Structure and Conformation of α'-Diphenylphosphinoyl Enones: X-Ray Structure of *E*-(5*SR*,6*SR*)-3,6-Dimethyl-5-diphenylphosphinoyl-7-triphenylmethoxyhept-2-en-4-one

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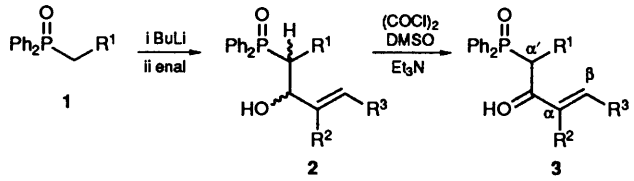
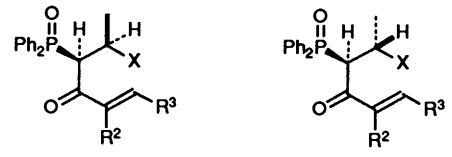
A series of α'-diphenylphosphinoyl enones has been prepared and their *s-cis* or *s-trans* conformations correlated with ^{1}H NMR and IR spectra and an X-ray crystal structure of the title compound. The effect of chelation to cerium(III) is correlated with the regio- and stereo-selectivity of reductions under the Luche conditions.

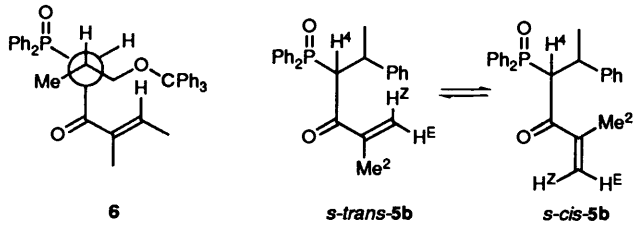
We have been studying stereoselective reactions of the α'-diphenylphosphinoyl (Ph_2PO)-enones **3**, **4** and **5**. New chiral centres can be generated with control at C=O by 1,2-reduction[1] with $NaBH_4$–$CeCl_3$ to give single diastereoisomers[2] of the allylic alcohols **2**, at C-α (in **3**) by 1,4-reduction with $NaBH_4$ or H_2–Pd–C, at C-β by Michael addition, at C-α and C-β by the Diels–Alder reaction, and at C=O and C-α by epoxidation of single diastereoisomers of the allylic alcohols **2** (R^3 = H). Prediction and explanation alike require a detailed knowledge not only of the configuration of **4** and **5**, but also of the conformation of all the enones in solution.



1 **2** **3**



4 **5**



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Many important stereoselective reactions[3] depend on the conformation of enones or related compounds. Diels–Alder reactions[4] on α'-hydroxy enones[5] and esters of acrylic acids[6] and Michael additions to chiral oxazolines[7] and sulfoxides[7] create new chiral centres by stereoselective attack on one face of a conformationally rigid grouping of C=C and C=O, though which conformation is often best deduced from the stereochemistry of the products. Masamune's α'-hydroxy enones[5] must react in the *s-cis* conformation, but Oppolzer[6] was able to show by X-ray crystal analysis[9] and IR spectroscopy[10] that his acrylate esters have the *s-trans* conformation in the solid state, exist as an equilibrium in solution, and that complexation to a Lewis acid catalyst may fix the molecule again in one, not necessarily the same, preferred conformation. We report that a combination of X-ray crystal analysis, ^{1}H NMR with NOE experiments and complexation to a Lewis acid, and IR spectra can be used to define the conformation of α'-Ph_2PO-enones in solution and hence explain or even predict the stereoselectivities of their reactions.

Table 1 Synthesis of α'-Ph_2PO-enones

Compound	R^1	R^2	R^3	X	Yield[a]
3a	H	Me	Me	—	50
3b	Bu^t	H	Me	—	46
3c	4-MeOC$_6$H$_4$	H	Me	—	67
3d	Me	Pr^i	H	—	77
3e	Bu^s	Me	Me	—	78
3f	C$_6$H$_{11}$[b]	Me	Me	—	58
4a	—	H	Me	Ph	21
5a	—	H	Me	Ph	20
4b	—	Me	H	Ph	25
5b	—	Me	H	Ph	23
4c	—	H	Me	CH_2OCPh_3	36
5c	—	H	Me	CH_2OCPh_3	21
4d	—	Me	H	CH_2OCPh_3	41
5d	—	Me	H	CH_2OCPh_3	23
4e	—	Me	Me	CH_2OCPh_3	42
5e	—	Me	Me	CH_2OCPh_3	27

[a] Compounds **4** and **5** were separated by HPLC from the *ca.* 1:1 mixture obtained in the Swern oxidation of **2**. [b] Cyclohexyl.

The enones **3** were prepared by addition of enals to the lithium derivatives of the phosphine oxides **1** to give mixtures of allylic alcohols **2** which were oxidised directly under Swern[11] conditions to the enones **3** (Table 1). Compounds with a chiral R^1 substituent were formed as a roughly 1:1 mixture and were separated by HPLC to give pure samples of the diastereoisomers **4** and **5**. X-Ray crystal structure analysis of **5e** (X = CH_2OCPh_3, R^2 = R^3 = Me) gave the relative configuration at the two chiral centres (Fig. 1).

Crystal Structure Determination of E-(5SR,6SR)-3,6-*Dimethyl-5-diphenylphosphinoyl-7-triphenylmethoxyhept-2-en-4-one* **5e**.—Suitable transparent crystals of the compound were grown after HPLC by crystallisation from ethyl acetate–light petroleum (b.p. 60–80 °C). The crystals contain a solvent molecule of acetone.

Crystal data. $C_{40}H_{39}O_3P$. C_3H_6O, M = 656.76, triclinic, a = 11.967(6), b = 12.380(8), c = 14.270(8) Å, α = 72.87(5), β = 87.71(4), δ = 67.38(4)°, v = 1858.5 Å^3 (by least-squares

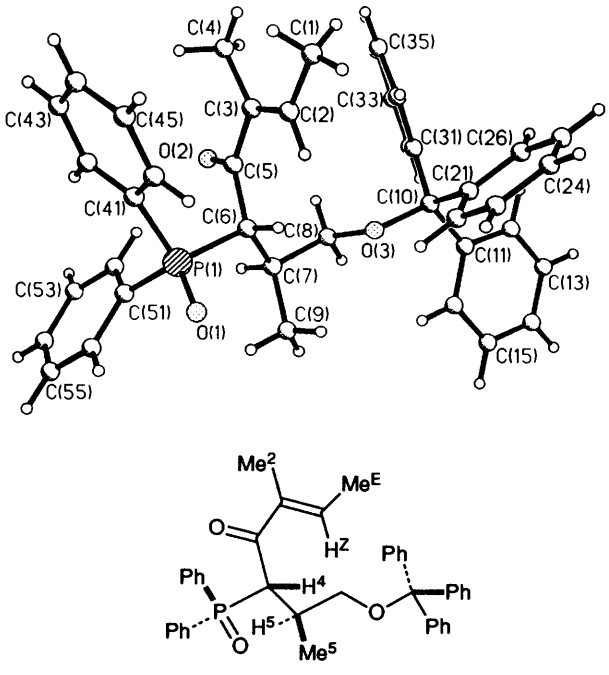


Fig. 1 Crystal structure of *E*-(5*SR*,6*SR*)-3,6-dimethyl-5-diphenylphosphinoyl-7-triphenylmethoxyhept-2-en-4-one **5e**. The formula is numbered as in Table 3.

refinement of diffractometer angles from 25 automatically centred reflections in the range $50 < 2\theta < 60°$, λ = 1.541 78 Å), $Z = 2$, $D_c = 1.173$ g cm^{-3}, space group $P\bar{1}$ (No. 2), $F(000) = 700$. Transparent block, dimensions 0.25 × 0.48 × 0.52 mm, μ(Cu-Kα) = 9.68 cm^{-1}.

Data collection and processing. Nicolet R3m$_\mu$ four-circle diffractometer, graphite-monochromated Cu-Kα radiation, 96-step ω–2θ scan mode, scan width from 1.0° below K$_\alpha$, to 1.0° above $K_{\alpha 2}$, scan speed 2.5–29.3° min^{-1}, 5300 reflections measured ($5.0 \leqslant 2\theta \leqslant 116.0°$, $\pm h$, $-k$, $\pm l$), 4949 unique, [R_{int} = 0.015 after empirical absorption correction using 311 azimuthal scan data and an ellipsoid model (transmission factors, minimum, maximum 0.495, 0.940)] 4203 with $F > 4\sigma(F)$. Three standard reflections showed no significant variation in intensity.

Structure analysis and refinement. Direct methods and subsequent Fourier difference synthesis for all non-hydrogen atoms. Hydrogen atoms placed in idealised positions (C–H, 0.96 Å) and allowed to ride on the relevant carbon; each type of H was assigned a common isotropic thermal parameter. Blocked cascade least-squares refinement with all non-hydrogen atoms anisotropic. The weighting scheme $w = \sigma^2(F) + 0.0012(F^2)$ gave satisfactory agreement analyses. The converged residuals were $R = 0.077$ and $R^1 = 0.081$, a final Fourier difference map showed no residual peaks above 0.57 eÅ^{-3}. Final atomic coordinates for the non-hydrogen atoms are given in Table 2.

The structure was solved and refined using the SHELXTL package[12] implemented on a Data General Desktop 30 computer. Additional material available from the Cambridge Crystallographic Data Centre* comprises H-atom co-ordinates, thermal parameters and full listings of bond lengths and angles.

Configuration and Conformation around the Two Chiral Centres in **4** *and* **5**.—Correlation of the configuration of *E*-**5e** with the other compounds **4** and **5** was established by ^{1}H NMR spectra (Table 3; protons are identified in the diagrams of **4** and **5** accompanying the Table) showing that, in all cases, the compound first eluted from HPLC was **4** and the second **5**. Among the key diagnostic features is the larger coupling constant between H^4 and H^5 for isomer **5**, $J_{4,5} \sim 10.5$ Hz, than for isomer **4**, $J_{4,5}$ 5.5–7.02 Hz, suggesting that the conformation revealed by the X-ray structure with H^4 and H^5 disposed *anti* (Fig. 1) is also preferred in solution. The preferred conformation for the isomers **4** may be **6** or it may exist as an equilibrium between several conformations.

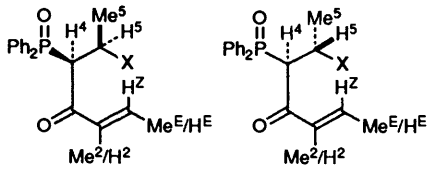
Conformation of the Enone Group.—The enone **5c** is revealed by the X-ray structure to be *s-trans*. This is the theoretically preferred conformation[13] and IR spectra[14] suggest it is maintained in solution. Enones typically show a C=C stretching frequency band at *ca.* 1620 cm^{-1} whatever the conformation, but the C=O stretching frequency is normally *ca.* 1680 cm^{-1} for *s-cis* enones and *ca.* 1650 cm^{-1} for *s-trans* enones. By this

Table 2 Atomic coordinates (× 10^4) for compound **5e**.

	x	*y*	*z*
C(1)	2 410(6)	9 278(6)	157(3)
C(2)	2 482(4)	8 955(5)	1 247(3)
C(3)	3 254(3)	7 920(4)	1 871(3)
C(4)	4 217(5)	6 857(6)	1 582(4)
C(5)	3 244(3)	7 672(3)	2 959(2)
C(6)	2 226(3)	8 521(3)	3 405(2)
C(7)	2 729(3)	8 801(3)	4 254(2)
C(8)	3 696(3)	9 323(3)	3 893(2)
C(9)	1 723(3)	9 659(3)	4 688(3)
C(11)	4 078(3)	11 784(3)	3 269(2)
C(12)	4 933(4)	12 304(4)	3 079(3)
C(13)	5 036(4)	13 038(4)	3 623(3)
C(14)	4 296(4)	13 262(4)	4 346(3)
C(15)	3 444(4)	12 768(3)	4 546(3)
C(16)	3 313(3)	12 038(3)	4 003(3)
C(21)	3 123(4)	12 006(3)	1 690(2)
C(22)	1 891(3)	12 302(3)	1 560(3)
C(23)	1 219(4)	13 154(4)	711(3)
C(24)	1 736(4)	13 736(4)	−17(3)
C(25)	2 957(4)	13 482(4)	97(3)
C(26)	3 647(3)	12 620(3)	944(3)
C(31)	5 066(3)	10 155(3)	2 383(3)
C(32)	6 161(3)	9 648(4)	2 967(3)
C(33)	7 162(4)	8 770(4)	2 755(4)
C(34)	7 119(4)	8 368(4)	1 966(4)
C(35)	6 038(4)	8 836(4)	1 393(3)
C(36)	5 045(3)	9 724(3)	1 595(3)
C(41)	1 013(3)	7 151(3)	2 848(2)
C(42)	1 703(4)	5 920(3)	3 002(3)
C(43)	1 751(4)	5 386(4)	2 267(3)
C(44)	1 085(4)	6 087(4)	1 381(3)
C(45)	400(4)	7 306(4)	1 212(3)
C(46)	349(3)	7 846(3)	1 947(3)
C(51)	1 357(3)	6 836(3)	4 927(2)
C(52)	2 519(4)	5 963(3)	5 307(3)
C(53)	2 685(5)	5 104(4)	6 223(3)
C(54)	1 740(7)	5 123(5)	6 764(4)
C(55)	578(7)	5 975(6)	6 412(4)
C(56)	380(4)	6 845(4)	5 492(3)
C(10)	3 891(3)	11 064(3)	2 623(2)
O(1)	−189(2)	8 968(2)	3 658(2)
O(2)	4 038(2)	6 779(2)	3 507(2)
O(3)	3 141(2)	10 409(2)	3 081(2)
P(1)	1 008(1)	7 946(1)	3 726(1)
O(61)	8 375(4)	1 192(4)	2 743(3)
C(61)	8 722(6)	1 716(6)	1 920(4)
C(62)	9 610(4)	1 221(5)	1 580(4)
C(63)	7 718(9)	3 019(6)	1 465(6)

* For full details of the CCDC deposition scheme see, 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1993, Issue 1.

Table 3 ^{1}H NMR structural correlation of α'-Ph_2PO-enones **4** and **5**[a]



Compound	R_T[b]	J_{PH^4}	J_{45}	δ_{H^5}	δ_{Me^5}	δ_{H^4}	δ_{Me^2}	δ_{H^2}	δ_{Me^E}	δ_{H^E}	δ_{H^Z}
4a	*c*	*d*	*d*	3.82[d]	1.26	3.82[d]	—	6.53	1.76	—	6.72
5a	*c*	12.6	12.6	3.72	1.25	4.07	—	5.80	1.49	—	6.24
4b	17	11.0	7.0	3.79	1.23	4.55	1.46	—	—	5.66	5.95
5b	23	16.4	9.4	3.68	1.36	4.59	1.08	—	—	5.28	5.52
4c	10	8.4	5.6	2.75[d]	1.00	3.96	—	6.20	1.66	—	6.64
5c	13	13.8	10.4	2.77[d]	1.09	3.84	—	5.83	1.49	—	6.36
4d	10	12.1	5.8	2.96	0.96	4.65	1.43	—	—	5.52	5.91
5d	13	17.2	10.5	1.56[d]	1.18	4.46	1.16	—	—	5.34	5.75
4e	13	13.1	7.0	2.79[d]	0.96	4.56	1.35	—	1.57	—	6.65
5e	17	18.5	10.7	2.68[d]	1.21	4.56	2.10	—	1.41	—	6.62

[a] Spectra recorded in $CDCl_3$ at 250 MHz, chemical shifts (δ) in ppm, coupling constants (J) in Hz. [b] Retention time (min) on HPLC (Dynamex prepacked column (2.14 mm internal diameter × 25 cm) with a Gilson model 303 pump operating at 12 cm^3 min^{-1}, eluting with EtOAc). [c] Separated by column chromatography on silica eluting with 1:1 EtOAc–light petroleum (b.p. 60–80 °C), **4a** had R_F 0.20 and **5a** R_F 0.16. [d] Not resolved.

Table 4 Conformation of the enone group by IR spectroscopy

		ν_{max}/cm^{-1}		
			C=O stretch	
Compound	Structural type	C=C stretch	*s-cis*	*s-trans*
3a	α,β-disubstituted	1630		1650
3b	β-monosubstituted	1620	1680	1645
3c	β-monosubstituted	1620	1680	1655
3d	α-monosubstituted	1650	—	1650
3e	α,β-disubstituted	1630	—	1650
3f	α,β-disubstituted	1630	—	1630
4a	β-monosubstituted	1620	1710	1670
5a	β-monosubstituted	1620	1670	1650
4b	α-monosubstituted	1620	—	1660
5b	α-monosubstituted	1620	—	1655
4c	β-monosubstituted	1615	1670	1650
5c	β-monosubstituted	1640	1670	1655
4d	α-monosubstituted	1650	—	1720
5d	α-monosubstituted	1650	—	1710
4e	α,β-disubstituted	1635	—	1650
5e	α,β-disubstituted	1705	—	1750

criterion (Table 4), enones **3**, **4**, and **5** with R^3 = H (*e.g.* **3d**, **4d**, **5d**) or with R^2 and $R^3 \neq$ H (*e.g.* **3f**, **4e**, **5e**) exist exclusively as the *s-trans* conformer, whereas enones with R^2 = H and $R^3 \neq$ H (*e.g.* **3b**, **4c**, **5c**) exist as equilibrium mixtures of *s-cis* and *s-trans*. One exception to the general rule is **5b** which, although having R^3 = H, nevertheless seems to exist as an *s-cis*, *s-trans* mixture by IR spectroscopy.

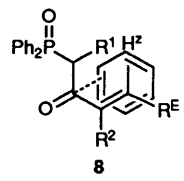
We hoped to confirm these assignments by solvent shift[15] data in the ^{1}H NMR spectra. In fact, all classes of enones **3**, even those with R^2 = H and $R^3 \neq$ H, gave similar upfield shifts for H^Z on changing the solvent from $CDCl_3$ to C_6D_6. This behaviour is expected only for the *s-trans* conformer which presents H^Z to the face of the solvating molecule of benzene **8**. The solvent shifts of other substituents agree: R^E (which may be H) shows a smaller upfield shift and R^2, which is on the border between the up- and down-field zones[15] shows little if any shift. Benzene solvent shifts are sadly of little help in assigning the conformation. It nevertheless seemed worthwhile to study the conformation of these open chain conformationally flexible molecules by a variety of methods and draw at least some tentative conclusions in view of the stereoselective reactions they exhibit.[2,16]

Relationship between the Enone and the Chiral Centres.—The various stereoselective reactions under investigation involve the approach of reagents to one face or the other of the enone plane governed by the disposition of the large groups (*e.g.* Ph_2PO) in the rest of the molecule. In the solid state, the X-ray structure of **5e** shows (Fig. 1; numbering as in Table 3) that H^4 and H^Z are *syn* planar with the Ph_2PO group on one face of the enone and the R^1 group on the other. This arrangement persists in solution as there is a clear NOE between H^4 and H^Z and *no* NOE between H^4 and either of the methyl groups on the enone. The other α,β-disubstituted enones, *i.e.* **3** with R^2 and $R^3 \neq$ H, and the α-substituted enones, those with $R^2 \neq$ H and R^3 = H, showed similar NOEs. Our previous exception, the enone **5b**, was also an *s-cis*, *s-trans* mixture by this technique as it showed an NOE both between H^Z and H^4 and between H^4 and Me^2.

Effect of Lewis Acids.—One of the reactions under study is the regioselective 1,2-reduction of the enones with $NaBH_4$ under the Luche[1] conditions ($CeCl_3$, MeOH, −78 °C) which gives high yields of the *erythro* alcohols[2] **9**. Without $CeCl_3$, the reduction occurs mostly 1,4 to give the saturated ketones **10**. We therefore studied the ^{1}H NMR spectra of the enones under the Luche reaction conditions without $NaBH_4$.

Though Ce^{3+} as a lanthanide might provide useful shift reagents, it has been little used[17] as it tends to be oxidised to Ce^{4+} which is paramagnetic. However, we found Ce^{3+} behaved very well. The spectrum of **4e** in [$^2H_4$]MeOH at −78 °C was essentially the same as that in $CDCl_3$ at 40 °C. Addition of $CeCl_3$ caused small but significant changes. The *ortho* protons (H° in **11**) were shifted downfield while the signal for Me^5 disappeared. This latter effect is presumably a relaxation phenomenon and suggest a complex such as **11** in which the enone conformation and the *syn* planarity of H^2 and H^6 are essentially unaltered but the Ph_2PO group has rotated to allow chelation of Ce^{3+} by C=O and P=O. Attack by $NaBH_4$ on a complex such as **11** accounts for the observed stereoselectivity of the reduction.[2]

It would be neither possible nor correct to define a single



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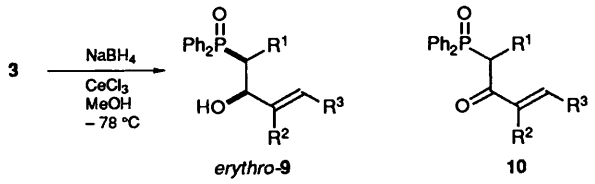

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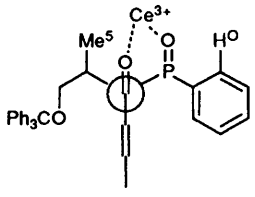

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conformation for any of these molecules in solution, but the general picture built up by these studies is consistent with the stereoselectivity of the reactions[2,16] and the approach of collecting tentative conclusions by a number of methods may be of value in attempts to understand other stereoselective reactions of open chain compounds.

Experimental

^{1}H NMR were recorded on Bruker WM-250, Bruker WP80-SY, or Varian Associates E. M. 90 spectrometers. Tetramethylsilane (TMS) or (deuterochloroform) $CDCl_3$ was used as an internal standard with chemical shifts (δ) given in parts per million (ppm) downfield from tetramethylsilane (δ = 0) and coupling constants (J) given in Hz. Low resolution mass spectra were recorded on a AEI-Kratos MS902 instrument, operating at 70 eV, and high resolution mass spectra were recorded on a AEI-Kratos MS30 double beam spectrometer with DS50 data system. Thin layer chromatography (TLC) was carried out on commercially prepared plates (Merck silica kieselgel $60F_{250}$), eluting with ethyl acetate (EtOAc) unless otherwise stated. Flash column chromatography[18] was carried out using Merck Kieselgel 60 (230–400 mesh) silica. Preparative high performance liquid chromatography (HPLC) was performed on a Dynamax prepack silica column (21.4 mm i.d. × 25 cm l), with a Gilson model 303 pump operating at 12 cm^3 min^{-1} and a Cecil Instruments CE 212A UV monitor measuring absorbance at 256 nm. R_T refers to the retention time. Melting points were determined on a Buchi 510 apparatus and are uncorrected. Micro-analyses were carried out by the Analytical Department of the University Chemical Laboratories, Cambridge. IR spectra were recorded in $CHCl_3$ solution unless otherwise stated using Perkin-Elmer 297, 1310 and 983 spectrophotometers. All solvents were distilled and dried in the usual manner.[19] THF was freshly distilled from lithium aluminium hydride ($LiAlH_4$) using benzophenone radical as an indicator. Dichloromethane was dried by distillation from P_2O_5. All non aqueous reactions were carried out under a dry nitrogen atmosphere. BuLi refers to commercial butyllithium (1.54 mol dm^{-3} solution in hexane).

3-Diphenylphosphinoyl-2-methylpropan-1-ol **1** (R = $CHMeCH_2OH$).—A solution of chlorodiphenylphosphine (33 g, 150 mmol) in dry Et_2O (150 cm^3) was added slowly to a solution of 2-methylprop-2-en-1-ol (10.8 g, 12.7 cm^3, 150 mmol) in Et_2O (200 cm^3) and dry pyridine (12 cm^3) at 0 °C. The addition took 30 min. A white solid appeared immediately and stirring was continued for 1 h. The mixture was filtered and the solvent removed at reduced pressure under N_2. The oily residue was redissolved in toluene (300 cm^3) and heated at reflux for 1 day. The solvent was removed under reduced pressure and the solid residue was purified by chromatography, eluting with EtOAc. The olefin[20] (24 g, 66%) was used directly in the following hydroboration[21] step.

A solution of the olefin in dry THF (150 cm^3) was added to a suspension of sodium borohydride (1.5 g, 4.0 mmol) in dry THF (30 cm^3) at room temperature. Boron trifluoride–diethyl ether (3.6 cm^3, 30 mmol) was added over 30 min with cooling. After 1 h, water (10 cm^3) was added, followed by sodium hydroxide (3 cm^3 of a 12% solution) in one portion, then H_2O_2 (3 cm^3 of a 100 volume solution) added gradually. After 1 h the reaction mixture was extracted with EtOAc (3 × 150 cm^3) and the organic portions dried (Na_2SO_4). Evaporation under reduced pressure and flash column chromatography, eluting with EtOAc, gave the *alcohol* (24 g, 59% based on methylpropenol) as prisms, m.p. 133–135 °C (from EtOAc) (Found: C, 69.9; H, 6.8; P. 11.2 $C_{16}H_{19}PO_2$ requires C, 70.1; H, 6.90; P, 11.3%); R_F (acetone) 0.5; ν_{max}/cm^{-1} 3270 (OH) and 1440 (P–Ph); $\delta_H(CDCl_3)$ 7.85–7.41 (10 H, m, Ph_2PO), 3.60 (1 H, dd, ABX, J_{HH} 11.5, 7.4, CHO), 3.44 (1 H, dd, ABX, J_{HH} 11.5, 7.4, CHO), 2.37–2.30 (2 H, m, CH_2P), 2.15–2.03 (1 H, m, C*H*Me) and 0.98 (3 H, dd, J_{HH} 7.0, J_{PH} 1.0, CH*Me*); *m*/*z* 274 (M, 10%), 256 (M − OH, 20%), 244 (M − CH_3O, 25%), 215 (Ph_2POCH_2, 85%) and 202 (Ph_2POH, 100%).

3-Diphenylphosphinoyl-2-methyl-1-triphenylmethoxypropane **1** (R = $CHMeCH_2OTr$).—A solution of 3-diphenylphosphinoyl-2-methylpropan-1-ol (3.0 g, 10.9 mmol) and trityl pyridinium tetrafluoroborate[22] (5.0 g, 12.1 mmol) in dry acetonitrile (150 cm^3) was stirred at room temperature for 20 h. The solvent was removed under reduced pressure and the solid residue purified by flash column chromatography, eluting with EtOAc. The *trityl ether* was obtained as microprisms (5.0 g, 87%), m.p. 157–160 °C (from EtOAc–light petroleum) (Found: C, 81.5; H, 6.5; P. 5.9. $C_{35}H_{33}PO_2$ requires C, 81.4; H, 6.40; P, 6.0%), R_F 0.50; ν_{max}/cm^{-1} 1580 (Ph) and 1175 (P=O); $\delta_H(CDCl_3)$ 7.81–7.18 (25 H, m, Ph_2PO and CPh_3) 3.05–2.91 (2 H, m, CH_2OTr), 2.56 (1 H, ddd, J_{HH} 3, J_{HH} 10, J_{PH} 15, CHP), 2.33–2.23 (1 H, m, C*H*Me), 2.04–1.86 (1 H, m, CHP) and 1.03 (3 H, d, J_{HH} 6.7, CH*Me*); *m*/*z* 273 (100%, M − trityl), 243 (25%, Ph_3C) and 201 (35%, Ph_2PO) (M^+ was observed in the FAB mass spectrum).

1-Diphenylphosphinoyl-2-phenylpropane **1** (R^1 = 1-phenylethyl).—2-Phenylpropan-1-ol (4 g) with toluene-*p*-sulfonyl chloride and 4-dimethylaminopyridine gave the toluene-*p*-sulfonate (90%), which with KI in dry THF gave 1-iodo-2-phenylpropane (80%). Lithium diphenylphosphide [from diphenylphosphine (3.14 cm^3, 18 mmol) and BuLi (12.7 cm^3, 19.6 mmol) in dry THF at −78 °C] was added to the iodide (4 g, 16.3 mmol) in dry THF (120 cm^3) at −78 °C. After 12 h, NH_4Cl (100 cm^3 saturated solution) was added and the layers separated. The aqueous layer was extracted with dichloromethane (3 × 50 cm^3). The combined organic layers were dried ($MgSO_4$) and the solvents removed under reduced pressure. The oil was dissolved in acetic acid (120 cm^3) and hydrogen peroxide (15 cm^3 of a 30% solution) added slowly. After 30 min the mixture was poured into ice–water with vigorous stirring. The solution was extracted with EtOAc (3 × 100 cm^3). The combined organic layers were washed with sodium carbonate (3 × 100 cm^3 of saturated solution), water (3 × 100 cm^3) and

brine (3 × 100 cm^3), dried ($MgSO_4$), and the solvents removed under reduced pressure. Recrystallisation from EtOAc gave the phosphine oxide (97%) which was identified spectroscopically.

General Procedure for the Preparation of the Enones.—BuLi (11 mmol) was added to a solution of the phosphine oxide (10 mmol) in dry THF (100 cm^3) at 0 °C with stirring. The coloured lithium derivative was cooled to −78 °C and the unsaturated aldehyde (11 mmol) added. After 30 min, NH_4Cl (50 cm^3) was added and the reaction mixture allowed to warm to room temperature. Separation of aqueous and organic layers and extraction of the aqueous layer with EtOAc (3 × 40 cm^3) gave, after drying (Na_2SO_4) and evaporation, the alcohol as a mixture of diastereoisomers. This was used in the Swern oxidation without further purification. DMSO (20 mmol) was added to a solution of oxalyl chloride (14 mmol) in dry CH_2Cl_2 (50 cm^3) at −55 °C. A solution of the alcohol was added slowly and the mixture stirred for 20 min. Triethylamine (50 mmol) was added and the mixture allowed to warm to room temperature. Evaporation of the solvent under reduced pressure and chromatography of the residue, eluting with EtOAc or EtOAc–light petroleum (b.p. 60–80 °C) gave the ketone. Diastereoisomers were separated by HPLC.

E-1-*Diphenylphosphinoyl*-3-*methylpent*-3-*en*-2-*one* **3a**. Methyldiphenylphosphine oxide (3 g, 13 mmol) and 2-methylbutenal (1.3 cm^3, 13 mmol) gave the *enone* as needles (1.9 g, 50%); m.p. 105–106 °C (from EtOAc–light petroleum) (Found: C, 72.3; H, 6.25; P, 10.4%; M^+, 298.1132. $C_{18}H_{19}PO_2$ requires C, 72.5; H, 6.4; P, 10.4%; *M*, 298.1211); R_F 0.45; ν_{max}/cm^{-1} 1650 (C=O), 1630 (C=C), 1580 (Ph) and 1440 (P–Ph); $\delta_H(CDCl_3)$ 7.81–7.41 (10 H, m, Ph_2PO), 6.91 (1 H, dq, J_{PH} 1.3, J_{HH} 6.9, =CH), 3.85 (2 H, d, J_{PH} 15.5, CHP), 1.84 (3 H, d, J_{HH} 6.9, =CMe) and 1.63 (3 H, s, =CMe); *m*/*z* 298 (M, 100%), 283 (M − Me, 30%), 215 (Ph_2POMe, 50%) and 201 (Ph_2PO, 70%).

E-6,6-*Dimethyl*-5-*diphenylphosphinoylhept*-2-*en*-4-*one* **3b**. 1-Diphenylphosphinoyl-2,2-dimethyl propane[23] (2 g, 7.4 mmol) and but-2-enal (0.63 cm^3, 7.4 mmol) gave after chromatography, eluting with EtOAc, the *enone* as needles (1.1 g, 46%); m.p. 196–197 °C (from EtOAc) (Found: C, 73.9; H, 7.4; P. 9.2. $C_{21}H_{25}PO_2$ requires C, 74.1; H, 7.35; P, 9.1%); R_F 0.66; ν_{max}/cm^{-1} 3060 (=CH), 1680 (C=O), 1654 (C=O), 1620 (C=C), 1435 (P–Ph), 1370 (P=O) and 1185; $\delta_H(CDCl_3)$ 7.88–7.34 (10 H, m, Ph_2PO), 6.50 (1 H, dq, J_{HH} 16, 6, =C*H*Me), 6.48 (1 H, br d, J_{HH} 16, =CH), 3.8 (1 H, br d, CHP), 1.65 (3 H, d, J_{HH} 6, Me) and 1.07 (9 H, s 3 × Me); *m z* 340 (M, 2%), 325 (M − Me, 2%), 284 (M − Bu, 15%), 201 (Ph_2PO, 40%) and 69 (C_4H_5O, 100%).

E-1-*Diphenylphosphinoyl*-1-(4-*methoxyphenyl*)*pent*-3-*en*-2-*one* **3c**. (4-Methoxyphenyl)methyldiphenylphosphine oxide[24] (5 g, 14.8 mmol) and but-2-enal (1.2 cm^3, 16 mmol) gave the *enone* as needles (4.1 g, 67%); m.p. 214–215 °C (from EtOAc–light petroleum) (Found: C, 73.3; H, 5.9; P, 7.7. $C_{24}H_{23}PO_3$ requires C, 73.85; H, 5.90; P, 9.95%); R_F 0.56; ν_{max}/cm^{-1} 3060 (=CH), 1680 (C=O), 1655 (C=O), 1620 (C=C), 1500 (Ph), 1435 (P–Ph) and 1175 (P=O); $\delta_H(CDCl_3)$ 7.83–7.26 (12 H, m, Ph_2PO and 2 H from Ar), 6.77 (1 H, dq, J_{HH} 7, J_{HH} 15.5, =CH), 6.74 (2 H, d, J_{HH} 7, Ar), 6.40 (1 H, d, J_{HH} 15.5, =CH), 4.83 (1 H, d, J_{PH} 9.1, CHP) and 1.75 (3 H, d, J_{HH} 7, Me); *m*/*z* 390 (M, 10%), 322 (M − C_4H_6O), 219 (Ph_2PO_2H, 10%), 201 (Ph_2PO, 50%) and 172 (M − Ph_2PO_2, 100%).

4-*Diphenylphosphinoyl*-2-*isopropylpent*-1-*en*-3-*one* **3d**. Ethyldiphenylphosphine oxide[24] (2 g, 8.7 mmol) and 2-isopropylpropenal (1.12 cm^3, 9.3 mmol) gave the *enone* as needles (2.2 g, 77%); m.p. 116–117 °C (from EtOAc–light petroleum) (Found: C, 73.9; H, 7.3; P. 9.3 $C_{20}H_{23}PO_2$ requires C, 73.6; H, 7.05; P, 9.5%); R_F 0.45; ν_{max}/cm^{-1} 1650 (C=C–C=O), 1580 (Ph) and 1440 (P–Ph); $\delta_H(CDCl_3)$ 7.96–7.37 (10 H, m, Ph_2PO), 6.04 (1 H, s, =CH), 5.68 (1 H, s, =CH), 4.34 (1 H, dq, J_{HH} 7.1, J_{PH} 14.4, CHP), 2.69 (1 H, quin, J_{HH} 6.7, C*H*Me_2), 1.43 (3 H, dd, J_{HH} 7.1, J_{PH} 16.2, PC*H*Me), 0.90 (3 H, d, J_{HH} 6.8, Me) and 0.72 (3 H, d, J_{HH} 6.8, Me); *m*/*z* 326 (M^+, 60%), 311 (M − Me, 50%), 283 (M − Pr^i, 30%), 219 (Ph_2PO_2H, 80%) and 201 (Ph_2PO, 100%).

E-3,7-*Dimethyl*-5-*diphenylphosphinoyloct*-2-*en*-4-*one* **3e**. (3-Methylbutyl)diphenylphosphine oxide[24] (3 g, 11 mmol) and 2-methylbut-2-enal (1.2 cm^3, 12 mmol) gave after flash column chromatography, eluting with EtOAc–light petroleum, the *enone* as needles (3.0 g, 78%); m.p. 170–172 °C (from EtOAc) (Found: C, 74.3; H, 7.75; P. 8.65. $C_{22}H_{27}PO_2$ requires C, 74.6; H, 7.65; P, 8.8%); R_F 0.37; ν_{max}/cm^{-1} 1650 (C=O), 1630 (C=C), 1580 (Ph) and 1440 (P–Ph); $\delta_H(CDCl_3)$ 7.94–7.37 (10 H, m, Ph_2PO), 6.61 (1 H, dq, J_{PH} 1.1, J_{HH} 6.8, =CH), 4.36 (1 H, ddd, J_{HH} 2.4, J_{HH} 7.2, J_{PH} 18.0, CHP), 2.22–2.12 (2 H, m, CH_2), 1.64 (3 H, dd, J_{PH} 1.1, J_{HH} 6.9, =CH*Me*), 1.51 (3 H, s, =CMe), 1.49–1.40 (1 H, m, C*H*Me_2), 0.82 (3 H, d, J_{HH} 6.5, CH*Me*) and 0.77 (3 H, d, J_{HH} 6.4, CH*Me*); $\delta_C(CDCl_3)$ 198.1 (C=O), 131–128.2 (m, Ph_2PO), 139.7 (s, =C), 139.0 (s, =C), 48.4 (d, J_{CP} 56.9, CHP), 36.6 (s, =CMe), 27.3 (d, J_{CP} 12, CHMe), 22.9 (s, =CMe), 21.5 (s, CHMe), 14.8 (s, Me) and 11.1 (s, Me); *m*/*z* 354 (M, 45%), 339 (M − Me, 20%), 298 (M − C_4H_8, 60%), 229 (85%), 219 (Ph_2PO_2H, 80%) and 201 (Ph_2PO, 100%).

E-1-*Cyclohexyl*-1-*diphenylphosphinoyl*-3-*methylpent*-3-*en*-2-*one* **3f**. (Cyclohexylmethyl)diphenylphosphine oxide[24] (2 g, 6.7 mmol) and 2-methylbut-2-enal (0.7 cm^3, 7.1 mmol) gave the *enone* as prisms (1.45 g, 58%); m.p. 178–180 °C (from EtOAc) (Found: C, 76.0; H, 7.7; P. 7.9. $C_{24}H_{29}PO_2$ requires C, 75.8; H, 7.6; P. 8.2%); R_F 0.44, ν_{max}/cm^{-1} 1630 (C=C–C=O), 1580 (Ph), and 1440 (P=O); $\delta_H(CDCl_3)$ 8.17–7.29 (10 H, m, Ph_2PO), 6.65 (1 H, dq, J_{PH} 1.1, J_{HH} 6.7, =CH), 4.16 (1 H, dd, J_{HH} 10.4, J_{PH} 17.5, CHP), 2.37–2.21 (1 H, m, CH), 2.02–1.90 (1 H, m, CH), 1.67 (3 H, dd, J_{PH} 1.1, J_{HH} 6.7, =CMe), 1.61–1.47 (4 H, m, 2 × CH_2), 1.24 (3 H, s, =CMe) and 1.21–0.86 (5 H, m, CH_2); *m*/*z* 380 (M, 80%), 365 (M − Me, 30%), 298 (M − C_5H_8O, 100%), 219 (Ph_2PO_2H, 85) and 201 (Ph_2PO, 95%).

E-5-*Diphenylphosphinoyl*-6-*phenylhept*-2-*en*-4-*one* **4a** *and* **5a**. 1-Diphenylphosphinoyl-2-phenylpropane (500 mg, 1.6 mmol) and but-2-enal (0.16 cm^3, 1.8 mmol) gave, after column chromatography, eluting with EtOAc–light petroleum, the first *diastereoisomer* of the enone as feathers (130 mg, 21%); m.p. 206–208 °C (from EtOAc–light petroleum) (Found: C, 77.5; H, 6.45; P. 7.8. $C_{25}H_{25}PO_2$ requires C, 77.3; H, 6.45; P, 8.0%); R_F 0.2 (EtOAc–light petroleum 1:1); ν_{max}/cm^{-1} 1710 (C=O), 1670 (C=O) and 1430 (P–Ph); $\delta_H(CDCl_3)$ 7.74–6.84 (15 H, m, Ph_2PO and Ph), 6.72 (1 H, dq, J_{HH} 6.8, J_{HH} 15.4, =CH), 6.53 (1 H, dd, J_{HH} 15.4, J_{PH} 1.1, =CH), 3.89–3.76 (2 H, m, CHP and C*H*Me), 1.76 (3 H, dd, J_{PH} 1.1, J_{HH} 6.8, Me) and 1.26 (3 H, d, J_{HH} 6.1, CH*Me*); *m*/*z* 388 (M, 2%), 319 (M − C_4H_5O, 10%), 219 (Ph_2PO_2H, 30%), 201 (Ph_2PO, 30%) and 84 (100%).

The second *diastereoisomer* was obtained as feathers (125 mg, 20%); m.p. 206–208 °C (from EtOAc–light petroleum) (Found: C, 77.5; H, 6.4; P. 7.9. $C_{25}H_{25}PO_2$ requires C, 77.3; H, 6.4; P, 8.0%); R_F 0.16 (EtOAC–light petroleum); ν_{max}/cm^{-1} 1670 (C=O), 1650 (C=O), 1615 (C=C) and 1440 (P–Ph); $\delta_H(CDCl_3)$ 8.09–7.07 (15 H, m, Ph_2PO and Ph), 6.24 (1 H, dq, J_{HH} 7, J_{HH} 15.4, =CH), 5.80 (1 H, d, J_{HH} 15.4, =CH), 4.07 (1 H, t, J_{PH} = J_{HH} = 12.6, CHP), 3.72 (1 H, m, C*H*Me), 1.49 (3 H, d, J_{HH} 6.8, =CH*Me*) and 1.25 (3 H, d, J_{HH} 6.8, Me); *m*/*z* 388 (M, 10%), 319 (M − C_4H_5O, 20%), 219 (Ph_2PO_2H, 70%) and 201 (Ph_2PO, 100%).

4-*Diphenylphosphinoyl*-2-*methyl*-5-*phenylhex*-1-*en*-3-*one* **4b** *and* **5b**. 3-Diphenylphosphinoyl-2-phenylpropane (1 g, 3.2 mmol) and 2-methylpropenal (0.26 cm^3, 3.2 mmol) gave after HPLC, eluting with EtOAc, the first *diastereoisomer* (R_T 17 min) as needles (310 mg, 25%); m.p. 175–177 °C (from EtOAc–light petroleum) (Found: C, 77.05; H, 6.37; P, 8.26. $C_{25}H_{25}PO_2$ requires C, 77.32; H, 6.44; P, 7.99%); R_F 0.65; ν_{max}/cm^{-1} 1660 (C=O), 1620 (C=C) and 1175 (P=O); $\delta_H(CDCl_3)$ 7.81–6.92 (15 H, m, Ph_2PO and Ph), 5.95 (1 H, s, C=CH), 5.66 (1 H, d, J_{PH}

1, C=CH), 4.55 (1 H, dd, J_{PH} 11, J_{HH} 9.5, CHP), 3.79 (1 H, sextet, $J_{HH} = J_{PH} = 7.0$, C*H*Me), 1.46 (3 H, s, =CMe) and 1.23 (3 H, d, J_{HH} 7.0, CH*Me*); $\delta_C(CDCl_3)$ 199 (C=O), 146 (C=C), 142 (C=C), 125.9–132.8 (ArC), 57.6 (d, J_{CP} 59, CP), 39.9 (d, J_{CP} 2, =CMe), 21.1 (d, J_{CP} 10, CPh) and 17.4 (Me); *m/z* 388 (2%, M), 319 (12%, M − C_4H_5O), 243 (20%) and 202 (100%, Ph_2POH).

The second *diastereoisomer* (R_T 23 min) was obtained as feathers (270 mg, 23%); m.p. 153–154 °C (from EtOAc–light petroleum) (Found: C, 77.09; H, 6.32; P, 7.97. $C_{25}H_{25}PO_2$ requires C, 77.32; H, 6.46; P, 7.99%); R_F 0.65; ν_{max}/cm^{-1} 1655 (C=O), 1620 (C=C), 1580 (Ph) and 1185 (P=O); $\delta_H(CDCl_3)$ 8.28–7.06 (15 H, m, Ph_2PO and Ph), 5.52 (1 H, s, =CH), 5.28 (1 H, d, J_{PH} 1.0, =CH), 4.59 (1 H, dd, J_{PH} 16.4, J_{HH} 9.4, CHP), 3.68 (1 H, m, CHPh), 1.36 (3 H, d, J_{HH} 7.0, CH*Me*) and 1.08 (3 H, s, =CMe); *m/z* 388 (2%, M), 319 (M − C_4H_5O, 15%), 243 (33%) and 202 (Ph_2POH, 100%).

E-5-*Diphenylphosphinoyl*-6-*methyl*-7-*triphenylmethoxyhept*-2-*en*-4-*one* **4c** *and* **5c**. 3-Diphenylphosphinoyl-2-methyl-1-triphenylmethoxypropane (2 g, 4 mmol) and but-2-enal (0.4 cm^3, 4.4 mmol) gave after HPLC, eluting with EtOAc, the first *diastereoisomer* (R_T 10 min) as prisms (820 mg, 36%); m.p. 162–163 °C (from EtOAc–light petroleum) (Found: C, 80.4; H, 6.6; P, 5.5. $C_{39}H_{37}PO_3$ requires C, 80.1; H, 6.3; P. 5.3%); R_F 0.27 (EtOAc–light petroleum 1:1); ν_{max}/cm^{-1} 1670 (C=O), 1650 (C=O), 1615 (C=C), 1600 (Ph) and 1440 (P–Ph); $\delta_H(CDCl_3)$ 7.83–7.16 (25 H, m, Ph_2PO and CPh_3), 6.64 (1 H, dq, J_{HH} 7, J_{HH} 15.4, =CH), 6.20 (1 H, dd, J_{PH} 1.5, J_{HH} 15.4, =CH), 3.96 (1 H, dd, J_{HH} 5.6, J_{PH} 8.4, CHP), 3.07–3.00 (1 H, m, CHOTr), 2.78–2.73 (2 H, m, CHOTr and C*H*Me), 1.66 (3 H, dd, J_{PH} 1.4, J_{HH} 7.0, =CH*Me*) and 1.00 (3 H, d, J_{HH} 9.1, CH*Me*); *m/z* 342 (M + H − trityl, 20%), 341 (M − trityl, 100%), 243 (trityl, 60%) and 201 (Ph_2PO, 35%).

The second *diastereoisomer* was obtained (R_T 13 min) as microcrystals (480 mg, 21%); m.p. 187–188 °C (from EtOAc–light petroleum) (Found: C, 80.2; H, 6.3; P, 5.2. $C_{39}H_{37}PO_3$ requires C, 80.14; H, 6.34; P, 5.3%); R_F 0.27 (EtOAc–light petroleum 1:1); ν_{max}/cm^{-1} 1670 (C=O), 1655 (C=O), 1640 (C=C), 1440 (P–Ph) and 1140 (P=O); $\delta_H(CDCl_3)$ 8.01–7.12 (25 H, m, Ph_2PO and CPh_3), 6.36 (1 H, dq, J_{HH} 7.0, J_{HH} 15.5, =C*H*Me), 5.83 (1 H, dd, J_{PH} 1.5, J_{HH} 15.5, =CH), 3.84 (1 H, dd, J_{HH} 10.4, J_{PH} 13.8, CHP), 3.00 (1 H, dd, ABX, J_{AB} 9, J_{AX} 4.0, CHOTr), 2.90 (1 H, dd, ABX, J_{AB} 9.0, J_{BX} 4.1, CHOTr), 2.80–2.74 (1 H, m, CHMe), 1.49 (3 H, dd, J_{PH} 1.5, J_{HH} 7.0, =CH*Me*) and 1.09 (3 H, d, J_{HH} 6.7, Me); *m/z* 341 (M − CPh_3, 90%), 243 (CPh_3, 100%), 201 (Ph_2PO, 85%) and 165 (90%).

4-*Diphenylphosphinoyl*-2,5-*dimethyl*-6-*triphenylmethoxyhex*-1-*en*-3-*one* **4d** *and* **5d**. 3-Diphenylphosphinoyl-2-methyl-1-triphenylmethoxypropane (400 mg, 0.78 mmol) and 2-methylpropenal (0.06 cm^3, 0.78 mmol) gave after HPLC, eluting with EtOAc, the first *diastereoisomer* (R_T 10 min) as needles (190 mg, 41%); m.p. 155–157 °C (from EtOAc–light petroleum) (Found: C, 79.9; H, 6.4; P. 5.1. $C_{39}H_{37}PO_3$ requires C, 80.1; H, 6.3; P, 5.3%); R_F 0.49; ν_{max}/cm^{-1} 1720 (C=O), 1650 (C=C), 1580 (Ph), 1430 (P–Ph) and 1150 (P=O); $\delta_H(CDCl_3)$ 7.89–7.09 (25 H, m, Ph_2PO and CPh_3), 5.52 (1 H, d, J_{PH} 1.4, =CH), 5.91 (1 H, s, =CH), 4.65 (1 H, dd, J_{HH} 5.8, J_{PH} 12.1, CHP), 2.98 (2 H, m, CH_2OTr), 2.96 (1 H, m, C*H*Me), 1.43 (3 H, s, =CMe) and 0.96 (3 H, d, J_{HH} 6.7, CH*Me*); *m/z* 342 M − $HCPh_3$, 30%), 341 (M − CPh_3, 90%), 243 (CPh_3, 100%), 219 (Ph_2PO_2H, 40%), 201 (Ph_2PO, 70%) and 165 (60%).

The second *diastereoisomer* was obtained (R_T 13 min) as needles (105 mg, 23%); m.p. 169–170 °C (from EtOAc–light petroleum) (Found: C, 80.4; H, 6.5; P. 5.4 $C_{29}H_{37}PO_3$ requires C, 80.1; H, 6.3; P. 5.3%); R_F 0.49; ν_{max}/cm^{-1} 1710 (C=O), 1650 (C=C) and 1580 (Ph); $\delta_H(CDCl_3)$ 8.14–8.06 and 7.71–7.31 (25 H, m, Ph_2PO and CPh_3), 5.75 (1 H, s, =CH), 5.34 (1 H, d, J_{PH} 1.5, =CH), 4.46 (1 H, dd, J_{HH} 10.5, J_{PH} 17.2, CHP), 2.98–2.74 (2 H, m, CH_2O), 1.72–1.41 (1 H, m, CHMe), 1.18 (3 H, d, J_{HH} 7.0, CH*Me*) and 1.16 (3 H, s, =CMe); *m/z* 341 (M − trityl, 100%), 243 (trityl, 75%), 219 (Ph_2PO_2H, 30%), 201 (Ph_2PO, 60%) and 165 (40).

E-5-*Diphenylphosphinoyl*-3,6-*dimethyl*-7-*triphenylmethoxyhept*-2-*en*-4-*one* **4e** *and* **5e**. 3-Diphenylphosphinoyl-2-methyl-1-triphenylmethoxypropane (1.1 g, 2.13 mmol) and 2-methylbutenal (0.14 cm^3, 2.3 mmol) gave after HPLC, eluting with EtOAc, the first *diastereoisomer* (R_T 13 min) as microprisms (530 mg, 42%); m.p. 163–165 °C (from EtOAc–light petroleum) (Found: C, 80.3; H, 6.0; P. 5.2. $C_{40}H_{39}PO_3$ requires C, 80.3; H, 6.5; P, 5.2%); R_F 0.43 (EtOAc–light petroleum); ν_{max}/cm^{-1} 1650 (C=O), 1635 (C=C), 1580 (Ph) and 1440 (P–Ph); $\delta_H(CDCl_3)$ 7.94–7.17 (25 H, m, Ph_2PO and CPh_3), 6.65 (1 H, q, J_{HH} 6.5, C=CH), 4.56 (1 H, dd, J_{HH} 7, J_{PH} 13.1, CHP), 3.04 (1 H, ABX, dd, J_{AB} 9.2, J_{AX} 7.2, CHOTr), 2.94 (1 H, ABX dd, J_{AB} 9.2, J_{BX} 7.2, CHOTr), 2.85–2.73 (1 H, m, CHMe), 1.57 (3 H, dd, J_{PH} 0.9, J_{HH} 6.9, =CH*Me*) and 0.96 (3 H, d, J_{HH} 6.8, CH*Me*); *m/z* 598 (M, 2%), 355 (M − CPh_3, 20%), 243 (CPh_3, 100%), 219 (Ph_2PO_2H, 90%) and 201 (Ph_2PO, 90%).

The second *diastereoisomer* (R_T 17 min) was obtained as prisms (342 mg, 27%); m.p. 156–157 °C (from EtOAc–light petroleum) (Found: C, 79.8; H, 6.55; P. 5.1. $C_{40}H_{39}PO_3$ requires C, 80.3; H, 6.5; P. 5.2%); R_F 0.43 (EtOAc–light petroleum, 1:1); ν_{max}/cm^{-1} 1750 (C=O), 1705 (C=O), 1630 (C=C), 1580 (Ph) and 1440 (P–Ph); $\delta_H(CDCl_3)$ 8.23–8.13 and 7.67–7.08 (25 H, m, Ph_2PO and CPh_3), 6.62 (1 H, q, J_{HH} 6.1, =CH), 4.56 (1 H, dd, J_{PH} 10.7, J_{HH} 18.5, CHP), 2.92 (1 H, dd ABX, J_{AB}, 9.9, J_{AX}, 3.0, CHOTr), 2.78 (1 H, dd, ABX, J_{AB} 9.9, J_{BX} 3.8, CHOTr), 2.70–2.66 (1 H, m, CHMe), 2.10 (3 H, s, =Me), 1.41 (3 H, d, J_{HH} 6.1, =CH*Me*) and 1.21 (3 H, d, J_{HH} 6.8, CH*Me*); *m/z* 598 (M, 20%), 355 (M − trityl, 100%) and 201 (Ph_2PO, 70%).

Acknowledgements

We thank the SERC for grants (to D. H. and N. S.), Schering Agrochemicals Ltd. for a CASE award (to D. H.) and Drs. A. D. Buss and P. Dudfield for many helpful discussions.

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Paper 2/03948F
Received 23*rd July* 1992
Accepted 13*th November* 1992