Diastereoselective Epoxidation of Allylic Phosphine Oxides

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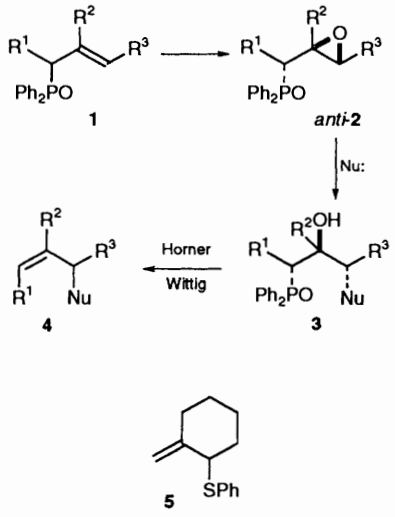
Allylic phosphine oxides are epoxidised *anti* selectively by *m*-CPBA, but this selectivity can be reversed if the allylic phosphine oxide is also an allylic alcohol.

The epoxides **2** of allylic phosphine oxides **1** are regiospecific equivalents of allylic cations. Nucleophilic attack on the epoxide reveals the hydroxyl group of a Horner–Wittig intermediate **3**, which can be collapsed stereospecifically[1] with a sodium or potassium base to the allylically functionalised alkene **4**. We have published[2] a synthesis of the unstable allylic sulfide **5** based on this strategy.

The stereochemistry of the final product **4** of this sequence[3] is determined by that of the epoxide **2** in two ways. The absolute configuration of the allylic chiral centre of **4** derives directly from the absolute configuration of the epoxide **2** by stereochemical inversion at the epoxide opening step. The asymmetric synthesis of epoxides **2** will be described in a future paper.[4] The



Scheme 1

stereospecificity of the Horner–Wittig elimination means that the geometry of the double bond of **4** reflects the relative stereochemistry between the diphenylphosphinoyl group and the epoxide of **2**. In this paper, we describe the diastereoselectivity of the epoxidation of allylic phosphine oxides **1** to give epoxides **2**.[5] The influence of an allylic chiral centre over reactions on the adjacent double bond is widely exploited in stereocontrolled synthesis, and has been the subject of a considerable amount of investigation.[6] We further demonstrate that the stereochemical directing properties of the diphenylphosphinoyl group can be significantly altered if the allylic phosphine oxide is also an allylic alcohol.

Allylic phosphine oxides **1a–f** were made by alkylation of a simpler allylic phosphine oxide[7] (**1a**, **b**), by silylation of the corresponding allylic alcohol[8] (**1c**), or by acid-catalysed dehydration[9] of β-hydroxy allylic phosphine oxides (**1d–f**). These six compounds, which each contain one chiral centre α to phosphorus, were epoxidised with *m*-CPBA in buffered dichloromethane.[10] The stereoselectivity observed in these reactions (measured by ^{1}H NMR of the crude product mixture) is shown in Table 1. For three cases the stereochemistry of the major epoxide was confirmed, either by comparison with known compounds (*anti* and *syn*-**2c** were desilylated to give known[4] epoxy alcohols), by stereospecific conversion into a *Z* allylic sulfide [*anti*-**2d** gave **4**; Nu = PhS (Scheme 1)], or by X-ray crystal structure (*anti*-**2e**, Fig. 1).

Table 1 Epoxidation of the allylic phosphine oxides

Starting material **1**	R^1	R^2	R^3	Epoxide **2** *anti*:*syn*
a	Me	H	Me	66:34
b	Pr	H	Me	85:15
c	Pr^i	H	$CH_2OSiMe_2Bu^t$	86:14
d[a]	Me	Me	Pr^i	90:10
e	Pentyl	Me	Et	91:9
f[a]	Me	Et	Me	80:20

[a] We have previously published some details of the epoxidation of **1d** and **1f** (see ref. 10). At that time we were not interested in the diastereoselectivity of the reactions. We have since re-examined the data, and report these diastereoselectivity for the first time.

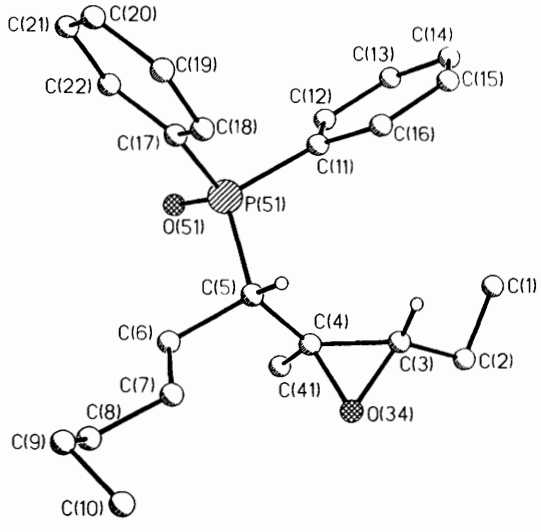
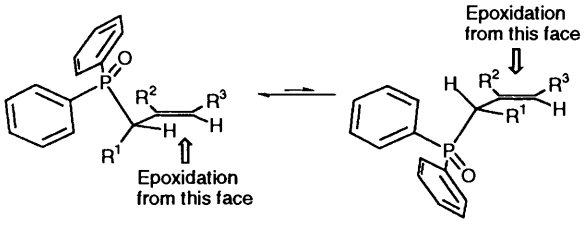


Fig. 1 The molecular conformation of *anti*-**2e** in the crystal with the atom numbering (only H atoms at chiral centres included)

In these reactions, the diphenylphospinoyl group exerts a clear *anti*-directing[11] effect. The most likely ground-state conformation for the allylic system,[6,12] depicted in **6a** has an eclipsing interaction between the hydrogen atom at the chiral centre and the double bond. Attack by *m*-CPBA on the top face of the double bond is hindered by the bulky diphenylphosphinoyl group, and *anti* epoxides result.

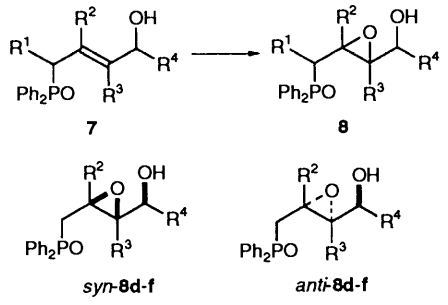
The poorer *anti* selectivity observed in the epoxidation of **1a** can be attributed to an alternative reactive conformation, **6b**, with R^1 eclipsing the double bond.[6] Epoxidation from the face of the double bond opposite to the diphenylphosphinoyl group in this conformation gives a *syn* epoxide. For epoxidation of **1b–f**, conformation **6b** is disfavoured by $A^{1,3}$ interactions between R^1 and the *cis* vinylic hydrogen atom. But for **1a** it is significantly populated because R^1 is only a methyl group.



6a **6b**

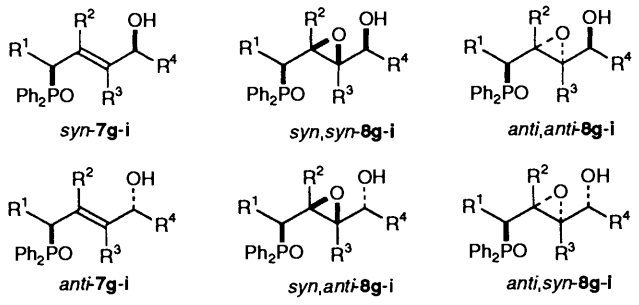
We have described methods[4,13] for the stereoselective synthesis of δ-hydroxy allylic phosphine oxides **7**. Our study of the stereoselective epoxidation of this class of allylic phosphine oxides begins with some simple compounds **7a–f**, which have R^1 = H, and therefore no chiral centre α to phosphorus. Any stereoselectivity in their epoxidation must, therefore, be due to the chiral centre bearing the hydroxy group. We epoxidised them with *m*-CPBA and, in some cases, with *tert*-butyl hydroperoxide catalysed by vanadyl acetoacetonate or titanium tetraisopropoxide. The results of these reactions are presented in Table 2. Stereoselectivities were measured by ^{1}H NMR of the crude product mixture, and the stereochemistry of the major stereoisomers inferred from precedent.[14]

The yields of the reactions using *m*-CPBA were generally excellent, with the exception of the epoxidation of **7a** to give the reactive* epoxide **8a**. The reactions using transition metal peroxide complexes were more capricous: **7d** did not epoxidise cleanly with Bu^{t}OOH–VO(acac)$_2$, while **7e** and **7f** did.



7 **8**

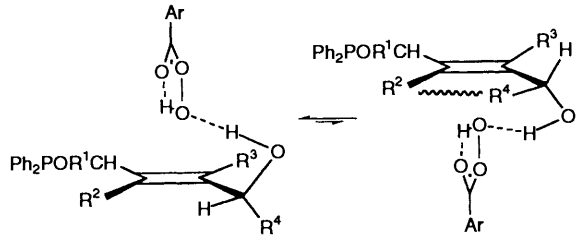
syn-**8d-f** *anti*-**8d-f**



syn-**7g-i** *syn,syn*-**8g-i** *anti,anti*-**8g-i**

anti-**7g-i** *syn,anti*-**8g-i** *anti,syn*-**8g-i**

The stereoselectivity of the epoxidation of allylic alcohols, both with peracids and with transition metal peroxide complexes, is well documented.[14] The widely accepted transition state for peracid epoxidations of allylic alcohols involves a hydrogen bond between the hydroxy group and the terminal oxygen atom of the peracid.[14b] With the ground state conformation shown in **9a**, a chiral secondary allylic alcohol generally epoxidises with *syn* selectivity. However, unless there is a substituent at R^3 ($R^3 \neq$ H) to lock the molecule into conformation **9a**, the *syn* selectivity is often poor.



9a **9b**

The selectivities observed in the epoxidations of **7d–f** can be compared with published results[14b,15] for similar substitution patterns which lack the diphenylphosphinoyl group. In no case, using either *m*-CPBA or Bu^{t}OOH–VO(acac)$_2$, does the presence of the diphenylphosphinoyl group perturb the stereoselectivity significantly.

Bearing in mind our two sets of results, the outcome of the next group of reactions is rather surprising. The compounds **7g**, **7h** and **7i** each have two chiral centres: one α to phosphorus and one α to oxygen. They therefore have features in common with both of our first two sets of allylic phosphine oxides. We took each diastereoisomer of the compounds **7g**, **7h** and **7i**, and epoxidised them to see whether they would demonstrate the stereochemical directing powers of the diphenylphosphinoyl group and of the hydroxyl group engaged, respectively, in cooperation and competition. The results of these reactions are presented in Table 3. Stereoselectivities were measured by ^{1}H NMR or by analytical HPLC of the crude product mixture (in the case of *syn*-**7g** and of *syn*- and *anti*-**7h**, after oxidation to epoxy ketones),[3a,16] and the major diastereoisomers identified by crystal structure (*anti,syn*-**8g**: Fig. 2, and *anti,syn*-**8h**),[17] by comparison of the epoxy ketones[3a,16] obtained by oxidation of compounds epimeric at the hydroxyl-bearing chiral centre (**8g** and **8h**), by stereospecific conversion into alkenes in the manner of Scheme 1 (**8h**),[3a,16] or by comparison with known compounds (**8i**).[4]

In each case, there was some degree of match/mismatch[18]

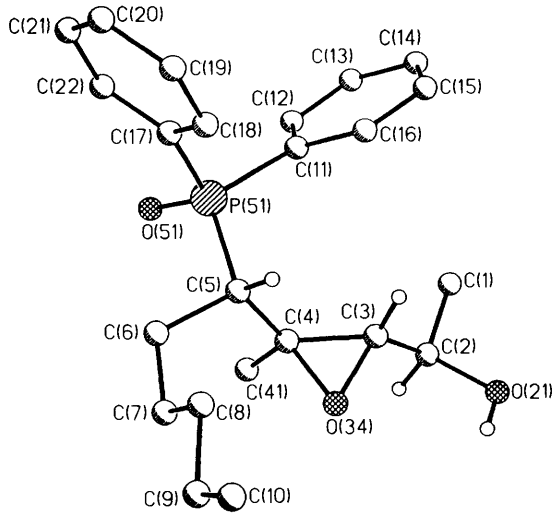


Fig. 2 The molecular conformation of one of the two independent molecules of *anti,syn*-**8g** in the crystal with the atom numbering (only H atoms at the chiral centres and the hydroxyl H atom included)

* The epoxide **8b** readily undergoes a base-catalysed rearrangement: see ref. 4.

Table 2 Epoxidation of simple δ-hydroxy allylic phosphine oxides

		Starting material						Product **8**	
Entry	7	R^1	R^2	R^3	R^4	Geometry	Reagent[a]	Yield (%)	Ratio *syn*:*anti*
1	**a**	H	H	H	H	*E*	A	40	—
2	**b**	H	Me	H	H	*E*	A	83	—
3	**b**						B	60	—
4	**c**	H	Me	H	H	*Z*	A	75	—
5	**d**	H	H	H	Me	*E*	A	100	62:38
6	**d**						C	15	—
7	**e**	H	H	Me	Me	*E*	A	94	54:46
8	**e**						C	97	0:100
9	**f**	H	Me	H	Pentyl	*E*	A	84	100:0
10	**f**						C	90	84:16

[a] Reagents: A, *m*-CPBA; B, Bu^{t}OOH, $Ti(OPr^i)_4$; C, Bu^{t}OOH, $VO(acac)_2$.

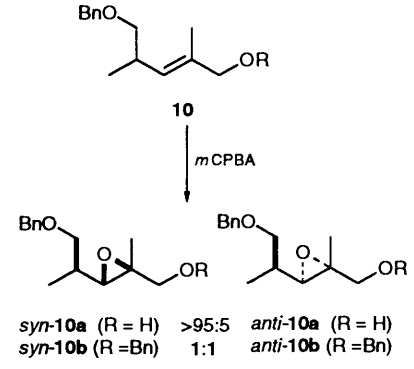
Table 3 Epoxidation of allylic alcohols with a chiral centre α to phosphorus

Entry	Starting material	R^1	R^2	R^3	R^4	**8**, ratio of diastereoisomers	Major diastereoisomer
1	*syn*-**7g**	Pentyl	Me	H	Me	93:7	*syn,syn*-**8g**
2	*anti*-**7g**	Pentyl	Me	H	Me	100:0	*anti,syn*-**8g**
3	*syn*-**7h**	Pentyl	H	H	Me	73:27	*syn,syn*-**8h**
4	*anti*-**7h**	Pentyl	H	H	Me	56:44	*anti,syn*-**8h**
5	*syn*-**7i**	Pr^i	H	H	Me	81:29	*syn,syn*-**8i**
6	*anti*-**7i**	Pr^i	H	H	Me	53:47	*anti,syn*-**8i**

between the two chiral centres. The relative directing powers of the two chiral centres were, however, quite dependent on the compound's substitution pattern. For both diastereoisomers of **7g**, the reaction was very *syn* selective with respect to the hydroxyl group. The methyl group R^2 so raises the energy of conformation **9b** that the configuration at the other chiral centre is almost irrelevant to the course of the reaction. The epoxidation of **7f** (Table 2, entry 9) has already demonstrated the very good hydroxyl-directed *syn* selectivity typical[14b,15] of reactions of this substitution pattern.

Without this *cis* methyl group, the directing power of the hydroxyl group is reduced and the influence of the diphenylphosphinoyl group revealed. Both **7h** and **7i** show a more marked match/mismatch effect in their epoxidations, with the effect being greater when the directing power of the diphenylphosphinoyl group is strengthened by a larger group R^1. The hydroxyl group is directing the epoxidation *syn*, as expected (compare the *m*-CPBA epoxidation of **7d** in Table 2, entry 5). But, surprisingly, the *syn* selectivity is greater when epoxidation is also *syn* to the diphenylphosphinoyl group. This contrasts with the *anti* directing effect of the diphenylphosphinoyl group in epoxidations of simple allylic phosphine oxides (Table 1).

We suppose that the ability of the diphenylphosphinoyl group to direct epoxidation *syn* in these systems arises from hydrogen bonding between the phosphoryl oxygen atom and the terminal hydrogen atom of the *m*-CPBA. Such hydrogen bonds, in which the polarity of the bond is opposite to that usually observed between peracids and hydroxyl groups, have been shown to direct the stereochemical course of epoxidation reactions of alkenes bearing a variety of electronegative functional groups.[19] The switch in selectivity in the presence of the δ-hydroxyl group is harder to explain, though a similar phenomenon has been noted by Kishi[21] in the epoxidation of homoallylic benzyl ethers. He found that the homoallylic benzyloxy group of allylic alcohol **10a** (the oxygen atom of which is the same number of bond-lengths from the double bond as the oxygen atom of an allylic phosphine oxide) could direct epoxidation *syn*. When the alcohol was protected as an ether **10b**, the reaction was unselective.

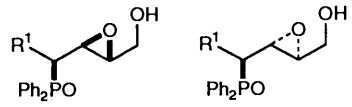


To investigate further the *syn* directing ability of the diphenylphosphinoyl group, we decided to remove the obscuring effect of the second, hydroxyl-carrying, chiral centre. δ-Hydroxyallylic phosphine oxides with primary hydroxyl groups are available by palladium(II)-catalysed allylic rearrangement.[8] The five examples **7j–m** were epoxidised with *m*-CPBA, the stereoselectivities measured by ^1H NMR or by analytical HPLC of the crude reaction products, and the diastereoisomers identified by comparison with known[4] compounds. The results of these reactions are presented in Table 4.

The selectivity was clearly strongly dependent on the substituent R^1. When R^1 was small (R^1 = Me, **7j**), the epoxidation was *anti* selective. When R^1 was an unbranched alkyl group (R^1 = Et, **7k** and R^1 = pentyl, **7l**), the reaction swung to being marginally *syn*-selective, and when R^1 was a branched alkyl group (R^1 = Pr^i, **7m** or R^1 = cyclohexyl, **7n**) the *syn* selectivity was fairly strong. Comparison of the match/mismatch effect for **7h** and **7i** reveals a similar increase in the *syn*-directing power of the diphenylphosphinoyl group with increased branching.

To account for these results in detail, we must again consider the most likely transition state conformations leading to each of the possible diastereoisomeric products. Diagram **11a** shows the lowest energy conformation of **7** (R^2 = R^3 = R^4 = H),

Table 4 Epoxidation of primary allylic alcohols with a chiral centre α to phosphorus

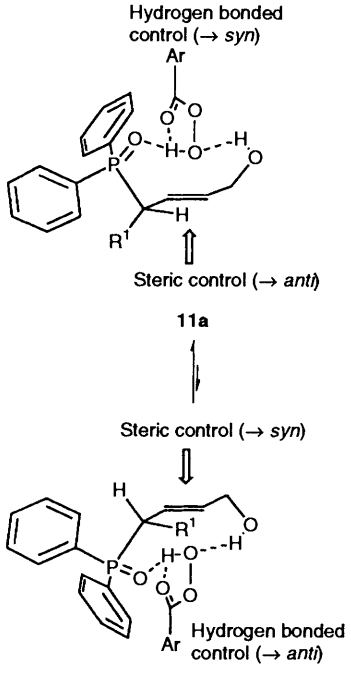


syn-**8j-n** *anti*-**8j-n**

Starting material **7**	R^1	R^2	R^3	R^4	Ratio *syn*-**8**:*anti*-**8**
j	Me	H	H	H	29:71
k	Et	H	H	H	53:47
l	Pentyl	H	H	H	54:46
m	Pr^i	H	H	H	73:27
n	Cyclohexyl	H	H	H	69:31

Table 5 Epoxidation of primary allylic alcohols with chiral centres α and β to phosphorus

Entry	Starting material	R	Ratio *syn*:*anti* **13**
1	*anti*-**12a**	Me	68:32
2	*syn*-**12a**	Me	72:28
3	*anti*-**12b**	OAc	56:44
4	*syn*-**12b**	OAc	56:44
5	*anti*-**12c**	OH	56:44
6	*syn*-**12c**	OH	18:82



11b

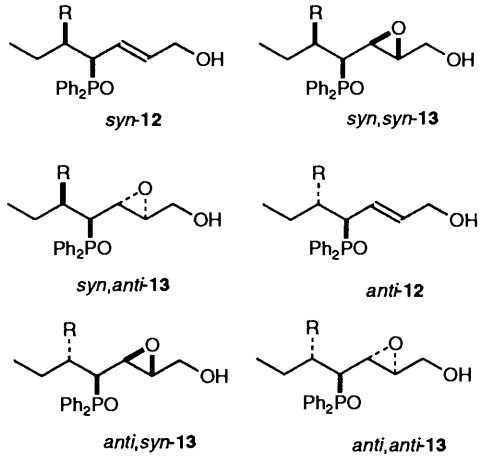
with H in the plane of the double bond.[6,12] As R^1 is always smaller than diphenylphosphinoyl, the next most populated conformation is **11b**, in which R^1 eclipses the double bond.

The free hydroxyl group appears to encourage formation of a hydrogen bond between the peracid and the diphenylphosphinoyl group, presumably in the cyclic structure shown in **11**.[20] When R^1 is branched (for example isopropyl or cyclohexyl; **7m** and **7n**) only conformation **11a** is significantly populated, and predominant attack of the peracid *syn* to diphenylphosphinoyl in this conformation leads to predominant formation of the *syn* epoxide *syn*-**7**. The 73:27 ratio for epoxidation of **7m** (R^1 = Pr^i) indicates that the *syn* directing effect is nonetheless fairly weak, and that a substantial proportion of attack still occurs on the other face of the double bond. With smaller R^1, conformation **11b** is populated, and the combined effect of this and the fact that the bottom face of conformation **11a** less hindered leads to a shift to *anti* selectivity. This change in the direction of the selectivity, despite conformation **11b** is being less populated than conformation **11a**, implies that sterically directed attack *anti* to the diphenylphosphinoyl group remains important even when modified by hydrogen bonding.

With a view to using some of these stereoselective reactions in the synthesis of compounds bearing remote chiral centres,[3c] we were also interested in the stereodirecting effect of a chiral centre in our δ-hydroxy allylic phosphine oxides β to phosphorus. Each diastereoisomer of compounds **12a–c** was available by palladium(II)-catalysed allylic ester rearrangement.[8,21] They were epoxidised with *m*-CPBA, the stereoselectivities measured by ^{1}H NMR of the crude product mixture, and the diastereoisomers identified by comparison with known[4] compounds. The results are presented in Table 5.

The *sec*-butyl-substituted compound **12a** (entries 1 and 2) behaved very similarly to the isopropyl-substituted compound **7m** (Table 4): the reaction was not significantly influenced by the new chiral centre, with both *anti*- and *syn*-**12a** giving good *syn* selectivity. The acetoxy-substituted compounds **12b** (entries 3 and 4) were less *syn* selective in their reactions, giving similar selectivities to the n-alkyl substituted **7k** and **7l** (Table 4). Conformation **11b** should not be significantly populated with a branched R^1 like this, so the reduced *syn* selectivity must be due to a greater tendency for the peracid to approach **11a** from the bottom face. The acetoxy group can favour attack from this side by providing an alternative site for the second hydrogen bond. There is no match/mismatch effect for this homoallylic chiral centre.

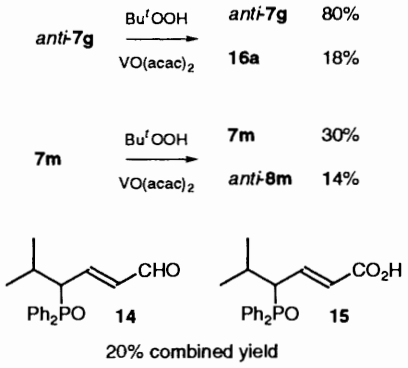
This was not the case for the diols **12c**: *anti*-**12c** gave the same ratio of epoxides as both diastereoisomers of **12b**. *syn*-**12c**



however, was epoxidised highly *anti* selectively. Homoallylic hydroxyl groups can direct stereoselective *m*-CPBA epoxidations of branched compounds.[20] The (mechanistic) *syn* directing effect of the hydroxyl group in *syn*-**12c** is completely overriding the weaker *syn* directing effect of the diphenylphosphinoyl group, and promoting attack of *m*-CPBA *syn* to R^1 in **11a**, giving mainly the *anti* epoxide *syn*,*anti*-**13c**. Presumably, for the other diastereoisomer (*anti*-**12c**), the conformation required for the hydroxyl group to deliver the *m*-CPBA to the double bond is too crowded for the interaction to be favourable.

Attempts were made to epoxidise allylic phosphine oxides with some other reagents. *tert*-Butyl hydroperoxide catalysed

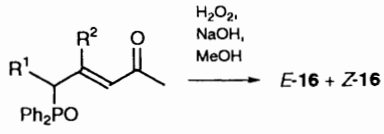
by $VO(acac)_2$ reacted with *anti*-**7g** and with **7m** to give products **16a** and a mixture of **14** and **15**, arising from oxidation of the hydroxyl group (Scheme 2). We have already remarked on the



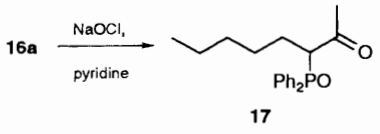
20% combined yield

Scheme 2

poor reaction between **7d** and Bu^tOOH–$VO(acac)_2$ (Table 2, entry 6). Allylic alcohols **7g** and **7h** were oxidised to enones[13c] **16a** and **16b** and epoxidation was attempted with alkaline hydrogen peroxide (Scheme 3). Only a mixture of the starting



E-**16a**; R^1 = pentyl, R^2 = Me *ca.* 30:70
E-**16b**; R^1 = pentyl, R^2 = H *ca.* 70:30



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Scheme 3

materials and their *Z* isomers was isolated from these reactions. Interestingly, for **16a**, the *Z* isomer predominated, probably because it was stabilised by chelation to the metal cation. With sodium hypochlorite in pyridine, over-oxidation of **16a** gave the keto-phosphine oxide **17**.

The *syn* epoxidation of branched δ-hydroxy allylic phosphine oxides with peracids is conveniently complementary to the *anti* selectivity with which they undergo Sharpless kinetic resolution.[4] We have made use of this in a general synthesis of optically active diphenylphosphinoyl epoxy alcohols, from which we have made unsaturated amino acids and a number of other allylically and homoallylically substituted alkenes.[3b,3c,16]

Experimental

Synthesis of New Starting Materials

(E)-4-*Diphenylphosphinoylhept-2-ene* **1b**.—Butyllithium (1.5 mol dm^{-3} solution in hexane) was added dropwise to a stirred solution of but-2-enyl(diphenyl)phosphine oxide[7] (384 mg, 1.5 mmol) in THF (20 cm^3) at 0 °C under nitrogen until a permanent red colour appeared; further butyllithium (1.05 cm^3, 1.5 mmol) was then added with cooling at 0 °C. 1-Bromopropane (247 mg, 2.0 mmol) was added dropwise to the solution which was then warmed to 10 °C for 30 min before being quenched with saturated aqueous ammonium chloride (10 cm^3). Water (50 cm^3) was added to the mixture which was then extracted with dichloromethane (2 × 40 cm^3). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure to give a white solid, recrystallisation of which from EtOAc–hexane gave the *phosphine oxide* (184 mg, 42%), m.p. 182–183 °C, R_F(EtOAc) 0.46; ν_{max}(Nujol)/cm^{-1} 1594 (C=C), 1440 (PPh) and 1168 (P=O); δ_H(100 MHz; $CDCl_3$) 7.3–8.0 (10 H, m, Ph_2PO), 5.0–5.6 (2 H, m, CH=CH), 2.7–3.1 (1 H, m, PCH), 1.48 (3 H, d, *J* 5.5, CH*Me*), 1.0–1.9 [4 H, m, $(CH_2)_2$] and 0.9 (3 H, t, *J* 7, CH_2*Me*) (Found: M^+, 298.1484. $C_{19}H_{23}OP$ requires *M*, 298.1487), *m/z* 298 (22%, M^+), 269 (2, M – Et), 256 (6, M – MeCH=CH_2), 202 (100, Ph_2POH) and 201 (98, Ph_2PO). Concentration of the mother liquor and preparative TLC gave (E)-4-*diphenylphosphinoyl*-4-*propylhept*-2-*ene* (144 mg, 28%), R_F(EtOAc) 0.59; ν_{max}(Nujol)/cm^{-1} 1590 (C=C), 1439 (PPh) and 1185 (P=O); δ_H(100 MHz; $CDCl_3$) 7.3–8.2 (10 H, m, Ph_2PO), 5.1–5.5 (2 H, m, CH=CH), 1.0–2.2 (11 H, m, 4 × CH_2 and CH*Me*) and 0.76 (6 H, br t, *J* 7, CH_2*Me*) (Found: M^+, 340.1969. $C_{22}H_{29}OP$ requires *M*, 340.1956); *m/z* 340 (28%, M^+), 311 (1, M – C_3H_7) and 202 (100, Ph_2POH). Lower running fractions from the TLC gave an oil which was a 1:1 mixture of α and γ alkylated products by NMR.

4-*Diphenylphosphinoyl*-5-*methylhex*-2-*enyl* tert-*Butyl*(*dimethyl*)*silyl Ether* **1c**.—The allylic alcohol[8] **7m** (275.5 mg, 0.876 mmol), *tert*-butyl(dimethyl)silyl chloride (154.6 mg, 1.03 mmol, 1.17 equiv.) and imidazole (119.2 mg, 1.75 mmol, 2 equiv.) were dissolved in dry DMF (1.5 cm^3). After the mixture had been stirred under nitrogen at room temperature for 80 min, water (6 cm^3) was added to it and the aqueous suspension was extracted with ethyl acetate (× 3). The combined extracts were washed with water (× 3) and brine, dried (Na_2SO_4), and evaporated under reduced pressure to give a white solid. Purification of this by flash chromatography, eluting with EtOAc–cyclohexane (1:1), gave the *silyl ether* **1c** as minute needles, m.p. 161–163.5 °C (from EtOAc–cyclohexane) (Found: C, 70.2; H, 9.0; P, 7.3%; M^+, 428.2316. $C_{25}H_{37}O_2PSi$ requires C, 70.05; H, 8.7; P, 7.23%; *M*, 428.2300); R_F(EtOAc) 0.50; ν_{max}(Nujol)/cm^{-1} 1440 (PPh), 1250 ($SiMe_2$) and 1180 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 5.80 (1 H, dddt, *J* 15.5, 11, 6.5 and 1, PCHC*H*=C), 5.48 (1 H, dq, *J* 15 and 4.5, C=C*H*CH_2OH), 4.05 (2 H, ABX m, CH_2OSi), 2.93 (1 H, dt, *J* 3.5 and 10.2, PCH), 2.3 (1 H, m, C*H*Me_2), 1.05 (3 H, d, *J* 7, CH*Me*$_A$$Me_B$), 0.96 (3 H, d, *J* 7, CHMe_A*Me*$_B$), 0.89 (9 H, s, CMe_3), 0.02 (3 H, s, Si*Me*$_A$$Me_B$) and 0.01 (3 H, s, $SiMe_A$*Me*$_B$); δ_C(100 MHz; $CDCl_3$) 136.7$^+$ ($^3J_{PC}$ 12.4, C=*C*HCH$_2$OSi), 132–127 (Ph_2PO), 121.2$^+$ ($^2J_{PC}$ 5.8, PCH*C*H=C), 63.4$^-$ ($^4J_{PC}$ 1.5, CH_2OSi), 49.6$^+$ ($^1J_{PC}$ 68.5, PCH), 27.5$^+$ ($^2J_{PC}$ 2.2, $CHMe_2$), 25.8$^+$ (*C*Me_3), 23.0$^+$ ($^3J_{PC}$ 13.1, CH*Me*$_A$$Me_B$), 18.7$^+$ ($^3J_{PC}$ 2.7, CHMe_A*Me*$_B$), 18.3$^-$ (*C*Me_3), –5.29$^+$ (Si*Me*$_A$$Me_B$) and –5.32$^+$ ($SiMe_A$*Me*$_B$); *m/z* 428 (1.5%, M^+), 371 (100, M – C_4H_9), 202 (16, Ph_2POH) and 201 (35, Ph_2PO).

(E)-5-*Diphenylphosphinoyl*-4-*methyldec*-3-*ene* **1e**.—Butyllithium (1.5 mol dm^{-3} solution in hexane) was added dropwise to a stirred solution of hexyl(diphenyl)phosphine oxide[19] (4.4 g, 15.4 mmol) in dry THF (50 cm^3) at –40 °C under nitrogen until a permanent red colour was formed; further butyllithium (11.0 cm^3, 17 mmol) was then added dropwise and the solution cooled to –78 °C and stirred for 10 min. Pentan-3-one (1.46 g, 1.8 cm^3, 17 mmol) was added dropwise to the reaction mixture, discharging the anion colour, and the solution was then allowed to warm to room temperature. After the reaction had been quenched by addition of saturated aqueous NH_4Cl (18 cm^3) to the mixture, the layers were separated and the aqueous layer extracted with EtOAc (3 × 20 cm^3). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure to give the crude phosphine oxide which was not purified but heated at reflux in TFA[9] (40 cm^3) under nitrogen for 45 min. The mixture was cooled and poured into water (100 cm^3) and this solution extracted with chloroform (3 × 50 cm^3). The combined extracts were washed with saturated aqueous $NaHCO_3$ (3 × 50 cm^3) and water (2 × 50 cm^3) dried and

evaporated under reduced pressure to give the *allylic phosphine oxide* (4.1 g, 76%) as a white crystalline solid, m.p. 110–112 °C [from light petroleum (b.p. 60–80 °C)/25% EtOAc], R_F(EtOAc) 0.51; ν_{max}/cm^{-1} 3053 (C=C–H), 1437 (P–Ph) and 1178 (P=O); δ_H(100 MHz, $CDCl_3$) 7.25–8.1 (10 H, m, Ph_2PO), 5.21 (1 H, br q, $J_{HP} = J_{HH} = 5$, C=CH), 2.9 (1 H, ddd, *J* 2, 7 and 9, PCH), 1.75–2.1 (2 H, CH_2CH=C), 1.66 (3 H, d, $J < 1$, *Me*C=CH), 0.82 (3 H, t, *J* 6, *Me*CH_2CH), 0.9–1.7 [8 H, m, $(CH_2)_4$] and 0.7 (3 H, t, *J* 7, *Me*CH_2CH_2) (Found: M^+, 354.2096. $C_{23}H_{31}OP$ requires *M*, 354.2113); *m/z* 354 (175%, M^+) 202 and (100, Ph_2POH).

General Procedure for the Epoxidation of Allylic Phosphine Oxides with m-*CPBA*.—Disodium hydrogen phosphate (355 mg, 2.5 mmol, 2.5 equiv.) or sodium hydrogen carbonate (210 mg, 2.5 mmol, 2.5 equiv.), and *m*-CPBA (*ca.* 65%; 530 mg, 2.0 mmol, 2.0 equiv.), were added to a stirred solution of the allylic phosphine oxide (1 mmol) in dry dichloromethane (10 cm^3) at room temperature. After 24 h, the suspension was diluted with dichloromethane and washed with water, 10% aqueous sodium sulfite (×2), saturated aqueous sodium hydrogen carbonate and brine, dried (Na_2SO_4) and evaporated under reduced pressure to yield a crude product.

Epoxidation of **1a**.—In this way, the allylic phosphine oxide[24] **1a** (1.553 g, 5.75 mmol) gave, after 48 h, an oil (1.57 g, 95%). ^{1}H NMR spectroscopy showed this material to consist of a 66:34 mixture of *anti*-**2a** and *syn*-**2a** (Found: M^+, 286.1136. $C_{17}H_{19}O_2P$ requires *M*, 286.1123); R_F 0.28 (major) and 0.24; δ_H(400 MHz; $CDCl_3$) 7.9–7.3 (10 $H^{anti+syn}$, m, Ph_2PO), 2.88 (1 H^{anti} + 2 H^{syn}), 2.49 (1 H^{syn}, sextet, *J* 7.2, PCH), 2.34 (1 H^{anti}, dq, *J* 2.2 and 5.2, MeC*H*O), 2.09 (1 H^{anti}, sextet, *J* 7.4, PCH), 1.36 (3 H^{anti}, dd, *J* 16.0 and 7.1, PCMe), 1.22 (3 H^{syn}, 3 H, d, *J* 5.2, MeCO), 1.15 (3 H^{syn}, dd, *J* 15.6 and 7.4, PCMe) and 0.89 (3 H^{anti}, d, *J* 5.2, MeCO); *m/z* 286 (0.1%, M^+), 243 (5, $Ph_2POCHCHO$), 219 (14, Ph_2POH_2), 202 (100, Ph_2POH) and 201 (60, Ph_2PO).

Epoxidation of **1b**.—By the general method above, the phosphine oxide **1b** (150 mg, 0.5 mmol) gave after 6 days 4-*diphenylphosphinoyl*-2,3-*epoxyheptane* **2b** (155 mg, 100%). Though this crude product was pure (NMR and TLC), recrystallisation (from EtOAc–hexane) gave the *epoxide* (30 mg, 19%), R_F(EtOAc) 0.35; δ_H(100 MHz, $CDCl_3$) 7.4–8.0 (10 H, m, Ph_2PO), 2.83 (1 H, dt, *J* 9, 2, PCHC*H*), 2.15 (1 H, dq, *J* 2, 5, MeC*H*), 2.00 (1 H, dq, *J* 3.5, 9, PCH), 1.1–2.0 [4 H, m, $(CH_2)_2$], 0.82 (3 H, d, *J* 7, CH*Me*) and 0.80 (3 H, d, *J* 5, CH*Me*) (Found: M^+ – Me, 299.1172. $C_{18}H_{20}O_2P$ requires M – Me, 299.1201); *m/z* 299 (0.5%, M^+), 257 [30, $Ph_2POCH(CH_2)_2Me$], 202 (100, Ph_2POH) and 201 (57, Ph_2PO).

Epoxidation of **1c**.—By the general method above, the phosphine oxide **1c** (79.8 mg, 0.186 mmol) gave, after 4 days, a crude product (82.7 mg, 100%), R_F(EtOAc) 0.28. The ^{1}H NMR spectrum of this material showed it to consist of an 86:14 mixture of the epoxides (2*RS*,3*SR*,4*SR*)-4-diphenylphosinoyl-2,3-epoxy-5-methylhexanyl (1,1-dimethylethyl)dimethylsilyl ether *anti*-**2c** and (2*RS*,3*SR*,4*RS*)-4-diphenylphosphinoyl-2,3-epoxy-5-methylhexanyl *tert*-butyl(dimethyl)silyl ether *syn*-**2c**; δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 $H^{anti+syn}$, m, Ph_2PO), 3.80 (1 H^{syn}, dd, *J* 12.0 and 4.0, CH_AH_BOSi), 3.62 (1 H^{syn}, dd, *J* 12.0 and 4.3, CH_AH_BOSi), 3.36 (1 H^{anti}, dd, *J* 11.0 and 1.0, CH_AH_BOSi), 3.30 (1 H^{anti}, dt, PCHC*H*O), 3.05 (1 H^{anti}, dd, *J* 11.5 and 7.0, CH_AH_BOSi), 2.90 (1 H^{syn}, m, C*H*OCH$_2$OSi), 2.35 (1 $H^{anti+syn}$, dt, *J* 3.0 and 10.5, CHP), 1.27 (3 $H^{anti+syn}$, d, *J* 6.8, Me), 1.16 (3 $H^{anti+syn}$, d, *J* 6.8, Me), 0.87 (3 H^{syn}, s, Bu^t), 0.85 (3 H^{anti}, s, Bu^t) and 0.0–0.1 (6 $H^{anti+syn}$, Me_2 × 2).

Tetrabutylammonium fluoride (1 mol dm^{-3} solution in THF; 0.15 cm^3, 0.15 mmol, 1.15 equiv.) was added to a stirred solution of some of this material (61.9 mg, 0.13 mmol) in dry THF (2 cm^3) under nitrogen. After 30 min, the solution was passed through a short column of silica, eluting with EtOAc and then EtOAc–2% MeOH to yield a product (37.2 mg, 87%). ^{1}H NMR showed this material to consist of an 87:13 mixture of *anti* and *syn* epoxides *anti*-**8m** and *syn*-**8m**, respectively. Analytical HPLC, eluting with $CHCl_3$–2% MeOH, showed the mixture to contain two compounds in a ratio 86:14.

Epoxidation of **1e**.—By the general method above, the allylic phosphine oxide **1e** (1.6 g, 5 mmol) gave, after 48 h, an oil which was a 10:1 mixture of diastereoisomers (by NMR). Flash chromatography (SiO_2/EtOAc–25% hexane) gave the major diastereoisomer of (3RS,4SR,5RS)-5-*diphenylphosphinoyl*-3,4-*epoxy*-4-*methyldecane* **2e** (1.42 g, 84%) as a white crystalline solid, m.p. 141.5–143.5 °C (from hexane/25% EtOAc) (Found: C, 74.5; H, 8.45%; M^+, 341.1670. $C_{23}H_{31}O_2P$ requires C, 74.6; H, 8.45%; *M*, 341.1666); R_F(EtOAc) 0.42; ν_{max}/cm^{-1} 1437 (P–Ph) and 1190 (P=O); δ_H(100 MHz, $CDCl_3$) 7.3–8.0 (10 H, m, Ph_2PO), 2.18 (1 H, dd, *J* 5 and 7, OC*H*CH$_2$), 2.04 (1 H, m, PCH), 0.90–2.0 (10 H, m br), 1.40 (3 H, s, Me), 0.80 (3 H, t, *J* 6, *Me*CH$_2$) and 0.59 (3 H, t, *J* 7, *Me*CH$_2$); δ_C(25 MHz, $CDCl_3$), 9.80 (q, *Me*CH$_2$CH) 13.57 (q, *Me*CH$_2$CH$_2$), 14.47 (q, *Me*CO), 21.11 and 22.00 (2 × t, MeCH$_2$CH$_2$), 25.29 (t, MeCH$_2$CH), 27.78 (dt, J_{PC} 65.6, PCH), 60.22 [d, J_{PC} 4.3, MeC(O)CH], 64.93 [d, MeC(O)CH] and 127.56–133.8 (12 C, m, Ph_2PO); *m/z* 341 (5%, M – Et) and 202 (100, Ph_2POH).

Epoxidation of **7a**.—By the general method above, the allylic alcohol[8] **7a** (39.2 mg, 0.144 mmol) gave the epoxide[4] **8a** as a crude product (16.7 mg, 40%).

Epoxidation of **7b**.—In the same way, the allylic alcohol[13b] **7b** (201 mg, 0.703 mmol) gave a crude product, which was purified by flash chromatography, eluting with CH_2Cl_2–6% MeOH, to yield the epoxide[4] **8b** (177 mg, 83%).

Epoxation of **7c**.—In the same way, the allylic alcohol[13b] **7c** (177.1 mg, 0.619 mmol) gave a crude product, which was purified by flash chromatography, eluting with EtOAc, to yield the epoxide[4] **8c** (135 mg, 72%).

Epoxidation of **7d**.—In the same way, the allylic alcohol[8,13b] **7d** (101.0 mg, 0.353 mmol) gave a crude product (109.5 mg, 103%) as an oil, R_F(EtOAc–10% MeOH) 0.32. The ^{1}H NMR spectrum of this material showed it to consist of a 62:38 mixture of the epoxide (2*RS*,3*SR*,4*RS*)-5-diphenylphosphinoyl-3,4-epoxypentan-2-ol *syn*-**8d** and the epoxide[4] *anti*-**8**; δ_H(250 MHz, $CDCl_3$) (signals due to *syn*-**8d**) 7.8–7.4 (10 H, m, Ph_2PO), 3.43 (1 H, quintet, *J* 6.5, C*H*OH), 3.20 (2 H, m, PCH$_2$C*H*O), 2.83 (1 H, m, PCH_AH_B), 2.67 (1 H, dd, *J* 5.0 and 2.0, OC*H*HOH), 2.34 (1 H, ddd, *J* 14.8, 12.7 and 7.2, PCH$_A$$H_B$) and 0.96 (3 H, d, *J* 6.5, Me).

Epoxidation of **7e**.—In the same way, the allylic alcohol[8] **7e** (99.6 mg, 0.33 mmol) gave a crude product (98.2 mg, 94%) as an oil, R_F(EtOAc) 0.19. The ^{1}H NMR spectrum of this material showed it to consist of a 54:46 mixture of the epoxide (2*RS*,3*SR*,4*RS*)-5-diphenylphosphinoyl-3,4-epoxy-3-methylpentan-2-ol *syn*-**8e** and the epoxide[4] *anti*-**8e**; δ_H(250 MHz; $CDCl_3$) (signals due to *syn*-**8e**) 7.8–7.3 (10 H, m, Ph_2PO), 3.4–3.2 (2 H, m, C*H*OH and PCH$_2$C*H*O), 2.65 (1 H, m, PCH_AH_B), 2.40 (1 H, ddd, *J* 15.5, 14.4 and 6.7, PCCH$_A$$H_B$), 1.07 (3 H, s, HOCC*Me*) and 0.96 (3 H, d, *J* 6.5, HOCH*Me*).

Epoxidation of **7f**.—In the same way, the allylic alcohol[8] **7f** (306.3 mg, 0.859 mmol) gave a crude product, the ^{1}H NMR spectroscopy of which showed it to contain one compound only. This material was purified by flash chromatography, eluting

with EtOAc, to give (2RS, 3SR,4RS)-1-*diphenylphosphinoyl*-2,3-*epoxy*-2-*methylnonan*-4-*ol syn*-**8f** (267.5 mg, 84%) as an unrecrystallisable solid (Found: M − $C_6H_{12}OH$, 271.0901. $C_{22}H_{29}O_3P$ requires *M* − $C_6H_{12}OH$, 271.0888); R_F(EtOAc) 0.30; ν_{max}($CHCl_3$)/cm^{-1} 3400 (OH), 1440 (PPh) and 1130 (P=O); δ_H(250 MHz; $CDCl_3$) 7.8–7.2 (10 H, m, Ph_2PO), 3.19 (1 H, dt, *J* 4.7 and 8.1, C*H*OH), 2.84 (1 H, t, *J* 14.6, PCH_AH_B), 2.56 (1 H, d, *J* 8.0, OC*H*CHOH), 2.22 (1 H, ddd, *J* 14.8 and 10.6, PCH_AH_B), 1.35 (3 H, s, OCMe), 1.4–0.9 [8 H, m, $(CH_2)_4$] and 0.80 (3 H, t, *J* 6.5, CH_2Me); δ_C(100 MHz; $CDCl_3$) 134–128 (Ph_2PO), 70.1$^+$ (CHOH), 67.0$^+$ (O*C*HCHOH), 58.6$^-$ (PCH_2C), 40.3$^-$ ($^1J_{PC}$ 66.7, PCH_2), 33.0$^-$, 31.6$^-$, 24.7$^-$ and 22.5$^-$ [$(CH_2)_4$], 19.4$^+$ (OC*Me*) and 14.1$^+$ (CH_2Me); *m*/*z* 271 (12%, M − $C_6H_{12}OH$), 259 [16, $Ph_2POCH_2C(OH)Me$], 219 (8, $Ph_2PO_2H_2$), 216 (4, Ph_2POMe), 215 (10, Ph_2POCH_2), 202 (100, Ph_2POH) and 201 (72, Ph_2PO).

Epoxidation of syn-**7g**.—In the same way, the allylic alcohol[13c] *syn*-**7g** 2.34 g, 6.32 mmol), gave after purification of the residual solid on a short fat column (SiO_2/CH_2Cl_2–4% MeOH),(2RS,3SR,4RS,5SR)-5-*diphenylphosphinoyl*-3,4-*epoxy*-4-*methyldecan*-2-*ol* **8g** (2.12 g, 87%) as a glassy solid, R_F(EtOAc) 0.21; ν_{max}/cm^{-1} 3300 (OH) and 1440 (P–Ph); δ_H(100 MHz, $CDCl_3$) 7.3–8.1 (10 H, m, Ph_2PO), 3.55 (1 H, quintet, *J* 7, C*H*OH), 2.85 [1 H, d, *J* 7, CH(O)C], 2.1–2.4 (1 H, m, PCH), 1.44 [3 H, s, MeC(O)C], 1.23 (3 H, d, *J* 6, *Me*CH), 1.1–2.0 [8 H, m, $(CH_2)_4$] and 0.80 (3 H, t, *J* 6, *Me*CH_2) (Found: M$^+$ − H, 385.1938. $C_{23}H_{30}O_3$ requires *M*, 385.1932); *m*/*z* 386 (2%, M$^+$), 385 (5, M − H), 368 (87, M − H_2O), 352 (42), 341 (21, M − MeCHOH) and 202 (100, Ph_2POH). Oxidation of the crude epoxide to the epoxy ketone revealed a *ca.* 13:1 mixture of diastereoisomers.

Epoxidation of anti-**7g**.—In the same way, the allylic alcohol[13c] *anti*-**7g** (0.525 g, 1.41 mmol) gave (2RS,3SR,4RS,-5SR)-5-*diphenylphosphinoyl*-3,4-*epoxy*-4-*methyldecan*-2-*ol* (0.39 g, 71%) as a white crystalline solid, m.p. 189.5–190.5 °C (from EtOAc–30% hexane), R_F 0.24; ν_{max}/cm^{-1} 3450 (OH), 1437 (P–Ph) and 1170 (P=O); δ_H(100 MHz; $CDCl_3$) 7.3–8.1 (10 H, m, Ph_2PO), 3.39 (1 H, dq, *J* 7.5 and 7, MeC*H*OH), 3.1–3.3 (1 H, br s, OH), 2.47 (1 H, d, *J* 7.5, C*H*CHOH), 1.9–2.3 (1 H, m, PCH), 1.45 (3 H, s, MeC), 1.0–2.0 [8 H, br m, $(CH_2)_4$], 0.8 (3 H, t, *J* 6, *Me*CH_2) and 0.55 (3 H, d, *J* 7, *Me*CH) (Found: M$^+$ − EtO, 341.1651. $C_{21}H_{26}O_3P$ requires 341.1670); *m*/*z* 341 (17%, M − EtO) and 202 (100, Ph_2POH). No evidence for any other diastereoisomers was observed in the ^{1}H NMR spectrum of the crude product.

Epoxidation of syn-**7h**.—In the same way, a 7:1 mixture of the allylic alcohols[13c] *syn*- and *anti*-**7h** gave a mixture of the epoxy alcohols (2*RS*,5*SR*)-5-diphenylphosphinoyl-3,4-epoxydecan-2-ol (3.40 g) which co-ran on TLC. Recrystallisation of this crude product (EtOAc–hexane) gave a white solid (2.4 g, 65%). Comparison of the signals at δ 0.80 in the ^{1}H NMR spectrum showed that this was a *ca.* 4:1 mixture. Further recrystallisation (EtOAc–hexane) gave, eventually, a low yield of the minor (2RS,3RS,4SR,5RS)-*diastereoisomer* as a white crystalline solid, m.p. 117–118 °C (from EtOAc–hexane); R_F(EtOAc) 0.20; ν_{max}/cm^{-1} 3350 (OH), 1447 (P–Ph) and 1184 (P=O); δ_H(100 MHz; $CDCl_3$) 7.3–7.9 (10 H, m, Ph_2PO), 3.47 (1 H, dq, *J* 4 and 6, C*H*OH), 3.15 (1 H, dt, *J* 8 and 2, C*H*CHP), 2.45 (1 H, dd, *J* 2 and 4, C*H*CHOH), 2.18 (1 H, m, PCH), 1.0–1.9 [8 H, m, $(CH_2)_4$], 0.85 (3 H, d, *J* 6, CH*Me*) and 0.78 (3 H, t, *J* 7, CH_2Me) (Found: M$^+$, 372.1853. $C_{22}H_{29}O_3P$ requires *M*, 372.1859); *m*/*z* 372 (0.3%, M$^+$), 327 (0.4, M − MeCHOH), 257 (43), 219 (22, $Ph_2PO_2H_2$), 202 (100, Ph_2POH) and 201 (70, Ph_2PO). The mother liquor from the second recrystallisation gave a 7:1 mixture of the (2*RS*,3*SR*,4*RS*,5*RS*)- and the major (2*RS*,3*RS*,4*SR*,5*RS*)-diastereoisomers as an oil. The major (2*RS*,3*RS*,4*SR*,5*RS*)-diastereoisomer had R_F(EtOAc) 0.2; ν_{max}/cm^{-1} 3600 and 3350 (OH), 1447 (P–Ph) and 1185 (P=O); δ_H(100 MHz; $CDCl_3$) 7.4–7.9 (10 H, m, Ph_2PO), 3.52 (1 H, distorted quintet, *J ca.* 6, C*H*OH), 3.10 (1 H, ddd, *J* 9, 5 and 3, C*H*CHP), 2.87 (1 H, br d, *J* 6, C*H*CHOH), 1.1–2.4 [9 H, m, $CH(CH_2)_4$], 1.21 (3 H, d, *J* 6, CH*Me*) and 0.80 (3 H, t, *J* 7, CH_2Me). Oxidation of a portion (0.34 g) of the crude epoxidation product gave a 7:3 mixture of diastereoisomeric epoxy ketones. This indicates a 2.7:1 stereoselectivity in the epoxidation of *syn*-**7h**.

Epoxidation of anti-**7h**.—In the same way, the allylic alcohol[13c] *anti*-**7h** (3.56 g, 10 mmol) gave a white solid (2*RS*,5*SR*)-5-diphenylphosphinoyl-3,4-epoxydecan-2-ol(3.40g, 95%). Fractional recrystallisation of a portion (2.04 g) of this crude product gave the separate epoxide diastereoisomers. The less soluble (2RS,3RS,4RS,5SR)-*diastereoisomer* (1.0 g, 45%) was a white crystalline solid, m.p. 163–164 °C (from EtOAc); R_F(EtOAc) 0.2; ν_{max}/cm^{-1} 3250 (OH), 1440 (P–Ph) and 1182 (P=O); δ_H(100 MHz; $CDCl_3$) 7.4–7.9 (10 H, m, Ph_2PO), 3.26 (1 H, dq, *J* 5.5 and 7, C*H*OH), 3.17 (1 H, dt, *J* 2 and 9.5, C*H*CHP) 2.38 (1 H, dd, *J* 2 and 5.5, C*H*CHOH), 2.13 (1 H, dq, *J* 3.5 and 9.5, PCH), 1.0–2.0 [8 H, m, $(CH_2)_4$], 0.83 (3 H, t, *J* 7, C*H*CH_2) and 0.78 (3 H, d, *J* 7, *Me*CH) (Found: M$^+$ − H, 371.1778. $C_{22}H_{28}O_3P$ requires *M* − H, 371.1776); *m*/*z* 371 (5%, M − H), 357 (22, M − Me), 354 (15, M − H_2O), 327 (12, M − EtO), 202 (100, Ph_2POH) and 201 (60, Ph_2PO). The more soluble (2RS,3SR,4SR,5SR)-*diastereoisomer* (0.70 g, 31%) was a white crystalline solid (contaminated with *ca.* 10% of the less soluble diastereoisomer), m.p. 132–133 °C (from hexane–20% EtOAc); R_F(EtOAc) 0.20; ν_{max}/cm^{-1} 3300 (OH), 1440 (P–PH) and 1178 (P=O); δ_H(100 MHz; $CDCl_3$) 7.4–7.9 (10 H, m, Ph_2PO), 3.81 (1 H, br quintet, *J* 6, C*H*OH), 2.15–2.25 and 2.92 (2 H, 2 × m, C*H*C*H*CHOH), 1.18 (3 H, d, *J* 6, *Me*CH), 1.0–2.4 (9 H, m) and 0.78 (3 H, t, *J* 7, *Me*CH_2) (Found: M − H, 371.1758, $C_{22}H_{28}O_3P$ requires 371.1776); *m*/*z* 372 (4%, M$^+$), 371 (5, M − H), 357 (10, M − Me), 327 (14, M − EtO), 202 (100, Ph_2POH) and 201 (80, Ph_2PO). To determine the epoxidation stereoselectivity, a portion of the crude epoxidation product was dissolved in acetone (15 cm^3) at 0 °C and Jones reagent (2.5 cm^3, 2.66 mol dm^{-3} in CrO_3, 6.5 mmol) was added in one portion with stirring to the solution. The resulting solution was allowed to warm to 10 °C over 30 min before being carefully poured into saturated aqueous $NaHCO_3$ (50 cm^3). The resulting solution was extracted with ether (100 cm^3). The ether fraction was washed with water (2 × 50 cm^3), dried ($MgSO_4$) and evaporated under reduced pressure to give an oil (340 mg, 92%). Comparison of the signals at δ 1.80 and 1.98 and also the signals due to the epoxide protons in the ^{1}H NMR spectrum showed this crude product to be a 9:7 mixture of the epoxy ketone diastereoisomers. The 10% impurity in the more soluble epoxy alcohol above was also determined by oxidation in a similar way.

Epoxidation of syn-**7i**.—In the same way, the allylic alcohol[8,13c] *syn*-**7i** (44.0 mg, 0.13 mmol) gave a crude product (47.6 mg, 106%) as an oil. The ^{1}H NMR spectrum of this material showed it to consist of a 81:19 mixture of the epoxide *syn*,*syn*-**8i** and the epoxide[4] *anti*,*anti*-**8i**. Analytical HPLC, eluting with $CHCl_3$–2% MeOH, showed it to consist of a 19:81 mixture of two compounds, retention times 10.1 and 15.4 min, respectively. Purification by HPLC, eluting with CH_2Cl_2–6% MeOH, gave *anti*,*anti*-**8i** (4.9 mg, 11%), retention time 15 min.

Also obtained was (2RS,3RS,4RS,5RS)-5-*diphenylphosphinoyl*-3,4-*epoxy*-6-*methylheptan*-2-*ol* syn,syn-**8i** (24.2 mg, 54%) as an oil, retention time 17 min (Found: M$^+$, 344.1565. $C_{20}H_{25}O_3P$ requires *M*, 344.1541); R_F(EtOAc) 0.04;

ν_{max}(neat)/cm^{-1} 3350 (OH), 1440 (PPh) and 1180 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H, m, Ph_2PO), 3.56 (1 H, qn, *J* 6.5, C*H*OH), 3.26 (1 H, ddd, *J* 8, 6 and 2.5, PCHC*H*O), 2.89 (1 H, d × fine m, *J* 6, OC*H*CHOH), 2.3 (1 H, m, C*H*Me_2), 2.2 (1 H, br s, OH), 2.06 (1 H, ddd, *J* 11, 8 and 3, PCH), 1.29 (3 H, d, *J* 7), 1.13 (3 H, d, *J* 7) and 1.08 (3 H, d, *J* 7) (CH*Me*$_2$ and HOCH*Me*); δ_C(100 MHz; $CDCl_3$) 134–128 (Ph_2PO), 67.8$^+$ (CHOH), 63.0$^+$ ($^3J_{PC}$ 12.3, OCHCHOH), 52.6$^+$ ($^2J_{PC}$ 3.7, PCH*C*HO), 46.7$^+$ ($^1J_{PC}$ 67.7, PCH), 27.1$^+$ ($^2J_{PC}$ 1.5, *C*HMe$_2$), 23.9$^+$ ($^3J_{PC}$ 12.4, CH*Me*$_A$Me$_B$), 19.6 (CHOH*Me*) and 19.2$^+$ ($^3J_{PC}$ 1.5, CHMe$_A$*Me*$_B$); *m/z* 344 (1%, M$^+$), 299 (6, M – C_2H_5O), 257 (48, $Ph_2POC_4H_8$), 219 (22, $Ph_2PO_2H_2$), 202 (70, Ph_2POH) and 201 (100, Ph_2PO).

Epoxidation of anti-**7i**.—In the same way, the allylic alcohol[8] *anti*-**7i** (63.4 mg, 0.19 mmol) gave a crude product (67.5 mg, 103%) as an oil, the ^{1}H NMR spectrum of which showed it to consist of a 53:47 mixture of the epoxides (2*RS*,3*SR*,4*RS*,5*SR*)-5-diphenylphosphinoyl-3,4-epoxy-6-methylheptan-2-ol *anti*,*syn*-**8i** *and* (2*RS*,3*RS*,4*SR*,5*SR*)-5-diphenylphosphinoyl-3,4-epoxy-6-methylheptan-2-ol *syn*,*anti*-**8i**. Analytical HPLC, eluting with $CHCl_3$–2% MeOH, showed it to consist of a 47:53 mixture of two compounds, retention times 10.1 and 12.2 min, respectively: R_F(EtOAc) 0.07 and 0.04; δ_H(400 MHz; $CDCl_3$) 7.9–7.4 (10 H$^{anti,anti\,+\,syn,anti}$, m, Ph_2PO), 3.79 (1 H^{syn,anti}, m, CHOH), 3.4–3.1 (1 H^{syn,anti} + 2 H^{anti,syn}, m), 2.88 (1 H^{syn,anti}, fine m, C*H*OCHOH), 2.4–2.2 (3 H^{anti,syn} + 2 H^{syn,anti}, m) and 1.8–0.7 (9 H$^{anti,anti\,+\,syn,anti}$, m, Me × 3).

Epoxidation of **7j**.—In the same way, the allylic alcohol[8] **7j** (45.4 mg, 0.159 mmol) gave a crude product (44.4 mg, 92%) as an oil, the ^{1}H NMR spectrum of which showed it to consist of a 29:71 mixture of epoxides (2*RS*,3*SR*,4*SR*)-4-diphenylphosphinoyl-2,3-epoxypentan-1-ol *syn*-**8j** and (2*RS*,3*SR*,4*RS*)-4-diphenylphosphinoyl-2,3-epoxypentan-1-ol *anti*-**8j**. Analytical HPLC, eluting with $CHCl_3$–2% MeOH, showed it to consist of a 71:29 mixture of two compounds, retention times 9 and 11 min; R_F(EtOAc – 2.5% MeOH) 0.12; δ_H(250 MHz; $CDCl_3$) 7.9–7.4 (10 H$^{syn\,+\,anti}$, m, Ph_2PO), 3.76 (1 H^{syn}, dd, *J* 13.0 and 4.0, C*H*$_A$H$_B$OH), 3.61 (1 H^{syn}, dd, *J* 13.0 and 4.4, CH$_A$*H*$_B$OH), 3.45 (1 H^{anti}, dd, *J* 13.0 and 3.0, C*H*$_A$H$_B$OH), 3.3–3.0 (2 H$^{syn\,+\,anti}$, m), 2.57 (1 H^{anti}, fine m, PCHC*H*O), 2.21 (1 H$^{anti\,+\,syn}$, m, PCH), 1.38 (3 H^{anti}, dd, *J* 16.5 and 7, Me) and 1.16 (3 H^{syn}, dd *J* 16.0 and 7.5, Me).

Epoxidation of **7k**.—In the same way, the allylic alcohol[8] **7k** (66.5 mg, 0.221 mmol) gave a crude product (64.2 mg, 92%) as an oil, R_F(EtOAc) 0.23, the ^{1}H NMR spectrum of which showed it to consist of a 54:46 mixture of the epoxides[4] *syn*-**8k** and *anti*-**8k**. Analytical HPLC, eluting with $CHCl_3$–2% EtOH, showed it to consist of a 47:53 mixture of two compounds, retention times 13 and 20 min.

Epoxidation of **7l**.—In the same way, the allylic alcohol[8] **7l** (73.4 mg, 0.214 mmol) gave a crude product (69.3 mg, 90%) as an oil, R_F(EtOAc) 0.31, the ^{1}H NMR spectrum of which showed it to consist of a 56:44 mixture of the epoxides[4] *syn*-**8l** and *anti*-**8l**. Analytical HPLC, eluting with $CHCl_2$–2% EtOH, showed it to consist of a 44:56 mixture of two compounds retention times 9 and 12 min.

Epoxidation of **7m**.—In the same way, the allylic alcohol[8] **7m** (158.9 mg, 0.51 mmol) gave a crude product (177 mg, 105%) as an oil, R_F(EtOAc–4% MeOH) 0.33, the ^{1}H NMR spectrum of which showed it to consist of a 73:27 mixture of the epoxide *syn*-**8m** and the epoxide[4] *anti*-**8m**. Purification by HPLC, eluting with CH_2Cl_2–6% MeOH, gave *anti*-**8m** (36.3 mg, 22%), retention time 18 min. Also obtained was (2RS,3SR,4SR)-4-*diphenylphosphinoyl*-2,3-*epoxy*-5-*methylhexan*-1-*ol* syn-**8m** (80.5 mg, 48%), as prisms, m.p. 126.5–128 °C (from EtOAc), retention time 22 min (Found: C, 68.7; H, 7.2; P. 9.5%; M$^+$, 330.1367. $C_{19}H_{23}O_3P$ requires C, 69.08; H, 7.02; P. 9.38%; *M*, 330.1384); R_F(EtOAc–4% MeOH) 0.33; ν_{max}($CDCl_3$)/cm^{-1} 3320 (OH), 1440 (PPh) and 1130 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 3.74 (1 H, dd, *J* 12.6 and 3, C*H*$_A$H$_B$OH), 3.63 (1 H, dd, *J* 12.6 and 4.3, CH$_A$*H*$_B$OH), 3.3 (1 H, br s, OH), 3.27 (1 H, ddd, *J* 9.3, 5.4 and 2.0, PCHC*H*O), 3.02 (1 H, fine m, OC*H*CH$_2$OH), 2.28 (1 H, d × septet, *J* 3.5 and 7.0, C*H*Me$_2$), 2.03 (1 H, ddd, *J* 9.4, 7.3 and 3.0, PCH), 1.08 (3 H, d, *J* 6.8, CH*Me*$_A$Me$_B$) and 1.02 (3 H, d, *J* 6.8, CHMe$_A$*Me*$_B$); δ_C(100 MHz; $CDCl_3$) 134–128 (Ph_2PO), 61.4$^-$ (CH_2OH), 59.3$^+$ ($^3J_{PC}$ 12.9, OCHCH$_2$OH), 51.7$^+$ (PCHCHO), 47.3$^+$ ($^1J_{PC}$ 67.8, PCH), 27.1$^+$ (*C*HMe$_2$), 23.8$^+$ ($^3J_{PC}$ 12.2, CH*Me*$_A$Me$_B$), and 19.2$^+$ (CHMe$_A$*Me*$_B$); *m/z* 330 (4%, M$^+$), 299 (6, Me – CH_2OH), 257 (68, M – CH_2OH – C_3H_6), 219 (34, $Ph_2PO_2H_2$), 202 (55, Ph_2POH) and 201 (100, Ph_2PO).

Epoxidation of **7n**.—In the same way, the allylic alcohol[8] **7n** (536.1 g, 1.513 mmol) gave a crude product, which was purified by flash chromatography, eluting with EtOAc and then EtOAc–5% MeOH, to yield a mixture of epoxides (3.32 g, 81%) as an oil. The ^{1}H NMR spectrum of this material showed it to consist of a 77:23 mixture of epoxide *syn*-**8n** and the epoxide[4] *anti*-**8n**. Further purification by HPLC, eluting with $CHCl_3$–3.5% MeOH, gave *anti*-**8n** (98.8 g, 18%), retention time 15 min. Also obtained was (2S,3R,4R)-4-*cyclohexyl*-4-*diphenylphosphinoyl*-2,3-*epoxybutan*-1-*ol* syn-**8n** (311.1 g, 56%) as a foam, retention time 17 min (Found: M + H, 371.1808. $C_{22}H_{27}O_3P$ requires *M* + H, 371.1776); R_F(EtOAc–2.5% MeOH) 0.29; ν_{max}($CHCl_3$)/cm^{-1} 3350, OH), 1440 (PPh) and 1160 (P=O); δ_H(250 MHz; $CDCl_3$) 7.9–7.3 (10 H, m, Ph_2PO), 3.89 (1 H, dd, *J* 13 and 1.5, C*H*$_A$H$_B$OH), 3.63 (1 H, dd, *J* 13 and 4.5, CH$_A$*H*$_B$OH), 3.32 (1 H, ddd, *J* 9, 5 and 2, PCHC*H*O), 3.04 (1 H, fine, m, OC*H*CH$_2$OH) and 2.2–1.0 (12 H, m, ring and PCH); δ_C(100 MHz; $CDCl_3$) 134–128 (Ph_2PO), 61.2$^-$ (CH_2OH), 59.2$^+$ ($^3J_{PC}$ 8.5, OCHCH$_2$OH), 52.1$^+$ ($^2J_{PC}$ 3.7, PCH*C*HO), 47.3$^+$ ($^1J_{PC}$ 67.0, PCH), 37.3$^+$ ($^2J_{PC}$ 1.5, PCH*C*HCH$_2$), 34.3$^-$ [$^3J_{PC}$ 11.0, PCHCH(*C*H$_2$)$_A$(CH$_2$)$_B$], 30.0$^-$ [$^3J_{PC}$ 2.2, PCHCH(CH$_2$)$_A$(*C*H$_2$)$_B$] and 26.9$^-$, 26.6$^-$ and 26.0$^-$ [(CH$_2$)$_3$]; *m/z* (+FAB) 371 (100%, M + H), 219 (42, $Ph_2PO_2H_2$) and 201 (60, Ph_2PO).

Epoxidation of anti-**12a**.—In the same way, *anti*-**12a** (171.1 mg, 0.521 mmol) gave, after filtration through a short column of silica, eluting with EtOAc, a crude product (190 mg). Analytical HPLC showed this to contain a 68:32 mixture of epoxides[4] *anti*,*syn*-**13a** and *anti*,*anti*-**13a**. Purification of some of this material by HPLC, eluting with $CHCl_3$–2.5% MeOH, gave separately the epoxides *anti*,*anti*-**13a** (34.9 mg) and *anti*,*syn*-**13a** (73.3 mg).

Epoxidation of syn-**12a**. In the same way, *syn*-**12a** (104.6 mg, 0.319 mmol; 80% ee) gave, after filtration through a short column of silica, eluting with EtOAc, a crude product (120 mg), analytical HPLC of which showed it to contain a 72:28 mixture of the epoxides[4] *syn*, *syn*-**13a** and *syn*,*anti*-**13a**. Purification of some of this material by HPLC, eluting with $CHCl_3$–2.5% MeOH, gave separately the epoxides *syn*,*anti*-**13a** (10.0 mg) and *syn*,*syn*-**13a** (26.9 mg).

Epoxidation of anti-**12b**.—In the same way, *anti*-**12b** (58 mg, 0.156 mmol) gave a 56:44 mixture (by ^{1}H NMR) of the epoxides[4] *anti*,*syn*-**13b** and *anti*,*anti*-**13b** (54.4 mg, 90%).

Epoxidation of syn-**12b**.—In the same way, *syn*-**12b** (56 mg, 0.150 mmol) gave a 56:44 mixture (by ^{1}H NMR) of the epoxides[4] *syn*,*syn*-**13b** and *syn*,*anti*-**13b** (45.6 mg, 78%).

Epoxidation of anti-**12c**.—In the same way, *anti*-**12c** (32.5 mg, 0.10 mmol) gave a 56:44 mixture (by ^{1}H NMR) of the epoxides (2RS,3SR,4SR,5SR)-4-*diphenylphosphinoyl*-2,3-*epoxyheptane*-1,5-*diol* anti,syn-**13c** and (2RS,3SR,4RS,5RS)-4-*diphenylphosphinoyl*-2,3-*epoxyheptane*-1,5-*diol* anti,anti-**13c** (30.0 mg, 90%) (Found: M − OH, 329.1335. $C_{19}H_{23}O_4P$ requires *M* − OH, 329.1307); R_F(EtOAc) 0.17; δ_H(400 MHz; $CDCl_3$) 7.9–7.4 (10 $H^{anti,anti+anti,syn}$, m, Ph_2PO), 4.08 (1 $H^{anti,anti+anti,syn}$, CHOH), 3.72 (1 $H^{anti,syn}$, dd, *J* 11.5 and 3.0, CH_AH_BOH), 3.60 (1 $H^{anti,syn}$ + 1 $H^{anti,anti}$, m), 3.39 (1 $H^{anti,syn}$, ddd, *J* 9.2, 4.8 and 1.9, PCHC*H*O), 3.23 (1 $H^{anti,anti}$, dd, *J* 12.8 and 2.3, CH_AH_BO), 3.05 (1 $H^{anti,anti}$, fine m, OC*H*CH_2O), 2.96 (1 $H^{anti,anti}$, dd, *J* 12.8 and 4.8, CH_AH_BO), 2.31 (1 $H^{anti,syn}$, fine m, OC*H*CH_2O), 2.2–1.4 (3 $H^{anti,anti+anti,syn}$, CH_2Me), 0.90 and 0.88 (3 $H^{anti,anti+anti,syn}$, t × 2, Me × 2).

Epoxidation of syn-**12c**.—By the general procedure above, *syn*-**12c** (34.8 mg, 0.11 mmol) gave a 82:18 mixture (by ^{1}H NMR) of the epoxides (2*RS*,3*SR*,4*RS*,5*SR*)-4-diphenylphosphinoyl-2,3-epoxyheptane-1,5-diol *syn,syn*-**13c** and (2*RS*,3*SR*,-4*SR*,5*RS*)-4-diphenylphosphinoyl-2,3-epoxyheptane-1,5-diol *syn,anti*-**13c** (35.1 mg, 96%); R_F(EtOAc) 0.17; δ_H(400 MHz, $CDCl_3$) 7.8–7.4 (10 $H^{syn,anti+syn,syn}$, m, Ph_2PO), 4.0 (2 $H^{syn,anti+syn,syn}$, m, C*H*OH), 3.73 (1 $H^{syn,syn}$, dd, *J* 12.0 and 3.0, CH_AH_BOH), 3.54 (1 $H^{syn,syn}$, dd, *J* 12.0 and 4.2, CH_AH_BOH), 3.30 (1 $H^{syn,anti}$, d × fine m, *J* 10.4, PCHC*H*O), 3.20 (1 $H^{syn,anti}$, dd, *J* 12.5 and 1.5, CH_AH_BOH), 3.12 (1 $H^{syn,syn}$, fine m, PCHC*H*O), 2.88 (1 $H^{syn,anti}$, dd, *J* 12.5 and 4.0, CH_AH_BOH), 2.76 (1 $H^{syn,syn}$, m, PCHC*H*O), 2.47 (1 $H^{syn,anti}$, m, PCHC*H*O), 2.42 (1 $H^{syn,syn}$, m, PCH), 2.30 (1 $H^{syn,anti}$, dt, *J* 3.5 and 9.6, PCH), 1.8–1.5 (2 $H^{syn,anti+syn,syn}$, m, CH_2Me) and 1.0–0.8 (3 $H^{syn,anti+syn,syn}$, t × 2, Me).

Epoxidation of **7b** *with* Bu^{t}OOH–Ti(OPr^i)$_4$.—Activated 4 Å powdered molecular sieves (*ca.* 0.5 g) were added to a stirred solution of the allylic alcohol **7b** (100 mg, 0.35 mmol) in dry dichloromethane (20 cm^3), and the suspension stirred under nitrogen at room temperature for 1–3 h. Meanwhile, *tert*-butyl hydroperoxide (3 mol dm^{-3} solution in 2,2,4-trimethylpentane; 1 cm^3) was placed in a separate vial over activated 4 Å powdered molecular sieves and allowed to stand for 1–3 h. The flask containing the allylic alcohol was cooled to between −16 and −20 °C and titanium tetraisopropoxide (0.10 cm^3, 0.34 mmol, 1.0 equiv.) was added. The mixture was stirred at *ca.* −20 °C for 30–40 min. A portion of the dried solution of *tert*-butyl hydroperoxide (0.25 cm^3, 0.75 mmol, 2.1 equiv.) was added dropwise, and the reaction stirred at −20 °C for 18 h. Water (40 cm^3) was added to the mixture which was then stirred vigorously as it was allowed to warm to room temperature. The aqueous layer was extracted with dichloromethane or ethyl acetate (3 × 40 cm^3) and the combined organic fractions were washed with brine, dried (Na_2SO_4) and evaporated under reduced pressure to yield a crude product. This was purified by flash chromatography, eluting with CH_2Cl_2–6% MeOH, to yield the epoxy alcohol **8b** (64 mg, 60%).

General Procedure for the VO(acac)$_2$*-Catalysed Epoxidation of Allylic Alcohols.*—*tert*-Butyl hydroperoxide (3 mol dm^{-3} solution in 2,2,4-trimethylpentane; 0.7 cm^3, 2 mmol, 2 equiv.) was added dropwise to a stirred suspension of the allylic alcohol (1 mmol), vanadylbis(acetoacetate) (6 mg, 2.5 mol%) and 4 Å molecular sieves (a spatula end) in dry dichloromethane (10 cm^3) at 0 °C under nitrogen. The stirred red mixture was allowed to warm to room temperature over 24 h, after which it was concentrated and passed through a short column of silica, eluting with EtOAc and then EtOAc–12% MeOH. The appropriate fractions were evaporated under reduced pressure to give a partially purified product.

Epoxidation of **7d**.—By the general method described above, the allylic alcohol **7d** (237.5 mg, 0.829 mmol), gave a product (38.2 mg, 15%), the ^{1}H NMR spectrum of which showed it to contain a 62:38 mixture of the *anti* and *syn* epoxides *anti*-**8d** and *syn*-**8d**.

Epoxidation of **7e**.—By the general method described above, the allylic alcohol **7e** (98.9 mg, 0.329 mmol), gave a product (100.95 mg, 97%), the ^{1}H NMR spectrum of which showed it to consist solely of the *anti* epoxide *anti*-**8e**.

Epoxidation of **7f**.—By the general method described above, the allylic alcohol **7f** (201.9 mg, 0.566 mmol), gave a product (189.6 mg, 90%), the ^{1}H NMR spectrum of which showed it to consist of an 84:16 mixture of *syn* and *anti* epoxides *syn*-**8f** and *anti*-**8f**.

Epoxidation of **7g**.—By the general method described above, the allylic alcohol **7g** (178 mg, 0.5 mmol) gave no epoxides but starting material (80%) and a low yield (16%) of 5-diphenylphosphinoyldec-3-en-2-one.

Epoxidation of **7m**. By the general method described above, the allylic alcohol **7m** gave, after 42 h, and after flash chromatography, eluting with $CHCl_3$–2% MeOH, material (39 mg, 20%) containing the aldehyde[4] **14** and a compound tentatively identified as 4-diphenylphosphinoyl-5-methylhex-2-enoic acid **15**; δ_H(250 MHz; $CDCl_3$) (signals due to **15**) 8.0–7.3 (10 H, m, Ph_2PO), 7.06 (1 H, m, C*H*=CHCO$_2$H), 5.70 (1 H, dd, *J* 16 and 4.5, C*H*CO$_2$H), 3.08 (1 H, ddd, *J* 11.0, 9.0 and 3.5, CHP), 2.30 (1 H, m, C*H*Me$_2$), 1.05 (3 H, d, *J* 6.8, CH*Me*$_A$Me$_B$) and 0.93 (3 H, d, *J* 6.8, CHMe$_A$*Me*$_B$).

Also obtained were *anti*-**8m** (29 mg, 14%) and starting material **7m** (40 mg, 30%).

Epoxidations with H_2O_2–NaOH.—*Epoxidation of the enone* **16a**. 30% Aqueous NaOH (0.1 cm^3, 0.75 mmol) was added dropwise to a stirred solution of the enone[13c] **16a** (552 mg, 1.5 mmol) and hydrogen peroxide (100 volume solution; 0.5 cm^3, 4.2 mmol) in methanol (3 cm^3) at room temperature. The red solution was heated under reflux for 4 h under nitrogen, after which it was cooled, diluted with water (20 cm^3) and extracted with EtOAc (3 × 10 cm^3). The combined extracts were dried (Na_2SO_4) and evaporated under reduced pressure to give an oil (0.55 g, 99%) which was shown (NMR) to be a 4:6 mixture of *E*- and *Z*-**16a**. Flash chromatography on silica eluting with EtOAc–hexane (1:1) of this mixture (183 mg) gave (*Z*)-5-*diphenylphosphinoyl*-4-*methyldec*-3-*en*-2-*one* *Z*-**16a** (65 mg, 35%) as an oil (Found: M$^+$, 368.1907. $C_{23}H_{29}O_2P$ requires *M*, 368.1905); R_F(EtOAc) 0.46; ν_{max}($CDCl_3$)/cm^{-1} 1675 and 1603 (enone), 1439 (PPh) and 1185 (P=O); δ_H(100 MHz; $CDCl_3$) 8.3–7.3 (10 H, m, Ph_2PO), 6.07 (1 H, br s, C=CH), 5.54 (1 H, ddd, J_{PH} 11, J_{HH} 8, 3, PCH), 2.03 (3 H, dd, J_{PH} 3, J_{HH} 1.5, *Me*C=CH), 1.99 (3 H, s, MeCO), 1.0–2.0 [8 H, m, $(CH_2)_4$] and 0.78 (3 H, t, *J* 6, *Me*CH_2); *m*/*z* 368 (5%, M$^+$), 325 (14, M − Ac), 219 (100, $Ph_2PO_2H_2$), 202 (65, Ph_2POH), 201 (70, Ph_2PO) and 166 (35, M − Ph_2PO).

Epoxidation of the Enone **16b**.—By the same method, the enone **16b** gave a mixture of products shown (NMR) to contain about 40% **16b** and no trace of epoxy ketone.

Epoxidation of the Enone **16a** *with* NaOCl–*Pyridine*.—14% Aqueous sodium hypochlorite (0.34 cm^3, 0.64 mmol) was added dropwise to a stirred solution of the enone **16a** (235 mg, 0.64 mmol) in pyridine (8 cm^3) at 0 °C. After 10 min saturated aqueous NH_4Cl and then water (50 cm^3) were added to the

solution which was then extracted with dichloromethane (3 × 40 cm^3). The combined extracts were washed with water (40 cm^3), dried (Na_2SO_4) and evaporated under reduced pressure to give an oily mixture of compounds shown (NMR) to contain no epoxy ketones. Chromatography on silica eluting with EtOAc followed by HPLC gave 3-diphenylphosphinoyloctan-2-one (60 mg, 30%), R_F(EtOAc) 0.26.

X-Ray Structure Analysis of anti-**2e**.—Molecular formula $C_{23}H_{31}O_2P$ (M_r = 370.5), crystals grown from acetone–hexane as long needles, crystal size 0.4 × 0.1 × 0.05 mm^3, monoclinic, space group $C2/c$, a = 39.63(1), b = 9.687(3), c = 11.592(5) Å, β = 100.75(3)°, V = 4372(2) $Å^3$, Z = 8, D_x = 1.126 g cm^{-3}, μ (Cu-Kα) = 1.20 mm^{-1}, F(000) = 1600, 3000 unique reflections collected on a Syntex $P2_1$ diffractometer, $2\theta_{max}$ = 115°, structure solved by inspection of a sharpened Patterson function (P atom) followed by tangent expansion, hydrogen atoms located in difference electron-density maps, least-squares refinement (on F^2) of 236 parameters with SHELXL-93,[22] all non-hydrogen atoms anisotropic, H atoms isotropic with fixed individual displacement parameters [U(H) = 1.2 U_{eq}(C) and 1.5 U_{eq}(C) for methyl groups, respectively] using a riding model, bond lengths and angles within the pentyl group slightly restrained due to high thermal motion, refinement converged at wR = 0.211 corresponding to R = 0.080 for 1541 observed reflections with $|F| > 4\sigma(F)$, S = 1.036, $\Delta\rho$ in final difference map within 0.29 and −0.28 e/$Å^3$, all relevant data deposited with the Cambridge Crystallographic Data Base.*

X-Ray Structure Analysis of anti,syn-**8g**.—Molecular formula $C_{23}H_{31}O_3P$ (M_r = 386.5), crystals grown from acetone–water as long needles, crystal size 0.4 × 0.15 × 0.05 mm^3, triclinic, space group $P\text{-}1$, a = 19.157(3), b = 11.637(2), c = 9.893(1) Å, α = 93.81(1)°, β = 90.05(1)°, γ = 94.85(1)°, V = 2192.6(6) $Å^3$, Z = 4, D_x = 1.171 g cm^{-3}, μ (Cu-Kα) = 1.26 mm^{-1}, F(000) = 832, 5988 unique reflections collected on a Syntex $P2_1$ diffractometer, $2\theta_{max}$ = 115°, structure solved by inspection of a sharpened Patterson function (P atoms) followed by tangent expansion, hydrogen atoms located in difference electron-density maps, least-squares refinement (on F^2) of 491 parameters with SHELXL-93,[22] all non-hydrogen atoms anisotropic, H atoms isotropic with fixed individual displacement parameters [U(H) = 1.2 U_{eq}(C) and 1.5 U_{eq}(C or O) for methyl and hydroxyl groups, respectively] using a riding model, refinement converged at wR = 0.173 corresponding to R = 0.064 for 3770 observed reflections with $|F| > 4\sigma(F)$, S = 0.978, $\Delta\rho$ in final difference map within 0.35 and −0.29 e/$Å^3$, all relevant data deposited with the Cambridge Crystallographic Data Base.

The crystal packing is stabilized by two intermolecular hydrogen bonds O(21)–H···O(21) (molecule 1) and O(21′)–H···O(34′) (molecule 2) with O···distances of 2.989(7) and 2.878(4) Å and O–H···O angles of 134(5) and 171(6)°, respectively, across inversion centres, such that dimeric complexes are formed. The conformations of the two independent molecules differ only in the torsion angles of the pentyl group and agree well with that of *anti*-**2e**. In all three molecules, the epoxy O atom is antiperiplanar to both C(1) and the phosphorus atom, and the P=O bond, which is antiperiplanar to H(C-5), is situated in the plane of the two phenyl rings.

* For details, see 'Instructions for Authors' (1994), *J. Chem. Soc., Perkin Trans. 1, 1994, Issue 1.*

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