Stereochemically Controlled Synthesis of Unsaturated Alcohols by the Horner–Wittig Reaction

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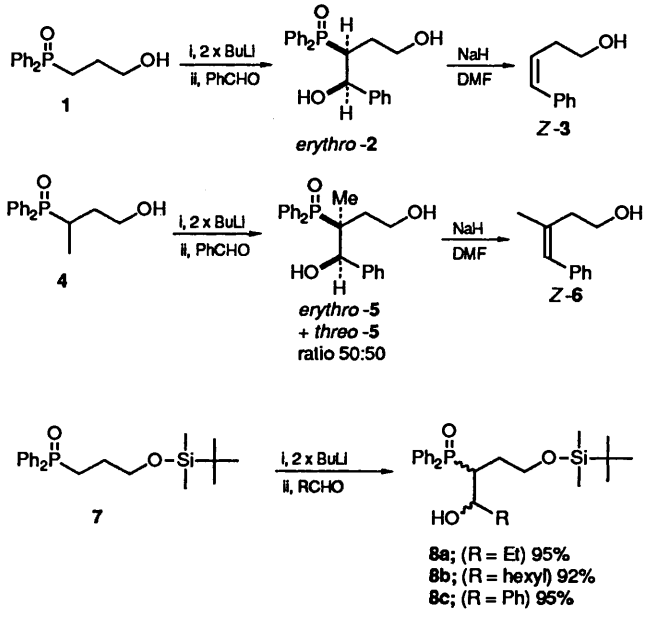
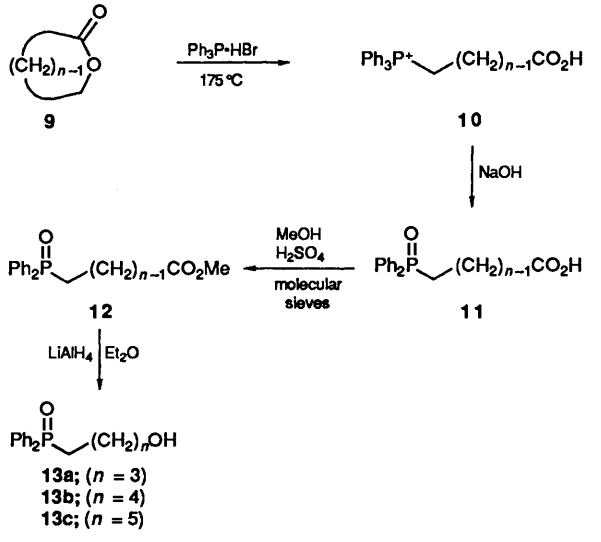
Single isomers (*E* or *Z*) of unsaturated alcohols with two to five carbon atoms between the double bond and the OH group may be made by the phosphine oxide version of the Horner–Wittig reaction. Hydroxyalkyldiphenylphosphine oxides react with aldehydes either directly or as silyl ethers to give a moderately *Z*-selective synthesis, while rearrangement of esters of the same alcohols by acyl transfer or acylation of alkyldiphenylphosphine oxides with lactones gives hydroxy ketones whose reduction and elimination leads to an *E*-selective synthesis. In most cases, separation of the diastereoisomers of the Horner–Wittig intermediates leads to the preparation of pure *E*- or *Z*-alkenols.

Unsaturated alcohols may be made by the Wittig reaction with the hydroxy group positioned either on the phosphonium salt or on the aldehyde.[1] This route is well suited to the synthesis of *Z* alkenols either by the attack of ylides on lactols or of protected hydroxyalkyl ylides on aldehydes. The stereoselectivity of reactions of ylides made from hydroxyalkylphosphonium salts depends on the position of the OH group and on whether it is protected or not.[2] Protected hydroxyalkyl ylides give *Z*-alkenols,[1,3] but alkoxyalkyl ylides tend to give *E*-alkenols *via* a Schlosser-like[4] equilibration, and 2-alkoxyalkyl ylides give the SCOOPY reaction.[1] The phosphine oxide version of the Horner–Wittig reaction,[5] as well as providing pure *E*- or *Z*-unsaturated alcohols,[6] is well suited to the synthesis of *E*-alkenols by the reduction of ketones formed either by the acylation of phosphine oxides with lactones,[7] or by acyl transfer.[8] We now give full details of these routes and outline the best approach to each type of unsaturated alcohol. The synthesis of dienols has already been described.[9]

The direct reaction of dilithium derivatives of hydroxyalkylphosphine oxides with aldehydes is limited to non-enolisable aldehydes since starting materials are recovered from attempted reactions with simple alkyl aldehydes. The *erythro*:*threo* selectivity is worse with **1** and benzaldehyde (70:30) than with Ph_2POPr and the same aldehyde (85:15), but 69% pure *erythro*-**2** was isolated, giving pure *Z*-4-phenylbut-3-en-1-ol **3** on elimination. The trisubstituted alkenes *E*- and *Z*-3-methyl-4-phenylbut-3-en-1-ol **6** were made by the same route in good yield but as expected[5,7] without any stereoselectivity. The *E*-isomers of both these alkenes can be made by acyl transfer.[8] Attempts to make lithium derivatives of the trimethylsilyl ethers of **1** and **4** led only to desilylation, but protection of the hydroxy group as the less reactive *tert*-butyldimethylsilyl ether **7** allowed a very high yield reaction with enolisable aldehydes though with no stereoselectivity.

A more general approach to hydroxyalkyl phosphine oxides **13** is outlined in Scheme 1, and the yields for each stage given in



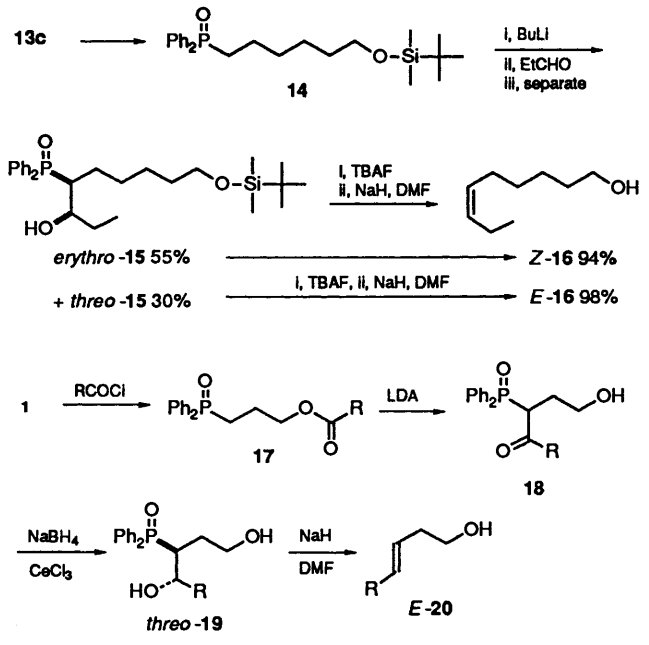


Scheme 1 Synthesis of hydroxyalkyl phosphine oxides

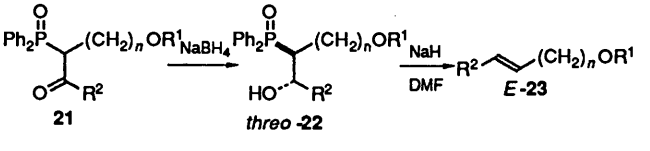
Table 1. The phosphine oxide **13d** ($n = 10$) was made by hydrolysis[5] of the triphenylphosphonium salt from available 11-bromoundecanol. With a longer distance [$(CH_2)_6$] between the OH group and the phosphorus atom **13c**, addition of the dilithium derivative to enolisable aldehydes was possible, but stereoselectivity was poor, and we could not separate the diastereoisomers of the adduct. The silyl ether **14** gave some selectivity (64:36) and, more important, easy separation of diastereoisomers **15**. Desilylation and elimination gave pure *Z*-non-6-en-1-ol *Z*-**16**, and pure *E*-**16**, better prepared by acylation and reduction.[7] If pure *Z*-alkenols are required this is a possible route, but Wittig routes are generally better.

Table 1 Synthesis of hydroxyalkyl phosphine oxides

n	Yield (%) 10	11	12	Product	Yield of product (%)
3	84	97	82	**13a**	72
4	81	98	89	**13b**	78
5	85	70	88	**13c**	95

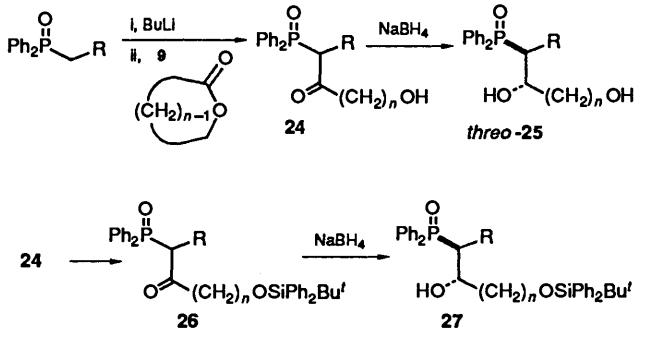


Acyl transfer routes[8] are available from 3- and 4-hydroxyalkylphosphine oxides, *e.g.* **1**, **4** or **13a**. These provide a *threo* selective route to alcohols **19** and hence *E*-**20** by acylation at oxygen and rearrangement of the esters **17** to the hydroxy ketones **18** in base. Reduction with $NaBH_4$ in the presence of $CeCl_3$ (Luche[10] reduction) is very *threo* selective for hydroxy ketones[11] of this particular structure: other β-Ph_2PO-ketones,[12] even those with a hydroxy group elsewhere **21** (R = H and see

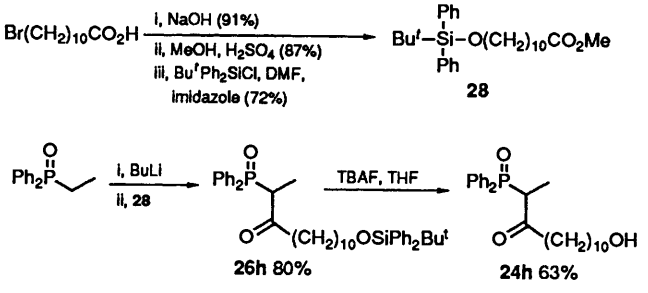


below) give reduced *threo*- or even *erythro*-selectivity in the presence of $CeCl_3$. Reductions of the free alcohols **21** (R = H) and of the silyl ethers **21** (R = $SiPh_2Bu^t$) by $NaBH_4$, with and without cerium, are summarised in Table 2.

Acylation of alkyldiphenylphosphine oxides with lactones **9**

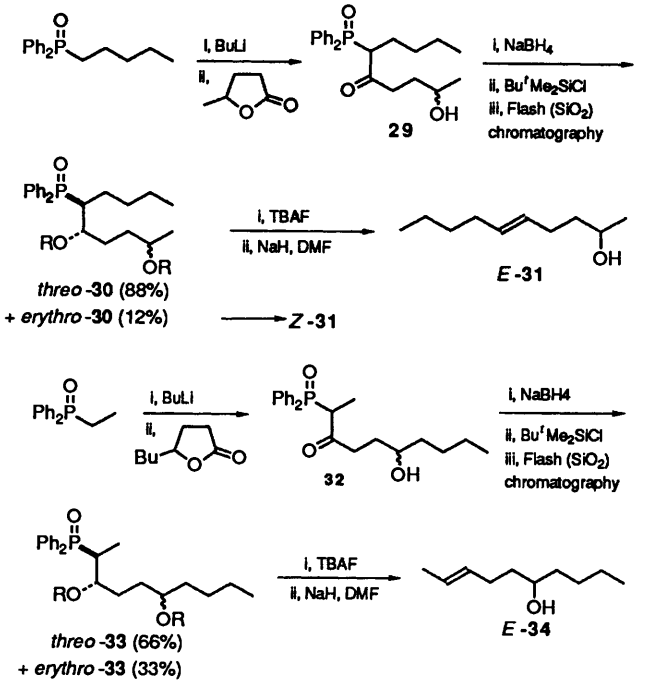


(*n* = 2–5, 14) gives hydroxy ketones **24** with the hydroxy group in the other side chain. Acylation is possible with propiolactone (*n* = 2) and cyclopentadecanolide (*n* = 14), but the yields are only moderate. Five-, six- and seven-membered lactones give clean acylation (Table 3); protected hydroxy esters (*e.g.* **28**) can



be used instead of lactones. Reduction with $NaBH_4$ alone is *threo*-selective, Luche reduction is virtually non-selective. The silyl ethers generally give lower *threo*- or even weak *erythro*-selectivity (Table 4).

Unsaturated secondary alcohols have the complication of a third chiral centre in the vital intermediate (*e.g.* **30** or **33**). We



have shown how acyl transfer may be used to control an extra chiral centre,[13] but we have now made *E*- and *Z*-isomers of two decenols **31** and **34** without such control. These examples were chosen so that substituents (Me and Bu) on the phosphine oxide and lactone starting materials were reversed in the two series. Acylation gave **29** and **32** which were reduced with good and fair selectivity respectively to give four diastereoisomers each of the diols **30** and **33** which we could not separate. The silyl ethers **30** and **33** (R = Bu^tMe_2Si) were easily separated by flash chromatography into a *threo* pair and an *erythro* pair, as shown by the clean elimination to *E*- or *Z*-isomers of the products. Evidently the silica binds selectively to the neighbouring silyl ether and Ph_2PO groups and essentially ignores the remote silyl ether. The alkenol **31** has been made by a Wittig reaction[14] in poor yield and 88:12 *Z*:*E* selectivity and by the Claisen rearrangement[15] in good yield but poor (53:47) selectivity. In neither case could the mixture of *E*- and *Z*-alkenols be separated.

Table 2a Reduction of keto alcohols **21**

Compound	*n*	R^1	R^2	Reduction method[a]	*threo*: *erythro*	Yield (%) *threo*
21a[b,c]	2	H	Me	A1	75:25	66
21b[b,c]	2	H	Et	A1	75:25	64
21c[b,d]	2	H	$(CH_2)_2CO_2Me$	A1	69:31	—
21c[b,d]	2	H	$(CH_2)_2CO_2Me$	B	>95:5	77
Various[e]	2	H	various[e]	B	>95:5	good
Various[f]	2	CPh_3	alkenyl	B	<5:95	0[g]
21d[b,c]	3	H	Ph	A1	>95:5	65

[a] Method A1: $NaBH_4$, MeOH, 0 °C; B: $NaBH_4$, $CeCl_3$, MeOH, −78 °C. [b] Prepared by acyl transfer. [c] See ref. 8. [d] See ref. 11. [e] See ref. 13. [f] See ref. 12, the carbon chain is branched: $CHMe{\cdot}CH_2OCPh_3$. [g] Good yields of *erythro* compounds.

Table 2b NMR Experiments on the effects of hydroxy protection on the reduction of keto alcohols **21** (R^2 = Me)

	Borohydride reduction[a]				Luche reduction[b]			
	R^1 = H		R^1 = $SiPh_2Bu^t$		R^1 = H		R^1 = $SiPh_2Bu^t$	
n	Yield (%)	*threo*: *erythro*	Yield (%)	*threo*: *erythro*	Yield (%)	*threo*: *erythro*	Yield (%)	*threo*: *erythro*
2	88	67:33	92	62:38	92	>95:5	90	73:27
3	98	64:36	97	59:41	90	55:45	80	47:53
4	87	63:37	87	48:52	94	56:44	84	63:37
10	65	37:63	79	34:66	76	72:28	—	—

[a] Method A: $NaBH_4$, MeOH, 0 °C. [b] Method B: $NaBH_4$, $CeCl_3$, MeOH, −78 °C.

Table 3 Acylation of diphenylalkylphosphine oxides with lactones **9**

R in starting material	*n* in Lactone **9**	Product	Yield (%)
Me	2	**24a**	29[a]
Me	3	**24b**	66
C_5H_{11}	3	**24c**	79
Bu	3[b]	**29**	71
Me	3[c]	**32**	73
Me	4	**24d**	57
Bu	4	**24e**	86[d]
Me	5	**24f**	74
Et	5	**24g**	81[d]
Me	10	**26h**	80[e]
Me	14	**24i**	49

[a] 71% Recovered starting material. [b] Lactone is γ-valerolactone, see text. [c] Lactone is γ-octanoic, see text. [d] See ref. 7. [e] Acylation by ester of protected hydroxy acid, see text.

Acylation with a lactone and reduction with $NaBH_4$ alone is thus the simplest route to *E*-unsaturated alcohols other than homoallylic alcohols **20** which are better made by acyl transfer and reduction with $NaBH_4$ and $CeCl_3$. Though pure *Z*-isomers of unsaturated alcohols are available by these methods, the only remotely *erythro*-selective route is the Horner–Wittig reaction on silyl ethers, and other routes such as the reduction of alkynes, are preferable.

Experimental

erythro-2-*Diphenylphosphinoyl*-1-*phenylbutane*-1,4-*diol* erythro-**2**.—Butyllithium (27.2 cm^3 of a 1.6 mol dm^{-3} solution in hexane) was added to a stirred solution of 3-diphenylphosphinoylpropan-1-ol[8] (2.0 g) in THF (5 cm^3) at −78 °C. After 1 h the dark red solution was quenched by the addition of benzaldehyde (2.06 cm^3). The mixture was allowed to warm to 0 °C over 4 h, quenched with water, and extracted with dichloromethane. Purification by flash chromatography[18] on silica gel eluting with EtOAc and removal of solvent under reduced pressure gave a solid which was repeatedly recrystallised from EtOAc to give the *diol* (1.94 g, 69%) as needles, m.p. 149.5–150 °C (Found: C, 72.3; H, 6.0; P, 8.4%; M^+, 365.1306. $C_{22}H_{23}O_3P$ requires C, 72.1; H, 6.3; P, 8.5%; *M*, 365.1307); $\nu_{max}(CDCl_3)/cm^{-1}$ 3350 (OH), 1440 (Ph–P) and 1180 (P=O); $\delta_H(CD_3OD)$ 8.2–7.2 (15 H, m, Ph_2PO and Ph), 5.15 (1 H, dd, J_{HH} 3 and J_{PH} 9, CHO), 3.2–2.8 (1 H, m, CHP), 3.0 (2 H, t, *J* 7, CH_2O) and 2.3–1.5 (2 H, m, CH_2CH_2OH); *m/z* 365 (10%, M^+), 260 (29), 229 (100, $Ph_2POHCH{=}CH_2$) and 202 (22, Ph_2POH).

2-*Diphenylphosphinoyl*-2-*methyl*-1-*phenylbutane*-1,4-*diol* **5**.—In the same way, butyllithium (9.8 cm^3 of a 1.6 mol dm^{-3} solution in hexane), 3-diphenylphosphinoylbutan-1-ol[8] **4** (2.0 g) in THF (40 cm^3) and benzaldehyde (1 cm^3) gave the *diol* (1.66 g, 60%) as a waxy 1:1 mixture of diastereoisomers, R_f (EtOAc) 0.19; $\nu_{max}(CDCl_3)/cm^{-1}$ 3300 (OH), 1440 (Ph–P) and 1180 (P=O); $\delta_H(CDCl_3)$ 8.3–7.1 (15 H, m, Ph_2PO and Ph), 5.05 and 4.95 (1 H, two d, *J* 8, *threo*-CHO and *J* 11, *erythro*-CHO respectively), 4.2 (2 H, br s, OHs), 4.0–3.1 (2 H, m, CH_2OH), 2.2–1.5 (2 H, m, CH_2CH_2OH), 1.3 and 1.05 (3 H, two d, J_{PH} 17, *threo*-Me, and J_{PH} 17, *erythro*-Me respectively) (Found: M^+, 380.1558. $C_{23}H_{25}O_3P$ requires *M*, 380.1541); *m/z* 380 (2%, M^+), 243 [100, $Ph_2POC(Me){=}CH_2$] and 202 (26, Ph_2POH).

(Z)-4-*Phenylbut*-3-*en*-1-*ol* Z-**3**.—Sodium hydride (100 mg of a 50% suspension in oil) was placed in a round bottom flask and freed from oil by decantation with pentane under nitrogen. The excess of pentane was removed in a stream of nitrogen and the residue taken up in dry dimethylformamide (DMF) (10 cm^3). *erythro*-**2** (250 mg) was added and the mixture stirred for 2 h. After this time a yellowish precipitate had formed. Water (40 cm^3) was added and the mixture was extracted with ether. The extract was washed with water and with brine, dried ($MgSO_4$), and the ether removed under reduced pressure to give the *alcohol* (96 mg, 95%) as a liquid; ν_{max}(neat film)/cm^{-1} 3320 (OH) and 795 (C=C); $\delta_H(CDCl_3)$ 7.4–7.2 (5 H, m, Ph), 6.6 [1 H, d, *J* 12 (and allylic coupling), PhC*H*=CH], 5.7 (1 H, dt, *J* 12 and 8, CH=C*H*CH_2), 3.7 (2 H, t, *J* 7, CH_2OH), 2.6 (2 H, dt, *J* 7 and 8, CH_2CH_2OH) and 1.6 (1 H, br s, OH) (Found: M^+, 148.0896.

Table 4 Effects of silylation and of $CeCl_3$ on the $NaBH_4$ reduction of hydroxy ketones **24** (R = Me)

Substrate:		Alcohol **24**			Bu^tPh_2Si ether **26**			Best yield[b] (%) of *threo*-**25**
n	Method[a]	Compound	*threo*: *erythro*	Yield (%)	Compound	*threo*: *erythro*	Yield (%)	
2	A1	**24a**	65:35	100	**26a**	67:33	100	68
2	B	**24a**	41:59	79	**26a**	50:50	81	—
3	A2	**24b**	74:26	76	**26b**	70:30	63	55
3	B	**24b**	44:56	77	**26b**	45:55	68	
4	A2	**24d**	75:25	78	**26d**	71:29	87	57
4	B	**24d**	48:52	77	**26d**	39:61	75	
5	A1	**24f**	74:26	76	**26f**	58:42	87	50
5	B	**24f**	48:52	77	**26f**	39:61	80	
5	C1	**24f**	67:33	78	**26f**	—	—	—
5	C2	**24f**	55:45	80	**26f**	—	—	—
10	A1	**24i**	64:36	85	**26i**	64:36	85	—
14	A1	**24i**	52:48	90	**26i**	—	—	—

[a] A1: $NaBH_4$ in MeOH at 0 °C; A2: as A1 but in EtOH; B: $NaBH_4$ and $CeCl_3$ in MeOH at −78 °C, see ref. 10; C1: $LiEt_3BH$ ('Super-Hydride®', see R. Baker, P. D. Ravenscroft, and C. J. Swain, *J. Chem. Soc., Chem. Commun.*, 1984, 74), THF, 0 °C; C2 as C1 but at −78 °C. [b] Highest yield of isolated pure *threo*-**25** from any of these reductions.

$C_{10}H_{12}O$ requires *M*, 148.0888); *m/z* 148 (28.7%, M^+), 117 (100, $PhCH{=}CHCH_2$) and 91 (17, $PhCH_2$).

Completion of the Horner–Wittig Reaction on Compound **5**: E- *and* Z-3-*Methyl*-4-*phenylbut*-3-*en*-1-*ol* **6**.—In the same way, sodium hydride (100 mg of a 50% dispersion in oil) and the phosphine oxide **5** (160 mg of a 1:1 mixture of diastereoisomers) gave, after HPLC on silica eluting with ether, *Z*-3-methyl-4-phenylbut-3-en-4-ol *Z*-**6** (27 mg, 39%) as a liquid; $\nu_{max}(CDCl_3)/cm^{-1}$ 3350 (OH), 1630 (C=C) and 1500 (Ph); $\delta_H(CDCl_3)$ 7.5–7.2 (5 H, m, Ph), 6.5 (1 H, br s, PhC*H*=C), 3.8 (2 H, t, *J* 7, CH_2OH), 2.5 (2 H, t, *J* 7, CH_2C=CH), 1.9 (3 H, s, Me) and 1.5 (1 H, br s, OH) (Found: M^+, 162.1041. $C_{11}H_{14}O$ requires *M*, 162.1044); *m/z* 162 (68%, M^+), 132 (100) and 91 (52), and *E*-3-methyl-4-phenylbut-3-en-4-ol *E*-**6** (31 mg, 46%).[8]

1-tert-*Butyldimethylsilyloxy*-3-*diphenylphosphinoylpropane* **7**.—A solution of the alcohol **1** (20 g), *tert*-butyldimethylsilyl chloride (13.94 g), and imidazole (13.08 g) in dry DMF (40 cm^3) was stirred at room temperature for 18 h. Water was added and the mixture extracted with dichloromethane. The extract was thoroughly washed with water, dried ($MgSO_4$), and the solvent removed under reduced pressure to give a waxy solid. Recrystallisation from EtOAc gave the *silyl ether* (23.6 g, 82%) as a waxy solid; $\nu_{max}(CDCl_3)/cm^{-1}$ 1440 (Ph–P) and 1180 (P=O); $\delta_H(CDCl_3)$ 8.0–7.4 (10 H, m, Ph_2PO), 3.65 (2 H, t, *J* 7, CH_2OSi), 2.6–2.1 (2 H, m, CH_2P), 2.1–1.5 (2 H, m, $CH_2CH_2CH_2$), 0.85 (9 H, s, Bu^t) and 0.0 (6 H, s, Me's) (Found: M^+, 374.1837. $C_{21}H_{31}O_2PSi$ requires *M*, 374.1831); *m/z* 374 (5%, M^+), 317 (100, M − Bu^t) and 201 (10, Ph_2PO).

6-tert-*Butyldimethylsilyloxy*-4-*diphenylphosphinoylhexan*-3-*ol* **8a**.—Butyllithium (1.8 cm^3 of a 1.6 mol dm^{-3} solution in hexane) was added to a stirred solution of the phosphine oxide **7** (1.0 g) in THF (40 cm^3) cooled to −78 °C in a Cardice-ethanol bath. After 10 min, propanal (115 mg) in THF (1 cm^3) was added. Stirring was continued for 1 h, the mixture was quenched with saturated aqueous ammonium chloride, and allowed to warm to room temperature. Extraction with dichloromethane, washing with water and with brine followed by drying ($MgSO_4$) and removal of the solvent under reduced pressure gave the crude alcohol **8a** (a 1:1 mixture of diastereoisomers by ^{13}C NMR spectroscopy) (1.10 g, 95%) as a waxy solid; $\delta_H(CDCl_3)$ 8.0–7.2 (10 H, m, Ph_2PO), 3.9–3.2 (3 H, m, CH_2OSi and C*H*OH), 3.0–2.6 (1 H, m, CHP), 2.2–1.4 (4 H, m, CH_2's), 2.0 (1 H, br s, OH), 0.9 (9 H, s, Bu^t), 0.9 (3 H, t, *J* 7, *Me*CH_2), 0.0 and −0.05 (6 H, two s, $SiMe_2$); $\delta_C(CDCl_3)$ 70.3 and 70.2 (CHOH), 60.19 and 60.16 (CHOSi), 40.1 and 37.0 (PCH, 2 d, J_{CP} 70 and 73).

1-tert-*Butyldimethylsilyloxy*-3-*diphenylphosphinoyldecan*-4-*ol* **8b**.—In the same way, butyllithium (1.3 cm^3 of a 1.6 mol dm^{-3} solution in hexane), the phosphine oxide **7** (710 mg), and heptanal (217 mg) in THF (1 cm^3) gave the crude alcohol **8b** (a 1:1 mixture of diastereoisomers from the ^{13}C NMR spectrum) (852 mg, 92%) as a waxy solid; $\delta_H(CDCl_3)$ 8.0–7.2 (10 H, m, Ph_2PO), 3.8–3.2 (3 H, m, CH_2OSi and C*H*OH), 3.0–2.6 (1 H, m, CHP), 2.2–0.9 (13 H, m, methylene envelope and OH), 0.9 (9 H, s, Bu^t), 0.85 (3 H, t, *J* 7, *Me*CH_2), 0.0 and −0.05 (6 H, two s, $SiMe_2$); $\delta_C(CDCl_3)$ 70.1 and 70.0 (CHOH), 60.18 and 60.2 (CHOSi), 40.1 and 37.0 (PCH, d, J_{CP} 70).

4-tert-*Butyldimethylsilyloxy*-2-*diphenylphosphinoyl*-1-*phenylbutan*-1-*ol* **8c**.—In the same way, butyllithium, the phosphine oxide **7** (520 mg), and benzaldehyde (220 mg) gave the crude alcohol **8c** (a 1:1 mixture of diastereoisomers by ^{13}C NMR spectroscopy) (634 mg, 95%) as a waxy solid; $\delta_H(CDCl_3)$ 8.3–7.2 (15 H, m, Ph_2PO and Ph), 5.3–4.9 (1 H, m, C*H*OH), 3.7–3.5 (2 H, m, CH_2OSi), 3.0–2.6 (1 H, m, CHP), 2.2–1.7 (2 H, m, $CHCH_2CH_2$), 1.9 (1 H, br s, OH), 0.9 (9 H, s, Bu^t), 0.0 and −0.05 (6 H, two s, $SiMe_2$); $\delta_C(CDCl_3)$ 70.4 and 70.1 (CHOH), 60.2 (CHOSi), 40.1 and 37.0 (CHP, two d, J_{CP} 68).

Synthesis of Hydroxyalkyldiphenylphosphine Oxides **13**.—The triphenylphosphoniocarboxylic acids **10** were prepared[16,17] from the lactones **9** and Ph_3P·HBr. The phosphonium salts were hydrolysed to the phosphine oxides **11** by refluxing in excess 30% NaOH for 30 min, distillation of benzene, acidification with conc. HCl, and washing with water and then ether.[5]

4-*Diphenylphosphinoylbutanoic acid* **11a** (*n* = 3). The phosphonium salt **10** (*n* = 3) (8.03 g, 18.7 mmol) gave the phosphine oxide (5.21 g, 97%); R_f (EtOAc–MeOH:0.88 ammonia, 5:1:1) 0.15, m.p. 160.5–161.5 °C (from EtOH–Et_2O); ν_{max}/cm^{-1} 3000–2500br (acid-OH) and 1725 (C=O); $\delta_H(CDCl_3)$ 8.0–7.25 (10 H, m, Ph_2PO), 2.49 (2 H, t, *J* 6, CH_2CO_2H) and 2.2–1.7 (4 H, m, remaining CH_2s).

5-*Diphenylphosphinoylpentanoic acid* **11b** (*n* = 4). The phosphonium salt **10** (*n* = 4) (4.48 g, 10.1 mmol) gave the phosphine oxide (2.99 g, 98%); R_f (EtOAc–MeOH:88 ammonia, 5:1:1) 0.11; *m/z* 302 (M^+), 225 (M − Ph) and 201 (Ph_2PO^+); ν_{max}/cm^{-1} 3000–2500br (acid-OH) and 1753 (C=O); $\delta_H(CDCl_3)$ 7.9–7.3 (10 H, m, Ph_2PO), 2.13 (2 H, t, *J* 6, CH_2CO_2H) and 1.9–1.3 (6 H, m, remaining CH_2s).

6-*Diphenylphosphinoylhexanoic acid* **11c** (n = 5). The phosphonium salt **10** (n = 5) gave the acid (9.4 g, 90%) as plates, m.p. 135–137 °C (from EtOAc–acetone) (Found: C, 68.0; H, 6.8; P, 9.65; M^+, 316.1234. $C_{18}H_{21}O_3P$ requires C, 68.3; H, 6.8; P, 9.8%; M, 316.1228); R_f (EtOAc–AcOH, 92:8) 0.45; ν_{max}/cm^{-1} 2800–2500 (OH), 1715 (C=O), 1440 (P–Ph) and 1160 (P=O); $\delta_H(CDCl_3)$ 10.65 (1 H, br s, CO_2H), 7.85–7.1 (10 H, m, Ph_2PO), 2.2 (4 H, m, PCH_2 and CH_2CO) and 1.5 [6 H, m, $(CH_2)_3$]; m/z 316 (4%, M^+), 257 (75), 215 (100, Ph_2POCH_2) and 201 (71, Ph_2PO).

Esterification of acids **11**. The acid **11** was refluxed overnight in alumina-dried methanol to which a few drops of conc. H_2SO_4 and some 4 Å molecular sieves had been added. The mixture was filtered and methanol removed under reduced pressure. The residue was dissolved in EtOAc, and washed with sodium hydrogen carbonate solution, water, and brine. The organic layer was dried ($MgSO_4$), the solvent removed under reduced pressure, and the product dried *in vacuo* to give:

Methyl 4-*diphenylphosphinoylbutanoate* **12a** (n = 3). The acid **11** (n = 3) (4.94 g, 16.4 mmol) gave the methyl ester (4.24 g, 82%), m.p. 108–109 °C (from EtOAc–40–60 light petroleum); R_f (5% MeOH in EtOAc) 0.24; ν_{max}/cm^{-1} 1730 (C=O); $\delta_H(CDCl_3)$ 8.0–7.4 (10 H, m, Ph_2PO), 3.63 (3 H, s, OMe), 2.46 (2 H, t, J 7, CH_2CO_2Me) and 2.2–1.8 (4 H, m, remaining CH_2s); m/z 302 (M^+), 271 (M − OMe) and 201 (Ph_2PO^+).

Methyl 5-*diphenylphosphinoylpentanoate* **12b** (n = 4). The acid **11** (n = 4) (3.61 g, 12.0 mmol) gave the methyl ester, as an oil (3.35 g, 89%); R_f (EtOAc–MeOH, 15:1) 0.38; ν_{max}/cm^{-1} 1735 (C=O); $\delta_H(CDCl_3$ 8.0–7.2 (10 H, m, Ph_2PO), 3.55 (3 H, s, OMe), 2.18 (2 H, t, J 6, CH_2CO_2Me) and 1.9–1.4 (6 H, m, remaining CH_2s).

Methyl 6-*diphenylphosphinoylhexanoate* **12c** (n = 5). The acid (5 g) in acidic MeOH gave the *ester* (5.0 g, 96%) as needles, m.p. 69–71 °C (from EtOAc–Et_2O) (Found: C, 68.9; H, 6.8; P, 9.15%; M^+, 330.1393. $C_{19}H_{23}O_3P$ requires C, 68.9; H, 7.05; P, 9.4%; M, 330.1385); R_f (acetone) 0.5; ν_{max}/cm^{-1} 1725 (ester), 1440 (P–Ph) and 1180 (P=O); $\delta_H(CDCl_3)$ 7.9–7.05 (10 H, m, Ph_2PO), 3.6 (3 H, s, OMe), 2.45–1.95 (4 H, m, PCH_2 and CH_2CO) and 1.8–1.25 [6 H, m, $(CH_2)_3$]; m/z 330 (8%, M^+), 257 (90), 216 (80), 215 (100, Ph_2POCH_2) and 201 (Ph_2PO).

Reduction of the esters **12** *to the alcohols* **13**. A dry ethereal solution of the ester was added dropwise to a stirred solution of one equiv. of lithium aluminium hydride in dry ether. After about 4 h, when all the ester had reacted (TLC), water was added cautiously, the layers were separated, and the aqueous layer extracted with ethyl acetate. The combined organic extracts were washed with brine and dried ($MgSO_4$). The solvent was removed under reduced pressure and the product dried *in vacuo*.

4-*Diphenylphosphinoylbutan*-1-*ol* **13a** (n = 3). The ester **12** (n = 3) (3.70 g, 12.2 mmol) gave the alcohol (2.42 g, 72%) as an oil; R_f (EtOAc–MeOH–0.88 ammonia, 5:1:1) 0.51; $\delta_H(CDCl_3)$ 7.9–7.2 (10 H, m, Ph_2PO), 3.54 (2 H, t, J 6, CH_2OH) and 2.5–1.5 (6 H, m, remaining CH_2s).

5-*Diphenylphosphinoylpentan*-1-*ol* **13b** (n = 4). The ester **12** (n = 4) (4.03 g, 12.8 mmol) gave the alcohol (2.87 g, 78%), m.p. 90–91 °C (from EtOAc–light petroleum, b.p. 40–60 °C); R_f (EtOAc–MeOH–0.88 ammonia, 5:1:1) 0.56; $\delta_H(CDCl_3)$ 7.9–7.3 (10 H, m, Ph_2PO) and 2.5–1.4 (8 H, m, other CH_2s).

6-*Diphenylphosphinoylhexan*-1-*ol* **13c** (n = 5). Reduction of the acid (5 g) with lithium aluminium hydride gave 75% and reduction of the methyl ester (2.0 g) with lithium borohydride in THF gave 94% of the alcohol, m.p. 70–72 °C (from EtOAc–light petroleum, b.p. 40–60 °C) (lit.,[19] 43–45 °C) (Found: C, 71.2; H, 7.7; P, 10.55%; M^+, 302.1454. Calc. for $C_{18}H_{23}O_2P$: C, 71.5; H, 7.7; P, 10.25%; M, 302.1436); R_f (acetone) 0.4; ν_{max}/cm^{-1} 3270 (OH), 1445 (P–Ph) and 1165 (P=O); $\delta_H(CDCl_3)$ 7.85–7.3 (10 H, m, Ph_2PO), 3.5 (2 H, t, J 6, CH_2CH_2OH), 3.3 (1 H, s, OH), 2.4–2.05 (2 H, m, PCH_2) and 1.8–1.2 [8 H, m, $(CH_2)_4$]; m/z 302 (3%, M^+), 215 (100, Ph_2POCH_2), 202 (58, Ph_2POH) and 201 (53, Ph_2PO).

1-(6-tert-*Butyldimethylsilyloxyhexyl*)*diphenylphosphine Oxide* **14**.—The alcohol **13c** (3.5 g), *tert*-butyldimethylsilyl chloride (2.1 g) and imidazole (2.0 g) in DMF (15 cm^3) gave the *silyl ether* (4.4 g, 92%) as an oil; R_f (acetone) 0.6; ν_{max}(film)/cm^{-1} 1440 (P–Ph), 1250 (Si–C), 1190 (P=O), 1105 (Si–O) and 840 (Si–C); $\delta_H(CDCl_3)$ 7.9–7.4 (10 H, m, Ph_2PO), 3.55 (2 H, t, J 6, CH_2CH_2OSi), 2.45–2.0 (2 H, m, PCH_2), 1.7–1.25 [8 H, m, $(CH_2)_4$], 0.9 (9 H, s, Bu^t) and 0.0 (6 H, s, $SiMe_2$); m/z 416 (3%, M^+), 359 (100, M − Bu^t) and 201 (15, Ph_2PO).

6-*Diphenylphosphinoylnonane*-1,7-*diol*.—Butyllithium (5.7 cm^3, 1.5 mol dm^{-3} in hexane) was added to the phosphine oxide **13c** (1.3 g) in THF (40 cm^3) at 0 °C. After 30 min, the solution was cooled to −78 °C and propanal (250 mg) added dropwise. After 4 h, addition of water (25 cm^3), removal of THF, addition of brine (15 cm^3) and extraction with dichloromethane gave a mixture of diastereoisomers of the *diol* (1.1 g, 73%) as needles, m.p. 120–137 °C (from EtOAc–light petroleum, b.p. 40–60 °C) (Found: C, 69.7; H, 8.1; P, 8.6%; M^+, 360.1841. $C_{21}H_{29}O_3P$ requires C, 69.9; H, 8.15; P, 8.6; M, 360.1854); R_f (acetone) 0.5; ν_{max}/cm^{-1} 3450 and 3300 (OH), 1440 (P–Ph) and 1170 (P=O); $\delta_H(CDCl_3)$ 8.0–7.25 (10 H, m, Ph_2PO), 3.9 (1 H, m, $CHOH$), 3.45 (2 H, 2 t, J 6, CH_2OH), 3.2 (1 H, br s, OH), 2.45 (1 H, m, CHP), 1.8–1.0 (10 H, m, CH_2s) and 0.85 (3 H, t, J 7, Me); m/z 360 (1%, M^+), 331 (39), 229 (50), 202 (100) and 201 (61). Elimination with sodium hydride and bulb-to-bulb distillation gave a mixture of *E*- and *Z*-alkenes **16** (81%) by NMR, GLC and IR.

9-tert-*Butyldimethylsilyloxy*-4-*diphenylphosphinoylnonan*-3-*ol* **15**.—In the usual way,[5] butyllithium (7.0 cm^3, 1.5 mol dm^{-3} in hexane), the phosphine oxide **14** (4.4 g), and propanal (614 mg) gave a crystalline mixture of diastereoisomers, separated by column chromatography on silica, eluting with EtOAc. The (3RS,4SR)-*alcohol* (*erythro*-**15**) (2.73 g, 55%) had m.p. 119–120 °C (from ether–hexane) (Found: C, 68.4; H, 8.95; P, 6.35. $C_{27}H_{43}O_3PSi$ requires C, 68.3; H, 9.15; P, 6.55%); R_f 0.5; ν_{max}/cm^{-1} 3370 (OH), 1440 (P–Ph), 1260 (Si–C), 1170 (P=O), 1110 (Si–O) and 840 (Si–C); $\delta_H(CDCl_3)$ 8.0–7.4 (10 H, m, Ph_2PO), 4.0 (1 H, m, $CHOH$), 3.8 (1 H, s, OH), 3.5 (2 H, m, CH_2OSi), 2.5–2.2 (1 H, m, CHP), 1.7–1.1 [10 H, m, $(CH_2)_5$], 0.95 (12 H, s and t, Bu^t and CH_2Me) and 0.05 (6 H, s, $SiMe_2$); m/z 417 (100%, M − Bu^t), 359 (37), 202 (58, Ph_2POH) and 201 (61, Ph_2PO). The (3RS,4RS)-*alcohol* (*threo*-**15**) (1.52 g, 30%) had m.p. 150–151 °C (from ether–hexane) (Found: C, 68.1; H, 9.0; P, 6.8. $C_{27}H_{43}O_3PSi$ requires C, 68.3; H, 9.15; P, 6.55%); R_f 0.4; ν_{max}/cm^{-1} 3350 (OH), 1440 (P–Ph), 1255 (Si–C), 1160 (P=O), 1100 (Si–C) and 830 (Si–C); $\delta_H(CDCl_3)$ 7.95–7.35 (10 H, m, Ph_2PO), 3.9 (1 H, m, $CHOH$), 3.7 (1 H, br s, OH), 3.45 (2 H, t, J 6, CH_2OSi), 2.4 (1 H, m, CHP), 1.6–1.1 [10 H, m, $(CH_2)_5$], 0.85 (12 H, s and t, Bu^t and CH_2Me) and 0.0 (6 H, s, $SiMe_2$); m/z 417 (98%, M − Bu^t), 359 (35), 202 (83, Ph_2POH) and 201 (100, Ph_2PO).

Z-Non-6-*en*-1-*ol* (**Z-16**) *by Deprotection and Elimination from* (3RS,4SR)-**15**.—Tetrabutylammonium fluoride (2.2 cm^3; 5 mol dm^{-3} in THF) was added by syringe to (3*RS*,4*SR*)-**15** (420 mg) in dry THF (5 cm^3) at 25 °C. After 2 h, the solvent was removed under reduced pressure, brine was added to the residue, and the mixture extracted with dichloromethane (3 × 20 cm^3). The organic extracts were dried ($MgSO_4$) and evaporated to give the solid diol (319 mg) which was dissolved in DMF (20 cm^3) and sodium hydride (53 mg, 80% dispersion in oil) was added. The solution was kept at 50 °C for 30 min. The mixture was cooled and water (25 cm^3) added to dissolve the precipitate. The solution was diluted with brine (15 cm^3) and extracted with

ether (3 × 40 cm^3). The organic extracts were washed with water (3 × 40 cm^3), dried ($MgSO_4$), and the solvent was removed under reduced pressure to give an oil. Bulb-to-bulb distillation (Kugelrohr) gave *Z*-non-6-en-1-ol **Z-16** (118 mg, 94%), previously made by a Wittig reaction as the major component of a mixture,[7,19] as a colourless liquid (118 mg, 94%); R_f 0.7; ν_{max}(film)/cm^{-1} 3340 (OH), 1050 (C–O) and 700 (*cis* CH=CH); δ_H(CCl_4) 5.2 (2 H, m, CH=CH), 3.4 (2 H, t, *J* 5, CH_2OH), 2.25 (1 H, s, OH), 1.9 (4 H, m, CH_2CH=$CHCH_2$), 1.25 [6 H, m, $(CH_2)_3$] and 0.85 (3 H, t, *J* 6, CH_2Me). GLC analysis showed *ca.* 5% of the *E*-isomer.

E-*Non*-6-*en*-1-*ol* (**E-16**) *by Deprotection and Elimination from* (3RS,4RS)-**15**.—In the same way, *threo*-**15** (140 mg) gave *E*-**16**[7] (41 mg, 98%).

11-tert-*Butyldiphenylsiloxyundecyldiphenylphosphine Oxide*.—11-Hydroxyundecyltriphenylphosphonium bromide[20] (12.18 g, 23.7 mmol) was refluxed in 30% NaOH (50 cm^3) for 30 min. Benzene was distilled out and the reaction cooled and neutralised cautiously with conc. HCl. Extraction with ethyl acetate, washing with water and drying ($MgSO_4$) gave impure 11-diphenylphosphinoylundecan-1-ol **13** (*n* = 10) (8.75 g oil, 99%) on removal of the solvent under reduced pressure. The crude alcohol (4.09 g, 11 mmol), imidazole (1.64 g, 2.2 equiv.) and *tert*-butyldiphenylsilyl chloride (4.53 g, 1.5 equiv.) were combined and the crude material was applied to a column [Merck 9385 silica gel, eluting with (i) EtOAc–light petroleum (b.p. 40–60 °C), 1:1 (1000 cm^3), (ii) EtOAc–light petroleum (b.p. 40–60 °C), 2:1 (500 cm^3), and (iii) EtOAc (1000 cm^3)]. The fractions containing the silyl ether were combined and the solvent removed under reduced pressure. Drying *in vacuo* gave an oil (6.32 g, 94%); R_f [EtOAc–light petroleum (b.p. 40–60 °C), 2:1] 0.42; δ_H($CDCl_3$) 8.0–7.1 (20 H, m, Ph_2PO and Ph_2Si), 3.62 (2 H, t, *J* 6, CH_2OSi), 2.21 (3 H, s, MeCO), 1.9–1.2 (20 H, m, remaining CH_2s) and 1.2 (9 H, s, Me_3CSi).

General Methods for the Synthesis of the Keto Alcohols **21** (R^1 = H, R^2 = Me) *and the Silyl Ethers* **21** (R^1 = $SiPh_2Bu^t$, R^2 = Me).—The alcohols described in Table 2a were prepared by known methods and silylated as follows: the keto alcohol and imidazole (2.2 equiv.) were dissolved in dry DMF. *tert*-Butyldiphenylsilyl chloride (1.1 equiv.) was added under nitrogen and the mixture was stirred overnight at 40 °C, quenched with brine, and extracted with ethyl acetate. The combined organic fraction were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The product was recrystallised from ethyl acetate–light petroleum (b.p. 40–60 °C) and dried *in vacuo*. In this way were prepared the following compounds identified by IR and NMR spectra:

5-tert-*Butyldiphenylsiloxy*-3-*diphenylphosphinoylpentan*-2-*one*. 3-Diphenylphosphinoyl-1-hydroxypentan-2-one (0.48 g, 1.59 mmol) gave the silyl ether (0.55 g, 64%), m.p. 133–134 °C [from EtOAc–light petroleum (b.p. 40–60 °C]; R_f [EtOAc–light petroleum (40–60 °C), 2:1] 0.48; ν_{max}/cm^{-1} 1705 (C=O) and 1100 (Si–C stretch); δ_H($CDCl_3$) 8.0–7.3 (20 H, m, Ph_2PO and Ph_2Si), 4.3 (1 H, dd, J_{PH} 13.3, J_{HH} 10.6, J_{HH} 2.7, Ph_2POCH), 3.57 (2 H, ABX_2 system, CH_2OSi), 2.5–1.5 (2 H, m, remaining CH_2), 2.20 (3 H, s, MeCO) and 1.05 (9 H, s, MeCSi).

6-tert-*Butyldiphenylsiloxy*-3-*diphenylphosphinoylhexan*-2-*one*. 3-Diphenylphosphinoyl-6-hydroxyhexan-2-one (0.257 g, 0.63 mmol) gave the silyl ether (0.33 g, 73%), m.p. 110.5–111.5 °C [from EtOAc–light petroleum (b.p. 40–60 °C)]; ν_{max}/cm^{-1} 1705 (C=O); δ_H($CDCl_3$) 8.0–7.25 (20 H, m, Ph_2PO and Ph_2Si), 3.57 (2 H, t, *J* 6, CH_2OSi obscures signal due to Ph_2POCH), 2.18 (3 H, s, MeCO), 1.95–1.25 (4 H, m, remaining CH_2s) and 0.97 (9 H, s, Me_3CSi).

General Method for the Borohydride Reduction of Keto Alcohols **21** (R^1 = H, R^2 = Me) *and the Silyl Ethers* **21** (R^1 = $SiPh_2Bu^t$, R^2 = Me) (*Table 2a*).—Ketone (*ca.* 100 mg) was dissolved in alumina-dried methanol. The solution was cooled with stirring to 0 °C and $NaBH_4$ (1 equiv.) added in one portion. The reaction was monitored by TLC; if starting material had not disappeared completely after 2 h, more borohydride was added. On completion, the reaction was quenched with NH_4Cl solution. The mixture was acidified (dil. HCl) and extracted with EtOAc. The extracts were dried ($MgSO_4$) and solvent was removed under reduced pressure, then *in vacuo* to give the reduced material in essentially quantitative yield. The alcohols were generally characterised only by NMR and the ratio of diastereoisomers measured by integration.

General Procedure for Acylation of Phosphine Oxides with Lactones.—Butyllithium (1.5 mol dm^{-3} solution in hexane) was added dropwise to a stirred solution of ethyldiphenylphosphine oxide in dry THF (*ca.* 30 cm^3 g^{-1}) under nitrogen at 0 °C. After 20 min the red solution was cooled to −78 °C (acetone–dry ice) and the lactone added dropwise at such a rate that the solution temperature was maintained at −78 °C. The pale yellow solution was quenched at −78 °C by the addition of saturated aqueous ammonium chloride. The mixture was allowed to warm to room temperature and then most of the THF was removed under reduced pressure. Water was added and the mixture was extracted with dichloromethane (3 × 25 cm^3). The combined extracts were washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by flash column chromatography[18] on silica gel eluting with dichloromethane–methanol (10:1) to give the ketone.

2-*Diphenylphosphinoyl*-5-*hydroxypentan*-3-*one* **24a**. Ethyldiphenylphosphine oxide (5.00 g, 0.022 mol) in dry THF (150 cm^3), butyllithium (15.7 cm^3 of a 1.5 mol dm^{-3} solution in hexane), and propiolactone (1.59 g, 0.022 mol) gave the *ketone* **24a** (R = Me, *n* = 2) (1.92 g, 29%). The 3,5-dinitrobenzoate was obtained in quantitative yield upon treatment with 3,5-dinitrobenzoyl chloride (1.1 mol equiv.) and DMAP (1.1 mol equiv.) in dichloromethane, flash column chromatography on silica gel eluting with EtOAc, and recrystallisation from EtOAc–light petroleum (b.p. 30–40 °C) as needles, m.p. 126–127 °C; R_f (CH_2Cl_2–MeOH, 10:1) 0.54; ν_{max}/cm^{-1} 1728 (C=O), 1540 (N=O) and 1160 (P=O); δ_H($CDCl_3$) 9.20 (1 H, t, J_{HH} 2, PhCO), 9.05 (2 H, d, J_{HH} 2, PhCO), 7.35–7.92 (10 H, m, Ph_2PO), 4.62 (2 H, t, J_{HH} 6, CH_2OCO), 3.75 (1 H, dq, J_{HH} 7, J_{PH} 15, PC*H*Me), 3.20 (2 H, t, J_{HH} 6, $COCH_2$) and 1.42 (3 H, dd, *J* 7 and 15, PCH*Me*) (Found: $M^+ - C_7H_4N_2O_6$, 284.079. $C_{24}H_{21}N_2O_8P$ requires $M - C_7H_4N_2O_6$, 284.2956); *m/z* 284 (30% M − $C_7H_4N_2O_6$) and 201 (100, Ph_2PO).

2-*Diphenylphosphinoyl*-6-*hydroxyhexan*-3-*one* **24b**. Ethyldiphenylphosphine oxide (5.0 g, 0.022 mol) in dry THF (150 cm^3), butyllithium (1.57 cm^3 of a 1.5 mol dm^{-3} solution in hexane) and γ-butyrolactone gave the *keto alcohol* **24b** (R = Me, *n* = 3) (4.53 g, 66%). 3,5-Dinitrobenzoyl chloride and DMAP in dichloromethane as above gave the 3,5-*dinitrobenzoate* as needles, m.p. 78–79 °C; R_f (CH_2Cl_2–MeOH, 10:1) 0.53; ν_{max}/cm^{-1} 1715 (C=O), 1545 (N=O) and 1160 (P=O); δ_H($CDCl_3$) 9.03–9.23 (3 H, m, PhCO), 7.38–7.98 (10 H, m, Ph_2PO), 4.29 (2 H, t, J_{HH} 6, CH_2OCO), 3.70 (1 H, dq, J_{HH} 7, J_{PH} 15, PC*H*Me), 2.85 (2 H, t, *J* 6, $COCH_2$), 1.74–2.20 (2 H, m, CH_2) and 1.39 (3 H, dd, *J* 7 and 15, PCH*Me*) (Found: M^+, 510.1156. $C_{25}H_{23}N_2O_8P$ requires *M*, 510.4414); *m/z* 510 (3%, M^+), 298 (28, M − $C_7H_4N_2O_6$) and 201 (100, Ph_2PO).

2-*Diphenylphosphinoyl*-7-*hydroxyheptan*-3-*one* **24d**. Ethyl diphenylphosphine oxide (5.00 g, 0.022 mol), butyllithium (15.7 cm^3 of a 1.5 mol dm^{-3} solution in hexane), and δ-valerolactone

(2.17 g, 0.022 mol) gave the *ketone* **24d** (R = Me, *n* = 4) (4.12 g, 57%). The 3,5-dinitrobenzoate was needles, m.p. 130–131.5 °C; R_f (CH_2Cl_2–MeOH, 10:1) 0.55; ν_{max}/cm^{-1} 1715 (C=O), 1540 (N=O) and 1170 (P=O); δ_H($CDCl_3$) 9.05–9.25 (3 H, m, PhCO), 7.38–7.97 (10 H, m, Ph_2PO), 4.34 (2 H, t, J_{HH} 6, CH_2OCO), 3.67 (1 H, dq, J_{HH} 7, J_{PH} 16, PC*H*Me), 2.72 (2 H, t, *J* 6, $COCH_2$) and 1.18–1.77 [7 H, m, $(CH_2)_2$ and PCH*Me*] (Found: C, 59.3; H, 4.9; N, 5.3%. $C_{26}H_{25}N_2O_8P$ requires C, 59.5; H, 4.8; N, 5.3%); *m*/*z* 524 (M^+), 312 (M − $C_7H_4N_2O_6$) and 201 (100%, Ph_2PO).

2-*Diphenylphosphinoyl*-8-*hydroxyoctan*-3-*one* **24f** (R = Me, *n* = 5). Ethyldiphenyl phosphine oxide (5.01 g, 0.022 mol), butyllithium (15.7 cm^3 of a 1.5 mol dm^{-3} solution in hexane), and ε-caprolactone (2.48 g, 0.022 mol) gave after recrystallisation from EtOAc–light petroleum (b.p. 30–40 °C) the *ketone* **24f** (R = Me, *n* = 5) as needles (4.55 g, 61%), m.p. 58–59 °C (lit.,[21] oil); R_f (CH_2Cl_2–MeOH, 10:1) 0.18 (Found: M^+, 344.1546. $C_{20}H_{25}O_3P$ requires *M*, 344.392); *m*/*z* 344 (8%, M^+), 326 (6, M − H_2O) and 201 (100, Ph_2PO). Other spectroscopic data were identical to those described in the literature.[21] The 3,5-dinitrobenzate had m.p. 101–102 °C; R_f (CH_2Cl_2–MeOH, 10:1) 0.5; ν_{max}/cm^{-1} 1720 (C=O), 1540 (N=O) and 1170 (P=O); δ_H($CDCl_3$), 9.05–9.25 (3 H, m, PhCO), 7.35–7.95 (10 H, m, Ph_2PO), 4.35 (2 H, t, J_{HH} CH_2OCO), 3.65 (1 H, dq, J_{HH} 7, J_{PH} 16, PC*H*Me), 2.64 (2 H, t, *J* 6, $COCH_2$) and 1.10–1.95 [9 H, m, $(CH_2)_3$ and PCH*Me*]; *m*/*z* 538 (M^+) and 201 (100%, Ph_2PO).

2-*Diphenylphosphinoyl*-17-*hydroxyheptadecan*-3-*one* **24i**. Ethyldiphenylphosphine oxide (1.00 g, 4.52 mmol), butyllithium (3.1 cm^3 of a 1.5 mol dm^{-3} solution in hexane) and a solution of cyclopentadecanolide (1.06 g, 4.52 mmol) in dry THF gave the *ketone* **24** (R = Me, *n* = 14) (1.0 g, 49%) as needles, m.p. 61–62 °C; R_F(CH_2Cl_2–MeOH, 10:1) 0.24 (Found: C, 74.1; H, 9.15. $C_{29}H_{43}O_3P$ requires C, 74.0; H, 9.2%); ν_{max}/cm^{-1} 3470 (OH), 1700 (C=O) and 1180 (P=O); δ_H($CDCl_3$) 7.39–7.90 (10 H, m, Ph_2PO), 3.63 (3 H, m, C*H*Me and C*H*$_2$OH), 2.51 (2 H, t, J_{HH} 6, $COCH_2$), 1.72 (1 H, br s, OH) and 0.93–1.72 [27 H, m, $(CH_2)_{12}$ and PCH*Me*]; *m*/*z* 470 (M^+), 452 (M − H_2O) and 201 (100%, Ph_2PO).

Preparation of the Silyl Ethers **26**.—A solution of the keto alcohol **24** (R = Me) in dry THF (*ca.* 10 cm^3 g^{-1}) was stirred at 40 °C under nitrogen with imidazole (2.2 mol equiv.) and *tert*-butylchlorodiphenylsilane (1.1 mol equiv.). The mixture was poured into water (25 cm^3) and extracted with Et_2O (3 × 15 cm^3). The combined extracts were washed with water, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with EtOAc. In this way the following silyl ethers were prepared:

5-tert-*Butyldiphenylsilyloxy*-2-*diphenylphosphinoylpentan*-3-*one* **26a**. 2-Diphenylphosphinoyl-5-hydroxypentan-3-one **24a** (1.00 g, 3.3 mmol), imidazole (0.49 g) and *tert*-butylchlorodiphenylsilane (1.00 g, 3.6 mmol) and 24 h gave, upon recrystallisation from EtOAc–light petroleum (b.p. 30–40 °C) the *silyl ether* (0.54 g, 30%) as needles, m.p. 113–114 °C; R_f (EtOAc) 0.50; ν_{max}/cm^{-1} 1700 (C=O), 1170 (P=O) and 1100 (Si–O) (Found: C, 73.1; H, 7.05; P, 5.7. $C_{33}H_{37}O_3PSi$ requires C, 73.3; H, 6.9; P, 5.7%); δ_H($CDCl_3$) 7.32–7.85 (20 H, m, Ph_2PO and Ph_2Si), 3.69–3.88 (3 H, m, PC*H*Me and CH_2OSi), 2.76 (2 H, m, $COCH_2$), 1.39 (3 H, dd, J_{HH} 7, J_{PH} 16, PCH*Me*) and 0.98 (9 H, s, Bu^t); *m*/*z* 483 (M − C_4H_9) and 201 (100%, Ph_2PO).

6-tert-*Butyldiphenylsilyloxy*-2-*diphenylphosphinoylhexan*-3-*one* **26b**. 2-Diphenylphosphinoyl-6-hydroxyhexan-3-one **24b** (1.09 g, 3.44 mmol), imidazole (0.51 g) and *tert*-butylchlorodiphenylsilane (1.03 g, 3.78 mmol) after 12 h and recrystallisation from EtOAc–light petroleum (b.p. 30–40 °C) gave the *silyl ether* (0.98 g, 51%) as needles, m.p. 108–109 °C; R_f (EtOAc) 0.5 (Found: C, 73.9; H, 7.1; P, 5.7. $C_{34}H_{39}O_3PSi$ requires C, 73.7; H, 7.1; P, 5.6%); ν_{max}/cm^{-1} 1700 (C=O), 1170 (P=O) and 1095 (Si–O); δ_H($CDCl_3$) 8.32–8.85 (20 H, m, Ph_2PO and Ph_2Si), 3.67 (1 H, dq, J_{HH} 7, J_{PH} 15, PC*H*Me), 3.51 (2 H, t, J_{HH} 6.5, CH_2OSi), 2.63 (2 H, t, *J* 6.5, $COCH_2$), 1.66 (2 H, m, CH_2), 1.38 (3 H, dd, *J* 7 and 15, PCH*Me*) and 1.01 (9 H, s, Bu^t); *m*/*z* 497 (M − C_4H_9) and 201 (100%, Ph_2PO).

7-tert-*Butyldiphenylsilyloxy*-2-*diphenylphosphinoylheptan*-3-*one* **26d**. 2-Diphenylphosphinoyl-7-hydroxyheptan-3-one **24d** (0.96 g, 2.9 mmol), imidazole (0.44 g) and *tert*-butylchlorodiphenylsilane (0.88 g, 3.2 mmol) after 6 h and recrystallisation from EtOAc–light petroleum (b.p. 30–40 °C) gave the *silyl ether* (0.49 g, 30%) as needles, m.p. 72.5–73.5 °C; R_f (EtOAc) 0.48 (Found: C, 74.1; H, 7.2; P, 5.5%; M^+ − C_4H_9, 511.1902. $C_{35}H_{49}O_3PSi$ requires C, 73.9; H, 7.3; P, 5.4%; M − C_4H_9, 511.655); ν_{max}/cm^{-1} 1705 (C=O), 1175 (P=O) and 1100 (Si–O); δ_H($CDCl_3$) 7.34–7.86 (20 H, m, Ph_2PO and Ph_2Si), 3.64 (1 H, dq, J_{HH} 7.5, J_{PH} 15, PC*H*Me), 3.54 (2 H, t, J_{HH} 6, CH_2OSi), 2.52 (2 H, t, *J* 6, $COCH_2$), 1.27–1.55 [7 H, m, $(CH_2)_2$ and PCH*Me*] and 1.01 (9 H, s, Bu^t); *m*/*z* 511 (100%, M^+ − C_4H_9) and 201 (94, Ph_2PO).

8-tert-*Butyldiphenylsilyloxy*-2-*diphenylphosphinoyloctan*-3-*one* **26f**. 2-Diphenylphosphinoyl-8-hydroxyoctan-3-one **24f** (0.5 g, 1.45 mmol), imidazole (0.22 g) and *tert*-butylchlorodiphenylsilane (0.48 g, 1.74 mmol) after 24 h gave the *silyl ether* (0.65 g, 76%) as an oil; R_f (EtOAc) 0.41; ν_{max}/cm^{-1} 1705 (C=O), 1175 (P=O) and 1100 (Si–O); δ_H($CDCl_3$) 7.33–7.87 (20 H, m, Ph_2PO and Ph_2Si), 3.66 (1 H, dq, J_{HH} 7.5, J_{PH} 15, PC*H*Me), 3.56 (2 H, t, J_{HH} 6, CH_2OSi), 2.51 (2 H, t, *J* 6, $COCH_2$), 1.07–1.52 [9 H, m, $(CH_2)_3$ and PCH*Me*] and 1.01 (9 H, s, Bu^t) (Found: M^+ − C_4H_9, 525.2031. $C_{36}H_{43}O_3PSi$ requires: M − C_4H_9, 525.682); *m*/*z* 525 (100%, M − C_4H_9) and 201 (46, Ph_2PO).

Methyl 11-tert-*Butyldiphenylsilyloxyundecanoate* **28**.—11-Bromoundecanoic acid (5.07 g, 0.019 mol) was refluxed in 30% aqueous sodium hydroxide (50 cm^3) for 48 h. The mixture was cooled and the pH adjusted to 3. The product was filtered and recrystallised from water to yield 11-hydroxyundecanoic acid as needles (3.52 g, 91%), m.p. 64–65 °C (lit.,[22] 64–66 °C); R_f (CH_2Cl_2–MeOH, 10:1) 0.06. The acid (1.5 g, 7.41 mmol) was refluxed in MeOH (20 cm^3) and Me_2SO_4 (2 cm^3) for 5 h. The volume was reduced *in vacuo* and water added to the residue. The pH was adjusted to 7 and the product extracted with EtOAc (3 × 25 cm^3). The extracts were washed with water (25 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was distilled at 8 mmHg to yield, on cooling, methyl 11-hydroxyundecanoate (1.4 g, 87%) as plates, m.p. 27–27.5 °C (lit.,[22] 27–27.5 °C); R_f (CH_2Cl_2–MeOH, 10:1) 0.36. A mixture of the ester (1.16 g, 5.36 mmol), dry DMF (12 cm^3), imidazole (0.80 g, 12 mmol) and *tert*-butylchlorodiphenylsilane (1.62 g, 5.9 mmol) was stirred at 40 °C under nitrogen for 24 h and poured into water (25 cm^3). The product was extracted into Et_2O (3 × 15 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with CH_2Cl_2 to yield the ester **28** as an oil (1.75 g, 72%); R_f (CH_2Cl_2–MeOH, 10:1) 0.78; ν_{max}/cm^{-1} 1745 (C=O) and 1105 (Si–O); δ_H($CDCl_3$) 7.32–7.85 (10 H, m, Ph_2Si), 3.58–3.78 (5 H, m, $SiOCH_2$ and CO_2Me), 2.30 (2 H, t, J_{HH} 7, CH_2CO_2), 1.13–1.79 [16 H, m, $(CH_2)_8$] and 1.05 (9 H, s, Bu^t); *m*/*z* 454 (M − OMe), 397 (M − OMe − Bu^t) and 199 (100%, Ph_2SiO).

13-tert-*Butyldiphenylsilyloxy*-2-*diphenylphosphinoyltridecan*-3-*one* **26h** (*n* = 10).—Butyllithium (2.14 cm^3 of a 1.5 mol dm^{-3} solution in hexane) was added dropwise to a stirred solution of ethyldiphenylphosphine oxide (0.50 g, 2.17 mmol) in dry THF (20 cm^3) under nitrogen at 0 °C. After 20 min the red mixture was cooled to −78 °C and the ester **28** (1.00 g, 2.19 mmol) was added dropwise at such a rate as to maintain the temperature at

−78 °C. The mixture was stirred at −78 °C for 30 min and then warmed slowly to room temperature. The yellow solution was quenched by saturated aqueous ammonium chloride (15 cm^3). The organic layer was separated and the aqueous layer extracted with dichloromethane (3 × 10 cm^3), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with EtOAc to give *ketone* **26h** (1.13 g, 80%); R_f (EtOAc) 0.45; ν_{max}/cm^{-1} 1708 (C=O), 1185 (P=O) and 1105 (Si–O); $\delta_H(CDCl_3)$ 7.31–7.86 (20 H, m, Ph_2PO and Ph_2Si), 3.56–3.70 (3 H, m, CH_2OSi and PC*H*Me), 2.51 (2 H, t, J_{HH} 6, $COCH_2$) and 1.05–1.56 [28 H, m, CHMe, $(CH_2)_8$ and Bu^t] (Found: $M^+ - C_4H_9$, 595.2796. $C_{41}H_{53}O_3PSi$ requires: $M - C_4H_9$, 595.817); *m*/*z* 595 (100%, $M - C_4H_9$) and 201 (34, Ph_2PO).

2-*Diphenylphosphinoyl*-13-*hydroxytridecan*-3-*one* **24h** (R = Me, *n* = 10).—A mixture of the ketone **26h** (0.5 g, 0.77 mmol) and tetrabutylammonium fluoride (0.84 cm^3 of a 1 mol dm^{-3} solution in THF) in dry THF (10 cm^3) under nitrogen was stirred for 48 h, and poured into water (15 cm^3). The organic layer was separated. The aqueous layer was saturated with salt and extracted with dichloromethane (3 × 15 cm^3). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with EtOAc to give the *ketone* **24h** (0.20 g, 62.5%) as an oil; R_f (CH_2Cl_2–MeOH, 10:1) 0.24; ν_{max}/cm^{-1} 3375br (OH), 1708 (C=O) and 1180 (P=O); $\delta_H(CDCl_3)$ 7.42–7.88 (10 H, m, Ph_2O), 3.58–3.73 (3 H, m, CH_2OH and PC*H*Me), 2.53 (2 H, t, J_{HH} 7, $COCH_2$) and 1.02–1.78 [20 H, m, PCH*Me*, $(CH_2)_8$, and OH] (Found: M^+, 414.2300. $C_{25}H_{35}O_3P$ requires *M*, 414.527); *m*/*z* 414 (3%, M^+) and 201 (100, Ph_2PO).

Reduction of the Keto Alcohols **24** *using Sodium Borohydride*.—In all cases an excess of sodium borohydride was used.

*Method A*1. Sodium borohydride (1.1 mol equiv.) was added in one portion to a stirred solution of the ketone in MeOH under nitrogen at 0 °C. The mixture was stirred at 0 °C for 90 min and further sodium borohydride added as required to ensure complete reduction of starting material (by TLC), with the temperature kept at 0 °C. The reaction was quenched at 0 °C by the addition of saturated aqueous ammonium chloride (15 cm^3) and the product extracted into dichloromethane (3 × 5 cm^3). The combined extracts were washed with water (5 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with CH_2Cl_2–MeOH (10:1) to give the dihydroxyalkylphosphine oxides **25** as a mixture of diastereoisomers.

*Method A*2. Method A1 in EtOH as solvent.

Method B. A solution of sodium borohydride in EtOH (*ca.* 0.02 g cm^{-3}) was added dropwise to a stirred solution of the ketone and cerium trichloride (1.1 mol equiv.) in MeOH under nitrogen at −78 °C. The solution was stirred at this temperature until reduction was complete (a few hours), and then quenched at −78 °C by the addition of saturated aqueous ammonium chloride (5 cm^3). The product was extracted into dichloromethane (3 × 5 cm^3) and the combined extracts dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with CH_2Cl_2–MeOH (10:1) to give the dihydroxyalkylphosphine oxide **25** as a mixture of diastereoisomers.

Reduction of 2-*diphenylphosphinoyl*-5-*hydroxypentan*-3-*one* **24a**. The ketone **24a** (0.17 g, 0.75 mmol) gave by method A1 a mixture of threo- and erythro-2-*diphenylphosphinoyl*-5-*hydroxypentan*-3-*ol* **25a** (0.17 g, 100%). Separation of 0.1 g by HPLC and recrystallisation of the more abundant isomer from EtOAc–light petroleum (b.p. 30–40 °C) gave the *threo*-diol **25a** (0.068 g, 68%) as needles, m.p. 139.5–140 °C; R_f (CH_2Cl_2–MeOH, 10:1) 0.08; ν_{max}/cm^{-1} 3250br (OH) and 1160 (P=O); $\delta_H(CDCl_3)$ 7.42–7.85 (10 H, m, Ph_2PO), 4.13 (1 H, m, C*H*OH), 3.81 (2 H, m, CH_2OH), 2.76 (1 H, m, PC*H*Me), 1.64–1.92 (2 H, m, CH_2) and 1.02 (3 H, dd, J_{HH} 7.5, J_{PH} 15, PCH*Me*) (Found: M^+, 304.1297. $C_{17}H_{21}O_3P$ requires *M*, 304.327); *m*/*z* 304 (7%, M^+), 286 (3, $M - H_2O$) and 201 (100, Ph_2PO).

Reduction of the ketone **24a** (0.20 g, 0.66 mmol) *via* method B gave 41:59 mixture of *threo*:*erythro* diols **25a** (0.16 g, 79%).

Reduction of 2-*diphenylphosphinoyl*-6-*hydroxyhexane*-3-*one* **24b**. The ketone (0.55 g, 1.74 mmol) gave by method A2 a mixture of diols (0.43 g, 78%). This mixture (0.058 g) gave pure threo-2-*diphenylphosphinoyl*-6-*hydroxyhexan*-3-*ol* (0.042 g, 72%) after HPLC and recrystallisation from EtOAc–light petroleum (b.p. 30–40 °C) as needles; m.p. 137–138 °C; R_f (CH_2Cl_2–MeOH, 10:1) 0.08 (Found: C, 67.7; H, 7.35; P, 9.4. $C_{18}H_{23}O_3P$ requires: C, 67.9; H, 7.3; P, 9.7%); ν_{max}/cm^{-1} 3250br (OH) and 1160 (C=O); $\delta_H(CDCl_3)$ 7.44–7.85 (10 H, m, Ph_2PO), 3.91 (1 H, m, CHOC), 3.61 (2 H, t, J_{HH} 6, CH_2OH), 2.75 (1 H, m, PC*H*Me), 1.44–1.87 [4 H, m, $(CH_2)_2$] and 1.02 (3 H, dd, J_{HH} 7.5, J_{PH} 15, PCH*Me*); *m*/*z* 318 (8%, M^+), 300 (10, $M - H_2O$) and 201 (100, Ph_2PO).

Reduction of the ketone **24b** (0.49 g, 1.55 mmol) using method B gave a 44:56 mixture of *threo*:*erythro* diols **25b** (0.38 g, 77%).

Reduction of 2-*Diphenylphosphinoyl*-7-*hydroxyheptan*-3-*one* **24d**. The ketone (0.55 g, 1.66 mmol) gave by method A a mixture of diols **24d** (0.43 g, 78%). This mixture (0.0516 g) gave pure threo-2-*diphenylphosphinoyl*-7-*hydroxyheptan*-3-*ol* (0.038 g, 74%) after HPLC and recrystallisation from EtOAc–light petroleum (b.p. 30–40 °C) as needles, m.p. 111–112 °C; R_f (CH_2Cl_2–MeOH, 10:1) 0.08; ν_{max}/cm^{-1} 3250br (OH) and 1160 (P=O); $\delta_H(CDCl_3)$ 7.44–7.85 (10 H, m, Ph_2PO), 3.86 (1 H, m, C*H*OH), 3.60 (2 H, t, J_{HH} 6, $3H_2OH$) and 2.69 (1 H, m, PC*H*Me); *m*/*z* 332 (1%, M^+), 314 (15, $M - H_2O$) and 201 (100, Ph_2PO).

Reduction of ketone **24d** (0.50 g, 1.51 mmol) by method B gave the diols **25d** (0.39 g, 77%) as a 48:52 mixture of *threo* and *erythro* isomers.

Reduction of 2-*diphenylphosphinoyl*-8-*hydroxyoctan*-3-*one* **24f**. The ketone (0.13 g, 0.38 mmol) gave by method A1 a mixture of diols **25f** (0.10 g, 76%). HPLC and recrystallisation from EtOAc–light petroleum (b.p. 30–40 °C) gave pure threo-3-*diphenylphosphinoyl*-8-*hydroxyoctan*-3-*ol* (66%) as needles, m.p. 104–105 °C; R_f (CH_2Cl_2–MeOH, 10:1) 0.07; ν_{max}/cm^{-1} 3250br (OH) and 1160 (P=O); $\delta_H(CDCl_3)$ 7.44–7.85 (10 H, m, Ph_2PO), 3.85 (1 H, m, C*H*OH), 3.59 (2 H, t, J_{HH} 6, CH_2OH), 2.68 (1 H, m, PC*H*Me), 1.20–1.62 [8 H, m, $(CH_2)_4$] and 1.01 (3 H, dd, J_{HH} 7.5, J_{PH} 15, PCH*Me*) (Found: $M^+ - H_2O$, 328.1631. $C_{20}H_{27}O_3P$ requires $M - H_2O$, 328.3923); *m*/*z* 328 ($M - H_2O$) and 201 (100%, Ph_2PO).

Reduction of the ketone **24f** (0.53 g, 1.54 mmol) by method B gave diols **25f** (0.41 g, 77%) as a 48.52 mixture of *threo* and *erythro* isomers.

Reduction of 2-*diphenylphosphinoyl*-13-*hydroxytridecan*-3-*one* **24h**. The ketone (0.0297 g, 0.07 mmol) was reduced by method A1 to give a mixture of diols **25h** (0.0253 g, 85%) which were inseparable by HPLC. Integration in the NMR spectrum at $\delta_H(CDCl_3)$ 2.69 (m, *threo* PC*H*Me) and 2.35 (m, *erythro* PC*H*Me) gave the ratio of *threo*:*erythro* isomers as 64:36.

Reduction of 2-*diphenylphosphinoyl*-17-*hydroxyheptadecan*-3-*one* **24i**. Reduction of the ketone (0.089 g, 0.19) by method A1 gave a mixture of diols **25i** (0.08 g, 90%). The composition was determined by integration of the NMR spectrum as 52:48 *threo*:*erythro*.

Reduction of α-*Diphenylphosphinoyl Ketones* **26**.—These siloxyketones were reduced using the same conditions as their

non-silylated precursors **24** to give mixtures of diastereoisomers. These were inseparable by HPLC and the *threo*:*erythro* ratio was measured by integration of two multiplets in the NMR spectrum between $\delta_H(CDCl_3)$ 2.0 and 3.0. The yields and isomer ratios are given in Table 3.

Reduction of 2-*Diphenylphosphinoyl*-8-*hydroxyoctan*-3-*one* **24f** *using Lithium Triethyl Borohydride* ('*Super-Hydride*®').—*Method C*1.—Lithium triethyl borohydride (1.12 cm^3 of a 1 mol dm^{-3} solution in THF) was added to a stirred solution of the ketone (0.128 g, 0.037 mmol) in dry THF (5 cm^3) under nitrogen at −78 °C at such a rate as to maintain the temperature at −78 °C. The mixture was stirred at this temperature for 3 h and quenched by addition of acetone (5 cm^3). A 1:1 mixture of 2 mol dm^{-3} aqueous sodium hydroxide and 28% hydrogen peroxide (5 cm^3) was added at room temperature, and stirring continued for 12 h. The pH was adjusted to 7 by addition of 30% HCl and the mixture extracted with dichloromethane (3 × 10 cm^3). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure. Purification by flash column chromatography on silica gel eluting with CH_2Cl_2–MeOH (10:1) gave the mixture of diols **26f** as an oil (0.100 g, 78%). Separation by HPLC gave the *threo*:*erythro* ratio as 67:33.

*Method C*2. The ketone **24f** (0.124 g, 0.036 mmol) was reduced by the same reagent at 0 °C to give a 55:45 *threo*:*erythro* mixture of diols **25f** (0.100 g, 80%).

6-*Diphenylphosphinoyl*-5-*oxodecan*-2-*ol* **29**.—Butyllithium (24 cm^3 of a 1.5 mol dm^{-3} solution in hexane, 36 mmol) was added dropwise to a stirred solution of diphenylpentylphosphine oxide[5] (10.12 g, 37.2 mmol) in dry THF (100 cm^3) at 0 °C. The solution was cooled to −78 °C and γ-valerolactone (2.3 cm^3, 24.3 mmol) was added dropwise over 15 min. After 30 min, cyclohexanone (1.4 cm^3, 13.5 mmol) was added to quench the red colour. After 15 min, saturated ammonium chloride solution (30 cm^3) was added and the mixture allowed to warm to room temperature. The THF was evaporated under reduced pressure and the aqueous residue was extracted with CH_2Cl_2 (3 × 100 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash column chromatography[18] eluting with EtOAc–hexane to give the *keto alcohol* (6.42 g, 71%) as needles (from EtOAc–hexane), m.p. 100–102 °C (Found: C, 70.6; H, 7.8; P, 8.6; $M^+ - H_2O$, 354.1748. $C_{22}H_{29}O_3P$ requires C, 70.9; H, 7.85; P, 8.3%; *M*, 354.1749); R_f 0.21; ν_{max}/cm^{-1} 3360 (OH), 1700 (C=O), 1435 (Ph–P) and 1160 (P=O); δ_H 8.1–7.3 (10 H, m, Ph_2PO), 4.4 (1 H, m, C*H*OH), 3.6 (1 H, m, CHP), 3.2 (1 H, br s, OH), 3.1–1.0 (10 H, m, remaining CH_2s), 1.1 (3 H, d, *J* 6, MeCO) and 0.75 (3 H, t, *J* 6, *Me*CH_2); *m*/*z* 354 (4%, M − H_2O), 229 (43) and 201 (100, Ph_2PO).

2-*Diphenylphosphinoyl*-6-*hydroxydecan*-3-*one* **32**.—In the same way butyllithium (8.7 cm^3 of a 1.5 mol dm^{-3} solution in hexane), ethyl diphenyl phosphine oxide[5] (2.99 g, 13 mmol), and γ-octanoic lactone (1.88 cm^3, 13 mmol) in THF (50 cm^3) gave, after recrystallisation from EtOAc–hexane, the *keto alcohol* (3.53 g, 73%) as needles, m.p. 85–87 °C (Found: C, 70.9; H, 7.6; P, 8.5; $M^+ - H_2O$, 354.1749. $C_{22}H_{27}O_2P$ requires C, 70.9; H, 7.85; P, 8.3%; *M*, 354.1749); R_f 0.48; ν_{max}/cm^{-1} 3300 (OH), 1700w (C=O), 1590 (Ph), 1440 (Ph–P) and 1120 (C–O). In $CDCl_3$ dehydration occurred to a *ca.* 3:1 mixture of *E* and *Z* exocyclic enol ethers; δ_H 7.8–7.3 (10 H, m, Ph_2PO), 4.27 (0.75 H, quintet, *J* 7, CHO), 4.05 (0.25 H, quintet, *J* 7, CHO), 2.9 (4 H, AA′BB′P m, PC=CCH_2CH_2CO), 2.15–1.0 [6 H, m, $(CH_2)_3$], 1.80 (0.75 H, d, J_{PH} 12, MeCP), 1.60 (2.25 H, dt, J_{PH} 13.3, J_t 1.5, MeCP), 0.91 (2.25 H, t, *J* 6.4, Me) and 0.74 (0.75 H, t, *J* 7, Me); *m*/*z* 354 (33%, M − H_2O), 339 (5), 297 (10), 230 (23, $EtPh_2PO$) and 201 (100, Ph_2PO).

5-*Diphenylphosphinoyl*-1-*hydroxydecan*-4-*one*.—In the same way, hexyl diphenyl phosphine oxide[23] (2.86 g) and butyrolactone (0.86 g) gave the *hydroxy ketone* (2.94 g, 79%), m.p. 92–95 °C (from EtOAc–hexane) (Found: C, 71.1; H, 7.85; P, 8.3. $C_{22}H_{29}O_3P$ requires C, 71.0; H, 7.85; P, 8.3%); R_f (EtOAc) 0.19; ν_{max}/cm^{-1} 3370 (OH), 1705 (C=O), 1440 (P–Ph) and 1165 (P=O); $\delta_H(CDCl_3)$ 8.1–7.3 (10 H, m, Ph_2PO), 3.7 (1 H, ddd, *J* 3, 12 and 14, PCH), 3.43 (2 H, t, *J* 6, CH_2OH), 3.05 (1 H, br s, OH), 2.7 (2 H, t, *J* 6, $COCH_2$), 2.3–0.8 [10 H, m, CH_2CHOH and $(CH_2)_4$] and 0.8 (3 H, m, Me); *m*/*z* 373 (2%, M^+), 354 (2), 29 (28), 216 (87), 215 (100), 202 (98) and 201 (79). Reduction of this ketone with sodium borohydride gave a 1:1 mixture of diastereoisomers of the diol as judged by ^1H NMR spectroscopy.

tert-*Butylsiloxy*-2,5-*dimethyl*-6-*diphenylphosphinoyldecane* **30**.—Sodium borohydride (220 mg, 5.79 mmol) was added to a stirred solution of ketone **29** (1.253 g, 3.37 mmol) in MeOH (10 cm^3) at 0 °C. The solution was stirred for 2 h, saturated ammonium chloride solution (10 cm^3) was added, and MeOH was evaporated under reduced pressure. The aqueous residue was acidified with dilute HCl and extracted with CH_2Cl_2 (3 × 25 cm^3). The organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue, imidazole (1.14 g, 16.8 mmol), and *tert*-butyldimethylsilyl chloride (1.27 g, 8.4 mmol) in dry DMF (30 cm^3) were warmed to 40 °C for 42 h. The solution was cooled, diluted with brine (30 cm^3), and extracted with ether (3 × 50 cm^3). The combined organic extracts were washed with water (3 × 50 cm^3), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was purified by flash chromatography[18] eluting with EtOAc–light petroleum, b.p. 40–60 °C (1:3) to give two sets of fractions. The first to elute was the (5*RS*,6*RS*)-pair of diastereoisomers (*threo*-**30**) (1.79 g, 88%) as an oil (Found: C, 67.5; H, 9.6; P, 4.9. $C_{34}H_{59}O_3PSi_2$ requires C, 67.7; H, 9.85; P, 5.1%); R_f 0.69; ν_{max}/cm^{-1} 1600 (Ph) and 1440 (Ph–P); δ_H 8.0–7.4 (10 H, m, Ph_2PO), 3.7 (2 H, m, 2 × CHOSi), 2.4 (1 H, m, CHP), 2.1–1.0 (10 H, m, remaining CH_2s), 1.1 (3 H, d, *J* 6, MeCO), 0.91–0.77 (21 H, m, 2 × Bu^t and Me), 0.02 (6 H, s, 2 × MeSi), −0.03 (3 H, s, MeSi) and −0.18 (3 H, s, MeSi); *m*/*z* 545 (100%, M − Bu^t), 272 (12, $Ph_2POPent$), 229 (15) and 201 (76, Ph_2PO). The second to elute was the (5*RS*,6*SR*)-pair of diastereoisomers (*erythro*-**30**) (0.24 g, 12%) as an oil; R_f 0.62; ν_{max}/cm^{-1} 1600 (Ph), 1435 (Ph–P) and 1160 (P=O); δ_H 8.0–7.4 (10 H, m, Ph_2PO), 4.2–3.6 (2 H, m, 2 × CHOSi), 2.15 (1 H, m, CHP), 2.0–1.0 (10 H, m, remaining CH_2s), 1.08 (3 H, d, *J* 6, MeCO), 0.86 (9 H, s, Bu^t), 0.85 (9 H, s, Bu^t), 0.0 (9 H, s, 3 × MeSi) and −0.3 (3 H, s, MeSi) [Found: $MH^+ - 2 \times Bu^t$) 489.2418. $C_{26}H_{42}O_3PSi_2$ requires M − C_8H_{17}, 489.2410]; *m*/*z* 489 [7%, MH − (2 × Bu^t)] 488 (8), 473 (15), 431 (55), 272 (40, $Ph_2POPent$), 229 (63) and 201 (100, Ph_2PO).

tert-*Butylsiloxy*-3,6-*dimethyl*-2-*diphenylphosphinoyldecane* **33**.—In the same way, sodium borohydride (150 mg, 3.9 mmol) and the ketone **32** (1.18 g, 3.2 mmol) in MeOH (10 cm^3) at 0 °C for 3 h, followed by *tert*-butyldimethylsilyl chloride (1.20 g, 7.9 mmol) and imidazole (1.08 g, 16 mmol) in dry DMF (40 cm^3) for 47 h gave, after flash chromatography[18] on silica gel eluting with EtOAc–hexane (1:3), two sets of fractions. The first to elute was the (2*RS*,3*RS*)-pair of diastereoisomers (*threo*-**33**) (1.27 g, 66%) as an oil (Found: C, 67.4; H, 9.85; P, 5.1%; M^+ − Me, 587.3452. $C_{33}H_{56}O_3PSi_2$ requires C, 67.7; H, 9.6; P, 6.9%; *M* − Me, 587.3508); R_f 0.74; ν_{max}/cm^{-1} 1440 (Ph–P) and 1170 (P=O); δ_H 7.98–7.37 (10 H, m, Ph_2PO), 4.03 (1 H, m, CHO), 3.6 (1 H, m, CHO), 2.35 (1 H, quintet, *J* 8, CHP), 1.8–1.1 (10 H, m, remaining CH_2s), 1.2 (3 H, dd, J_{HP} 18 and J_{HH} 8, MeCP), 1.0–0.8 (21 H, m, 2 × Bu^t and Me), 0.03 (6 H, s, Me_2Si) and −0.02 (6 H, s, Me_2Si); *m*/*z* 587 (1%, M − Me), 545 (100, M − Bu^t), 230 (9, Ph_2POEt) and 201 (20, Ph_2PO). The second to elute was

the (2*RS*,3*SR*)-pair of diastereoisomers (*erythro*-**33**) (648 mg, 33%) as an oil (Found: C, 68.0; H, 9.6. $C_{34}H_{59}O_3PSi_2$ requires C, 67.7; H, 9.6%); R_f 0.63; ν_{max}/cm^{-1} 1590 (Ph), 1440 (Ph–P) and 1160 (P=O); δ_H 7.86–7.39 (10 H, m, Ph_2PO), 3.60 (2 H, m, 2 × CHO), 2.55 (1 H, m, CHP), 1.8–1.2 (10 H, m, remaining CH_2s), 1.2 (3 H, dd, J_{HP} 16 and J_{HH} 7.3, MeCP), 0.93–0.85 (21 H, m, 2 × Bu^t and Me) and 0.08–0.12 (12 H, m, 4 × MeSi); *m*/*z* 545 (1%, M − Bu^t), 431 (80), 230 (54, Ph_2POEt) and 201 (100, Ph_2PO).

(5RS,6RS)-6-*Diphenylphosphinoyldecane*-2,5-*diol* (threo-**30**; R = H).—Tetrabutylammonium fluoride (TBAF) (11.9 cm^3 of a 1 mol dm^{-3} solution in THF, 11.9 mmol) was added to a stirred solution of the silyl ether (*threo*-**30**) (1.79 g, 2.97 mmol) in dry THF (20 cm^3) at 0 °C. The solution was allowed to warm to room temperature and was stirred for 16 h. The THF was evaporated under reduced pressure, the residue was diluted with brine (30 cm^3) and extracted with EtOAc (3 × 50 cm^3). The combined organic extracts were washed with water (50 cm^3) and brine (50 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Recrystallisation from EtOAc gave the *diol* (758 mg, 68%) as needles, m.p. 167–167.5 °C (Found: C, 70.9; H, 8.35; P, 8.1%; M^+ − OH, 357.1990. $C_{22}H_{31}O_3P$ requires C, 70.6; H, 8.35; P, 8.3%; M − OH, 357.1983); R_f 0.10; ν_{max}/cm^{-1} 3350 (OH), 1590 (Ph), 1440 (Ph–P) and 1155 (P=O); $\delta_H(CDCl_3)$ 7.86–7.69 (4 H, m, Ph_2PO *ortho*-protons), 7.52–7.41 (6 H, m, Ph_2PO *meta* and *para* protons), 3.96 (1 H, m, CHO), 3.68 (1 H, m, CHO), 2.5 (2 H, m, 2 × OH), 2.46 (1 H, m, CHP), 1.69–1.0 (10 H, m, remaining CH_2s), 1.07 (1.5 H, d, *J* 6.2, MeCO), 1.05 (1.5 H, d, *J* 6.1, MeCO) and 0.71 (3 H, t, *J* 6.9, Me); *m*/*z* 357 (1%, M − OH), 341 (1), 301 (63), 272 (38, $Ph_2POPent$), 229 (100, $Ph_2POC_2H_4$), 202 (90, Ph_2POH) and 201 (88, Ph_2PO). The mother liquor was purified by flash chromatography [18] on silica gel eluting with EtOAc–MeOH (9:1) to give additional product (240 mg, total yield 90%).

(5RS,6SR)-6-*Diphenylphosphinoyldecane*-2,5-*diol* (erythro-**30**; R = H).—In the same way, TBAF (1.6 cm^3, 1.6 mmol) and the silyl ether (*erythro*-**30**) (0.24 g, 0.4 mmol) in THF (5 cm^3) for 16 h gave, after flash chromatography [18] on silica gel eluting with EtOAc–MeOH (9:1), the *diol* (130 mg, 87%) as needles (from EtOAc), m.p. 132–133 °C (Found: C, 70.4; H, 8.3; P, 8.0%; MH^+, 375.2067. $C_{22}H_{31}O_3P$ requires C, 70.6; H, 8.35; P, 8.3%; *M*H, 375.2089); R_f 0.08; ν_{max}/cm^{-1} 3370 (OH), 1590 (Ph), 1440 (Ph–P) and 1180 (P=O); δ_H 7.87–7.72 (4 H, m, Ph_2PO *ortho* protons), 7.58–7.42 (6 H, m, Ph_2PO *meta* and *para* protons), 4.06 (1 H, m, CHO), 3.74 (1 H, m, CHO), 3.0 (1 H, d, *J* 3, OH), 2.14 (1 H, m, CHP), 2.04–0.91 (10 H, m, remaining CH_2s), 1.68 (1 H, s, OH), 1.14 (1.2 H, d, *J* 6.2, MeCO), 1.13 (1.8 H, d, *J* 6.3, MeCO) and 0.67 (3 H, t, *J* 7, Me); *m*/*z* 375 (0.3%, MH^+), 356 (0.5, M − H_2O), 341 (2), 301 (38), 272 (45, $Ph_2POPent$), 229 (100, $Ph_2POC_2H_4$), 202 (91, Ph_2POH) and 201 (78, Ph_2PO).

(2RS,3RS)-2-*Diphenylphosphinoyldecane*-3,6-*diol* (threo-**33**; R = H).—In the same way, TBAF (5.9 cm^3, 5.9 mmol) and the silyl ether (*threo*-**33**) (890 mg, 1.48 mmol) in THF (10 cm^3) for 16 h gave, after flash chromatography [18] on silica gel eluting with EtOAc–MeOH (9:1), the *diol* (440 mg, 80%) as needles (from EtOAc), m.p. 135–137 °C (Found: C, 70.4; H, 8.45; P, 8.4%; M^+ − H_2O 356.1896. $C_{22}H_{31}O_3P$ requires C, 70.6; H, 8.35; P, 8.3%; M − H_2O 356.1905); R_f 0.33; ν_{max}/cm^{-1} 3330 (OH), 1590 (Ph), 1440 (Ph–P) and 1150 (P=O); δ_H 7.82–7.69 (4 H, m, Ph_2PO *ortho* protons), 7.58–7.45 (6 H, m, Ph_2PO *meta* and *para* protons), 3.88 (1 H, m, CHO), 3.53 (1 H, m, CHO), 3.11 (2 H, m, 2 × OH), 2.72 (1 H, m, CHP), 1.88–1.27 (10 H, m, remaining CH_2s), 1.03 (3 H, dd, J_{HP} 17.6 and J_{HH} 7.6, MeCP) and 0.88 (3 H, t, *J* 6.3, Me); *m*/*z* 356 (1%, M − H_2O), 299 (15), 259 (55), 230 (70, Ph_2POEt), 202 (90, Ph_2POH) and 201 (100, Ph_2PO).

(2RS,3SR)-2-*Diphenylphosphinoyldecane*-3,6-*diol* (erythro-**33**; R = H).—In the same way, TBAF (3.6 cm^3, 3.6 mmol) and the silyl ether (*erythro*-**33**) (160 mg, 0.27 mmol) in THF (10 cm^3) for 16 h gave, after flash chromatography [18] on silica gel eluting with EtOAc–MeOH (9:1), the *diol* (80 mg, 80%) as an oil which solidified on prolonged standing (Found: C, 70.3; H, 8.55; P, 8.4%; M^+ − H_2O), 356.1913. $C_{22}H_{31}O_3P$ requires C, 70.6; H, 8.35; P, 8.3%; M^+ − H_2O, 356.1905); R_f 0.30; ν_{max}/cm^{-1} 3370 (OH), 1590 (Ph), 1440 (Ph–P) and 1160 (P=O); δ_H (7.85–7.70 (4 H, m, Ph_2PO *ortho* protons), 7.57–7.44 (6 H, m, Ph_2PO *meta* and *para* protons), 4.4 (2 H, br, m, 2 × OH), 4.05 (1 H, m, CHO), 3.52 (1 H, m, CHO), 2.35 (1 H, quintet, *J* 7, CHP), 1.87–1.15 (10 H, m, remaining CH_2s), 1.18 (3 H, dd, J_{HP} 17 and J_{HH} 7.3, MeCP) and 0.87 (3 H, t, *J* 7, Me); *m*/*z* 356 (5%, M − H_2O), 299 (14), 259 (59), 230 (90, Ph_2POEt), 202 (99, Ph_2POH) and 201 (100, Ph_2PO).

E-*Dec*-5-*en*-2-*ol* (E-**31**).—Sodium hydride (152 mg of a 60% dispersion in oil, 3.8 mmol) was added to a stirred solution of the diol (*threo*-**30**; R = H) (567 mg, 1.52 mmol) in dry DMF (30 cm^3) and was warmed to 55 °C for 2 h. After cooling, the thick white precipitate was dissolved by the addition of water (30 cm^3) and brine (30 cm^3), and the mixture was extracted with Et_2O (3 × 30 cm^3). The combined organic extracts were washed with water (3 × 30 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure. Kugelrohr distillation of the residue gave the *E*-alkene (229 mg, 97%) as a clear oil, b.p. 105–110 °C/0.1 mmHg (lit.,[15] b.p. 83 °C/5 mmHg) (Found: C, 76.5; H, 12.95%; M^+, 156.1501. $C_{10}H_{20}O$ requires C, 76.9; H, 12.90%; M, 156.1505); R_f 0.49; ν_{max}(neat)/cm^{-1} 3330 (OH), 1660 (C=C) and 975 (*E*-HC=CH def.); δ_H 5.42 (2 H, ABm, J_{AB} 15.2, HC=CH), 3.80 (1 H, m, CHO), 2.06 (2 H, m, CH_2C=), 1.96 (2 H, m, CH_2C=), 1.60–1.25 (7 H, m, remaining CH_2s and OH), 1.17 (3 H, d, *J* 6.1, MeCO) and 0.87 (3 H, t, *J* 7, Me); δ_C 131.1, 129.7, 67.8, 39.1, 32.1, 31.8, 29.0, 23.4, 22.2 and 13.8; *m*/*z* 156 (3%, M^+), 138 (5, M − H_2O), 109 (10), 95 (49), 81 (49) and 67 (100). GLC analysis showed the *E*:*Z* ratio to be >40:1.

Z-*Dec*-5-*en*-2-*ol* (*Z*-**31**).—In the same way, sodium hydride (40 mg of a 50% dispersion, 0.83 mmol) and the diol (*erythro*-**30**; R = H) (102 mg, 0.27 mmol) in dry DMF (4 cm^3) at 70 °C for 5 h followed by flash chromatography [18] on silica gel eluting with EtOAc gave the *Z*-alkene (36 mg, 86%) as a clear oil, b.p. 90–100 °C/0.2 mmHg (lit.,[15] b.p. 59 °C/1 mmHg) (Found: C, 76.8; H, 12.9%; M^+, 156.1504. $C_{10}H_{20}O$ requires C, 76.9; H, 12.9%; *M*, 156.1514); R_f 0.51; ν_{max}/cm^{-1} 3400 (OH), 1460, 1380 and 920; δ_H 5.37 (2 H, ABm, J_{AB} 10.8, HC=CH), 3.81 (1 H, sextet, *J* 6.2, CHO), 2.14–2.02 (4 H, m, CH_2C=CCH_2), 1.54–1.27 (6 H, m, remaining CH_2s), 1.18 (3 H, d, *J* 6.3, MeCO) and 0.88 (3 H, t, *J* 7, Me); δ_C 130.6, 129.1, 67.9, 39.2, 31.9, 29.7, 26.9, 23.6, 22.3 and 13.9; *m*/*z* 156 (7%, M^+), 138 (10), 109 (11), 95 (41), 82 (49), 81 (50) and 67 (100). GLC analysis showed the *Z*:*E* ratio to be >30:1.

E-*Dec*-2-*en*-6-*ol* (E-**34**).—In the same way, sodium hydride (77 mg of a 60% dispersion, 1.93 mmol) and the diol (*threo*-**33**) (288 mg, 0.77 mmol) in dry DMF (20 cm^3) at 60 °C for 1 h gave, after Kugelrohr distillation, the E-*alkene* (94 mg, 78%) as a clear oil, b.p. 100–110 °C/0.1 mmHg (Found: C, 76.7; H, 13.05%; M^+ − H_2O 138.1411. $C_{10}H_{20}O$ requires C, 76.9; H, 12.9%; *M* − H_2O, 138.1408); ν_{max}/cm^{-1} 3350 (OH) and 975 (*E*-HC=CH def.); δ_H 5.4 (2 H, ABm, J_{AB} 15.2, HC=CH), 3.59 (1 H, m, CHO), 2.17–2.00 (2 H, m, CH_2C=), 1.63 (3 H, dt, *J* 4.7 and 1.3, MeC=), 1.61–1.23 (9 H, m, OH and remaining CH_2s) and 0.89 (3 H, t, *J* 7, Me); δ_C 131.1, 125.2, 71.6, 37.2, (2 C), 28.9, 27.8,

22.7, 17.7 and 13.9; *m/z* 138 (20%, M − H_2O), 81 (77) and 68 (100).

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