Titanium as a Regio- and Stereo-selective Control Element in the Reaction of α-Alkoxyallylic Phosphine Oxide Anions with Carbonyl Compounds

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A general method is described for directing the condensation of α-methoxyallylphosphine oxide anions (2) with aldehydes, preferentially at the α-position of the allyl system. The procedure, which employs the formation of the titanium ate complex, yields pure diastereoisomers with high stereoselectivity, and these can be used in Horner-Wittig reactions to provide an efficient and convenient synthesis of conjugated methoxydienes of defined geometry. Under the same conditions, acyl halides yield γ-adducts.

There is considerable current interest in the synthetic applications of allylic carbanions.[1] One of the most fascinating aspects of their chemistry, the regioselectivity of their reactions, has received considerable attention.[2] In particular, control of α versus γ substitution by electrophiles in heteroatom-stabilized allylic anions appears to depend upon the complex interplay between the nature of the heteroatom(s),[3] charge delocalization,[4] steric effects,[5] solvation,[6] the type of electrophile,[7] and the counterion.[8] These difficulties are illustrated by the observation that halides and carbonyl systems often exhibit opposite regioselectivities.[9]

In this context a wealth of practical synthetic methods has evolved around the use of phosphorus-stabilized carbanions for carbon-carbon bond construction. However, no definitive treatment of the regioselectivity of the anions of α-oxygenated allylphosphine oxides with electrophiles has been presented. Preliminary studies,[10] and work carried out in this study, have indicated that reaction of lithium anions (2) of α-methoxyallylphosphine oxides (1a—c) with aldehydes proceeds with predominant γ-regioselectivity to give compound (3) rather than compound (5) (see Scheme 1). These anions have been found to react with other electrophiles[11] to produce γ-adducts which are related to phosphonic acid derivatives recently developed as homoenolate equivalents.[12] On the other hand it

has been shown[13] that the anion of oxide (1d) undergoes reaction with carbonyl compounds at the α-position with subsequent production of methoxydienes (6). No intermediate β-hydroxyalkylphosphine oxides were observed in those reactions and the ease of the *in situ* Wittig-Horner elimination[14] step meant that stereoselective diene preparation was difficult to achieve.

We have been seeking a simple and synthetically useful method for controlling the α-regiochemistry of carbonyl additions to these anions. It appeared to us that titanium(IV) isopropoxide[15] might react with anion (2) at the γ-site, where it would undergo preferential co-ordination to the methoxy group, to produce the corresponding -ate complex (4). Subsequent carbon-carbon bond formation would then take place at the α-position. This proved to be practical, and we now report that titanium ate complexes (4) of α-methoxyallylic phosphine oxides, generated *in situ* from the corresponding lithium anions, condense with aldehydes exclusively at the α-position to produce the alcohols (5). These are generally stable, crystalline compounds, easily separated into pure diastereoisomers by chromatography (flash column) and crystallisation. Subsequent elimination of the water soluble $Ph_2PO^-_2$ from the anions of these diastereoisomeric β-hydroxy-α-alkoxyphosphine oxides provides a method for stereospecific alkene synthesis.
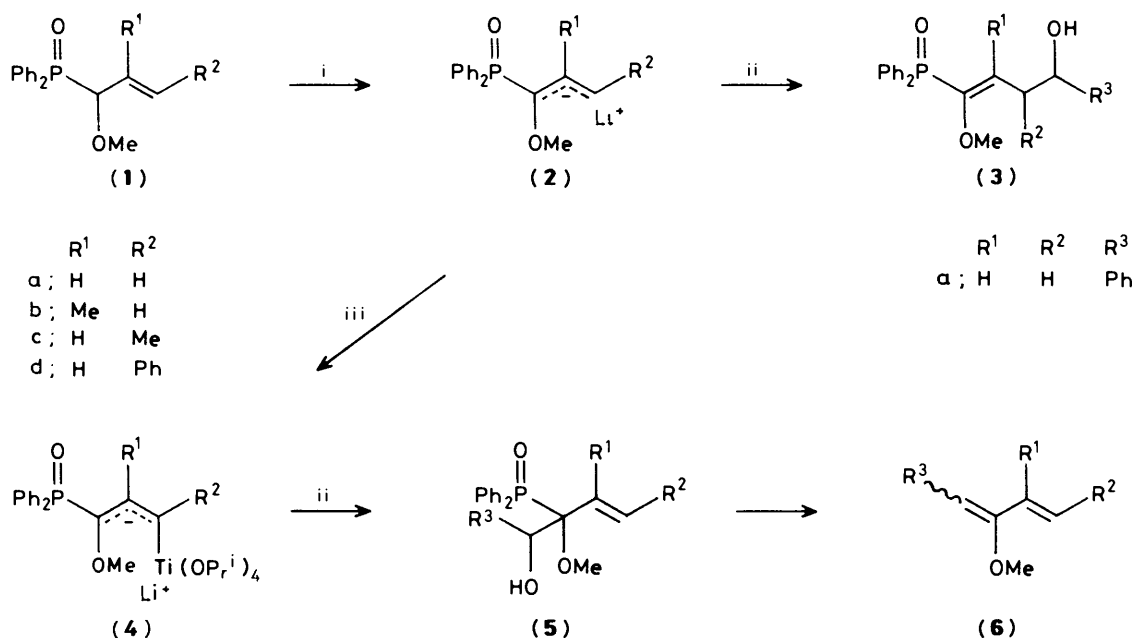
Scheme 1. *Reagents:* i, BuLi or LDA; ii, R^3CHO then H_2O; iii, $Ti(OPr^i)_4$

Results and Discussion

α-Methoxyallyldiphenylphosphine oxides (1) were prepared in a one-pot sequence from chlorodiphenylphosphine and the dimethyl acetal of the appropriate α,β-unsaturated aldehyde, in yields >75%, by a modification of the method earlier reported by Miller et al.[16] Preparative details, and extensive spectroscopic evidence for the structure assignments for these phosphine oxides have been presented elsewhere.[13] The corresponding anions (2) were formed readily from these oxides by their treatment with either lithium di-isopropylamide (1.1 equiv., THF, −78 °C) or with butyl-lithium (1.1 equiv. −78 °C).

With benzaldehyde, lithium anions (2a—c) reacted regio-

Moreover, while the methyl group in (1c) was observed at δ 1.69 as a double doublet with a coupling constant $^5J_{PH}$ 6 Hz, in product (3c) that methyl group appeared at δ 1.08 as a doublet with no observable long-range phosphorus coupling.[19]

On the other hand, lithio anions (2a,c), when treated first with titanium(IV) isopropoxide and then with benzaldehyde, yielded, in addition to the γ-adducts (3a,c), significant amounts isomers (S,R)—(5) and (7) and (R,R)—(5) and (7)* (see Scheme 2). Exchanging the lithium cation with titanium tri-isopropoxide (from chlorotitanium tri-isopropoxide) gave better yields of the α-products, but the best results, were achieved on transmetallation with dichlorotitanium di-isopropoxide, when
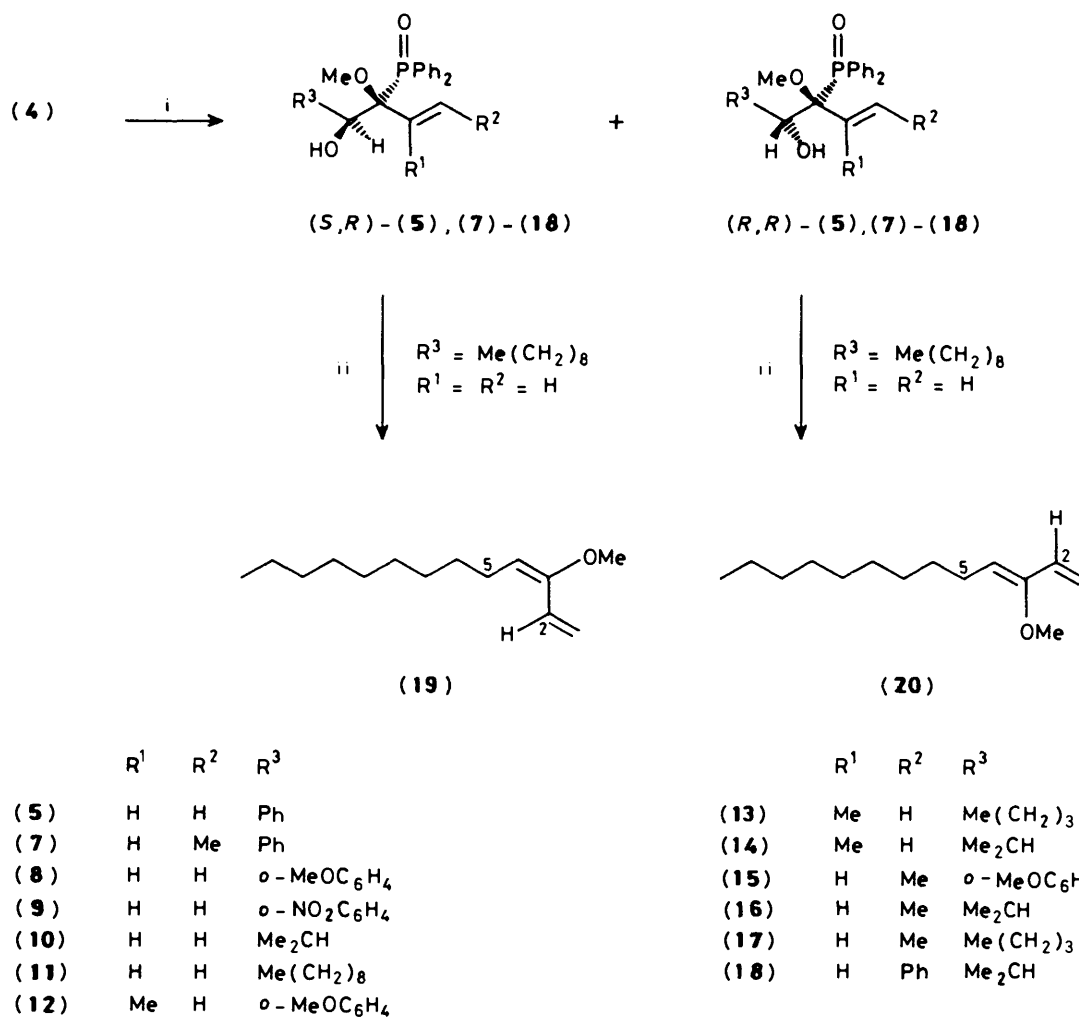
Scheme 2. Reagents: i, R³CHO; ii, KOBuᵗ in THF

specifically to provide the γ-adducts (3a—c) as the E-isomers, thus confirming the trend observed in earlier work.[10] These products were assigned as γ-adducts on the basis of their ¹H and ¹³C n.m.r. spectra. Typically, the starting allylphosphine oxides (1) displayed in their ¹H n.m.r. a singlet at δ 3.25 for the methoxy protons, while in the products (3) these protons appeared at δ 3.4, a downfield shift characteristic of the transition from an ether to an enol ether.[17] Further evidence for the assignments came from the observed phosphorus-hydrogen coupling constants. Thus coupling constants J_{PH} 10 Hz in (3a,c) were indicative of a hydrogen atom cis to the phosphorus entity.[18]

>10:1 stereoselectivity of (S,R):(R,R) was obtained with aromatic aldehydes (see Table 1). In general, slightly poorer stereoselectivity was achieved with aliphatic aldehydes, although in the case of (1b) there was still a predominance of the (S,R)-product, even when R³ was aliphatic.
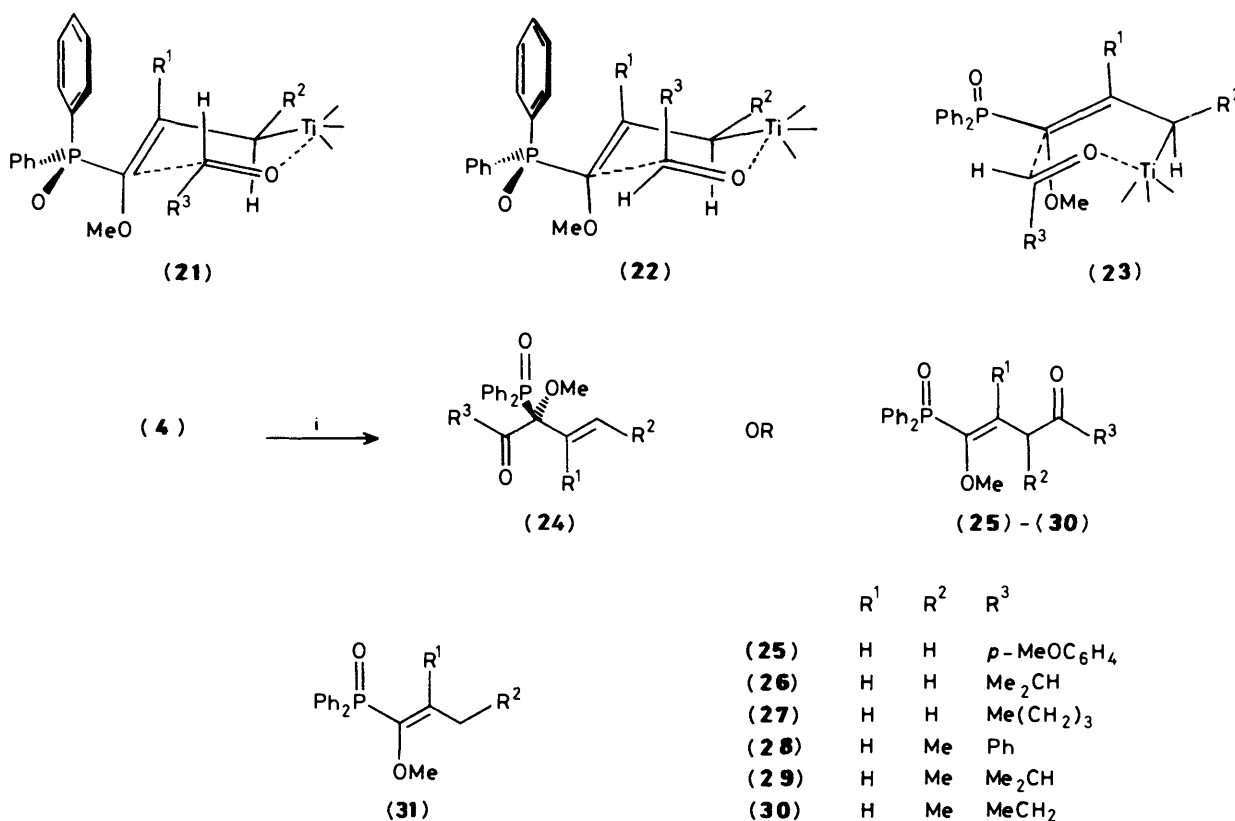
Products (5), and (7)—(18) were assigned as α-adducts on the

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* The diastereoisomers defined (S,R) and (R,R) are in fact racemic mixtures although only one enantiomer is drawn for each enantiomeric pair, i.e., the compound designated (R,R) is in fact a racemic mixture of the (R,R) and (S,S) enantiomers.

Table 1. Reaction of α-methoxyallylic phosphine oxide titanium ate complexes with aldehydes

Substrate	Additive[a]	Aldehyde (R³)	Regioselectivity[b]	α-Adduct	Ratio[c] S,R:R,R	Total yield of mixture (%)
(1a)	None	Ph	γ			71
(1b)	None	Ph	γ			69
(1c)	None	Ph	γ			85
(1a)	Ti(OPr^i)$_4$	Ph	γ:α = 65:35	(5)	2.5:1	60
(1c)	Ti(OPr^i)$_4$	Ph	γ:α = 75:25	(7)	2.5:1	88
(1a)	TiCl(OPr^i)$_3$	Ph	α	(5)	3:1	70
(1a)	TiCl(OPr^i)$_3$	o-MeOC$_6$H$_4$	α	(8)	>10:1[d]	65
(1a)	TiCl(OPr^i)$_3$	o-NO$_2$C$_6$H$_4$	α	(9)	>10:1[d]	58
(1a)	TiCl$_2$(OPr^i)$_2$	Me$_2$CH	α	(10)	2.5:1	65
(1a)	TiCl$_2$(OPr^i)$_2$	Me(CH$_2$)$_8$	α	(11)	2.5:1	74
(1b)	TiCl$_2$(OPr^i)$_2$	o-MeOC$_6$H$_4$	α	(12)	>10:1[d]	65
(1b)	TiCl$_2$(OPr^i)$_2$	Me(CH$_2$)$_3$	α	(13)	>10:1[d]	74
(1b)	TiCl$_2$(OPr^i)$_2$	Me$_2$CH	α	(14)	>10:1[d]	60
(1c)	TiCl$_2$(OPr^i)$_2$	Ph	α	(7)	>10:1[d]	63
(1c)	TiCl$_2$(OPr^i)$_2$	o-MeOC$_6$H$_4$	α	(15)	>10:1[d]	56
(1c)	TiCl$_2$(OPr^i)$_2$	Me$_2$CH	α	(16)	1.5:1	65
(1c)	TiCl$_2$(OPr^i)$_2$	Me(CH$_2$)$_3$	α	(17)	1.5:1	72
(1d)	TiCl$_2$(OPr^i)$_2$	Me$_2$CH	α	(18)	1:1	63

[a] None indicates the normal reaction of the lithium anion without the additive. [b] Where only the entry α or γ appears, the crude reaction products were virtually a single regioisomer (≥95%) by n.m.r. [c] Yields of isolated purified products. [d] Only one diastereoisomer was isolated and purified.

(21)   (22)   (23)

(4) ——i——> (24)   OR   (25)-(30)

	R¹	R²	R³
(25)	H	H	p-MeOC$_6$H$_4$
(26)	H	H	Me$_2$CH
(27)	H	H	Me(CH$_2$)$_3$
(28)	H	Me	Ph
(29)	H	Me	Me$_2$CH
(30)	H	Me	MeCH$_2$

(31)

Scheme 3. *Reagent:* i, R³COCl

basis of spectral evidence. All compounds showed peaks at 3 200—3 400(OH), 1 430—1 435 (PPh), and 1 160—1 180 cm⁻¹ (P=O) in the i.r. In the ¹³C n.m.r. these compounds displayed the quaternary carbon as resonating in the range 80—90 p.p.m., with J_{PC} 85—90 Hz when the introduced group was aromatic, and J_{PC} 75—85 Hz, when that group was aliphatic. The stereochemistry about the double bond in the products was

assigned as (*E*) on the basis of the observed coupling constants of the alkenyl protons ($^3J_{HH}$ 16 Hz). The assignment of the stereochemistries of the (*S*,*R*)- and (*R*,*R*)-isomers was made by reference to the configuration of the dienes produced by Horner-Wittig elimination.

The relevant Horner-Wittig reactions were carried out by stirring a solution of the pure diastereoisomer in THF and

Table 2. Reaction of α-methoxyallylic phosphine oxide titanium ate complexes[a] with acyl halides

Substrate	Acyl halide (R³)	γ-Adduct	Yield [b] (%)
(1a)	p-MeOC₆H₄	(25)	75
(1a)	Me₂CH	(26)	72
(1a)	Me(CH₂)₃	(27)	74
(1c)	Ph	(28)	68
(1c)	Me₂CH	(29)	71
(1c)	MeCH₂	(30)	78

[a] TiCl₂(OPrⁱ)₂ as additive. [b] Yield of isolated product.

adding potassium t-butoxide in THF at room temperature. The potassium salt of diphenylphosphinic acid precipitated out almost immediately and t.l.c. showed the presence of only one isomer of the diene which was isolated in virtually quantitative yield. Typically, diastereoisomers (3R,4S)-(11) and (3R,4R)-(11) afforded dienyl ethers (19) and (20) respectively, as single isomers whose structures were confirmed by their n.m.r. spectra and in particular from difference n.O.e. experiments. In the product obtained from the (R,S)-alcohol, irradiation of the signal at δ_H 2.06 (5-H) resulted in a n.O.e. enhancement of 2-H, while in the other diene from the (R,R)-hydroxy compound no effect was observed at 2-H upon irradiation of 5-H. This effect defines the stereochemistry of (19) and (20) unambiguously, since only the stereoisomer (19) permits the proximity of 2-H and 5-H. The ability to isolate and purify the intermediate hydroxy compounds from α-attack of aldehydes on α-methoxyallylphosphine ylides can therefore be used to prepare pure isomers of conjugated methoxydienes of defined geometry (E,E)- from the (R,S)-diastereoisomer and (Z,E)- from the (R,R)-diastereoisomer. It is also interesting to note that these reactions establish the operational equivalence between α-methoxyallyldiphenylphosphine oxides and vinylacyl anion equivalents.[20] The fact that the diastereoisomeric hydroxy compounds can be isolated, despite the extremely facile nature of the Horner–Wittig elimination on addition of potassium t-butoxide, could be due to tight co-ordination between the titanium species and the methoxy oxygen.

The diastereoselectivities shown in Table 1 can be reasonably explained by considering a transition state of the type (21) in which it is assumed that the titanium group is bonded to the γ-position of the allylic system and in which the bulky phosphorus entity takes up an equatorial or pseudo-equatorial position. The alternative transition state (22) would then be destabilized relative to (21) by increase of the 1,3-interactions. Increased steric interaction due to the methyl group in (1b) presumably accounts for the predominance of the (R,S)-diastereoisomer when this phosphine oxide reacts with aliphatic aldehydes. If, as we have already assumed, titanium is complexed tightly to the O-methyl group, then the boat transition state (23) might be involved.

The possibility of extending the methodology to the synthesis of α-diphenylphosphinoyl ketones (24) by using acid chlorides instead of aldehydes, was next considered, particularly in view of the known methods available for the stereoselective reduction of such species.[21] To our surprise, repetition of the above conditions, employing acid chlorides as the electrophilic species, afforded the respective γ-adducts (25)—(30), as oils, in good to excellent yield (see Table 2, Scheme 3), after separation from traces of isomerized starting material (31) which presumably arises by γ-protonation of the titanium ate complex. The general pattern of the spectrum of each of these products was comparable to the spectra of the previously obtained γ-adducts. The methoxy singlet had moved downfield and the J_{PH} coupling

constant between the vinylic proton and the phosphorus group was between 8—9 Hz, indicating that the product was *trans*. Absorptions for the keto carbon atoms were observed in the ¹³C n.m.r., and in each case the α-carbon resonated in the region 150—155 p.p.m. with ¹J_{PC} 120—125 Hz, indicating that this carbon was vinylic. The remaining resonances confirmed the structural assignments.

Why the regioselectivity of the reaction of titanated anions (4) should change so completely on changing the electrophile from an aldehyde to an acyl halide is not immediately obvious. We suspect that the difference is due to steric effects (see Scheme 4); thus in the case of aldehydes the hydrogen atom attached to the
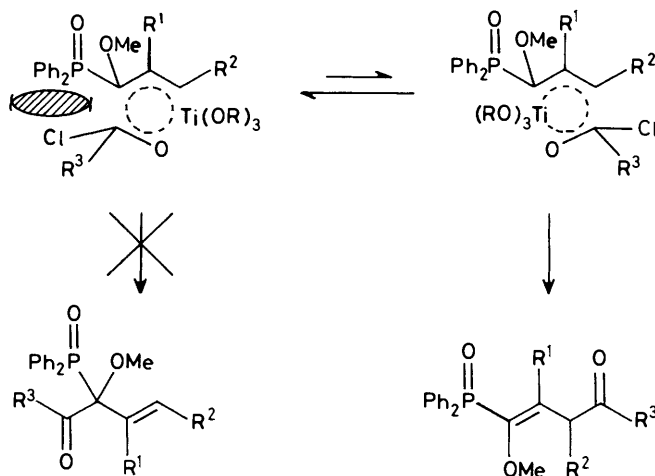
Scheme 4.

carbonyl group does not interfere greatly with the bulky phosphorus group, but with acyl halides the relatively large chlorine atom may prevent close approach to the hindered α-position.

Experimental

M.p.s were determined on an Electrothermal melting point apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 298 machine, and are for Nujol mulls. Mass spectra were determined with an A.E.I. MS9 Spectrometer. N.m.r. spectra were recorded on either Varian EM360 (60 MHz) or Bruker HX90 (90 MHz) (for ¹H) and Bruker WP 60 F.T. (15.1 MHz) (for ¹³C) spectrometers. Unless otherwise stated the samples were dissolved in CDCl₃ and the chemical shifts are expressed in p.p.m. downfield from tetramethylsilane as internal standard.

General Procedures for the Generation of the Lithium Anion of α-Methoxyallyldiphenylphosphine Oxides.—Method (a). A solution of the α-methoxyallyldiphenylphosphine oxide in anhydrous THF in a flame dried flask under a positive pressure of nitrogen was cooled to −78 °C. Butyl-lithium (1.1—1.2 mol equiv.) in hexane was added slowly and the resulting solution stirred at this temperature for 30 min.

Method (b). A solution of di-isopropylamine (1.1—1.2 mol equiv.) in anhydrous THF in a flame dried flask under a positive pressure of nitrogen was cooled to −78 °C. Butyl-lithium (1.1—1.2 mol equiv.) in hexane was added slowly and the resulting solution stirred at this temperature for 15 min. The α-methoxyallyldiphenylphosphine oxide in anhydrous THF was then added slowly to the LDA solution which was stirred for a further 30 min at −78 °C.

Dichlorotitanium Di-isopropoxide.—Titanium(IV) iso-propoxide (0.75 mol) was added slowly under nitrogen to a stirred solution of titanium tetrachloride (0.75 mol) in carbon tetrachloride (500 ml) at 0 °C. The solution was allowed to warm to 20 °C and stirred for 1 h at this temperature after which time the solvent was evaporated off at atmospheric pressure. Distillation of the residue afforded dichlorotitanium di-isopropoxide (168.8 g, 95%), b.p. 105—110 °C at 0.1 mmHg. The product solidified on cooling and was carefully (exothermic) dissolved in anhydrous THF (250 ml) and made up to produce a 2.85M solution.

(E)-4-*Diphenylphosphinoyl*-4-*methoxy*-1-*phenylbut*-3-*en*-1-*ol* (3a).—Phosphine oxide (1a) (2.72 g, 10 mmol) in dry THF (25 ml) was converted into its lithium anion by method (b). Benzaldehyde (1.06 g, 10 mmol) was added to the deep red anion solution and stirring was continued at −78 °C for 30 min after which time the solution was allowed to warm to room temperature. A saturated solution of NH₄Cl (25 ml) was then added, the layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 30 ml). The combined organic layers were washed with saturated NaCl solution, dried (Na₂SO₄), and evaporated under reduced pressure. The residual syrup was purified by flash chromatography (EtOAc as eluant) to give the title compound (3a) as a white solid (2.7 g, 82%), m.p. 131—132 °C (from toluene–hexane) (lit.,[10] 121.5—123 °C); $\nu_{max.}$ 3 290 (OH), 1 431 (PPh), and 1 161 cm⁻¹ (P=O); δ_H 2.70 (2 H, ddd, J_H 6, 7, and J_{PH} 2 Hz, CH_2CHOH), 3.34 (3 H, s, OMe), 3.52 (1 H, br s, OH), 4.69 (1 H, t, J_H 6 Hz, CHOH), 5.81 (1 H, d of t, J_H 7, and J_{PH} 9 Hz, C=CHCH₂), and 7.03—7.89 (15 H, m, 3 × Ph); δ_C 156.6, 148.3, 144.2, 132.2, 128.8, 128.3, 128.0, 126.0 (Ar and alkenyl carbons), 74.6 (CHOH), 61.2 (OMe), and 36.0 (d, J_{PC} 9 Hz, CH₂CHOH) (Found: C, 73.0; H, 6.1. Calc. for C₂₃H₂₃O₃P: C, 73.0; H, 6.13%).

4-*Diphenylphosphinoyl*-4-*methoxy*-3-*methyl*-1-*phenylbut*-3-*en*-1-*ol* (3b).—Phosphine oxide (1b) (2.86 g, 10 mmol) was subjected to the procedure outlined above. The crude product was purified by crystallisation from benzene–hexane to give the *title compound* (2.4 g, 61%), m.p. 110—111 °C; $\nu_{max.}$ 3 300 (OH), 1 435 (PPh), and 1 164 cm⁻¹ (P=O); δ_H 2.01 (3 H, d, J_{PH} 2 Hz, Me), 2.88 (2 H, m, CH_2CHOH), 3.02 (3 H, s, OMe), 4.99 (1 H, dt, J_H 6, and J_{PH} 1 Hz, CHOH), and 7.21—8.10 (15 H, m, 3 × Ph); δ_C 144.5, 143.8, 142.6, 142.1, 136.4, 133.4, 132.1, 131.7, 131.4, 129.6, 128.8, 128.4, 128.0, 127.5, 126.1 (Ar and alkenyl carbons), 71.9 (CHOH), 60.8 (OMe) 43.0 (d, J_P 6 Hz, CH₂CHOH), and 17.5 (Me) (Found: C, 73.1; H, 6.3. C₂₄H₂₅O₃P requires C, 73.47; H, 6.38%).

4-*Diphenylphosphinoyl*-4-*methoxy*-2-*methyl*-1-*phenylbut*-3-*en*-1-*ol* (3c).—Phosphine oxide (1c) (2.86 g, 10 mmol) was subjected to the procedure outlined above. Identical work-up as for compound (3a) afforded an oil which was purified on a dry silica gel column [Et₂O–CH₂Cl₂ (1:1) R_F 0.2] and crystallised from toluene–hexane to give the *title compound* (E)-(3c) (3.2 g, 85%) as a mixture of diastereoisomers, m.p. 94—96 °C; $\nu_{max.}$ 3 290 (OH), 1 440 (PhP), and 1 179 cm⁻¹ (P=O). Major isomer: δ_H 1.08 (3 H, d, J_H 7 Hz, Me), 2.72 (1 H, s, OH), 3.18 (1 H, m, CHMe), 3.31 (3 H, s, OMe), 4.45 (1 H, d, J_H 6 Hz, CHOH), 5.62 (1 H, m, J_H 10, and J_{PH} 11 Hz, C=CH), and 7.03—7.92 (15 H, m, 3 × Ph); δ_C 139.2 (d, J_{PC} 123 Hz, PC=CH), 133.9, 133.4, 132.9, 132.3, 129.6, 128.9, 128.3, 128.0, 126.9 (ArC and C=CH), 75.6 (CHOH), 61.5 (OMe), 39.5 (d, J_{PC} 8 Hz, CHMe), and 17.3 (Me) (Found: C, 73.2; H, 6.2. C₂₄H₂₅O₃P requires C, 73.47; H, 6.38%).

General Procedure for the Reactions of Titanium Ate Complexes of α-Methoxyallyldiphenylphosphine Oxides with Aldehydes.—One of the following (1.1 mol equiv.) (i) freshly distilled

titanium(IV) isopropoxide, (ii) chlorotitanium tri-isopropoxide in dry THF or (iii) dichlorotitanium di-isopropoxide in dry THF was added to a solution of the phosphine oxide lithium anion, and the resulting mixture was stirred at −78 °C for 2 h. Aldehyde (1 mol equiv.) was added, and the mixture was stirred for an additional 1 h at that temperature, and then quenched by pouring into a saturated aqueous solution of NH₄Cl–KF (25 ml). Inorganic material was removed by filtration and washed with CH₂Cl₂, the THF layer was evaporated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 25 ml). The combined organic extracts were washed with a saturated solution of NaCl (25 ml), dried (Na₂SO₄), and the solvent evaporated off to give a crude syrup which was separated by flash column chromatography [hexane–Et₂O–CH₂Cl₂ (1:3:6)] into the γ-adduct and the α-adduct, the latter as a mixture of two diastereoisomers. The products were finally purified by recrystallisation from toluene–hexane. Method (iii) proved to be the best (see Table 1 for details).

(1S,2R)- and (1R,2R)-2-*Diphenylphosphinoyl*-2-*methoxy*-1-*phenylbut*-3-*en*-1-*ol* (5). (1S,2R): m.p. 152—153 °C (from toluene–hexane); $\nu_{max.}$ 3 240 (OH), 1 430 (PPh), and 1 165 cm⁻¹ (P=O); δ_H 2.8 (3 H, s, OMe), 4.6—5.4 (3 H, m, OH, CH=CH_2), 5.4 (1 H, d, J_{PH} 8.5 Hz, CHOH), 6.13 (1 H, m, J_H 11, 17, and J_{PH} 5 Hz, CH=CH₂), and 6.9—8.2 (15 H, m, 3 × Ph); δ_C(CDCl₃–CD₃OD) 139.23, 137.9, 133.59, 131.82, 130.27, 127.63 (ArC and CH=CH₂), 120.99 (d, J_{PC} 9 Hz, CH=CH₂), 85.23 (d, J_{PC} 85 Hz, PCOMe), 74.61 (d, J_{PC} 5 Hz, CHOH), and 53.14 (d, J_{PC} 9 Hz, OMe) (Found: C, 73.0; H, 6.1. C₂₃H₂₃O₃P requires C, 73.0; H, 6.08%).

(1R,2R): m.p. 115—117 °C (from toluene–hexane); $\nu_{max.}$ 3 170 (OH), 1 590 (C=C), 1 430 (PPh), and 1 165 cm⁻¹ (P=O); δ_H 3.7 (3 H, s, OMe), 5.06—5.44 (3 H, m, OH, CH=CH_2), 5.34 (1 H, d, J_{PH} 8.5 Hz, CHOH), 5.64 (1 H, m, J_H 10, 17, and J_{PH} 3 Hz CH=CH₂), and 7.0—8.05 (15 H, m, 3 × Ph) (Found: C, 72.9; H, 6.0).

(1S,2R)-2-*Diphenylphosphinoyl*-2-*methoxy*-1-(2-*methoxy-phenyl*)but-3-*en*-1-*ol* (8). M.p. 131.5—132.5 °C (from toluene–hexane); $\nu_{max.}$ 3 250 (OH), 1 650, 1 593, 1 582 (C=C), 1 431 (PPh), and 1 150 cm⁻¹ (P=O); δ_H 2.86 (3 H, s, PCOMe), 3.66 (3 H, s, ArOMe), 4.83 (1 H, m, J_H 2, 18, and J_{PH} 5 Hz, *cis* C=CH_2), 4.95 (1 H, br s, OH), 5.38 (1 H, m, J_H 2, 11.5, and J_{PH} 5 Hz, *trans* C=CH_2), 5.93 (1 H, d, J_{PH} 10 Hz, CHOH), 6.51 (1 H, m, J_H 11.5, 18, and J_{PH} 5 Hz, CH=CH₂), and 6.72—8.45 (14 H, m, 3 × Ph); δ_C 157.08 (ArCOMe), 133.95, 132.73, 131.52, 128.79, 128.06, 127.51 (ArC and C=CH₂), 120.62 (d, J_{PC} 9 Hz, C=CH_2), 120.35, 110.21 (ArC), 85.53 (d, J_{PC} 87 Hz, PCOMe), 67.05 (d, J_{PC} 5 Hz, CHOH), 55.15 (ArOMe), and 52.55 (d, J_{PC} 10 Hz, OMe) (Found: C, 70.2; H, 6.0; P. 7.6. C₂₄H₂₅O₄P requires C, 70.59; H, 6.13; P, 7.59%).

(1S,2R)-2-*Diphenylphosphinoyl*-2-*methoxy*-1-(2-*nitrophenyl*)-but-3-*en*-1-*ol* (9). Pale yellow crystals, m.p. 138—139.5 °C (from toluene–hexane); $\nu_{max.}$ 3 185 (OH), 1 620, 1 600, 1 581, 1 570 (C=C), 1 523, 1 348 (NO₂), 1 430 (PPh), and 1 160 cm⁻¹ (P=O); δ_H 2.8 (3 H, s, OMe), 4.66—5.53 (3 H, m, OH, C=CH_2), 5.6—6.33 (1 H, m, CH=CH₂), 5.88 (1 H, d, J_{PH} 10 Hz, CHOH), and 7.0—8.25 (14 H, m, 3 × Ph); δ_C 150.1 (C NO₂), 132.43, 130.04, 128.12, 125.47, 123.08 (ArC and CH=CH₂), 123.24 (d, J_{PC} 9 Hz, C=CH₂), 84.28 (d, J_{PC} 84 Hz, PCOMe), 69.35 (d, J_{PC} 5 Hz, CHOH), and 54.05 (d, J_{PC} 8 Hz, OMe) (Found: C, 65.4; H, 5.2; N, 3.4. C₂₃H₂₂NO₅P requires C, 65.25; H, 5.20; N, 3.30%).

(3S,4R)- and (3R,4R)-4-*Diphenylphosphinoyl*-4-*methoxy*-2-*methylhex*-5-*en*-3-*ol* (10). (3S,4R): m.p. 137—138 °C (from hexane); $\nu_{max.}$ 3 230 (OH), 1 622, 1 582 (C=C), 1 430 (PPh), and 1 165 cm⁻¹ (P=O); δ_H 0.93 (6 H, d, J_H 6 Hz, 2 × Me), 1.8 (1 H, m, J_H 2 and 6 Hz, CHMe₂), 3.27 (3 H, s, OMe), 4.38 (1 H, m, CHOH), 4.7—5.66 (3 H, m, OH, CH=CH_2) 5.7—6.35 (1 H, m, J_H 9, 17, and J_{PH} 3 Hz, CH=CH₂), and 7.0—8.1 (10 H, m, 2 × Ph); δ_C 136.77, 136.1, 135.11, 132.46, 131.46, 128.15 (ArC

and $CH=CH_2$), 115.94 (d, J_{PC} 10 Hz, $CH=CHCH_2$), 87.14 (d, J_{PC} 77 Hz, PCOMe), 73.23 (CHOH), 52.97 (d, J_{PC} 2.5 Hz, OMe), 29.59 (d, J_{PC} 7.5 Hz, CHMe$_2$), and 19.99 and 18.47 (2 × Me) (Found: C, 69.6; H, 7.2. $C_{20}H_{25}O_3P$ requires C, 69.77; H, 7.27%).

(3R,4R): M.p. 119—121 °C (from hexane); $\nu_{max.}$ 3 260 (OH), 1 583 (C=C), 1 433 (PPh), and 1 173 cm^{-1} (P=O); δ_H 0.97 (6 H, dd, J_H 7, and J_{PH} 5 Hz, 2 × Me), 1.88 (1 H, m, J_H 7 Hz, CHMe$_2$), 3.66 (3 H, s, OMe), 4.0 (1 H, dd, J_H 3, and J_{PH} 6.5 Hz, CHOH), 4.9—5.61 (4 H, m, OH, CH=CH_2), and 7.1—8.25 (10 H, m, 2 × Ph); δ_C 134.92, 132.19, 131.70, 128.55, 127.76 (ArC and CH=CH$_2$), 117.80 (d, J_{PC} 9 Hz, CH=CH$_2$), 84.59 (d, J_{PC} 75 Hz, PCOMe), 78.58 (CHOH), 55.65 (d, J_{PC} 5 Hz, OMe), 29.21 (d, J_{PC} 7.5 Hz, CHMe$_2$), and 21.94 and 15.99 (2 × Me) (Found: C, 69.5; H, 7.1).

(3R,4S)- and (3R,4R)-3-*Diphenylphosphinoyl-3-methoxytri-dec-1-en-4-ol* (**11**). (3R,4S): M.p. 96—97 °C (from hexane); $\nu_{max.}$ 3 295 (OH), 1 625, 1 585 (C=C), 1 430 (PPh), and 1 170 cm^{-1} (P=O); δ_H 0.82 (3 H, t, J_H 6 Hz, CH$_2$Me), 0.96—1.82 [16 H, m, (CH$_2$)$_8$], 3.3 (3 H, s, OMe), 4.72 (1 H, m, CHOH), 5.24—5.69 (3 H, m, OH, CH=CH_2), 6.07 (1 H, m, J_H 11, 18, and J_{PH} 3.5 Hz, CH=CH$_2$), and 7.31—8.29 (10 H, m, 2 × Ph) (Found: C, 72.8; H, 8.5. $C_{26}H_{37}O_3P$ requires C, 72.90; H, 8.64%).

(3R,4R): As an oil; $\nu_{max.}$ 3 340 (OH), 1 625, 1 585 (C=C), 1 430 (PPh), and 1 165 cm^{-1} (P=O); δ_H 0.85 (3 H, t, J_H 6 Hz, CH$_2$Me), 1.0—1.72 [16 H, m, (CH$_2$)$_8$], 3.52 (3 H, s, OMe), 3.55 (1 H, br s, OH), 4.12 (1 H, m, CHOH), 5.34 (2 H, m, CH=CH_2), 5.86 (1 H, m, J_H 10, 18, and J_{PH} 3.5 Hz, CH=CH$_2$), and 7.3—8.34 (10 H, m, 2 × Ph) (Found: C, 72.7; H, 8.6. $C_{26}H_{37}O_3P$ requires C, 72.90; H, 8.64%).

(1S,2R)-2-*Diphenylphosphinoyl-2-methoxy-3-methyl-1-(2-methoxyphenyl)but-3-en-1-ol* (**12**). M.p. 151—152 °C (from toluene–hexane); $\nu_{max.}$ 3 230 (OH), 1 625, 1 598, 1 582 (C=C), 1 430 (PPh), and 1 185 cm^{-1} (P=O); δ_H 2.03 (3 H, br s, CH$_2$=CMe), 2.85 (1 H, br s, OH), 3.33 (3 H, s, OMe), 3.6 (3 H, s, ArOMe), 4.78 (1 H, d, J_H 4.8 Hz, C=CH_2), 5.0 (1 H, d, J_H 4.8 Hz, C=CH_2), 6.01 (1 H, d, J_{PH} 6.5 Hz, CHOH), and 6.3—8.0 (14 H, m, 3 × Ph); δ_C(CDCl$_3$–CD$_3$OD) 156.41 (ArCOMe), 139.23, 134.68, 134.26, 132.49, 131.50, 131.27, 130.61, 129.82, 138.73, 138.12, 137.45, 126.72, 123.51 (ArC), 119.62 (C=CH$_2$), 118.79, 109.43 (ArC), 88.99 (d, J_{PC} 89 Hz, PCOMe), 67.28 (d, J_{PC} 8 Hz, CHOH), 54.36 (2 × OMe), and 21.75 (CH$_2$=CMe) (Found: C, 71.0; H, 6.3. $C_{25}H_{27}O_4P$ requires C, 71.09; H, 6.40%).

(3R,4S)-3-*Diphenylphosphinoyl-3-methoxy-2-methyloct-1-en-4-ol* (**13**). M.p. 140.5—141 °C (from toluene–hexane); $\nu_{max.}$ 3 280 (OH) 1 625, 1 583 (C=C), 1 433 (PPh), and 1 173 cm^{-1} (P=O); δ_H 0.66—1.0 (3 H, t, CH$_2$Me), 1.0—1.66 [6 H, m, (CH$_2$)$_3$], 1.9 (3 H, d, J_{PH} 1.5 Hz, CH$_2$=CMe), 3.32 (3 H, s, OMe), 4.23 (1 H, d, J_{PH} 3 Hz, CHOH), 4.57 (1 H, br s, OH), 5.07 (2 H, m, C=CH_2), and 7.16—8.27 (10 H, m, 2 × Ph); δ_C 140.93, 135.83, 134.62, 131.98, 129.99, 128.33 (ArC and CH$_2$=CMe), 117.24 (d, J_{PC} 7 Hz, C=CH$_2$), 87.81 (d, J_{PC} 84 Hz, PCOMe), 72.21 (d, J_{PC} 5 Hz, CHOH), 53.93 (d, J_{PC} 7.5 Hz, OMe), 32.38 (CH$_2$CHOH), 28.37 (CH$_2$CH$_2$CHOH), 22.36 (CH$_2$Me), 20.97 (CH$_2$=CMe), and 13.98 (CH$_2$$Me$) (Found: C, 70.7; H, 7.9. $C_{22}H_{29}O_3P$ requires C, 70.97; H, 7.80%).

(3S,4R)-4-*Diphenylphosphinoyl-4-methoxy-2,5-dimethylhex-5-en-3-ol* (**14**). M.p. 152—154 °C (from toluene–hexane); $\nu_{max.}$ 3 300 (OH), 1 625 (C=C), 1 432 (PPh), and 1 170 cm^{-1} (P=O); δ_H 0.93 (6 H, J_H 6 Hz, CHMe_2), 1.7 (3 H, d, J_{PH} 2 Hz, CH$_2$=CMe), 1.88 (1 H, m, CHMe$_2$), 3.18 (3 H, s, OMe), 4.46 (1 H, m, J_{PH} 4 Hz, CHOH), 4.53 (1 H, s, OH), 5.03 (1 H, m, C=CH_2), 5.25 (1 H, m, C=CH_2), and 7.3—8.24 (10 H, m, 2 × Ph); δ_C 141.66, 135.86, 134.70, 132.31, 128.48, 128.0 (ArC and C=CH_2), 117.56 (d, J_{PC} 8 Hz, C=CH$_2$), 87.49 (d, J_{PC} 80 Hz, PCOMe), 74.75 (CHOH), 53.81 (d, J_{PC} 5 Hz, OMe), 30.02 (d, J_{PC} 8 Hz, CHMe$_2$), 21.14 (CH$_2$=CMe), and 21.63 and 16.96 (2 × Me) (Found: C, 70.3; H, 7.5. $C_{21}H_{27}O_3P$ requires C, 70.39; H, 7.54%).

(E)-(1S,2R)-2-*Diphenylphosphinoyl-2-methoxy-1-phenylpent-3-en-1-ol* (**7**). M.p. 176.5—177 °C (from toluene–hexane); $\nu_{max.}$ 3 250 (OH), 1 652, 1 585 (C=C), 1 430 (PPh), and 1 165 cm^{-1} (P=O); δ_H(CDCl$_3$–CD$_3$OD) 1.68 (3 H, dd, J_H 6, and J_{PH} 6 Hz, CH=CHMe), 3.07 (3 H, s, OMe), 4.05 (1 H, s, OH), 5.15 (1 H, d, J_{PH} 9 Hz, CHOH), 5.31 (1 H, m, J_H 6, 16, and J_{PH} 2 Hz, CH=CHMe), 5.73 (1 H, m, J_H 16, and J_{PH} 5.5 Hz, CH=CHMe), and 7.1—8.2 (15 H, m, 3 × Ph); δ_C(CDCl$_3$–CD$_3$OD) 139.51, 137.39, 135.45, 132.53, 131.96, 129.13, 128.11, 122.68 (ArC and CH=CHMe and CH=CHMe), 85.54 (d, J_{PC} 85 Hz, PCOMe), 75.53 (d, J_{PC} 5 Hz, CHOH), 52.71 (d, J_{PC} 8 Hz, OMe), and 18.44 (Me) (Found: C, 73.1; H, 6.2. $C_{24}H_{25}O_3$ requires C, 73.47; H, 6.38%).

(E)-(1S,2R)-2-*Diphenylphosphinoyl-2-methoxy-1-(2-methoxyphenyl)pent-3-en-1-ol* (**15**). M.p. 163—164 °C (from toluene–hexane); $\nu_{max.}$ 3 220 (OH), 1 595, 1 582 (C=C), 1 432 (PPh), and 1 165 cm^{-1} (P=O); δ_H 1.6 (3 H, m, CH=CHMe), 2.75 (3 H, s, OMe), 3.65 (3 H, s, ArOMe), 4.95 (1 H, br s, OH), 4.75—5.25 (1 H, m, CH=CHMe), 5.72 (1 H, d, J_{PH} 11.5 Hz, CHOH), 6.0 (1 H, J_H 16, and J_{PH} 2 Hz, CH=CHMe), and 6.55—8.3 (14 H, m, 3 × Ph); δ_C 157.20 (ArCOMe), 134.62, 133.77, 132.98, 129.03, 128.03 (ArC and CH=CHMe), 121.29 (d, J_{PC} 7.5 Hz, CH=CHMe), 110.88 (Ar), 86.02 (d, J_{PC} 90 Hz, PCOMe), 67.35 (d, J_{PC} 5 Hz, CHOH), 55.15 (ArCOMe), 51.87 (d, J_{PC} 9 Hz, OMe), and 18.42 (CH=CHMe) (Found: C, 71.1; H, 6.2. $C_{25}H_{27}O_4P$ requires C, 71.09; H, 6.40%).

(E)-(3S,4R)- and (E)-(3R,4R)-4-*Diphenylphosphinoyl-4-methoxy-2-methylhept-5-en-3-ol* (**16**). (E)-(3S,4R): M.p. 143.5—144.5 °C (from hexane); $\nu_{max.}$ 3 250 (OH), 1 660, 1 585 (C=C), 1 430 (PPh), and 1 170 cm^{-1} (P=O); δ_H 0.95, 0.98 (6 H, 2 × d, J_H 7 Hz, 2 × Me), 1.9 (1 H, m, CHMe$_2$), 2.7 (3 H, t, J_H 5, and J_{PH} 5 Hz, CH=CHMe), 3.35 (3 H, s, OMe), 4.47 (1 H, m, J_H 5, 7, and J_{PH} 5 Hz, CHOH), 5.39 (1 H, d, J_H 5 Hz, OH), 5.75 (2 H, m, CH=CHMe), and 7.15—8.3 (10 H, m, 2 × Ph); δ_C 136.72, 135.93, 132.59, 131.98, 131.5, 130.04, 128.46, 128.22, 127.74, 127.43, 127.01 (ArC and CH=CH), 86.44 (d, J_{PC} 78 Hz, PCOMe), 74.56 (d, J_{PC} 2 Hz, CHOH), 53.04 (d, J_{PC} 4 Hz, OMe), 29.59 (d, J_{PC} 8 Hz, CHMe$_2$), and 20.58, 18.27, and 18.03 (2 × Me, CH=CHMe) (Found: C, 70.0; H, 7.4. $C_{21}H_{27}O_3P$ requires C, 70.39; H, 7.54%).

(E)-(3R,4R): M.p. 123—124 °C (from hexane); $\nu_{max.}$ 3 270 (OH), 1 650, 1 585 (C=C), 1 435 (PPh), and 1 170 cm^{-1} (P=O); δ_H 0.89 (3 H, d, J_H 7 Hz, Me), 0.95 (3 H, d, J_H 7 Hz, Me), 1.64 (3 H, t, J_H 6, and J_{PH} 6 Hz, CH=CHMe), 1.9 (1 H, m, CHMe$_2$), 3.67 (3 H, s, OMe), 3.95 (1 H, m, CHOH), 5.1 (1 H, m, CH=CHMe), 5.2 (1 H, br s, OH), 5.7 (1 H, m, CH=CHMe), and 7.25—8.25 (10 H, m, 2 × Ph); δ_C 135.57, 134.57, 132.41, 131.86, 129.62, 127.86 (ArC and CH=CMe), 84.57 (d, J_{PC} 77 Hz, PCOMe), 79.23 (CHOH), 54.49 (d, J_{PC} 5 Hz, OMe), 29.20 (d, J_{PC} 7 Hz, CHMe$_2$), 22.1 and 16.57 (2 × Me), and 18.15 (CH=CHMe) (Found: C, 70.1; H, 7.3).

(E)-(4R,5S)- and (E)-(4R,5R)-4-*Diphenylphosphinoyl-4-methoxynon-2-en-5-ol* (**17**). (E)-(4R,5S): M.p. 145.5—146.5 °C (from hexane); $\nu_{max.}$ 3 280 (OH), 1 660, 1 585 (C=C), 1 430 (PPh), and 1 170 cm^{-1} (P=O); δ_H 0.82 (3 H, t, J_H 6.5 Hz, CH$_2$Me), 1.2—1.6 [6 H, m, (CH$_2$)$_3$], 1.71 (3 H, dd, J_H 5, and J_{PH} 5 Hz, CH=CHMe), 3.34 (3 H, s, OMe), 4.52 (1 H, m, CHOH), 5.06 (1 H, br s, OH), 5.5—5.95 (2 H, m, CH=CH), and 7.31—8.29 (10 H, m, 2 × Ph); δ_C 136.07, 135.41, 132.43, 131.88, 131.22, 129.88, 128.30, 128.06, 127.57, 127.27, 125.69 (ArC and CH=CH), 84.95 (d, J_{PC} 82 Hz, PCOMe), 71.60 (CHOH), 52.70 (d, J_{PC} 5 Hz, OMe), 30.71 (CH$_2$CHOH), 28.31 (CH$_2$CH$_2$CHOH), 22.60 (CH$_2$CH$_3$), 18.05 (CH=CHMe), and 13.86 (Me) (Found: C, 70.7; H, 7.6. $C_{22}H_{29}O_3P$ requires C, 70.97; H, 7.80%).

(E)-(4R,5R): M.p. 122.5—123.5 °C (from hexane); $\nu_{max.}$ 3 280 (OH), 1 650, 1 580 (C=C), 1 435 (PPh), and 1 170 cm^{-1} (P=O); δ_H 0.78 (3 H, J_H 5.5 Hz, CH$_2$Me), 1.0—1.55 [6 H, m, (CH$_2$)$_3$], 1.63 (3 H, m, J_H 5, and J_{PH} 4.5 Hz, CH=CHMe), 3.47 (3 H, s,

OMe), 4.04 (1 H, m, J_H 7.5, and J_{PH} 7.5 Hz, CHOH), 5.01 (1 H, d, J_H 7 Hz, OH), 5.40—5.75 (2 H, m, CH=CH), and 7.33—8.33 (10 H, m, 2 × Ph); δ_C 135.45, 132.29, 131.99, 131.74, 128.59, 128.40, 127.86, 125.67 (ArC and CH=CH), 83.61 (d, J_{PH} 85 Hz, PCOMe), 75.16 (CHOH), 52.63 (d, J_{PC} 7 Hz, OMe), 32.66 (CH$_2$CHOH), 28.96 (CH$_2$CH$_2$CHOH) 22.46 (CH$_2$Me), 18.27 (CH=CHMe), and 13.84 (Me) (Found: C, 71.0; H, 7.9. C$_{22}$H$_{29}$O$_3$P requires C, 70.97; H, 7.88%).

(E)-(3S,4R)- and (E)-(3R,4R)-4-Diphenylphosphinoyl-4-methoxy-2-methyl-6-phenylhex-5-en-3-ol (18). (E)-(3S,4R): M.p. 133.5—134.5 °C (from toluene–hexane); v_{max} 3 260 (OH), 1 595, 1 585, 1 568 (C=C), 1 433 (PPh), and 1 170 cm^{-1} (P=O); δ_H 1.04 (6 H, m, J_H 6.5 Hz, CHMe$_2$), 1.93 (1 H, m, CHMe$_2$), 3.48 (3 H, s, OMe), 4.6 (1 H, m, J_H 5.5 and 6 Hz, CHOH), 5.42, (1 H, br s, CHOH), 6.5 (1 H, m, J_H 17 Hz, CH=CHPh), 6.88 (1 H, m, CH=CHPh), and 7.15—8.33 (15 H, m, 3 × Ph); δ_C 136.75, 131.71, 132.25, 128.2, 127.27, 125.54 (Ar and alkenyl carbons), 86.81 (d, J_{PC} 74 Hz, PCOMe), 74.35 (CHOH), 53.46 (OMe), 29.59 (d, J_{PC} 10 Hz, CHMe$_2$), and 20.5 and 28.64 (CHMe_2) (Found: C, 74.0; H, 6.7. C$_{26}$H$_{29}$O$_3$P requires C, 74.29; H, 6.90%).

(E)-(3R,4R): M.p. 137—138 °C (from toluene–hexane); v_{max} 3 315 (OH), 1 595, 1 583, 1 572 (C=C), 1 433 (PPh), and 1 170 cm^{-1} (P=O); δ_H 1.10 (6 H, dd, J_H 7 Hz, CHMe$_2$, 1.9 (1 H, m, CHMe$_2$), 3.81 (3 H, s, OMe), 4.2 (1 H, dd, J_{PH} 6 and 3 Hz, CHOH), 5.73 (1 H, s, OH), 5.76 (1 H, m, J_H 16, and J_{PH} 4.5 Hz, CH=CHPh), 6.87 (1 H, m, J_H 16, and J_{PH} 5 Hz, CH=CHPh), and 7.18—8.29 (15 H, m, 3 × Ph); δ_C 136.01, 134.86, 131.58, 128.18, 127.45, 125.59 (Ar and alkenyl carbons), 84.01 (d, J_{PC} 72.5 Hz, PCOMe), 78.64 (CHOH), 55.57 (d, J_{PC} 5 Hz, OMe), 29.65 (d, J_{PC} 7.5 Hz, CHMe$_2$), and 21.33 and 15.62 (CHMe_2) (Found: C, 74.1; H, 6.8).

(E)-2-Methoxy-1-phenylbuta-1,3-diene (6).—The alcohol (1S,-2R)-(5) (1.89 g, 5 mmol) was dissolved in anhydrous THF (60 ml) in a flame dried flask under a positive pressure of nitrogen at room temperature. Potassium t-butoxide (0.68 g, 6 mmol) dissolved in THF (10 ml) was added quickly to the well-stirred reaction mixture, when a thick white precipitate separated out. The reaction mixture was quenched after 30 min by the addition of water (25 ml), and thoroughly extracted with ether (3 × 25 ml). The organic layers were combined, washed successively with saturated solutions of NaHCO$_3$ (25 ml) and NaCl (25 ml), and dried (MgSO$_4$). Evaporation of the solvent afforded (E)-2-methoxy-1-phenylbuta-1,3-diene (0.76 g, 95%) as an oil which was purified by dry column chromatography on silica gel [light petroleum (b.p. 40—60 °C) as eluant]; δ_H 3.70 (3 H, s, OMe), 5.19 (1 H, dt, J_H 1.5, 2, and 11 Hz, trans CH=CH$_2$), 5.77 (1 H, dd, J_H 0.75, 2, and 17 Hz, cis CH=CH$_2$), 5.82 (1 H, br s, PhCH=C), 6.65 (1 H, dd, J_H 11 and 17 Hz, CH=CH$_2$), and 7.26 (5 H, br s, Ph) (Found: C, 82.3; H, 7.4. C$_{11}$H$_{12}$O requires C, 82.50; H, 7.50%).

Potassium t-butoxide treatment of the alcohol (3R, 4S)-(11) was analogous to that of compound (6). Chromatography [silica gel; light petroleum (40—60 °C)] afforded (E)-3-methoxytrideca-1,3-diene (19), 96%, as a colourless oil; δ_H 0.9 (3 H, t, CH$_2$Me), 1.09—1.66 [14 H, m, (CH$_2$)$_7$], 2.06 (2 H, m, C=CHCH$_2$), 3.54 (3 H, s, OMe), 4.53 (1 H, m, J_H 7 and 0.75 Hz C=CHCH$_2$), 5.05 (1 H, dt, J_H 0.75, 2, and 11 Hz, trans CH=CH$_2$), 5.50 (1 H, dd, J_H 2 and 17 Hz, cis CH=CH$_2$), and 6.43 (1 H, dd, J_H 11 and 17 Hz, CH=CH$_2$) (Found: C, 79.7; H, 12.2. C$_{14}$H$_{26}$O requires C, 80.0; H, 12.38%).

Similarly, the alcohol (3R,4R)-(11) yielded (Z)-3-methoxy-trideca-1,3-diene (20) (93%), as a colourless oil; δ_H 0.89 (3 H, t, CH$_2$Me), 1.07—1.64 [14 H, m, (CH$_2$)$_7$], 2.11 (2 H, m, C=CHCH$_2$), 3.53 (3 H, s, OMe), 4.88 (1 H, t, C=CHCH$_2$), 4.94 (1 H, dd, J_H 2 and 10 Hz, trans CH=CH$_2$), 5.25 (1 H, dd, J_H 2 and 16 Hz, cis CH=CH$_2$), and 5.98 (1 H, dd, J_H 10 and 16 Hz,

CH=CH$_2$) (Found: C, 79.8; H, 12.1. C$_{14}$H$_{26}$O requires C, 80.0; H, 12.38%).

General Procedure for the Reaction of Titanium Ate Complexes of α-Methoxyallyldiphenylphosphine Oxides with Acyl Chlorides.—BuLi (1.1 equiv.) was added slowly to a stirred solution of the phosphine oxide (10 mmol) in anhydrous THF (50 ml) at −78 °C. Stirring was continued for 30 min, chlorotitanium tri-isopropoxide (1.2 equiv.) in THF (10 ml) was added and after a further 30 min at −78 °C, the acyl halide (1.1 equiv.) in THF (5 ml) was rapidly introduced. Stirring was continued for a further 30 min after which time the reaction mixture was quenched with 20% KF solution (50 ml). Inorganic material was removed by filtration and washed with CH$_2$Cl$_2$, the THF layer was evaporated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 × 30 ml). The combined organic extracts were washed successively with saturated aqueous NaHCO$_3$ (2 × 25 ml) and saturated aqueous NaCl (25 ml), dried (Na$_2$SO$_4$), and the solvent evaporated off. The residual syrup was purified by dry column chromatography [1% MeOH in CH$_2$Cl$_2$–Et$_2$O (1:1)].

(E)-4-Diphenylphosphinoyl-4-methoxy-1-(4-methoxyphenyl)-but-3-en-1-one (25): v_{max} 1 675 (C=O), 1 595, 1 570 (C=C), 1 435 (PPh), and 1 170 cm^{-1} (P=O); δ_H 3.63 (3 H, s, OMe), 3.74 (3 H, s, OMe), 3.89 (2 H, dd, J_H 7, and J_{PH} 2.5 Hz, CH_2CO), 6.0 (1 H, dt, J_H 7, and J_{PH} 9 Hz, C=CHCH$_2$), and 6.88—8.1 (14 H, m, 3 × Ph) (Found: C, 70.7; H, 5.4. C$_{24}$H$_{23}$O$_4$P requires C, 70.94; H, 5.66%).

(E)-6-Diphenylphosphinoyl-6-methoxy-2-methylhex-5-en-3-one (26): v_{max} 1 705 (C=O), 1 620, 1 585 (C=C), 1 432 (PPh), and 1 175 cm^{-1} (P=O); δ_H 1.07 (6 H d, J_H 7 Hz, CHMe$_2$), 2.63 (1 H, m, J_H 7 Hz, CHMe$_2$), 3.4 (2 H, dd, J_H 7, and J_{PH} 2.5 Hz, CH_2CO), 3.61 (3 H, s, OMe), 5.78 (1 H, m, J_H 7, and J_{PH} 9 Hz, C=CHCH$_2$), and 7.23—8.0 (10 H, m, 2 × Ph) (Found: C, 70.1; H, 6.6. C$_{20}$H$_{23}$O$_3$P requires C, 70.17; H, 6.72%).

(E)-1-Diphenylphosphinoyl-1-methoxyoct-1-en-4-one (27): v_{max} 1 705 (C=O), 1 625, 1 585 (C=C), 1 435 (PPh), and 1 175 cm^{-1} (P=O); δ_H 0.84 (3 H, t, J_H 6 Hz, CH$_2$Me), 1.07—1.86 (4 H, m, CH$_2$CH$_2$), 2.44 (2 H, t, J_H 7 Hz, CH$_2$CO), 3.38 (2 H, dd, J_H 7, and J_{PH} 2.5 Hz, =CHCH$_2$CO), 3.59 (3 H, s, OMe), 5.87 (1 H, m, J_H 7, and J_{PH} 9 Hz, CH=C), and 7.3—8.0 (10 H, m, 2 × Ph) (Found: C, 70.4; H, 7.0. C$_{21}$H$_{25}$O$_3$P requires C, 70.79; H, 7.02%).

(E)-4-Diphenylphosphinoyl-4-methoxy-2-methyl-1-phenylbut-3-en-1-one(28): v_{max} 1 685(C=O), 1 595, 1 575(C=C), 1 433(PPh), and 1 185 cm^{-1} (P=O); δ_H 1.33 (3 H, d, J_H 7 Hz, CHMe), 3.7 (3 H, s, OMe), 4.7 (1 H, m, J_H 7 and 9.5 Hz, CHMe), 5.69 (1 H, dd, J_H 9.5, and J_{PH} 10 Hz, C=CH), and 7.28—8.1 (15 H, m, 3 × Ph); δ_C 198.91 (C=O), 153.52 (d, J_{PC} 117.5 Hz, PCOMe), 135.41, 132.43, 131.34, 130.67, 128.18, 127.88, 127.70 (Ar and alkenyl carbons), 60.37 (OMe), 56.36 (d, J_{PC} 10 Hz, =CCHMe), and 16.11 (Me) (Found: C, 73.6; H, 5.7. C$_{24}$H$_{23}$O$_3$P requires C, 73.85; H, 5.90%).

(E)-6-Diphenylphosphinoyl-6-methoxy-2,4-dimethylhex-5-en-3-one (29): v_{max} 1 710 (C=O), 1 623, 1 585 (C=C), 1 435 (PPh), and 1 180 cm^{-1} (P=O); δ_H 0.98—1.28 (9 H, m, CHMe and CHMe$_2$), 2.8 (1 H, m, J_H 7 Hz, CHMe$_2$), 3.64 (3 H, s, OMe), 3.92 (1 H, m, CHMe), 5.53 (1 H, dd, J_H 9.5, and J_{PH} 10 Hz, C=CH), and 7.3—8.1 (10 H, m, 2 × Ph) (Found: C, 70.7; H, 6.8. C$_{21}$H$_{25}$O$_3$P requires C, 70.79; H, 7.02%).

(E)-6-Diphenylphosphinoyl-6-methoxy-4-methylhex-5-en-3-one (30): v_{max} 1 710 (C=O), 1 625, 1 585 (C=C), and 1 180 cm^{-1} (P=O); δ_H 1.03 (3 H, t, J_H 7 Hz, CH$_2$Me), 1.2 (3 H, d, J_H 7 Hz, CHMe), 2.53 (2 H, q, J_H 7 Hz, CH$_2$Me), 3.63 (3 H, s, OMe), 3.89 (1 H, m, CHMe), 5.64 (1 H, t, J_H 9.5 Hz, C=CH), and 7.3—8.0 (10 H, m, 2 × Ph) (Found: C, 71.8; H, 6.0. C$_{22}$H$_{23}$O$_3$P requires C, 72.13; H, 6.28%).

References
1 For example, see B. Lythgoe, T. A. Moran, M. E. N. Nambudiry, S. Ruston, J. Tideswell, and P. W. Wright, *Tetrahedron Lett.*, 1975, 3863; W. Dumont, C. Vermeyen, and A. Krief, *ibid.*, 1984, **25**, 2883; M. R. Binns, R. K. Haynes, A. A. Katsifis, P. A. Schober, and S. C. Von-Willer, *ibid.*, 1985, **26**, 1565.
2 D. Seebach and K.-H. Geiss, 'New Applications of Organometallic Reagents in Organic Synthesis,' ed. D. Seyferth, Elsevier, Amsterdam, 1976, p. 1; S. F. Martin, *Synthesis*, 1979, 633; J.-F. Biellmann and J.-B. Ducep, *Org. React.*, 1982, **27**, 1.
3 Y. Yamamoto, H. Yatagai, Y. Saito, and K. Maruyama, *J. Org. Chem.*, 1984, **49**, 1096.
4 V. Rautenstrauch, *Helv. Chim. Acta*, 1974, **57**, 496; R. Gompper and H.-U. Wagner, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 321; D. Hoppe, *ibid.*, 1984, **23**, 932.
5 D. A. Evans, G. C. Andrews, T. T. Fujimoto, and D. Wells, *Tetrahedron Lett.*, 1973, 1385, 1389; S. Warren and A. H. Davidson, *J. Chem. Soc., Chem. Commun.*, 1975, 148.
6 W. H. Glaze, J. E. Hanicak, J. Chaudhuri, M. L. Moore, and D. P. Duncan, *J. Organomet. Chem.*, 1973, **51**, 13; P. M. Atlani, J.-F. Biellmann, S. Dube, and J. J. Vicens, *Tetrahedron Lett.*, 1974, 2665.
7 L. E. Overmann, C. B. Campbell, and F. M. Knoll, *J. Am. Chem. Soc.*, 1978, **100**, 4822; H. Ahlbrecht, B. Konig, and H. Simon, *Tetrahedron Lett.*, 1978, 1191.
8 D. A. Evans, G. C. Andrews, and B. Buckwalter, *J. Am. Chem. Soc.*, 1974, **96**, 5560; W. C. Still and T. L. Macdonald, *J. Org. Chem.*, 1976, **41**, 3620.
9 G. Rauschwalbe and H. Ahlbrecht, *Synthesis*, 1974, 663; W. C. Still and T. L. Macdonald, *J. Am. Chem. Soc.*, 1974, **96**, 5561.
10 M. Maleki, J. A. Miller, and O. W. Lever, *Tetrahedron Lett.*, 1981, **22**, 3789.
11 D. K. Devchand, A. W. Murray, and E. Smeaton, *Tetrahedron Lett.*, 1986, **27**, 4635.
12 T. Hata, M. Nakajima, and M. Sekine, *Tetrahedron Lett.*, 1979, 2047; D. A. Evans, J. M. Takacs, and K. M. Hurst, *J. Am. Chem. Soc.*, 1979, **101**, 371.
13 E. F. Birse, M. Maleki, J. A. Miller, and A. W. Murray, *J. Chem. Res.*, 1988, (*S*), 85; (*M*), 0864.
14 L. Horner, H. Hoffmann, H. G. Wippel, and G. Klahre, *Chem. Ber.*, 1959, **92**, 2499.
15 M. T. Reetz and B. Wenderoth, *Tetrahedron Lett.*, 1982, **23**, 5259; A. Murai, A. Abiko, N. Shimada, and T. Masamune, *ibid.*, 1984, **25**, 4951; C. Siegel and E. R. Thornton, *ibid.*, 1986, **27**, 457.
16 M. Maleki, J. A. Miller, and O. W. Lever, *Tetrahedron Lett.*, 1981, **22**, 365.
17 D. H. Williams and I. Fleming, 'Spectroscopic Methods in Organic Chemistry,' 3rd Edition, McGraw-Hill, Maidenhead, 1980, p. 136.
18 W. Kemp 'Organic Spectroscopy,' MacMillan, London, 1979, p. 207.
19 A. H. Davidson, C. Earnshaw, J. I. Grayson, and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1452.
20 P. Bakuzis, M. L. F. Bakuzis, and T. F. Weingarter, *Tetrahedron Lett.*, 1978, 2371; Y. Nagao, K. Seno, and E. Fujita, *ibid.*, 1979, 3167; H. J. Cristau, B. Chabaud, and C. Niangoran, *J. Org. Chem.*, 1983, **48**, 1527; P. Tuchinda, V. Prapansiri, W. Naengchomnong, and V. Reutrakul, *Chem. Lett.*, 1984, 1427.
21 A. D. Buss and S. Warren, *J. Chem. Soc., Chem. Commun.*, 1981, 100; R. S. Torr and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1173; A. D. Buss, N. Greeves, D. Levin, P. Wallace, and S. Warren, *Tetrahedron Lett.*, 1984, **25**, 357; N. Greeves and S. Warren, *ibid.*, 1986, **27**, 259.