Acyl Transfer Reactions with Phosphine Oxides: Synthesis of *E*-Homoallylic Alcohols, Cyclopropyl Ketones, and γ-Hydroxy Ketones

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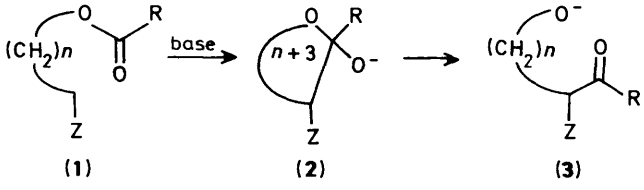
Esters of 3-hydroxypropylphosphine oxides rearrange in base by O to C acyl (RCO) transfer to give the hydroxy ketones (**8**). *threo*-Selective reduction of (**8**) leads to pure *E*-homoallylic alcohols whilst C to O acyl (Ph_2PO) transfer leads to γ-hydroxy ketones with nucleophilic aqueous base or cyclopropyl ketones with $KOBu^t$–$HOBu^t$.

Carbon–carbon bond formation by O to C acyl transfer, that is capture of an acyl group by a carbanion with displacement of RO^-, is common enough when RO^- leaves *exo* from the cyclic intermediate during cyclisation reactions such as the Dieckmann condensation, but rare when the RO^- functionality is retained in the product (**3**), that is when RO^- leaves *endo* from the cyclic intermediate (**2**). The chief requirement for successful acyl transfer, (**1**) ⟶ (**3**), is a group Z which is more anion-stabilising than an ester [so that, if R = alkyl, enolisation of the ester in (**1**) does not occur] but not too anion-stabilising as O^- must be more stable than the Z-stabilised carbanion or the intermediate (**2**) will decompose to (**1**) rather than (**3**). Known examples include Z = ArCO in the Baker-Venkataraman reaction,[1] Z = $ArSO_2$,[2] and Z = alkyl CO.[3] One simple case is reported to rearrange in the reverse direction,[4] *i.e.* (**3**; R = Ph, Z = COPh, *n* = 3) gives (**1**; R = Ph, Z = COPh, *n* = 3) in base. The obvious advantage of this synthetic strategy, that a fixed functional group relationship, *i.e.* a hydroxy ketone in (**3**), is automatically established as the new carbon–carbon bond is formed, is increased if the group Z can be used to assemble the starting material (**1**) and can be removed from the product (**3**) in a variety of ways. We report that the diphenylphosphinoyl (Ph_2PO) group as Z fulfills all these requirements.[5]



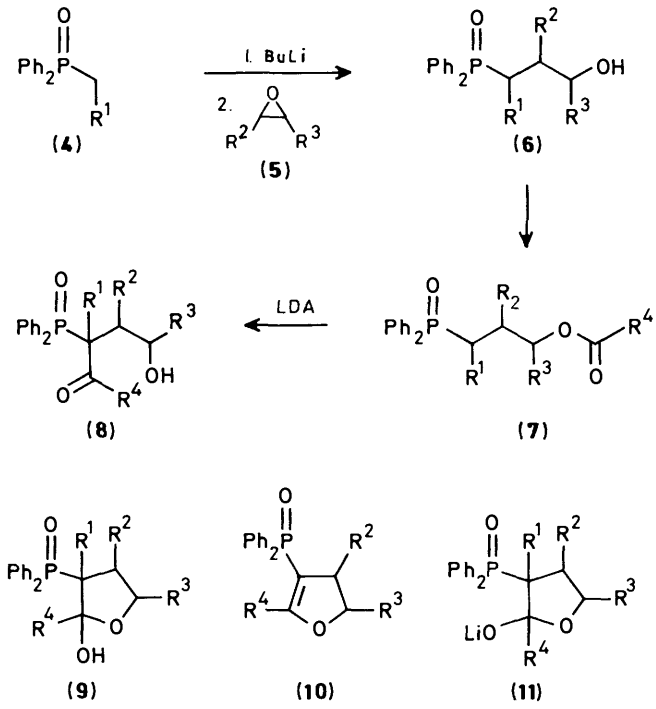
The starting materials, 3- and 4-hydroxyalkyldiphenylphosphine oxides such as (**6**), were made by straightforward routes, the most general being the opening of epoxides (**5**) by a phosphine oxide anion (Table 1). The styrene oxide adducts (**6f**) and (**6g**) were formed with considerable 1,3-diastereoselectivity, though this is irrelevant to their application here and the preferred structure has not yet been determined.

Acyl Transfer Reactions.—Treatment of esters (**7**) derived from these alcohols (**6**) with lithium di-isopropylamide (LDA) gave in all cases good yields of the rearranged hydroxy ketones (**8**) (Table 2). The esterifying group may be aryl or alkyl, so enolisation, if it occurs, must be reversible, and the reaction is not driven by the formation of a stable enolate anion from the product, as is the case with the Claisen ester condensation,[6] since compound (**8f**), which is fully blocked between C=O and P=O, is formed in good yield. The n.m.r. spectra of the products (**8**) showed that hemiacetals and, if R^1 = H, enol ethers (**10**)

Table 1. Synthesis of 3-hydroxyalkyldiphenylphosphine oxides (**6**) from epoxides (**5**)

Compound	R^1	R^2	R^3	Yield (%)	Stereo
(**6a**)	H	H	Me	70	
(**6b**)	H	H	Ph	79	
(**6c**)	H	Me	Me	88[a]	100:0[b]
(**6d**)	Me	H	H	85	
(**6e**)	Me	H	Me	80[c]	50:50
(**6f**)	Me	H	Ph	71[a]	91:9
(**6g**)	Et	H	Ph	96[a]	>96:4
(**6h**)	Bu	H	H	27	

[a] Yield of single isomer. [b] (**5c**) Is *trans*-2,3-dimethyloxirane. [c] Mixture of diastereoisomers not separated.



form readily, unless the solvent is carefully freed from traces of acid, and it may be that the lithium derivative (**11**) of the hemiacetal is the true product of the rearrangement, by analogy with the Horner-Wittig reaction.[7] One hydroxy ketone (**8c**) was characterised as its benzoate, which was formed without difficulty. Products with $R^3 \neq H$ (**8d,e**) appear from their n.m.r. spectra to be single diastereoisomers, though the spectra are

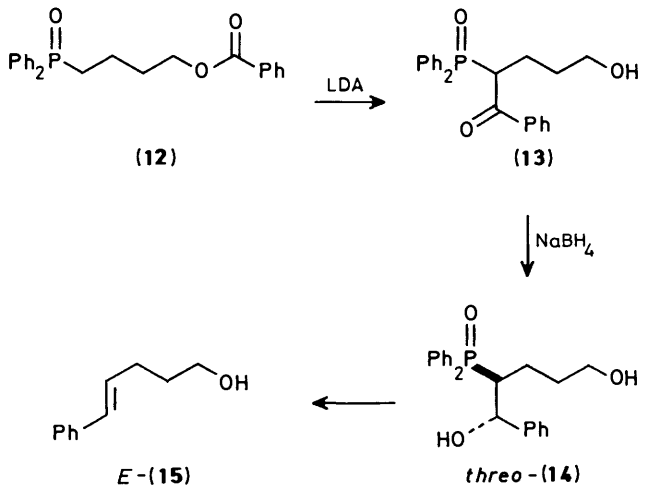
Table 2. Rearrangement of esters (7) to γ-hydroxy ketones (8) with lithium di-isopropylamide (LDA)

	Starting material					Yield
	R^1	R^2	R^3	R^4	Product[a]	(%)
(7a)	H	H	H	Me	(8a)	83
(7b)	H	H	H	Et	(8b)	73
(7c)	H	H	H	Ph	(8c)	95
(7d)	H	H	Me	n-C_6H_{13}	(8d)	80
(7e)	H	H	Ph	C_3H_5[a]	(8e)	73
(7f)	Me	H	H	Ph	(8f)	82

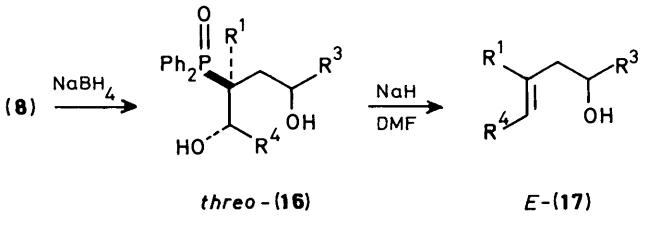
[a] Mixtures of open (8) and closed (9) forms, see text. [b] Cyclopropyl.

complicated by the presence of hydroxy ketone (8) and hemiacetal (9) forms and by the extra chiral centre in the hemiacetal form.

The success of this rearrangement suggested that the reported[4] rearrangement of (3; R = Ph, Z = COPh) to (1; R = Ph, Z = COPh) in weak base might be reversed in strong base, but treatment of (1; R = Ph, Z = COPh) with LDA returned starting material. One acyl transfer was also successful through a six-membered cyclic intermediate, the ester (12) giving the δ-hydroxy ketone (13) in 71% yield with LDA.



Horner-Wittig Reactions.[8]—We have already shown[9] that reduction of α-diphenylphosphinoyl ketones is *threo*-selective and can be used to make *E*-alkenes. In this way the ketone (13) gave the alcohol *E*-(15) *via* the diol (14) and the hydroxy ketones (8) gave the *threo*-diols (16) and hence *E*-homoallylic alcohols (17). The stereoselectivity of these reductions is good (Table 3): the hydroxy group may assist by chelation to boron.



Removal of Ph_2PO *by Phosphinoyl Transfer.*—Just as acyl (COPh) transfer occurred in the rearrangement[4] of (3; R = Ph, Z = COPh) so C to O phosphinoyl transfer occurs when the

Table 3. *E*-Homoallylic alcohols by acyl transfer

Starting ester	*threo*:*erythro*	Isolated *threo* (16) (%)	Yield alkene *E*-(17) (%)
(8a)	75:25[a]	66	
(8b)	75:25[a]	64	85
(8c)	92:8	92	82
(8d)		90[b]	80[b]
(8f)	75:25[a]	75	90
(13)	75:25	65	80

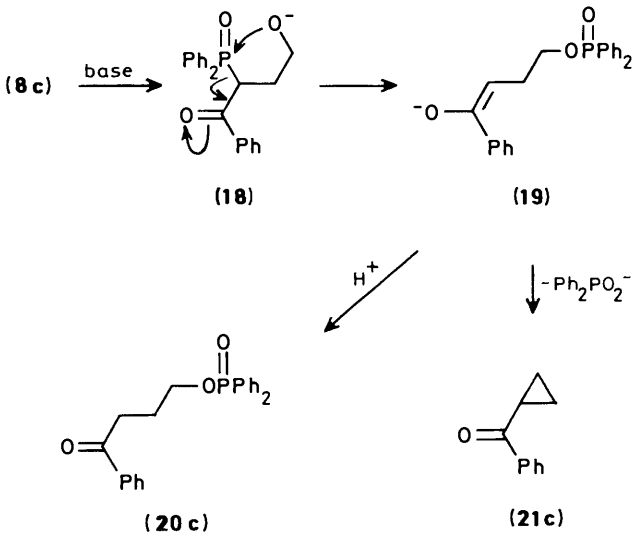
[a] By n.m.r. [b] Mixture of isomers.

Table 4. Synthesis of cyclopropyl ketones (21) and γ-hydroxy ketones (22) by C to O Ph_2PO transfer

Starting material (see Table 2)	Yield of cyclopropyl ketone (21)	Yield of γ-hydroxy ketone (22)
(8a)	81	53
(8b)	100[a]	60
(8c)	100	69
(8d)	91	65
(8e)	99	
(8f)	91	

[a] As 2,4-dinitrophenylhydrazone.

hydroxy ketones (8) are treated with a sodium or potassium base: evidently a lithium counter-ion masks the oxygen atom in the alkoxide of (8) or (11) during its formation, as it does in the Horner-Wittig reaction itself.[7] Sodium hydride, the base used to complete the Horner-Wittig reaction,[9] gives a mixture of the phosphinate (20c) and the cyclopropyl ketone (21c) from (8c) suggesting that the enolate (19) is a common intermediate. We have now found sets of conditions to give the cyclopropyl ketones (21) or the hydroxy ketones (22) derived by hydrolysis of the phosphinates (20) as the only products.

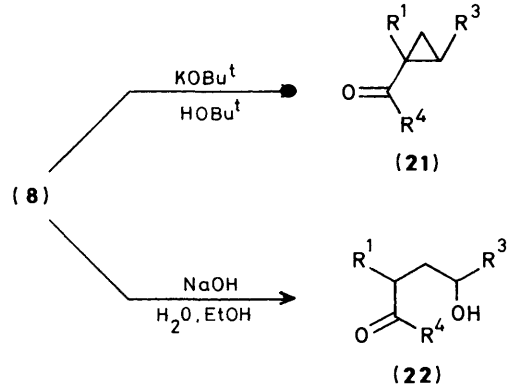


Cyclopropyl Ketone Synthesis.—Treatment of the hydroxy ketones (8) with Bu^{t}OK–Bu^{t}OH (Table 4) gives high yields of the cyclopropyl ketones (21). Evidently this medium is not acidic enough to protonate the enolate and not nucleophilic enough to cleave the phosphinate ester in (19). The phosphonium salt analogue[10] of (7c) also gives (21c) on

treatment with base, and the anion of triethyl phosphonoacetate reacts with ethylene oxide to give ethyl cyclopropanecarboxylate.[11] Both reactions occur in one step and cannot be diverted to make other products, 1,2-diphenylcyclopropane has been made from a phosphine oxide[12] and enamines of α-diphenylphosphinoyl ketones react with epoxides to give cyclopropyl ketones.[13]

The range of cyclopropyl ketones available by our route includes those with alkyl or aryl substituents, with a quaternary centre next to the carbonyl group (**21f**), and with a second substituent (R^3) on the cyclopropyl ring. In these cases (**21d,e**) only one compound is formed and the ^1H n.m.r. spectrum of (**21e**) suggests that this is *trans*. We made (**21e**) because of the potential of such compounds in Murphy's tetralone synthesis.[14]

Synthesis of γ-Hydroxy Ketones.—The intermediate (**19**) is diverted to a third product, the hydroxy ketone (**22**), if the enolate anion can be protonated and the phosphinate ester hydrolysed to deprive the intermediate both of its nucleophile and its leaving group. Aqueous sodium hydroxide with enough ethanol to dissolve the phosphine oxide (**8**) gives reasonable yields of the hydroxy ketone (**22**) (Table 4), though some cyclopropyl ketone (**21**) is usually formed as well. The strategy of these synthetic methods revolves around the carbon atom attached to the Ph_2PO group as two new C–C bonds are made to this atom, acyl transfer being used for the second.



Attempts at C to O phosphinoyl transfer on the homologue (**13**) failed. Evidently carboxy groups can be transferred *via* five- or six-membered intermediates but phosphinoyl groups only *via* their preferred[15] five-membered rings. For the 3-hydroxypropyl series (**8**) these simple examples define conditions of general use for making three classes of molecules.

Experimental

Thin layer chromatography was run on silica gel, n.m.r. spectra were recorded at 90 or 250 MHz, and mass spectra by electron impact.

3-*Diphenylphosphinoylpropan*-1-*ol*.—We prefer the phosphonium salt[9] method: 3-bromopropanol (47.7 g) and triphenylphosphine (90 g) in dry dimethylformamide (200 ml) were heated under reflux for 18 h and allowed to cool to room temperature. The precipitated phosphonium bromide was filtered off, washed with a little ether, dried under reduced pressure, dissolved in 30% aqueous sodium hydroxide (200 ml), and heated under reflux for 3 h. The mixture was cooled and neutralised by 10M hydrochloric acid. It was then extracted with dichloromethane and the extract dried ($MgSO_4$) and evaporated under reduced pressure and the residue triturated with ether (3 × 100 ml) and recrystallised from EtOAc to give the alcohol (80.1 g, 89%) as needles, m.p. 99.5—100.5 °C, (lit.,[16] 103 °C), R_F(EtOAc) 0.21; $\delta_H(CDCl_3)$[17] 8.0—7.3 (10 H, m, Ph_2PO), 4.4 (1 H, s, OH), 3.65 (2 H, t, *J* 7 Hz, CH_2O), 2.6—2.2 (2 H, m, CH_2P), and 2.1—1.6 (2 H, m, other CH_2s) (Found: $M^+ - H$, 259.0901. $C_{15}H_{17}O_2P$ requires $M - H$, 259.0888); *m/z* 259 (6.9%, $M^+ - H$), 242 (26, $M^+ - H_2O$), 230 (67, $M^+ - CH_2O$), 215 (88, $M^+ - CH_2CH_2OH$), and 202 (100, Ph_2POH).

3-*Diphenylphosphinoylbutan*-1-*ol* (**6d**).—Butyl-lithium (1.6M solution in hexane; 20.1 ml) was added to a stirred solution of ethyldiphenylphosphine oxide (6.9 g) in THF (80 ml) at −20 °C. Stirring was continued for 30 min after which ethylene oxide (2.5 ml) was added in one portion and the mixture stirred at −20 °C for 2 h. Excess of water was added and the mixture extracted with dichloromethane. The extract was washed with water and brine, dried ($MgSO_4$), and evaporated under reduced pressure. Recrystallisation of the residue from EtOAc gave the *alcohol* (6.99 g, 85%) as prisms, m.p. 104—107 °C (Found: C, 70.2; H, 7.05; P, 11.3. $C_{16}H_{19}O_2P$ requires C, 70.1; H, 6.93; P, 11.3%); R_F(EtOAc) 0.18; $\nu_{max.}(CDCl_3)$ 3 250 (OH), 1 600 (Ph), 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); $\delta_H(CDCl_3)$ 8.1—7.3 (10 H, m, Ph_2PO), 4.8 (1 H, br s, OH), 3.7 (2 H, br t, *J* 5 Hz, CH_2OH), 2.9—2.6 (1 H, m, MeC*H*P), 2.3—1.4 (2 H, m, CH_2CHP), and 1.3—1.0 (3 H, dd, J_{PH} 17 Hz and J_{HH} 7 Hz, Me) (Found: M^+, 274.1125. $C_{16}H_{19}O_2P$ requires *M*, 274.1122); *m/z* 274 (0.6%, M^+), 244 (16, $M^+ - CH_2O$), 230 (45, Ph_2PCH_2Me), and 201 (100, Ph_2PO).

3-*Diphenylphosphinoyl*-1-*phenylpentan*-1-*ol* (**6g**).—In the same way, BuLi (1.6M solution in hexane; 27.5 ml), propyldiphenylphosphine oxide (10 g) in THF at 0 °C, and styrene oxide (4.7 ml) gave the *alcohol* (16.3 g, 96%) as prisms, m.p. 210—211 °C (from EtOAc) (Found: C, 75.5; H, 6.85; P, 8.16. $C_{23}H_{25}O_2P$ requires C, 75.8; H, 6.87; P, 8.52%); R_F(EtOAc) 0.14; $\nu_{max.}(CDCl_3)$ 3 350 (OH), 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); $\delta_H(CDCl_3)$ 8.0—7.2 (15 H, m, Ph_2PO and Ph), 5.3 (1 H, br s, OH), 5.0—4.8 (1 H, m, CH–O), 2.5—1.5 (5 H, m, CH_2CHCH_2), and 0.9 (3 H, t, *J* 6 Hz, Me); *m/z* 258 (9%, $M^+ - PhCHO$), 229 (49), and 202 (100, Ph_2POH).

4-*Diphenylphosphinoylpentan*-2-*ol* (**6e**).—In the same way, BuLi (1.6M solution in hexane; 23.6 ml), ethyldiphenylphosphine oxide (8.08 g) at 0 °C, and propylene oxide (2.46 ml) gave the *alcohol* (a 1:1 mixture of diastereoisomers by integration of the ^{13}C n.m.r. spectrum) as an oil (8.06 g, 80%); $\delta_H(CDCl_3)$ 8.0—7.3 (10 H, m, Ph_2PO), 4.6 (1 H, br s, OH), 4.1—3.8 (1 H, m, C*H*OH), 3.1—2.6 (1 H, m, CHP), 1.9—1.6 (2 H, m, CH_2), and 1.3—0.9 (6 H, m, Me's); $\delta_C(CDCl_3)$ major isomer 64.0 (J_{CP} 1.5 Hz), 38.5, 29.3 (J_{CP} 70.0 Hz), 24.0, and 11.3; minor isomer 62.8 (J_{CP} 1.5 Hz), 37.8, 27.6 (J_{CP} 70.0 Hz), 20.5, and 13.6 p.p.m.

3-*Diphenylphosphinoyl*-1-*phenylpropan*-1-*ol* (**6b**).—In the same way, BuLi (1.6M solution in hexane; 9.3 ml), methyldiphenylphosphine oxide (3.0 g) at 0 °C, and styrene oxide (1.7 ml) gave an oil, recrystallised from EtOAc to give the *alcohol* (3.72 g, 79%) as needles, m.p. 144—145 °C (from EtOAc) (Found: C, 74.8; H, 6.26; P, 9.41. $C_{21}H_{21}O_2P$ requires C, 75.0; H, 6.25; P, 9.23%); R_F(EtOAc) 0.11; $\nu_{max.}(CDCl_3)$ 3 350 (OH), 1 440 (Ph–P), 1 400s, and 1 020s cm^{-1}; $\delta_H(CDCl_3)$ 7.8—7.2 (15 H, m, Ph_2PO and Ph), 4.75 (1 H, t, *J* 7 Hz, CH–O), 4.7 (1 H, br s, OH), and 2.6—1.8 (4 H, m, CH_2CH_2) (Found: M^+, 336.1283. $C_{21}H_{21}O_2P$ requires *M*, 336.1279); *m/z* 336 (0.74%, M^+), 201 (100, Ph_2PO), and 77 (72, Ph).

4-*Diphenylphosphinoylbutan*-2-*ol* (**6a**).—In the same way, BuLi (1.6M solution in hexane; 25 ml), methyldiphenylphosphine oxide (8.03 g) in THF (100 ml) at 0 °C, and propylene oxide (2.6

ml) gave an oil. Recrystallisation of this from EtOAc gave the *alcohol* (7.1 g, 70%) as needles, m.p. 101—102 °C (from EtOAc) (Found: C, 70.3; H, 7.19; P, 11.09. $C_{16}H_{19}O_2P$ requires C, 70.1; H, 6.93; P, 11.3%); R_F(EtOAc) 0.15; $\nu_{max.}$($CDCl_3$) 3 320 (OH), 1 590 (Ph), 1 440 (Ph–P), and 1 170 cm^{-1} (P=O); δ_H($CDCl_3$) 7.9—7.4 (10 H, m, Ph_2PO), 4.1—3.7 (1 H, m, CH–O), 2.9 (1 H, br s, OH), 2.6—2.2 (2 H, m, CH_2P), 2.0—1.4 (2 H, m, CH_2CH–O), and 1.15 (3 H, d, *J* 6 Hz, Me) (Found: $M^+ - H$, 273.1052. $C_{16}H_{19}O_2P$ requires $M^+ - H$, 273.1044); *m/z* 273 (1.3%, $M^+ - H$), 215 (63, Ph_2POHMe), and 202 (100, Ph_2POH).

3-*Diphenylphosphinoyl*-1-*phenylbutan*-1-*ol* (**6f**).—In the same way, BuLi (1.6M solution in hexane: 34 ml), ethyldiphenylphosphine oxide (10.62 g) in THF (100 ml) at 0 °C, and styrene oxide (5.8 g) gave an oil. Recrystallisation of this from EtOAc gave the *alcohol* (11.45 g, 71%) as needles, m.p. 154—157 °C; R_F(EtOAc) 0.20; $\nu_{max.}$($CDCl_3$) 3 320 (OH), 1 600 (Ph), 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); δ_H($CDCl_3$) 7.9—7.2 (15 H, m, Ph_2PO and Ph), 5.1 (1 H, br s, OH), 4.8 (1 H, t, *J* 7 Hz, CH–O), 2.6—2.2 (1 H, m, CHP), 2.2—1.8 (2 H, m, CH_2CHP), and 1.3—1.0 (3 H, dd, J_{PH} 17 Hz and J_{HH} 7 Hz, Me) (Found: M^+, 350.1435. $C_{22}H_{23}O_2P$ requires *M*, 350.1435); *m/z* 350 (0.13%, M^+) and 202 (100, Ph_2POH).

3-*Diphenylphosphinoylheptan*-1-*ol* (**6h**).—In the same way, BuLi (1.6M solution in hexane; 13.4 ml), pentyldiphenylphosphine oxide (5.44 g) in THF (80 ml) at 0 °C for 1.5 h, and ethylene oxide (2.0 ml) at −60 °C, and a further portion of ethylene oxide (1 ml) at −5 °C gave a waxy solid which was purified by flash chromatography on silica gel eluting with EtOAc and recrystallised from EtOAc to give the *alcohol* (1.7 g, 27%) as a waxy solid (Found: C, 72.1; H, 7.9; P, 10.05. $C_{19}H_{25}O_2P$ requires C, 72.15; H, 7.91; P, 9.81%); R_F(EtOAc) 0.29; $\nu_{max.}$($CDCl_3$) 3 250 (OH), 1 440 (Ph–P), and 1 170 cm^{-1} (P=O); δ_H($CDCl_3$) 8.0—7.2 (10 H, m, Ph_2PO), 4.4 (1 H, s, OH), 3.9—3.3 (2 H, m, CH_2OH), 2.7—2.2 (1 H, m, CHP), and 2.2—0.5 (11 H, m, Me and other CH_2s) (Found: M^+, 316.1566. $C_{19}H_{25}O_2P$ requires *M*, 316.1593); *m/z* 316 (1.6%, M^+), 229 (76, Ph_2POCH_2Me), and 202 (100, Ph_2POH).

(1R2S,1S2R)-3-*Diphenylphosphinoyl*-1,2-*dimethylpropan*-1-*ol* (**6c**).—In the same way, BuLi (1.6M solution in hexane; 9.37 ml), methyldiphenylphosphine oxide (3.02 g) at 0 °C, and *trans*-2,3-epoxybutane (1.24 ml) gave an oil. Recrystallisation of this from EtOAc gave the *alcohol* (3.54 g, 88%), m.p. 195—196 °C; $\nu_{max.}$($CDCl_3$) 3 250 (OH), 1 440 (Ph–P), and 1 170 cm^{-1} (P=O); δ_H($CDCl_3$) 7.9—7.3 (10 H, m, Ph_2PO), 3.9 (1 H, br s, OH), 4.0—3.6 (1 H, m, on D_2O exchange becoming dq, *J* 6.5 and 3 Hz, CH–O), 2.8—1.8 (3 H, m, $CHCH_2P$), 1.1 (3 H, t, *J* 6 Hz, *Me*CHOH), and 0.9 (3 H, dt, J_{PH} 1 Hz and J_{HH} 6.5 Hz, Me) (Found: M^+, 288.1266. $C_{17}H_{21}O_2P$ requires *M*, 288.1279), *m/z* 288 (2.5%, M^+), 215 (62, Ph_2POHMe), and 202 (100, Ph_2POH).

3-*Diphenylphosphinoylpropyl Acetate* (**7a**).—Acetyl chloride (790 mg) and 3-diphenylphosphinoylpropan-1-ol (2.6 g) in pyridine (25 ml) gave the *ester* (2.8 g, 93%) as a waxy solid; R_F(EtOAc) 0.20; $\nu_{max.}$($CDCl_3$) 1 720 (C=O), 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); δ_H($CDCl_3$) 8.0—7.3 (10 H, m, Ph_2PO), 4.1 (2 H, t, *J* 6 Hz, CH_2–O), and 2.7—1.7 (4 H, m, CH_2CH_2P) overlaid by 2.0 (3 H, s, Me) (Found: M^+, 302.1070. $C_{17}H_{19}O_3P$ requires *M*, 302.1071); *m/z* 302 (0.08%, M^+), 259 (85, M − MeCO), 242 [83, $Ph_2POC(Me)=CH_2$], 215 (100, Ph_2POCH_2), and 201 (80, Ph_2PO).

3-*Diphenylphosphinoylpropyl Benzoate* (**7c**).—In the same way, benzoyl chloride (1.5 g), the phosphine oxide (2.6 g), and pyridine (35 ml) gave the *ester* (3.35 g, 92%) as needles, m.p. 127—128.5 °C (Found: C, 72.4; H, 5.69; P, 8.53. $C_{22}H_{21}O_3P$ requires C, 72.5; H, 5.77; 8.52%); R_F(EtOAc) 0.30; $\nu_{max.}$($CDCl_3$) 1 715 (C=O), 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); δ_H($CDCl_3$) 8.2—7.3 (15 H, m, Ph_2PO and Ph), 4.4 (2 H, t, *J* 7 Hz, CH_2O), and 2.7—1.9 (4 H, m, CH_2CH_2P) (Found: M^+, 364.1234. $C_{22}H_{21}O_3P$ requires *M*, 364.1228); *m/z* 364 (0.83%, M^+), 259 (100, M − PhCO), 201 (67, Ph_2PO), and 105 (76, PhCO).

3-*Diphenylphosphinoylbutyl Benzoate* (**7f**).—In the same way, benzoyl chloride (0.9 g), 3-diphenylphosphinoylbutan-1-ol (**6d**) (1.57 g), and pyridine (25 ml) gave the *ester* (1.84 g, 85%) as needles, m.p. 133—134 °C (Found: C, 73.3; H, 6.36; P, 7.94. $C_{23}H_{23}O_3P$ requires C, 73.0; H, 6.08; P, 8.20%); R_F(EtOAc) 0.31; $\nu_{max.}$($CDCl_3$) 1 710 (C=O), 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); δ_H($CDCl_3$) 8.2—7.3 (15 H, m, Ph_2PO and Ph), 4.45 (2 H, dd, *J* 5 and 7 Hz, CH_2O), 2.9—2.5 (1 H, m, CHP), 2.5—1.6 (2 H, m, CH_2CHP), and 1.3 (3 H, dd, J_{PH} 17 and J_{HH} 7.5 Hz, Me) (Found: M^+, 378.1380. $C_{23}H_{23}O_3P$ requires *M*, 378.1385); *m/z* 378 (0.46%, M^+), 256 (56), 230 (73, Ph_2POCH_2Me), and 201 (100, Ph_2PO).

3-*Diphenylphosphinoylpropyl Propionate* (**7b**).—BuLi (1.6M solution in hexane; 4.6 ml) was added dropwise to a stirred solution of 1-diphenylphosphinoylpropan-1-ol (1.75 g) in THF cooled to 0 °C in an ice–salt bath until a permanent orange colour was formed. Stirring was continued for 5 min and a solution of propionyl chloride (623 mg) in THF (10 ml) was added. After a further 15 min the THF was removed under reduced pressure and the residue dissolved in dichloromethane. The extract was washed with water and with brine, dried ($MgSO_4$), and evaporated under reduced pressure to give the *ester* (2.0 g, 93%) as an oil; R_F(EtOAc) 0.19; $\nu_{max.}$($CDCl_3$) 1 720 (C=O), 1 440 (Ph–P), and 1 185 cm^{-1} (P=O); δ_H($CDCl_3$) 7.8—7.2 (10 H, m, Ph_2PO), 4.0 (2 H, t, *J* 6 Hz, CH_2O), 2.4—1.5 (4 H, m, CH_2s) overlain by 2.1 (2 H, q, *J* 8 Hz, CH_2Me), and 0.9 (3 H, t, *J* 8 Hz, Me) (Found: $M^+ - CH_2CH_2CO$, 259.0901. $C_{18}H_{21}O_3P$ requires $M - CH_2CH_2CO$, 259.0898); *m/z* 259 (0.84%, M^+), 242 [30, $Ph_2POC(Me)=CH_2$], 215 (25, Ph_2POCH_2), 201 (23, Ph_2PO), and 56 (100, CH_2CH_2CO).

3-*Diphenylphosphinoyl*-1-*phenylpropyl Cyclopropanecarboxylate* (**7e**).—In the same way, BuLi (1.6M solution in hexane; 4.1 ml), the phosphine oxide (**6b**) (2.0 g) in THF (30 ml), and cyclopropanecarbonyl chloride (625 mg) in THF (10 ml) gave the *ester* (1.93 g, 80%) as needles, m.p. 156—157 °C (Found: C, 74.0; H, 6.19; P, 7.80. $C_{25}H_{25}O_3P$ requires C, 74.3; H, 6.19; P, 7.67%); R_F(EtOAc) 0.32; $\nu_{max.}$($CDCl_3$) 1 720 (C=O), 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); δ_H($CDCl_3$) 7.8—7.3 (10 H, m, Ph_2PO), 5.9—5.7 (1 H, m, CH–O), 2.4—1.9 (4 H, m, CH_2CH_2P), 1.8—1.5 (1 H, m, COCH), and 1.1—0.7 (4 H, m, cyclopropyl CH_2s) (Found: M^+ − cyclopropyl − CO, 335.1198. $C_{25}H_{25}O_3P$ requires $M - C_3H_5CO$, 335.1201), *m/z* 335 (80%, $M^+ - C_3H_5CO$), 201 (100, Ph_2PO), and 69 (48, C_3H_5CO).

3-*Diphenylphosphinoylbutyl Heptanoate* (**7d**).—In the same way, BuLi (1.6M solution in hexane; 4.9 ml), the phosphine oxide (**6a**) (2.0 g) in THF (30 ml), and heptanoyl chloride (1.09 g) in THF (10 ml) gave the *ester* (2.53 g, 90%) as an oil; R_F(EtOAc) 0.20; $\nu_{max.}$($CDCl_3$) 1 720 (C=O), 1 590 (Ph), 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); δ_H($CDCl_3$) 7.9—7.4 (1 H, m, Ph_2PO), 4.9 (1 H, sextet, *J* 6 Hz, OCH), 2.5—1.0 (23 H, m, CH_2s) overlain by 1.2 (3 H, d, *J* 6 Hz, *Me*CH), and 0.9 (3 H, t, *J* 5 Hz, $MeCH_2$) (Found: M^+, 386.2033. $C_{23}H_{31}O_3P$ requires M^+, 386.2010); *m/z* 386 (0.63%, M^+), 273 (100, $M^+ - C_6H_{13}CO$), and 201 (42, Ph_2PO).

Acyl Transfer Products.—The n.m.r. spectra of these compounds usually reveals a mixture of acyclic hydroxy ketone (**8**) and cyclic hemiacetal (**9**).

3-*Diphenylphosphinoyl*-5-*hydroxypentan*-2-*one* (**8a**).—To a stirred solution of di-isopropylamine (919 mg) in THF (10 ml) cooled to 0 °C in an ice–salt bath was added dropwise a solution of BuLi (1.6M solution in hexane; 5.59 ml). Stirring was continued at 0 °C for 15 min after which the solution was cooled to −78 °C. The resulting solution of lithium di-isopropylamide was added *via* a double-ended needle over a period of 5 min to a stirred solution of the ester (**7a**) (2.29 g) in THF (40 ml) cooled to −78 °C. Stirring was continued for 15 min and the mixture quenched with saturated aqueous ammonium chloride. The solution was allowed to warm to room temperature when the THF was removed under reduced pressure and the residue dissolved in dichloromethane. The solution was dried ($MgSO_4$) and evaporated under reduced pressure to give an oil which was purified by flash chromatography on silica gel eluting with acetone to give the *ketone* (1.9 g, 83%) as an oil; R_F(EtOAc) 0.20; $\nu_{max.}$($CDCl_3$) 3 500 (OH), 1 700 (C=O), 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); δ_H($CDCl_3$) 8.1—7.3 (10 H, m, Ph_2PO), 4.3—3.8 (2 H, m), and 3.7—3.4 (1.5 H, m) [CH_2O (**8a**), CH_2OH and PCHC=O (**9a**)], 3.1—2.7 [0.5 H, m, PCHC–O (**8a**)], 2.7—1.5 (2 H, m, CH_2CHP) overlaid by 2.1 [2 H, s, MeC=O (**8a**)], and 1.2 [1 H, s, MeC–O (**9a**)] (Found: M^+, 302.1077. $C_{17}H_{19}O_3P$ requires *M*, 302.1072); *m/z* 302 (0.18%, M^+), 284 (20, $M^+ - H_2O$), 259 (37, $MH - CH_2CH_2O$), and 201 (100, Ph_2PO).

4-*Diphenylphosphinoyl*-6-*hydroxyhexan*-3-*one* (**8b**).—In the same way, the ester (**7b**) (2.0 g) gave a pale yellow solid. Recrystallisation from EtOAc–hexane gave the *ketone* (1.46 g, 73%), as needles, m.p. 160—161 °C (Found: C, 68.6; H, 6.75; P, 9.70. $C_{18}H_{21}O_3P$ requires C, 68.4; H, 6.65; P, 9.81%); R_F(EtOAc) 0.20; $\nu_{max.}$($CDCl_3$) 3 350 (OH), 1 710 (C=O), 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); δ_H($CDCl_3$) 7.9—7.3 (10 H, m, Ph_2PO), 4.35 (2 H, t, *J* 9 Hz, CH_2O), 2.8—2.1 (1 H, m, CHP), 2.6 (2 H, dt, *J* 9 and 1 Hz, CH_2CHP), 2.35 (2 H, q, *J* 7 Hz, CH_2CO), 1.9 (1 H, br s, OH), and 1.0 (3 H, t, *J* 7 Hz, Me) (Found: $M^+ - H_2O$, 298.1130. $C_{18}H_{21}O_3P$ requires $M - H_2O$, 298.1122); *m/z* 298 (100%, $M^+ - H_2O$) and 201 (67, Ph_2PO).

2-*Diphenylphosphinoyl*-4-*hydroxy*-1-*phenylbutan*-1-*one* (**8c**).—In the same way, the ester (**7c**) (300 mg) gave a waxy solid which was recrystallised from chloroform–EtOAc to give the *ketone* (287 mg, 95%) as needles, m.p. 138—141 °C (Found: C, 71.7; H, 5.33; P, 8.59. $C_{22}H_{21}O_3P$ requires C, 72.5; H, 5.77; P, 8.52%); R_F(EtOAc) 0.13; $\nu_{max.}$($CDCl_3$) 3 340 (OH), 1 710, 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); δ_H($CDCl_3$) 8.1—6.9 (15 H, m, Ph_2PO and Ph), 5.0 [0.5 H, ddd, J_{PH} 17 Hz, J_{HH}a 9, and J_{HH}b 3 Hz, CHP (**8c**)], 4.5 (2 H, t, *J* 9 Hz, CH_2OH), 3.9—3.3 [1 H, m, CH_2CHP (**9c**)], 2.8 [0.5 H, dt, J_{PH} 10 Hz and J_{HH} 3 Hz, OCHC–O (**9c**)], and 2.7—1.8 [1 H, m, CH_2CHP (**8c**)] (Found: M^+, 364.1233. $C_{22}H_{21}O_3P$ requires *M*, 364.1228); *m/z* 364 (0.59%, M^+), 345 (36, $M - H_2O$), 320 (42, $M - CH_2CH_2OH$), and 202 (100, Ph_2POH).

2-*Diphenylphosphinoyl*-4-*hydroxy*-2-*methyl*-1-*phenylbutan*-1-*one* (**8f**).—In the same way, the ester (**7f**) (700 mg) gave an oil. Recrystallisation from EtOAc–light petroleum gave the *ketone* (574 mg, 82%) as needles, m.p. 148—149 °C (Found: C, 73.15; H, 6.15; P, 8.0. $C_{23}H_{23}O_3P$ requires C, 73.0; H, 6.08; P, 8.20%); R_F(EtOAc) 0.19; $\nu_{max.}$($CDCl_3$) 3 250 (OH), 1 710, 1 420 (Ph–P), and 1 240 cm^{-1} (P=O); δ_H($CDCl_3$) 8.1—6.9 (15 H, m, Ph_2PO and Ph), 4.5—4.0 (2 H, m, CH_2OH), 4.2 (1 H, br s, OH), 3.5—2.9 (1 H, m, CH_AH_BCP), 1.9—1.5 (1 H, m, CH_AH_BCP), and 1.2 (3 H, d, J_{PH} 17 Hz, Me) (Found: M^+, 378.1388. $C_{23}H_{23}O_3P$ requires *M*, 378.1385); *m/z* 378 (0.28%, M^+), 243 (69, $M - CH_2CH_2OH$), 201 (75, Ph_2PO), and 105 (100, PhCO).

2-*Diphenylphosphinoyl*-1-*cyclopropyl*-4-*hydroxy*-4-*phenylbutan*-1-*one* (**8e**).—In the same way, the ester (**7e**) (1.5 g) gave an oil. Recrystallisation of this from EtOAc–hexane gave the *ketone* (1.1 g, 73%); $\nu_{max.}$($CHCl_3$) 3 350 (OH), 1 710 (C=O), and 1 442 cm^{-1} (Ph–P); δ_H($CDCl_3$) 8.0—7.0 (15 H, m, Ph_2PO and Ph), 5.5 (1 H, dd, *J* 10 and 8.5 Hz, C*H*OH), 3.3–1.9 (4 H, m, $CH_2CHPCOCH$), 2.0 (1 H, br s, OH), and 1.2—0.5 (4 H, m, cyclopropyl CH_2s) (Found: $M^+ - H_2O$, 386.1409. $C_{25}H_{25}O_3P$ requires $M - H_2O$, 386.1436); *m/z* 386 (10%, $M^+ - H_2O$), and 202 (100, Ph_2POH).

4-*Diphenylphosphinoyl*-2-*hydroxyundecan*-5-*one* (**8d**).—In the same way, the ester (**7d**) (2.8 g) gave an oil. Recrystallisation of this from EtOAc gave the *ketone* (2.23 g, 80%) as needles, m.p. 122—123 °C (Found: C, 71.5; H, 7.91; P, 8.21. $C_{23}H_{31}O_3P$ requires C, 71.5; H, 8.03; P, 8.03%); R_F(EtOAc) 0.18; $\nu_{max.}$($CDCl_3$) 3 350 (OH), 1 710 (C=O), 1 440 (Ph–P), and 1 175 cm^{-1} (P=O); δ_H($CDCl_3$) 8.1—7.3 (10 H, m, Ph_2PO), 4.6—3.5 (1 H, m, CH–O), 3.2—0.9 (16 H, m, other Hs) overlaid by 1.7 (1 H, br s, OH), and 0.85 (3 H, t, *J* 5 Hz, $MeCH_2$) (Found: M^+, 386.2020. $C_{23}H_{31}O_3P$ requires 386.2010); *m/z* 386 (0.05%, M^+), 368 (22, $M - H_2O$), 229 (100, $Ph_2POCH_2CH_2$), and 202 (60, Ph_2POH).

3-*Benzoyl*-3-*diphenylphosphinoylpropyl Benzoate.*—Benzoyl chloride (21 mg) and the alcohol (**8c**) (50 mg) in pyridine (5 ml) gave the *ester* (55 mg, 85%) as needles, m.p. 147—148 °C (from EtOAc) (Found: C, 74.1; H, 5.49; P, 6.59. $C_{29}H_{25}O_4P$ requires C, 74.4; H, 5.34; P, 6.62%); $\nu_{max.}$($CDCl_3$) 1 715 (C=O), 1 700 (C=O), 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); δ_H($CDCl_3$) 8.1—7.1 (15 H, m, Ph_2PO and Ph), 5.0—4.6 (1 H, ddd, *J* 3, 10, and 13 Hz, C*H*PCH_2), 4.4—4.2 (2 H, m, CH_2O), and 3.1—2.0 (2 H, m, CH_2CHP) (Found: M^+, 468.1505. $C_{29}H_{25}O_4P$ requires *M*, 468.1519); *m/z* 468 (1%, M^+), 346 (27), 320 (32), and 201 (100, Ph_2PO).

4-*Diphenylphosphinoylbutyric Acid.*—An intimate mixture of triphenylphosphine hydrobromide (17.15 g) and γ-butyrolactone (4.3 g) was heated in an oil bath to 180 °C for 5 h. The resulting solid was allowed to cool to room temperature when 30% aqueous sodium hydroxide (150 ml) was added to it; the mixture was then heated under reflux for 3 h. The solution was cooled to room temperature, carefully acidified with 10M hydrochloric acid, and extracted with dichloromethane. The extract was washed with water and with brine, dried ($MgSO_4$), and evaporated under reduced pressure to give an oil. Recrystallisation of this from EtOAc–methanol gave the acid (9.1 g, 63%) as needles, m.p. 158—159 °C (from EtOAc–methanol) (lit.,[18] m.p. 155—156 °C).

Methyl 4-*Diphenylphosphinoylbutyrate.*—A solution of the above acid (5.76 g) and trimethylsilyl chloride (4.8 g) in methanol (40 ml) was stirred under nitrogen for 18 h. Methanol was removed under reduced pressure to give an oil which was purified by flash chromatography on silica gel eluting with EtOAc. Evaporation under reduced pressure gave a yellow solid which was recrystallised from EtOAc to give the ester (4.1 g, 68%) as needles, m.p. 138—139 °C; $\nu_{max.}$($CDCl_3$) 1 730 (C=O), 1 440 (Ph–P), 1 180 (P=O), and 1 120s cm^{-1}; δ_H($CDCl_3$) 7.9—7.4 (10 H, m, Ph_2PO), 3.6 (3 H, s, Me), 2.45 (2 H, t, *J* 6 Hz, CH_2CO), and 2.5—1.6 (4 H, m, CH_2CH_2P).

4-*Diphenylphosphinoylbutan*-1-*ol.*—Lithium aluminium hydride (500 mg) was added to a stirred solution of the above ester (2.5 g) in THF (40 ml). The mixture was heated under

reflux for 2 h, cooled to room temperature, and excess of lithium aluminium hydride destroyed by the careful addition of EtOAc. Water (40 ml) was added and the mixture extracted with dichloromethane. The extract was washed with water and with brine, dried ($MgSO_4$), and evaporated under reduced pressure to give the alcohol (1.6 g, 71%) as an oil; R_F(EtOAc) 0.13; $\nu_{max.}$($CDCl_3$) 3 350 (OH), 1 440 (Ph–P), and 1 170 cm^{-1} (P=O); δ_H($CDCl_3$) 7.9—7.0 (10 H, m, Ph_2PO), 3.3 (2 H, t, *J* 6 Hz, CH_2O), and 2.6—1.3 (6 H, m, $CH_2CH_2CH_2P$).

4-*Diphenylphosphinoylbutyl Benzoate* (**12**).—Benzoyl chloride (4.89 g) and 4-diphenylphosphinoylbutan-1-ol (9.53 g) in pyridine gave a yellow oil. Trituration with sodium-dried diethyl ether and evaporation under reduced pressure gave a waxy solid which was recrystallised from EtOAc–diethyl ether to give the *ester* (11.97 g, 92%) as needles, m.p. 106—107 °C; R_F(EtOAc) 0.32 (Found: C, 72.9; H, 5.89; P, 7.96. $C_{23}H_{23}O_3P$ requires C, 73.0; H, 6.08; P, 8.20%); $\nu_{max.}$($CDCl_3$) 1 710 (C=O), 1 440 (Ph–P), 1 280s, and 1 180 cm^{-1} (P=O); δ_H($CDCl_3$) 8.0—7.3 (10 H, m, Ph_2PO), 4.3 (2 H, t, *J* 6 Hz, CH_2O), 2.6—2.1 (2 H, m, CH_2P), and 2.1—1.5 (4 H, m, other CH_2s) (Found: M^+, 378.1358. $C_{23}H_{23}O_3P$ requires *M*, 378.1384); *m/z* 378 (0.56%, M^+), 257 (100), and 201 (48, Ph_2PO).

2-*Diphenylphosphinoyl*-5-*hydroxy*-1-*phenylpentan*-1-*one* (**13**).—BuLi (1.6M solution in hexane; 7.41 ml) was added dropwise to a stirred solution of di-isopropylamine (1.67 ml) in THF (18 ml) cooled to 0 °C in an ice–salt bath. The resulting solution was stirred at room temperature for 15 min, cooled to 78 °C, and added *via* a double-ended needle to a stirred solution of the above ester (3.8 g) in THF (40 ml) cooled to −78 °C. Stirring was continued for 1 h when the mixture was quenched with saturated aqueous ammonium chloride and allowed to warm to room temperature. The solvent was removed under reduced pressure and the residue taken up in dichloromethane. The organic extract was washed with water and with brine, dried ($MgSO_4$), and evaporated under reduced pressure to give an oil. Recrystallisation of this from EtOAc gave the *ketone* (2.7 g, 71%) as needles, m.p. 105.5—108 °C (Found: C, 73.1; H, 6.28; P, 8.00. $C_{23}H_{23}O_3P$ requires C, 73.0; H, 6.08; P, 8.20%); R_F(EtOAc) 0.19; $\nu_{max.}$($CDCl_3$) 3 350 (OH), 1 700 (C=O), 1 440 (Ph–P), and 1 185 cm^{-1} (P=O); δ_H($CDCl_3$) 8.0—7.0 (15 H, m, Ph and Ph_2PO), 4.7 (1 H, ddd, J_{PH} 16 Hz, J_{HH} 10 and 4 Hz, CHP), 3.5 (2 H, t, *J* 6 Hz, CH_2O), 2.7 (1 H, br s, OH), 2.5—1.9 (2 H, m, CH_2CHP), and 1.8—1.3 (2 H, m, CH_2CH_2O) (Found: $M^+ - H_2O$, 360.1279. $C_{23}H_{23}O_3P$ requires $M - H_2O$, 360.1279), *m/z* 360 (0.93%, $M^+ - H_2O$), 202 (86, Ph_2POH), 105 (74, PhCO), and 77 (100, Ph).

threo-3-*Diphenylphosphinoylpentane*-1,4-*diol* (**16a**).—Sodium borohydride (100 mg) was added in one portion to a stirred solution of the ketone (**8a**) (1.28 g) in methanol (30 ml). Stirring was continued for 2 h and the solvent removed under reduced pressure. Water (30 ml) was added and the mixture extracted with dichloromethane. The extract was washed with water and with brine, dried ($MgSO_4$), and evaporated under reduced pressure to give a white solid [1.2 g; a 3:1 mixture of diastereoisomers by integration of the ^1H n.m.r. doublets at δ 1.3 (*J* 7 Hz, major) and δ 1.15 (*J* 7 Hz, minor)]. Recrystallisation from EtOAc gave the *diol* (770 mg, 66%) as needles, m.p. 166—168 °C (Found: C, 67.0; H, 6.69; P, 10.45. $C_{17}H_{21}O_3P$ requires C, 67.1; H, 6.91; P, 10.20%); $\nu_{max.}$($CDCl_3$) 3 350 (OH), 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); δ_H(CD_3OD) 8.2—7.4 (10 H, m, Ph_2PO), 4.4—3.9 (1 H, m, CH–O), 3.6 (2 H, t, *J* 7 Hz, CH_2OH), 3.2—2.5 (1 H, m, CHP), 2.3—1.5 (2 H, m, CH_2CHP), and 1.3 (3 H, d, *J* 7 Hz, Me); *m/z* 305 (4.1%, MH^+), 229 (86, $Ph_2POHCH{=}CH_2$), 202 (49, Ph_2POH), and 201 (49, Ph_2PO).

threo-3-*Diphenylphosphinoylhexane*-1,4-*diol* (**16b**).—In the same way, the ketone (**8b**) gave a white solid [440 mg; a 3:1 mixture of diastereoisomers by integration of the ^{13}C n.m.r. doublets at δ 40.2 p.p.m. (J_{PC} 70 Hz, major) and δ 37.1 p.p.m. (J_{PC} 70 Hz, minor)]. Recrystallisation from EtOAc gave the *diol* as prisms, m.p. 194—195 °C (Found: C, 67.6; H, 7.25; P, 9.35. $C_{18}H_{23}O_3P$ requires C, 67.9; H, 7.23; P, 9.75%); $\nu_{max.}$($CDCl_3$) 3 350 (OH), 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); δ_H(CD_3OD) 8.0—7.3 (10 H, m, Ph_2PO), 4.1—3.3 (3 H, m, CH_2OH and CHOH), 3.0—2.5 (1 H, m, CHP), 2.3—1.0 (4 H, m, other CH_2s), and 0.9 (3 H, t, *J* 8 Hz, Me) (Found: MH^+, 319.1449. $C_{18}H_{23}O_3P$ requires MH^+, 319.1463); *m/z* 319 (0.29%, MH^+), 229 (100, $Ph_2POHCHCH_2$), and 201 (77, Ph_2PO).

threo-2-*Diphenylphosphinoyl*-1-*phenylbutane*-1,4-*diol* (**16c**).—In the same way, the ketone (**8c**) (100 mg) gave a white solid. Recrystallisation from EtOAc gave the *diol* (92 mg, 92%) as needles, m.p. 198—199.5 °C (Found: C, 72.0; H, 6.10; P, 8.69. $C_{22}H_{23}O_3P$ requires C, 72.1; H, 6.28; P, 8.47%); R_F(EtOAc) 0.14; $\nu_{max.}$($CDCl_3$) 3 350 (OH), 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); δ_H(CD_3OD) 8.1—7.2 (15 H, m, Ph_2PO and Ph), 5.0 (1 H, dd, J_{PH} 13 Hz and J_{HH} 7 Hz CHOH), 3.4—3.1 (1 H, m, CHP) overlaid by 3.3 (2 H, t, *J* 7 Hz, CH_2OH), and 2.2—1.4 (2 H, m, CH_2CHP) (Found: M^+, 366.1366. $C_{22}H_{23}O_3P$ requires *M*, 336.1385); *m/z* 366 (0.06%, M^+), 260 (30, M^+ − PhCHO), 229 (100, $Ph_2POHCH{=}CH_2$), and 202 (35, Ph_2POH).

threo-2-*Diphenylphosphinoyl*-2-*methyl*-1-*phenylbutane*-1,4-*diol* (**16f**).—In the same way, the ketone (**8f**) (208 mg) gave a white solid [200 mg; a 3:1 mixture of diastereoisomers by integration of the ^1H n.m.r. doublets at δ 1.25 (*J* 17 Hz, major) and δ 1.15 (*J* 17 Hz, minor)]. Recrystallisation from EtOAc gave the *diol* (159 mg, 75%) as needles, m.p. 178—179 °C (Found: C, 72.3; H, 6.65; P, 7.95. $C_{23}H_{25}O_3P$ requires C, 72.6; H, 6.58; P, 8.16%); R_F(EtOAc) 0.10; $\nu_{max.}$($CDCl_3$) 3 350 (OH), 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); δ_H(CD_3OD) 8.4—7.2 (15 H, m, Ph_2PO and Ph), 5.05 (1 H, d, J_{PH} 8 Hz, CH–O), 3.6—3.2 (2 H, m, CH_2–O), 2.0—1.5 (2 H, m, CH_2CH_2OH), and 1.25 (3 H, d, J_{PH} 17 Hz, Me); *m/z* 332 (38), 318 (46), 243 [100, Ph_2POH-(Me)=CH_2], and 202 (28, Ph_2POH).

4-*Diphenylphosphinoylundecane*-2,5-*diol* (**16d**).—In the same way, the ketone (**8d**) (0.36 g) gave a white solid. Recrystallisation from EtOAc gave the *diol* (mixture of diastereoisomers) (200 mg, 56%) as needles, m.p. 164—165 °C (Found: C, 70.9; H, 8.50; P, 8.22. $C_{23}H_{33}O_3P$ requires C, 71.1; H, 8.51; P, 7.99%); $\nu_{max.}$($CDCl_3$) 3 350 (OH), 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); δ_H($CDCl_3$) 8.0—7.3 (10 H, m, Ph_2PO), 4.2—3.2 (2 H, m, CH–O), 3.2—2.4 (1 H, m, CHP), 1.3—0.9 (12 H, m, other CH_2s) overlaid by 1.7 (2 H, br s, OHs) and by 1.1 (3 H, d, *J* 6.5 Hz, *Me*CH), and 0.9 (3 H, t, *J* 5 Hz, *Me*CH_2) (Found: $M^+ - H_2O$, 370.2087. $C_{23}H_{33}O_3P$ requires $M - H_2O$, 370.2062); *m/z* 370 (1.29%, $M^+ - H_2O$), 229 (100, $Ph_2POHCH{=}CH_2$), 202 (100, Ph_2POH), 201 (98, Ph_2PO), and 128 (62).

threo-2-*Diphenylphosphinoyl*-1-*phenylpentane*-1,5-*diol* (**14**).—In the same way, the ketone (**13**) gave an oil which solidified under high vacuum. Recrystallisation from EtOAc gave the *diol* (327 mg, 65%) as needles, m.p. 137.5—139 °C (Found: C, 72.3; H, 6.62; P, 8.08. $C_{23}H_{25}O_3P$ requires C, 72.6; H, 6.58; P, 8.16%); R_F(EtOAc) 0.12; $\nu_{max.}$($CDCl_3$) 3 350 (OH), 1 440 (Ph–P), and 1 180 cm^{-1} (P=O); δ_H($CDCl_3$) 7.9—7.0 (15 H, m, Ph_2PO and Ph), 5.3—4.8 (3 H, m, CHOH and OH), on CD_3OD exchange becoming 4.9 (1 H, dd, J_{PH} 14 Hz and J_{HH} 7 Hz), 3.3 (3 H, t, *J* 6 Hz, CH_2OH), 3.0—2.6 (1 H, m, CHP), and 1.8—1.0 (4 H, m, CH_2CH_2CHP) (Found: M^+, 380.1555. $C_{23}H_{25}O_3P$ requires *M*, 380.1541); *m/z* 380 (0.44%, M^+), 229 (74, $Ph_2POHCH{=}CH_2$), 202 (85, Ph_2POH), and 77 (100, Ph).

(E)-*Hex*-3-*en*-1-*ol* (**17b**).—Sodium hydride (50% suspension in oil; 100 mg) was freed from oil by decantation with pentane under nitrogen. Excess of pentane was removed in a stream of nitrogen and the residue taken up in dry THF (10 ml). The phosphine oxide (**16b**) (150 mg) was added and the mixture stirred for 2 h. Water (10 ml) was added and the mixture was extracted with ether. The extract was washed with water and with brine, dried ($MgSO_4$), and evaporated under reduced pressure to give the olefin (57 mg, 85%) as a liquid whose ^1H and ^{13}C spectra were identical with those published.[19]

(E)-4-*Phenylbut*-3-*en*-1-*ol* (**17c**).—In the same way, the phosphine oxide (**16c**) (830 mg) gave the olefin (275 mg, 82%) as a liquid; $\nu_{max.}$(neat film) 3 325 (OH) and 970 cm^{-1} (C=C); $\delta_H(CDCl_3)$ 7.5–7.2 (5 H, m, Ph), 6.5 (1 H, d, *J* 17 Hz, PhC*H*=CH), 6.2 (1 H, dt, *J* 17 and 7 Hz, CH=C*H*CH_2), 3.7 (2 H, t, *J* 7 Hz, CH_2OH), 2.5 (2 H, q, *J* 7 Hz, C$H_2$$CH_2$OH), and 1.5 (1 H, br s, OH) (Found: M^+, 148.0882. $C_{10}H_{12}O$ requires *M*, 148.0888); *m/z* 148 (30.8, M^+), 117 (100, PhCH=$CHCH_2$), and 91 (26, $PhCH_2$).

(E)-3-*Methyl*-4-*phenylbut*-3-*en*-1-*ol* (**17f**).—In the same way, the phosphine oxide (**16f**) (152 mg) gave the olefin (52 mg, 80%) as a liquid; $\nu_{max.}(CDCl_3)$ 3 350 (OH), 1 630 (C=C), and 1 500 cm^{-1} (Ph); $\delta_H(CDCl_3)$ 7.4—7.2 (5 H, m, Ph), 6.4 (1 H, br s, PhCH=C), 3.8 (2 H, t, *J* 7 Hz, CH_2OH), 2.45 (2 H, t, *J* 7 Hz, CH_2C=CH). 1.9 (3 H, s, Me), and 1.6 (1 H, br s, OH); pre-irradiation of the vinylic proton at δ 6.4 gave a 5% positive n.O.e. to the signal at δ 2.45 (Found: M^+, 162.1044. $C_{11}H_{14}O$ requires *M*, 162.1044); *m/z* 162 (70%, M^+), 132 (100), and 91 (45).

Undec-4-*en*-2-*ol* (**17d**).—In the same way, the phosphine oxide (**16d**) (388 mg) gave the olefin (140 mg, 82%) identified by its ^1H n.m.r. spectrum; $\delta_H(CDCl_3)$ 5.7—5.2 (2 H, m, CH=CH), 4.9—4.6 (1 H, m, C*H*OH), 2.2—1.8 (4 H, m, allylic CH_2s), 1.8 (1 H, br s, OH). 1.7—1.0 (8 H, m, methylene envelope) overlain by 1.2 (3 H, d, *J* 7 Hz, *Me*CH) and 0.9 (3 H, distorted t, *J* 6.5 Hz, *Me*CH_2).

(E)-5-*Phenylpent*-4-*en*-1-*ol* (**15**).—In the same way, the phosphine oxide (**14**) (120 mg) gave the olefin (74 mg, 80%) as a liquid whose ^1H n.m.r. spectrum was identical with that published.[20]

4-*Diphenylphosphinoyloxy*-1-*phenylbutan*-1-*one* (**20c**).—Sodium hydride (50% suspension in oil; 60 mg) was freed from oil by repeated decantation from pentane. Excess of pentane was removed in a stream of nitrogen and the residue suspended in THF (15 ml). A solution of phosphine oxide (**8c**) (230 mg) in THF (2 ml) was added and stirring continued for 1 h. Water was added and the mixture extracted with dichloromethane. The extract was washed with water and with brine, dried ($MgSO_4$), and evaporated under reduced pressure to give an oil. Purification by flash chromatography on silica gel eluting with EtOAc gave the *phosphinate* (80 mg, 35%) as needles, m.p. 111.5—112 °C (from EtOAc) (Found: C, 72.7; H, 6.0; P, 8.5. $C_{22}H_{21}O_3P$ requires C, 72.5; H, 5.77; P, 8.52%); $\delta_H(CDCl_3)$ 8.0—7.3 (15 H, m, Ph_2PO and Ph), 4.1 (2 H, q, J_{PH} = J_{HH} 7 Hz, CH_2CH_2OP), 3.1 (2 H, t, *J* 7 Hz, CH_2C=O), and 2.2 (2 H, quintet, *J* 7 Hz, C$H_2$$CH_2OP$) (Found: M^+, 364.1231. $C_{22}H_{21}O_3P$ requires *M*, 364.1228); *m/z* 364 (1.1%, M^+), 219 [100, $Ph_2P(OH)_2$], 201 (29, Ph_2PO), and 105 (33), and cyclopropyl phenyl ketone (**21c**) (32 mg, 35%).

6-*Diphenylphosphinoyloxyhexan*-3-*one* (**20b**).—In the same way, the phosphine oxide (**17b**) (200 mg) gave an oil. Purification by flash chromatography on silica gel eluting with EtOAc the *phosphinate* (85 mg, 43%) as a waxy solid; $\nu_{max.}(CDCl_3)$ 1 710 (C=O), 1 440 (Ph–P), 1 230s, and 1 140s cm^{-1}; $\delta_H(CDCl_3)$ 7.8—7.2 (10 H, m, Ph_2PO), 3.95 (2 H, q, J_{HH} = J_{PH} 7 Hz, CH_2CH_2OP), 2.5 (2 H, t, *J* 7 Hz, $COCH_2CH_2$), 2.3 (2 H, q, *J* 7 Hz, $COCH_2Me$), 1.95 (2 H, q, *J* 7 Hz, $COCH_2CH_2CH_2$), and 0.9 (3 H, t, *J* 7 Hz, Me) (Found: M^+, 316.1241. $C_{18}H_{21}O_3P$ requires *M*, 316.1228); *m/z* 316 (5%, M^+), 219 [100, $Ph_2P(OH)_2$], and 201 (24, Ph_2PO).

Hydrolysis of the Phosphinate Ester (**20c**).—4M Aqueous sodium hydroxide (10 ml) was added to a stirred solution of the phosphinate (**20c**) (50 mg) in ethanol (1 ml). The mixture was heated under reflux for 30 min, and allowed to cool to room temperature. The solution was extracted with ether, and the extract washed with water and with brine, dried ($MgSO_4$), and evaporated under reduced pressure to give an oil (12 mg, 53%) whose ^1H n.m.r. spectrum was identical with that of (**22c**).

Hydrolysis of the Phosphinate Ester (**20b**).—In the same way, the phosphinate (**20b**) (50 mg) gave an oil (15 mg, 82%) whose ^1H n.m.r. spectrum was identical with that of (**22b**).

Cyclopropyl Methyl Ketone (**21a**).—Potassium t-butoxide (186 mg) was added in one portion to a stirred solution of the phosphine oxide (**8a**) (250 mg) in t-butyl alcohol (20 ml). The solution was kept mobile by immersion in a bath of warm water as required. Stirring was continued for 2 h and the mixture poured into water (50 ml) and extracted with ether. The extract was washed with water and with brine, dried ($MgSO_4$), and evaporated under reduced pressure to give the ketone (56 mg, 81%) as a liquid with an n.m.r. spectrum identical with that reported.[21]

Cyclopropyl Ethyl Ketone 2,4-*Dinitrophenylhydrazone*.—In the same way, potassium t-butoxide (70 mg) and the phosphine oxide (**8b**) (100 mg) in t-butyl alcohol (15 ml) followed by 2,4-dinitrophenylhydrazine (64 mg) and 5 drops of concentrated sulphuric acid gave the 2,4-dinitrophenylhydrazone (89 mg, 100%) as needles, m.p. 158—160 °C (lit.,[22] m.p. 161—162 °C).

Cyclopropyl Phenyl Ketone (**21c**).—In the same way, the phosphine oxide (**8c**) (500 mg) gave the ketone (200 mg, 100%) as a liquid; $\nu_{max.}$(neat film) 1 665 (C=O), 1 540s, 1 380s, and 1 220s cm^{-1}; $\delta_H(CDCl_3)$ 8.2—7.1 (5 H, m, Ph), 2.9—2.4 (1 H, m, CH), and 1.4—0.8 (4 H, m, CH_2CH_2) (Found: M^+, 146.0740. $C_{10}H_{10}O$ requires *M*, 146.0732); *m/z* 146 (11.8%, M^+), 122 (23), 105 (100, PhCO), and 77 (26, Ph).

1-*Benzoyl*-1-*methylcyclopropane* (**21f**).—In the same way, the phosphine oxide (**8f**) (200 mg) gave the ketone (77 mg, 91%) as a liquid; $\nu_{max.}(CDCl_3)$ 1 670 (C=O), and 910s cm^{-1}: $\delta_H(CDCl_3)$ 8.0—7.3 (5 H, m, Ph), 1.6—1.0 (2 H, m, cyclopropyl CH *trans* to Me) overlaid by 1.4 (3 H, s, Me), and 1.0—0.5 (2 H, m, cyclopropyl CH *cis* to Me) (Found: M^+, 160.0885. $C_{11}H_{12}O$ requires *M*, 160.0889); *m/z* 160 (44.7%, M^+), 105 (100, PhCO), and 77 (45, Ph).

trans-1-*Cyclopropylcarbonyl*-2-*phenylcyclopropane* (**21e**).—In the same way, the phosphine oxide (**8e**) (300 mg) gave the *ketone* (138 mg, 99%) as a liquid; R_F(ether) 0.9; $\nu_{max.}(CDCl_3)$ 1 670 (C=O) and 1 605 cm^{-1} (Ph); $\delta_H(CDCl_3)$ 7.5—7.2 (5 H, m, Ph), 2.8 [1 H, ddd, $J_{Ha,Hb}$(*trans*) 4.5, $J_{Ha,Hc}$(*cis*) 8.5, and $J_{Ha,Hd}$(*trans*) 5.5 Hz, $PhCH_a$], 2.4 (1 H, ddd, $J_{Ha,Hb}$ 4.5, $J_{Hb,Hc}$ 6.5, and $J_{Hb,Hd}$ 9 Hz, $COCH_bCH_aPh$), 2.2 (1 H, m, $COCHCH_2CH_2$), 1.8 (1 H, ddd, $J_{Ha,Hc}$ 8.5, $J_{Hb,Hc}$ 6.5, and $J_{Hc,Hd}$ 4.5 Hz, $CH_cH_dCH_aPh$), 1.5 (1 H, ddd, $J_{Ha,Hd}$ 5.5, $J_{Hb,Hd}$ 9, and $J_{Hc,Hd}$ 4.5 Hz, $CHC_cH_dCH_aPh$), 1.2 (2 H, m), and 1.0 (2 H, m) ($COCHCH_2CH_2$) (Found: M^+, 186.1029. $C_{13}H_{14}O$ requires

M, 186.1045), *m/z* 186 (54%, M^+), 117 (45), and 69 (100, C_3H_5CO).

1-*Heptanoyl*-2-*methylcyclopropane* (**21d**).—In the same way, the phosphine oxide (**8d**) (202 mg) gave the ketone (80 mg, 91%) as an oil; $\nu_{max.}(CDCl_3)$ 1 695 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 2.5 (2 H, t, *J* 7.5 Hz, CH_2CO), 1.8—0.5 (12 H, m, other Hs) overlaid by 1.1 (3 H, d, *J* 4 Hz, *Me*CH), and 0.9 (3 H, t, *J* 6 Hz, *Me*CH_2) (Found: M^+, 168.1513. $C_{11}H_{20}O$ requires *M*, 168.1513); *m/z* 168 (1.3%, M^+), 98 (54), 83 (100, $M^+ - C_6H_{13}$), and 55 (42).

5-*Hydroxypentan*-2-*one* (**22a**).—4M Aqueous sodium hydroxide (20 ml) was added to a stirred solution of the phosphine oxide (**8a**) (302 mg) in ethanol (10 ml). The mixture was warmed to 60 °C, maintained at this temperature for 3 h with vigorous stirring, and then allowed to cool to room temperature. Water was added and the mixture extracted with dichloromethane. The extract was washed with water and with brine and evaporated under reduced pressure to give a pale yellow oil. Column chromatography of this on silica gel eluting with EtOAc gave the ketone (53 mg, 53%) as a liquid whose ^1H n.m.r. spectrum was identical to that published.[23]

6-*Hydroxyhexan*-3-*one* (**22b**).—In the same way, the phosphine oxide (**8b**) gave an oil. Column chromatography on silica gel eluting with EtOAc gave the ketone (22 mg, 60%) as a liquid; $\nu_{max.}$(neat film) 3 400 (OH) and 1 715 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 3.6 (2 H, t, *J* 6 Hz, CH_2OH), 2.7—2.2 (4 H, m, CH_2COCH_2), 2.2—1.5 (3 H, m, other CH_2 and OH), and 1.1 (3 H, t, *J* 7 Hz, Me) (Found: $M^+ - OH$, 99.0811. $C_6H_{12}O_2$ requires $M - OH$, 99.0810); *m/z* 99 (18.4%, $M^+ - OH$), 98 (18, $M^+ - H_2O$), and 57 ($EtCO^+$, 100).

4-*Hydroxy*-1-*phenylbutan*-1-*one* (**22c**).—In the same way, the phosphine oxide (**8c**) (250 mg) gave the ketone (66 mg, 69%) as an oil; $\nu_{max.}$(neat film) 3 400 (OH) and 1 700 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 8.1—7.2 (5 H, m, Ph), 3.7 (2 H, t, *J* 6 Hz, CH_2OH), 3.4 (1 H, br s, OH), 3.1 (2 H, t, *J* 6 Hz, $CH_2C{=}O$), and 2.0 (2 H, quintet, *J* 6.5 Hz, CH_2CH_2OH) (Found: $M^+ - H_2O$, 146.0739. $C_{10}H_{12}O_2$ requires $M^+ - H_2O$, 146.0732); *m/z* 146 (11.4%, $M^+ - H_2O$), 105 (100, PhC=O), and 77 (57, Ph).

2-*Hydroxyundecan*-5-*one* (**22d**).—In the same way, the phosphine oxide (**8d**) (386 mg) gave the ketone (121 mg, 65%) as a liquid; $\nu_{max.}$(neat film) 3 350 (OH) and 1 715 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 3.8 (1 H, sextet, *J* 6 Hz, *CH*OH), 2.7—2.2 (4 H, m, CH_2COCH_2), 2.2—0.7 (10 H, m, other CH_2s) overlaid by 1.8 (1 H, br s, OH), 1.2 (3 H, d, *J* 6 Hz, *Me*CH), and 0.9 (3 H, t, *J* 6 Hz, *Me*CH_2) (Found: $M^+ - H_2O$, 168.1511. $C_{11}H_{22}O_2$ requires $M - H_2O$, 168.1514); *m/z* 168 (9.0%, $M^+ - H_2O$), 111 (47), 98 (62), and 83 (100, C_5H_7O).

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