Synthesis of Single Isomers (*E* or *Z*) of Protected γ,δ-Unsaturated Ketones by the Horner-Wittig Reaction

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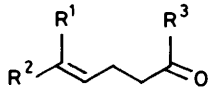
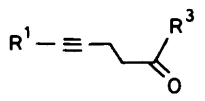
The lithium derivative of the γ-diphenylphosphinoyl ketal (**10a**) added to aldehydes and ketones to give stable Horner-Wittig intermediates (**11**) which were separated and converted into single isomers (*E* or *Z*) or γ,δ-unsaturated ketals (**12**). *erythro*-Adducts (**11**), and hence *Z*-(**12**), were selectively formed by addition of aldehydes and *threo* adducts (**11**), and hence *E*-(**12**), by reduction of the corresponding α-diphenylphosphinoyl ketones (**13**), prepared by acylation of the same γ-diphenylphosphinoyl ketal (**10a**).

γ,δ-Unsaturated aldehydes and ketones (**1**) occur naturally and have been used as intermediates in the synthesis of juvenile hormone,[1-3] rethrolones,[4] insect pheromones,[5-8] terpenes,[9] trisporic acids,[10] and prostaglandins.[11] Most of the natural products have a specific double bond geometry, a feature also required of the synthetic intermediates.

E-Isomers are often made by the Claisen-Cope or Carroll rearrangements which give good stereoselectivity in ketones (**1**) where R^1 and R^2 are very different in size,[12] but not if they are similar in size but different in electronic demand.[13,14] The strategy of this approach is the allylation of a ketone.



(**1**)



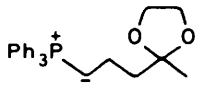
(**2**)

If the double bond is derived from a triple bond by reduction,[4,8] full stereochemical control may be achieved by suitable reduction methods.[6] For many years,[15] addition of an acetylene to an enone was not among the available approaches to γ,δ-ynones (**2**) but alkynyl aluminium[15] and boron[7,16] reagents are now known to add to cisoid enones to give ketones (**2**).

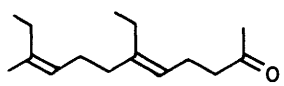
The Michael addition of vinyl anion equivalents to enones is one of the simplest strategies but vinylboranes add thus only to cisoid enones.[17] Full stereochemical control can be achieved by the addition of a vinyl cuprate, even to cyclopentenones.[11] Trisubstituted double bonds can be made by addition of an alkylcopper to an acetylene and Michael addition of the resulting stereospecific vinyl cuprate.[18]

The Wittig reaction of the ylide (**3**) with aldehydes and ketones was one of the first approaches.[19] Under the right conditions, highly selective *cis* olefination is possible with aldehydes[4] but isomer ratios of 75:25 to 45:55 (*E*:*Z*) are found with ketones.[2,3,9,10,14,20]

In one example,[2] a Claisen rearrangement followed by a Wittig reaction between the ylide (**3**) and a ketone gave a 15:23:25:37 mixture of geometrical isomers of the ketone (**4**). The worst aspect of these two otherwise excellent methods is that separation of geometrical isomers must be attempted by g.l.c.,[2] t.l.c.,[10] repetitive continuous elution chromatography,[9] or spinning band distillation.[3,13] Column chromatography gave either incomplete separation[14] or decomposition.[9]

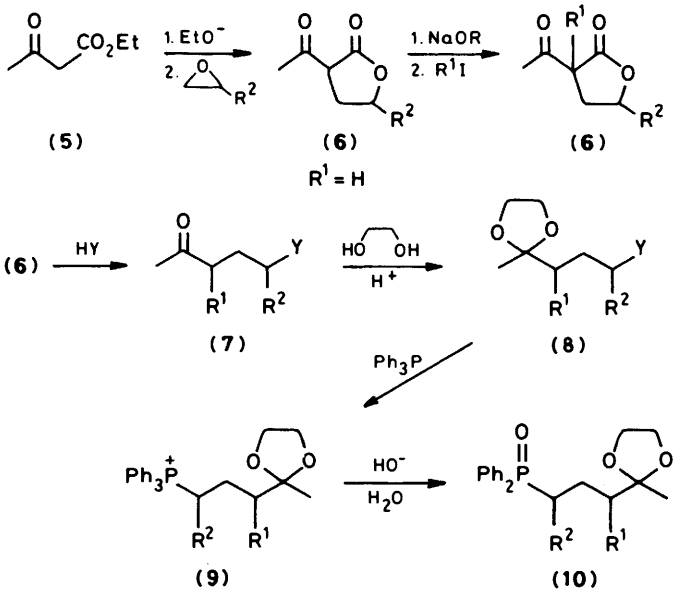


(**3**)



Z,*E*-(**4**)

We report[21] that the Horner-Wittig reaction with the γ-diphenylphosphinoyl ketals (**10**) may be used stereoselectively in reactions with aldehydes and ketones to produce *E* or *Z* isomers of γ,δ-unsaturated ketals without separation of the final products. Instead flash chromatography[22] and crystallisation of the intermediates on a gram scale gains exclusive entry to one stereochemical family.



Scheme 1. Synthesis of protected γ-diphenylphosphinoyl ketones

The phosphonium salt (**9a**) had been made[2,4,23] in the usual way from the protected γ-halogeno ketone (**8a**). Alkyldiphenylphosphine oxides are usually made from phosphonium salts by alkaline hydrolysis[24] and γ-halogeno ketals can be assembled by the reactions in Scheme 1. Addition of an epoxide to the keto ester (**5**) gave keto lactones (**6**; R^1 = H),[25] which were alkylated[26] if required. These keto lactones (**6**) can be converted directly into γ-halo ketones[2,27] (**7**) with HCl, HBr, or HI. Yields were generally better with HCl and the chloro ketone (**7**; Y = Cl) gave the highest yields of ketal (**8**), but the reaction with triphenylphosphine was so slow (Table 1) that the best compromise was to use the bromo compounds (**8**; Y = Br).

Table 1. Synthesis of γ-diphenylphosphinoyl ketals (**10**)

Series	R^1	R^2	Yield (**6**) (%)	Y	Yield (**7**) (%)	Yield (**8**) (%)	Time[a] (days)	Yield (**10**) (%)
a	H	H	78	Cl	88	83	3[b]	65
				Br	73	72	2	72
				I	68	70	2	54
b	H	Me	55	Cl	91	80	—	—
				Br	80	64	5	38
c	H	Et	42	Br	78	58	4	43
d	Me	H	72[c]	Cl	83	69	—	—
				Br	61	49	2	52
e	Me	Me	—	Br	31[d]	28[d]	—	*e*

[a] Time of refluxing a toluene solution of (**8**) with Ph_3P. [b] With NaI: without NaI, 7 days gave < 5% (**9a**). [c] From (**6a**) by alkylation. [d] Mixture of diastereoisomers. [e] < 10% (**9e**) after 7 days: (**10e**) was not prepared.

Alkaline hydrolysis of the phosphinium salts (**9**) gave the crystalline phosphine oxides (**10**).

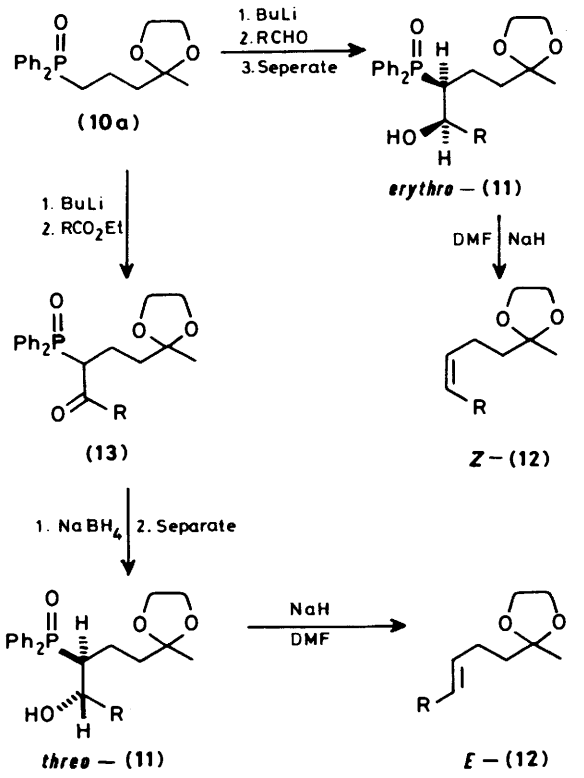
The phosphine oxide (**10a**) was also prepared from γ-chloro ketal (**8a**; Y = Cl) by an Arbuzow reaction with Ph_2POEt (this route has been used for the corresponding diethyl phosphine oxide[28]) and the phosphine oxide (**10b**) by methylation (BuLi, TMEDA, MeI) of (**10a**) but both routes gave low yields and chromatography was required to purify the products and the route of Scheme 1 was preferred.

Synthesis of Protected γ,δ-Unsaturated Ketals.—Our stereoselective Horner-Wittig reaction[29] uses direct addition of aldehydes to the lithium derivatives of phosphine oxides for stereoselective formation of the *erythro* intermediates and hence *Z*-alkenes.[30] Acylation of the same lithium derivative and reduction of the resulting α-diphenylphosphinoyl ketones stereoselectively gives the *threo* intermediates and hence *E*-alkenes.[31] We have already used this route to make protected β,γ-unsaturated ketones[32] but stereoselectivity in the aldehyde addition was very poor. Fortunately, stereoselectivity with the present series of phosphine oxides (**10**) (Scheme 2) is much improved.

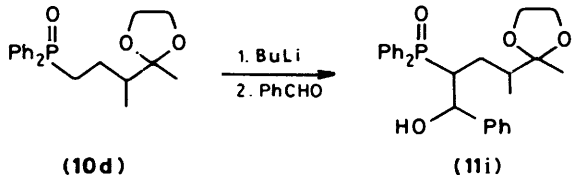
Treatment of the γ-diphenylphosphinoyl ketal (**10a**) with butyl-lithium (BuLi) in tetrahydrofuran (THF) at 0 °C gave the deep red lithium derivative which was cooled to −78 °C and treated with aldehydes to give mixtures of diastereoisomers of the adducts (**11**) (Scheme 2). Flash column chromatography[22] (SiO_2, EtOAc) gave pure *erythro* and *threo* adducts (**11**). The acetaldehyde (**11b**) and benzaldehyde (**11g**) adducts were formed with good *erythro* stereoselectivity. This decreased slightly for longer unbranched chains (**11c—e**) and disappeared for branched chains (**11f,h**). The adducts (**11c**; R = Et) were not separated by this chromatographic system. In all other cases yields of pure crystalline *erythro* adducts (**11**) of *ca.* 50% were achieved.

One Horner-Wittig reaction was attempted with the methylated γ-phosphinoyl ketal (**10d**) whose lithium derivative added to benzaldehyde to give two diastereoisomers of adduct (**11i**). This compound has three chiral centres, the yield was poor (42%), and this compound was not studied further.

Though stereoselectivity in the addition of aldehydes to the lithium derivatives of ketal (**10a**) is less than that observed for many unfunctionalised compounds (Table 3), it compares favourably with that observed for the better analogy (**15**) and for other functionalised phosphine oxides (Table 3). Chelation of the first formed lithium derivative (**22**) may be responsible for the fall in stereoselectivity but it seems more likely that this, or chelation in the transition state[29] (**23**), occurs with nearer [(**16**)—(**18**), Table 2] or more active (**19**) functional groups, and



Scheme 2. Stereocontrolled synthesis of protected γ,δ-unsaturated ketones

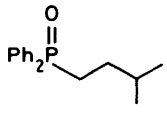


that the ketal exerts a mainly steric effect. The transition state geometry (**23**) probably results[29] from the large Ph_2PO group remaining *anti* to the developing solvated O^- and when R^1 contains a quaternary carbon atom, as in (**10a**), it begins to rival Ph_2PO in size. When the same functionality is one atom closer to the reaction site (**18**), separation of diastereoisomers of

Table 2. Stereoselectivity of Horner-Wittig reactions with γ-diphenylphosphinoyl ketal (**10a**)

Product	R	Yield (**11**)	*erythro*: *threo*	Yield (%)[a] *erythro*-(**11**)	Yield (%) *Z*-(**12**)	Yield (%)[a] *threo*-(**11**)	Yield (%) *E*-(**12**)
(**11a**)	H	68	—	—	63[b]	—	63[b]
(**11b**)	Me	75	3.2:1	57	76	18	80
(**11c**)	Et	62	2.5:1	*c*	81[c]	*c*	81[c]
(**11d**)	Pr^n	67	2.2:1	46	76	21	85
(**11e**)	Bu^n	78	1.7:1	49	83	29	72
(**11f**)	Pr^i	79	1:1	39	77	40	79
(**11g**)	Ph	72	3.8:1	57	90	15	83
(**11h**)	C_6H_{11}[d]	71	1:1	36	58	35	—

[a] Yield of isolated crystalline diastereoisomers. [b] Yield (**12a**): no geometry. [c] Diastereoisomers not separated: ratio by n.m.r. [d] Cyclohexyl.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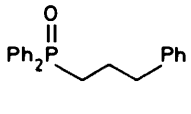
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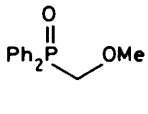
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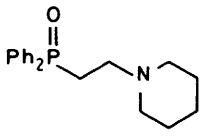
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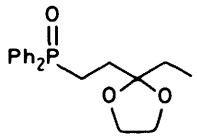
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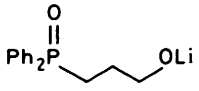
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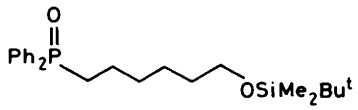
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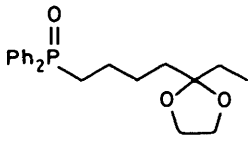
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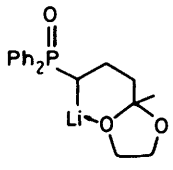
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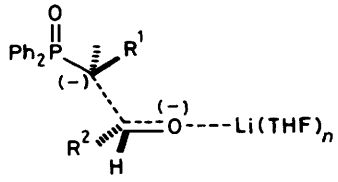
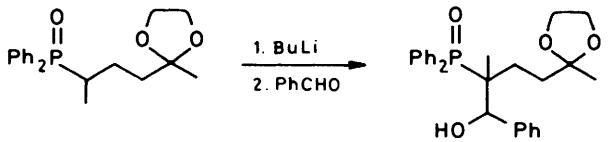

(23)

Horner-Wittig adducts or even estimation of their ratio by n.m.r. becomes very difficult.[32]

The *threo* adducts (**11**) were also isolated as minor products (15—40%) from aldehyde addition, but better yields were obtained by reduction of the α-diphenylphosphinoyl ketones (**13**) (Table 4). Acylation[33] of the lithium derivative of γ-diphenylphosphinoyl ketal (**10a**) with ethyl esters gave good yields of the ketones (**13**). These ketones are, in fact, half-protected diketones, but no dioxolane transfer was observed on storage and they were reduced with sodium borohydride in aqueous ethanol to give three of the adducts (**11b,d,g**) with *threo* selectivity. Yields were high and allowed the isolation of good yields (57—71%) of pure crystalline *threo* adducts.

Both *erythro* and *threo*-adducts (**11**) gave stereospecific elimination of $Ph_2PO_2^-$ on treatment with sodium hydride in dimethylformamide (DMF) for *ca.* 1 h to give γ,δ-unsaturated ketals (**12**). Each isomer had a different ^1H n.m.r. spectrum and in the case of (**12g**) and *Z*-(**12h**) the coupling constants between the vicinal olefinic protons confirmed the stereochemical assignment.

Synthesis of Trisubstituted Olefins.—Trisubstituted olefins[34] are best approached *via* ketone adducts of the simple phosphine oxide (**10a**), but one experiment with the methylated phosphine oxide (**10b**) showed that this route was also reasonable: a 1:1 mixture of the two benzaldehyde adducts was separated to give 35 and 37% yields of the two diastereoisomers (**24**).


(10b) (24)

Addition of ketones to the lithium derivative of γ-phosphinoyl ketal (**10a**) was more generally satisfactory. Yields (Table 5) were reasonable, even with the highly enolisable ketones cyclopentanone and acetophenone. Symmetrical ketones gave single adducts (**25**) and unsymmetrical ketones gave a *ca.* 1:1 mixture of diastereoisomers, as they do with unfunctionalised phosphine oxides.[34]

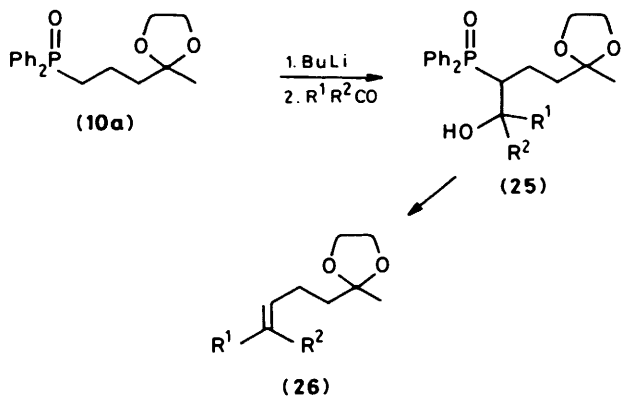

(10a) (25) (26)

Table 3. Diastereoselectivity in Horner-Wittig reactions

Phosphine Oxide	Aldehyde	Isolated yield (%) adduct	*erythro*: *threo*	Yield (%) *erythro*	Yield (%) *Z*-alkene	Ref.
(14)	PhCHO	81	80:20	65	65	29
(15)	MeCHO	95	58:42	56	81	29
(16)	4-$MeOC_6H_4$	85	45:55	39	70	*a*
(17)	PhCHO	80	52:48	42	72	*b*
(17)	MeCHO	69	51:49	35	74	*b*
(18)	MeCHO	73	*c*	*c*	—	32
(19)	PhCHO	92	75:25	69	95	*d*
(20)	EtCHO	85	64:36	55	94	*d*
(21)	EtCHO	71	60:40	*e*	—	*f*

[a] C. Earnshaw, C. J. Wallis, and S. Warren, *J. Chem. Soc., Perkin Trans 1*, 1979, 3099. [b] D. J. Cavalla and S. Warren, *Tetrahedron Lett.*, 1982, **23**, 4505. [c] Diastereoisomers could not be separated. [d] A. D. Buss, N. Greeves, D. Levin, P. Wallace, and S. Warren, *Tetrahedron Lett.*, 1984, **25**, 357. [e] *Erythro* Diastereoisomer not obtained pure. [f] C. A. Cornish and S. Warren, unpublished work.

Table 4. Stereoselectivity of reduction of ketones (**13**)

Adduct	R	Yield (%) (**13**)	Yield (%) (**11**)	*threo*: *erythro*	Yield (%) *threo*-(**11**)	Yield (%) *E*-(**12**)	Yield (%)[a] *erythro*-(**11**)
(11b)	Me	71	91	3.5:1	71	80	20
(11d)	Pr	51	81	2.4:1	57	85	24
(11g)	Ph	64[b]	84	3.0:1	63	83	21

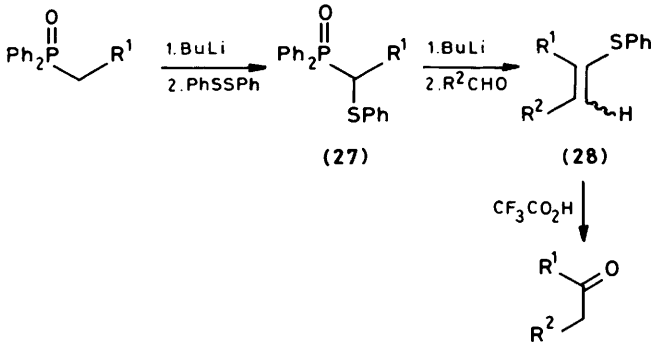
[a] For yield of *Z*-(**12**) see Table 2. [b] 55% PhCOCl as electrophile.

Table 5. Trisubstituted alkenes

Adduct	R^1	R^2	Yield (%) (**25**)	Isomer ratio	Yield (%) of products: Isomer (**25A**)	Isomer (**26A**)	Isomer (**25B**)	Isomer (**26B**)
(25a)	Me	Me	70	—	—	84	—	84[a]
(25b)	Et	Et	48	—	—	—	–	—
(25c)		$(CH_2)_4$	51	—	—	—	—	—
(25d)		$(CH_2)_5$	70	—	—	89	—	89[a]
(25e)	Me	Et	77	1:1	39	73	38	81
(25f)	Me	Pr^n	56	1:1	28	—	28	—
(25g)	Me	Pr^i	62	0.9:1	29	82	33	67
(25h)	Me	Ph	71	1.1:1	37	—	34	—

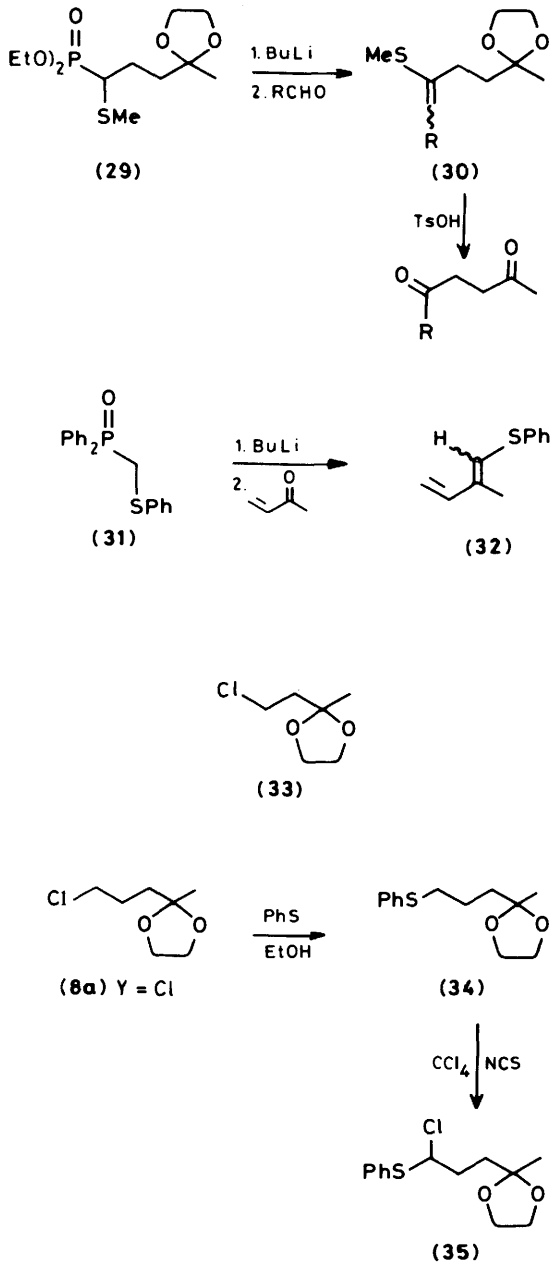
[a] Isomer (**26B**) is the same as isomer (**26A**)

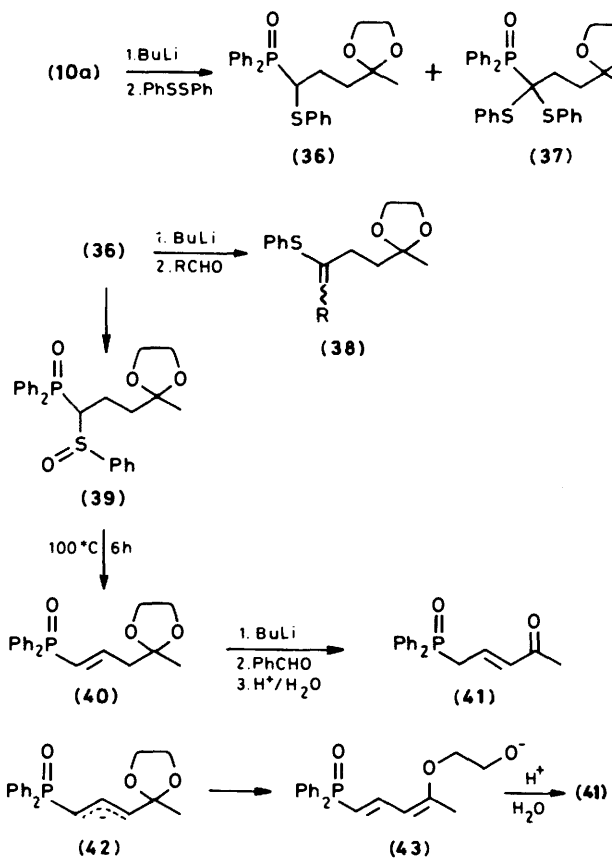
Elimination of $Ph_2PO_2^-$ from adducts of symmetrical ketones gave γ,δ-unsaturated ketals and each diastereoisomer of the adducts of unsymmetrical ketones (**25e**) and (**25g**) gave a distinct isomer (*E* or *Z*: geometry not definitely assigned.).



α-(*Phenylthio*)*alkylphosphine Oxides*.—We have used α-phenylthioalkyldiphenylphosphine oxides (**27**) to make allyl sulphides (**28**) and hence ketones.[35] Mikolajczyk [36] has used the α-(methylthio)phosphonate (**29**) to synthesise the masked 1,4-diketones (**30**), unmasked simply on treatment with toluene-*p*-sulphonic acid (TsOH) and converted into cyclopentenones. We have prepared the analogous γ-phenylthio-γ-phosphinoyl ketal (**36**) by sulphenylation of the γ-phosphinoyl ketal (**10a**) and confirmed that it too can be used in the synthesis of masked 1,4-diketones (**38**).

Several attempts to make the sulphenylated phosphine oxide (**36**) failed. Attempted Michael addition of phenylthiomethyldiphenylphosphine oxide (**31**) to butenone gave only the 1-phenylthio diene (**32**) in 86% yield. We have previously made 1-phenylthio dienes from γ-phenylthioallylphosphine oxides.[37] Attempted alkylation of the same phosphine oxide (**31**) with β-chloro ketal (**33**) gave starting material. The phenylthio ketal (**34**) gave (**35**) by α-chlorination[38] with *N*-chlorosuccinimide (NCS), but an attempted Arbuzow reaction with $Ph_2P(O)Et$[39] failed. Direct sulphenylation of the lithium derivative of the γ-diphenylphosphinoyl ketal (**10a**) with diphenyl disulphide gave starting material (**10a**) (27%), product (**36**) (41%), and the bisphenylthio compound (**37**) (24%) which were separated by chromatography on a gram scale. Sulphenylation with PhSCl





gave (**10a**) (21%), (**36**) (46%), and (**37**) (14%). Evidently proton exchange between (**36**) and the anion of (**10a**) is roughly as fast as sulphenylation.

The Horner-Wittig reaction of the γ-phenylthio-γ-diphenylphosphinoyl ketal (**36**) with aldehydes gave good yields of the masked 1,4-diketones (**38**) (R = Me, 72%; Et, 75%; Pr^i, 79%; Ph, 65%). Isolation of vinyl sulphides rather than adducts analogous to (**11**) is normal with α-phenylthioalkylphosphine oxides, *e.g.* (**31**), even when the counter-ion is lithium, as the PhS group accelerates the elimination of $Ph_2PO_2^-$.[35] The adducts can be isolated at low temperature.[40]

Oxidation to the sulphoxide (**39**) and thermal elimination gave the vinyl phosphine oxide (**40**). We had hoped to use the anion (**42**) as a γ-extended enolate[41] but treatment with BuLi followed by benzaldehyde gave only the enone (**41**). Presumably elimination gives the dienol ether (**43**) which hydrolyses to the enone (**41**) on work-up.

Experimental

M.p.s were determined on a Reichart Kofler block and are uncorrected. N.m.r. spectra were recorded for solutions in deuteriochloroform, unless otherwise stated, on Varian Associates HA 100D (100 MHz), EM 390 (90 MHz), EM 360A (60 MHz), and CFT 20 (80 MHz) machines. I.r. spectra were obtained for chloroform solutions, thin films, or Nujol mulls on a Perkin-Elmer 257 or 297 spectrophotometer. Mass spectra were run on A.E.I. MS902 and MS30 spectrometers. High-resolution mass spectra were recorded using a DS 50 S data system. Diastereotopic protons are marked with an asterisk.

T.l.c. was performed on silica GF_{254} (0.25 mm) plates, p.l.c. on silica GF_{254} (1 mm) plates. Visualisation was by u.v., iodine, or vanillin spray (for alcohols). Column chromatography was performed on Merck Silica Kieselgel 60, either on 60—230 mesh or 230—400 mesh for flash chromatography.[22]

THF refers to freshly distilled dry tetrahydrofuran; distilled off lithium aluminium hydride directly into the reaction vessel. Ether refers to dry diethyl ether, distilled off lithium aluminium hydride and stored over sodium wire. EtOAc refers to distilled ethyl acetate. TMEDA refers to dry tetramethylethylenediamine, over calcium hydride. MCPBA refers to *m*-chloroperbenzoic acid (100%, as supplied by B.D.H. Chemicals). TsOH refers to toluene-*p*-sulphonic acid monohydrate (microanalytical grade, ex. B.D.H. Chemicals). BuLi refers to n-butyllithium (15% solution in hexane).

3-*Acetyldihydrofuran*-2-(3H)-*one* (**6a**; $R^1 = R^2 = H$).—In a three-necked, 2-l flask fitted with a thermometer and mechanical stirrer immersed in a cooling bath at 0 °C, sodium hydroxide (40 g, 1.0 mol) was dissolved in water (300 ml). After dissolution, ethanol (110 ml) was added. The stirred solution was cooled to −5 °C, and a cooled mixture of ethylene oxide

(44.0 g, 1.0 ml) and methyl acetoacetate (116.0 g, 1.0 mol) added dropwise over 2 h so that the internal temperature remained in the range −5 °C to 0 °C. The solution was then stirred for 48 h so that the temperature remained in this range. Glacial acetic acid (60.0 g, 1.0 mol) was added and the solution extracted with benzene (2 × 100 ml, 2 × 50 ml). The combined extracts were evaporated under reduced pressure. The residue was distilled to give the lactone (**6a**) (99.8 g, 78%) as a clear liquid, b.p. 125—128 °C/15 mmHg (lit.,[25] 107—108 °C/5 mmHg), $\nu_{max.}$(film) 1 770 and 1 710 cm^{-1}; δ($CDCl_3$) 4.01 (2 H, t, *J* 5.5 Hz, CH_2O), 3.55 (1 H, dd, *J* 8, 9 Hz, $CHCH_2$), 2.25 (2 H, complex AB systems, $CHCH_2CH_2$), and 2.0 (3 H, s, MeCO).

3-*Acetyl*-5-*methyldihydrofuran*-2(3H)-*one* (**6b**; R^1 = H, R^2 = Me).—To a cooled solution of sodium (9.2 g, 0.4 mol) in absolute ethanol (150 ml), ethyl acetoacetate (52.0 g, 0.4 mol) was added rapidly. The solution was cooled in an ice bath and 2-methyloxirane (propylene oxide) (23.2 g, 0.4 mol) added dropwise over 30 min. After being stirred at 0 °C overnight, the solution was allowed to warm to room temperature and stirred for 4 h. The solvent was removed under reduced pressure, and the residue neutralised with aqueous acetic acid (1:1). The solution was extracted with ether (4 × 50 ml), dried (Na_2SO_4), and evaporated under reduced pressure. The residue was distilled to give the lactone (**6b**) (31.25 g, 55%) as a clear liquid, b.p. 130—134 °C/15 mmHg (lit.,[41] 112 °C/11 mmHg), $\nu_{max.}$(film) 1 775 and 1 710 cm^{-1}; δ($CDCl_3$) 4.4 (1 H, m, C*H*Me), 3.7 (1 H, dd, *J* 8, 9 Hz, COC*H*CO), 2.5 and 2.10 (2 H, complex AB system, $CHCH_2^*CH$), 2.12 (3 H, s, MeCO), and 1.15 (3 H, d, *J* 6 Hz, *Me*CH).

The following were prepared in a similar way.

3-*Acetyl*-5-*ethyldihydrofuran*-2(3H)-*one* (**6c**; R^1 = H, R^2 = Et). From ethyl acetoacetate (28.6 g, 0.22 mol) and 2-ethyloxirane (butylene oxide) (15.9 g, 0.22 mol), as a colourless liquid (14.1 g, 42%), b.p. 180 °C (oven temp.)/20 mmHg (lit.,[42] 98—103 °C/0.3 mmHg), $\nu_{max.}$(film) 1 770 and 1 710 cm^{-1}; δ($CDCl_3$) 4.27 (1 H, sym m, MeC*H*O), 3.72 (1 H, dd, *J* 7, 9 Hz, COC*H*CO), 2.42 and 2.09 (2 H, complex AB system, $CHCH_2^*CH$), 2.08 (3 H, s, MeCO), 1.92 and 1.82 (2 H, complex AB system, $CHCH_2Me$), and 0.93 (3 H, t, *J* 7 Hz, CH_2Me).

3-*Acetyl*-3-*methyldihydrofuran*-2(3H)-*one* (**6d**; R^1 = Me, R^2 = H). A benzene solution of sodium 2-methylbutan-2-olate (1.5M; 325 ml) was added dropwise to a stirred mixture of the lactone (**6a**) (64.0 g, 0.5 mol) and methyl iodide (78.0 g, 0.55 mol) at room temperature. The solution was stirred for 24 h and water (200 ml) added. The solution was separated and the aqueous phases extracted with benzene (3 × 50 ml). The combined organic phases were dried (Na_2SO_4) and evaporated. The residue was distilled to give the lactone (**6d**) as a colourless liquid (51.5 g, 72%), b.p. 120—124 °C/17 mmHg (lit.,[43] 128 °C/20 mmHg), $\nu_{max.}$(soln.) 1 770 and 1 710 cm^{-1}; δ($CDCl_3$) 4.10 and 4.03 (2 H, complex AB system, CH_2^*O), 2.7 and 2.4 (2 H, complex AB system, CH_2CH_2O), 2.10 (3 H, s, *Me*CO), and 1.3 (3 H, s, *Me*CCOMe).

5-*Chloropentan*-2-*one* (**7a**; Y = Cl).—This compound was prepared by the published method from the lactone (**6**; R^1 = H) as a colourless liquid, (88%), b.p. 71—74 °C/21 mmHg (lit.,[27a,44] 70—71 °C/20 mmHg), $\nu_{max.}$(film) 1 715 cm^{-1}; δ($CDCl_3$) 3.50 (2 H, t, *J* 7 Hz, CH_2Cl), 2.60 (2 H, t, *J* 7 Hz, $COCH_2$), 2.05 (3 H, s, MeCO), and 1.85 (2 H, quintet, *J* 7 Hz, $CH_2CH_2CH_2Cl$).

The following were made in a similar manner.

5-*Bromopentan*-2-*one* (**7a**; Y = Br). From the lactone (**6a**) and hot aqueous hydrobromic acid, the bromide was obtained as a pale yellow liquid (73%), b.p. 87—89 °C/25 mmHg (lit.,[27b] 79—81 °C/21 mmHg), $\nu_{max.}$(film) 1 710 cm^{-1}; δ($CDCl_3$) 3.35 (2 H, t, *J* 6.5 Hz, CH_2Br), 2.70 (2 H, t, *J* 7 Hz, $COCH_2$), 2.10 (3 H, s, MeCO), and 2.0 (2 H, m, $CH_2CH_2CH_2Br$).

5-*Iodopentan*-2-*one* (**7a**; Y = I). The lactone (**6a**) and aqueous hydriodic acid gave the iodide as a yellow liquid (68%), b.p. 101—106 °C/17—20 mmHg (lit.,[2,27d,e] 94 °C/14 mmHg), $\nu_{max.}$(soln.) 1 710 cm^{-1}; δ($CDCl_3$) 3.30 (2 H, t, *J* 6.5 Hz, CH_2I), 2.75 (2 H, t, *J* 7.5 Hz, $COCH_2$), 2.25 (3 H, s, MeCO), and 2.10 (2 H, m, $CH_2CH_2CH_2I$).

5-*Chlorohexan*-2-*one* (**7b**; Y = Cl). The lactone (**6b**) in aqueous hydrochloric acid gave the *chloride* as a colourless liquid (91%), b.p. 80 °C/13 mmHg, $\nu_{max.}$(film) 1 710 cm^{-1}; δ($CDCl_3$) 3.85 (1 H, m, CHCl), 2.50 (2 H, t, *J* 7 Hz, $COCH_2$), 1.95 (3 H, s, MeCO), 1.8 (2 H, complex AB system, CH_2CHCl), and 1.35 (3 H, d, *J* 6 Hz, *Me*CH); *m*/*z* 134, 136 (M^+, 15, 5%), 76, 78 ($C_3H_5Cl^+$, 25%), and 43 ($MeCO^+$, 100%).

5-*Bromohexan*-2-*one* (**7b**; Y = Br). The lactone (**6b**) in aqueous hydrobromic acid gave the *bromide* as a colourless liquid (80%), b.p. 102—104 °C/14 mmHg, $\nu_{max.}$(film) 1 710 cm^{-1}, δ($CDCl_3$) 4.32 (1 H, m, C*H*Br), 2.52 (2 H, t, *J* 7 Hz, $COCH_2$), 2.21 (3 H, s, *Me*CO), 1.68 (2 H, complex AB system, CH_2CHBr), and 1.2 (3 H, d, *J* 7 Hz, *Me*CH); *m*/*z* 178, 180 (M^+, 9, 8%), 99 (M − Br, 14%), and 43 ($MeCO^+$, 100%).

5-*Bromoheptan*-2-*one* (**7c**; Y = Br). The lactone (**6c**) and aqueous hydrobromic acid gave the *bromide* as a pale yellow liquid (78%), b.p. 128—133 °C/15 mmHg, $\nu_{max.}$(soln.) 1 710 cm^{-1}; δ($CDCl_3$) 4.2 (1 H, m, CHBr), 2.4 (2 H, t, *J* 6.5 Hz, $COCH_2$), 2.2 (3 H, s, MeCO), 1.8 (2 H, complex AB system, $CH_2CH_2^*CHBr$), 1.5 (2 H, complex AB system, $MeCH_2^*CHBr$), and 0.9 (3 H, t, *J* 7.3 Hz, CH_2Me); *m*/*z* 192, 194 (M^+, 2, 2.5%), 113 (M − Br, 45%), and 43 ($MeCO^+$, 100%).

5-*Chloro*-3-*methylpentan*-2-*one* (**7d**; Y = Cl). The lactone (**6d**) in aqueous hydrochloric acid gave the chloride as a colourless liquid (83%), b.p. 67—70 °C/15 mmHg (lit.,[44] 64—69 °C/13—17 mmHg), $\nu_{max.}$(soln.) 1 710 cm^{-1}; δ($CDCl_3$) 3.50 (2 H, t, *J* 6.5 Hz, CH_2Cl), 2.65 (1 H, m, C*H*Me), 2.08 (3 H, s, MeCO), 1.93 and 1.60 (2 H, complex AB systems, $CHCH_2^*CH_2Cl$), and 1.05 (3 H, d, *J* 7 Hz, *Me*CH); *m*/*z* 134, 136 (M^+, 17, 5%), 99 (M − Cl, 8%), 62, 64 ($C_2H_3Cl^+$, 19%), and 43 ($MeCO^+$, 100%).

5-*Bromo*-3-*methylpentan*-2-*one* (**7d**; Y = Br). The lactone (**6d**) in aqueous hydrobromic acid gave the bromide as a colourless liquid (61%), b.p. 98—100 °C/19 mmHg (lit.,[44] 68—71 °C/5 mmHg), $\nu_{max.}$ 1 715 cm^{-1}; δ($CDCl_3$) 3.36 (2 H, t, *J* 7 Hz, CH_2Br), 2.58 (1 H, m, C*H*Me), 2.14 (3 H, s, MeCO), 1.82 and 1.72 (2 H, complex AB system, $CHCH_2^*CH_2Br$), and 1.07 (3 H, d, *J* 7 Hz, *Me*CH); *m*/*z* 178, 180 (M^+, <1%), 163, 165 (M − Me, 4%), 106/108 ($C_2H_3Br^+$, 10%), 99 (M − Br, 70%), 84 ($C_5H_8O^+$, 41%), and 43 ($MeCO^+$, 100%).

5-*Bromo*-3-*methylhexan*-2-*one* (**7e**; Y = Br). The lactone (**6e**) in hydrobromic acid gave the bromide as a yellow liquid (31%, as a mixture of diastereoisomers), b.p. 88—91 °C/16 mmHg, $\nu_{max.}$ 1 715 cm^{-1}; δ($CDCl_3$) 4.21 (1 H, m, CHBr), 2.47 (1 H, m, MeC*H*), 2.14 (3 H, s, *Me*CO), 1.8—1.55 (2 H, m, $CHCH_2CH$), and 1.13 and 1.07 (2 × 3 H, d, *Me*CHBr and *Me*CHCO); *m*/*z* 192, 194 (M^+, 2, 2%), 114 (M − Br, 40%), 99 ($C_6H_{10}O^+$, 28%), and 43 ($MeCO^+$, 100%).

5-*Chloropentan*-2-*one Ethylene Acetal* (**8a**; Y = Cl).—A solution of the ketone (**7a**; Y = Cl) (60.0 g, 0.49 mol), ethylene glycol (31.0 g, 0.50 mol), and TsOH (100 mg) in toluene (400 ml) was heated at reflux for 24 h under a Dean-Stark trap. After being cooled, the solution was poured into aqueous sodium hydrogen carbonate (1% soln.; 200 ml). The organic phase was separated and the aqueous phase extracted with toluene (2 × 50 ml). The combined organic phases were washed with water (2 × 50 ml), dried (Na_2SO_4), and evaporated under reduced pressure, to give the ethylene acetal (**8a**; Y = Cl) as a colourless liquid (66.9 g, 83%), b.p. 95—99 °C/21 mmHg (lit.,[48] 73—76 °C/7 mmHg), $\nu_{max.}$(film) 1 060 cm^{-1} (C–O); δ($CDCl_3$) 3.78 (4 H, s, OCH_2CH_2O), 3.5 (2 H, t, *J* 6.5 Hz, CH_2Cl), 1.6—2.2

(4 H, m, $CH_2CH_2CH_2Cl$), and 1.31 (3 H, s, MeC); *m/z* 164, 166 (M^+, 1, 0.4%), 149, 151 (M − Me, 100, 35%), and 86 ($C_4H_6O_2^+$, 15%).

The following were prepared in a similar manner.

5-Bromopentan-2-one ethylene acetal (**8a**; Y = Br). As a colourless liquid (72%), b.p. 103—105 °C/20 mmHg (lit.,[27b] 102—105 °C/20 mmHg), $\nu_{max.}$(film) 1 060 cm^{-1} (C–O); δ($CDCl_3$) 3.85 (4 H, s, OCH_2CH_2O), 3.4 (2 H, t, *J* 6.5 Hz, CH_2Br), 1.6—2.2 (4 H, m, CH_2CH_2Br), and 1.3 (3 H, s, MeC); *m/z* 208, 210 (M^+, absent), 193, 195 (M − Me, 100%), 129 (M − Br, 41%), and 86 ($C_4H_6O_2^+$, 8%).

5-Iodopentan-2-one ethylene acetal (**8a**; Y = I). As a dark brown liquid (70%), b.p. 105 °C/0.2 mmHg (lit.,[2] 76 °C/0.05 mmHg), δ($CDCl_3$) 3.8 (4 H, s, OCH_2CH_2O), 3.2 (2 H, t, *J* 6.5 Hz, CH_2I), 1.6—2.2 (4 H, m, $CH_2CH_2CH_2Br$), and 1.3 (3 H, s, MeC); *m/z* 256 (*M*, absent), 241 (M − Me, 100%), 155 ($C_2H_4I^+$, 20%), 129 (M − I, 75%), 87 (M − $CH_2CH_2CH_2I$, 35%), and 86 ($C_4H_6O_2^+$, 30%).

5-Chlorohexan-2-one ethylene acetal (**8b**; Y = Cl). As a colourless liquid (80%), b.p. 95 °C/12.5 mmHg, $\nu_{max.}$(film) 1 075 cm^{-1} (C–O); δ($CDCl_3$) 3.7 (4 H, s, OCH_2CH_2O), 3.45 (1 H, m, CHCl), 1.4—1.8 (4 H, m, CH_2CH_2CHCl), 1.35 (3 H, d, *J* 6 Hz, *Me*CHBr), and 1.15 (3 H, s, MeC); *m/z* 178, 180 (M^+, 5.2%), 163, 165 (M − Me, 100, 35%), 143 (M − Cl, 20%), and 86 ($C_4H_6O_2^+$, 10%).

5-Bromohexan-2-one ethylene acetal (**8b**; Y = Br). As a yellow–orange liquid (64%), b.p. 126—128 °C/11 mmHg, $\nu_{max.}$(film) 1 065 cm^{-1} (C–O); δ($CDCl_3$) 3.83 (4 H, s, OCH_2CH_2O), 3.42 (1 H, m, CHBr), 1.36—1.72 (4 H, m, CH_2CH_2CHBr), 1.24 (3 H, d, *J* 6.3 Hz, *Me*CHBr), and 1.12 (3 H, s, MeC); *m/z* 221, 223 (M^+, <1%), 206, 208 (M − Me, 100%), and 142 (M − Br, 75%).

5-Bromoheptan-2-one ethylene acetal (**8c**; Y = Br). As an orange liquid (58%), b.p. 114—118 °C/3 mmHg, $\nu_{max.}$(soln.) 1 050 cm^{-1} (C–O); δ($CDCl_3$) 3.84 (4 H, s, OCH_2CH_2O), 3.5—3.3 (1 H, m, CHBr), 1.8—1.2 (6 H, m, $CH_2CH_2^*CHBrCH_2^*$), 1.22 (3 H, s, MeC), and 0.96 (3 H, t, *J* 7 Hz, $MeCH_2$); *m/z* 235, 237 (M^+, absent), 220, 222 (M − Me, 100%), 156 (M − Br, 80%), 142 ($C_8H_{15}O_2^+$, 10%), and 86 ($C_4H_6O_2^+$, 15%).

5-Chloro-3-methylpentan-2-one ethylene acetal (**8d**; Y = Cl). As a colourless liquid (69%), b.p. 52—57 °C/1.3 mmHg (lit.,[44] 66—71 °C/3 mmHg), $\nu_{max.}$(film) 1 080 cm^{-1} (C–O); δ($CDCl_3$) 3.7 (4 H, s, OCH_2CH_2O), 3.55 (2 H, t, *J* 6.5 Hz, CH_2Cl), 1.5—1.25 (3 H, m, $MeCHCH_2^*$), 1.3 (3 H, s, MeC), and 1.0 (3 H, d, *J* 7 Hz, *Me*CH); *m/z* 208, 210 (M^+, 6, 2%), 193, 195 (M − Me, 100%), 178, 180 ($C_6H_9O_2Cl^+$, 15, 5%), and 87 ($C_4H_7O_2^+$, 35%).

5-Bromo-3-methylpentan-2-one ethylene acetal (**8d**; Y = Br). As a brown liquid (49%), b.p. 77—82 °C/4 mmHg (lit.,[44] 71—74 °C/3 mmHg), $\nu_{max.}$(film) 1 050 cm^{-1}; δ($CDCl_3$) 3.8 (4 H, s, OCH_2CH_2O), 3.35 (2 H, t, *J* 7 Hz, CH_2Br), 1.5—1.1 (6 H, m, including s at 1.25 p.p.m., $CHCH_2^*$ and *Me*C), and 0.95 (3 H, d, *J* 7 Hz, *Me*CH).

5-Bromo-3-methylhexan-2-one ethylene acetal (**8e**; Y = Br). As a yellow liquid (28%, a mixture of diastereoisomers), b.p. 93—97 °C/1.2 mmHg, $\nu_{max.}$(film) 1 060 cm^{-1}; δ($CDCl_3$) 3.4—3.7 (4 H, sym m, OCH_2CH_2O), 3.3 (1 H, m, CHBr), 1.6—1.1 (6 H, m, including s at 1.2 p.p.m., *Me*C and $CHCH_2CHBr$), 0.97 (3 H, d, *J* 6.5 Hz, *Me*CHBr), and 0.92 (3 H, d, *J* 7.5 Hz, $MeCHCH_2Br$).

5-Diphenylphosphinoylpentan-2-one Ethylene Acetal (**10a**).—(*a*) A solution of the ethylene acetal (**8a**; Y = Br) (62.7 g, 0.3 mol) and triphenylphosphine (78.0 g, 0.297 mol) in toluene (500 ml) was heated at reflux for 2 days. The crystalline precipitate was filtered off and washed with ether (3 × 100 ml). The solid was heated at reflux with aqueous sodium hydroxide (30% w/v; 400 ml) for 2 h after which the apparatus was adapted for distillation and benzene (25 ml, 85% theoretical) distilled out. The solution was cooled, and the organic phase separated. The aqueous phase was extracted with ethyl acetate (3 × 100 ml). The combined organic phases were dried (Na_2SO_4) and evaporated under reduced pressure to give the *phosphine oxide* (**10a**) (71.3 g, 72%) as needles, m.p. 94.5—95 °C (from EtOAc), R_F 0.09 (EtOAc), $\nu_{max.}$(Nujol) 1 440 (P–Ph) and 1 165 cm^{-1} (P=O); δ($CDCl_3$) 7.2—8.0 (10 H, m, Ph_2PO), 3.8 (4 H, s, OCH_2CH_2O), 2.3 (2 H, dt, J_{HH} 7 Hz, J_{HP} 10 Hz, CH_2P), 1.70—1.75 (4 H, m, $CH_2CH_2CH_2P$), and 1.2 (3 H, s, *Me*C); *m/z* 330 (M^+, 8%), 244 ($Ph_2POCH_2CH_2CH_2^+$, 27%), 201 (Ph_2PO^+, 55%), and 87 ($C_4H_7O_2^+$, 100%) (Found: M^+, 330.1398; $C_{19}H_{23}O_3P$ requires *M*, 330.1385).

(*b*) The same compound was also prepared from the iodide (**8a**; Y = I) with triphenylphosphine heated at reflux for 2 days, followed by hydrolysis, in 54% yield.

(*c*) Reaction of the chloride (**8a**; Y = Cl) with triphenylphosphine at 110 °C gave very low yields of the corresponding phosphonium salt even after 7 days. Hydrolysis was not attempted.

(*d*) A solution of the chloride (**8a**; Y = Cl) (8.2 g, 0.05 mol), sodium iodide (7.50 g, 0.05 mol), and triphenylphosphine (13.1 g, 0.05 mol) was heated at reflux in toluene (200 ml) for 3 days. An oil slowly separated. The oil was hydrolysed with sodium hydroxide as above, to give the phosphine oxide (**10a**) in 65% yield.

(*e*) The chloride (**8a**; Y = Cl) (16.45 g, 10 mmol) and ethyl diphenylphosphinite (23.0 g, 10 mmol) were heated at 140 °C overnight. Cooling gave a gummy solid which was purified by chromatography [SiO_2/EtOAc–MeOH (9:1)] to give the phosphine oxide (**10a**) (18.5 g, 56%).

5-Diphenylphosphinoylhexan-2-one Ethylene Acetal (**10b**).—From the ethylene acetal (**8b**; Y = Br) (4.45 g, 20 mmol) and triphenylphosphine (5.12 g, 20 mmol) in toluene (50 ml) heated at reflux for 5 days, a crystalline phosphonium salt was obtained; this, after hydrolysis as above, gave the *phosphine oxide* (**10b**) as off-white needles (2.56 g, 38%), m.p. 108—110 °C (from EtOAc), R_F 0.06 (EtOAc), $\nu_{max.}$(Nujol) 1 440 (P–Ph) and 1 165 cm^{-1} (P=O); δ($CDCl_3$) 7.98—7.11 (10 H, m, Ph_2PO), 3.78 (4 H, s, OCH_2CH_2O), 2.40 (1 H, m, CHP), 2.10—1.50 (4 H, m, $CH_2CH_2^*CHP$), 1.23 (3 H, s, MeC), and 1.18 (3 H, dd, J_{PH} 16 Hz, J_{HH} 7 Hz, PCH*Me*); *m/z* 344 (M^+, 3%), 256 ($Ph_2POCHMeCH_2CH_2^+$, 15%), and 201 (Ph_2PO^+, 100%).

5-Diphenylphosphinoylheptan-2-one Ethylene Acetal (**10c**).—The bromo-acetal (**8c**; Y = Br) (2.36 g, 10 mmol) and triphenylphosphine (2.61 g, 10 mmol) in toluene (50 ml) were heated at reflux for 4 days to give a crystalline precipitate, hydrolysis of which gave the *phosphine oxide* (**10c**) as needles (1.54 g, 43%), m.p. 112—114 °C (from EtOAc–hexane, 9:1), R_F 0.07 (EtOAc), $\nu_{max.}$(Nujol) 1 440 (P–Ph) and 1 160 cm^{-1} (P=O); δ($CDCl_3$) 8.0—7.1 (10 H, m, Ph_2PO), 3.8 (4 H, s, OCH_2CH_2O), 2.3 (1 H, m, CHP), 2.0—1.5 (6 H, m, $CH_2^*CH_2^*CHPCH_2^*$), 1.2 (3 H, s, MeC), and 0.95 (3 H, dd, J_{HH} 7 Hz, J_{PH} 4 Hz, CH_2Me).

5-Diphenylphosphinoyl-3-methylpentan-2-one Ethylene Acetal (**10d**).—The bromo ketal (**8d**; Y = Br) (2.50 g, 11.2 mmol) and triphenylphosphine (2.90 g, 11.0 mmol) in toluene (30 ml) heated at reflux for 2 days gave a crystalline precipitate, which was filtered off and hydrolysed in alkaline solution to give the *phosphine oxide* (**10d**) (1.96 g, 52%) as needles, m.p. 117—119 °C (from EtOAc), R_F 0.10 (EtOAc), $\nu_{max.}$(Nujol) 1 440 (P–Ph), 1 440 (P–Ph), 1 165 (P=O), and 1 055 cm^{-1} (C–O); δ($CDCl_3$) 7.9—7.0 (10 H, m, Ph_2PO), 3.8 (4 H, s, OCH_2CH_2O), 2.4—2.2 (2 H, m, CH_2P), 1.8—1.4 (3 H, m, $MeCHCH_2^*$), 1.2 (3 H, s, MeC), and 0.95 (3 H, d, *J* 7 Hz, *Me*CH); *m/z* 344 (M^+, 1%), 329 (M − Me, 55%), 257 ($Ph_2POCH_2CHCHMe^+$, 20%), and 201 (Ph_2PO^+, 100%).

Alkylation of 5-Diphenylphosphinoylpentan-2-one Ethylene Acetal (**10a**).—BuLi (7.0 ml, 1.08 mmol) was added to a solution of the phosphine oxide (**10a**) (330 mg, 1.0 mmol) in a mixture of THF (15 ml) and TMEDA (130 mg, 1.12 mmol) at 0 °C under nitrogen. After 15 min, the solution was cooled to −78 °C, and methyl iodide (0.5 ml, excess) added. The solution was allowed to warm to room temperature and was then diluted with water (5 ml). The organic phase was separated, and the aqueous phase washed with ether (5 × 10 ml). The combined organic phase was dried (Na_2SO_4) and evaporated under reduced pressure to give a pale yellow oil. P.l.c. (EtOAc–MeOH, 9:1) gave the *phosphine oxide* (**10b**) (103 mg, 30%) and *5-diphenylphosphinoyl-5-methylhexan-2-one ethylene acetal* (39 mg, 11%), as pale yellow needles, m.p. 84—87 °C, δ($CDCl_3$) 7.9—7.2 (10 H, m, Ph_2PO), 3.7 (4 H, s, OCH_2CH_2O), 1.8—1.5 (4 H, m, CH_2CH_2CP), 1.25 (3 H, s, MeC), and 1.15 (6 H, d, J_{PH} 15 Hz, Me_2CP).

5-Diphenylphosphinoyl-6-hydroxyhexan-2-one Ethylene Acetal (**11a**; R = H).—BuLi (3.5 ml, 5.5 mol) was added to a solution of the phosphine oxide (**10a**) (1.65 g, 5.0 mmol) in THF (25 ml) under nitrogen at 0 °C. After 15 min, the orange solution was cooled to −78 °C and paraformaldehyde (0.5 g, excess) added. The decolourised solution was allowed to warm to room temperature when aqueous ammonium chloride (saturated, 10 ml) was added. The solution was extracted with ether (3 × 30 ml, 2 × 50 ml) and the combined organic phases were dried (Na_2SO_4) and evaporated under reduced pressure to give, after chromatography, (SiO_2/EtOAc), the *alcohol* (**11a**) as plates (1.22 g, 68%), m.p. 99—101 °C (from EtOAc), R_F 0.55 (EtOAc–MeOH, 9:1), $\nu_{max.}$(Nujol) 3 300 (O–H), 1 440 (P–Ph), 1 165 (P=O), and 1 055 cm^{-1} (C–O); δ($CDCl_3$) 7.9—7.1 (10 H, m, Ph_2PO), 4.3 (1 H, br s, O*H*), 4.2—3.9 (2 H, complex AB system, CH_2^*OH), 3.8—3.6 (4 H, sym m, OCH_2CH_2O), 2.2—1.4 (5 H, m, CH_2CH_2CHP), and 1.2 (3 H, s, MeC).

5-Diphenylphosphinoyl-6-hydroxyheptan-2-one Ethylene Acetal (**11b**; R = Me).—In a similar manner, the lithium anion of the phosphine oxide (**10a**) (4.7 g, 14.2 mmol) was quenched with a solution of acetaldehyde (1.0 g, 1.6 equiv.) in THF saturated with LiBr (10 ml) to give, after chromatography (SiO_2, eluted with EtOAc), the HR_F *diastereoisomer* (3.03 g, 57%) as needles, m.p. 114—115 °C (from EtOAc), R_F 0.45 (EtOAc), $\nu_{max.}$(Nujol) 3 320 (O–H), 1 440 (P–Ph), and 1 170 cm^{-1} (P=O); δ($CDCl_3$) 7.8—7.1 (10 H, m, Ph_2PO), 4.4—4.2 (2 H, m, including *J* 12, 7 Hz, CHOH), 3.7 (4 H, s, OCH_2CH_2O), 2.7 (1 H, dq, J_{HH} 7 Hz, J_{PH} 12 Hz, CHP), 1.9—1.5 (4 H, m, $CH_2CH_2^*CHP$), 1.3 (3 H, s, MeC), and 1.25 (3 H, dd, J_{HH} 7 Hz, J_{PH} 15 Hz, *Me*CH); *m/z* 374 (*M*$^+$, 0.2%), 359 (*M* − Me, 10%), 330 (*M* − MeCHO, 30%), 202 (Ph_2POH^+, 20%), and 201 (Ph_2PO^+, 100%) (Found: *M*$^+$, 374.1655. $C_{21}H_{27}O_4P$ requires *M*, 374.1647); and the LR_F *diastereoisomer* (0.95 g, 18%) as needles, m.p. 124—126 °C (from EtOAc), R_F 0.37 (EtOAc), $\nu_{max.}$(Nujol) 3 300 (O–H), 1 440 (P–Ph), 1 165 (P=O), and 1 055 cm^{-1} (C–O); δ($CDCl_3$) 7.85—7.15 (10 H, m, Ph_2PO), 4.7 (1 H, br s, OH), 4.3 (1 H, m, including *J* 7 Hz, C*H*OH), 3.8 (4 H, s, OCH_2CH_2O), 2.45 (1 H, m, CHP), 1.9—1.5 (4 H, m, $CH_2CH_2^*CHP$), 1.25 (3 H, s, MeC), and 1.2 (3 H, dd, J_{HH} 7 Hz, J_{PH} 12 Hz, *Me*CH); *m/z* 374 (*M*$^+$, 0.7%), 359 (*M* − Me, 30%), 330 (*M* − MeCHO, 20%), and 201 (Ph_2PO^+, 100%) (Found: *M*$^+$, 374.1650. $C_{21}H_{27}O_4P$ requires *M*, 374.1647).

In a similar way the following were obtained.

5-Diphenylphosphinoyl-6-hydroxyoctan-2-one ethylene acetal (**11c**, R = Et). The phosphine oxide (**10a**) (990 mg, 3 mmol), BuLi (2.10 ml, 3.25 mmol), and propionaldehyde (0.5 ml, excess) gave the *phosphine oxide* (**11c**) as a mixture of diastereoisomers (721 mg, 62%), $\nu_{max.}$(soln.) 3 350 (O–H), 1 440 (P–Ph), 1 165 (P=O), and 1 050 cm^{-1} (C–O); δ($CDCl_3$) 7.7—7.3 (10 H, m, Ph_2PO), 4.55 (1 H, br s, O*H*), 4.1, 3.8 (1 H, 2 × m, C*H*OH), 3.7—3.4 (4 H, sym m, OCH_2CH_2O), 1.74—1.37 (7 H, m, $CH_2CH_2^*CHCHCH_2^*$), 1.05 and 1.00 (3 H, 2 × s, *Me*C), 0.84 and 0.78 (3 H, 2 × t, *J* 6.5, 7 Hz, *Me*CH_2), ratio of diastereoisomers 2.5:1 by integration; *m/z* 388 (*M*$^+$, 0.5%), 373 (*M* − Me, 40%), 330 (*M* − EtCHO, 35%), and 201 (Ph_2PO^+, 100%).

5-Diphenylphosphinoyl-6-hydroxynonan-2-one ethylene acetal (**11d**; R = Pr). The phosphine oxide (**10a**) (1.50 g, 4.55 mmol), BuLi (3.2 ml, 1.1 equiv.), and butyraldehyde (1.0 ml, excess) gave, after chromatography (SiO_2, eluted with EtOAc–MeOH, 9:1), the HR_F *diastereoisomer* as prisms (840 mg, 46%), m.p. 121—123 °C (from EtOAc), R_F 0.62 (EtOAc–MeOH, 9:1), $\nu_{max.}$(Nujol) 3 320 (O–H), 1 435 (P–Ph), 1 155 (P=O), and 1 055 cm^{-1} (C–O); δ($CDCl_3$) 7.7—7.1 (10 H, m, Ph_2PO), 4.5 (1 H, s, OH), 4.3—4.1 (1 H, m, C*H*OH), 3.8 (4 H, s, OCH_2CH_2O), 2.1—1.4 (9 H, m, $CH_2CH_2^*CHCHCH_2^*CH_2Me$), 1.3 (3 H, s, Me), and 0.9 (3 H, t, *J* 7 Hz, *Me*CH_2); *m/z* 402 (*M*$^+$, absent), 387 (*M* − Me, 35%), 330 (*M* − PrCHO, 20%), 201 (Ph_2PO^+, 100%), and the LR_F *diastereoisomer* as needles (383 mg, 21%), m.p. 136—140 °C (from EtOAc–hexane), R_F 0.50 (EtOAc–MeOH, 9:1), $\nu_{max.}$(Nujol) 3 300 (O–H), 1 440 (P–Ph), 1 160 (P=O), and 1 050 cm^{-1} (C–O); δ($CDCl_3$) 7.9—7.3 (10 H, m, Ph_2PO), 4.4—4.1 (2 H, m, CHOH), 3.8—3.6 (4 H, m, OCH_2CH_2O), 1.9—1.4 (9 H, m, $CH_2CH_2^*CHCHCH_2^*CH_2Me$), 1.3 (3 H, s, MeC), and 0.9 (3 H, t, *J* 7 Hz, *Me*CH_2); *m/z* 402 (*M*$^+$, 0.4%), 387 (*M* − Me, 50%), 330 (*M* − PrCHO, 10%), and 201 (Ph_2PO^+, 100%) (Found: *M*$^+$, 402.1961; $C_{23}H_{31}O_4P$ requires *M*, 402.1958).

5-Diphenylphosphinoyl-6-hydroxydecan-2-one ethylene acetal (**11e**; R = Bu). The phosphine oxide (**10a**) (660 mg, 2 mmol), BuLi (1.4 ml, 2.16 mmol), and valeraldehyde (0.5 ml, excess), gave after chromatography (SiO_2, eluted with EtOAc), the HR_F *diastereoisomer* (407 mg, 49%) as needles, m.p. 122—125 °C (from EtOAc–Pr^i_2O), R_F 0.35 (EtOAc), $\nu_{max.}$(Nujol) 3 300 (O–H), 1 440 (P–Ph), 1 165 (P=O), and 1 060 cm^{-1} (C–O); δ($CDCl_3$) 7.9—7.4 (10 H, m, Ph_2PO), 4.3—3.6 (6 H, m, OCH_2CH_2O, CHOH), 2.1—1.5 (9 H, m, $CH_2CH_2^*CHCH$-$CH_2^*CH_2Et$), 1.35—1.15 (5 H, m, including sharp s at 1.3 p.p.m., *Me*C, MeCH_2CH_2), and 0.9 (3 H, t, *J* 7 Hz, *Me*CH_2); *m/z* 416 (*M*$^+$, absent), 401 (*M* − Me, 70%), 387 (*M* − C_2H_5, 12%), 330 (*M* − BuCHO, 30%), 202 (Ph_2POH^+, 20%), 201 (Ph_2PO^+, 80%), and 87 ($C_4H_7O_2^+$, 100%); and the LR_F *diastereoisomer* (240 mg, 29%) as a gummy solid, m.p. 100—107 °C, R_F 0.30 (EtOAc), $\nu_{max.}$(soln.) 3 340 (O–H), 1 440 (P–Ph), 1 160 (P=O), and 1 055 cm^{-1} (C–O); δ($CDCl_3$) 7.9—7.3 (10 H, m, Ph_2PO), 4.4—4.1 (m, C*H*OH), 3.9—3.7 (4 H, sym m, OCH_2CH_2O), 2.0—1.4 (9 H, m, $CH_2CH_2^*CHCHCH_2^*CH_2Et$), 1.28 (2 H, quintet, *J* 7 Hz, MeCH_2), 1.20 (3 H, s, MeC), and 0.94 (3 H, t, *J* 7 Hz, *Me*CH_2).

5-Diphenylphosphinoyl-6-hydroxy-7-methyloctan-2-one, ethylene acetal (**11f**; R = Pr^i). The phosphine oxide (**10a**) (830 mg, 2.51 mmol), BuLi (1.75 ml, 2.73 mmol), and isobutyraldehyde (1.0 ml, excess) after chromatography (SiO_2, eluting with EtOAc–MeOH, 9:1—8:2), gave the HR_F *diastereoisomer* (394 mg, 39%) as needles, m.p. 102—103.5 °C (from EtOAc–Pr^i_2O), R_F 0.65 (EtOAc–MeOH, 9:1), δ($CDCl_3$) 7.8—7.4 (10 H, m, Ph_2PO), 4.8 (1 H, br s, O*H*), 4.2 (1 H, ddd, J_{HH} 6 Hz, 7 Hz, J_{HP} 16 Hz, PCH_ACHCH_B), 3.8 (4 H, s, OCH_2CH_2O), 2.3—2.1 (1 H, m, including *J* 6, 7 Hz, C*H*P), 1.7—1.4 (4 H, m, CH_2CH_2CHP), 1.35 (1 H, m, *J* 7 Hz, C*H*Me_2), 1.2 (3 H, s, MeC), and 0.9 (6 H, d, *J* 7 Hz, Me_2CH); *m/z* 402 (*M*$^+$, 0.5%), 387 (*M* − Me, 50%), 330 (*M* − Pr^iCHO, 100%), 244 ($Ph_2POC_3H_7^+$, 10%), and 201 (Ph_2PO^+, 70%) (Found: *M*$^+$, 402.1957. $C_{23}H_{31}O_4P$ requires *M*, 402.1958; and the LR_F *diastereoisomer* (404 mg, 40%) as needles, m.p. 137—138 °C (from EtOAc), R_F 0.55 (EtOAc–MeOH, 9:1) (Found: C, 68.8%; H, 7.89%; P, 7.8%. $C_{23}H_{31}O_4P$ requires C, 68.64%; H, 7.76%; P, 7.7%), $\nu_{max.}$(Nujol) 3 300 (O–H), 1 440

(P–Ph), and 1 165 cm^{-1} (P=O); δ($CDCl_3$) 7.9—7.4 (10 H, m, Ph_2PO), 4.5 (1 H, s, OH), 4.3—4.1 (1 H, m, including *J* 7, 16 Hz, C*H*OH), 3.8 (4 H, s, OCH_2CH_2O), 2.1—1.5 (6 H, m, $CH_2CH_2^*CHPCHCHMe_2$), 1.2 (3 H, s, MeC), and 0.9 (6 H, d, *J* 7 Hz, Me_2CH); *m/z* 402 (M^+ absent), 387 (*M* – Me, 30%), 330 (*M* – Pr^iCHO, 60%), and 201 (Ph_2PO^+, 100%).

5-Diphenylphosphinoyl-6-hydroxy-6-phenylhexan-2-one ethylene acetal (**11g**; R = Ph). The phosphine oxide (**10a**) (4.00 g, 12.1 mmol), BuLi (8.5 ml, 13.3 mmol), and benzaldehyde (1.5 g, 14.2 mmol) gave, after chromatography (SiO_2, eluting with EtOAc), the HR_F *diastereoisomer* (3.00 g, 57%) as prisms, m.p. 184—187 °C (from EtOAc), R_F 0.45 (EtOAc), $\nu_{max.}$(soln.) 3 320 (O–H), 1 605, 1 585 (Ph), 1 440 (P–Ph), and 1 165 cm^{-1} (P=O); δ($CDCl_3$) 7.86—7.06 (15 H, Ph_2PO and Ph), 5.16 (1 H, d, *J* 10 Hz, C*H*OH), 4.62 (1 H, br s, OH), 3.57—3.27 (4 H, sym m, OCH_2CH_2O), 2.43 (1 H, quintet, $J_{HH} = J_{PH}$ 5.3 Hz, CHP), 1.74 (2 H, m including *J* 5.3, 6.7 Hz, CH_2^*CHP), 0.94 (2 H, t, *J* 6.7 Hz, CH_2CH_2CHP), and 0.76 (3 H, s, *Me*C); *m/z* 436 (M^+, 5%), 329 (*M* – PhCHOH, 30%), and 201 (Ph_2PO^+, 100%); and the LR_F *diastereoisomer* (790 mg, 15%) as needles, m.p. 197—200 °C (from EtOAc), R_F 0.35 (EtOAc), $\nu_{max.}$(soln.) 3 350 (O–H), 1 600 (Ph), 1 440 (P–Ph), and 1 165 (P=O); δ($CDCl_3$) 7.85—6.97 (15 H, m, Ph_2PO and Ph), 4.9 (1 H, dd, J_{HH} 6.5 Hz, C*H*OH), 4.93 (1 H, br s, CHO*H*), 3.74—3.40 (4 H, sym m, OCH_2CH_2O), 2.64 (1 H, dq, J_{HH} 6.5 Hz, J_{PH} 13 Hz, CHP), and 1.97—1.07 (4 H, m, $CH_2CH_2^*CHP$), and 0.85 (3 H, s, MeC).

6-Cyclohexyl-5-diphenylphosphinoyl-6-hydroxyhexan-2-one ethylene acetal (**11h**; R = cyclohexyl). The phosphine oxide (**10a**) (330 mg, 1 mmol), BuLi (0.7 ml, 1.08 mmol) and cyclohexanecarbaldehyde (200 mg, 1.75 mmol) gave after p.l.c. (SiO_2, triple elution with EtOAc), the HR_F *diastereoisomer* (159 mg, 36%), m.p. 164—167 °C, R_F 0.37 (EtOAc), δ($CDCl_3$) 7.5—7.1 (10 H, m, Ph_2PO), 4.3 (1 H, dt, J_{HP} 16 Hz, J_{HH} 7 Hz, C*H*OH), 3.8—3.4 (4 H, m, OCH_2CH_2O), and 1.8—1.0 (19 H, m including sharp s at 1.2 p.p.m., *Me*C, $CH_2CH_2^*CHP$, cyclohexyl H); and the LR_F *diastereoisomer* (155 mg, 35%), m.p. 181—182 °C, R_F 0.3 (EtOAc), δ($CDCl_3$) 7.5—7.1 (10 H, m, Ph_2PO), 4.6 (1 H, br s, OH), 4.3 (1 H, dt, J_{HP} 13 Hz, J_{HH} 7 Hz, C*H*OH), 3.7—3.4 (4 H, m, OCH_2CH_2O), and 1.8—1.0 (19 H, m including sharp s at 1.25 p.p.m., *Me*C, $CH_2CH_2^*CHP$, cyclohexyl H).

5-Diphenylphosphinoylheptane-2,6-dione 2-Ethylene Acetal (**13b**; R = Me).—BuLi (4.8 ml, 7.5 mmol) was added to a solution of the phosphine oxide (**10a**) (2.31 g, 7 mmol) in THF (40 ml) under nitrogen at 0 °C. After 30 min, the solution was cooled to −78 °C and ethyl acetate (0.7 g, 8 mmol) added dropwise to the orange anion over a period of 1 min. The solution was allowed to warm to room temperature, when saturated aqueous ammonium chloride (20 ml) was added. The solution was extracted with EtOAc (4 × 50 ml) and the combined organic phases dried (Na_2SO_4) and evaporated under reduced pressure to give the *ketone* (1.85 g, 71%) as needles, m.p. 162—166 °C (from EtOAc), R_F 0.24 (EtOAc–MeOH, 9:1), $\nu_{max.}$(soln.) 1 705 (C=O), 1 440 (P–Ph), and 1 180 cm^{-1} (P=O); δ($CDCl_3$) 7.9—7.4 (10 H, m, Ph_2PO), 3.8 (4 H, s, OCH_2CH_2O), 3.7 (1 H, dd, J_{HH} 7.5 Hz, J_{PH} 12 Hz, PC*H*), 2.35 (3 H, s, *Me*CO), 1.8—1.4 (4 H, m, $CH_2CH_2^*CHP$), and 1.2 (3 H, s, MeC); *m/z* 372 (M^+, 8), 357 (*M* – Me, 20%), 329 (*M* – MeCO, 35%), and 201 (Ph_2PO^+, 100%) (Found: M^+, 372.1490. $C_{21}H_{25}O_4P$ requires *M*, 372.1491).

The following were prepared in a similar way.

5-Diphenylphosphinoyl-6-phenylhexane-2,6-dione 2-ethylene acetal (**13g**). The phosphine oxide (**10a**) (2.31 g, 7 mmol), BuLi (4.8 ml, 7.5 mmol), and ethyl benzoate (1.2 g, 8 mmol) gave, after chromatography (SiO_2, eluted with EtOAc), the *ketone* (**13g**) (1.94 g, 64%) as needles, m.p. 194—197 °C (from EtOAc–hexane), R_F 0.20 (EtOAc) (Found: C, 72.2; H, 6.5; P, 6.95; $C_{26}H_{27}O_4P$ requires C, 71.9; H, 6.3; P, 7.1%), $\nu_{max.}$ 1 680 (C=O), 1 430 (P–Ph), 1 180 (P=O), and 1 055 cm^{-1} (C–O); δ($CDCl_3$) 8.1—6.9 (15 H, m, Ph_2PO and PhCO), 4.0 (1 H, dd, J_{HH} 8 Hz, J_{PH} 10 Hz, PC*H*), 3.8—3.5 (4 H, m, OCH_2CH_2O), 2.3—1.8 (2 H, complex AB system, CH_2^*CHP), 1.7—1.3 (2 H, m, CH_2CH_2CHP), and 1.1 (3 H, d, *J* 3 Hz, MeC); *m/z* 434 (M^+, 35%), 329 (*M* – PhCO, 70%), and 201 (Ph_2PO^+, 100%).

Likewise, the phosphine oxide (**10a**) (660 mg, 2 mmol), BuLi (1.4 ml, 2.2 mmol), and benzoyl chloride (300 mg, 2.12 mmol) gave the *ketone* (**13g**) (477 mg, 55%) after p.l.c.

5-Diphenylphosphinoylnonane-2,6-dione 2-ethylene acetal (**13d**; R = Pr). The phosphine oxide (**10a**) (3.30 g, 10 mmol), BuLi (7.0 ml, 11 mmol), and ethyl butyrate (1.50 g, 11.5 mmol) gave, after chromatography, the *ketone* (**13d**) (2.42 g, 51%) as needles, R_F 0.18 (EtOAc), $\nu_{max.}$ (Nujol) 1 705 (C=O), 1 440 (P–Ph), and 1 200 cm^{-1} (P=O); δ($CDCl_3$) 8.1—7.4 (10 H, m, Ph_2PO), 3.8 (4 H, s, OCH_2CH_2O), 3.6 (1 H, m, CHP), 2.5 (2 H, t, *J* 7.5 Hz, CH_2CO), 2.0—1.1 (9 H, m including sharp s at 1.2 p.p.m., *Me*C; $CH_2CH_2CHCOCH_2CH_2Me$), and 0.8 (3 H, t, *J* 7 Hz, $MeCH_2$).

Reduction of 5-Diphenylphosphinoylheptane-2,6-dione 2-Ethylene Acetal (**13b**).—A solution of the sodium borohydride (90 mg, 2.4 mmol) in aqueous sodium hydroxide [1M-NaOH (2 ml) and water (2 ml)] was added dropwise to a stirred solution of the ketone (**13b**) (1.50 g, 4 mmol) in ethanol (5 ml) at 0 °C. The solution was stirred for 30 min and then allowed to warm to room temperature. The solvent was evaporated under reduced pressure and the residue was dissolved in ether (50 ml). The solution was washed rapidly with dilute sulphuric acid (1M-solution; 2 × 5 ml), aqueous sodium hydrogen carbonate (5% solution; 2 × 20 ml), and finally with water (2 × 10 ml). The organic phase was dried (Na_2SO_4) and evaporated under reduced pressure to give 5-diphenylphosphinoyl-6-hydroxyheptan-2-one ethylene acetal (**11b**). After chromatography (SiO_2, eluting with EtOAc), the HR_F diastereoisomer (300 mg, 20%) and the LR_F diastereoisomer (1.06 g, 71%) were obtained.

The following were treated similarly.

Reduction of 5-diphenylphosphinoyl-6-phenylhexane-2,6-dione 2-ethylene acetal (**13g**). The ketone (1.10 g, 2.53 mmol) and sodium borohydride (55 mg, 1.5 mmol) gave, after chromatography (SiO_2, eluting with EtOAc), 5-diphenylphosphinoyl-6-hydroxy-6-phenylhexan-2-one ethylene acetal (**11g**) HR_F diastereoisomer (232 mg, 21%) and the LR_F diastereoisomer (695 mg, 63%).

Reduction of 5-diphenylphosphinoyldecane-2,6-dione 2-ethylene acetal (**13d**). The ketone (2.0 g, 4.83 mmol) and sodium borohydride (110 mg, 3.0 mmol) gave, after chromatography (SiO_2, eluting with EtOAc), 5-diphenylphosphinoyl-6-hydroxydecan-2-one ethylene acetal (**11d**), HR_F diastereoisomer (480 mg, 24%) and the LR_F diastereoisomer (1.145 g, 57%).

Hex-5-en-2-one Ethylene Acetal (**12a**).—Sodium hydride (50% in oil) (145 mg, 1.1 equiv.) was added to a solution of the alcohol (**10a**) (1.0 g, 2.77 mmol) in DMF (10 ml). The solution was heated at 50 °C for 1 h and then poured into a mixture of ether (30 ml) and water (20 ml). The aqueous phase was extracted with ether (2 × 10 ml). The combined organic phases were dried (Na_2SO_4) and evaporated under reduced pressure, to give the olefin (**12a**) as a colourless liquid (85 mg, 63%), b.p. 65—67 °C/25 mmHg (lit.,[46] 52 °C/14 mmHg), $\nu_{max.}$(film) 1 650 (C=C) and 1 050 cm^{-1} (C–O); δ($CDCl_3$) 5.8 (1 H, m, C*H*=CH_2), 4.9 (2 H, complex AB system, CH=CH_2), 3.8 (4 H, s, OCH_2CH_2O), 2.1 (2 H, q, *J* 7 Hz, CH_2CH=CH_2), 1.7 (2 H, t, *J* 7 Hz, CH_2CH_2CH), and 1.2 (3 H, s, MeC).

Sometimes also isolated from the above was hex-5-en-2-one (18%), b.p. 42 °C/28 mmHg (lit.,[47] 69 °C/100 mmHg),

$\nu_{max.}$(film) 1 710 (C=O) and 1 650 cm^{-1} (C=C); $\delta(CDCl_3)$ 5.8 (1 H, m, C*H*=CH_2), 5.0 (2 H, m, AB system, CH=CH_2), 2.7—2.3 (m, including t, *J* 7.5 Hz at 2.4 p.p.m., CH_2CH_2CH=CH_2), and 2.1 (3 H, s, CH_3CO).

In a similar way the following were prepared.

(Z)-*Hept-5-en-2-one ethylene acetal Z*-(**12b**). The HR_F diastereoisomer of alcohol (**11b**) (1.38 g, 3.69 mmol) and sodium hydride (50% in oil) (177 mg, 3.70 mmol) gave the olefin *Z*-(**12b**) as a colourless liquid (437 mg, 76%), b.p. 72—76 °C/20 mmHg (lit.,[51] 70—75 °C/18 mmHg, $\nu_{max.}$(film) 1 650 (C=C) and 1 055 cm^{-1} (C–O); $\delta(CDCl_3)$ 5.35 (2 H, m, C*H*=C*H*), 3.85 (4 H, s, OCH_2CH_2O), 2.4—1.4 (7 H, m, CH_2CH_2CH=CH*Me*), and 1.25 (3 H, s, MeC).

Oct-5-en-2-one ethylene acetal (**12c**). A mixture of the diastereoisomers of the alcohol (**11c**) (500 mg, 1.29 mmol) and sodium hydride (62 mg, 1.30 mmol) gave a mixture of olefins (177 mg, 81%), b.p. 75—82 °C/12 mmHg (lit.,[4] *Z*: 74—80 °C/12 mmHg, *E*: 82—83 °C/10 mmHg), $\nu_{max.}$(film) 1 660 (C=C) and 1 060 cm^{-1} (C–O); $\delta(CDCl_3)$ 5.4—5.2 (2 H, m, CH=CH), 3.8 (4 H, br s, OCH_2CH_2O), 2.2—1.4 (6 H, m, CH_2CH_2CH=CHCH_2), 1.2 (3 H, s, MeC), and 0.95 (3 H, t, *J* 7.5 Hz, *Me*CH_2).

(Z)-*Non-5-en-2-one ethylene acetal Z*-(**12d**). The HR_F diastereoisomer of the alcohol (**11d**) (700 mg, 1.75 mmol) and sodium hydride (84 mg, 1.75 mmol) gave the *olefin Z*-(**12d**) as a colourless liquid (245 mg, 76%), b.p. 87—90 °C/14 mmHg, $\nu_{max.}$(soln.) 1 650 cm^{-1} (C=C); $\delta(CDCl_3)$ 5.2 (2 H, m, CH=CH), 3.85 (4 H, s, OCH_2CH_2O), 2.4—1.3 (8 H, m, CH_2CH_2-CH=CHCH_2CH_2), 1.2 (3 H, s, MeC), and 1.0 (3 H, t, *J* 7 Hz, *Me*CH_2).

(Z)-*Dec-5-enone ethylene acetal Z*-(**12e**). The HR_F diastereoisomer of the alcohol (**11e**) (350 mg, 0.84 mmol) and sodium hydride (41 mg, 0.84 mmol) gave the *olefin Z*-(**11e**) as a colourless liquid (138 mg, 83%), b.p. 105 °C (oven temp.)/15 mmHg, $\nu_{max.}$(soln.) 1 645 (C=C) and 1 070 cm^{-1} (C–O); $\delta(CDCl_3)$ 5.3 (2 H, m, CH=CH), 3.7 (4 H, s, OCH_2CH_2O), 2.5—1.5 (10 H, m, 5 × CH_2), 1.2 (3 H, s, MeC), and 1.0 (3 H, t, *J* 7 Hz, *Me*CH_2) (Found: C, 72.92; H, 11.01. $C_{12}H_{22}O_2$ requires C, 72.68; H, 11.18%).

(Z)-7-*Methyloct-5-en-one ethylene acetal Z*-(**12f**). The HR_F diastereoisomer of the alcohol (**11f**) (350 mg, 0.87 mmol) and sodium hydride (42 mg, 0.88 mmol) gave the *olefin Z*-(**12f**) as a colourless liquid (123 mg, 77%), b.p. 105—108 °C/20 mmHg, $\delta(CDCl_3)$ 5.2 (2 H, m, CH=CH), 3.8 (4 H, m, OCH_2CH_2O), 2.4—2.2 (5 H, m, CH_2CH_2CH=CHC*H*), 1.3 (3 H, s, MeC), and 0.85 (6 H, d, 7 Hz, Me_2CH).

(Z)-6-*Phenylhex-5-en-2-one ethylene acetal Z*-(**12g**). The HR_F diastereoisomer of the alcohol (**11g**) (2.0 g, 4.58 mmol) and sodium hydride (220 mg, 4.6 mmol) gave the *olefin Z*-(**12g**) as a colourless liquid (898 mg, 90%), b.p. 82—85 °C (oven temp.)/2 mmHg, $\nu_{max.}$(film) 1 620 (C=C) and 1 080 cm^{-1} (C–O); $\delta(CDCl_3)$ 7.35 (5 H, s, *Ph*CH), 6.35 (1 H, dt, J_{HH} 10 Hz, 7 Hz, CH_2CH=CHPh), 5.6 (1 H, dt, J_{HH} 10 Hz, 1 Hz, CH_2-CH=C*H*Ph), 2.3 (2 H, q, *J* 7 Hz, CH_2CH=CH), 2.0 (2 H, t, *J* 7 Hz, CH_2CH_2CH=CHPh), and 1.0 (3 H, s, MeC); *m/z* 218 (M^+, 10%), 203 (*M* − Me, 45), 117 (PhCH=$CHCH_2^+$, 20), 87 ($C_4H_7O_2^+$, 15%), and 77 (Ph^+, 100%).

(Z)-6-*Cyclohexylhexan-2-one ethylene acetal Z*-(**12h**). The HR_F diastereoisomer of the alcohol (**11h**) (140 mg, 0.31 mmol), and sodium hydride (18 mg, 1.18 equiv.) gave the *olefin Z*-(**12h**) as an oil (40 mg, 58%), $\delta(CDCl_3)$ 5.7 (1 H, d, *J* 9 Hz, CH=C*H*C_6H_{11}), 5.45 (1 H, dt, *J* 9 Hz, *J* 7 Hz, CH_2CH=CH), 3.8 (4 H, s, OCH_2CH_2O), 2.5—2.0 [5 H, m, CH_2CH_2-CH=CHC*H*$(CH_2)_5$], and 1.5—1.0 [13 H, m, including sharp s at 1.1 p.p.m., MeC and $(CH_2)_5$ envelope].

(E)-*Hept-5-en-2-one ethylene acetal E*-(**12b**). As for the HR_F diastereoisomers, the LR_F diastereoisomer of the alcohol (**11b**) (500 mg, 1.33 mmol) and sodium hydride (64 mg, 1.33 mmol) gave the olefin *E*-(**12b**) as a colourless liquid (166 mg, 80%) b.p. 90 °C (oven temp.)/20 mmHg (lit.,[4] 79—84 C/18 mmHg), $\nu_{max.}$(soln.) 1 060 cm^{-1} (C–O); $\delta(CDCl_3)$ 5.35 (2 H, m, CH=CH), 3.8 (4 H, s, OCH_2CH_2O), 2.3—1.5 (7 H, m, CH_2CH_2CH=CH*Me*), and 1.21 (3 H, s, MeC).

(E)-*Non-5-en-2-one ethylene acetal E*-(**12d**). The LR_F diastereoisomer of the alcohol (**11d**) (320 mg, 0.8 mmol) and sodium hydride (39 mg, 0.8 mmol) gave the *olefin E*-(**12d**) as an oil (125 mg, 85%), $\nu_{max.}$(soln.) 1 080 cm^{-1} (C–O), $\delta(CDCl_3)$, 5.3 (2 H, m, CH=CH), 3.8 (4 H, s, OCH_2CH_2O), 2.3—1.7 (8 H, m, 4 × CH_2), 1.2 (3 H, s, MeC), and 0.95 (3 H, t, *J* 7 Hz, *Me*CH_2).

(E)-*Dec-5-en-2-one ethylene acetal E*-(**12e**). The LR_F diastereoisomer of the alcohol (**11e**) (416 mg, 1.0 mmol) and sodium hydride (48 mg, 1.0 mmol) gave the olefin *E*-(**12e**) as a colourless liquid (142 mg, 72%), b.p. 125 °C (oven temp.)/14 mmHg, $\nu_{max.}$(soln.) 1 070 cm^{-1} (C–O); $\delta(CDCl_3)$ 5.3 (2 H, m, CH=CH), 3.7 (4 H, s, OCH_2CH_2O), 2.5—1.5 (10 H, m, 5 × CH_2), 1.2 (3 H, s, MeC), and 1.0 (3 H, t, *J* 7 Hz, *Me*CH_2).

(E)-7-*Methyloct-5-en-2-one ethylene acetal E*-(**12f**). The LR_F diastereoisomer of the alcohol (**11f**) (300 mg, 0.75 mmol) and sodium hydride (36 mg, 0.75 mmol) gave the *olefin E*-(**12f**) as an oil (109 mg, 79%), $\delta(CDCl_3)$ 5.4 (2 H, m, CH=CH), 3.85 (4 H, s, OCH_2CH_2O), 2.3—1.8 (5 H, m, CH_2CH_2CH=CHC*H*), 1.2 (3 H, s, MeC), and 0.95 (6 H, d, *J* 7 Hz, Me_2CH).

(E)-6-*Phenylhex-5-en-2-one ethylene acetal E*-(**12g**). The LR_F diastereoisomer of the alcohol (**11g**) (500 mg, 1.15 mmol) and sodium hydride (56 mg, 1.15 mmol) gave the *olefin E*-(**12g**) as a colourless liquid (208 mg, 83%), b.p. 105 °C (oven temp.)/2 mmHg, $\nu_{max.}$(soln.) 1 080 cm^{-1} (C–O); $\delta(CDCl_3)$ 7.85—7.3 (5 H, s, *Ph*CH), 6.4 (1 H, d, J_{HH} 16 Hz, CH=C*H*Ph), 6.1 (1 H, dt, J_{HH} 16, 7 Hz, CH_2CH=CHPh), 2.3—1.9 (4 H, m, CH_2CH_2-CH=CHPh), and 1.2 (3 H, s, MeC).

5-Diphenylphosphinoyl-6-hydroxy-5-methyl-6-phenylhexan-2-one Ethylene Acetal (**24**).—BuLi (0.7 ml, 1.08 mmol) was added to a solution of the phosphine oxide (**10b**) (344 mg, 1.0 mmol), in THF (15 ml) at 0 °C under nitrogen. After 15 min the solution was cooled to −78 °C and benzaldehyde (150 mg, 1.4 mmol) added. The solution was allowed to warm to room temperature and aqueous ammonium chloride (20 ml, saturated solution) added. The organic phase was separated, and the aqueous phase extracted with ether (4 × 20 ml). The combined organic phases were dried (Na_2SO_4) and evaporated under reduced pressure to give, after p.l.c., the alcohol (**24**); HR_F *diastereoisomer* (166 mg, 37%) as needles, m.p. 160—162 °C (from EtOAc–Pr^i_2O), R_F 0.40 (EtOAc), $\nu_{max.}$(soln.) 3 300 (O–H), 1 440 (P–Ph), and 1 170 cm^{-1} (P=O); $\delta(CDCl_3)$ 8.1—7.1 (15 H, m, Ph_2PO and Ph), 5.1 (1 H, br s, OH), 4.9 (1 H, d, J_{PH} 14 Hz, C*H*OH), 3.7—3.5 (4 H, m, OCH_2CH_2O), 2.7—1.7 (4 H, m, $CH_2CH^*_2CMeP$), 1.4 (3 H, d, J_{PH} 18 Hz, MeCP), and 0.9 (3 H, s, MeC); *m/z* 450 (M^+, 5%), 343 (*M* − PhCHOH, 35%), 337 (*M* − $C_4H_6O_2$, 10%), and 201 (Ph_2PO^+, 100%); and LR_F *diastereoisomer* (157 mg, 35%) as needles, m.p. 183—185 °C (from EtOAc), R_F 0.35 (EtOAc), $\nu_{max.}$(soln.) 3 250 (O–H), 1 420 (P–Ph), and 1 155 cm^{-1} (P=O); $\delta(CDCl_3)$ 8.1—7.2 (15 H, m, Ph_2PO and Ph), 5.3 (1 H, d, J_{PH} 16 Hz, C*H*OH), 5.2 (1 H, br s, O*H*), 3.8 (4 H, s, OCH_2CH_2O), 2.6—2.0 (5 H, m including d, J_{PH} 17 Hz at 2.4 p.p.m., CH^*_2CMeP), 1.8 (2 H, t, *J* 7 Hz, CH_2CH_2CMeP), and 1.0 (3 H, s, MeCO); *m/z* 450 (M^+, 20%), 343 (*M* − PhCHOH, 45%), and 201 (Ph_2PO^+, 100%).

The following were prepared in a similar manner.

5-Diphenylphosphinoyl-6-hydroxy-3-methyl-6-phenylhexan-2-one ethylene acetal (**11i**). The phosphine oxide (**10d**) (345 mg, 1.0 mmol), BuLi (0.7 ml, 1.08 mmol), and benzaldehyde (150 mg, 1.4 mmol) gave after p.l.c., two diastereoisomers of the alcohol (**11i**): HR_F *diastereoisomer* (207 mg, 46%), m.p. 174—181 °C (from EtOAc–hexane), R_F 0.33 (EtOAc), $\nu_{max.}$(soln.) 3 220 (O–H), 1 440 (P–Ph), and 1 170 cm^{-1} (P=O); $\delta(CDCl_3)$ 8.1—7.3 (15 H, m, Ph_2PO and Ph), 5.0 (1 H, dd, J_{HH} 6 Hz, J_{PH} 16 Hz, C*H*OH),

4.5 (1 H, br s, OH), 3.8 (4 H, sym m, OCH_2CH_2O), 2.4 (1 H, m, CHP), 1.9—1.5 (3 H, m, $CHCH_2^*CHP$), 1.2 (3 H, s, MeC), and 1.0 (3 H, d, *J* 7 Hz, *Me*CH); and the LR_F *diastereoisomer* (72 mg, 16%) as an oil, R_F 0.25 (EtOAc), δ($CDCl_3$) 7.9—6.9 (15 H, m, Ph_2PO and Ph), 5.3 (1 H, dd, J_{HH} 6 Hz, J_{PH} 12 Hz, C*H*OH), 3.6—3.3 (4 H, m, OCH_2CH_2O), 2.3—1.4 (4 H, m, MeC*H*-CH_2^*CHP), 1.2 (3 H, s, MeC), and 0.95 (3 H, d, *J* 6.5 Hz, *Me*CH).

5-*Diphenylphosphinoyl*-6-*hydroxy*-6-*methylheptan*-2-*one ethylene acetal* (**25a**; $R^1 = R^2 =$ Me). The phosphine oxide (**10a**) (3.30 g, 10 mmol), BuLi (7.2 ml, 1.1 equiv.), and acetone (1 ml, excess) gave the *alcohol* (**25a**) (2.72 g, 70%) as needles, m.p. 118—119 °C (from EtOAc—Pr^i_2O), R_F 0.40 (EtOAc–MeOH, 9:1), $\nu_{max.}$(Nujol) 3 400 (O–H), 1 440 (P–Ph), and 1 165 cm^{-1} (P=O); δ($CDCl_3$) 8.0—7.3 (10 H, m, Ph_2PO), 4.9 (1 H, br s, O*H*), 3.7 (4 H, s, OCH_2CH_2O), 2.35 (1 H, td, J_{HH} 7 Hz, J_{PH} 5 Hz, C*H*P), 2.0—1.45 (4 H, m, $CH_2CH_2^*CHP$), 1.35 (3 H, s, MeCO), and 1.15 (6 H, d, J_{PH} 16 Hz, Me_2COH); *m*/*z* 388 (M^+, 0.2%), 329 (M − Me_2COH, 80%), and 201 (Ph_2PO^+, 100%) (Found: M^+, 388.1800. $C_{22}H_{29}O_4P$ requires *M*, 388.1803).

5-*Diphenylphosphinoyl*-6-*hydroxy*-6-*methyloctan*-2-*one ethylene acetal* (**25e**; R^1 = Me, R^2 = Et). The phosphine oxide (**10a**) (1.0 g, 3.03 mmol), BuLi (2.10 ml, 1.08 equiv.), and butanone (0.5 ml, 1.8 equiv.), after chromatography (SiO_2, eluted with EtOAc–MeOH, 9:1), gave the HR_F *diastereoisomer* (**25e**) (475 mg, 39%) as needles, m.p. 110—112 °C (from EtOAc–Pr^i_2O), R_F 0.40 (EtOAc–MeOH, 9:1), $\nu_{max.}$(soln.) 3 350 (O–H), 1 440 (P–Ph), 1 160 (P=O), and 1 055 cm^{-1} (C–O); δ($CDCl_3$) 7.9—7.2 (10 H, m, Ph_2PO), 4.5 (1 H, s, O*H*), 3.8 (4 H, s, OCH_2CH_2O), 2.5 (1 H, ddd, J_{PH} 5 Hz, J_{HH} 2, 8 Hz, CH_2^*CHP), 2.0—1.5 (6 H, m, 3 × CH_2^*), 1.3 (3 H, s, MeC), 1.25 (3 H, d, J_{PH} 15 Hz, *Me*COH), and 0.9 (3 H, t, 7 Hz, *Me*CH_2) (Found: C, 68.51; H, 7.94; P, 8.13; $C_{23}H_{31}O_4P$ requires C, 68.64; H, 7.76; P, 7.70%); and the LR_F *diastereoisomer* (**25e**) (463 mg, 38%) as needles, m.p. 121—124 °C (from EtOAc), R_F 0.32 (EtOAc–MeOH, 9:1), δ($CDCl_3$) 7.9—7.1 (10 H, m, Ph_2PO), 4.1 (1 H, br s, O*H*), 3.8 (4 H, s, OCH_2CH_2O), 2.45 (1 H, ddd, J_{PH} 5 Hz, J_{HH} 4, 5 Hz, CH_2^*CHP), 2.0—1.5 (6 H, m, 3 × CH_2^*), 1.3 (3 H, s, MeC), 1.2 (3 H, d, J_{PH} 12 Hz, *Me*COH), and 1.0 (3 H, dt, J_{PH} 2 Hz, J_{HH} 7 Hz, *Me*CH_2).

5-*Diphenylphosphinoyl*-6-*ethyl*-6-*hydroxyoctan*-2-*one ethylene acetal* (**25b**; $R^1 = R^2$ = Et). The phosphine oxide (**10a**) (2.30 g, 6.97 mmol), BuLi (4.9 ml, 7.5 mmol), and pentan-3-one (650 mg, 7.55 mmol) gave the *alcohol* (**25a**) (1.39 g, 48%) as a gum, which crystallised very slowly (*ca.* 2 months), $\nu_{max.}$(soln.) 3 400 (O–H), 1 440 (P–Ph), and 1 160 cm^{-1} (C–O); δ($CDCl_3$) 8.0—7.2 (10 H, m, Ph_2PO), 3.8 (4 H, s, OCH_2CH_2O), 2.4 (1 H, dt, J_{PH} 6 Hz, CHP), 1.9—1.4 (8 H, m including q, *J* 7 Hz at 1.55 p.p.m., 4 × CH_2), 1.25 (3 H, s, MeC), and 1.0 (6 H, t, *J* 7 Hz, 2 × *Me*CH_2).

5-*Diphenylphosphinoyl*-6-*hydroxy*-6-*methylnonan*-2-*one ethylene acetal* (**25f**; R^1 = Me, R^2 = Pr^n). The phosphine oxide (**10a**) (330 mg, 1.0 mmol), BuLi (0.7 ml, 1.1 mmol), and pentan-2-one (100 mg, 1.2 mmol) after chromatography (SiO_2 eluted with EtOAc–MeOH, 9:1) gave the HR_F *diastereoisomer* (**25f**) (117 mg, 28%) as needles, R_F 0.35 (EtOAc–MeOH, 9:1), δ($CDCl_3$), 7.8—7.1 (10 H, m, Ph_2PO), 4.5 (1 H, s, OH), 3.75 (4 H, sym m, OCH_2CH_2O), 2.3 (1 H, ddd, J_{PH} 6 Hz, J_{HH} 3, 6 Hz, CH_2^*CHP), 1.9—1.4 (8 H, m, 4 × CH_2), 1.3 (3 H, d, J_{PH} 16 Hz, *Me*COH), 1.25 (3 H, s, MeC), and 0.9 (3 H, t, J_{HH} 7 Hz, *Me*CH_2); and the LR_F *diastereoisomer* (**25f**) (116 mg, 28%) as prisms, m.p. 144—147 °C (from EtOAc), R_F 0.27 (EtOAc–MeOH, 9:1), $\nu_{max.}$(soln.) 3 350 (O–H), 1 440 (P–Ph), 1 170 (P=O), and 1 060 cm^{-1} (C–O); δ($CDCl_3$) 7.9—7.1 (10 H, m, Ph_2PO), 4.9 (1 H, br s, O*H*), 3.8 (4 H, s, OCH_2CH_2O), 2.4 (1 H, ddd, J_{PH} 8 Hz, J_{HH} 3, 8.5 Hz, CH_2^*CHP), 1.9—1.4 (8 H, m, 4 × CH_2), 1.3—1.1 (6 H, m, including s at 1.2, *Me*C and *Me*C–OH), and 1.0 (3 H, t, J_{HH} 7 Hz, *Me*CH_2).

5-*Diphenylphosphinoyl*-6-*hydroxy*-6,7-*dimethoxyoctan*-2-*one ethylene acetal* (**25**; R^1 = Me, R^2 = Pr^i). The phosphine oxide (**10a**) (1.65 g, 5 mmol), BuLi (3.5 ml, 5.5 mmol), and 3-methylbutan-2-one (500 mg, 5.8 mmol) gave, after chromatography (SiO_2 eluted with EtOAc), the HR_F *diastereoisomer* (603 mg, 29%), as prisms, m.p. 97—100 °C (from EtOAc), R_F 0.35 (EtOAc), $\nu_{max.}$(Nujol) 3 250 (O–H), 1 435 (P–Ph), and 1 165 cm^{-1} (P=O); δ($CDCl_3$) 8.0—7.2 (10 H, m, Ph_2PO), 4.8 (1 H, s, OH), 3.8 (4 H, s, OCH_2CH_2O), 2.4 (1 H, ddd, J_{PH} 6 Hz, J_{HH} 3, 8 Hz, CH_2^*CHP), 1.9—1.3 (5 H, m, $CH_2CH_2^*CHP$, $CHMe_2$), 1.2 (3 H, d, J_{PH} 15 Hz, *Me*C–OH), 1.15 (3 H, s, MeC), and 1.0 (6 H, d, J_{HH} 6 Hz, Me_2CH); *m*/*z* 416 (M^+, absent), 329 (M − $MePr^iCOH$, 80%), and 201 (Ph_2PO^+, 100%); and the LR_F *diastereoisomer* (686 mg, 33%) as needles, m.p. 91—95 °C (from EtOAc), R_F 0.28 (EtOAc) (Found: C, 68.95, H, 8.04. $C_{24}H_{33}O_4P$ requires C, 69.21%; H, 7.98%), δ($CDCl_3$) 8.0—7.2 (10 H, m, Ph_2PO), 4.2 (1 H, s, OH), 3.8 (4 H, sym m, OCH_2-CH_2O), 2.3 (1 H, m including *J* 7 Hz, CH_2^*CHP), 2.0—1.3 (5 H, m, $CH_2CH_2^*CHP$, $CHMe_2$), 1.3 (3 H, d, J_{PH} 13 Hz, *Me*C–OH), 1.15 (3 H, s, MeC), and 0.95 (6 H, d, J_{HH} 6.5 Hz, Me_2CH).

5-*Diphenylphosphinoyl*-6-*hydroxy*-6-*phenylheptan*-2-*one ethylene acetal* (**25h**; R^1 = Me, R^2 = Ph). The phosphine oxide (**10a**) (1.32 g, 4 mmol), BuLi (2.8 ml, 4.4 mmol), and acetophenone [1 ml in lithium bromide-saturated THF (10 ml)], gave, after chromatography (SiO_2, eluted with EtOAc), the HR_F *diastereoisomer* (665 mg, 37%), as needles, m.p. 170—175 °C (from EtOAc–hexane), R_F 0.4 (EtOAc), $\nu_{max.}$(soln.) 3 400 (O–H), 1 440 (P–Ph), and 1 165 cm^{-1} (P=O); δ($CDCl_3$) 7.9—7.0 (15 H, m, Ph_2PO and Ph), 4.3 (1 H, br s, O*H*), 3.5 (4 H, m, OCH_2CH_2O), 2.85 (1 H, ddd, J_{PH} 10 Hz, J_{HH} 4, 6 Hz, CH_2^*CHP), and 1.7—1.2 (10 H, m, *Me*C, $CH_2CH_2^*CHP$, *Me*COH); *m*/*z* 450 (M^+, absent), 435 (M − Me, 10%), 329 (M − PhCMeOH, 95%), and 201 (Ph_2PO^+, 100%); and the LR_F *diastereoisomer* (610 mg, 34%), as needles, m.p. 210—217 °C (from EtOAc), R_F 0.35 (EtOAc), $\nu_{max.}$(soln.) 3 380 (O–H), 1 440 (P–Ph), 1 160 (P=O), and 1 050 cm^{-1} (C–O); δ($CDCl_3$) 8.1—7.1 (15 H, m, Ph_2PO and Ph), 3.7—3.3 (4 H, m, OCH_2CH_2O), 2.5 (1 H, ddd, J_{PH} 7 Hz, J_{HH} 2, 8 Hz, CH_2^*CHP), and 1.7—1.1 (10 H, m, *Me*C, $CH_2CH_2^*CHP$, and *Me*COH).

5-*Diphenylphosphinoyl*-5-(1-*hydroxycyclohexyl*)*pentan*-2-*one ethylene acetal* [**25d**; $R^1R^2 = (CH_2)_5$]. The phosphine oxide (**10a**) (3.30 g, 10 mmol), BuLi (7.1 ml, 11.0 mmol), and cyclohexanone (1.5 ml, 14.5 mmol) gave the *phosphine oxide* (**25d**) as plates (3.00 g, 70%), m.p. 147—149 °C (from EtOAc–Pr^i_2O), $\nu_{max.}$(Nujol) 3 250 (O–H), 1 440 (P–Ph), and 1 170 cm^{-1} (P=O); δ($CDCl_3$) 7.8—7.0 (10 H, m, Ph_2PO), 4.0—3.8 (5 H, m including sharp s at 3.85, OH, OCH_2CH_2O), 2.5 (1 H, m, including *J* 8 Hz, CHP), and 1.8—1.1 [17 H, m including sharp s at 1.3, *Me*C, $CH_2CH_2^*CHP$, $(CH_2)_5$]; *m*/*z* 428 (M^+, 1%), 329 [M − $(CH_2)_5COH$, 100%], and 201 (Ph_2PO^+, 80%) (Found: M^+, 428.2117. $C_{23}H_{33}O_4P$ requires *M*, 428.2115).

5-*Diphenylphosphinoyl*-5-(1-*hydroxycyclopentyl*)*pentan*-2-*one ethylene acetal* [**25c**; $R^1R^2 = (CH_2)_4$]. The phosphine oxide (**10a**) (1.40 g, 4.25 mmol), BuLi (3.0 ml, 4.6 mmol), and a solution of cyclopentanone in LiBr-saturated THF (1.0 ml in 10 ml) gave, after chromatography (SiO_2, eluted with EtOAc–MeOH 9:1), the *phosphine oxide* (**25c**) as needles (897 mg, 51%), m.p. 131—133 °C (from EtOAc), R_F 0.35 (EtOAc–MeOH, 9:1), δ($CDCl_3$) 8.0—7.1 (10 H, m, Ph_2PO), 4.5 (1 H, br s, OH), 3.8 (4 H, s, OCH_2CH_2O), 2.5 (1 H, dt, J_{PH} 5 Hz, J_{HH} 7 Hz, CHP), and 1.9—1.2 [15 H, m, including sharp s at 1.25, *Me*C, $CH_2CH_2^*CHP$, $(CH_2)_4$]; *m*/*z* 414 (M^+, 0.2%), 329 [M − $(CH_2)_4COH$, 60%], and 202 (Ph_2POH^+, 100%) (Found: *M*, 414.1942. $C_{24}H_{31}O_4P$ requires *M*, 414.1959).

6-*Methylhept*-5-*en*-2-*one Ethylene Acetal* (**26a**; $R^1 = R^2 =$ Me).—Sodium hydride (50% in oil) (310 mg, 6.56 mmol) was added to a solution of the alcohol (**25a**) (2.5 g, 6.45 mmol) in

DMF (20 ml). The solution was heated at 50 °C for 1 h and then poured into a mixture of ether (50 ml) and water (30 ml). The organic layer was separated and the aqueous layer was washed with ether (2 × 25 ml). The combined organic layers were washed with water (20 ml), dried (Na_2SO_4), and evaporated under reduced pressure, to give the olefin (**26a**) as a colourless liquid (926 mg, 84%), b.p. 91—95 °C/14 mmHg (lit.,[48] 86—89 °C/12 mmHg), R_F 0.95 (Et_2O), $\nu_{max.}$(soln.) 1 675 (C=C) and 1 060 cm^{-1} (C–O); δ($CDCl_3$) 5.2 (1 H, t, *J* 7 Hz, C*H*=CMe$_2$), 3.9 (4 H, s, OCH_2CH_2O), 2.4—1.5 (10 H, m including 2 × sharp s at 1.7 and 1.6, CH_2CH_2CH=C*Me*$_2$), and 1.05 (3 H, s, MeCO), *m/z* 170 (M^+, 5%), 155 (*M* − Me, 5%), 88 ($C_4H_8O^+$, 5%), and 87 ($C_4H_7O^+$, 100%).

The following were prepared similarly.

(Z)-6-*Methyloct-5-en-2-one ethylene acetal*[49] (**26e**; R^1 = Me, R^2 = Et). The HR_F diastereoisomer of the alcohol (**25e**) (402 mg, 1.0 mmol) and sodium hydride (48 mg, 1.0 mmol) in DMF (5 ml) gave the olefin (**26e**) as a colourless oil (134 mg, 73%), R_F 0.85 (Et_2O), $\nu_{max.}$(soln.) 1 070 cm^{-1} (C–O); δ($CDCl_3$) 5.0 (1 H, t, *J* 7 Hz, C*H*–CMeEt) 3.7 (4 H, s, OCH_2CH_2O), 1.7—1.3 (7 H, m, including s at 1.6 p.p.m., CH_2CH=C*Me*CH_2Me), 1.2 (3 H, s, MeCO), and 0.9 (3 H, t, *J* 7 Hz, *Me*CH_2).

(E)-6-*Methyloct-5-en-2-one ethylene acetal* (**26e**; R^1 = Et, R^2 = Me). The LR_F diastereoisomer of the alcohol (**25e**) (402 mg, 1.0 mmol) and sodium hydride (48 mg, 1.0 mmol) in DMF (5 ml) gave the olefin (**26e**) as a colourless oil (149 mg, 81%), b.p. 84—88 °C (oven temperature/15 mmHg) (lit.,[49] 44 °C/2 mmHg), R_F 0.85 (Et_2O), δ($CDCl_3$) 5.05 (1 H, t, *J* 6.5 Hz, C*H*=CMeEt), 3.8 (4 H, s, OCH_2CH_2O), 1.8—1.2 (9 H, m, including sharp s at 1.5 p.p.m., CH_2CH_2C=C*Me*CH_2Me), 1.15 (3 H, s, MeCO), and 0.9 (3 H, t, *J* 7 Hz, *Me*CH_2).

(Z)-6,7-*Dimethyloct-5-en-2-one ethylene acetal* (**26g**). The HR_F diastereoisomer of the alcohol (**25g**) (500 mg, 1.2 mmol) and sodium hydride (58 mg, 1.2 mmol) in DMF (8 ml) gave the *olefin* (**26g**) as a colourless oil (195 mg, 82%), R_F 0.80 (Et_2O), $\nu_{max.}$(soln.) 1 650 (C=C) and 1 070 cm^{-1} (C–O); δ($CDCl_3$) 5.0 (1 H, t, *J* 7 Hz, C*H*=CMePr^i), 3.8 (4 H, s, OCH_2CH_2O), 1.8—1.4 (8 H, m, CH_2CH_2CH=C*Me*C*H*Me$_2$), 1.2 (3 H, s, MeCO), and 1.0 (6 H, d, *J* 6 Hz, *Me*$_2$CH).

(E)-6,7-*Dimethyloct-5-en-2-one ethylene acetal* (**26g**). The LR_F diastereoisomer of the alcohol (**25g**) (500 mg, 1.2 mmol) and sodium hydride (58 mg, 1.2 mmol) in DMF (8 ml) gave the olefin (**26g**) as a pale yellow oil (159 mg, 67%), R_F 0.77 (Et_2O), $\nu_{max.}$(film) 1 635 (C=C) and 1 060 cm^{-1} (C–O).

5-*Cyclohexylidenepentan-2-one ethylene acetal* [**26c**; R^1, R^2 = $(CH_2)_5$]. The alcohol (**25c**) (2.5 g, 5.84 mmol) and sodium hydride (280 mg, 5.84 mmol) in DMF (20 ml) gave the olefin (**26c**) as a colourless liquid (1.09 g, 89%), b.p. 95—100 °C (oven temperature/1 mmHg, R_F 0.70 (Et_2O), $\nu_{max.}$(film) 1 055 cm^{-1} (C–O); δ($CDCl_3$) 5.0 [1 H, t, *J* 7 Hz, C*H*=C$(CH_2)_5$], 3.65 (4 H, m, OCH_2CH_2O), 1.7 (2 H, t, *J* 7 Hz, CH_2CH_2CH=C), and 1.5—1.0 [15 H, m, including sharp s at 1.2 p.p.m., *Me*C, CH_2CH=C($CH_2)_5$]; *m/z* 210 (M^+, 2%), 195 (*M* − Me, 60%), 109 [$(CH_2)_5C$=$CHCH_2^+$, 30%], and 87 ($C_4H_7O_2^+$, 100%) (Found: M^+, 210.1620. $C_{13}H_{22}O_2$ requires *M*, 210.1616).

5-*Diphenylphosphinoyl-5-phenylthiopentan-2-one Ethylene Acetal* (**36**).—A solution of the lithium anion of the phosphine oxide (**10a**) made from the addition of BuLi (7.0 ml, 10 mmol), to the phosphine oxide (**10a**) (3.30 g, 10 mmol) in THF (40 ml) at 0 °C was cooled to −78 °C and added very slowly to a solution of diphenyl disulphide (2.18 g, 10 mmol) in THF (50 ml) at −78 °C. When the addition was complete (4 h), the solution was allowed to warm slowly to room temperature. Saturated aqueous ammonium chloride (30 ml) was added and the organic phase separated. The aqueous phase was extracted with ether (3 × 20 ml). The combined organic phases were dried (Na_2SO_4) and concentrated under reduced pressure to give, after chromatography (SiO_2, eluting with EtOAc), starting material (790 mg, 27%), the sulphide (**36**) (1.75 g, 41%) and the disulphenylated material (**37**) (1.31 g, 24%). The *sulphide* (**36**) was obtained as needles, m.p. 134—136 °C (from EtOAc), R_F 0.4 (EtOAc), $\nu_{max.}$(soln.) 1 480 (Ph–S), 1 440 (Ph–P), 1 185 (P=O), and 1 060 cm^{-1} (C–O); δ($CDCl_3$), 7.85, 7.4—7.25 (10 H, m, Ph_2PO), 7.12 (5 H, s, PhS), 3.8 (4 H, sym m, OCH_2CH_2O), 2.3—1.8 (5 H, m, $CH_2CH_2^*CHP$), and 1.20 (3 H, s, MeC); *5-diphenylphosphinoyl-5,5-bisphenylthiopentan-2-one ethylene acetal* (**37**) was obtained as needles, R_F 0.47 (EtOAc), $\nu_{max.}$(soln.) 1 480 (Ph–S), 1 440 (Ph–P), 1 175 (P=O), and 1 060 cm^{-1} (C–O); δ($CDCl_3$) 8.3 (4 H, m) and 7.5—7.0 (16 H, m) (2 × PhS, Ph_2PO), 3.8—3.4 (4 H, sym, m, OCH_2CH_2O), 2.10 (2 H, t, *J* 6 Hz, CH_2CH_2CP), 1.60 (2 H, dt, J_{PH} 15 Hz, J_{HH} 6 Hz, CH_2CH_2CP), and 0.95 (3 H, s, MeC).

The same products were formed by addition of the lithium anion of the phosphine oxide (**10a**) to phenylsulphenyl chloride in the following yields: starting material (21%), sulphide (**36**) (46%), and bissulphide (**37**) (14%).

5-*Phenylthiopentan-2-one Ethylene Acetal* (**34**).—A solution of 5-chloropentan-2-one ethylene acetal (**8**; Y = Cl) (8.2 g, 50 mmol) and sodium thiophenoxide (6.6 g, 50 mmol) in absolute ethanol (100 ml) was heated at reflux overnight. The precipitate was filtered off and the liquors evaporated under reduced pressure to give the *sulphide* (9.8 g, 82.5%) as a colourless liquid, b.p. 160 °C (oven temp.)/3 mmHg, R_F 0.70 (Et_2O), $\nu_{max.}$(film) 1 585, 1 480 (SPh), and 1 060 cm^{-1} (C–O); δ($CDCl_3$) 7.2 (5 H, m, SPh), 3.8 (4 H, s, OCH_2CH_2O), 2.8 (2 H, t, *J* 7 Hz, CH_2SPh), 1.9—1.6 (4 H, m, $CH_2CH_2CH_2$SPh), and 1.2 (3 H, s, MeC); *m/z* 238 (M^+, 15%), 223 (*M* − Me, 25%), 137 (PhS $CH_2CH_2^+$, 10%), 110 (PhSH$^+$, 85%), and 109 (PhS$^+$, 100%).

5-*Chloro-5-phenylthiopentan-2-one Ethylene Acetal* (**35**).—A solution of 5-phenylthiopentan-2-one ethylene acetal (4.76 g, 20 mmol) in carbon tetrachloride (20 ml) was added dropwise to a suspension of *N*-chlorosuccinimide (2.67 g, 20 mmol) in carbon tetrachloride (20 ml) under nitrogen at 0 °C. The mixture was stirred overnight and allowed to warm to room temperature. The white precipitate was filtered off and the liquors evaporated under reduced pressure to give the *chloro sulphide* (**35**) as a colourless liquid (3.38 g, 60%), b.p. 145 °C (oven temperature)/1 mmHg, $\nu_{max.}$(soln. in CCl_4) 1 490 (SPh) and 1 075 cm^{-1} (C–O); δ(CCl_4) 7.1 (5 H, m, SPh), 5.0 [1 H, t, *J* 6.5 Hz, C*H*Cl(S)Ph], 3.7 (4 H, s, OCH_2CH_2O), 1.8—1.4 (4 H, m, CH_2CH_2CH), and 1.15 (3 H, s, MeC).

5-*Diphenylphosphinoyl-5-phenylsulphinylpentan-2-one Ethylene Acetal* (**39**).—A solution of *m*-chloroperbenzoic acid (1.81 g, 10.5 mmol) in chloroform (30 ml) was added dropwise to a solution of the sulphide (**36**) (2.19 g, 5 mmol) in chloroform (20 ml) at room temperature. The solution was stirred for 2 h, water (30 ml) was added, and the organic layer separated. The aqueous layer was extracted with chloroform (3 × 20 ml). The combined organic phases were washed with water (20 ml), dried (Na_2SO_4), and evaporated under reduced pressure to give the *sulphoxide* (**39**) (1.92 g, 85%) as a pale oil, R_F 0.2 (EtOAc), $\nu_{max.}$(soln.) 1 570, 1 480n (SPh), 1 440 (P–Ph), 1 165 (P=O), 1 060 (C–O), and 1 040 cm^{-1} (S=O); δ($CDCl_3$) 8.2—7.3 (15 H, m, Ph_2PO and PhSO), 4.0—3.5 (5 H, m, OCH_2CH_2O, CHPS), 2.3—1.4 (4 H, m, CH_2CH_2CHPOS), and 1.0 (3 H, s, MeC).

(E)-5-*Diphenylphosphinoylpent-4-en-2-one Ethylene Acetal* (**40**).—The sulphoxide (**39**) (454 mg, 1.0 mmol) was heated in toluene (3 ml) at 100 °C for 6 h. The mixture was cooled and the crude product chromatographed (SiO_2/EtOAc) to give the *vinyl phosphine oxide* (**40**) (327 mg, 95%) as prisms, m.p. 156—158 °C, R_F 0.15 (EtOAc), $\nu_{max.}$(Nujol) 1 640 (C=C), 1 440 (P–Ph), and

1 165 cm^{-1} (P=O); δ($CDCl_3$) 7.85—7.35 (10 H, m, Ph_2PO), 6.65 (1 H, ddt, J_{PH} 33, J_{HH} 18, 7 Hz, CH_2CH=CHP), 6.4 (1 H, dd, J_{PH} 42, J_{HH} 18 Hz, CH=CHP), 3.85 (4 H, s, OCH_2CH_2O), 2.6 (2 H, d, J_{HH} 7 Hz, CH_2CH), 1.3 (3 H, s, MeC).

5-Diphenylphosphinoylpent-3-en-2-one (**41**).—Butyl-lithium (0.7 ml, 1.1 equiv.) was added dropwise to a stirred solution of the vinyl phosphine oxide acetal (**40**) (344 mg, 1.0 mmol) in THF (5 ml) under nitrogen at −60 °C. An instantaneous orange colour formed at the surface as the butyl-lithium drop touched it, but stirring caused the colour to disappear. After the butyl-lithium had been added, the solution was cooled to −78 °C and benzaldehyde (115 mg, 1.1 equiv.) was added. After 20 min at −78 °C the cooling bath was removed and the solution allowed to warm to room temperature. Water (3 ml) and ether (10 ml) were added and the organic layer separated. The aqueous phase was extracted with ether (2 × 10 ml). The combined organic phases were dried (Na_2SO_4) and evaporated to give the *enone* (**41**) (213 mg, 75%) as pale yellow needles, R_F 0.6 (EtOAc), $\nu_{max.}$(soln.) 1 675 (C=O), 1 635 (C=C), 1 440 (P–Ph), and 1 165 cm^{-1} (P=O); δ($CDCl_3$) 7.9—7.2 (10 H, m, Ph_2PO), 6.9—6.3 (1 H, m, including J_{HH} 16 Hz, COCH=CH), 6.1 (1 H, dd, J_{HH} 16 Hz, J_{HP} 4 Hz, COCH=CH), 3.25 (2 H, dd, J_{HH} 6 Hz, J_{PH} 14 Hz, $CHCH_2P$), and 2.1 (3 H, s, MeC=O).

5-Phenylthiohept-5-en-2-one Ethylene Acetal (**38**; R = Me).—BuLi (1.4 ml, 2.16 mmol) was added to a solution of the sulphide (**36**) (976 mg, 2.0 mmol) in THF (20 ml) under nitrogen at 0 °C. After 15 min the solution was cooled to −78 °C and acetaldehyde (1 ml, excess) added. As the mixture warmed to room temperature a cloudy precipitate began to settle. Saturated aqueous ammonium chloride (10 ml) was added and the organic phase separated. The aqueous phase was extracted with ether (3 × 30 ml); the combined organic phases were dried (Na_2SO_4) and evaporated under reduced pressure to give a mixture of isomers of the *vinyl sulphide* (**38**; R = Me) (380 mg, 72%) as a colourless oil, R_F 0.8 (CH_2Cl_2), $\nu_{max.}$(soln.) 1 630 (C=C), 1 580, 1 480 (SPh), and 1 060 cm^{-1} (C–O); δ($CDCl_3$) 7.2 (5 H, m, SPh), 5.35, 5.15 [1H, 2 × q, *J* 7 Hz, ratio *ca.* 1:1, MeCH=C(SPh)CH_2], 3.8 (4 H, s, OCH_2CH_2O), 2.3 (2 H, t, *J* 7 Hz, CH_2CH_2C=C), and 1.8—1.5 (5 H, m, MeCH and CH_2CH_2C=C).

The following were prepared in a similar way.

6-Phenyl-5-phenylthiohex-5-en-2-one ethylene acetal (**38**; R = Ph). The phosphine oxide (**36**) (438 mg, 1 mmol), BuLi (0.7 ml, 1.1 mmol), and benzaldehyde (0.15 ml, 1.5 equiv.) gave after p.l.c. (eluted with CH_2Cl_2), a mixture of isomers of the *vinyl sulphide* (**38**; R = Ph) as a yellow oil (212 mg, 65%), R_F 0.75 and 0.68 (CH_2Cl_2); δ($CDCl_3$) 7.5—7.0 (10 H, m, SPh and Ph), 6.28 and 6.06 (1 H, 2 × s, ratio *ca.* 1:2, CHPh), 3.8—3.6 (4 H, m, OCH_2CH_2O), 2.3 (2 H, t, *J* 7 Hz, CH_2CH_2CSPh), 1.7 (2 H, t, *J* 7 Hz, CH_2CH_2CSPh), and 1.2 (3 H, s, MeCO).

7-Methyl-5-phenylthio-octan-5-en-2-one ethylene acetal (**38**; R = Pr^i). The phosphine oxide (**36**) (438 mg, 1.0 mmol), BuLi (0.7 ml, 1.1 mmol), and isobutyraldehyde (0.2 ml, 2.5 mmol), gave, after p.l.c. (SiO_2, eluted with CH_2Cl_2), a mixture of isomers of the *vinyl sulphide* (**38**; R = Pr^i) as a yellow oil (233 mg, 79%), R_F 0.7 (CH_2Cl_2), $\nu_{max.}$(soln.) 1 640 (C=C), 1 585, 1 480 (SPh), and 1 065 cm^{-1} (C–O); δ($CDCl_3$) 7.3 (5 H, m, SPh), 5.4—5.1 (1 H, m, Pr^iCH=C), 3.8 (4 H, sym m, OCH_2CH_2O), 2.3 (2 H, t, *J* 7 Hz, CH_2CH_2C=C), 2.2 (1 H, dm, *J* 7 Hz, Me_2CH–CH=C), 1.7 (2 H, t, *J* 7 Hz, $CH_2CH_2CH_2C$=C), 1.25 (3 H, s, MeC), and 0.95 (6 H, d, *J* 6 Hz, Me_2CH).

Reaction of the Anion of (**36**) *with Ketones.*—Typically, the lithium anion of the sulphide (**36**) (made from addition of BuLi to a solution of the sulphide in THF at 0 °C), reacted with a ketone at −78 °C to decolourise the orange anion. The solution was allowed to warm to room temperature and then worked-up in the manner described above, to give, after chromatography (SiO_2, eluted with CH_2Cl_2), starting material (**36**) (*ca.* 70% recovery).

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