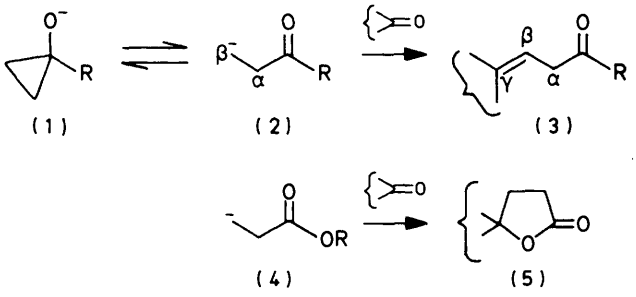
Synthesis of Protected β,γ-Unsaturated Ketones from β-Diphenylphosphinoyl Ketones

Chris Earnshaw, Richard S. Torr, and Stuart Warren *
University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW

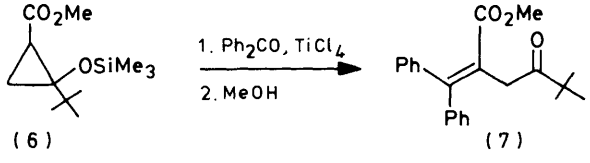
Ketals of β-diphenylphosphinoyl ketones combine with aldehydes and ketones in the Horner-Wittig reaction to give ketals of β,γ-unsaturated ketones.

Aldols and α,β-unsaturated ketones result from enolate attack on aldehydes or ketones. Synthesis of γ-hydroxy carbonyl compounds ('homoaldols') and β,γ-unsaturated ketones (3) by an analogous strategy requires the attack of a homoenolate [1] (2), or its synthetic equivalent, on a carbonyl compound. Homoenolates of acid derivatives [2] (4) give γ-lactones (5) by the same reaction. Reaction of (2) with alkyl halides has potential as a chain extension of ketones.



Scheme 1.

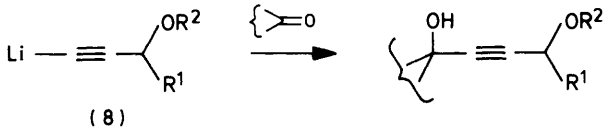
True homoenolisation, the stabilisation of (2) as a cyclopropane (1), is too weak a phenomenon to be synthetically useful and is overwhelmed by normal enolisation unless the α-carbon atom is quaternary.[3] Many types of homoenolate equivalent have therefore been devised,[1,4] mostly for homoenolates of aldehydes (2; R = H) or acid derivatives (4), but a few are available for ketone homoenolates and includes a representative from each main type (Schemes 2—8).



Scheme 2.

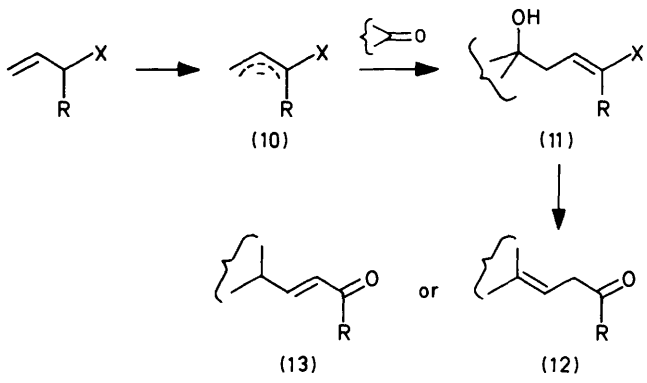
Derivatives of (1), such as silyl ether [5] (6), react with carbonyl compounds to give, in this special case, a β,γ-unsaturated ketone (7). The regioselectivity of the cyclopropane opening is controlled by the ester group but otherwise only compounds unsubstituted at the α or β carbon atoms of (3) can be made.[2] The regio- and stereo-selectivity of double bond formation depends on dehydration of the intermediate tertiary alcohol.

Acetylenes could provide a natural link between the carbonyl group and the anion in (2) but normally the alcohol



Scheme 3.

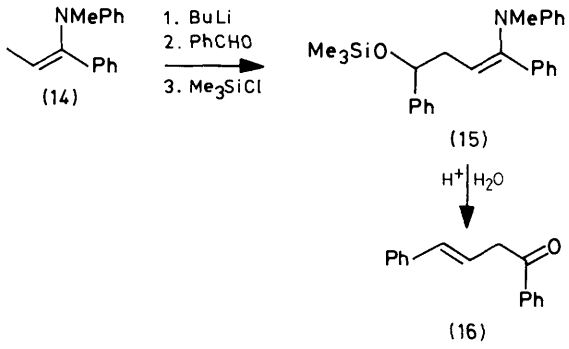
oxidation state (8) is preferred [6] to avoid self-condensation (Scheme 3). Reduction of the triple bond, oxidation of the ether, and dehydration of the alcohol are needed to give (3). No substituents are possible on the α or β carbon atoms and there is again no built-in control in the dehydration.



Scheme 4.

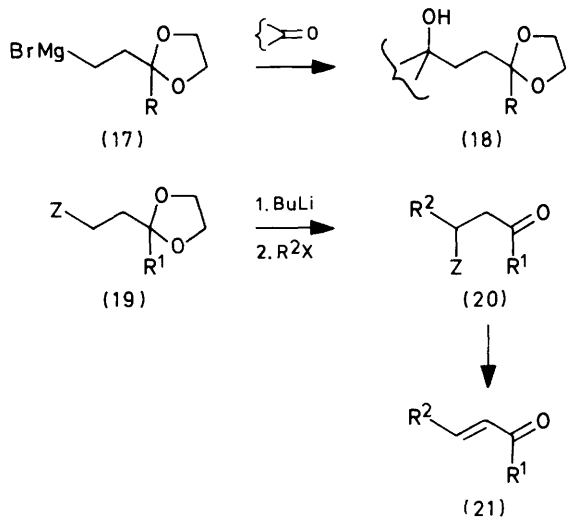
The most versatile homoenolate equivalents [4,7,8] are those based on allyl anions with a heteroatom at one end (10; X = B, N, O, S, Si, *etc.*). Providing γ-selectivity in addition of electrophiles can be assured, the product (11) is a masked ketone. Dehydration of (11) normally gives an α,β (13) rather than a β,γ-unsaturated ketone (12). The most extensively studied anions (10) are those derived from enamines,[4,9] *e.g.* (14), usually in reactions with alkyl halides to give an extended carbon chain. One case of a ketone derivative (14) reacting with benzaldehyde has been reported.[10] This gives a β,γ-unsaturated ketone (16) as the regioselectivity of dehydration of (15) is controlled by the phenyl group. Anions (10; X = PhS) react at the γ-position with carbonyl compounds when R = H to give aldehyde derivatives but prefer to react at the α-position when R = alkyl so that ketone derivatives cannot be made this way.[8]

The most widely used ketone homoenolate equivalents are those with an anion-stabilising group on the β carbon atom and with the ketone protected to avoid self-condensation. Grignard reagents [11] (17) give alcohols (18) which may be dehydrated to α,β- or β,γ-unsaturated ketones depending on the structure. Sulphones [1,12] (19; Z = $ArSO_2$) and nitriles [13]



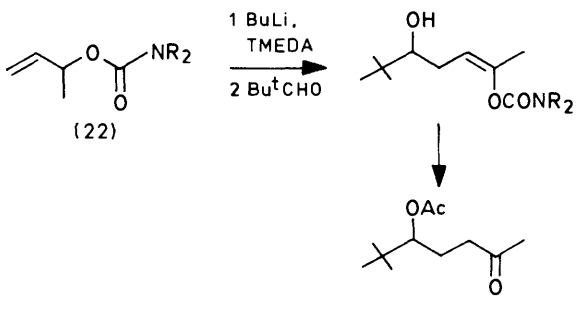
Scheme 5.

(19; Z = CN) can be alkylated at the β carbon atom: removal of the activating and protecting groups from (20) gives an α,β-unsaturated ketone (21) (Scheme 6).



Scheme 6.

Current interest [14] in the homoaldol reaction, in which anions of (10; X = OR) react with aldehydes or ketones, derives from its stereoselectivity. One such anion, from (22), gives a γ-hydroxyketone on reaction with an aldehyde (Scheme 7).[15]



Scheme 7.

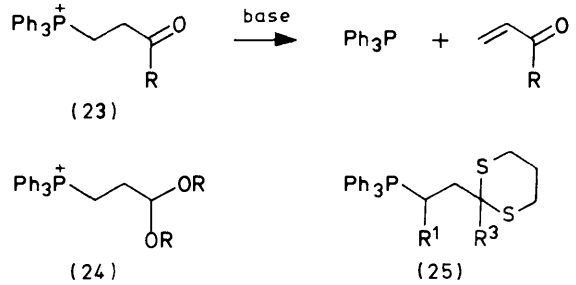
Control over double bond position in the product is most obviously exercised by a Wittig reaction. Ketones (23) cannot be used as they eliminate [16] or rearrange [17] too easily in base.

Table 1. Synthesis of ketals (28) from ketones (27)

Ketone	Ketal	R^1	R^2	R^3	Yield (%)
a	(28a)	H	H	Me	46
(27b)	(28b)	H	H	Et	88
(27c)	(28c)	H	H	Ph	91
(27d)	(28d)	Me	H	Me	96 (74) [a]
(27e)	(28e)	Me	H	Ph	91
a	(28f)	Me	Me	Me	85
a	(28g)	H	Me	Me	12
(27h)	(28h)	*b*	H	*b*	83 (80) [a]

[a] By alternative route shown in Scheme 2. [b] $R^1R^3 = (CH_2)_4$; (28h) is shown in Scheme 2.

Protected aldehydes (24) have been used [18] in *cis*-selective Wittig reactions, and there is one instance of ketones, protected as dithianes (25; R^3 = Me, Ph),* being used [19] to synthesise protected β,γ-unsaturated ketones (Scheme 8). Attempts to remove the dithiane from the product have begun.[20]

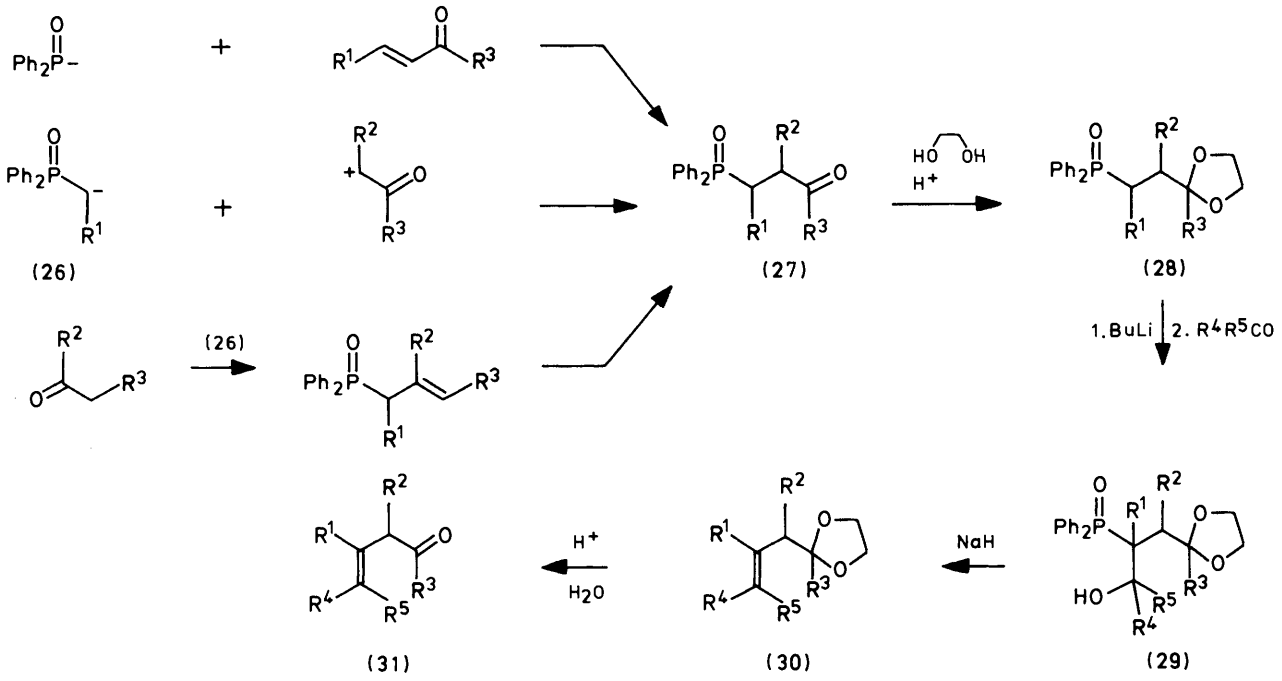


Scheme 8.

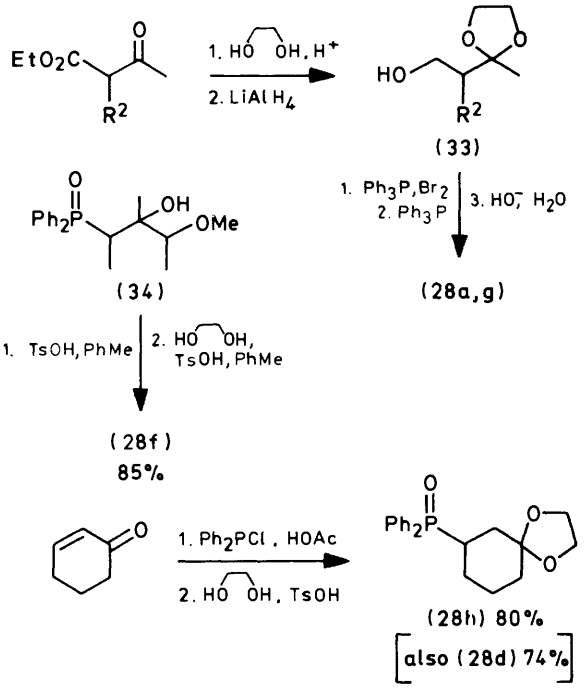
We have already reported [21] the synthesis of β-diphenylphosphinoyl (Ph_2PO) ketones (27) by three main methods (Scheme 9). We now report [22,23] that anions of the corresponding ketals (28) take part in Horner-Wittig reactions [24,25] in a regiospecific synthesis of β,γ-unsaturated ketones (31). Some control over stereochemistry is also possible.

Conversion of ketones (27) into the stable crystalline ketals (28) is routine—glycol, toluene-*p*-sulphonic acid (TsOH) in benzene or toluene under reflux—and gives good yields even with the most crowded ketones (Table 1). The only low yields in the Table are for conversion of alcohols (33) into ketals (28a) and (28g) by a three-step procedure: [21] ketones (27a) and (27g) are not intermediates. In two other cases (Scheme 10) direct conversion of ketone precursors into ketals (28) gives higher yields than if ketones (28) are isolated. Thus the conditions for transposition of (34) to (27) can be made the same as those for ketal formation, giving 85% of (28f). The ketone (27f) can be isolated in only 80% yield from this route. The Conant reaction (Scheme 10) gives (27h) in 66% yield: [21] ketalisation of (27h) occurs in 83% yield (55% for the two steps). If the ketone (27h) is not isolated, (28h) can be obtained in 80% overall yield. The same route was used for (28d).

* R^1, R^2, and R^3 refer to substituents on carbon atoms 1, 2, and 3 throughout this paper.



Scheme 9.



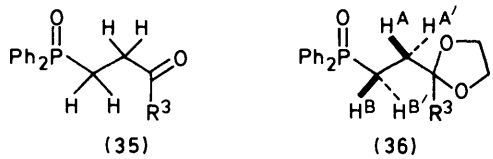
Scheme 10.

Structure.—Ketones (27; $R^1 = R^2 = H$) have a broad singlet in the ^1H n.m.r. spectrum where all four protons marked H in (35) resonate at about the same chemical shift, *e.g.* at δ 2.6 for (35; R^3 = Et), since the carbonyl and Ph_2PO groups are about equally electron-withdrawing. The ketals of the same substitution pattern (36) no longer have the same coincidence of chemical shifts and the expected multiplets for an AA'BB'P system are observed, *e.g.* for (36; R^3 = Et) at δ 2.96 (2 H, m, PCH_2CH_2) and 3.34 (2 H, m, PCH_2CH_2).

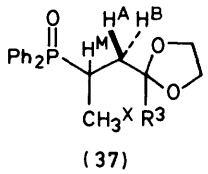
Table 2. Chemical shifts and coupling constants (in Hz) in the ^1H n.m.r. spectrum of (37; R^3 = Me)

δ^A	2.08	J_{PM}	8	J_{AB}	15
δ^B	1.77	J_{PA}	15	J_{AM}	3
δ^M	2.66	J_{PB}	9	J_{BM}	2
δ^X	1.31	J_{PX}	17	J_{MX}	7

($J_{AX} = J_{BX} = 0$).



Ketals with a chiral centre next to the phosphorus atom (37) have characteristic ABMP systems with $J_{AP} \sim J_{AB} > J_{BP} > J_{MP}$. Both J_{AM} and J_{BM} are small (*ca.* 2—3 Hz) perhaps because of the electronegative substituents or conformational restrictions. Hence proton A is a double triplet, B a double double doublet, and M a double double quartet if R^1 = Me. For (37; R^3 = Me), all signals can clearly be seen: δ and *J*



values appear in Table 2. For all ketals in Table 1, the protons of the dioxolane ring appear as a symmetrical multiplet at *ca.* δ 4 except for (28b) which has a sharp singlet at that position.

Table 3. Horner-Wittig adducts (29) from (28) and R^3R^5CO

Ketal (28)	R^1	R^2	R^3	R^4	R	Product	Yield (%)
(28a)	H	H	Me	$(CH_2)_5$		(29a)	81
(28b)	H	H	Et	H	Me	(29b)	73
	H	H	Et	H	Et	(29c)	39 (72) [a]
	H	H	Et	H	Pr^n	(29d)	76
	H	H	Et	H	*p*-$MeOC_6H_4$	(29e)	81
	H	H	Et	Et	Et	(29f)	77
	H	H	Et	$(CH_2)_5$		(29g)	85
(28c)	H	H	Ph	H	Me	(29h)	38 [b]
	H	H	Ph	Me	Me	(29i)	66
(28d)	Me	H	Me	H	Ph	(29j)	81
	Me	H	Me	H	*p*-$MeOC_6H_4$	(29k)	78
	Me	H	Me	H	Pr^n	(29l)	55
(28g)	H	Me	Me	H	Ph	(29m)	42
(28h)	Me	Me	Me	H	Me	(29n)	80 [b]

[a] Based on recovered starting material. [b] Single diastereoisomer, see text.

Table 4. Completion of the Horner-Wittig reaction on adduct (29)

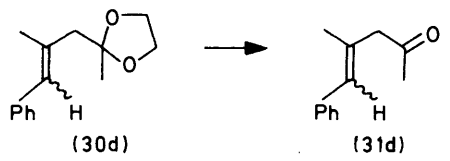
Adduct	R^1	R^2	R^3	R^4	R^5	Temp.	Product	Yield
(29f)	H	H	Et	Et	Et	reflux	(30a)	74 (12) [a]
(29g)	H	H	Et	$(CH_2)_5$		reflux	(30b)	83
(29i)	H	H	Ph	Me	Me	room	(30c)	55 (24) [a]
(29j)	Me	H	Me	H	Ph	room	(30d) [b]	96
(29k)	Me	H	Me	H	*p*-$MeOC_6H_4$	room	(30e) [b]	75 (trace) [a]
(29l)	Me	H	Me	H	Pr^n	reflux	(30f) [b]	76 (7) [a]

[a] Yield (%) of recovered starting material. [b] See discussion on stereoselectivity.

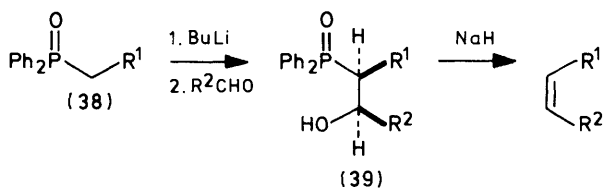
Horner-Wittig Reactions of Ketals (28).—The ketals (28) form deep red lithium derivatives on treatment with butyllithium (BuLi) in tetrahydrofuran (THF) at −78 °C. These anions are stable at −78 to 0 °C, unlike the corresponding phosphonium ylides.[16] Addition of aldehydes or ketones at −78 °C (R^1 = H) or at 0 °C (R^1 = Me) gives good yields of adducts (29) (Scheme 9 and Table 3). The products are easily separated from starting materials by column chromatography on silica, with ethyl acetate as eluant. Enolisable aldehydes and ketones give as good yields as aromatic aldehydes, though a lower yield was obtained in one case (29l) with an enolisable aldehyde and a secondary alkyl phosphine oxide. Losses due to enolisation may be minimised by using ether saturated with anhydrous lithium bromide as solvent (29n).

Treatment of adducts (29) with sodium hydride in THF causes elimination of sodium diphenylphosphinate and formation of the β,γ-unsaturated ketals (30) (Scheme 9 and Table 4). A side reaction is sometimes the reversion of adducts (29) to (28) and carbonyl compound, but pure (30) can be separated from these and from other impurities by chromatography on silica, except in the case of (30e) which contained traces of anisaldehyde. Elimination is regiospecific, giving for example an exocyclic double bond in (30b), and stereospecific, each diastereoisomer of (29) giving a single geometrical isomer of (30) as described below.

Removal of the dioxolane group from compounds such as (30) is known [26] to be possible without moving the double bond into conjugation with the developing carbonyl group, though the corresponding aldehydes present a more serious problem.[18] Reagents such as aqueous acetic or oxalic acid have been used [26] and in one case we confirmed that (30d) could be hydrolysed to (31d) with dilute aqueous sulphuric acid in THF. The presence of alkyl and aryl groups on the γ, and to a lesser extent, the β atom ' anchors ' the double bond in (31).



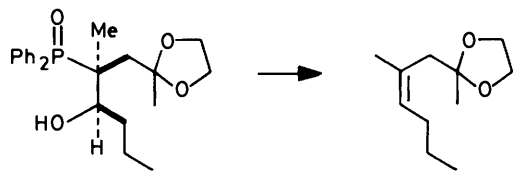
Stereoselectivity.—Addition of anions of primary alkyl phosphine oxides (38) to aldehydes normally [27] favours ' *erythro* ' adducts (39) but stereoselectivity is usually poor if R^1 is large, and particularly if it is branched near the reaction site. There is also evidence that a polar group in R^1 can reduce or even invert this selectivity,[25,27,28] whilst an extra substituent at either carbon atom also reduces stereoselectivity in the synthesis of trisubstituted alkenes.[29]



Scheme 11.

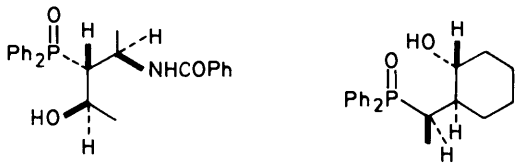
It is not therefore surprising that stereoselectivity was found to be low in the reactions (28) to (29) in those few cases that we were able to assess. The separation of pure diastereoisomers of adducts (29) proved to be more difficult than usual. Neither chromatography nor fractional crystallisation was entirely successful in all cases. Adduct (29l) was separated into diastereoisomers, the ratio being 2 : 1 in favour of the ' erythro '

adduct (40). Elimination was stereospecific giving only *Z*-(41). One diastereoisomer of (29h) was isolated by chromatography in 38% yield but the other could not be separated from impurities. Adduct (29j) was formed in an approximately 5 : 3 mixture of diastereoisomers and gave a 5 : 3 mixture of olefins (both by n.m.r.).



(40) (41)

In the one case we investigated with an R^2 substituent (29n), a single diastereoisomer, as judged by chromatography, sharp m.p., and n.m.r. spectrum, was isolated in high yield. This is remarkable as (29n) has three chiral centres. Two other hydroxyphosphine oxides (42) [28] and (43),[30] also having three chiral centres, are formed in similar reactions also with high stereoselectivity. This phenomenon is under investigation.



(42) (43)

We recommend these homoenolate equivalents (29) for the synthesis of β,γ-unsaturated ketones because of the ease of synthesis of the starting materials (28) by a wide variety of methods,[22] the clean reaction with enolisable aldehydes and ketones, and the regiospecificity of double bond formation. However, for stereochemical control each compound must be tackled as a special case.

Experimental

General spectroscopic and chromatographic procedures have been described previously.[21]

Synthesis of Ketals (28) (*see Table* 1).—*1-Diphenylphosphinoylpentan-3-one ethylene acetal* (28b). 1-Diphenylphosphinoylpentan-3-one (27b) (0.98 g, 3.43 mmol) was heated under reflux, in dry benzene in a Dean-Stark apparatus, with an excess of ethylene glycol (0.52 g, 10 mmol) and a catalytic amount of TsOH (50 mg), under nitrogen, for 24 h. The solution was cooled, washed with 10% aqueous sodium hydroxide (2 × 50 ml)and water (2 × 100 ml), dried (Na_2SO_4), and evaporated under reduced pressure to give an oil. Column chromatography of this on silica (eluted with EtOAc) gave the *acetal* (28b) (894 mg, 79%) as needles, m.p. 91.5—92.5 °C (from EtOAc) (Found: C, 68.9; H, 7.05; P, 9.4. $C_{19}H_{23}O_3P$ requires C, 69.1; H, 7.00; P, 9.4%), R_F 0.14 (EtOAc), δ ($CDCl_3$) 1.66 (3 H, t, J_{HH} 7 Hz, CH_2Me), 2.64 (2 H, q, J_{HH} 7 Hz, CH_2Me), 2.96 (2 H, m, PCH_2CH_2), 3.34 (2 H, m, PCH_2CH_2), 3.90 (4 H, s, OCH_2CH_2O), and 7.36—7.86 (10 H, m, Ph_2PO); $\nu_{max.}$ 1 445 (P–Ph) and 1 180 cm^{-1} (P=O); *m/z* 330 (M^+, 0.7%), 301 (M − Et, 100), and 201 (Ph_2PO, 52) (Found: M^+, 330.1375. $C_{19}H_{23}O_3P$ requires *M*, 330,1385).

4-Diphenylphosphinoylpentan-2-one ethylene acetal (28d). In the same way 4-diphenylphosphinoylpentan-2-one (27d) (574 mg, 201 mmol) gave, after column chromatography on silica (eluted with EtOAc), the *acetal* (28d) (576 mg, 87%) as a waxy solid (see below).

3-Diphenylphosphinoylcyclohexanone ethylene acetal (28h). In the same way 3-diphenylphosphinoylcyclohexanone (27h) (0.5 g, 1.68 mmol) gave, after column chromatography on silica (eluted with EtOAc), the *acetal* (28h) (0.47 g, 82%) as a waxy solid, R_F 0.21 (EtOAc), δ ($CDCl_3$) 1.30—2.80 (9 H, m, ring CH's), 3.80 (4 H, br s, OCH_2CH_2O), and 7.20—8.05 (10 H, m, Ph_2PO); $\nu_{max.}$ 1 440 (P–Ph) and 1 185 cm^{-1} (P=O); *m/z* 342 (M^+, 10%), 201 (Ph_2PO^+, 75), and 141 (M − Ph_2PO, 100) (Found: M^+, 342.1388. $C_{20}H_{23}O_3P$ requires *M*, 342.1385)

4-Diphenylphosphinoylpentan-2-one ethylene acetal (28d). Ketone (27d) (3 g), ethylene glycol (15 ml), and TsOH (1.2 g) were heated together in benzene under reflux for 1 day. The mixture was then cooled, poured into ether (150 ml), washed with aqueous sodium hydrogen carbonate (3 × 50 ml), dried, and evaporated. Column chromatography (EtOAc–5% MeOH) gave the *acetal* (28d) (3.3 g, 96%) as a gum, R_F 0.2, δ ($CDCl_3$) 1.3 (3 H, s, CMe), 1.31 (3 H, dd, J_{HH} 7, J_{PH} 17 Hz, PCH*Me*), 1.77 (1 H, ddd, J_{HH} 3, J_{PH} 9, and J_{AB} 15 Hz, PCH-CH_2*), 2.08 (1 H, dt, J_{HH} 2, J_{PH} = J_{AB} 15 Hz, PCHCH_2*), 2.66 (1 H, dddq, J_{PH} 8, J_{HH} 2, 3, and 7 Hz, PCH), 3.6—4.0 (4 H, m, OCH_2CH_2O), and 7.3—8.0 (10 H, m, Ph_2PO); $\nu_{max.}$ 1 435 (P–Ph) and 1 190 cm^{-1} (P=O); *m/z* 330 (M^+, 4%), 288 (20), and 202 ($Ph_2PO_2H^+$, 100) (Found: M^+, 330.1409. $C_{19}H_{23}O_3P$ requires *M*, 330.1385).

1-Diphenylphosphinoylpentan-3-one ethylene acetal (28b). Ketone (27b) (3.1 g), ethylene glycol (15 ml), and TsOH (1.2 g) in benzene gave, in a similar way to the above, the acetal (28b) (3.2 g, 88%) purified by column chromatography (EtOAc–10% MeOH).

3-Diphenylphosphinoyl-1-phenylbutan-1-one ethylene acetal (28e). In a similar way, ketone (27e) (300 mg), ethylene glycol (3 ml), and TsOH (200 mg) in benzene under reflux gave, after evaporation, the *acetal* (28e) (310 mg, 91%) as needles, m.p. 169—171 °C (from EtOAc), R_F 0.3, δ ($CDCl_3$) 7.2—7.8 (15 H, m, Ph_2PO and Ph), 3.6—4.1 (4 H, symmetrical m, OCH_2-CH_2O), 2.4—2.7 (1 H, m, PCH), 2.29 (1 H, ddd, J_{HH} 2 Hz and $J_{PH} \approx J_{AB} \approx$ 14 Hz, PCHCH^*_2), 1.97 (1 H, ddd, J_{HH} 3 Hz, J_{PH} 10 Hz and J_{AB} 14 Hz, PCHCH^*_2), and 1.23 (3 H, dd, J_{HH} 7 Hz and J_{PH} 17 Hz, PCH*Me*); *m/z* 392 (M^+, 0.5%), 350 (2), 306 (2), 201 (Ph_2PO^+, 19), and 149 ($C_9H_9O_2^+$, 100) (Found: C, 73.6; H, 6.7; P, 7.6. $C_{24}H_{25}O_3P$ requires C, 73.5; H, 6.4; P, 7.9%).

3-Diphenylphosphinoyl-1-phenylpropan-1-one ethylene acetal (28c). In the same way, ketone (27c) (300 mg), ethylene glycol (3 ml) and TsOH (200 mg) in benzene under reflux gave the *acetal* (28c) (310 mg, 91%), m.p. 187—188 °C (from EtOAc), R_F 0.3, δ ($CDCl_3$) 7.2—7.9 (15 H, m, Ph_2PO and Ph), 3.72—4.16 (4 H, symmetrical m, OCH_2CH_2O), and 2.0—2.4 (4 H, m, PCH_2CH_2); *m/z* 378 (M^+, 2%), 350 (2), 335 (26), and 201 (Ph_2PO^+, 100) (Found: C, 72.8; H, 6.4; P, 8.1 $C_{23}H_{23}O_3P$ requires C, 73.0; H, 6.1; P, 8.2%).

Conversion of the Methoxy Alcohol (34) *into the Ketone* (27; R^1 = R^2 = R^3 = Me) *with* TsOH.—The alcohol [21] (34) (250 mg) was heated under reflux in dry toluene (50 ml) with TsOH (150 mg) for 4 h. The solution was poured into ether (100 ml), washed with saturated aqueous sodium hydrogen carbonate (3 × 25 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give the ketone [21] (27; R^1 = R^2 = R^3 = Me).

Direct Conversion of the Methoxy Alcohol (34) *into 4-Diphenylphosphinoyl-3-methylpentan-2-one Ethylene Acetal* (28f). —The alcohol [21] (34) (250 mg) was heated under reflux in dry

toluene (50 ml) with TsOH (150 mg) for 4 h, or until no alcohol remained (t.l.c.); ethylene glycol (6 ml) was then added and the solution refluxed for a further 30 h. The solution was poured into ether (100 ml), washed with saturated aqueous sodium hydrogen carbonate (3 × 25 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give the *acetal* (28f) (220 mg, 85%), m.p. 99—101 °C, R_F 0.4 (EtOAc), $\nu_{max.}$ 1 440 (PPh), and 1 175 cm^{-1} (P=O); δ ($CDCl_3$) 7.4—8.1 (10 H, m, Ph_2PO), 3.5—4.0 (4 H, m, OCH_2CH_2O), 2.95 (1 H, m, PC*H*Me), 2.0—2.5 (1 H, m, PCHC*H*Me), 1.35 (3 H, s, CMe), 1.25 (3 H, dd, J_{PH} 18, J_{HH} 7 Hz, PCH*Me*), and 1.25 (3 H, d, J_{HH} 7 Hz, CH*Me*); *m/z* 344 (M^+, 1.5%), 299 (6), 288 (30), 258 (16), and 201 (Ph_2PO, 100).

Horner-Wittig Adducts from Acetals (28) (*Table* 3).—5-*Diphenylphosphinoyl*-6-*hydroxyheptan*-3-*one ethylene acetal* (29b). The acetal (28b) (330 mg, 1.0 mmol) was stirred with BuLi (0.71 ml, 1.1 mmol) in dry THF (10 ml), at −78 °C and under nitrogen, for 10 min. An excess of acetaldehyde (*ca.* 0.1 ml) was added dropwise at −78 °C and the solution allowed to warm to room temperature; aqueous NH_4Cl (20 ml) was then added. The layers were separated, the aqueous layer extracted with EtOAc (3 × 20 ml), and the combined organic layers dried (Na_2SO_4) and evaporated under reduced pressure to give an oil. Column chromatography on silica (eluted with EtOAc) gave the *alcohol* (29b) (273 mg, 73%) as needles, m.p. 145—147 °C (from EtOAc) (Found: C, 67.6; H, 7.30; P, 8.3. $C_{21}H_{27}O_4P$ requires C, 67.4; H, 7.30; P, 8.3%), R_F 0.32 (EtOAc); δ ($CDCl_3$) 0.69 (3 H, t, J_{HH} 8 Hz, CH_2Me), 1.22 (3 H, d, J_{HH} 7 Hz, CH*Me*), 1.46 (2 H, q, J_{HH} 8 Hz, CH_2-Me), 1.80—2.50 (2 H, m, PCHCH_2), 2.60 (1 H, m, PCH), 3.82 (4 H, m, OCH_2CH_2O), 4.14 (1 H, br s, OH), 4.30 (1 H, d quint, J_{HH} and J_{PH} 7 Hz, C*H*Me), and 7.36—7.96 (10 H, m, Ph_2PO) (the protons giving signals at 1.46, 1.80, 2.60, and 4.30 are diastereotopic); $\nu_{max.}$ 3 310 (OH), 1 440 (P–Ph), and 1 165 cm^{-1} (P=O); *m/z* M^+ absent, 345 (M − Et, 15%), 202 (Ph_2POH^+, 100), and 201 (Ph_2PO^+, 86).

5-*Diphenylphosphinoyl*-6-*hydroxynonan*-3-*one ethylene acetal* (29d). In the same way the acetal (28b) (330 mg, 1 mmol), BuLi (0.71 ml, 1 mmol), and n-butanal (0.08 g, 1.1 mmol) gave, after column chromatography on silica (eluted with EtOAc) the *alcohol* (29d) (305 mg, 76%) as microcrystals, m.p. 122—124 °C (from EtOAc) (Found: C, 68.6; H, 7.80; P, 7.8. $C_{23}H_{31}O_4P$ requires C, 68.6; H, 7.75; P, 7.8%), R_F 0.38 (EtOAc), δ ($CDCl_3$) 0.56—1.02 (6 H, m, 2 × Me), 1.20—1.84 (6 H, m, 3 × CH_2), 1.88—2.64 (3 H, m, $PCHCH_2$), 3.84 (4 H, m, OCH_2CH_2O), 3.96 (1 H, br s, OH), and 4.06 (1 H, m, C*H*OH); $\nu_{max.}$ 3 320 (OH), 1 440 (P–Ph), and 1 165 cm^{-1} (P=O); *m/z* M^+ absent, 387 (M − Me, 10%), 373 (M − Et, 12), 330 (M − $CH_3CH_2CH_2CHO$, 60), and 287 (M − $C_6H_{11}O_2$, 100) (Found: M^+ − Me, 387.1739. $C_{22}H_{28}O_4P$ requires M − Me, 387.1725).

5-*Diphenylphosphinoyl*-6-*ethyl*-6-*hydroxyoctan*-3-*one ethylene acetal* (29f). In the same way, the acetal (28b) (330 mg, 1 mmol), BuLi (0.71 ml, 1.1 mmol), and pentan-3-one (0.1 g, 1.1 mmol) gave, after column chromatography on silica (eluted with EtOAc) the *alcohol* (29f) (322 mg, 77%) as a waxy solid, R_F 0.49 (EtOAc), δ ($CDCl_3$) 0.54 (3 H, t, J_{HH} 7 Hz, CH_2Me), 0.82 (6 H, t, J_{HH} 7 Hz, 2 × CH_2Me), 1.10—2.30 (8 H, m, 4 × CH_2), 2.94 (1 H, ddd, J_{HH_A} 4 and 6 Hz, J_{PH} 10 Hz, PCH), 3.26—3.96 (4 H, m, OCH_2CH_2O), 4.85 (1 H, br s, OH), and 7.36—8.00 (10 H, m, Ph_2PO); $\nu_{max.}$ 3 320 (OH), 1 440 (P–Ph) and 1 165 cm^{-1} (P=O); *m/z* 406 (M^+, 3%) and 387 (M − Et, 100).

5-*Diphenylphosphinoyl*-5-(1-*hydroxycyclohexyl*)*pentan*-3-*one ethylene acetal* (29g). In the same way, the acetal (28b) (330 mg, 1 mmol), BuLi (0.71 ml, 1.1 mmol), and cyclohexanone (0.11 g, 1.1 mmol) gave, after column chromatography on silica (eluted with EtOAc), the *alcohol* (29g) (365 mg, 85%) as needles, m.p. 112—113 °C (from EtOAc) (Found: C, 70.1; H, 7.65; P, 7.2. $C_{25}H_{33}O_4P$ requires C, 70.1; H, 7.75; P, 7.2%), R_F 0.52 (EtOAc), δ ($CDCl_3$) 1.64 (3 H, t, J_{HH} 7 Hz, CH_2Me), 1.00—2.40 (14 H, m, 7 × CH_2), 2.68 (1 H, ddd, J_{HH} 3 and 5 Hz, J_{HP} 9 Hz, PCH), 3.82 (4 H, m, OCH_2CH_2O), 4.62 (1 H, br s, OH), and 7.36—8.00 (10 H, m, Ph_2PO); $\nu_{max.}$ 3 130 (OH), 1 440 (P–Ph), and 1 150 cm^{-1} (P=O); *m/z* 428 (M^+, 1%) and 399 (M − Et, 100).

5-*Diphenylphosphinoyl*-6-*hydroxybutan*-3-*one ethylene acetal* (29c). In the same way the anion from acetal (28b) (100 mg) and BuLi (0.22 ml; 1.5M in hexane) was treated with a solution of propionaldehyde (dried by passage through alumina) in dry THF was added dropwise until the red anion colour had discharged. After warming to room temperature, saturated aqueous ammonium chloride (10 ml) was added and the mixture extracted with ether (4 × 10 ml). The ether solution was dried and evaporated to a gum which was separated by preparative t.l.c. (EtOAc) into unchanged acetal (28b) (46 mg, 46%) and the *adduct* (29c) (46 mg, 39%, equivalent to 72% based on recovered starting material), R_F 0.3, δ ($CDCl_3$) 7.2—8.0 (10 H, m, Ph_2PO), 3.6—4.2 (6 H, m, CHOH and OCH_2CH_2O), 2.4—2.7 (1 H, m, PCH), 1.6—2.4 (2 H, m, PCHCH_2*), 1.2—1.6 (4 H, m, both CH_2Me), and 0.61 and 0.81 (each 3 H, t, J 7 Hz, both CH_2Me); *m/z* 388 (M^+, <1%), 359 (29), 229 (100), and 202 (Ph_2POH*, 77) (Found: M − Et, 359.1418. $C_{20}H_{24}O_4P$ requires M, 359.1412).

5-*Diphenylphosphinoyl*-6-p-*methoxyphenylhexan*-3-*one ethylene acetal* (29e). Similarly, acetal (28b) (100 mg), n-butyllithium (0.22 ml; 1.5M in hexane) in THF and anisaldehyde, added after cooling the anion solution to −78 °C, gave, after the usual work-up followed by preparative t.l.c. (EtOAc), the *adduct* (29e) (115 mg, 81%) as a gum, R_F 0.45, δ ($CDCl_3$) 7.3—8.1 (10 H, m, Ph_2PO), 7.28 (2 H, d, J_{AB} 9 Hz, protons *ortho* to MeO on *p*-methoxyphenyl ring), 6.74 (2 H, d, J_{AB} 9 Hz, protons *meta* to MeO on *p*-methoxyphenyl ring), 5.22 (1 H, dd, J_{HH} 2 Hz and J_{PH} 11 Hz, PCHC*H*Ar), 4.61 (1 H, br, OH), 3.71 (3 H, s, OMe), 2.9—3.9 (4 H, m, OCH_2CH_2O), 2.7—2.9 (1 H, m, PCH), 1.7—2.5 (2 H, m, PCHCH_2*), 0.87 (2 H, q, J 8 Hz, CH_2Me), and 0.48 (3 H, t, J 8 Hz, CH_2Me); *m/z* 466 (M^+, 1%), 350 (6), 265 (12), 229 (100), 202 (Ph_2POH^+, 66), and 101 ($C_5H_9O_2^+$, 100) (Found: M^+, 466.1911. $C_{27}H_{31}O_5P$ requires M, 466.1909).

4-*Diphenylphosphinoyl*-5-*hydroxy*-3-*methyl*-5-*phenylpentan*-2-*one ethylene acetal* (29m). Similarly acetal (28g) (0.2 g), BuLi (0.45 ml; 1.5M), in THF (10 ml) with benzaldehyde gave a yellow oil which was separated by p.l.c. to give the alcohol (29m) (0.11 g, 42%) as a mixture of diastereoisomers identified by n.m.r. spectroscopy; δ ($CDCl_3$) 1.1 (3 H, d, J_{HH} 7 Hz, CH*Me*), 1.2 (3 H, s, CMe), 1.8—2.9 (2 H, m, PC*HCH*Me), 3.6 (1 H, m, PhCH), 3.8 (4 H, m, OCH_2CH_2O), and 7.3—8.0 (15 H, m, ArH).

4-*Diphenylphosphinoyl*-5-*hydroxy*-4-*methyl*-5-*phenylpentan*-2-*one ethylene acetal* (29j). n-Butyl-lithium (0.27 ml; 1.5M in hexane) was added at 0 °C to a stirred solution of acetal (28d) (120 mg) in dry THF (5 ml) under nitrogen. After 5 min benzaldehyde was added dropwise to the solution until the red anion colour had been discharged and the mixture was then stirred for a further 10 min before saturated aqueous ammonium chloride was added. The aqueous layer was extracted with ether and the combined organic solutions dried and evaporated. Preparative t.l.c. (EtOAc) gave the alcohol (29j) as an approximately 3 : 1 mixture of diastereoisomers (n.m.r.) (134 mg, 82%), m.p. 185—190 °C (from EtOAc–MeOH), R_F 0.35, δ ($CDCl_3$) 7.2—8.0 (15 H, m, Ph_2PO and Ph), 5.5 (1 H, br, OH), 5.26 and 4.92 (1 H, two d, J_{PH} 15 Hz and 12 Hz, respectively, CHOH), 3.2—4.0 (4 H, m, OCH_2CH_2O), 2.44 and 1.9—2.4 (2 H, d, J_{PH} 16 Hz and m, respectively, $PCCH_2$),

1.62 and 1.45 (3 H, d, J_{PH} 16 Hz and 18 Hz, respectively, PCMe), and 1.01 and 0.94 (3 H, two s, CMe); *m/z* 437 (M + H, 1%), 421 (3), 330 (33), 243 (82), and 201 (Ph_2PO^+, 100) (Found: M − Me, 421.1576. $C_{25}H_{26}O_4P$ requires M, 421.1569).

4-*Diphenylphosphinoyl*-5-*hydroxy*-4-*methyl*-5-p-*methoxyphenylpentan*-2-*one ethylene acetal* (29k). In a similar way, acetal (28d) (600 mg), n-butyl-lithium (1.4 ml; 1.5M in hexane) and anisaldehyde in dry THF at 0 °C gave, after column chromatography (EtOAc), the *adduct* (29k) (662 mg, 78%) as a gummy mixture of diastereoisomers (*c*, 3 : 1 by n.m.r.), R_F 0.3, δ ($CDCl_3$) 7.3—8.2 (10 H, m, Ph_2PO), 7.26 and 7.28 (2 H, two d, J_{AB} 8 Hz and 9 Hz, respectively, protons *ortho* to MeO on *p*-methoxyphenyl ring), 6.71 and 6.74 (2 H, two d, J_{AB} 9 Hz and 8 Hz, respectively, protons *meta* to MeO on *p*-methoxyphenyl ring), 4.8—5.6 (1 H, br, OH), 4.94 and 5.24 (1 H, two d, J_{PH} 15 Hz and 12 Hz, respectively, PCCHAr), 3.3—4.0 (4 H, m, OCH_2CH_2O), 3.76 (3 H, s, OMe), 2.44 and 1.9—2.4 (2 H, d, J_{PH} 15 Hz and m, respectively, $PCCH_2$*), 1.47 and 1.64 (3 H, two d, J_{PH} 16 Hz and 18 Hz, respectively, PCMe), 1.00 and 1.06 (3 H, s, CMe), *m/z* 467 (M + H, <1%), 362 (1), 330 (4), 243 (45), and 202 (Ph_2POH*, 100) (Found: M − H_2O, 448.1795. $C_{27}H_{29}O_4P$ requires M, 448.1804).

3-*Diphenylphosphinoyl*-4-*hydroxy*-1-*phenylpentan*-1-*one ethylene acetal* (29h). In the same say, n-butyl-lithium (0.4 ml; 1.5M in hexane) was added to a solution of acetal (28c) (200 mg) in dry ether and the mixture stirred for 5 min. Acetaldehyde was added dropwise to discharge the colour and the reaction worked up as usual, the crude product being separated by preparative t.l.c. (EtOAc) into a gum (125 mg), R_F 0.6 (EtOAc), which may contain some of the HR_F *isomer* of the *adduct* (29h) (84 mg, 38%), m.p. 181—184 °C (from EtOAc), R_F 0.5 (EtOAc), δ ($CDCl_3$) 7.0—8.0 (15 H, m, Ph_2PO and Ph), 4.36 (1 H, s, OH), 4.33 (1 H, ddq, J_{PH} 12 Hz, J_{HH} 2 Hz and 7 Hz, C*H*Me), 3.54—3.95 (4 H, symmetrical m, OCH_2CH_2O), 2.62—2.83 (1 H, m, PCH), 1.9—2.6 (2 H, m, $PCHCH_2$*), and 1.15 (3 H, d, J_{HH} 7 Hz, CH*Me*); *m/z* 422 (M^+, <1%), 407 (1), 335 (2), 229 (96), 201 (Ph_2PO^+, 10), and 149 ($C_9H_9O_2^+$, 100) (Found: M − Me, 407.1414. $C_{24}H_{24}O_4P$ requires M, 407.1413 (Found: C, 71.0; H, 6.4; P, 7.1. $C_{25}H_{27}O_4P$ requires C, 71.1; H, 6.4; P, 7.3%).

3-*Diphenylphosphinoyl*-4-*hydroxy*-4-*methyl*-1-*phenylpentan*-1-*one ethylene acetal* (29i). In the same way, n-butyl-lithium (0.4 ml; 1.5M in hexane) was added to a solution of acetal (28c) (200 mg) in dry THF. After 5 min acetone was added to discharge the anion colour and the mixture was worked up as usual. Preparative t.l.c. (EtOAc) gave unchanged starting material (38 mg, 16%) and the *adduct* (291) (152 mg, 66%), m.p. 141—144 °C (from EtOAc), R_F 0.5 (EtOAc), δ ($CDCl_3$) 6.9—8.1 (15 H, m, Ph_2PO and Ph), 4.84 (1 H, br, OH), 3.4—4.1 (4 H, m, OCH_2CH_2O), 2.99 (1 H, ddd, *J* 4, 5, and 9 Hz, $PCHCH_2$*), 1.9–2.6 (2 H, m, $PCHCH_2$*), 1.28 and 1.36 (each 3 H, s, CMe_2*); *m/z* 436 (M^+, 0.5%), 421 (2), 229 (100), and 201 (Ph_2PO^+, 12) (Found: M^+, 436.1801; C, 71.6; H, 6.71; P. 6.9. $C_{26}H_{29}O_4P$ requires M, 436.1803; C, 71.5; H, 6.70; P, 7.10%).

4-*Diphenylphosphinoyl*-5-*hydroxy*-5-*methyl*-5-*phenylpentan*-2-*one ethylene acetal* (29j). In the same way the acetal (28d) (680 mg, 2.06 mmol), BuLi (1.46 ml, 2.26 mmol), and benzaldehyde (0.24 g, 2.54 mmol) gave, after column chromatography on silica (eluted with EtOAc) the *alcohol* (29j) (710 mg, 79%) as needles, m.p. 197—199 °C (from EtOAc) (Found: P, 7.3. $C_{26}H_{29}O_4P$ requires P, 7.1%), R_F 0.35 (EtOAc), δ ($CDCl_3$) (major isomer), 0.94 (3 H, s, Me), 1.46 (3 H, d, J_{PH} 18 Hz, PCMe), 1.60—2.30 (2 H, m, $PCCH_2$), 3.60 (4 H, m, OCH_2CH_2O), 4.93 (1 H, d, J_{PH} 14 Hz, C*H*OH), 5.04 (1 H, br s, OH), 7.08—8.14 (15 H, m, Ph and Ph_2PO), (minor isomer), 1.00 (3 H, s, Me), 1.60—2.30 (2 H, m, $PCCH_2$), 2.42 (3 H, m, J_{PH} 17 Hz, PCMe), 3.60 (4 H, m, OCH_2CH_2O), 5.04 (1 H, br s, OH), 5.24 (1 H, d, J_{PH} 16 Hz, C*H*OH), and 7.08—8.14 (15 H, m, Ph_2PO and Ph) (isomer ratio equals 5 : 3 by n.m.r.); $\nu_{max.}$ 3 150 (OH), 1 440 (P–Ph), and 1 160 cm^{-1} (P=O); *m/z* 436 (M^+, 6%), 329 (M − $PhCOH_2$, 30), and 201 (Ph_2PO^+, 100).

4-*Diphenylphosphinoyl*-5-*hydroxy*-4-*methyloctan*-2-*one ethylene acetal* (29l). In the same way, the acetal (28d) (760 mg, 2.30 mmol), BuLi (1.65 ml, 2.56 mmol) and n-butanal gave, after column chromatography on silica (eluted with EtOAc) recovered starting material (130 mg, 17%) and the *alcohol* (29l) (508 mg, 55—66% based on recovered starting material). *Major isomer:* oil (350 mg, 38—46% based on recovered starting material), R_F 0.25 (EtOAc), δ ($CDCl_3$) 1.34 (3 H, s, Me), 0.62—1.64 (7 H, m, CH_2CH_2Me), 1.45 (3 H, d, J_{PH} 17 Hz, PCMe), 2.28 (1 H, dd, $J_{H_AH_B}$ 15 Hz, J_{PH_A} 15 Hz, $PCCH_AH_B$), 2.50 (1 H, dd, $J_{H_AH_B}$ 15 Hz, J_{PH_B} 10 Hz, $PCCH_AH_B$), 3.60—4.04 (5 H, m, C*H*OH and OCH_2CH_2O), 4.82 (1 H, br s, OH), and 7.30—8.20 (10 H, m, Ph_2PO); $\nu_{max.}$ 3 300 (OH), 1 535 (P–Ph), and 1 160 cm^{-1} (P=O). *Minor isomer:* oil (158 mg, 17—21% based on recovered starting material), R_F 0.18 (EtOAc), δ ($CDCl_3$) 0.64—1.80 (7 H, m, CH_2CH_2Me), 1.32 (3 H, s, Me), 1.52 (3 H, d, J_{PH} 18 Hz, PCMe), 2.04 (1 H, dd, $J_{H_AH_B}$ 16 Hz, J_{PH_B} 6 Hz, $PCCH_AH_B$), 2.62 (1 H, dd, $J_{H_AH_B}$ 16, J_{PH_A} 14 Hz, PCH_AH_B) 3.70—3.96 (5 H, m, C*H*OH and OCH_2CH_2O), 4.20 (1 H, br s, OH), and 7.30—8.14 (10 H, m, Ph_2PO); $\nu_{max.}$ 3 320 (OH), 1 440 (P–Ph) and 1 160 cm^{-1} (P=O) (mixture); *m/e* M^+ absent, 387 (M − Me, 11), 359 (M − CH_2CH_2Me, 62), and 201 (Ph_2PO^+, 100) (Found: M^+ − Me, 387.1739. $C_{22}H_{29}O_4P$ requires M − Me, 387.1725).

4-*Diphenylphosphinoyl*-4-(1-*hydroxycyclohexyl*)*butan*-2-*one ethylene acetal* (29a). In the same way, the acetal (28a) (600 mg, 1.90 mmol), BuLi (1.4 ml, 2.2 mmol), and cyclohexanone (0.21 g, 2.1 mmol) gave, after column chromatography on silica (eluted with EtOAc), the alcohol (29a) (636 mg, 81%) as needles, m.p. 170—171 °C (from EtOAc), R_F 0.43 (EtOAc), δ ($CDCl_3$) 1.03 (3 H, s, Me), 1.20—2.06 (10 H, m, ring CH_2's), 2.10—2.54 (2 H, m, $PCHCH_2$), 3.70 (1 H, ddd, J_{HH} 4 and 6 Hz, J_{PH} 10 Hz, PCH), 3.50—4.00 (4 H, m, OCH_2CH_2O), 4.71 (1 H, br s, OH), and 7.28—8.00 (10 H, m, Ph_2PO); $\nu_{max.}$ 3 320 (OH), 1 440 (P–Ph), and 1 165 cm^{-1} (P=O); *m/z* 414 (M^+, 1%), 399 (M − Me, 30), 202 (Ph_2POH^+, 78), and 201 (Ph_2PO^+, 100).

4-*Dimethylphosphinoyl*-5-*hydroxy*-3,4-*dimethylhexan*-2-*one ethylene acetal* (29n). In the same way, the acetal (28h) (800 mg) in dry ether (50 ml), BuLi (1.5 ml; 2M in hexane) and a solution of acetaldehyde in ether saturated with lithium bromide gave an oil which was separated by p.l.c. to give a single diastereoisomer of the *alcohol* (29n) (320 mg, 80%), m.p. 153—155 °C (from EtOAc–Pr^i_2O), R_F 0.4, $\nu_{max.}$ 3 340 (OH), 1 435 (PPh), and 1 160 cm^{-1} (P=O); δ ($CDCl_3$) 1.15 (3 H, d, J_{HH} 8 Hz, CH*Me*), 1.25 (3 H, d, J_{HH} 7 Hz, CHOHMe), 1.4 (3 H, s, MeCO), 1.65 (3 H, d, J_{PH} 19 Hz, PCMe), 2.4 (1 H, dq, J_{PH} 13, J_{HH} 8 Hz, C*H*Me), 4.5 (1 H, dq, J_{PH} 21, J_{HH} 7 Hz, C*H*OHMe), 5.05 (1 H, br, OH), and 7.4—8.2 (10 H, m, Ph_2PO); *m/z* 388 (M^+, 4%), 360 (11), 257 (100), and 201 (Ph_2PO, 70) (Found: C, 67.9; H, 7.55; P, 8.3. $C_{20}H_{29}O_4P$ requires C, 68.0; H, 7.5; P, 8.0%).

Completion of Horner-Wittig Reactions (*Table* 4).—6-*Ethyloct*-5-*en*-3-*one ethylene acetal* (30a). The alcohol (29f) (307 mg, 0.76 mmol) was heated under reflux with sodium hydride (73 mg, 1.52 mmol) in dry THF (10 ml), under nitrogen, for 1 h. Saturated aqueous sodium hydrogen carbonate (25 ml) was carefully added to the mixture after cooling, the layers separated, and the aqueous layer extracted with $CHCl_3$ (4 × 20 ml). The combined organic layers were dried (K_2CO_3) and evaporated under reduced pressure to give an oil. P.l.c. on silica (eluted with EtOAc), gave the acetal

(28b) (30 mg, 12%) together with the alkene (30a) (110 mg, 74%) as an oil, R_F 0.71 (I_2) (EtOAc), δ ($CDCl_3$) 0.80—1.20 (9 H, m, 3 × Me), 1.30—2.20 (6 H, m, 3 × CH_2), 2.35 (2 H, d, J_{HH} 8 Hz, =CHCH_2), 4.00 (4 H, s, OCH_2CH_2O), and 5.17 (1 H, br t, J_{HH} 8 Hz, =CH); $\nu_{max.}$ 2 880 cm^{-1} (OCH_2CH_2O).

1-(*Cyclohexylidene*)*pentan*-3-*one ethylene acetal* (30b). In the same way as above, the alcohol (29g) (110 mg, 0.26 mmol) and sodium hydride (25 mg, 0.52 mmol) gave, after p.l.c. on silica (eluted with EtOAc), the alkene (30b) (45 mg, 83%) as an oil, R_F 0.67 (I_2) (EtOAc), δ ($CDCl_3$) 0.84 (3 H, t, J_{HH} 7 Hz, CH_2Me), 1.10—2.24 (12 H, m, 6 × CH_2), 2.28 (2 H, d, J_{HH} 8 Hz, =CHCH_2), 3.90 (4 H, s, OCH_2CH_2O), and 5.05 (1 H, t, J_{HH} 8 Hz, =CH); *m/z* 210 (M^+, 2.3%) and 101 ($C_5H_9O_2^+$, 100) (Found: M^+, 210.1621. $C_{13}H_{22}O_2$ requires *M*, 210.1620).

4-*Methyloct*-4-*en*-2-*one ethylene acetal* (30f). Using the same method as above, the LR_F diastereoisomer of alcohol (29l) (164 mg, 0.41 mmol) and sodium hydride (39 mg, 0.82 mmol) gave, after p.l.c. on silica (eluted with EtOAc), the acetal (28d) (9 mg, 7%) together with a single geometrical isomer of the alkene (30f) (57 mg, 76%) as an oil, R_F 0.68 (I_2) (EtOAc), δ ($CDCl_3$) 0.88 (3 H, t, J_{HH} 7 Hz, CH_2Me), 1.10—2.20 (10 H, m, =CMe, Me and CH_2CH_2), 2.33 (2 H, s, =CMeCH_2), 3.84 (4 H, s, OCH_2CH_2O), and 5.20 (1 H, t, J_{HH} 7 Hz, =CH).

4-*Benzylidenepentan*-2-*one ethylene acetal* (30d). Using the same method as above, a mixture of diastereoisomers of the alcohol (29j) (330 mg, 0.76 mmol), in the ratio 5 : 3, and sodium hydride (80 mg, 1.66 mmol) gave, after p.l.c. on silica (eluted with EtOAc), the acetal (28d) (15 mg, 6%) together with the alkene (30 d) (122 mg, 74%) as a 5 : 3 mixture of geometrical isomers (see below for characterisation)

In another experiment an approximately 2 : 1 mixture of diastereoisomers of adduct (29j) (200 mg) and sodium hydride (from 70 mg of 50% dispersion in oil) were stirred together in dry THF under nitrogen for 30 min. The gelatinous precipitate of sodium diphenylphosphinate was filtered off through Hyflo, washed with ether and the combined organic solutions evaporated to give the *acetal* (30d) (96 mg, 96%) as a yellow liquid, R_F 0.66. The n.m.r. spectrum indicated an approximately 2 : 1 mixture of geometrical isomers, δ ($CDCl_3$) 7.12—7.34 (5 H, m, Ph), 6.45 (major) and 6.36 (minor) (1 H, both br s, PhC*H*), 3.95 (minor) and 3.90 (major) (4 H, two s, OCH_2CH_2O), 2.62 (major) and 2.50 (2 H, two s, C=CCH_2), 2.00 and 1.96 (3 H, each d, $J_{allylic}$ 2 Hz, CH=C*Me*), and 1.38 and 1.28 (3 H, two s, CMe); $\nu_{max.}$ 2 880 cm^{-1} (OCH_2CH_2O); *m/z* 218 (M^+, <1%), 203 (11), 143 (18), 131 (67), and 115 (100) (Found: M^+, 218.1304. $C_{14}H_{18}O_2$ requires *M*, 218.1334).

Hydrolysis of acetal (30d). The 2 : 1 mixture of geometrical isomers of (30d) from the above experiment (90 mg) and dilute aqueous sulphuric acid (5 ml; 0.25M) were stirred together in THF (5 ml) for 2 days and then poured into saturated aqueous sodium hydrogen carbonate and extracted with ether. The organic solution was dried ($MgSO_4$) and evaporated to give a mixture of geometrical isomers of 4-*methyl*-5-*phenylpent*-4-*en*-2-*one* (31d) (61 mg, 85%) as a yellow liquid, $\nu_{max.}$ (CCl_4) 1 710 (C=O), 1 655 (C=C), 1 603, 1 578, and 1 491 cm^{-1} (Ph); δ ($CDCl_3$) 7.05—7.4 (5 H, m, Ph), 6.54 (major) and 6.39 (minor) (1 H, both br s, PhC*H*), 3.32 (major) and 3.26 (minor) (2 H, two s, $COCH_2$), 2.21 (minor) and 2.13 (major) (3 H, two s, COMe), and 1.91 (3 H, d, $J_{allylic}$ 2 Hz, CH=C*Me*); *m/z* 174 (M^+, 31%), 131 ($M - C_2H_3O$, 100), 115 (31), and 91 (71) (Found: M^+, 174.1049. $C_{12}H_{14}O$ requires *M*, 174.1044).

5-p-*Methoxyphenyl*-4-*methylpent*-4-*en*-2-*one ethylene acetal* (30e). Adduct (29k) (200 mg) and sodium hydride (70 mg; 50% dispersion in oil) washed with light petroleum (b.p. 30—40 °C) were stirred together in dry THF under nitrogen for 1 h. The slurry was filtered through Hyflo, the residue rinsed with ether, and the solution evaporated. N.m.r. suggested that the crude mixture contained some acetal (28d) (dd at δ 1.31) and anisaldehyde in addition to the expected product. Preparative t.l.c. (EtOAc) removed (28d), giving a mixture of geometrical isomers of the acetal (30e) (80 mg, *ca.* 75%) identified by n.m.r. still contaminated with traces of anisaldehyde, R_F 0.65, δ ($CDCl_3$) 7.21 (major) and 7.17 (minor) (2 H, each d, J_{AB} 9 Hz, protons *ortho* to MeO on *p*-methoxyphenyl ring), 6.84 (minor) and 6.82 (major) (2 H, each d, J_{AB} 9 Hz, protons *meta* to MeO on *p*-methoxyphenyl ring), 6.38 (major) and 6.28 (minor) (1 H, two br s, ArC*H*), 3.96 (minor) and 3.92 (major) (4 H, two s, OCH_2CH_2O), 3.86 (minor) and 3.79 (major) (3 H, two s, OMe), 2.62 (major) and 2.48 (minor) (2 H, two s, C=CCH_2), 1.97 (3 H, d, $J_{allylic}$ 2 Hz, CH=C*Me*), 1.38 (minor) and 1.29 (major) (3 H, two s, CMe); *m/z* 248 (M^+, 9%), 204 (9), 166 (48), 137 (34), and 87 ($C_4H_7O^+_2$, 100).

5-*Methyl*-1-*phenylpent*-3-*en*-2-*one ethylene acetal* (30c). Adduct (29c) (152 mg) and sodium hydride (from 70 mg of 50% dispersion in oil) were stirred together in dry THF for 20 h. The slurry was filtered through Hyflo, the residue washed with ether, and the organic solution evaporated to give a yellow solid. Preparative t.l.c. (EtOAc) gave the acetal (28c) (32 mg, 24%) and the *acetal* (30c) (42 mg, 55%), m.p. 48—51 °C (from pentane), R_F 0.67, δ ($CDCl_3$) 7.2—7.55 (5 H, m, Ph), 5.16 (1 H, dq, J_{HH} 7 Hz and $J_{allylic}$ 1 Hz, CH_2CH), 3.68—4.12 (4 H, symmetrical m, OCH_2CH_2O), 2.63 (2 H, d, J_{HH} 7 Hz, $CHCH_2$), 1.68 and 1.47 (each 3 H, br s and s, respectively, CMe_2); *m/z* 218 (M^+, <1%), 175 (4), and 149 ($C_9H_9O_2^+$, 100) (Found: C, 76.9; H, 8.28. $C_{14}H_{18}O_2$ requires C, 77.0; H, 8.31%).

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