) of the double doublets at δ 0.81 and 0.51 and analytical HPLC (eluting with ethyl acetate–3% methanol) showed that this was a 93:7 mixture of the (2*RS*,3*SR*)-*anti*-**22** and (2*RS*,3*RS*)-*syn*-**24** adducts. Recrystallisation from ethyl acetate–light petroleum (b.p. 40–60 °C) gave the (2*RS*,3*SR*)-adduct *anti*-**24** (72 mg, 72%).

(2RS,3SR; E)-3-(3,5-*Dinitrobenzoyloxy*)-2-(5-*oxodibenzophosphol*-5-*yl*)*oct*-4-*ene* anti-**25**.—3,5-Dinitrobenzoyl chloride (0.849 g, 3.68 mmol) was added under argon to a stirred solution of the enol *anti*-**24** (1.0 g, 3.07 mmol) and 4-dimethylaminopyridine (0.45 g, 3.68 mmol) in dichloromethane (10 cm^3) at 0 °C. The mixture was stirred at room temperature for 1 h and then purified by flash column chromatography on silica gel (3 cm), eluting with ethyl acetate to give the *ester* (1.46 g, 91%) as needles [from CH_2Cl_2–light petroleum (b.p. 40–60 °C)], m.p. 196–197 °C (Found: C, 62.6; H, 5.25; N, 5.3; P, 6.2%; M^+, 520.1364. $C_{27}H_{25}N_2O_7P$ requires C, 62.3; H, 4.85; N, 5.4; P, 6.0%; *M*, 520.1399); R_F(EtOAc) 0.32; $\nu_{max}(CHCl_3)/cm^{-1}$ 3100–2850 (CH), 1735 (C=O), 1665 (C=C), 1630, 1600 (Ph) and 1545 and 1345 (NO_2); δ_H(250 MHz, $CDCl_3$) 9.16 (1 H, t, *J* 2.0, Ar-4-H), 8.74 (2 H, d, *J* 2.0, Ar-2,6-H), 7.91–7.28 (8 H, m, dibenzo-H), 5.60 (2 H, m, OC*H*CH=C*H*CH_2), 5.42 (1 H, dd, *J* 14.4, 6.3, OCHC*H*=CH), 2.70 (1 H, m, PCH), 1.92 (2 H, br, q, *J ca.* 7, CH=CHCH_2), 1.60 (3 H, dd, J_{PH} 15.6, J_{HH} 7.3, PCH*Me*), 1.29 (2 H, sextet, *J* 7.3, CH_2Me) and 0.81 (3 H, t, *J* 7.3, CH_2*Me*) (irradiation of the signal at δ 0.81 led to a simplification of the signal at δ 1.29; irradiation of the signal at δ 1.29 led to a simplification of the signals at δ 0.89 and 1.92; irradiation of the signal at δ 1.60 led to a simplification of the signal at δ 2.70; irradiation of the signal at δ 1.92 led to a simplification of the signals at δ 1.29 and 1.60; and irradiation of the signal at δ 2.70 led to a simplification of the signals at δ 1.60 and 5.60); *m*/*z* 520 (6%, M^+), 308 (32, M − $ArCO_2H$), 200 (58, Ar_2POH) and 199 (100, Ar_2PO).

(2RS,3SR; E)-3-(3,5-*Dinitrobenzoyloxy*)-2-(5-*oxodibenzophosphol*-5-*yl*)*oct*-4-*ene* syn-**25**.—In the same way, 3,5-dinitrobenzoyl chloride (0.849 g, 3.68 mmol), the enol *syn*-**24** (1.0 g, 3.07 mmol) and 4-dimethylaminopyridine (0.45 g, 3.68 mmol) in dichloromethane (10 cm^3) gave, after purification by flash column chromatography on silica gel (3 cm) eluting with ethyl acetate, the *ester* (1.50 g, 94%) as needles [from CH_2Cl_2–light petroleum (b.p. 40–60 °C)], m.p. 175–176 °C (Found: C, 62.3; H, 4.9; N, 5.4; P, 5.9%; M^+, 520.1422. $C_{27}H_{25}N_2O_7P$ requires C, 62.3; H, 4.85; N, 5.4; P, 6.0%; *M*, 520.1399); R_F (EtOAc) 0.40; ν_{max}/cm^{-1} ($CHCl_3$) 3100–2870 (CH), 1730 (C=O) 1665 (C=C), 1630, 1600 (Ph), 1545, 1345 (NO_2) and 1160 (P=O); δ_H(250 MHz, $CDCl_3$) 9.14 (1 H, t, *J* 2.1, Ar-4-H), 8.79 (2 H, d, *J* 2.1, Ar-2,6-H), 7.94–7.29 (8 H, m, dibenzo-H), 5.79 (1 H, dt, J_d 14.3, J_t 7.0, OCHCH=C*H*), 5.43 (2 H, m, OCHCH), 3.01 (1 H, m, PCH), 1.95 (2 H, br q, *J ca.* 7, CH=CHCH_2), 1.33 (2 H, sextet, *J* 7.3, CH_2Me), 1.28 (3 H, dd, J_{PH} 16.2, J_{HH} 7.4, PCH*Me*) and 0.83 (3 H, t, *J* 7.3, CH_2*Me*); *m*/*z* (20%, M^+), 309 (46, M − $ArCO_2$) and 308 (100, M − $ArCO_2H$).

(2RS,5SR; E)-2-(5-*Oxodibenzophosphol*-5-*yl*)*oct*-3-*en*-5-*ol* anti-**26**.—The enol *anti*-**25** (200 mg, 0.38 mmol) in benzonitrile (15 cm^3) was heated to 150 °C for 1 h, cooled and the solvent evaporated under reduced pressure (high vacuum). The residue was dissolved in methanol (10 cm^3) and potassium carbonate (300 mg) was added to the solution. The mixture was stirred at room temperature for 1 h after which saturated aqueous ammonium chloride (10 cm^3) was added to it, methanol removed by evaporation under reduced pressure and the residue extracted with dichloromethane (4 × 10 cm^3). The combined organic fractions were washed with saturated aqueous sodium hydrogen carbonate (2 × 10 cm^3) and water (10 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give a yellow oil. This was purified by flash column chromatography on silica gel (2 cm^3), eluting with ethyl acetate–5% methanol. The first product to be eluted was (2*Z*,4*E*)-2-(5-oxodibenzophosphol-5-yl)octa-2,4-diene *Z*,*E*-**27** (9 mg, 8%) as a colourless oil, R_F (EtOAc–5% MeOH) 0.46; δ_H(250 MHz, $CDCl_3$) 7.81–7.22 (9 H, m, dibenzo-H and PC=CH.C*H*=CH), 6.85 (1 H, dd, J_{PH} 37.4, J_{HH} 11.6, PC=C*H*CH=CH), 5.87 (1 H, dt, J_d 14.7, J_t 7.4, PC=CH.CH=C*H*), 2.19 (2 H, q, *J* 7.4, =CHCH_2), 1.44 (2 H, m, CH_2Me), 1.36 (3 H, d, J_{PH} 14.4, PC*Me*) and 0.93 (3 H, t, *J* 7.4, CH_2*Me*) (irradiation of the signal at δ 2.19 led to a simplification of the signals at δ 1.44 and 5.87; irradiation of the signal at δ 5.87 led to a simplification of the signals at δ 2.19 and 7.64; irradiation of the signal at δ 6.85 led to a simplification of the signal at δ 7.64; irradiation of the signal at δ 7.64 led to a simplification of the signals at δ 5.87 and 6.85) (Found: M^+, 308.1331. $C_{20}H_{21}OP$ requires, *M*, 308.1331); *m*/*z* 308 (77%, M^+), 265 (69, M − CH_2CH_2Me), 200 (100, Ar_2POH), 199 (75, Ar_2PO), 183 (60, Ar_2P), and 152 (46, Ar_2). The second product to be eluted was the *alcohol anti*-**26** (94 mg, 76%), as a gum R_F (EtOAc–5% MeOH) 0.16; $\nu_{max}/CHCl_3)/cm^{-1}$ 3340br (OH), 3000–2840 (CH), 1660 (C=C), 1600 (Ph), and 1150 (P=O); δ_H(250 MHz, $CDCl_3$) 7.83–7.36 (8 H, m, dibenzo-H), 5.47 (1 H, ddd, J_{PH} 4.1, J_d 15.5, 7.1, PCHC*H*=CH), 5.36 (1 H, ddd, *J* 15.5, 6.2, 4.1, PCHCH=C*H*), 3.90 (1 H, m, CHO), 3.00 (1 H, d quint, J_{PH} 17.1, J_q 7.1, PCH), 1.8 (1 H, br s, exchanges with D_2O, OH), 1.30 (3 H, dd, J_{PH} 7.1, PCH*Me*), 1.30–0.94 (4 H, m, CH_2CH_2Me) and 0.82 (3 H, t, *J* 7.1, CH_2*Me*) (irradiation of the signal at δ 1.30 led to a simplification of the signals at δ 0.82, 3.00 and 3.90; irradiation of the signal at δ 3.00 led to a simplification of the signals at δ 3.00 and 5.47; irradiation of the signal at δ 3.90 led to a simplification of the signal at δ 5.36) (Found: M^+, 326.1425. $C_{20}H_{23}O_2P$ requires *M*, 326.1435); *m*/*z* 326 (10%, M^+), 283 (30, M − CH_2CH_2Me), 200 (98, Ar_2POH), 199 (100, Ar_2PO) and 152 (20, Ar_2). Analytical HPLC (eluting with ethyl acetate–5% methanol) showed that this contained *ca.* 5% of the (2*RS*,5*RS*)-adduct *syn*-**26**.

(2RS,5SR; E)-2-(5-*Oxodibenzophosphol*-5-*yl*)*oct*-3-*en*-5-*ol* syn-**26**.—(2*RS*,3*RS*; E)-3-(3,5-Dinitrobenzoyloxy)-2-)-5-oxodibenzophosphol-5-yl)oct-4-ene *syn*-**25** (90 mg, 0.17 mmol) in benzonitrile (5 cm^3) was heated to 150 °C for 1 h, cooled and the solvent evaporated under reduced pressure (high vacuum). The residue was dissolved in methanol (5 cm^3) and potassium carbonate (150 mg) was added to the solution. The mixture was stirred at room temperature for 1 h after which saturated aqueous ammonium chloride (10 cm^3) was added to it, the methanol removed by evaporation under reduced pressure and the residue extracted with dichloromethane (4 × 10 cm^3). The combined organic fractions were washed with saturated aqueous sodium hydrogen carbonate (2 × 10 cm^3) and water

($10\ cm^3$), dried ($MgSO_4$) and evaporated under reduced pressure to give a yellow oil. This was purified by flash column chromatography on silica gel (1 cm), eluting with ethyl acetate–5% methanol. The first product to be eluted was identified at (2E,4E)-2-(5-*oxodibenzophosphol*-5-*yl*)*octa*-2,4-*diene* E,E-**27** (3 mg, 6%) as a colourless oil, R_F (EtOAc–5% MeOH) 0.46; δ_H(250 MHz, $CDCl_3$) 7.80–7.31 (9 H, m, dibenzo-H and PC=C*H*CH=CH), 6.35 (1 H, ddd, J_{PH} 1.8, J_{HH} 14.7, 11.0, PC=CHC*H*=CH), 6.12 (1 H, dt, J_d 14.7, J_t 7.3, PC=CHCH=C*H*), 2.15 (2 H, q, *J* 3, =CHCH_2), 1.48 (2 H, m, C*H*Me), 1.41 (3 H, d, J_{PH} 15.2, PCMe) and 0.92 (3 H, t, *J* 7.4, CH_2*Me*) (irradiation of the signal at δ 1.48 led to a simplification of the signal at δ 2.15; irradiation of the signal at δ 2.15 led to a simplification of the signals at δ 2.15 and 6.35; irradiation of the signal at δ 6.35 led to a simplification of the signals at δ 6.12 and 7.30; irradiation of the signal at δ 7.30 led to a simplification of the signal at δ 6.35) (Found: M^+, 308.1334. $C_{20}H_{21}OP$ requires *M*, 308.1331); *m*/*z* 308 (37%, M^+), 265 (47, M – CH_2CH_2Me), 200 (100, Ar_2POH), 199 (83, Ar_2PO), 183 (60, Ar_2) and 152 (27, Ar_2). The second product to be eluted was the *alcohol syn*-**26** (38 mg, 67%), as a gum R_F (EtOAc–5% MeOH) 0.16; $\nu_{max}(CHCl_3)/cm^{-1}$ 3370 br (OH), 3000–2840 (CH), 1660 (C=C), 1600 (Ph) and 1155 (P=O); δ_H(250 MHz, $CDCl_3$) 7.84–7.37 (8 H, m, dibenzo-H), 5.46 (1 H, ddd, J_{PH} 3.9, J_d 15.5, 6.9, PCHC*H*=CH), 5.37 (1 H, ddd, *J* 15.5, 4.8, 3.7, PCHCH=C*H*), 3.91 (1 H, m, CHO), 3.03 (1 H, d quint, J_{PH} 18.2, J_q 6.9, PCH), 1.8 (1 H, br s, exchanges with D_2O, OH), 1.25 (3 H, dd, J_{PH} 17.2, J_{HH} 7.0, PCH*Me*), 1.41–1.05 (4 H, m, CH_2CH_2Me), and 0.83 (3 H, t, *J* 7.1, CH_2*Me*) (Found: M^+, 326.1425. $C_{20}H_{23}O_2P$ requires *M*, 326.1435); *m*/*z* 326 (3%, M^+), 228 (100, Ar_2POEt), 200 (72, Ar_2POH), 199 (66, Ar_2PO), 183 (20, Ar_2P) and 152 (23, Ar_2). Analytical HPLC (eluting with ethyl acetate–5% methanol) showed that this contained *ca.* 9% of the (2*RS*,5*SR*)-adduct *anti*-**26**.

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