Additions of Lithiated β-Hydroxy Alkyldiphenylphosphine Oxides to Aldehydes, and Palladium(II)-catalysed Allylic Transpositions of Bis-acetoxy Alkyldiphenylphosphine Oxides: Synthesis of *O*-Protected (*E,E*)- and (*E,Z*)-Hepta-2,4-dien-1-ol and of Alkyldiphenylphosphine Oxides Bearing Remotely Related Chiral Centres

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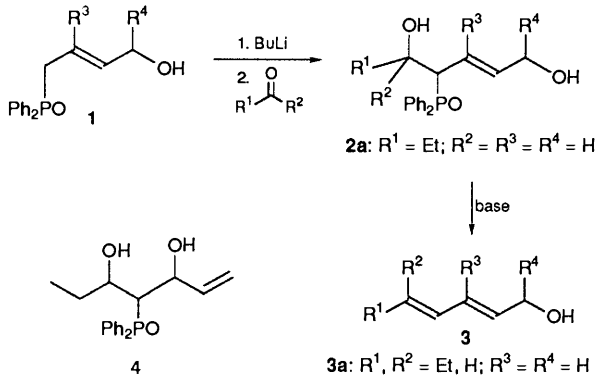
Saturated and unsaturated β- and δ-hydroxyalkyldiphenylphosphine oxides give adducts with aldehydes after treatment with an excess of butyllithium. Normal Horner–Wittig reactions lead to *O*-trityl (*E,E*)- and (*E,Z*)-hepta-2,4-dien-1-ols. Allylic rearrangement of the corresponding acetates catalysed by Pd^{II} can be used to control remote (1,4 or 1,7) relative stereochemistry across *E* alkenes.

We have reported the stereocontrolled synthesis of the dienols[1] **3** by the stereochemically controlled Horner–Wittig reaction.[2] We made use of the δ-hydroxyallylic phosphine oxides **1**, which were lithiated twice (once on oxygen, once on carbon) and added to aldehydes or ketones to give the diols **2**. Subsequent Horner–Wittig elimination gave the dienols **3**. One-step Horner–Wittig olefinations have been used to give the thermodynamically favoured *E*-polyenes,[3] but we hoped that separation of the diastereoisomeric diols **2** would enable us to control the geometry of one of the double bonds in the dienol **1**



by taking advantage of the stereospecificity of the Horner–Wittig elimination.[2] Unfortunately, for the substitution pattern under investigation, the diastereoisomers of the diol **2**, their bis-acetates, and their bis-silyl ethers, were inseparable.

We now report that the diastereoisomeric bis-acetates of the diol **2a** are readily separable by chromatography, providing a new route to the hepta-2,4-dien-1-ols **3a**, important intermediates in the synthesis of the pheromones of the silk worm and grape vine moths.[4] We also describe palladium(II)-catalysed allylic transposition[5,6] of β,β′-dihydroxyphosphine oxides such as **4**, which are made by a novel addition of lithiated β-hydroxy phosphine oxides to aldehydes, as an alternative route to the diols **2a**. We have extended the scope of this addition–transposition strategy to the synthesis of alkyldiphenylphosphine oxides bearing 1,7-related chiral centres.

Propionaldehyde was added to the dilithium derivative of the phosphine oxide **5** to give an inseparable 60:40 mixture of the diols **2a**. Monoprotection of the primary hydroxy group was more successful with a trityl group than with a triisopropylsilyl or a *tert*-butyldimethylsilyl group, but the two diastereoisomers of the trityl ether **6** showed only a very small difference in R_F by TLC. Peracetylation (excess of acetic anhydride, pyridine), on the other hand, gave two easily separated diastereoisomeric diacetates *anti*-**7** and *syn*-**7** in 54 and 32% yield, respectively. Similarly, addition of crotonaldehyde to the doubly lithiated phosphine oxide **5** gave an inseparable mixture of the diols **8**. After acetylation, the two diastereoisomers of the diacetate **9** were separated by HPLC.

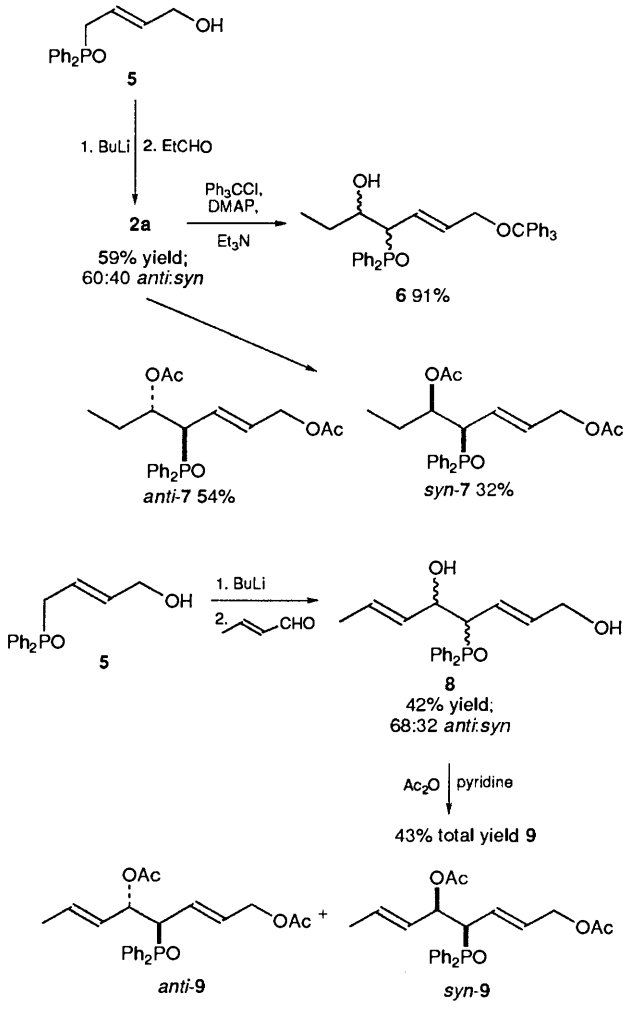
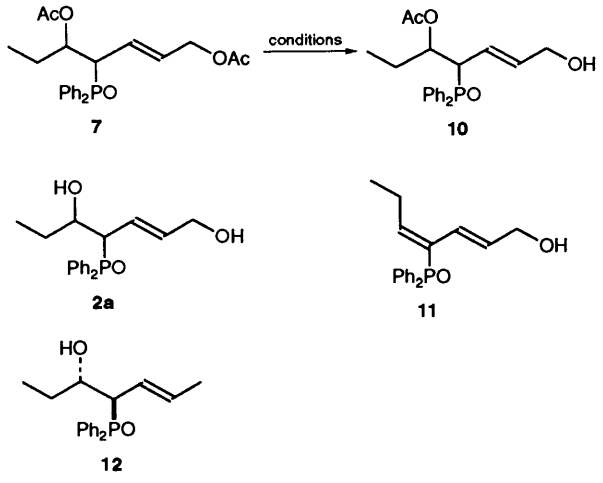


Table 1 Hydrolysis of the acetates **7** and **10**

Entry	Starting material	Method[a]	% in Crude product (by NMR) Diacetate **7**	Monoacetate **10**	Diol **2a**	Diene **11**	Isolated product (% yield)
1	*anti*-**7**	A	0	35	25	40	
2	*anti*-**7**	B	0	65	10	25	
3	*anti*-**7**	C	0	50	5	45	
4	*anti*-**7**	D		Complex mixture			
5	*anti*-**7**	E	0	10	90	0	
6	*anti*-**7**	F	0	0	100	0	*anti*-**2a** (73)
7	*anti*-**7**	G	0	90	10	0	
8	*anti*-**7**	H	100[b]	0[b]	0	0	
9	*anti*-**7**	I	Major[b]	Minor[b]	0	0	
10	*anti*-**7**	J	0	100	0	0	*anti*-**10** (85)
11	*anti*-**7**	K	*c*	—	—	—	**12** (44)
12	*anti*-**10**	K	0	0	90	10	*anti*-**2a** (69)
13	*syn*-**7**	F	*c*	—	—	—	*syn*-**2a** (64)
14	*syn*-**7**	J	*c*	—	—	—	*syn*-**10** (54)

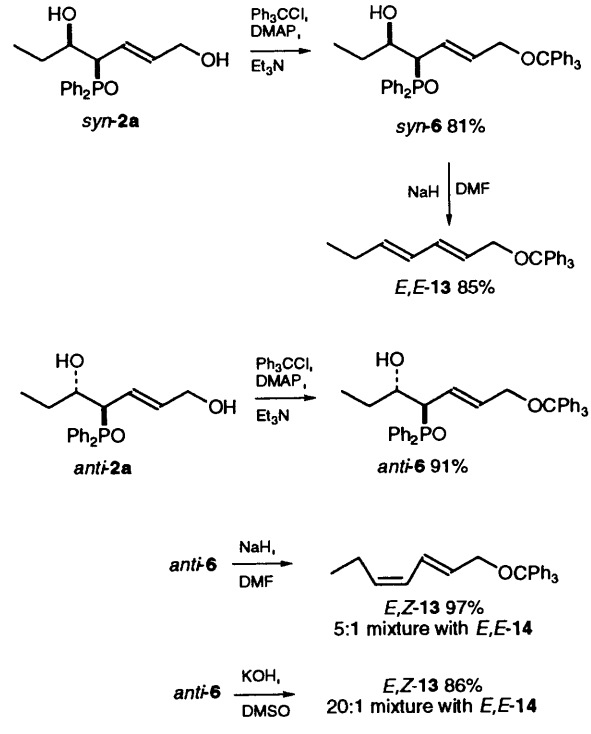
[a] Methods: A, NaOH, H_2O, MeOH; B, K_2CO_3, MeOH; C, NH_3, H_2O, MeOH; D, KCN, MeOH; E, HCl, MeOH, 20 °C; F, HCl, MeOH, 50 °C; G, NH_3, MeOH; H, isopropylamine, CH_2Cl_2: I, cyclohexylamine, CH_2Cl_2; J, cyclohexylamine, MeOH; K, $LiBH_4$, MeOH, THF (see ref. 7). [b] By TLC. [c] Crude ratio not determined.

Hydrolysis of the diacetate *anti*-**7** was attempted using the range of conditions shown in Table 1. Standard basic methods (entries 1–3) gave mixtures of products, which often included the monoacetate *anti*-**10**, the diol *anti*-**2a**, and an elimination product, believed to be the diene **11**. An acid-catalysed reaction (conc. HCl, MeOH; entry 5) was much cleaner. The crowded secondary acetate proved much more resilient than the primary one, but heating to 50 °C for 24 h (entry 6) cleanly removed both, giving the diol *anti*-**2a** in good yield.

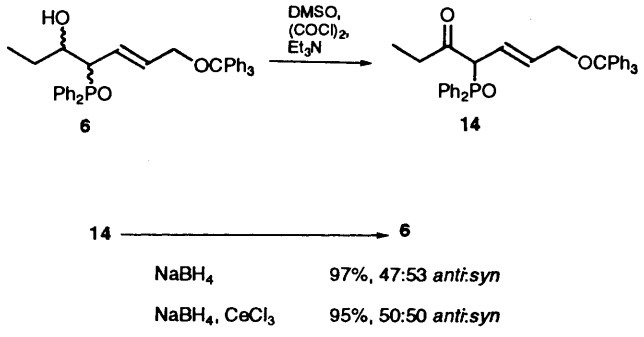


Treatment of the diacetate *anti*-**7** with anhydrous ammonia in methanol was, interestingly, almost completely selective for the primary acetate (entry 7). By using more bulky cyclohexylamine it was possible to isolate the monoacetate *anti*-**10** in high yield free from diol *anti*-**2a** and diene **11** (entry 10). Earlier attempts to use diisopropylamine or cyclohexylamine in dichloromethane gave very slow reactions (entries 8 and 9). While reduction of the diacetate *anti*-**7** with lithium borohydride[7] completely removed the primary allylic acetate by hydride substitution (entry 11), reduction of the monoacetate **10** cleanly gave the diol *anti*-**2a** (entry 12). The two successful methods were applied to the *syn* diastereoisomer *syn*-**7** to give the diol *syn*-**2a** in 64% yield (entry 13) and the monoacetate *syn*-**10** in 54% yield (entry 14).

Before the final Horner–Wittig elimination step, the diols *syn*-**2a** and *anti*-**2a** were tritylated (Ph_3CCl, DMAP, Et_3N) in high yield to remove the second acidic proton and to facilitate isolation of the diene products. Elimination of sodium diphenylphosphinate from the *syn*-diastereoisomer (with sodium hydride in DMF)[2] gave an 85% yield of the *E,E*-diene *E,E*-**13**. Under these conditions, the Horner–Wittig elimination of the *anti* diastereoisomer *anti*-**6** was only partially stereospecific, giving a 5:1 mixture of *E,Z* and *E,E* dienes **13**. With potassium hydroxide in DMSO, the stereospecificity was much better, and *E,Z*-**13** was isolated in 86% yield, contaminated with only 5% *E,E*-**13**.



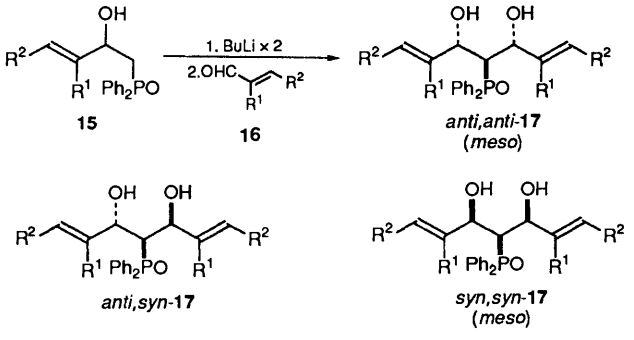
Some of our previous stereoselective syntheses of *Z* alkenes have made use of *anti*-selective reductions of β-keto phosphine oxides.[2,8] Careful Swern oxidation of the diastereoisomeric mixture of the trityl ethers **6** gave an excellent yield of the base-sensitive ketone **14**. But reduction of the ketone with sodium



borohydride, both in the absence[8] and presence[9] of cerium chloride, was not stereoselective, giving almost equal amounts of the alcohols *anti*-**6** and *syn*-**6**.

The δ-hydroxy allylic phosphine oxide **5** (which was lithiated and added to propionaldehyde in the first step of the sequence) was made by palladium(II)-catalysed rearrangement of an allylic acetate.[6] Reversing the order of these two steps, by performing an addition followed by a rearrangement, would provide an alternative route to the key diols **2a**. The addition of a lithiated β-hydroxy phosphine oxide to an aldehyde is an unknown reaction. However, it bears some similarity to Corey's remarkably stereoselective SCOOPY reaction.[10]

Our first attempts to use a phosphine oxide equivalent of the SCOOPY reaction were directed towards the synthesis of the symmetrical β,β′-dihydroxy phosphine oxides **17**, which can exist as only three diastereoisomers, two of which are *meso*, simplifying identification of the products by NMR. Lithiation of the β-hydroxy phosphine oxides **15a–c**,[1,6] with 2 equiv. of butyllithium at 0 °C gave an orange coloured solution (the colour appearing only after complete addition of the first equivalent of butyllithium). The aldehydes **16a–c** were added in excess to this solution at −70 °C, and after warming back to 0 °C, the reactions were quenched with ammonium chloride. The products **17** were isolated by chromatography, and



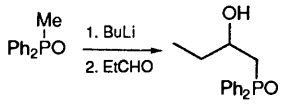
identified by their ^{1}H NMR spectra.* The results of these reactions are shown in Table 2. In all cases, conversion was poor and large amounts of starting material were recovered. None of the *syn,syn*-**17** diastereoisomers was observed, but otherwise there was little stereoselectivity in the reactions.

Further experiments showed that more starting material was consumed when 3 equiv. of base were used, and more of the required products **17** were formed if the aldehydes was added not at −70 °C but at 0 °C. These new conditions were employed in two syntheses of the unsymmetrical β,β′-dihydroxy phosphine oxides **20**. Addition of propionaldehyde to lithiated methyldiphenylphosphine oxide **18** gave the left-hand portion

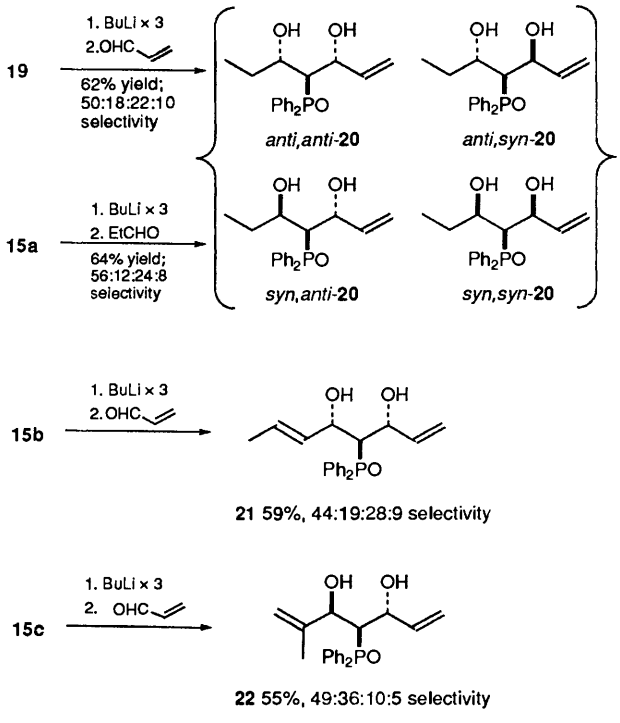
* The size of the coupling constant $^3J_{PCHCHOH}$ is a reliable indicator of the relative stereochemistry of a β-hydroxy phosphine oxide.

Table 2 Additions of the aldehydes **16** to the β-hydroxy phosphine oxides **15**

Starting material **15**	R^1	R^2	Yield *anti,anti*-**17**	Yield *anti,syn*-**17**	Recovered starting material (%)
a	H	H	10	10	33
b	H	Me	14.5	11	51
c	Me	H	16	8.6	37



19, which was lithiated and added to acrolein. Lithiation of **16a** and addition of propionaldehyde also gave **20**, with almost identical stereoselectivity. Separation of the four diastereoisomers was carried out by HPLC, and their stereochemistries assigned by analysis of their ^{1}H NMR spectra.[11] Stereoisomeric mixtures of two further compounds, **21** and **22**, were also made by this method.



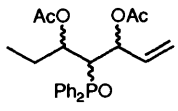
Some of these diols were bis-acetylated in the usual manner (acetic anhydride, pyridine) as shown in Table 3. The bis-acetates, and the two diastereoisomers of **9** described above, were treated with $Pd(MeCN)_2Cl_2$ to promote allylic transposition of one or both of the acetate groups.[5,6]

Rearrangement of **23** provided an alternative route to the two diastereoisomers *syn*- and *anti*-**7**. The presence of the second, non-allylic, acetate presented no problems. When **24** was treated with the palladium catalyst, only the right-hand side acetate was transposed, giving a single isolated diastereoisomer **25**. The γ methyl group on the left-hand side of the molecule blocks rearrangement on that side.[6] The diacetate **27** could be made as an inseparable mixture of diastereoisomers by tandem rearrangement of both allylic acetates of **26**. Alternatively, each diastereoisomer of **9** could be rearranged stereospecifically to one diastereoisomer of the product **27**. More spectacularly, *anti,anti*-**28** and *anti,syn*-**28** underwent tandem stereospecific

Table 3 Allylic transpositions of bis acetates

Entry	Diol	Bis-acetate (%)	Transposed bis-acetate (%)
1	**20**	**23** (79)	*anti*-**7** (42), *syn*-**7** (19)
2	**21**	**24** (72)	**25** (44)
3	**22**	**26** (72)	**27** (54)
4		*anti*-**9**	*anti*-**27** (54)
5		*syn*-**9**	*syn*-**27** (48)
6	*anti,anti*-**17b**	*anti,anti*-**28** (53)	*anti,anti*-**29** (76)
7	*anti,syn*-**19b**	*anti,syn*-**29** (100)	*anti,syn*-**29** (75)

rearrangement to give single diastereoisomers of *anti,anti*- and *anti,syn*-**29**. These compounds contain 1,7-related chiral centres, the remotest chiral relationship yet to have been controlled by the diphenylphosphinoyl group.



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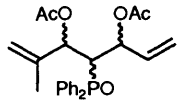

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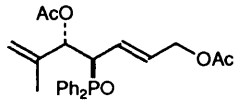

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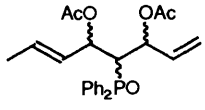

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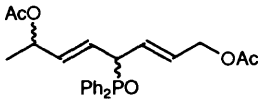

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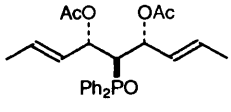
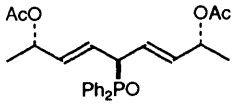
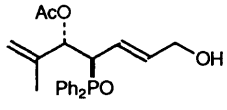


anti,anti-**28**



anti,anti-**29**



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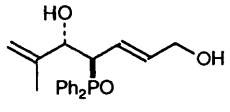

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The two acetate groups of rearranged diacetate **25** were distinguished by our selective aminolysis method: cyclohexylamine in methanol hydrolysed only the primary acetate group to give the monoacetate **30** in 71% yield. Conc. HCl in methanol removed both acetate groups to give the diol **31** in 72% yield. The secondary acetate group of **28** is less crowded than that of **25**, and hydrolysis of **28** with cyclohexylamine in methanol gave a complex mixture of hydrolysis and elimination products.

Experimental

General methods were introduced in a previous paper.[1] In the ^{13}C NMR spectra, + and − refer to the attached proton test (APT): a signal such as 72.4^+ is a CH or CH_3 group while 72.4^- is C or CH_2.

(4RS,5SR) *and* (4RS,5RS)-(E)-4-*Diphenylphosphinoylhept*-2-*ene*-1,5-*diol* syn- *and* anti-**2a**.—Butyllithium (1.4 mol dm^{-3} solution in hexane; 1.5 cm^3, 2.1 mmol, 2.1 equiv.) was added dropwise to a stirred solution of the phosphine oxide **5**[6] (274 mg, 1.0 mmol) in dry THF (10 cm^3) under nitrogen at 0 °C. The solution remained colourless until after 1 equiv. had been added, when it became deep red. Propionaldehyde was distilled directly into the reaction flask until the colour faded to lemon yellow. The temperature was maintained at 0 °C for a further 10 min before the mixture was allowed to warm to room temperature. Saturated aqueous ammonium chloride (10 cm^3) and water (10 cm^3) were added to the mixture after which most of the THF was removed under reduced pressure. The aqueous suspension was extracted with dichloromethane (× 3), and the combined extracts were washed with saturated brine, dried (Na_2SO_4), and evaporated under reduced pressure to yield the crude product, which was purified by flash chromatography, eluting with EtOAc–7% MeOH, to yield the *diols* **2a** (194.6 mg, 59%) as an oil; a 60:40 mixture of *anti* and *syn* diastereoisomers (by ^1H NMR). Further material (44.7 mg) was isolated, the ^1H NMR spectrum of which showed signals characteristic of starting material **5** and of vinylphosphine oxides.

(4RS,5SR)-*and*(4RS,5RS)-(E,E)-4-*Diphenylphosphinoylocta*-2,6-*diene*-1,5-*diol* syn- *and* anti-**8**.—In a similar way, the phosphine oxide **5**[6] (811 mg, 2.98 mmol) and distilling crotonaldehyde at −10 °C gave a crude product which was purified by flash chromatography, eluting with EtOAc–7% MeOH, to yield the *diols* **8** (431.6 mg, 42%) as an oil; a 54:46 mixture of *anti* and *syn* diastereoisomers (by ^1H NMR) (Found: M − H_2O, 324.1300. $C_{20}H_{23}O_3P$ requires *M* − H_2O, 324.1279); R_F(EtOAc) 0.24; δ_H(400 MHz; $CDCl_3$) (distinctive signals) 3.44 (1 H^{syn}, dd, *J* 11 and 9, C*H*OH), 3.10 (1 H^{anti}, t, *J* 9, C*H*OH), 1.59 (3 H^{anti}, d, *J* 7, Me) and 1.52 (3 H^{syn}, d, *J* 7, Me); *m*/*z* 324 (5%, M − H_2O), 314 (31, M − C_2H_4), 255 (60, $Ph_2POC_4H_6$), 219 (91, $Ph_2PO_2H_2$), 202 (42, Ph_2POH) and 201 (100, Ph_2PO).

Starting material **5** (211 mg, 26%) was also recovered.

Acetylation of the Mixture of anti- *and* syn-**2a**.—A 60:40 mixture of the diols *anti*- and *syn*-**2a** (171.03 mg, 0.520 mmol) was dissolved in pyridine (1.2 cm^3) and acetic anhydride (1.2 cm^3) and stirred under nitrogen for 65 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 hydrogencarbonate, 20% aqueous copper sulfate and brine, dried ($MgSO_4$) and evaporated under reduced pressure to yield a crude product. This was purified by flash chromatography, eluting with 3:1 EtOAc–hexane and then EtOAc, to give the *acetates syn*-**7** (69.2 mg, 32%) and *anti*-**7** (117.0 mg, 54%) separately.

(4RS,5SR)-*and*(4RS,5RS)-(E,E)-4-*Diphenylphosphinoylocta*-2,6-*diene*-1,5-*diyl Diacetate* syn-**9** *and* anti-**9**.—In a similar way, the diastereoisomeric mixture of the diols **8** (401.3 mg, 1.172 mmol) gave, after 65 h, a crude product. This was purified by flash chromatography, eluting with EtOAc, to yield the *diacetates anti*-**9** and *syn*-**9** (213.0 mg, 43%) as an oil. ^1H NMR spectroscopy showed the mixture to consist of a 68:32 ratio of *anti*-**9** and *syn*-**9**. Some of this mixture (about 140 mg) was purified further by HPLC (eluting with EtOAc) to yield firstly the *diacetate syn*-**9** (43.9 mg) as an oil, retention time 26 min (Found: M^+, 426.1564. $C_{24}H_{27}O_5P$ requires *M*, 426.1595); R_F(EtOAc) 0.39; $\nu_{max}(CDCl_3)/cm^{-1}$ 1730 (C=O), 1430 (PPh) and 1165 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 5.9–5.3 (5 H, m, CH=CH × 2 and C*H*OAc), 4.38 (2 H, m, CH_2OAc), 3.29 (1 H, dt, *J* 4 and 12, CHP), 1.97 (3 H, s), 1.64 (3 H, s) (OAc × 2) and 1.53 (3 H, d, *J* 7, CH*Me*); δ_C(250 MHz; $CDCl_3$) 170.5^-, 169.4^- (C=O × 2), 133–125 (Ph_2PO

and C=C × 2), 72.4$^+$ ($^2J_{PC}$ 4.2, *C*HOAc), 64.1$^-$ (*C*H_2OAc), 49.3$^+$ ($^1J_{PC}$ 66.1, CHP), 20.8$^+$, 20.7$^+$ (CO*Me* × 2) and 17.6$^+$ (*Me*CH); *m/z* 426 (6%, M$^+$), 314 (75, $Ph_2POCH_2CHCHCH_2$OAc), 255 (82, $Ph_2POC_4H_6$), 219 (75, $Ph_2PO_2H_2$), 202 (35, Ph_2POH) and 201 (100, Ph_2PO).

Also obtained was the *diacetate anti*-**9** (89.3 mg) as an oil, retention time 30 min (Found: M$^+$, 426.1625. $C_{24}H_{27}O_5P$ requires *M*, 426.1595); R_F(EtOAc) 0.39; $\nu_{max}(CDCl_3)/cm^{-1}$ 1725 (C=O), 1430 (PPh) and 1165 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 5.74 (1 H, ddd, *J* 16, 10 and 5, PCHC*H*=CH), 5.6 (3 H, m, MeC*H*=CH and C*H*OAc), 5.33 (1 H, ddt, *J* 16, 6 and 4, CH=C*H*CH_2OAc), 4.3 (2 H, m, CH_2OAc), 3.53 (1 H, ddd, *J* 10, 8 and 6, CHP), 1.93 (3 H, s), 1.68 (3 H, s) (OAc × 2) and 1.63 (3 H, d, *J* 6, CH*Me*); δ_C(250 MHz; $CDCl_3$) 170.4$^-$, 169.7$^-$ (C=O × 2), 133–125 (Ph_2PO and C=C × 2), 72.9$^+$ (*C*HOAc), 64.0$^-$ (*C*H_2OAc), 47.7$^+$ ($^1J_{PC}$ 65.8, CHP), 20.8$^+$, 20.7$^+$ (CO*Me* × 2) and 17.7$^+$ (*Me*CH); *m/z* 426 (2%, M$^+$), 314 (82, $Ph_2POCH_2CHCHCH_2$OAc), 255 (100, $Ph_2POC_4H_6$), 219 (48, $Ph_2PO_2H_2$), 202 (35, Ph_2POH) and 201 (92, Ph_2PO).

General Procedure for the Acid-catalysed Methanolysis of Diacetates.—Concentrated hydrochloric acid (1.5 cm^3) was added to a stirred solution of the diacetate (1 mmol) in methanol (30 cm^3). The mixture was heated to 50 °C, stirred at this temperature under nitrogen for 24 h and then poured into saturated aqueous sodium hydrogencarbonate (100 cm^3) and extracted with dichloromethane (150 cm^3 × 4). The combined organic fractions were washed with saturated brine, dried ($MgSO_4$), and evaporated under reduced pressure to give a residue which was purified by flash chromatography.

(4RS,5SR)-(E)-4-*Diphenylphosphinoylhept*-2-*ene*-1,5-*diol* anti-**2a**. In this way, the diacetate *anti*-**7** (1.481 g, 3.574 mmol) gave, after purification by flash chromatography, eluting with EtOAc–2.5% MeOH and then EtOAc–5% MeOH, the *diol anti*-**2a** (0.8627 g, 73%) as needles, m.p. 129–132 °C (from EtOAc) (Found: C, 69.2; H, 7.1; P. 9.4%; M − C_3H_6O, 272.0963. $C_{19}H_{23}O_3P$ requires C, 69.08; H, 7.02; P, 9.38%; *M* − C_3H_6O, 272.0996); R_F (EtOAc – 10% MeOH) 0.32; $\nu_{max}(CDCl_3)/cm^{-1}$ 3200–3500 (OH), 1430 (PPh) and 1150 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 6.02 (1 H, ddd, *J* 16, 11 and 6, PCHC*H*=CH), 5.62 (1 H, dq, *J* 16 and 6, CH=C*H*CH_2OH), 4.0 (3 H, m, C*H*OH and CH_2OH), 3.1 (2 H, br s, OH × 2), 3.09 (1 H, t, *J* 9, CHP), 1.65 (1 H, dqn, *J* 14 and 7, C$H_A$$H_B$Me), 1.45 (1 H, dqn, *J* 14 and 7, CH_AH_BMe) and 0.90 (3 H, t, *J* 7, Me); δ_C(100 MHz; $CDCl_3$) 137.0$^+$ ($^3J_{PC}$ 11.3, CH=*C*HCH_2OH), 136–128 (Ph_2PO), 121.8$^+$ ($^2J_{PC}$ 6.1, PCH*C*H=CH), 71.2$^+$ (CHOH), 63.1$^-$ (CH_2OH), 47.1$^+$ ($^1J_{PC}$ 67.8, CHP), 28.2$^-$ ($^3J_{PC}$ 11.6, *C*H_2Me) and 9.9$^+$ (CH_2*Me*); *m/z* 272 (100%, M − $MeCH_2CHO$), 255 (40, M − $MeCH_2CHO$ − H_2O), 219 (20, $Ph_2PO_2H_2$), 202 (45, Ph_2POH) and 201 (78, Ph_2PO).

(4RS,5SR)-(E)-4-*Diphenylphosphinoylhept*-2-*en*-1,5-*diol* syn-**2a**. In the same way, the diacetate *syn*-**7** (553 mg, 1.33 mmol) gave, after purification by flash chromatography, eluting with EtOAc–2% MeOH and then EtOAc–5% MeOH, the *diol* syn-**2a** (279.4 mg, 64%) as a wax, m.p. 119–126 °C (Found: M + H, 331.1435. $C_{19}H_{24}O_3P$ requires *M*, 331.1463); R_F (EtOAc – 10% MeOH) 0.34; $\nu_{max}(CDCl_3)/cm^{-1}$ 3200–3500 (OH), 1430 (PPh) and 1150 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 5.66 (1 H, dq, *J* 15 and 5, CH=C*H*CH_2OH), 5.41 (1 H, ddd, *J* 15, 10 and 5, PCHC*H*=CH), 4.05 (3 H, m, C*H*OH and CH_2OH), 3.38 (1 H, dt, *J* 9 and 11, CHP), 3.1 (2 H, br s, OH × 2), 1.71 (1 H, ddq, *J* 14, 3 and 7, C$H_A$$H_B$Me), 1.40 (1 H, dqn, *J* 14 and 7, CH_AH_BMe) and 1.00 (3 H, t, *J* 7, Me); δ_C(100 MHz; $CDCl_3$) 135.6$^+$ ($^3J_{PC}$ 12.0, CH=*C*HCH_2OH), 136–128 (Ph_2PO), 123.9$^+$ ($^2J_{PC}$ 5.3, PCH*C*H=CH), 71.8$^+$ (CHOH), 62.8$^-$ (CH_2OH), 50.0$^+$ ($^1J_{PC}$ 66.9, CHP), 28.3$^-$ ($^3J_{PC}$ 8.8, *C*H_2Me) and 9.2$^+$ (CH_2*Me*); *m/z* 331 (1%, M + H), 272 (100, M − $MeCH_2CHO$), 255 (40, M − $MeCH_2CHO$ − H_2O), 219 (30, $Ph_2PO_2H_2$), 202 (45, Ph_2POH) and 201 (72, Ph_2PO).

(4RS,5SR)-(E)-4-*Diphenylphosphinoyl*-6-*methylhepta*-2,6-*diene*-1,5-*diol* **31**. In the same way, the diacetate **25** (202 mg, 0.474 mmol) gave, after purification by flash chromatography, eluting with EtOAc–5% MeOH and then EtOAc–10% MeOH, the *diol* **31** (115.9 mg, 71%) as an oil (Found: M$^+$, 342.1396. $C_{20}H_{23}O_3P$ requires *M*, 342.1385); R_F (EtOAc) 0.18; $\nu_{max}(CHCl_3)/cm^{-1}$ 3350 (OH), 1440 (PPh) and 1160 (P=O); δ_H(250 MHz; $CDCl_3$) 8.0–7.4 (10 H, m, Ph_2PO), 5.94 (1 H, ddd, *J* 15, 10 and 5, PCHC*H*=C), 5.49 (1 H, dq, *J* 15 and 5, CH=C*H*CH_2OH), 5.07 (1 H, s, C=C$H_A$$H_B$) 4.89 (1 H, s, C=$CH_AH_B$), 4.56 (1 H, d, *J* 9, C*H*OH), 3.92 (2 H, m, CH_2OH), 3.21 (1 H, t, *J* 9, CHP) and 1.63 (3 H, s, MeC=C); δ_C(100 MHz; $CDCl_3$) 143.4$^-$ ($^3J_{PC}$ 12.2, *C*=CH_2), 136.5$^+$ ($^3J_{PC}$ 11.0, CH=*C*HCH_2OH), 133–128 (Ph_2PO), 121.0$^+$ ($^2J_{PC}$ 6.0, PCH-*C*H=CH), 111.7$^-$ (C=*C*H_2), 72.1$^+$ ($^2J_{PC}$ 3.5, *C*HOH), 62.8$^-$ ($^4J_{PC}$ 1.7, CH_2OH), 46.5$^+$ ($^1J_{PC}$ 67.0, CHP) and 19.2$^+$ (C=C*Me*); *m/z* 342 (0.5%, M$^+$), 272 (25, Ph_2POCH_2CHCH-CH_2OH), 219 (20, $Ph_2PO_2H_2$), 202 (44, Ph_2POH) and 201 (100, Ph_2PO).

General Procedure for the Cyclohexylaminolysis of Diacetates.—Cyclohexylamine (1.1 mmol) was added to the solution of the diacetate (1.0 mmol) in dry methanol (10 cm^3). The mixture was stirred under nitrogen at room temperature for 48 h after which the solvent was evaporated under reduced pressure, and the residue purified by flash chromatography.

(4RS,5SR)-(E)-5-*Acetoxy*-4-*diphenylphosphinoylhept*-2-*en*-1-*ol* anti-**10**. In this way, the diacetate *anti*-**7** (436.6 mg, 1.054 mmol) and cyclohexylamine (0.125 cm^3, 1.09 mmol, 1.04 equiv.) gave, after purification by flash chromatography, eluting with EtOAc and then EtOAc–4% MeOH, the *monoacetate anti*-**10** (332.9 mg, 85%) as prisms, m.p. 178–179 °C (from EtOAc–MeOH) (Found: C, 67.6; H, 6.8; P, 8.4%; M$^+$, 372.1492. $C_{21}H_{25}O_4P$ requires C, 67.7; H, 6.77; P, 8.32%; *M*, 372.1490); R_F (EtOAc) 0.12; $\nu_{max}(CHCl_3)/cm^{-1}$ 3300 (OH), 1730 (C=O), 1440 (PPh) and 1170 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 5.87 (1 H, ddd, *J* 15, 10 and 5, PCHC*H*=CH), 5.54 (1 H, dq, *J* 15 and 5, CH=C*H*CH_2OH), 5.23 (1 H, ddt, *J* 14, 3 and 7, C*H*OAc), 3.99 (2 H, ABX m, CH_2OH), 3.25 (1 H, ddd, *J* 13, 10 and 2, CHP), 2.58 (1 H, br s, OH), 1.73 (3 H, s, OAc), 1.8–1.5 (2 H, m, CH_2Me) and 0.78 (3 H, t, *J* 7, CH_2*Me*); δ_C(100 MHz; $CDCl_3$) 170.0$^-$ (C=O), 137.4$^+$ ($^3J_{PC}$ 10.7, CH=*C*HCH_2OH), 136–128 (Ph_2PO), 121.5$^+$ ($^2J_{PC}$ 5.6, PCH*C*H=CH), 72.2$^+$ (*C*HOAc), 62.8$^-$ (CH_2OH), 47.6$^+$ ($^1J_{PC}$ 67.5, CHP), 26.2$^-$ ($^3J_{PC}$ 8.9, *C*H_2Me), 20.7$^+$ (*Me*CO) and 9.8$^+$ (CH_2*Me*); *m/z* 372 (20%, M$^+$), 219 (100, $Ph_2PO_2H_2$), 202 (40, Ph_2POH) and 201 (72, Ph_2PO).

(4RS,5RS)-(E)-5-*Acetoxy*-4-*diphenylphosphinoylhept*-2-*en*-1-*ol* syn-**10**. In the same way, the diacetate *syn*-**7** (603.3 mg, 1.46 mmol) and cyclohexylamine (0.18 cm^3, 1.57 mmol, 1.1 equiv.) gave, after purification by flash chromatography, eluting with EtOAc–4% MeOH, the *monoacetate syn*-**10** (293.2 mg, 54%) as needles, m.p. 165–166.5 °C (from EtOAc) (Found: C, 67.8; H, 6.7; P, 8.25%; M$^+$, 372.14652. $C_{21}H_{25}O_4P$ requires C, 67.7; H, 6.77; P, 8.32%; *M*, 372.1490); R_F (EtOAc) 0.16; $\nu_{max}(CHCl_3)/cm^{-1}$ 3300 (OH), 1730 (C=O), 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, 10 and 6, PCHC*H*=CH), 5.41 (1 H, dq, *J* 15 and 5, CH=C*H*CH_2OH), 4.93 (1 H, ddt, *J* 8, 2 and 5, C*H*OAc), 3.90 (2 H, ABX m, CH_2OH), 3.57 (1 H, dt, *J* 6 and 10, CHP), 3.1 (1 H, br s, OH), 1.99 (1 H, m, C$H_A$$H_B$Me), 1.74 (3 H, s, OAc), 1.67 (1 H, m, CH_AH_BMe) and 0.73 (3 H, t, *J* 7, CH_2*Me*); δ_C(100 MHz; $CDCl_3$) 170.8$^-$ (C=O), 137.4$^+$ ($^3J_{PC}$ 10.7, CH=*C*HCH_2-OH), 136–128 (Ph_2PO), 121.1$^+$ ($^2J_{PC}$ 7.6, PCH*C*H=CH), 74.6$^+$ (*C*HOAc), 62.8$^-$ (CH_2OH), 46.8$^+$ ($^1J_{PC}$ 65.5, CHP), 24.3$^-$ ($^3J_{PC}$

2.5, CH_2Me), 20.7$^+$ (*Me*CO) and 9.9$^+$ (CH_2*Me*); *m/z* 372 (6%, M$^+$), 219 (100, $Ph_2PO_2H_2$), 202 (38, Ph_2POH) and 201 (95, Ph_2PO).

(4RS,5SR)-(E)-5-*Acetoxy*-4-*diphenylphosphinoyl*-6-*methylhepta*-2,6-*dien*-1-*ol* **30**. In the same way, the diacetate **25** (173.5 mg, 0.407 mmol) and cyclohexylamine (56 mm^3, 0.489 mmol, 1.2 equiv.) gave, after purification by flash chromatography, eluting with EtOAc and then EtOAc–5% MeOH, the *monoacetate* **30** (112.7 mg, 72%) as prisms, m.p. 159.5–160.5 °C (from EtOAc–MeOH) (Found: C, 68.8; H, 6.6; P, 8.2%; M − AcO, 325.1356. $C_{22}H_{25}O_4P$ requires C, 68.74; H, 6.55; P, 8.06%; *M* − AcO, 325.1357); R_F (EtOAc − 10% MeOH) 0.43; $\nu_{max}(CHCl_3)$/cm^{-1} 3350 (OH), 1735 (C=O), 1650 (C=C), 1440 (PPh) and 1150 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.4 (10 H, m, Ph_2PO), 5.81 (1 H, ddd, *J* 15, 10 and 4, PCHC*H*=C), 5.64 (1 H, d, *J* 8, C*H*OAc), 5.43 (1 H, dq, *J* 15 and 5, CH=C*H*CH_2OH), 4.80 (1 H, s, C=CH_AH_B), 4.72 (1 H, s, C=CH_AH_B), 3.99 (2 H, m, CH_2OH), 3.28 (1 H, ddd, *J* 13, 10 and 2, CHP), 2.5 (1 H, br s, OH), 1.76 (3 H, s, OAc) and 1.63 (3 H, s, MeC=C); δ_C(100 MHz; $CDCl_3$) 169.1$^-$ (C=O), 141.3$^-$ ($^3J_{PC}$ 10.5, C=CH_2), 137.3$^+$ ($^3J_{PC}$ 10.6, CH=CHCH_2OH), 133–128 (Ph_2PO), 120.8$^+$ ($^2J_{PC}$ 5.1, PCH*C*H=CH), 112.3$^-$ (C=CH_2), 72.9$^+$ ($^2J_{PC}$ 3.5, *C*HOAc), 62.6$^-$ ($^4J_{PC}$ 1.8, CH_2OH), 47.4$^+$ ($^1J_{PC}$ 66.4, CHP), 20.5$^+$ (*Me*CO) and 19.4$^+$ (C=C*Me*); *m/z* 325 (21%, M − AcO), 272 (30, $Ph_2POCH_2CHCHCH_2OH$), 219 (52, $Ph_2PO_2H_2$), 202 (49, Ph_2POH) and 201 (100, Ph_2PO).

Aminolysis of the Diacetate anti-**7** *with* NH_3–H_2O–MeOH.—Concentrated ammonia (*d* 0.880, 1 cm^3) was added to a solution of *anti*-**7** (87.5 mg, 0.211 mmol) in methanol (1 cm^3). The solution was stirred at room temperature under nitrogen for 25.5 h, before it was diluted with dichloromethane, washed with dilute hydrochloric acid and saturated aqueous sodium hydrogencarbonate, dried ($MgSO_4$) and evaporated under reduced pressure to give a crude product (68.9 mg) as an oil. ^{1}H NMR analysis of this material showed it to consist of 50% of the monoacetate *anti*-**10**, 5% of the diol *anti*-**2a**, and 45% of a by-product tentatively identified as the dienol (*E*,*E*)-4-diphenylphosphinoylhepta-2,4-dien-1-ol **11**; R_F (EtOAc–10% MeOH) 0.43; δ_H(250 MHz; $CDCl_3$) (signals not assigned as monoacetate *anti*-**10** or diol *anti*-**2a**) 7.9–7.3 (11 H, Ph_2PO and PC=CH), 6.43 (1 H, t, *J* 16, PC–C*H*=CH), 6.15 (1 H, ddt, *J* 16, 2 and 5, C*H*CH_2OH), 4.05 (2 H, d, *J* 5, CH_2OH), 2.30 (2 H, d × quintet, *J* 3 and 7, CH_2Me) and 0.93 (3 H, t, *J* 7, Me).

Reduction of the Diacetate anti-**7** *with* $LiBH_4$–MeOH–THF.—Dry methanol (40 mm^3, 0.99 mmol, 3.4 equiv.) and then lithium borohydride (19 mg, 0.87 mmol, 3 equiv.) were added to a stirred solution of *anti*-**7** in dry THF (5 cm^3) under nitrogen after which the mixture was heated to 50 °C. After 25 min, further lithium borohydride (15 mg) and methanol (100 mm^3) were added to the mixture. After a further 1 h, the reaction mixture was cooled to 0 °C, carefully diluted with water (10 cm^3), and extracted with dichloromethane (× 3). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash chromatography, eluting with EtOAc, to yield the *alcohol* **12** (40 mg, 44%) as needles, m.p. 159–162 °C (from EtOAc) (Found: C, 72.65; H, 7.6; P, 9.7%; M$^+$, 314.1427. $C_{19}H_{23}O_2P$ requires C, 72.51; H, 7.37; P, 9.85%; *M*, 314.1435); R_F (EtOAc) 0.39; $\nu_{max}(CDCl_3)$/cm^{-1} 3400 (OH), 1440 (PPh) and 1160 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 5.69 (1 H, dddq, *J* 15, 10, 5 and 2, PCHC*H*=CH), 5.37 (1 H, ddq, *J* 15, 4 and 6, CH=C*H*Me), 4.3 (1 H, br s, OH), 3.93 (1 H, dt, *J* 9 and 7, C*H*OH), 2.94 (1 H, dd, *J* 10.0 and 9, CHP), 1.75–1.25 (2 H, m, CH_2Me), 1.54 (3 H, ddd, *J* 6, 5 and 2, CH*Me*) and 0.81 (3 H, t, *J* 7, CH_2*Me*); δ_C(100 MHz; $CDCl_3$) 133.1$^+$ ($^3J_{PC}$ 11.9, CH=*C*HMe), 136–128 (Ph_2PO), 120.3$^+$ ($^2J_{PC}$ 6.2, PCH*C*H=CH), 70.4$^+$ ($^2J_{PC}$ 3.9, CHOH), 47.3$^+$ ($^1J_{PC}$ 67.8, CHP), 28.0$^-$ ($^3J_{PC}$ 12.0, CH_2Me), 18.2 (CH*Me*) and 9.9$^+$ (CH_2*Me*); *m/z* 314 (8%, M$^+$), 256 (100, M − $MeCH_2CHO$), 202 (39, Ph_2POH) and 201 (45, Ph_2PO).

Reduction of the Monoacetate anti-**10** *with* $LiBH_4$–MeOH–THF.—In the same way, the monoacetate *anti*-**10** (104.4 mg, 0.280 mmol), with methanol (25 mm^3, 0.625 mmol, 2.2 equiv.) and lithium borohydride (15 mg, 0.682 mmol, 2.4 equiv.) gave, after 70 min at 50 °C, a crude product. This was purified by flash chromatography, eluting with EtOAc–5% MeOH, to yield the diol *anti*-**2a** (63.4 mg, 69%) contaminated with 10% (by ^{1}H NMR) of a by-product presumed to be the dienol **11**.

(3RS,4RS)-4-*Diphenylphosphinoyl*-1-*triphenylmethoxyhept*-5-*en*-3-*ol* syn-**6**.—Trityl chloride (92 mg, 0.33 mmol, 1.4 equiv.), DMAP (2 mg) and triethylamine (65 mm^3, 0.46 mmol, 2.0 equiv.) were added to a solution of the diol *syn*-**2a** in dry dichloromethane (3 cm^3), and the mixture was stirred at room temperature under nitrogen for 7.5 h. The solvent was evaporated under reduced pressure, and the residue purified by flash chromatography, eluting with 1:1 EtOAc–hexane and then 3:1 EtOAc–hexane, to yield the *trityl ether* syn-**6** (108.25 mg, 81%) as a foam (Found: M + Na, 595.2340. $C_{38}H_{37}O_3P$ requires *M* + Na, 595.2378); R_F (EtOAc) 0.47; $\nu_{max}(CDCl_3)$/cm^{-1} 3400 (OH), 1430 (PPh) and 1150 (P=O); δ_H(250 MHz; $CDCl_3$) 8.0–7.2 (25 H, m, Ph_2PO and Ph_3CO), 5.66 (1 H, dq, *J* 15 and 5, CH=C*H*CH_2O), 5.48 (1 H, m, PCHC*H*=CH), 5.45 (1 H, br s, OH), 4.07 (1 H, dt, *J* 7 and 9, C*H*OH), 3.55 (2 H, ABX m, CH_2O), 3.39 (1 H, dt, *J* 13 and 9, CHP), 1.70 (1 H, m, CH_AH_BMe), 1.41 (1 H, m, CH_AH_BMe) and 1.00 (3 H, t, *J* 7, Me); δ_C(100 MHz; $CDCl_3$) 143.9$^-$ (Ph_3C *ipso*), 133.1$^+$ ($^3J_{PC}$ 12.4, CH=*C*HCH_2O), 133–127 (Ph_2PO and Ph_3C), 123.9$^+$ ($^2J_{PC}$ 5.0, PCH*C*H=CH), 86.7$^-$ (*C*Ph_3), 71.3$^+$ ($^2J_{PC}$ 4.2, CHOH), 63.8$^-$ (CH_2OCPh_3), 50.1$^+$ ($^1J_{PC}$ 67.3, CHP), 28.3$^-$ ($^3J_{PC}$ 10.3, *C*H_2Me) and 8.9$^+$ (CH_2*Me*); *m/z* (+FAB) 595 (100%, M + Na).

(3RS,4SR)-4-*Diphenylphosphinoyl*-1-*triphenylmethoxyhept*-5-*en*-3-*ol* anti-**6**.—In this way, the diol *anti*-**2a** (160.7 mg, 0.486 mmol), trityl chloride (191 mg, 0.69 mmol, 1.4 equiv.), DMAP (5 mg) and triethylamine (0.140 cm^3, 1.00 mmol, 2.1 equiv.) gave, after 6.5 h, a crude product. This was purified by flash chromatography, eluting with 1:1 EtOAc–hexane and then 3:1 EtOAc–hexane, to yield the *trityl ether anti*-**6** (253.8 mg, 91%) as a foam (Found: M + Na, 595.2378. $C_{38}H_{37}O_3P$ requires *M* + Na, 595.2378); R_F (EtOAc) 0.49; $\nu_{max}(CDCl_3)$/cm^{-1} 3400 (OH), 1430 (PPh) and 1150 (P=O); δ_H(250 MHz; $CDCl_3$) 8.0–7.2 (25 H, m, Ph_2PO and Ph_3CO), 6.05 (1 H, ddd, *J* 15, 10 and 5, PCHC*H*=CH), 5.65 (1 H, dq, *J* 15 and 4, CH=C*H*CH_2O), 4.6 (1 H, br s, OH), 4.07 (1 H, dt, *J* 9 and 7, C*H*OH), 3.48 (2 H, ABX m, CH_2O), 3.13 (1 H, t, *J* 9, CHP), 1.64 (1 H, dqn, *J* 15 and 7, CH_AH_BMe), 1.43 (1 H, dqn, *J* 15 and 7, CH_AH_BMe) and 0.90 (3 H, t, *J* 7, Me); δ_C(100 MHz; $CDCl_3$) 144.0$^-$ (Ph_3C *ipso*), 134.6$^+$ ($^3J_{PC}$ 11.7, CH=*C*HCH_2O), 136–126 (Ph_2PO and Ph_3C), 122.1$^+$ ($^2J_{PC}$ 6.1, PCH*C*H=CH), 86.6$^-$ (CPh_3), 71.3$^+$ (CHOH), 64.5$^-$ (CH_2OCPh_3), 47.3$^+$ ($^1J_{PC}$ 68.0, CHP), 28.1$^-$ ($^3J_{PC}$ 11.7, CH_2Me) and 9.9$^+$ (CH_2*Me*); *m/z* (+FAB) 595 (100, M + Na).

(E,E)-1-*Triphenylmethoxyhepta*-2,4-*diene* E,E-**13**.—Sodium hydride (60% suspension; 8 mg, 0.2 mmol, 2.6 equiv.) was added to a stirred solution of the alcohol *syn*-**6** (44.7 mg, 0.0781 mmol) in dry DMF (1 cm^3) under nitrogen. The mixture was warmed to 30 °C for 20 min, when a thick white precipitate formed. The suspension was cooled to 0 °C, quenched with saturated aqueous ammonium chloride and diluted with water. The aqueous mixture was extracted into ether (× 3) and the combined extracts were washed with water (× 3), dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by PTLC, eluting with EtOAc, to give the *trityl ether E,E*-**13** (23.5 mg, 85%) as prisms (Found: M − $C_7H_{11}O$,

243.1161. $C_{26}H_{26}O$ requires M − $C_7H_{11}O$, 243.1162); R_F (4:1 hexane–EtOAc) 0.64; ν_{max}(film)/cm^{-1} 1600 (Ph); δ_H(250 MHz; $CDCl_3$) 7.6–7.2 (15 H, m, Ph_3CO), 6.38 (1 H, dd, *J* 15 and 10, $MeCH_2CH{=}CH$), 6.13 (1 H, dd, *J* 15 and 10, $CH{=}CHCH_2O$), 5.81 (1 H, dt, *J* 15 and 7, $MeCH_2CH$), 5.76 (1 H, dt, *J* 15 and 6, OCH_2CH), 3.69 (2 H, d, *J* 6, CH_2O), 2.18 (2 H, qn, *J* 7, CH_2Me) and 1.09 (3 H, t, *J* 7, Me); δ_C(62.9 MHz; $CDCl_3$) 144.1$^-$ (Ph_3C *ipso*), 136.2$^+$, 131.4$^+$, 128.7$^+$, 127.4$^+$ [$(CH)_4$], 128.5$^+$, 127.7$^+$ (Ph_3C *ortho* and *meta*), 126.9 (Ph_3C *para*), 86.7$^-$ (CPh_3), 64.5$^-$ (CH_2OCPh_3), 25.5$^-$ (CH_2Me) and 13.4$^+$ (Me); *m*/*z* (+FAB) 243 (100%, Ph_3C) and 165 (50).

(E,Z)-1-*Triphenylmethoxyhepta*-2,4-*diene* E,Z-**13**.—Potassium hydroxide (85%; 9 mg, 0.16 mmol, 3.4 equiv.) was added to a stirred solution of the alcohol *anti*-**6** (26.8 mg, 0.047 mmol) in dry DMSO (1.5 cm^3) under nitrogen. The mixture was stirred at room temperature for 10 min, and then heated to 60 °C for 75 min. The resulting orange coloured solution was cooled to room temperature, quenched with saturated aqueous ammonium chloride and diluted with water. The aqueous mixture was extracted into ether (×3) and the combined extracts were washed with water (×3), dried (Na_2SO_4), evaporated under reduced pressure. The residue was purified by PTLC, eluting with EtOAc, to give the *trityl ether E,Z*-**13** (14.3 mg, 86%) as plates, contaminated with 5% *E,E*-**13** (by ^1H NMR) (Found: M^+, 354.1962. $C_{26}H_{26}O$ requires *M*, 354.1984); R_F (4:1 hexane–EtOAc) 0.64; ν_{max}(film)/cm^{-1} 1600 (Ph); δ_H(400 MHz; $CDCl_3$) 7.5–7.2 (15 H, m, Ph_3CO), 6.57 (1 H, dd, *J* 15 and 11, $OCH_2CH{=}CH$), 5.97 (1 H, t, *J* 11, $MeCH_2CH{=}CH$), 5.77 (1 H, dt, *J* 15 and 6, OCH_2CH), 5.41 (1 H, dt, *J* 11 and 7, $MeCH_2CH$), 3.66 (2 H, d, *J* 6, CH_2O), 2.19 (2 H, dqn, *J* 1 and 7, CH_2Me) and 0.99 (3 H, t, *J* 7, Me); δ_C(100 MHz; $CDCl_3$) 144.1$^-$ (Ph_3C *ipso*), 134.0–126.6 [Ph_3C and $(CH)_4$], 86.8$^-$ (CPh_3), 64.8$^-$ (CH_2OCPh_3), 21.1$^-$ (CH_2Me) and 14.5$^+$ (Me); *m*/*z* 354 (2%, M^+), 243 (100, Ph_3C) and 165 (78).

In another experiment, using the procedure described above for the synthesis of *E,E*-**13**, with 1.6 equiv. of sodium hydride, and stirring at room temperature for 18 min, a 97% yield of a 5:1 mixture (by ^1H NMR) of *Z,E*- and *E,E*-**13** was obtained.

(E)-4-*Diphenylphosphinoyl*-7-*triphenylmethoxyhept*-5-*en*-3-*one* **14**.—Oxalyl chloride (0.7 cm^3, 8.0 mmol, 1.7 equiv.) was added dropwise to a stirred solution of DMSO (0.7 cm^3, 10.0 mmol, 2.0 equiv.) in dry dichloromethane (25 cm^3) under nitrogen at −70 °C. After 10 min, a solution of the trityl ethers **6** (2.77 g, 4.84 mmol) in dry dichloromethane (30 cm^3) was added to the mixture, the temperature being maintained between −60 and −70 °C. After 5 min, diisopropylethylamine (2.5 cm^3) was added to the mixture which was then stirred for a further 10 min at −70 °C before warming to 0 °C over 50 min, and then to room temperature over 30 min. Aqueous sodium bisulfate (0.1 mol dm^{-3} solution; 100 cm^3) was added to the mixture, after which the two layers were separated; the aqueous layer was extracted with dichloromethane (×3). The combined extracts were washed with 0.1 mol dm^{-3} aqueous sodium hydrogen sulfate and water, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by flash chromatography, eluting with 1:1 EtOAc–hexane, to yield the *ketone* **14** (2.4833 g, 90%) as a foam (Found: M + H, 571.2385. $C_{38}H_{35}O_3P$ requires *M* + H, 571.2402); R_F (EtOAc) 0.52; ν_{max}($CDCl_3$)/cm^{-1} 1700 (C=O), 1430 (PPh) and 1150 (P=O); δ_H(400 MHz; $CDCl_3$) 8.0–7.2 (25 H, m, Ph_2PO and Ph_3CO), 6.09 (1 H, dddt, *J* 15, 10, 6 and 2, PCHC*H*=CH), 5.54 (1 H, dq, *J* 15 and 5, CH=C*H*CH_2O), 4.6 (1 H, br s, OH), 4.36 (1 H, dd, *J* 15 and 10, PCH), 3.48 (2 H, m, CH_2O), 2.67 (2 H, ABX_3P m, CH_2Me) and 0.93 (3 H, t, *J* 7, Me); δ_C(100 MHz; $CDCl_3$) 205.2$^-$ (C=O), 143.9$^-$ (Ph_3C *ipso*), 133.8$^+$ ($^3J_{PC}$ 10.9, CH=*C*HCH$_2$O), 132–126 (Ph_2PO and Ph_3C), 121.5$^+$ ($^2J_{PC}$ 7.1, PCH*C*H=CH), 86.8$^-$ (*C*Ph_3), 63.9$^-$ (*C*H_2OCPh_3), 61.5$^+$ ($^1J_{PC}$ 55.1, CHP), 37.4$^-$ (*C*H_2Me) and 7.4$^+$ (CH_2*Me*); *m*/*z* (+FAB) 571 (1%, M + H), 243 (100, Ph_3C) and 201 (20, Ph_2PO).

Sodium Borohydride Reduction of the Ketone **14**.—Sodium borohydride (9 mg, 0.238 mmol, 5.9 equiv.) was added to a stirred solution of the ketone **14** (23.1 mg, 0.0403 mmol) in dry methanol (1 cm^3) at −12 °C under nitrogen. The mixture was stirred at a temperature between −12 and −18 °C for 18 h before being quenched with saturated aqueous ammonium chloride and water. The aqueous suspension was extracted with dichloromethane (×4), and the combined extracts fractions were dried ($MgSO_4$) and evaporated under reduced pressure to yield a crude product (22.4 mg, 97%). ^1H NMR analysis showed this material to consist of a 53:47 mixture of *syn*-**6** and *anti*-**6**.

Luche Reduction of the Ketone **14**.—Sodium borohydride (*ca.* 5 mg) was added to a stirred solution of the ketone **14** (6.0 mg, 0.0105 mmol) and cerium chloride heptahydrate (6 mg, 0.015 mmol, 1.5 equiv.) in dry methanol (1 cm^3) at −70 °C under nitrogen. The mixture was stirred at −70 °C for 1 h before being warmed to room temperature. Saturated aqueous ammonium chloride (5 cm^3) was added to it and the aqueous suspension was extracted with dichloromethane (×2). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure to yield a crude product (5.7 mg, 95%). ^1H NMR analysis showed this material to consist of a 50:50 mixture of *syn*-**6** and *anti*-**6**.

General Procedure for the Addition of Lithiation and Addition of β-Hydroxy Phosphine Oxides to Aldehydes.—Butyllithium (1.5 mol dm^{-3} solution in hexane; 7.0 cm^3, 10.5 mmol, 2.1 equiv.) was added dropwise to a stirred solution of the β-hydroxy phosphine oxide (5.0 mmol) in dry THF (30 cm^3) under nitrogen at a temperature between 0 and −70 °C. The solution remained colourless until after 1 equiv. had been added, when it became orange–yellow. The solution was then cooled to −70 °C, and the aldehyde was distilled directly into the reaction flask until the colour faded to lemon yellow. The temperature was maintained at −70 °C for a further 10 min before the mixture was allowed to warm to room temperature. Saturated aqueous ammonium chloride (25 cm^3) and water (25 cm^3) were then added to the mixture after which most of the THF was removed under reduced pressure. The aqueous suspension was extracted with dichloromethane (×3), and the combined extracts were washed with saturated brine, dried (Na_2SO_4), and evaporated under reduced pressure to yield the crude product.

(3RS,5RS)-*and*(3RS,4SR,5SR)-4-*Diphenylphosphinoylhepta*-1,6-*diene*-3,5-*diol* syn,anti-**17a** *and* anti,anti-**17a**.—In this way, the phosphine oxide **15a**[6] (1.36 g, 5.0 mmol) and acrolein gave a crude product which was purified by flash chromatography, eluting with 3:1 EtOAc–hexane and then EtOAc, to give a mixture of the *diols* **17a** (462.5 mg, 28%) (54:46 by ^1H NMR) as an oil, plus recovered starting material (455.3 mg, 33%). Further purification by HPLC, eluting with EtOAc, gave the *diol syn,anti*-**17a** (170 mg, 10%) as an unrecrystallisable solid, retention time 25 min (Found: M − OH, 311.1180. $C_{19}H_{21}O_3P$ requires *M* − OH, 311.1201); R_F (EtOAc) 0.41; ν_{max}(film)/cm^{-1} 3600–3100 (OH), 1440 (PPh) and 1180 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 5.82 (1 H, ddd, *J* 17, 11 and 4, C*H*=CH_2 on *anti* side), 5.53 (1 H, ddd, *J* 17, 10 and 5, C*H*=CH_2 on *syn* side), 5.43 (2 H, dt, *J* 17 and 2, CH=CH_AH_B on *anti* side), 5.24 (1 H, d × fine m, *J* 11, CH=CH_AH_B on *anti* side), 5.07 (1 H, dt, *J* 17 and 2, CH=CH_AH_B on *syn* side), 4.80 (1 H, dt, *J* 10 and 2, CH=CH_AH_B on *syn* side), 4.79 (1 H, ddd, *J* 23, 6 and 2, C*H*OH *syn*), 4.51 (1 H, ddd, *J* 10, 4 and 2, C*H*OH *anti*), 3.5 (2 H, br s, OH × 2) and 2.58 (1 H, dt, *J* 8 and 2, PCH); δ_C(100 MHz; $CDCl_3$) 138.8$^+$, 138.1$^+$ ($^3J_{PC}$ 11.5) (*C*H=CH_2 × 2),

133–128 (Ph_2PO), 116.5$^-$, 115.2$^-$ (CH=CH_2 × 2), 71.7$^+$ (CHOH × 2) and 47.6$^+$ ($^1J_{PC}$ 66.8, PCH); *m/z* 311 (3%, M − OH), 272 (8, M − CH_2CHCOH), 271 (7.5, M − CH_2CH-CHOH), 256 (11, $Ph_2POC_4H_7$), 255 (16, $Ph_2POC_4H_6$), 254 (13, $Ph_2POC_4H_5$), 253 (6, $Ph_2POC_4H_4$), 245 (8), 227 (8), 203 (13, Ph_2POH_2), 202 (100, Ph_2POH) and 201 (39, Ph_2PO).

Irradiation of the multiplet at δ 5.82 in the NMR spectrum results in simplification of the signals at δ 5.43 and 5.24 to fine multiplets. Irradiation of the multiplet at δ 4.51 results in simplification of the signal at δ 5.82 to a double doublet.

Also obtained was the *diol anti,anti*-**17a** (171 mg, 10%) as prisms, m.p. 125.5–127 °C (from EtOAc), retention time 32 min (Found: C, 69.5; H, 6.4; P, 9.45%; M − OH, 311.1227. $C_{19}H_{21}O_3P$ requires C, 69.5; H, 6.44; P, 9.43%; M − OH, 311.1201); R_F (EtOAc) 0.41; ν_{max}(Nujol)/cm^{-1} 3400 (OH), 3150 (OH), 1440 (PPh) and 1175 (P=O); δ_H(250 MHz; $CDCl_3$) 7.85 (4 H, ddd, *J* 11, 8 and 2, Ph_2PO *ortho*), 7.6–7.2 (6 H, m, Ph_2PO *meta* and *para*), 6.01 (2 H, ddd, *J* 17, 11 and 5, C*H*=CH_2 × 2), 5.12 (2 H, dt, *J* 17 and 2, CH=CH_AH_B × 2), 4.97 (2 H, d × fine m, *J* 11, CH=CH_AH_B × 2), 4.71 (2 H, ddd, *J* 11, 5 and 2, C*H*OH × 2), 4.1 (2 H, br s, OH × 2) and 2.65 (1 H, dt, *J* 8 and 2, PCH); δ_C(100 MHz; $CDCl_3$) 140.0$^+$ ($^3J_{PC}$ 11.7, *C*H=CH_2 × 2), 133–128 (Ph_2PO), 114.9$^-$ (CH=*C*H_2 × 2), 71.3$^+$ (CHOH × 2) and 48.5$^+$ ($^1J_{PC}$ 66.4, PCH); *m/z* 311 (3%, M − OH), 271 (7.5, M − $CH_2CHCHOH$), 256 (3, $Ph_2POC_4H_7$), 255 (13, $Ph_2POC_4H_6$), 254 (18, $Ph_2POC_4H_5$), 253 (6, $Ph_2POC_4H_4$), 203 (16, Ph_2POH_2), 202 (100, Ph_2POH) and 201 (39, Ph_2PO).

(4RS,6RS)- *and* (4RS,5SR,6SR)-(E,E)-5-*Diphenylphosphinoylnona*-2,7-*diene*-4,6-*diol* syn,anti-**17b** *and* anti,anti-**17b**.—In the same way, the phosphine oxide **15b**[1,6] (1.423 g, 5.0 mmol) and crotonaldehyde gave a crude product. This was purified by flash chromatography, eluting with 3:1 EtOAc–hexane and then EtOAc, to give a mixture of the *diols* **17b** (550 mg, 31%) as an oil, plus recovered starting material (730 mg, 51%). Further purification by HPLC, eluting with CH_2Cl_2–4% MeOH, gave the *diol syn,anti*-**17b** (193.1 mg, 11%) as minute needles, m.p. 199–202 °C (from EtOAc–MeOH), retention time 20 min (Found: C, 70.7; H, 7.05; P, 8.8%; M − OH, 339.1488. $C_{21}H_{25}O_3P$ requires C, 70.77; H, 7.07; P, 8.69%; *M* − OH, 339.1514); R_F (EtOAc) 0.32; ν_{max}(Nujol)/cm^{-1} 3400 (OH), 3200 (OH), 1450 (PPh) and 1160 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 5.74 (1 H, ddq, *J* 15, 7 and 2, CH=C*H*Me on *anti* side), 5.6–5.4 (2 H, m, CHOHC*H*=CH on *anti* side and CH=C*H*Me on *syn* side), 5.14 (1 H, ddd, *J* 15, 6 and 2, CHOHC*H*=CH on *syn* side), 4.75 (1 H, d × fine m, *J* 22, C*H*OH *syn*), 4.46 (1 H, d × fine m, *J* 11, C*H*OH *anti*), 2.54 (1 H, dt, *J* 9 and 3, PCH), 1.63 (3 H, d, *J* 7, Me on *anti* side) and 1.32 (3 H, d, *J* 7, Me on *syn* side); δ_C(100 MHz; $CDCl_3$) 134–128 (Ph_2PO and CH=CH × 2), 71.7$^+$, 71.6$^+$ (CHOH × 2), 48.3$^+$ ($^1J_{PC}$ 66.8, PCH), 17.6$^+$ and 17.4$^+$ (Me × 2); *m/z* 339 (1.5%, M − OH), 286 (1.7, $Ph_2POCH_2CHOHC_3H_5$), 285 (2.2, $Ph_2POCHCHOHC_3H_5$), 268 (21, $Ph_2POC_5H_7$), 253 (18, $Ph_2POC_4H_4$), 203 (19, Ph_2POH_2), 202 (58, Ph_2POH), 201 (31, Ph_2PO) and 85 (100).

Irradiation of the multiplet at δ 5.14 in the ^{1}H NMR spectrum results in simplification of the multiplet at δ 5.6–5.4, but no change in the multiplet at δ 5.74. Irradiation of the multiplet at δ 5.74 results in simplification of the multiplet at δ 5.6–5.4 and simplification of the doublet at δ 1.63 to a singlet, but no change either in the multiplet at δ 5.14 or in the doublet at δ 1.32. Irradiation of the signal at δ 4.75 simplifies the signal at δ 5.14 to a doublet (*J* 16).

Also obtained was the *diol anti,anti*-**17b** (256.7 mg, 14.5%) as an unrecrystallisable solid, retention time 24 min (Found: M − OH, 339.1512. $C_{21}H_{25}O_3P$ requires *M* − OH, 339.1514); R_F (EtOAc) 0.32; ν_{max}($CDCl_3$)/cm^{-1} 3600–3200 (OH), 1440 (PPh) and 1190 (P=O); δ_H(250 MHz; $CDCl_3$) 7.82 (4 H, ddd, *J* 11.2, 7.0 and 1.7, Ph_2PO *ortho*), 7.6–7.4 (6 H, m, Ph_2PO *meta* and *para*), 5.62 (2 H, ddd, *J* 15, 6.0 and 2, CHOHC*H*=CH × 2), 5.46 (2 H, ddq, *J* 15, 3 and 6, CH=C*H*Me × 2), 4.69 (2 H, d × fine m, *J* 11, CHOH × 2), 2.9 (2 H, br s, OH × 2), 2.61 (1 H, dt, *J* 7 and 3, PCH) and 1.56 (6 H, d, *J* 6, Me × 2); δ_C(100 MHz; $CDCl_3$) 134–128 (Ph_2PO and CH=CH × 2), 70.8$^+$ (CHOH × 2), 49.0$^+$ ($^1J_{PC}$ 65.9, PCH) and 17.5$^+$ (Me × 2); *m/z* 339 (1%, M − OH), 286 (4, Ph_2POCH_2-$CHOHC_3H_5$), 268 (23, $Ph_2POC_5H_7$), 253 (19, $Ph_2POC_4H_4$), 219 (6, $Ph_2PO_2H_2$), 216 (7, Ph_2POMe), 215 (16, Ph_2POCH_2), 203 (21, Ph_2POH_2), 202 (100, Ph_2POH) and 201 (53, Ph_2PO).

(3RS,4SR,5SR)- *and* (3RS,5RS)-4-*Diphenylphosphinoyl*-2,6-*dimethylhepta*-1,6-*diene*-3,5-*diol* anti,anti-**17c** *and* syn,anti-**17c**. In the same way, the phosphine oxide **15c**[6] (1.43 g, 5.0 mmol) and methacrolein gave a crude product. This was purified by flash chromatography, eluting with 1:1 EtOAc–hexane, to give firstly the *diol anti,anti*-**17c** (283.6 mg, 16%) as an oil (Found: M − OH, 339.1497. $C_{21}H_{25}O_3P$ requires *M* − OH, 339.1514); R_F (EtOAc) 0.50; ν_{max}(film)/cm^{-1} 3600–3200 (OH), 1640 (C=C), 1440 (PPh) and 1165 (P=O); δ_H(250 MHz; $CDCl_3$) 7.87 (4 H, ddd, *J* 11, 8 and 2, Ph_2PO *ortho*), 7.6–7.3 (6 H, m, Ph_2PO *meta* and *para*), 4.95 (2 H, s, C=CH_AH_B × 2), 4.75 (2 H, s, C=CH_AH_B × 2), 4.60 (2 H, d × fine m, *J* 11, C*H*OH × 2), 2.92 (1 H, dt, *J* 8 and 3, PCH) and 1.61 (6 H, s, Me × 2); δ_C(62.9 MHz; $CDCl_3$) 144.3$^-$ ($^3J_{PC}$ 10.4, Me*C*=CH_2 × 2), 133–128 (Ph_2PO), 112.6$^-$ (MeC=*C*H_2 × 2), 73.1$^+$ (CHOH × 2), 41.8$^+$ ($^1J_{PC}$ 66.7, PCH) and 19.4$^+$ (Me); *m/z* 339 (3%, M − OH), 286 (5, $Ph_2POCH_2CHOHC_3H_5$), 285 (8, Ph_2-$POCHCHOHC_3H_5$), 270 (9, $Ph_2POC_5H_9$), 269 (22, Ph_2-POC_5H_8), 268 (22, $Ph_2POC_5H_7$), 267 (9, $Ph_2POC_5H_6$), 245 (21, Ph_2POCH_2CHOH), 219 (10, $Ph_2PO_2H_2$), 216 (7, Ph_2POMe), 215 (12, Ph_2POCH_2), 203 (16, Ph_2POH_2), 202 (100, Ph_2POH) and 201 (60, Ph_2PO).

The next compound to be eluted from the column was the *diol syn,anti*-**17c** (152.5 mg, 8.6%) as an oil (Found: M − OH, 339.1500. $C_{14}H_{25}O_3P$ requires *M* − OH, 339.1514); R_F-(EtOAc) 0.43; ν_{max}(film)/cm^{-1} 3600–3200 (OH), 1640 (C=C), 1440 (PPh) and 1180 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 5.32 (1 H, s), 5.09 (1 H, s), 4.82 (1 H, s) (C=CH_XH_Y × 3), 4.58 (1 H, dd, *J* 25 and 6, C*H*OH *syn*), 4.48 (1 H, s, C=CH_XH_Y), 4.34 (1 H, d × fine m, *J* 7, C*H*OH *anti*), 2.74 (1 H, dt, *J* 9 and 2, PCH), 1.64 (3 H, s, Me) and 1.35 (3 H, s, Me); δ_C(62.9 MHz; $CDCl_3$) 143.1$^-$ ($^3J_{PC}$ 11.9), 142.9$^-$ (Me*C*=CH_2 × 2), 134–128 (Ph_2PO), 113.3$^-$, 112.4$^-$ (MeC=*C*H_2 × 2), 74.3$^+$, 73.2$^+$ ($^2J_{PC}$ 4.3) (CHOH × 2), 40.9$^+$ ($^1J_{PC}$ 68.5, PCH), 19.6$^+$ and 19.5$^+$ (Me × 2); *m/z* 339 (0.7%, M − OH), 286 (4, $Ph_2POCH_2CHOHC_3H_5$), 285 (8, Ph_2-$POCHCHOHC_3H_5$), 270 (2, $Ph_2POC_5H_9$), 269 (11, Ph_2-POC_4H_8), 268 (19, $Ph_2POC_5H_7$), 267 (5, $Ph_2POC_5H_6$), 245 (9, Ph_2POCH_2CHOH), 203 (6, Ph_2POH_2), 202 (46, Ph_2POH), 201 (25, Ph_2PO) and 150 (100).

Also obtained was recovered starting material (532.4 mg, 37%).

Improved Procedure for the Lithiation and Addition of β-*Hydroxy Phosphine Oxides to Aldehydes.*—Butyllithium (1.5 mol dm^{-3} solution in hexane; 10 cm^3, 15 mmol, 3.0 equiv.) was added dropwise to a stirred solution of the β-hydroxy phosphine oxide (5.0 mmol) in dry THF (50 cm^3) under nitrogen at 0 °C. The solution remained colourless until after 1 equiv. had been added, when it became orange–yellow; after 2 equiv. had been added, it became deep burgundy red. The aldehyde was distilled directly into the reaction flask at 0 °C until the colour faded to lemon yellow. Sometimes, when acrolein was used, a very dark purple–red colour developed which later faded rapidly to pale lemon yellow. The mixture was allowed to warm to room temperature, after which saturated aqueous ammonium chloride (50 cm^3) and water (50 cm^3) were

added to it. Most of the THF was then removed under reduced pressure. The aqueous suspension was extracted into dichloromethane (× 3), and the combined extracts were washed with saturated brine, dried (Na_2SO_4) and evaporated under reduced pressure to yield the crude product. This was purified by flash chromatography to yield a mixture of the diols.

(3RS,4RS,5RS)-, (3RS,4SR,5SR)-, (3RS,4SR,5RS)- *and* (3RS,4RS,5SR)-4-*Diphenylphosphinoylhept*-1-*ene*-3,5-*diol* **20** (*by Addition of Acrolein to the Propionaldehyde Adduct* **19**).—In this way, the phosphine oxide **19** (1.807 g, 6.59 mmol) and acrolein gave, after flash chromatography, eluting with 2:1 EtOAc–hexane, the *diols* **20** (1.445 g, 66%) as an oil. ^{1}H NMR analysis of this mixture at 400 MHz showed it to contain a 50:18:22:10 ratio of the four diols *anti,anti-*, *anti,syn-*, *syn,anti-* and *syn,syn*-**20** plus 6% remaining starting material (by integration of the CHP signals). The individual diols were identified by further purification of a small sample (*ca.* 220 mg) of this mixture by HPLC, eluting with EtOAc, which gave *syn,anti*-**20** (31.8 mg) as a waxy solid, retention time 16 min (Found: M^+, 330.1402. $C_{19}H_{23}O_3P$ requires *M*, 330.1384); R_F (EtOAc) 0.39; ν_{max}(film)/cm^{-1} 3600–3100 (OH), 1440 (PPh) and 1165 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 5.78 (1 H, ddd, *J* 17, 11 and 4, C*H*=CH$_2$), 5.42 (1 H, dd, *J* 17 and 2, CH=C*H*$_A$H$_B$), 5.22 (1 H, d, *J* 11, CH=CH$_A$*H*$_B$), 4.9 (1 H, br s, OH), 4.6 (1 H, br s, OH), 4.43 (1 H, d × fine m, *J* 9, CH$_2$=CHC*H*OH), 4.15 (1 H, d × m, *J* 24, CH$_2$C*H*OH), 2.48 (1 H, dt, *J* 8 and 2, PCH), 1.6–1.1 (2 H, m, C*H*$_2$Me) and 0.76 (3 H, t, *J* 7, Me); δ_C(100 MHz; $CDCl_3$) 138.6$^+$ ($^3J_{PC}$ 12.8, *C*H=CH$_2$), 134–128 (Ph_2PO), 116.0$^-$ (CH=*C*H$_2$), 73.6$^+$, 71.9$^+$ (*C*HOH × 2), 46.3$^+$ ($^1J_{PC}$ 67.2, PCH), 30.2$^-$ (*C*H$_2$Me) and 10.7$^+$ (Me); *m*/*z* 331 (3%, M + H), 330 (0.8, M^+), 301 (27, M − Et), 274 (32, $Ph_2POCH_2CHOHEt$), 257 (14, $Ph_2POCHCH_2CH_2Me$), 246 (20, $Ph_2POCH_2CH_2OH$), 202 (100, Ph_2POH) and 77 (52, Ph).

Fractions containing the next eluted compound were evaporated to give *syn,syn*-**20** (17.5 mg, contaminated with 40% *syn,anti*-**20**) as a solid, retention time 17 min; R_F (EtOAc) 0.35; δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 5.72 (1 H, ddd, *J* 17, 10 and 6, C*H*=CH$_2$), 5.08 (1 H, d, *J* 17, CH=C*H*$_A$H$_B$), 4.91 (1 H, d, *J* 10, CH=CH$_A$*H*$_B$), 4.60 (1 H, d × m, *J* 18), CH$_2$=CHC*H*OH), 3.92 (1 H, ddt, *J* 18, 9 and 4, CH$_2$C*H*OH), 2.75 (1 H, dt, *J* 9 and 4, PCH), 1.8–1.4 (2 H, m, C*H*$_2$Me) and 0.80 (3 H, t, *J* 7, Me).

Fractions containing the next eluted compound were evaporated to give *anti,syn*-**20** (41.1 mg) as an oil, retention time 21 min (Found: M^+, 330.1386. $C_{19}H_{23}O_3P$ requires *M*, 330.1384); R_F (EtOAc) 0.27; ν_{max}(film)/cm^{-1} 3600–3100 (OH), 1640 (C=C), 1440 (PPh) and 1170 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 5.51 (1 H, ddd, *J* 17, 11 and 6, C*H*=CH$_2$), 5.04 (1 H, d, *J* 17, CH=C*H*$_A$H$_B$), 4.84 (1 H, d × fine m, *J* 18, CH$_2$=CHC*H*OH), 4.78 (1 H, d, *J* 10, CH=CH$_A$*H*$_B$), 3.91 (1 H, m, maximum *J* 11, CH$_2$C*H*OH), 2.60 (1 H, dt, *J* 9 and 2, PCH), 1.9–1.4 (2 H, m, C*H*$_2$Me) and 0.86 (3 H, t, *J* 7, Me); δ_C(62.9 MHz; $CDCl_3$) 139.2$^+$ (*C*H=CH$_2$), 133–128 (Ph_2PO), 114.8$^-$ (CH=*C*H$_2$), 72.7$^+$, 71.1$^+$ ($^2J_{PC}$ 4.0) (*C*HOH × 2), 46.8$^+$ ($^1J_{PC}$ 68.1, PCH), 28.3$^-$ ($^3J_{PC}$ 10.3, CH$_2$Me) and 10.9$^+$ (Me); *m*/*z* 331 (2, M + H), 330 (0.2%, M^+), 301 (8, M − Et), 274 (11, $Ph_2POCH_2CHOHEt$), 257 (12, $Ph_2POCHCH_2CH_2Me$), 246 (15, $Ph_2POCH_2CH_2OH$), 215 (11, Ph_2POMe), 202 (72, Ph_2POH) and 77 (100, Ph).

Fractions containing the last compound to be eluted were evaporated to give *anti,anti*-**20** (115.5 mg) as needles, m.p. 125.5–127 °C (from EtOAc) (Found: C, 69.1; H, 7.1; P, 9.4%; M^+, 330.1405. $C_{19}H_{23}O_3P$ requires C, 69.08; H, 7.02; P, 9.38%; *M*, 330.1384); R_F (EtOAc) 0.27; ν_{max}(film)/cm^{-1} 3600–3100 (OH), 1640 (C=C), 1440 (PPh) and 1170 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 5.99 (1 H, ddd, *J* 17, 10 and 5, C*H*=CH$_2$), 5.15 (1 H, d, *J* 17, CH=C*H*$_A$H$_B$), 5.02 (1 H, d, *J* 10, CH=CH$_A$*H*$_B$), 4.67 (1 H, ddd, *J* 13, 5 and 2, CH$_2$=CHC*H*OH), 4.6 (2 H, br s, OH × 2), 4.08 (1 H, m, maximum *J* 14, CH$_2$C*H*OH), 2.56 (1 H, dt, *J* 9 and 2, PCH), 1.9–1.5 (2 H, m, C*H*$_2$Me) and 0.80 (3 H, t, *J* 7, Me); δ_C(62.9 MHz; $CDCl_3$) 140.5$^+$ ($^3J_{PC}$ 12.6, *C*H=CH$_2$), 133–128 (Ph_2PO), 114.6$^-$ (CH=*C*H$_2$), 72.6$^+$ ($^2J_{PC}$ 1.0), 71.1$^+$ (CHOH × 2), 46.7$^+$ ($^1J_{PC}$ 67.4, PCH), 30.3$^-$ ($^3J_{PC}$ 10.7, *C*H$_2$Me) and 10.9$^+$ (Me); *m*/*z* 331 (2.5, M + H), 330 (0.7%, M^+), 301 (7, M − Et), 286 (19), 257 (18, $Ph_2POCHCH_2CH_2Me$), 246 (22, $Ph_2POCH_2CH_2OH$), 215 (11, Ph_2POMe), 201 (100, Ph_2POH) and 77 (96, Ph).

(3RS,4RS,5RS)-, (3RS,4SR,5SR)-, (3RS,4SR,5RS)- *and* (3RS,4RS,5SR)-4-*Diphenylphosphinoylhept*-1-*ene*-3,5-*diol* **20** (*by Addition of Propionaldehyde to the Acrolein Adduct* **15a**).—In the same way, the phosphine oxide **15a**[6] (550 mg, 2.02 mmol) and propionaldehyde gave, after flash chromatography, eluting with 2:1 EtOAc–hexane and then EtOAc, the *diols* **20** (507.4 mg, 76%) as an oil. ^{1}H NMR analysis of this mixture at 400 MHz showed it to be a 56:12:24:8 ratio of the four diols *anti,anti-*, *anti,syn*, *syn,anti* and *syn*, *syn*-**20** plus 16% of unchanged starting material (by integration of the CHP signals).

(3RS,4RS,5RS)-, (3RS,4SR,5SR)-, (3RS,4SR,5RS)- *and* (3RS,4RS,5SR)-(E)-4-*Diphenylphosphinoylocta*-1,6-*ene*-3,5-*diol* **21**.—In the same way, the phosphine oxide **15b**[6] (2.830 g, 9.88 mmol) and acrolein gave, after flash chromatography, eluting with 3:1 EtOAc–hexane and then EtOAc, the *diols* **21** (199.3 mg, 59%) as an oil. ^{1}H NMR analysis of this mixture at 400 MHz showed it to contain a 44:28:19:9 ratio of the four diols *anti,anti-*, *anti,syn-* or *syn,anti-*, *syn,anti-* or *anti,syn-* and *syn,syn*-**21** (by integration of the CHP signals) (Found: M^+, 342.1376. $C_{20}H_{23}O_3P$ requires *M*, 342.1385); R_F (EtOAc) 0.33; δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 6.0–4.2 (7 H, m, C*H*=C*H* + C=C*H*$_2$ + 2 × C*H*OH), 2.80 (1 H^{syn,syn}, m, CHP), 2.66 (1 H^{anti,anti}, m, CHP), 2.64 (1 H^{syn,anti}, m, CHP), 2.57 (1 H^{anti,syn}, m, *J* 9.6, CHP) and 1.6–1.2 (3 H, d × 4, *J* 7, Me); *m*/*z* 342 (1.5%, M^+), 325 (2, M − OH), 272 (13, $Ph_2POCH_2CHOHCHCH_2$), 245 (9, Ph_2POCH_2CO), 215 (5, Ph_2POCH_2), 202 (100, Ph_2POH) and 201 (48, Ph_2PO).

(3RS,4RS,5RS)-, (3RS,4SR,5RS)-, (3RS,4SR,5SR)- *and* (3RS,4RS,5SR)-4-*Diphenylphosphinoyl*-2-*methylhepta*-1,6-*diene*-3,5-*diol* **22**.—In the same way, the phosphine oxide **15c**[6] (5.700 g, 19.9 mmol) and acrolein gave, after flash chromatography, eluting with 1:1 EtOAc–hexane and then EtOAc, the *diols* **22** (4.2692 g, 63%) as a foam. ^{1}H NMR analysis of this mixture at 400 MHz showed it to contain a 49:36:10:5 ratio of the four diols *anti,anti-*, *anti,syn-*, *syn,anti-* and *syn,syn*-**22** plus 13% of unchanged starting material (by integration of the CHP signals); R_F (EtOAc) 0.42; δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 6.2–4.0 (7 H, m, C*H*=C*H*$_2$ + MeC=C*H*$_2$ + 2 × C*H*OH), 2.92 (1 H^{syn,syn}, m, CHP), 2.78 (1 H^{anti,anti}, d × m, *J* 9, CHP), 2.74 (1 H^{syn,anti}, m, CHP), 2.64 (1 H^{anti,syn}, d × fine m, *J* 10, CHP) and 1.9–1.4 (3 H, 4 × s, Me).

(3RS,4RS,5RS)-, (3RS,4SR,5SR)-, (3RS,4SR,5RS)- *and* (3RS,4RS,5SR)-4-*Diphenylphosphinoylhept*-1-*ene*-3,5-*diyl Diacetate* **23**.—The diastereoisomeric mixture of diols **20** (14.57 g, 44.1 mmol) were dissolved in pyridine (100 cm^3) and acetic anhydride (100 cm^3) and the mixture 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 hydrogencarbonate, 20% aqueous copper sulfate and brine. The organic fractions were dried ($MgSO_4$) and evaporated under reduced pressure to yield a crude product. This was purified by flash chromatography, eluting with 1:1 EtOAc–hexane and then EtOAc, to give the *acetates* **23** (14.39 g, 79%) as a white solid (Found: M − MeCO, 371.1390. $C_{23}H_{27}O_5P$ requires *M* − MeCO, 371.1412); R_F

(EtOAc) ≈ 0.44; *m/z* 371 (1%, M − Ac), 355 (50, M − AcO), 219 (55, $Ph_2PO_2H_2$), 202 (80, Ph_2POH) and 201 (100, Ph_2PO).

(3RS,4RS,5RS)-, (3RS,4SR5RS)- (3RS,4SR,5SR)- *and* (3RS,4RS,5SR)-4-*Diphenylphosphinoyl*-2-*methylhepta*-1,6-*diene*-3,5-*diyl Diacetate* **24**.—In the same way, the diastereoisomeric mixture of the diols **21** (4.269 g, 12.47 mmol) gave, after 21.5 h, a crude product. This was purified by flash chromatography, eluting with 1:1 EtOAc–hexane and then EtOAc, to give the *acetates* **24** (3.83 g, 72%) as an oil (Found: M^+, 426.1596. $C_{24}H_{27}O_5P$ requires *M*, 426.1596); R_F(EtOAc) 0.48; *m/z* 426 (3%, M^+), 383 (5, M − Ac), 367 (100, M − AcO), 219 (18, $Ph_2PO_2H_2$), 202 (45, Ph_2POH) and 201 (60, Ph_2PO).

(3RS,4RS,5RS)-, (3RS,4SR,4SR)-, (3RS,4SR,5RS)- *and* (3RS,4RS,5SR)-(E)-4-*Diphenylphosphinoyloct*-1-*ene*-3,5-*diyl Diacetate* **26**.—In the same way, the diastereoisomeric mixture of the diols **22** (1.92 g, 5.61 mmol) gave, after 22 h, a crude product. This was purified by flash chromatography, eluting with 1:1 EtOAc–hexane and then 3:1 EtOAc–hexane, to give the *acetates* **26** (1.72 g, 72%) as a solid (Found: M^+, 426.1574. $C_{24}H_{27}O_5P$ requires *M*, 426.1596); R_F (EtOAc) 0.38–0.52; *m/z* 426 (2%, M^+), 383 (16, M − Ac), 367 (78, M − AcO), 219 (32, $Ph_2PO_2H_2$), 202 (70, Ph_2POH) and 201 (100, Ph_2PO).

(4RS,5SR,6SR)-(E,E)-5-*Diphenylphosphinoylnona*-2,7-*diene*-4,6-*diyl Diacetate* anti,anti-**28**.—In the same way, *anti,anti*-**17b** (94.2 mg, 0.264 mmol) gave, after 15 h, a crude product. This was purified by flash chromatography, eluting with 3:2 EtOAc–hexane and then EtOAc, to yield the *diacetate anti,anti*-**28** (62.2 mg, 53%) as a solid (Found: M^+, 440.1733. $C_{25}H_{29}O_5P$ requires *M*, 440.1753); R_F (EtOAc) 0.44; ν_{max}-($CDCl_3$)/cm^{-1} 1720 (C=O), 1430 (PPh) and 1160 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 5.7–5.4 (6 H, m, CH=CH × 2 and CHO × 2), 3.11 (1 H, dt, *J* 10 and 5, PCH), 1.73 (6 H, s, Ac × 2) and 1.48 (6 H, d, *J* 5, CH*Me* × 2); δ_C(100 MHz; $CDCl_3$) 169.4$^-$ (C=O), 134–127 (Ph_2PO and CH=CH × 2), 72.3$^+$ (*C*HOAc × 2), 46.5$^+$ ($^1J_{PC}$ 68.1, PCH), 20.9$^+$ (OCO*Me* × 2) and 17.6$^+$ (Me × 2); *m/z* 440 (14%, M^+), 397 (19, M − MeCO), 381 (79, M − AcO), 285 (10, Ph_2POCH_2-CHOCHCHCH$_3$), 269 (51, $Ph_2POCH_2CHCHCHCH_3$), 219 (39, $Ph_2PO_2H_2$), 202 (84, Ph_2POH) and 201 (90, Ph_2PO).

(4RS,6RS)-(E,E)-5-*Diphenylphosphinoylnona*-2,7-*diene*-4,6-*diyl Diacetate* anti,syn-**28**.—In the same way, *anti,syn*-**17b** (13.3 mg, 0.0373 mmol) gave, after 21 h, and without further purification, the *acetate anti,syn*-**28** (16.55 mg, 101%) as a solid (Found: M^+, 440.1730. $C_{25}H_{29}O_5P$ requires *M*, 440.1752); R_F (EtOAc) 0.50; ν_{max}(Nujol)/cm^{-1} 1735 (C=O), 1445 (PPh) and 1180 (P=O); δ_H(250 MHz; $CDCl_3$) 8.0–7.3 (10 H, m, Ph_2PO), 5.7–5.4 (6 H, m, CH=CH × 2 and CHO × 2), 3.29 (1 H, m, PCH), 1.78 (3 H, s), 1.64 (3 H, s) (Ac × 2), 1.62 (3 H, d, *J* 6) and 1.54 (3 H, d, *J* 6) (CH*Me* × 2); δ_C(100 MHz; $CDCl_3$) 169.7$^-$, 169.6$^-$ (C=O × 2), 135–127 (Ph_2PO and CH=CH × 2), 72.8$^+$, 72.4$^+$ (CHO × 2), 45.9$^+$ ($^1J_{PC}$ 66.9, PCH), 20.9$^+$ (CO*Me* × 2) and 17.8$^+$ and 17.7$^+$ (CH*Me* × 2); *m/z* 440 (26%, M^+), 397 (27, M − MeCO), 379 (100, M − $AcOH_2$), 286 (10, $Ph_2POCH_2CHOHCHCHCH_3$), 269 (43, $Ph_2POC_5H_8$), 219 (22, $Ph_2PO_2H_2$), 202 (58, Ph_2POH) and 201 (92, Ph_2PO).

General Procedure for the Rearrangement of Allylic Acetates 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 periods in the range 1 h to 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.

(4RS,5SR)-*and*(4RS,5RS)-(E)-4-*Diphenylphosphinoylhept*-2-*ene*-1,5-*diyl Diacetate* anti-**7** *and* syn-**7**.—In this way, the diastereoisomeric mixture of the diacetates **23** (1.20 g, 2.90 mmol) and $Pd(MeCN)_2Cl_2$ (51 mg, 0.22 mmol, 7.5 mol%) was stirred at room temperature for 10 min, refluxed for a further 6 h, and then stirred at room temperature overnight to give a crude product. This was purified by flash chromatography, eluting with 2:1 EtOAc–hexane and then EtOAc, to give the *syn acetate syn*-**7** (222.7 mg, 19%) as minute needles, m.p. 120.5–121 °C (from EtOAc) (Found: C, 66.9; H, 6.65; P, 7.5%; M^+, 414.1615. $C_{23}H_{27}O_5P$ requires C, 66.66; H, 6.57; P, 7.47%; *M*, 414.1596); R_F (EtOAc) 0.40; ν_{max}($CHCl_3$)/cm^{-1} 1730 (C=O), 1440 (PPh) and 1160 (P=O); δ_H(250 MHz; $CDCl_3$) 8.0–7.3 (10 H, m, Ph_2PO), 5.87 (1 H, ddd, *J* 16, 10 and 6, PCH=C*H*), 5.37 (1 H, ddt, *J* 16, 4 and 6, CH=C*H*CH$_2$OAc), 4.95 (1 H, ddt, *J* 10, 3 and 5, C*H*OAc), 4.34 (2 H, m, CH_2OAc), 3.57 (1 H, dt, *J* 9 and 5, PCH), 2.08 (1 H, m, CH_AH$_B$Me), 1.96 (3 H, s), 1.79 (3 H, s) (OAc × 2), 1.69 (1 H, m, CH$_A$$H_B$Me) and 0.77 (3 H, t, *J* 7, CH$_2$*Me*); δ_C(100 MHz; $CDCl_3$) 170.7$^-$, 170.5$^-$ (C=O × 2), 133–128 (Ph_2PO and CH=*C*HCH$_2$OAc), 124.7$^+$ ($^2J_{PC}$ 7.1, PCH*C*H=CH), 74.5$^+$ (*C*HOAc), 64.0$^-$ (*C*H$_2$OAc), 47.1$^+$ ($^1J_{PC}$ 65.5, PCH), 24.3$^-$ ($^3J_{PC}$ 8.5, *C*H$_2$Me), 20.8$^+$, 20.6$^+$ (CO*Me* × 2) and 9.9$^+$ (CH$_2$*Me*); *m/z* 414 (11%, M^+), 355 (29, M − AcO), 313 (29, $Ph_2POCHCHCHCH_2OAc$), 255 (19, $Ph_2POC_4H_6$), 219 (100, $Ph_2PO_2H_2$), 202 (18, Ph_2POH) and 201 (62, Ph_2PO).

Also obtained was the anti *acetate anti*-**7** (504.0 mg, 42%) as an unrecrystallisable wax (Found: M^+, 414.1593. $C_{23}H_{27}O_5P$ requires *M*, 414.1596); R_F (EtOAc) 0.31; ν_{max}(film)/cm^{-1} 1740 (C=O), 1660 (C=C), 1445 (PPh) and 1190 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.3 (10 H, m, Ph_2PO), 5.83 (1 H, ddd, *J* 15, 10 and 5, PCH=C*H*), 5.39 (1 H, dq, *J* 15 and 6, CH=C*H*CH$_2$OAc), 5.20 (1 H, m, C*H*OAc), 4.33 (2 H, m, CH_2OAc), 3.18 (1 H, ddd, *J* 13, 10 and 2, PCH), 1.87 (3 H, s), 1.62 (3 H, s) (OAc × 2), 1.6–1.4 (2 H, m, CH_2Me) and 0.67 (3 H, t, *J* 7, CH$_2$*Me*); δ_C(100 MHz; $CDCl_3$) 170.3$^-$, 169.6$^-$ (C=O × 2), 132–128 (Ph_2PO and CH=*C*HCH$_2$OAc), 125.5$^+$ ($^2J_{PC}$ 4.9, PCH*C*H=CH), 71.7$^+$ (*C*HOAc), 63.8$^-$ (*C*H$_2$OAc), 47.7$^+$ ($^1J_{PC}$ 67.1, PCH), 26.1$^-$ ($^3J_{PC}$ 8.5, *C*H$_2$Me), 20.6$^+$, 20.4$^+$ (CO*Me* × 2) and 9.5$^+$ (CH$_2$*Me*); *m/z* 415 (4%, M + H), 414 (1, M^+), 372 (1, M − Ac), 355 (8, M − AcO), 313 (19, $Ph_2POCHCHCHCH_2OAc$), 255 (10, $Ph_2POC_4H_6$), 219 (100, $Ph_2PO_2H_2$), 202 (13, Ph_2POH) and 201 (52, Ph_2PO).

Mixed fractions from the column gave further material (130 mg, 11%).

(4RS,5SR)-(E)-4-*Diphenylphosphinoyl*-6-*methylhepta*-2,6-*diene*-1,5-*diyl diacetate* **25**. In the same way, the diastereoisomeric mixture of the acetates **24** (2.98 g, 7.00 mmol) and $Pd(MeCN)_2Cl_2$ (150 mg, 0.58 mmol, 8.25 mol%) was stirred at room temperature for 10 min and then refluxed for 65 h to give a crude product. This was purified by flash chromatography, eluting with 2:1 EtOAc–hexane and then EtOAc, to yield the *mono-rearranged diacetate anti*-**25** (1.2982 g, 44%) as minute needles, m.p. 121–123 °C (from EtOAc) (Found: C, 67.6; H, 6.45; P, 7.3%; M^+, 426.1610. $C_{24}H_{27}O_5P$ requires C, 67.60; H, 6.38; P, 7.26%; *M*, 426.1594); R_F (EtOAc) 0.30; ν_{max}($CHCl_3$)/cm^{-1} 1730 (C=O), 1650 (C=C), 1445 (PPh) and 1165 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 5.87 (1 H, ddd, *J* 15, 10 and 5, PCH=C*H*), 5.71 (1 H, dd, *J* 8 and 2, C*H*OAc), 5.36 (1 H, ddt, *J* 15, 4 and 6, CH=C*H*OAc), 4.81 (1 H, s, C=CH_AH$_B$), 4.73 (1 H, s, CH$_A$$H_B$), 4.42 (2 H, ABX m, C$H_2$OAc), 3.26 (1 H, ddd, *J* 14, 10 and 2, PCH), 1.98 (3 H, s), 1.75 (3 H, s) (OAc × 2) and 1.64 (3 H, s, CH$_2$=C*Me*); δ_C(62.9 MHz; $CDCl_3$) 170.5$^-$, 170.0$^-$ (C=O × 2), 141.1$^-$ ($^3J_{PC}$ 10.1, CH$_2$=*C*Me), 132–128 (Ph_2PO and CH=*C*HCH$_2$OAc), 125.5$^+$ ($^2J_{PC}$ 4.7, PCH*C*H=CH), 112.4$^-$ (*C*H$_2$=CMe), 72.7$^+$ (*C*HOAc), 64.0$^-$

(CH_2OAc), 47.6$^+$ ($^1J_{PC}$ 66.0, PCH), 21.3$^+$, 20.8$^+$ (CO*Me* × 2) and 19.5$^+$ (C=C*Me*); *m/z* 426 (1%, M$^+$), 367 (18, M − AcO), 313 (15, $Ph_2POCHCHCHCH_2OAc$), 255 (10, $Ph_2POC_4H_6$), 219 (40, $Ph_2PO_2H_2$), 202 (30, Ph_2POH), 201 (80, Ph_2PO) and 43 (100, MeCO).

Further fractions from the column contained a mixture of the unrearranged and mono-rearranged acetates **24** and **25**.

Allylic rearrangement of the diacetates **26**. In the same way, the diastereoisomeric mixture of the diacetates **26** (1.71 g, 4.13 mmol) and $Pd(MeCN)_2Cl_2$ was stirred at room temperature for 30 min and then refluxed for 4 h to give a crude product. This was purified by flash chromatography to yield the rearranged acetates ^{1,4}*anti*- and ^{1,4}*syn*-**27** (0.9313 g, 54%) in a 73:27 ratio (by ^{1}H NMR). Attempts to separate the two diastereoisomers by HPLC, eluting with EtOAc–5% MeOH, CH_2Cl_2–6% MeOH or $CHCl_3$–3% MeOH were unsuccessful.

(4RS,7SR)-(E,E)-4-*Diphenylphosphinoylocta*-2,5-*diene*-1,7-*diyl diacetate anti*-**27**. In the same way, the diacetate *anti*-**9** (64.8 mg, 0.152 mmol) and $Pd(MeCN)_2Cl_2$ (*ca.* 10 mg) was stirred at room temperature for 7 h to give a crude product. This was purified by flash chromatography, eluting with EtOAc, to yield the *rearranged diacetate anti*-**27** (34.7 mg, 54%) as an oil (Found: M$^+$, 426.1625. $C_{24}H_{27}O_5P$ requires *M*, 426.1596); R_F (EtOAc) 0.35; $\nu_{max}(CDCl_3)/cm^{-1}$ 1730 (C=O), 1445 (PPh) and 1190 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 5.75–5.60 (2 H, m, PCHC*H*=CH × 2), 5.64 (1 H, ddq, *J* 16, 6 and 1, CH=C*H*CH_2OAc), 5.48 (1 H, ddd, *J* 16, 6 and 4, CH=C*H*CHOAc), 5.25 (1 H, dqn, *J* 1 and 7, C*H*OAc), 4.50 (2 H, m, C*H*$_2$OAc), 3.85 (1 H, dt, *J* 14 and 8, PCH), 2.05 (3 H, s), 2.02 (3 H, s) (OAc × 2) and 1.13 (3 H, d, *J* 7, CH*Me*); δ_C(100 MHz; $CDCl_3$) 170.6$^+$, 170.1$^+$ (C=O × 2), 135–124 (Ph_2PO and C=C × 2), 70.3$^+$ (*C*HOAc), 64.2$^-$ (*C*H_2OAc), 48.5$^+$ ($^1J_{PC}$ 64.9, PCH), 21.2$^+$, 20.9$^+$ (CO*Me* × 2) and 20.0$^+$ (Me); *m/z* 426 (5%, M$^+$), 366 (12, M − AcOH), 307 (20, M − AcOH − AcO), 219 (50, $Ph_2PO_2H_2$), 202 (20, Ph_2POH) and 201 (100, Ph_2PO).

(4RS,7RS)-(E,E)-4-*Diphenylphosphinoylocta*-2,5-*diene*-1,7-*diyl diacetate* syn-**27**. In the same way, the diacetate *syn*-**9** (35.1 mg, 0.082 mmol) and $Pd(MeCN)_2Cl_2$ (*ca.* 8 mg) was stirred at room temperature for 5.5 h to give a crude product. This was purified by flash chromatography, eluting with EtOAc, to yield the *rearranged diacetate syn*-**27** (16.7 mg, 48%) as an oil (Found: M$^+$, 426.1585. $C_{24}H_{27}O_5P$ requires *M*, 426.1596); R_F (EtOAc) 0.35; $\nu_{max}(CDCl_3)/cm^{-1}$ 1730 (C=O), 1445 (PPh) and 1190 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 5.9–5.4 (4 H, m, CH=CH × 2), 5.19 (1 H, dqn, *J* 3 and 6, C*H*OAc), 4.41 (2 H, m, C*H*$_2$OAc), 3.79 (1 H, dt, *J* 14 and 8, PCH), 1.98 (3 H, s), 1.94 (3 H, s) (OAc × 2) and 1.12 (3 H, d, *J* 6, CH*Me*); δ_C(100 MHz; $CDCl_3$) 170.6$^+$, 170.0$^+$ (C=O × 2), 135–124 (Ph_2PO and C=C × 2), 70.0$^+$ (*C*HOAc), 64.2$^-$ (*C*H_2OAc), 48.3$^+$ ($^1J_{PC}$ 64.7, PCH), 21.2$^+$, 20.8$^+$ (CO*Me* × 2) and 19.9$^+$ (Me); *m/z* 426 (8%, M$^+$), 366 (15, M − AcOH), 307 (13, M − AcOH − AcO), 219 (60, $Ph_2PO_2H_2$), 202 (22, Ph_2POH) and 201 (100, Ph_2PO).

(2RS,5SR,8SR)-(E,E)-5-*Diphenylphosphinoylnona*-3,6-*diene*-2,8-*diyl diacetate* anti,anti-**29**. In the same way, the *anti,anti*-diacetate *anti,anti*-**28** (38.0 mg, 0.0863 mmol) and $Pd(MeCN)_2Cl_2$ (*ca.* 2 mg) gave, after 1 h at room temperature, a crude product. This was purified by flash chromatography, eluting with EtOAc, to yield the *diacetate anti,anti*-**29** (28.9 mg, 76%) as a solid (Found: M$^+$, 440.1740. $C_{25}H_{29}O_5P$ requires *M*, 440.1753); R_F (EtOAc) 0.38; $\nu_{max}(CHCl_3)/cm^{-1}$ 1720 (C=O), 1440 (PPh) and 140 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.3 (10 H, m, Ph_2PO), 5.74 (2 H, ddd, *J* 15, 8 and 6, PCHC*H*=CH × 2), 5.41 (2 H, ddd, *J* 15, 6 and 4, CH=C*H*CHOAc × 2), 5.18 (2 H, d × quintet, *J* 1 and 6, C*H*OAc × 2), 3.68 (1 H, dt, *J* 13 and 8, PCH), 1.94 (6 H, s, Ac × 2) and 1.06 (6 H, d, *J* 6, CH*Me* × 2); δ_C(100 MHz; $CDCl_3$) 170.1$^-$ (C=O × 2), 134.8$^+$ ($^3J_{PC}$ 10.8, CH=*C*HCHOAc × 2), 132–128 (Ph_2PO), 124.9$^+$ ($^2J_{PC}$ 7.5, PCH*C*H=CH × 2), 70.3$^+$ (*C*HOAc × 2), 48.5$^+$ ($^1J_{PC}$ 64.6, PCH), 21.3$^+$ (OCO*Me* × 2) and 20.0$^+$ (Me × 2); *m/z* 440 (38%, M$^+$), 379 (77, M − AcO), 327 (58, M − AcOCHCHCHMe), 286 (60, Ph_2POCH_2-$CHOHC_3H_5$), 269 (43, $Ph_2POC_5H_8$), 202 (80, Ph_2POH) and 137 (100).

(2SR,8SR)-(E,E)-5-*Diphenylphosphinoylnona*-3,6-*diene*-2,8-*diyl diacetate* anti,syn-**29**. In the same way, the *anti,syn* diacetate *anti,syn*-**28** (11.9 mg, 0.027 mmol) and $Pd(MeCN)_2Cl_2$ (*ca.* 2 mg) gave, after 2.5 h at room temperature, a crude product. This was purified by flash chromatography, eluting with EtOAc, to yield the *diacetate anti,syn*-**29** (8.9 mg, 75%) as minute needles (Found: M$^+$, 440.1763. $C_{25}H_{29}O_5P$ requires *M*, 440.1752); R_F (EtOAc) 0.42; $\nu_{max}(CHCl_3)/cm^{-1}$ 1720 (C=O), 1440 (PPh) and 1140 (P=O); δ_H(400 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 5.75 (2 H, m, PCHC*H*=CH × 2), 5.41 (2 H, m, CH=C*H*CHOAc × 2), 5.20 (2 H, m, C*H*OAc × 2), 3.72 (1 H, dt, *J* 14 and 8, PCH), 1.950 (3 H, s), 1.946 (3 H, s) (Ac × 2), 1.13 (3 H, d, *J* 7), 1.06 (3 H, d, *J* 7) (CH*Me* × 2); δ_C(100 MHz; $CDCl_3$) 170.1$^-$ (C=O × 2), 134.8$^+$ ($^3J_{PC}$ not resolvable, CH=*C*HCHOAc × 2), 132–128 (Ph_2PO), 124.9$^+$ ($^2J_{PC}$ not resolvable, PCH*C*H=CH × 2), 70.4$^+$ and 70.1$^+$ (*C*HOAc × 2), 48.5 ($^1J_{PC}$ 64.6, PCH), 21.3$^+$ (OCO*Me* × 2) and 20.0$^+$ (Me × 2); *m/z* 440 (29%, M$^+$), 381 (77, M − AcO), 321 (46), 261 (86, $Ph_2POHOAc$), 219 (54, $Ph_2PO_2H_2$), 202 (25, Ph_2POH) and 201 (90, Ph_2PO).

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