Organic Synthesis with a Migrating Functional Group: Scope and Limitations of Diphenylphosphinoyl Migration

By **Alan H. Davidson, Chris Earnshaw, J. Ian Grayson, and Stuart Warren,*** University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

Diphenylphosphinoyl (Ph_2PO) migration occurs during the acid-catalysed dehydration of β-Ph_2PO-alcohols having primary or secondary alkyl groups, alkenyl groups, or aryl groups at the migration terminus and, in another series of compounds, a five- or a four-membered ring at the migration origin. The allylphosphine oxide products form anions which add electrophiles, chiefly carbonyl compounds, mostly at the α-position (to phosphorus) but at the γ-position in some cases. A method to cause α-addition is described.

ANIONS of s-alkylphosphine oxides (1) can be used to form new carbon–carbon bonds in the first stage of the Wittig–Horner reaction.[1] The alcohols (2) produced rearrange in acid by diphenylphosphinoyl (Ph_2PO) migration to give allylphosphine oxides (3) whose anions may be used to form further carbon–carbon bonds.[2] This process [(1) ⟶ (3)] is a versatile synthetic sequence in that it makes possible the assembly of a carbon framework step-by-step from electrophilic fragments using the same anion stabilising group,[3] but it will work only if (a) the substitution pattern of the alcohols (2) is such that the rearrangement (2) ⟶ (3) occurs, (b) the allyl- (3) not the vinyl- (4) phosphine oxide is formed, and (c) the

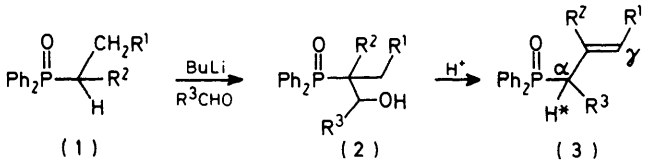
[1] L. Horner, H. Hoffmann, H. G. Wippel, and G. Klahre, *Chem. Ber.*, 1959, **92**, 2499.

[2] A. H. Davidson, P. K. G. Hodgson, D. Howells, and S. Warren, *Chem. and Ind.*, 1975, 455.

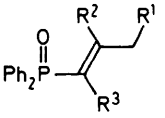
[3] A. H. Davidson and S. Warren, *J.C.S. Chem. Comm.*, 1975, 148.

anion of the allylphosphine oxide reacts with electrophiles at the α-position [see (3)].

We have shown that these conditions are satisfied when the substituents at the migration origin [R^1CH_2 and R^2 in (2)] are the same ($R^1CH_2 = R^2 = Me$),[4] different ($R^1CH_2 = Me$, R^2 = alkyl),[3-6] or form a six-membered ring ($R^1CH_2R^2 = [CH_2]_5$),[3,7] and when the



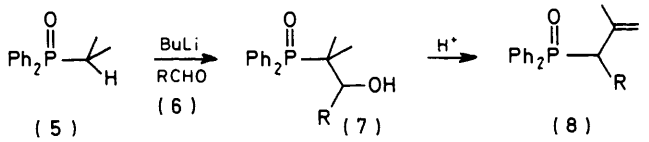
(1) (2) (3)



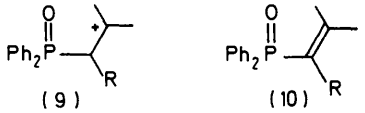
(4)

substituent at the migration terminus [R^3 in (2)] is methyl[4-7] or phenyl.[3,6] We now report that the scope of the method extends to other substituents at the migration terminus and to five- and even four-membered rings at the migration origin, but that limitations are imposed by each of the three conditions [(a)—(c) above] in some compounds.

Substituents at the Migration Terminus.—Using the simplest migration origin [$R^1CH_2 = R^2 = Me$ in (2)]—also the one which least encourages rearrangement[6]—we have explored how variations at the migration terminus affect the rearrangement. Addition of the aldehydes (6; R = Me, Et, Pr^n, Pr^i, Bu^t, or Ph) to the anion of isopropyldiphenylphosphine oxide (5) gave the



(5) (6) (7) (8)



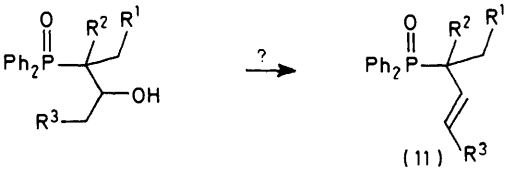
(9) (10)

alcohols (7), each of which we attempted to rearrange in acid solution.

The secondary benzyl alcohol (7; R = Ph) or its tosylate rearranged rapidly in trifluoroacetic acid (TFA) to the allyl compound (8; R = Ph), and this more slowly isomerised to the vinylphosphine oxide (10; R = Ph). The vinylphosphine oxide (10; R = Ph) was the only product when the alcohol (7; R = Ph) was dissolved in 98% sulphuric acid at room temperature.

This is the most favourable case for the isomerisation of the allyl to the vinyl compound, as the allyl compound (8; R = Ph) is a relatively unstable 1,1-disubstituted olefin whereas the vinyl compound (10; R = Ph) has a double bond conjugated with the benzene ring. Even here it is easily possible to stop the reaction after conversion into the allyl compound is complete and before any substantial conversion into the vinyl compound has occurred. In other cases, where the allyl compound is a trisubstituted olefin [*e.g.* (3; $R^1 = R^2 = R^3 = Me$)], the isomerisation does not occur,[6] and with the alkyl compound (8; R = Me) it is very slow. This is then clearly not a limitation to our methods.

All the compounds with a primary alkyl group at the migration terminus (7; R = Me, Et, or Pr^n) rearranged with toluene-*p*-sulphonic acid (TsOH) in benzene under reflux to give the allylphosphine oxides (8; R = Me, Et, or Pr^n) as the only products. We had feared that elimination without rearrangement might compete since it would give relatively stable 1,2-disubstituted olefins [*e.g.* (11; $R^1 = H$, $R^2 = R^3 = Me$)]. This factor does influence the dehydration of alcohols with a secondary migration origin (12; $R^1 = R^2 = H$, R^3 = Me or Et) and influences rearrangement in similar compounds otherwise controlled by a trimethylsilyl group (12; $R^1 = Me_3Si$, $R^2 = H$, R^3 = Me or Et).[6,8] In the compounds with a tertiary migration origin described in this



(11)

paper, this factor is not important. Either the driving force for the rearrangement—the formation of a stable tertiary allyl cation (9)[6]—is too large, or else the unrearranged allyl compound is formed reversibly. In any case, this again is not a limitation to our method.

We have already shown[9] that migration of a methyl group from an alternative migration origin can supplant Ph_2PO migration as the main reaction pathway. Thus the solvolysis of the mesylate (12; R = Me, X = SO_2Me) gives only the alcohol (14) since the cation formed by methyl migration (13) has the electronegative Ph_2PO group as far removed from the positive charge as possible.[9] The same migration occurred when we treated the alcohol (12; R = Me, X = H) with TsOH in benzene to give some (27%) of the same rearranged alcohol (14; R = Me), but the major product was the olefin (16) (50%) formed by methyl migration and loss of a proton from the resulting cation (13; R = Me). The third product was the olefin (15; R = Me) formed by Ph_2PO migration. This was formed in only 18% yield, however,

[4] P. F. Cann, D. Howells, and S. Warren, *J.C.S. Perkin II*, 1972, 304; D. Howells and S. Warren, *ibid.*, 1973, 1472.

[5] A. H. Davidson and S. Warren, *J.C.S. Chem. Comm.*, 1976, 181.

[6] A. H. Davidson, I. Fleming, J. I. Grayson, A. Pearce, R. L. Snowden, and S. Warren, *J.C.S. Perkin I*, 1977, 550.

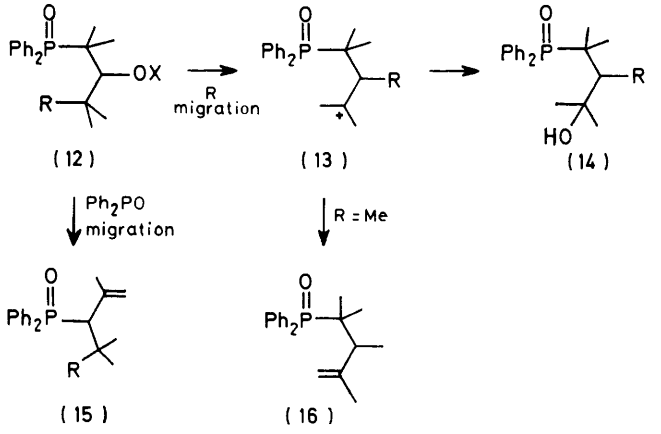
[7] A. H. Davidson and S. Warren, *J.C.S. Perkin I*, 1976, 639.

[8] I. Fleming, A. Pearce, and R. L. Snowden, *J.C.S. Chem. Comm.*, 1976, 182.

[9] D. Howells and S. Warren, *J.C.S. Perkin II*, 1973, 1645.

and it remains a limitation of our method that alkyl migration from an alternative tertiary migration origin successfully competes with Ph_2PO migration. We feared that even an alternative secondary migration origin [*e.g.* in (12; R = X = H)] might lead to hydride rather than Ph_2PO migration. Hydride shifts occur only half as rapidly as methyl migrations on solvolysis of simple alkyl tosylates in TFA when the same tertiary alkyl cation results.[10] In the event we were relieved to find that the isobutyraldehyde adduct (12; R = X = H) rearranged with TsOH in benzene by Ph_2PO migration to give only the allylphosphine oxide (15; R = H).

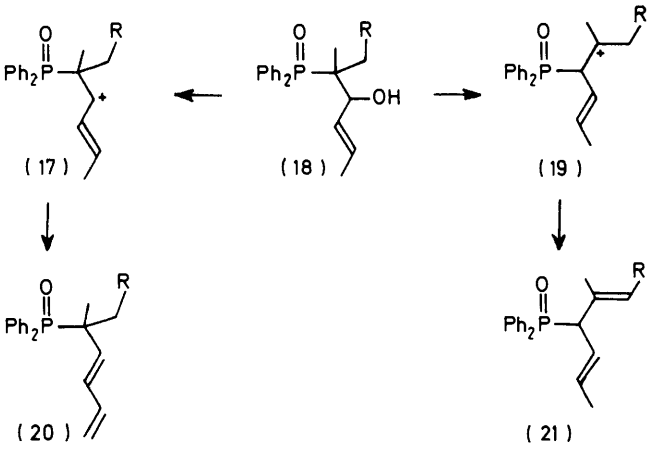
The crotonaldehyde adduct (18) was made to explore two other possible limitations—that αβ-unsaturated aldehydes might add in the Michael sense, and that the secondary allyl cation (17) might be more stable than the rearranged tertiary cation (19) so that the rearrangement did not occur. In fact only the simple 1,2-adduct



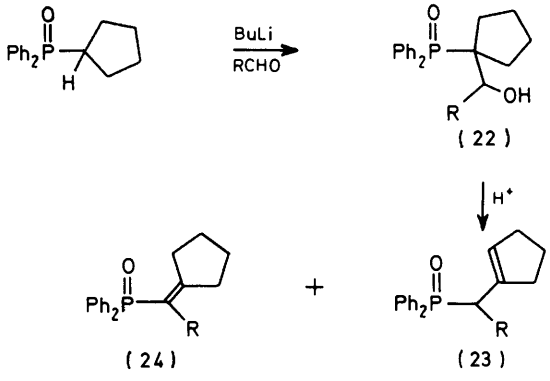
(18) was formed, as it is with other αβ-unsaturated aldehydes and ketones,[11,12] and other Ph_2PO-stabilised anions.[11,12] Dehydration of the allyl alcohol (18; R = H) with TsOH in benzene gave a *ca.* 1 : 3 mixture of the rearranged (21; R = H) and unrearranged (20; R = H) dienes. This is in fact an equilibrium mixture: when the products (21; R = H) and (20; R = H) were separated and each was treated with TsOH in benzene, a mixture of the same compounds in about the same proportions was formed. It therefore appears that equilibration occurs by Ph_2PO migration between the cations (17) and (19), in either direction, the diene (20; R = H) being preferred because of conjugation.

With an ethyl group at the migration origin (18; R = Me), the proportion of rearranged product (21; R = Me) increases as it now contains a trisubstituted double bond, whereas the unrearranged product (20; R = Me) is no more stable than before. The ratio of (20; R = Me) to (21; R = Me) was 1 : 2 after 20 h, the yield of isolated (21; R = Me) being 36%. So, while there appears to be no problem in making adducts (18) from αβ-unsaturated aldehydes, the rearrangement is a route to the phosphine oxides (21) only when both ends of the pentadienyl system carry alkyl groups [both methyl groups in (21; R = Me)].

Substituents at the Migration Origin.—Important substituents we had not explored were smaller rings at the migration origin, since here again the migration might not occur so readily and might give vinyl products.



Cyclopentyldiphenylphosphine oxide (made from cyclopentyl Grignard reagent and diphenylphosphinoyl chloride) was added to either benzaldehyde or acetaldehyde in good yield. The benzaldehyde adduct (22; R = Ph) rearranged in TFA to give only the allyl compound (23; R = Ph), but either the alcohol (22; R = Ph) or the allyl compound (23; R = Ph) gave a 9 : 1 mixture of the vinyl- (24; R = Ph) and allyl- (23; R = Ph) phosphine oxides with TsOH in benzene. Clearly the exocyclic double bond is more stable here than it is in the



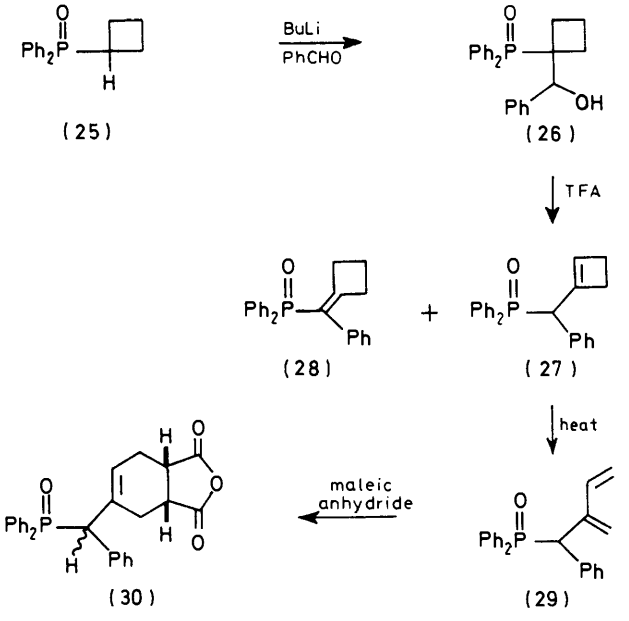
cyclohexyl series.[3,7] The acetaldehyde adduct (22; R = Me) also rearranged with TsOH in benzene by Ph_2PO migration to give a mixture of the allyl (23; R = Me) and vinyl (24; R = Me) compounds in which the allyl compound predominated (2.5 : 1) and which could easily be separated by t.l.c. to give the pure allyl compound.

[10] I. L. Reich, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, 1969, **91**, 5635.

[11] L. Horner, H. Hoffmann, W. Klink, H. Ertel, and V. G. Toscano, *Chem. Ber.*, 1962, **95**, 581.

[12] P. Blatcher, J. I. Grayson, and S. Warren, *J.C.S. Chem. Comm.*, 1976, 547; C. Earnshaw and S. Warren, unpublished observations.

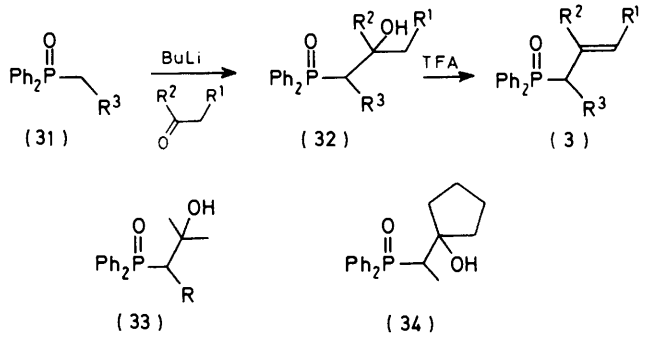
Cyclobutyldiphenylphosphine oxide (25) (made by hydrolysis of the phosphonium salt [13]) again adds to benzaldehyde, and the adduct (26) rearranges in TFA by Ph_2PO migration to a mixture of the allyl- (27) and vinyl- (28) phosphine oxides, the proportion of the vinyl compound increasing with time. We were able to isolate the allyl compound (27) in rather low yield and, by



(25) (26) (28) (27) (30) (29)

heating it under reflux in xylene, isomerised it to the butadiene (29), which was trapped as the Diels–Alder adduct (30). The smaller ring is not therefore a serious limitation in the rearrangement step, but other problems remain (see below).

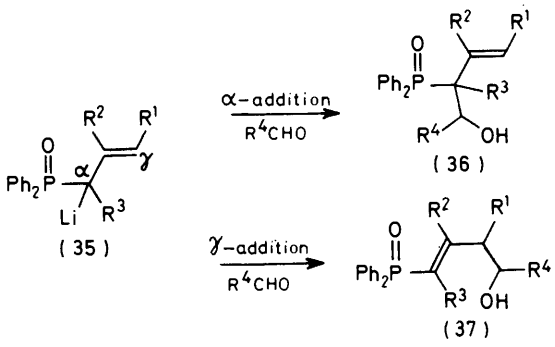
Alternative Routes to Allylphosphine Oxides.—We have previously shown [5-7] that allylphosphine oxides [*e.g.* (3)] may alternatively be made from the ketone adducts (32) of (primary alkyl)diphenylphosphine oxides (31) by



(31) (32) (3) (33) (34)

dehydration in TFA without rearrangement. We have checked that this route is available for some of the allylphosphine oxides described in this paper. The acetone adducts (33; R = Me or Et) give (8; R = Me or Et), and the cyclopentanone adduct (34) gives (23; R = Me) with TFA, all in high yield. This route is normally shorter and higher yielding than the rearrangement route to (3), providing that the ketone is available and that R^3 is an alkyl and not an aryl group. We particularly noted the satisfactory formation and dehydration of the adduct (34) in view of the difficulties sometimes experienced in Wittig reactions with cyclopentanone.[14]

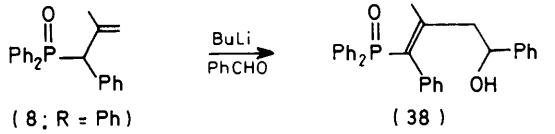
Reactions of Allylphosphine Oxide Anions with Electrophiles: α- vs. γ-Addition.—Allylphosphine oxide 'anions' (35; R^1 = alkyl) give mostly the α-adduct (36) with aldehydes.[3-6] However, the γ-adduct (37) is a vinylphosphine oxide and we may expect that the same



(35) (36) (37)

factors which cause some compounds to give vinylphosphine oxides on rearrangement would also increase the tendency for γ-addition.

The allylphosphine oxide anions which will be particularly susceptible to γ-addition will be those unsubstituted at the γ-carbon atom (35; R^1 = H), those with an aryl or other conjugating group at the α-carbon atom [*e.g.* (8; R = Ph)], and those with a small ring {*e.g.* (3; R^1R^2 = $[CH_2]_2$ or $[CH_2]_3$}. The aryl compound (8; R = Ph) does in fact give mostly the γ-adduct (38) with benzaldehyde, but this is an extreme case. The alkyl analogues, even with one methyl group at the γ-position (3; R^1 = Me) still give some γ-adduct (41; R^1 = Me, R^2 = Me or Ph) but the main product is the α-adduct (40; R^1 = Me, R^2 = Me or Ph). The α : γ



(8; R = Ph) (38)

ratios are about 5 : 1 (R^2 = Me) and 3 : 2 (R^2 = Ph). With a larger alkyl group at the γ-position [*e.g.* (39; R^1 = Pr^i or n-pentyl)], virtually no γ-addition occurs.[15]

In the smaller ring series, even with the cyclopentenyl compound (23; R = Me), we have already passed from almost complete α-addition (for the cyclohexenyl compound [7]) to almost complete γ-addition. Reaction of the anion of (23; R = Me) with carbon dioxide or benzaldehyde gave only the γ-adducts (42) and (43).

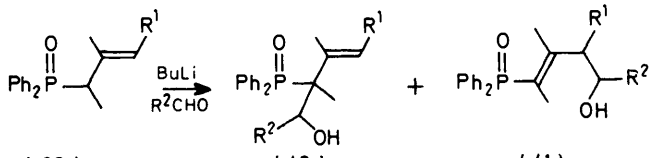
[13] E. E. Schweizer, J. G. Thompson, and T. A. Ulrich, *J. Org. Chem.*, 1968, **33**, 3082.

[14] E. J. Corey and J. I. Shulman, *J. Org. Chem.*, 1970, **35**, 777; D. R. Coulson, *Tetrahedron Letters*, 1964, 3323; G. Wittig, W. Böll, K-H. Krück, *Chem. Ber.*, 1962, **95**, 2514; G. Fodor and I. Tömösközi, *Tetrahedron Letters*, 1961, 579.

[15] A. H. Davidson and S. Warren, unpublished observations.

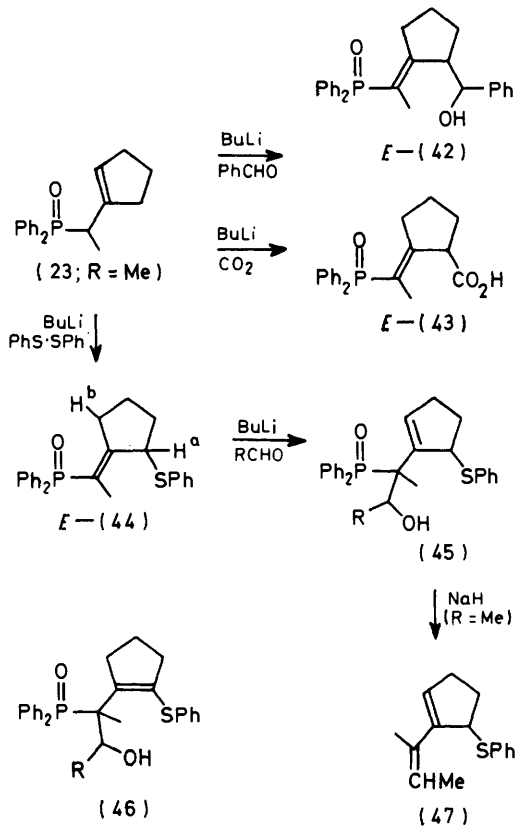
Only one geometrical isomer is formed in each case,* which we assume to be the *E*-isomer both on the basis of comparison with the sulphide *E*- (**44**) and because of the considerable steric crowding in the *Z*-series.

The γ-addition problem is one worth solving in this case in view of the importance of five-membered cyclic compounds, and we decided to try and overcome it by



(39) (40) (41)

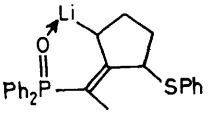
introducing an electrophile in the γ-position which would itself direct addition back to the α-position, and which could later be removed. We chose the phenylthio-group to fill this role on the grounds that the expected adduct (**44**) might then lose the proton [H^a in (**44**)] next to sulphur when treated with butyl-lithium and give the masked ketone (**46**) with an aldehyde. Reaction of the anion



(23; R = Me) *E*—(42) *E*—(43) *E*—(44) (45) (46) (47)

from (**23**; R = Me) with diphenyl disulphide did give a single sulphide which we showed to be *E*- (**44**) by n.m.r. spectroscopy in the presence of a shift reagent. A second treatment with butyl-lithium gave an anion which was quenched with acetaldehyde or benzaldehyde to give not the adduct (**46**) but instead (**45**) in rather low yield. Either (**46**) is too crowded, or else the intermediate lithium derivative (**48**) is stabilised by chelation of a type we have observed in other cases.[6] Though not the structure we had expected, (**45**) is nevertheless an α-adduct, and treatment [of (**45**; R = Me)] with sodium hydride gave a single isomer of the dienyl sulphide (**47**). Allyl sulphides have considerable potential in synthesis,[16] being synthons for allyl alcohols and hydroxy-carbonyl compounds.[17]

Conclusions.—The main limitations to our method are then (i) Ph_2PO migration no longer occurs when an



(48)

alternative tertiary migration origin is available in the molecule, and (ii) compounds with aryl groups at the migration terminus or small (four- or five-membered) rings at the migration origin tend to give vinyl- rather than allyl-phosphine oxides on rearrangement and to give γ- rather than α-addition when the anions of the rearranged allylphosphine oxides are added to carbonyl compounds. Neither limitation is very serious: the first excludes only a relatively obscure group of compounds and the second can to a certain extent be overcome. In the wide range of other structures we have now explored [2-7,9,12] all three conditions outlined at the start of this paper are satisfied.

EXPERIMENTAL

General spectroscopic and chromatographic details have been described previously.[6] R_F Values are given for development in ethyl acetate unless otherwise stated. All reactions with butyl-lithium were carried out under nitrogen. THF refers to tetrahydrofuran, distilled off lithium aluminium hydride immediately before use; TsOH refers to toluene-*p*-sulphonic acid monohydrate and TFA to trifluoroacetic acid. Petrol refers to light petroleum (b.p. 60—80 °C). N.m.r. signals marked with an asterisk belong to diastereotopic groups of protons. Except where otherwise stated, alkyldiphenylphosphine oxides were made by alkylation of triphenylphosphine and alkaline hydrolysis of the resulting phosphonium salt.[6,7,18]

2-Diphenylphosphinoyl-2-methyl-1-phenylpropan-1-ol (**7**; R = Ph). Isopropyldiphenylphosphine oxide (2 g) in dry ether (100 ml) was stirred with n-butyl-lithium (7 ml; 1.5M-solution in hexane) under nitrogen for 0.5 h. The solution was cooled to −78 °C and benzaldehyde (1.25 g) in dry ether was added over 10 min, discharging the red colour. The solution was allowed to warm to room temperature and water (100 ml) was added. The aqueous layer was extracted

* Though both diastereoisomers of *E*- (**42**) are formed.

[16] D. A. Evans and G. C. Andrews, *Accounts Chem. Res.*, 1974, **7**, 147.

[17] P. Brownbridge and S. Warren, *J.C.S. Chem. Comm.*, 1975, 820; *J.C.S. Perkin I*, 1977, 1131.

[18] K. Sasse in Houben-Weyl, 'Methoden der Organischen Chemie,' Stuttgart, 1963, vol. 12/1, pp. 144—150; L. Horner, H. Hoffmann, and H. G. Wippel, *Chem. Ber.*, 1958, **91**, 64.

with chloroform (3 × 50 ml) and the combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give the *alcohol* (7; R = Ph) (2 g, 70%), m.p. 225—228 °C (from EtOAc), R_F 0.4, $\nu_{max.}$ 3 300 (OH), 1 440 (PPh), and 1 150 cm^{-1} (P=O), τ ($CDCl_3$) 1.7—2.5 (10 H, m, Ph_2PO), 2.8 (5 H, s, Ph), 4.5 (1 H, s, OH), 5.1 (1 H, d, J_{PH} 10 Hz, PhC*H*OH), 8.8 (3 H, d, J_{PH} 16 Hz, $PCMe_2$*), and 9.0 (3 H, d, J_{PH} 16 Hz, $PCMe_2$*), *m/e* 350 (M^+, 1%), 242 ($Ph_2POCMe_2^+$, 100), and 201 (Ph_2PO, 50) (Found: C, 75.6; H, 6.5; P, 9.1. $C_{22}H_{23}O_2P$ requires C, 75.4; H, 6.6; P, 8.8%).

Trifluoroacetolysis of the Alcohol (7; R = Ph).—The alcohol (7; R = Ph) (270 mg) was kept at 70 °C in TFA (5 ml) for 20 min. The solution was poured into water (100 ml) and extracted with chloroform (3 × 25 ml). The extracts were washed with saturated sodium hydrogen carbonate solution (3 × 25 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give 3-*diphenylphosphinoyl*-2-*methyl*-3-*phenylpropene* (8; R = Ph) (250 mg, 98%), m.p. 190—192 °C (from EtOAc), R_F 0.5, $\nu_{max.}$ 1 440 (PPh) and 1 180 cm^{-1} (P=O), τ ($CDCl_3$) 2.0—2.9 (15 H, m, Ar), 4.6br (1 H, s, CH_2=C), 5.2br (1 H, s, CH_2=C), 5.9 (1 H, d, J_{PH} 8 Hz, PC*H*Ph), and 8.2 (3 H, s, *Me*C=CH_2), *m/e* 332 (M^+, 40%) and 201 (Ph_2PO, 100) (Found: C, 79.5; H, 6.5; P, 9.3. $C_{22}H_{21}OP$ requires C, 79.5; H, 6.3; P, 9.4%). Trifluoroacetolysis of the alcohol (7; R = Ph) (270 mg) under the same conditions as above for 36 h led to 1-*diphenylphosphinoyl*-2-*methyl*-1-*phenylpropene* (10; R = Ph) (240 mg, 90%), m.p. 130—132 °C (from EtOAc), R_F 0.2, $\nu_{max.}$ 1 615 (C=C), 1 440 (PPh), and 1 185 cm^{-1} (P=O), τ ($CDCl_3$) 2.1—3.2 (15 H, m, Ar), 7.7br (3 H, s, C=CMe_2), and 8.2br (3 H, s, C=CMe_2), *m/e* 332 (M^+, 70%) and 201 (Ph_2PO, 100) (Found: C, 79.3; H, 6.3; P, 9.2. $C_{22}H_{21}OP$ requires C, 79.5; H, 6.3; P, 9.4%).

Dehydration of the Alcohol (7; R = Ph) *in* 98% *Sulphuric Acid*.—The alcohol (7; R = Ph) (100 mg) was stirred at room temperature in 98% sulphuric acid (10 ml) for 15 min. The solution was then slowly poured into water (100 ml), and extracted with ether (3 × 50 ml). The extracts were washed with saturated sodium hydrogen carbonate solution (3 × 25 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give the vinylphosphine oxide (10; R = Ph) (90 mg, 91%).

Rearrangement of the Alcohol (7; R = Me) *with* TsOH.—The alcohol (7; R = Me) (100 mg) was heated under reflux in a Dean–Stark apparatus with TsOH (100 mg) for 10 h. The mixture was cooled and poured into ether (50 ml); the resulting solution was washed with saturated sodium hydrogen carbonate solution (3 × 25 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was recrystallised from ethyl acetate to give 3-diphenylphosphinoyl-2-methylbut-1-ene (8; R = Me) (80 mg, 79%), m.p. 112—114 °C (lit.,[4] 113—114 °C). Longer heating gives increasing amounts of 2-diphenylphosphinoyl-3-methylbut-2-ene (10; R = Me).

2-*Diphenylphosphinoyl*-2-*methylpentan*-3-*ol* (7; R = Et).—n-Butyl-lithium (4.4 ml; 1.8M-solution in hexane) was added dropwise to a stirred solution of diphenylisopropylphosphine oxide (2 g) in dry ether (100 ml) at room temperature. After 30 min, a solution of propionaldehyde (1 ml) in dry ether (25 ml) saturated with anhydrous lithium bromide was added dropwise over 10 min. Saturated aqueous ammonium chloride (30 ml) was added, and the aqueous layer was separated and extracted with ether (4 × 25 ml). The combined ether layers were dried ($MgSO_4$) and evaporated to give needles of the *alcohol* (7; R = Et) (1.32 g, 50%), m.p. 138—142 °C (from EtOAc), R_F 0.35, $\nu_{max.}$ ($CHCl_3$) 3 350 (OH), 1 439 (P–Ph), and 1 146 cm^{-1} (P=O), τ ($CDCl_3$) 1.8—2.7 (10 H, m, Ph_2PO), 4.83 (1 H, s, OH), 6.3 (1 H, ddd, J_{PH} 10, J_{HH} 7 and 5 Hz, PCC*H*CH_2*), 8.5—9.0 (2 H, m, CHCH_2*Me), 8.70 (3 H, d, J_{PH} 8 Hz, $PCMe_2$*), 8.97 (3 H, d, J_{PH} 10 Hz, $PCMe_2$*), and 9.02 (3 H, t, J_{PH} 7 Hz, CH_2*Me*), *m/e* 302 (M^+, 1%), 273 (M − Et, 17), 244 (M − C_3H_6O, 100), and 201 (Ph_2PO^+, 59) (Found: C, 71.3; H, 7.85; P, 10.3. $C_{18}H_{23}O_2P$ requires C, 71.5; H, 7.65; P, 10.2%).

Rearrangement of the Alcohol (7; R = Et) *with* TsOH.—The alcohol (7; R = Et) (150 mg) and TsOH (100 mg) were heated under reflux in dry benzene (30 ml) in a Dean–Stark apparatus for 6 days. The mixture was poured into ether (30 ml), and the resulting solution was washed with sodium hydrogen carbonate solution (2 × 20 ml), dried ($MgSO_4$), and evaporated to give 3-*diphenylphosphinoyl*-2-*methylpent*-1-*ene* (8; R = Et) (80 mg, 57%), m.p. 175—179 °C (from Pr^i_2O), R_F 0.4, $\nu_{max.}$ ($CHCl_3$) 1 640 (C=C), 1 439 (P–Ph), and 1 172 cm^{-1} (P=O), τ ($CDCl_3$) 1.9—2.8 (10 H, m, Ph_2PO), 5.08 and 5.16 (each 1 H, m, C=CH_2), 7.12 (1 H, ddd, J_{PH} 10, J_{HH} 4 and 8 Hz, PC*H*CH_2*), 7.9—8.5 (2 H, m, CH_2*Me), 8.25 (3 H, dd, J_{HH} 1 and 2 Hz, H_2C=C*Me*), and 8.08 (3 H, t, J_{HH} 8 Hz, CH_2*Me*), *m/e* 284 (M^+, 35%), 255 (M − Et, 18), and 201 (Ph_2PO^+, 201) (Found: C, 76.1; H, 8.6; P, 10.7. $C_{19}H_{21}OP$ requires C, 76.0; H, 7.45; P, 10.9%).

2-*Diphenylphosphinoyl*-2-*methylhexan*-3-*ol* (7; R = Pr^n).—This compound was prepared in the same way as (7; R = Et) from diphenylisopropylphosphine oxide (2 g) and n-butyraldehyde (1.5 ml) to give the *alcohol* (7; R = Pr^n) (0.75 g, 27%) after trituration with di-isopropyl ether; it had m.p. 112—114 °C (from EtOAc), R_F 0.32, $\nu_{max.}$ ($CHCl_3$) 3 340 (OH), 1 439 (P–Ph), and 1 144 cm^{-1} (P=O), τ ($CDCl_3$) 1.8—2.7 (10 H, m, Ph_2PO), 4.51 (1 H, s, OH), 6.2 (1 H, m, PCC*H*CH_2*), 8.1—8.9 (4 H, m, CHCH_2*CH_2*Me), 3.75 (3 H, d, J_{PH} 9 Hz, P*C*Me_2*), 8.85 (3 H, d, J_{PH} 10 Hz, P*C*Me_2*), and 9.15 (3 H, t, J_{HH} 7 Hz, CH_2*Me*), *m/e* 316 (M^+, 1%), 273 (M − Pr, 28), 244 (M − BuO, 100), and 201 (Ph_2PO^+, 39) (Found: C, 72.2; H, 8.2; P, 9.9. $C_{19}H_{25}O_2P$ requires C, 72.1; H, 8.0; P, 9.8%).

Rearrangement of the Alcohol (7; R = Pr^n) *with* TsOH.—The alcohol (7; R = Pr^n) (150 mg) and TsOH (100 mg) were heated under reflux in dry benzene (30 ml) in a Dean–Stark apparatus for 5 days. The mixture was poured into ether (30 ml), and the solution was washed with sodium hydrogen carbonate solution (2 × 20 ml), dried ($MgSO_4$), and evaporated to give needles of 3-*diphenylphosphinoyl*-2-*methylhex*-1-*ene* (8; R = Pr^n) (60 mg, 40%), m.p. 150—152 °C (from EtOAc), R_F 0.4, $\nu_{max.}$ ($CHCl_3$) 1 434 (P–Ph), and 1 168 cm^{-1} (P=O), τ ($CDCl_3$) 1.9—2.8 (10 H, m, Ph_2PO), 5.0—5.3 (2 H, m, C=CH_2), 6.98 (1 H, ddd, J_{PH} 11, J_{HH} 3 and 8 Hz, PC*H*CH_2*), 7.8—9.0 (4 H, m, PCCH_2*CH_2*Me), 8.25 (3 H, s with fine splitting, MeC=C), and 9.14 (3 H, t, J_{PH} 6 Hz, CH_2*Me*), *m/e* 298 (M^+, 35%), 269 (M − Et, 7), 255 (M − Pr, 21), and 201 (Ph_2PO^+, 100) (Found: C, 76.5; H, 7.75; P, 10.1. $C_{19}H_{23}OP$ requires C, 76.5; H, 7.77; P, 10.4%).

Rearrangement of the Alcohol (12; R = Me, X = H) *with* TsOH.—2-Diphenylphosphinoyl-2,4,4-trimethylpentan-3-ol [9,*] (150 mg) and TsOH (100 mg) were heated under reflux in dry benzene (30 ml) in a Dean–Stark apparatus for 24 h. The solution was poured into ether (30 ml) and the

* We previously reported [9] the m.p. of this alcohol as 98—99 °C, but both the old samples and those prepared for this work have in fact m.p. 124—127 °C (from EtOAc).

resulting solution washed with sodium hydrogen carbonate (2 × 20 ml), dried ($MgSO_4$), and evaporated. Preparative t.l.c. (elution with ethyl acetate) gave 4-diphenylphosphinoyl-2,3,4-trimethylpentan-2-ol [9] (14; R = Me) (38 mg, 27%), R_F 0.4; *4-diphenylphosphinoyl-2,3,4-trimethylpent-1-ene* (16) (75 mg, 50%), m.p. 145—147 °C (from EtOAc), R_F 0.45, τ ($CDCl_3$) 1.8—2.7 (10 H, m, Ph_2PO), 5.22br and 5.36br (each 1 H, s, H_2C=C), 7.2 (1 H, dq, J_{PH} 9, J_{HH} 7 Hz, PCC*H*Me), 8.29 (3 H, s, C=CMe), 8.64 (3 H, d, J_{PH} 16 Hz, $PCMe_2$*), 8.81 (3 H, d, J_{PH} 18 Hz, $PCMe_2$*), and 8.95 (3 H, d, J_{PH} 7 Hz, CH*Me*), *m/e* 312 (M^+, 25%), 297 (M − Me, 8), 243 (M − C_5H_9, 37), and 201 (Ph_2PO^+, 100) (Found: C, 76.6; H, 8.25; P, 9.7. $C_{20}H_{25}OP$ requires C, 76.9; H, 8.05; P, 9.9%); and *3-diphenylphosphinoyl-2,4,4-trimethylpent-1-ene* (15; R = Me) (25 mg, 18%), sublimes at 205—208 °C (from EtOAc), R_F 0.55, τ ($CDCl_3$) 1.9—2.8 (10 H, m, Ph_2PO), 4.5br (1 H, s, HC=C), 5.0br (1 H, s, HC=C), 7.2 (1 H, d, J_{PH} 8 Hz, PCH), 8.38br (3 H, s, C=CMe), and 8.92 (9 H, s, CMe_3), *m/e* 312 (M^+, 12%), 297 (M − Me, 6), 255 (M − Bu^t, 100), and 201 (Ph_2PO^+, 88) (Found: M^+, 312.1640. $C_{20}H_{25}OP$ requires M, 312.1642).

Rearrangement of the Alcohol (12; X = R = H) *in Acid.*—2-Diphenylphosphinoyl-2,4-dimethylpentan-3-ol [9] (12; X = R = H) (150 mg) and TsOH (100 mg) were heated in dry benzene (30 ml) under reflux in a Dean–Stark apparatus for 2 days. The solution was poured into ether and washed with sodium hydrogen carbonate solution (2 × 20 ml); the organic layer was separated, dried ($MgSO_4$), and evaporated *in vacuo* to give *3-diphenylphosphinoyl-2,4-dimethylpent-1-ene* (15; R = H) (90 mg, 60%), m.p. 176—178 °C (from Pr^i_2O), R_F 0.45, $\nu_{max.}$ ($CHCl_3$) 1 438 (PPh) and 1 198 cm^{-1} (P=O), τ ($CDCl_3$) 1.8—2.9 (10 H, m, Ph_2PO), 5.0br and 5.20br (each 1 H, s, H_2C=C), 7.25 (1 H, t, J_{HP} = J_{HH} = 7 Hz, PC*H*CH), 7.7 (1 H, m, C*H*Me_2), 8.42 (3 H, s, C=CMe), and 9.08 and 9.20 (each 3 H, d, J_{HH} 10 Hz, CHMe_2*), *m/e* 298 (M^+, 25%), 283 (M − Me, 5), 255 (M − Pr, 95), and 201 (Ph_2PO^+, 100) (Found: C, 76.5; H, 7.80; P, 20.2. $C_{19}H_{23}OP$ requires C, 76.5; H, 7.75; P, 10.4%).

2-Diphenylphosphinoyl-2-methylhex-4-en-3-ol (18; R = H).—n-Butyl-lithium (4.4 ml; 1.8M-solution in hexane) was added dropwise to a stirred solution of diphenyl isopropylphosphine oxide (2 g) in dry ether (100 ml) at room temperature. After 30 min a solution of crotonaldehyde (1 ml) in dry ether (20 ml) saturated with anhydrous lithium bromide was added dropwise over 10 min. Saturated ammonium chloride solution (50 ml) was added, the layers were separated, and the aqueous layer was extracted with ether (3 × 30 ml). The combined organic layers were dried ($MgSO_4$) and evaporated to give the *alcohol* (18; R = H) (0.74 g, 27%), m.p. 170—173 °C (from EtOAc), R_F 0.35, $\nu_{max.}$ ($CHCl_3$) 3 340 (OH), 1 439 (PPh), and 1 150 cm^{-1} (P=O), τ ($CDCl_3$) 1.8—2.6 (10 H, m, Ph_2PO), 4.2—4.7 (2 H, m, CHC*H*=C*H*Me), 4.76 (1 H, s, OH), 5.76 [1 H, dd, J_{PH} 11, J_{HH} 6 Hz, PCC*H*(OH)CH], 8.36 (3 H, d, J_{HH} 5 Hz, C=CH*Me*), and 8.73 and 8.89 (each 3 H, d, J_{PH} 16 Hz, $PCMe_2$*), *m/e* 314 (M^+, 1%), 244 (85), and 201 (Ph_2PO^+, 100) (Found: C, 72.3; H, 7.55; P, 9.8. $C_{19}H_{23}O_2P$ requires C, 72.6; H, 7.35; P, 9.9%).

Treatment of the Alcohol (18; R = H) *with* TsOH.—The alcohol (18; R = H) (150 mg) and TsOH (100 mg) were heated under reflux in dry benzene (20 ml) in a Dean–Stark apparatus for 1 h. The mixture was poured into ether (30 ml) and the solution was washed with sodium hydrogen carbonate solution (2 × 20 ml), dried ($MgSO_4$), and evaporated. Preparative t.l.c. (ethyl acetate) gave *5-diphenylphosphinoyl-5-methylhexa-1,3-diene* (20; R = H) (80 mg, 55%) as a gum, R_F 0.3, τ ($CDCl_3$) 1.8—2.8 (10 H, m, Ph_2PO), 3.4—4.2 and 4.6—5.9 (5 H, m, H_2C=C*H*·C*H*=C*H*), and 8.63 (6 H, d, J_{PH} 15 Hz, $PCMe_2$), *m/e* 296 (M^+, 33%), 281 (M − Me, 5), and 201 (Ph_2PO^+, 100) (Found: M^+, 296.1342. $C_{19}H_{21}OP$ requires M, 296.1329); and *3-diphenylphosphinoyl-2-methylhexa-1,4-diene* (21; R = H) (27 mg, 19%), m.p. 162—164 °C (from EtOAc), R_F 0.45, τ ($CDCl_3$) 2.0—2.8 (10 H, m, Ph_2PO), 4.1—4.9 (2 H, m, MeC*H*=C*H*), 5.06—5.22 (2 H, m, CH_2=C), 6.36 (1 H, t, J_{PH} = J_{HH} = 9 Hz, PC*H*CH), 8.22 (3 H, s, MeC=C), and 8.44 (3 H, t, J_{PH} = J_{HH} = 5 Hz, *Me*CH=CCP), *m/e* 296 (M^+, 37%), 281 (M − Me, 29), and 201 (Ph_2PO^+, 100) (Found: M^+, 296.1331. $C_{19}H_{21}OP$ requires M, 296.1329).

Equilibration of the Dienes (20; R = H) *and* (21; R = H).—The diene (20; R = H) (80 mg) was heated under reflux with TsOH (60 mg) in dry benzene in a Dean–Stark apparatus for 1 day. The mixture was worked up as above; t.l.c. and n.m.r. showed the presence of the dienes (20; R = H) and (21; R = H) in about a 4 : 1 ratio. The diene (21; R = H) (60 mg) was heated at 70 °C in TFA (0.5 ml) in an n.m.r. tube. Again both dienes (20; R = H) and (21; R = H) were present in about a 4 : 1 ratio.

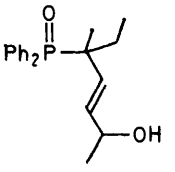
3-Diphenylphosphinoyl-3-methylhept-5-en-4-ol (18; R = Me).—n-Butyl-lithium (2.1 ml; 2.4M-solution in hexane) was added dropwise to a stirred solution of diphenyl-s-butylphosphine oxide [6] (1.3 g) in dry ether (50 ml) under dry nitrogen at 0 °C. After 30 min crotonaldehyde (0.7 ml) in dry ether (10 ml) was added dropwise over 5 min at 0 °C. The mixture was stirred for 10 min, then saturated ammonium chloride solution (20 ml) was added. The layers were separated and the aqueous layer was extracted with ether (3 × 20 ml). The ether layers were combined, dried ($MgSO_4$), and evaporated *in vacuo* to give the *alcohol* (18; R = Me) (0.89 g, 54%) as fine needles, m.p. 141—143 °C (from Pr^i_2O–EtOAc) (Found: C, 72.9; H, 7.75; P, 9.2, $C_{20}H_{25}O_2P$ requires C, 73.1; H, 7.65; P, 9.4%), R_F 0.45, τ ($CDCl_3$) 1.8—2.6 (10 H, m, Ph_2PO), 4.1—4.8 (2 H, m, CH=CH), 4.76 (1 H, d, J 5 Hz, CHO*H*), 5.5—5.9 (1 H, two m, C*H*OH), 7.8—8.3 (2 H, m, J 7 Hz and further splitting, CH_2Me), 8.36—8.5 (3 H, two d, J 5 Hz, *Me*CH=C), 8.55—8.85 (3 H, two d, J_{PH} 16 Hz, PCMe), and 9.1 (3 H, t, J 7 Hz, CH_2*Me*), *m/e* 329 (M + H, 15%), 328 (M^+, 11), 311 (M − OH, 11), 258 (M − C_4H_6O, 89), and 201 (Ph_2PO^+, 100).

Treatment of the Alcohol (18; R = Me) *with* TsOH *for* 45 *min*.—The alcohol (18; R = Me) (150 mg) and TsOH (100 mg) were heated together in benzene under reflux for 45 min. The mixture was poured into ether (30 ml) and the solution washed with sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated *in vacuo*. P.l.c. (EtOAc) yielded three products: (i) *4-diphenylphosphinoyl-3-methylhepta-2,5-diene* (21; R = Me), as needles (21 mg, 14%), m.p. 178—184 °C (from EtOAc) (Found: C, 77.1; H, 7.60; P, 9.7. $C_{20}H_{23}OP$ requires C, 77.4; H, 7.45; P, 10.0%), R_F 0.45, τ ($CDCl_3$) 2.0—2.7 (10 H, m, Ph_2PO), 4.0—4.9 (3 H, m, CH=CH and C=CH), 6.4 (1 H, t, J_{PH} 8.5, J_{HH} 8.5 Hz, PC*H*CH), and 8.2—8.6 (9 H, m, three Me), *m/e* 310 (M^+, 16%), 309 (M − H, 100), and 201 (Ph_2PO^+, 99); (ii) *5-diphenylphosphinoyl-5-methylhepta-1,3-diene* (20; R = Me), a gum (65 mg, 50%), R_F 0.4, τ (CCl_4) 2.0—2.9 (10 H, m, Ph_2PO), 3.4—4.0 (5 H, m, H_2C=CH·CH=CH), 7.8—8.3 (2 H, m, J 7 Hz and further splitting, PCCH_AH_BMe), 8.8 (3 H, d, J_{PH} 15 Hz, PCMe), and 9.25 (3 H, t, J 7 Hz, CH_2*Me*) (Found: M^+, 310.1494. $C_{20}H_{23}OP$ requires M, 310.1485), *m/e* 310 (50%),

295 (M − Me, 5), and 201 (Ph_2PO^+, 100); and (iii) a compound tentatively identified as the allylically rearranged alcohol, *5-diphenylphosphinoyl-5-methylhept-3-en-2-ol* (49) a gum (40 mg, 27%), R_F 0.3, τ (CCl_4) 1.8—2.8 (10 H, m, Ph_2PO), 4.27 (1 H, dd, J_{AB} 15, J 4 Hz, CH_A=CH_B), 4.65 (1 H, dt, J_{AB} 15, J 4 and 4 Hz, CH_A=CH_B), 5.2—5.8 (2 H, m, *CHOH*), 8.0—8.6 (2 H, m, J 7 Hz and further splittings $PCCH_2$*Me), 8.77 [3 H, d, J 5 Hz, CH(OH)*Me*], 8.85 (3 H, d, J_{PH} 16 Hz, POMe), and 9.25 (3 H, t and some further fine splitting, J 7 Hz, CH_2*Me*) (Found: M^+, 328.1592. $C_{20}H_{25}O_2P$ requires M, 328.1592), m/e 328 (1.5%), 327 (M − H, 3), 310 (M − H_2O, 18), 284 (M − C_2H_4O, 23), 202 (Ph_2POH^+, 100), and 201 Ph_2O^+, 46).

Treatment of the Alcohol (18; R = Me) *with* TsOH *for* 20 *h.*—The alcohol (18; R = Me) (150 mg) and TsOH were heated together in dry benzene under reflux (Dean–Stark head) for 20 h. The mixture was poured into ether (30 ml) and the solution was washed with sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated *in vacuo*. P.l.c. yielded the same products as above: (21; R = Me) (51 mg, 36%), (20; R = Me) (20 mg, 14%), and the alcohol (49) (8 mg, 5%).

Treatment of the Alcohol (18; R = Me) *with TFA*.—The alcohol (18; R = Me) (100 mg) was dissolved in neat TFA. The reaction was monitored by n.m.r. After 1½ h at 20 °C no apparent reaction had occurred. The mixture was heated to 70 °C for 4 h after which all starting material had been consumed. The mixture was poured into sodium hydrogen carbonate solution (30 ml), which was then



(49)

extracted with chloroform (3 × 30 ml). The extracts were dried ($MgSO_4$) and evaporated *in vacuo*. P.l.c. yielded compounds (21; R = Me) (35 mg, 37%) and (20; R = Me) (7 mg, 7.4%).

Cyclopentyldiphenylphosphine Oxide.—The Grignard route [19] was used. Diphenylphosphinic acid [20] (7.2 g, 0.03 mol) was heated under reflux in toluene with thionyl chloride (8 ml) for 1.5 h. The excess of thionyl chloride was removed with the toluene by evaporation under reduced pressure. The residue was dissolved in dry ether (70 ml) and added dropwise over 0.5 h to cyclopentylmagnesium bromide [from cyclopentyl bromide (7.3 g, 0.05 mol) and magnesium (1.18 g, 0.05 mol)] in ether (100 ml). The solution was heated under reflux for 2 h, cooled, and worked up with ammonium chloride solution. The layers were separated and the aqueous layer was washed with chloroform (3 × 50 ml). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was recrystallised from ethyl acetate to give the phosphine oxide (7.3 g, 82%), m.p. 128—129 °C (lit.,[21] 126—128°), R_F 0.27, $\nu_{max.}$ ($CHCl_3$) 1 440 (P–Ph) and 1 170 cm^{-1} (P=O) τ ($CDCl_3$) 2.3—2.6 (10 H, m, Ph_2PO), 7.3 (1 H, m, P–CH), and 8.25 (8 H, m, cyclopentyl ring), m/e 270 (M^+, 30%), 229 ($Ph_2PO{\cdot}CH_2{\cdot}CH_2^+$, 100), and 202 ($Ph_2POH$, 85).

(1-*Diphenylphosphinoylcyclopentyl*)*phenylmethanol* (22; R = Ph).—Cyclopentyldiphenylphosphine oxide (2 g, 7.4 mmol) in dry THF (50 ml) was stirred at −78 °C under nitrogen with n-butyl-lithium (3.4 ml; 2.4M in hexane) for 0.25 h. The deep red anion was quenched with benzaldehyde (0.4 ml, 4 mmol) and the solution allowed to warm to room temperature before the addition of water (1 ml). The solution was evaporated and the residue extracted from water (40 ml) with chloroform (3 × 30 ml). The extract was dried ($MgSO_4$) and evaporated under reduced pressure to give the *alcohol* (2.33 g, 84%), m.p. 240—241 °C (from toluene–petrol), R_F 0.52, $\nu_{max.}$ ($CHCl_3$) 3 400 (OH), 1 440 (P–Ph), and 1 150 cm^{-1} (P=O), τ ($CDCl_3$) 2.1—2.6 (10 H, m, Ph_2PO), 2.8 (5 H, m, PhC), 4.9 (1 H, d, J_{HP} 12 Hz, PCCH·O), 5.2 (1 H, s, OH), 7.7—8.2 (4 H, m, $PCCH_2$), and 8.9—9.1 (4 H, m, other ring protons), m/e 376 (M^+, 2%), 358 (M − H_2O, 13), 270 (M − PhCHO, 100), 229 ($Ph_2PO{\cdot}CH_2CH_2$, 80), and 202 (Ph_2POH, 90) (Found: C, 76.4; H, 6.8; P, 8.3. $C_{24}H_{25}O_2P$ requires C, 76.6; H, 6.7; P, 8.5%).

1-(*Diphenylphosphinoylbenzyl*)*cyclopentene* (23; R = Ph).—The alcohol (22; R = Ph) (0.5 g) was heated under reflux with TFA (10 ml) for 1 h. The solution was poured into water (50 ml) and the product extracted with chloroform (3 × 20 ml). The extracts were washed with sodium hydrogen carbonate solution (15 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give the *allylphosphine oxide* (425 mg, 90%), m.p. 282—283 °C (from EtOAc), R_F 0.54, $\nu_{max.}$ ($CHCl_3$) 1 440 (P–Ph) and 1 180 cm^{-1} (P=O), τ ($CDCl_3$) 2.1—2.6 (10 H, m, Ph_2P), 2.8 (5 H, m, PhC), 4.1 (1 H, m, CH=C), 5.71 (1 H, d, J_{PH} 8 Hz, PCH), 7.8 (4 H, m, allyl CH_2), and 8.3 (2 H, quintet, J_{HH} 6 Hz, non-allylic CH_2), m/e 358 (M^+, 100%) and 201 (Ph_2PO, 48) (Found: C, 80.4; H, 6.45; P, 8.3. $C_{24}H_{23}OP$ requires C, 80.4; H, 6.45; P, 8.6%).

Solvolysis of the Alcohol (22; R = Ph) *in* TsOH. The alcohol (22; R = Ph) (0.5 g, 1.3 mmol) and TsOH (0.7 g, 3.6 mmol) were heated together under reflux in dry benzene in a Dean–Stark apparatus for 16 h. The solution was poured into aqueous sodium hydrogen carbonate (50 ml), the layers were separated, and the aqueous layer was extracted with chloroform (3 × 20 ml). The organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give a mixture of the vinyl- (24; R = Ph) and allyl- (23; R = Ph) phosphine oxides (9 : 1 by t.l.c.). The vinylphosphine oxide was separated by preparative t.l.c. (ethyl acetate as eluant; R_F 0.40) but on recrystallisation from di-isopropyl ether, it equilibrated to a mixture of the vinyl- and allyl-phosphine oxides (9 : 1) (400 mg, 84%), m.p. 137—140 °C, τ ($CDCl_3$) 2.5—3.2 (15 H, m, Ph_2P and PhC), 4.15 (m, from allyl isomer), 5.72 (d, from allyl isomer), 7.3 (2 H, m, allyl CH_2), 7.75 (2 H, m, allyl CH_2), and 8.35 (4 H, m, non-allylic ring protons), m/e 358 (M^+, 100%) and 201 (Ph_2PO, 30). When the allylphosphine oxide (23; R = Ph) was treated under the same conditions (3 equiv. of TsOH in benzene under reflux for 18 h) it was converted into the same equilibrium mixture (9 : 1 vinyl : allyl).

1-(1-*Diphenylphosphinoylcyclopentyl*)*ethanol* (22; R = Me). Cyclopentyldiphenylphosphine oxide (1 g, 3.7 mmol) was stirred at −78 °C under nitrogen in dry THF with n-butyl-lithium (2.3 ml; 1.8M in hexane) for 0.25 h. The red anion was titrated with a solution of acetaldehyde in dry THF saturated with anhydrous lithium bromide until the colour changed to pale yellow. After allowing the mixture to warm to room temperature, water (1 ml) was

[19] D. C. Morrison, *J. Amer. Chem. Soc.*, 1950, **72**, 4820.

[20] B. B. Hunt and B. C. Saunders, *J. Chem. Soc.*, 1957, 2413.

[21] M. Epstein and S. A. Buckler, *Tetrahedron*, 1962, **18**, 1231.

added and the solution evaporated under reduced pressure. The residue was dissolved in water (20 ml) and extracted with chloroform (3 × 20 ml). The extracts were dried ($MgSO_4$)and evaporated to give the *alcohol* (0.96 g, 83%), m.p. 164—165 °C (from ethyl acetate–petrol), R_F 0.25, $\nu_{max.}$ ($CHCl_3$) 3 350 (OH), 1 440 (P–Ph), and 1 150 cm^{-1} (P=O), τ ($CDCl_3$) 2.1—2.5 (10 H, m, Ph_2PO), 4.95 (1 H, s, OH), 5.7 (1 H, m, PC·C*H*Me), 7.8—9.1 (8 H, m, cyclopentyl ring), and 8.90 (3 H, d, J_{HH} 6 Hz, *Me* CH), *m/e* 314 (M^+, 7%), 296 ($M - H_2O$, 5), 270 (M − MeCHO, 85), and 202 (Ph_2POH, 100) (Found: C, 72.4; H, 7.4; P, 9.7. $C_{19}H_{23}O_2P$ requires 72.6; H, 7.4; P, 9.85%).

Solvolysis of the Alcohol (22; R = Me) *in* TsOH.—The alcohol (22; R = Me) (350 mg, 1.1 mmol) and TsOH (425 mg, 2.2 mmol) were heated together in dry benzene under reflux in a Dean–Stark apparatus for 18 h. The solution was poured into aqueous sodium hydrogen carbonate (50 ml) and the resulting solution extracted with chloroform (3 × 30 ml). The extract was dried ($MgSO_4$) and evaporated under reduced pressure to give an oily mixture of the vinyl- (24; R = Me) and allyl- (23; R = Me) phosphine oxides (yields of isolated material 1 : 2.5). These were separated by preparative t.l.c. (ethyl acetate). The higher R_F isomer was 1-(1-*diphenylphosphinoylethyl*)*cyclopentene* (23; R = Me) (170 mg, 52%), m.p. 132—133 °C (from cyclohexane), R_F 0.40, $\nu_{max.}$ ($CHCl_3$) 1 440 (P–Ph) and 1 175 cm^{-1} (P=O), τ ($CDCl_3$) 2.2—2.6 (10 H, m, Ph_2PO), 4.5 (1 H, m, CH=C), 6.7 (1 H, m, PC*H*Me), 7.8 (4 H, m, allyl CH_2 in ring), 8.25 (2 H, quintet, J_{HH} 7 Hz, non-allylic CH_2 in ring), and 8.65 (3 H, dd, J_{HP} 16, J_{HH} 6 Hz, PCH*Me*), *m/e* 296 (M^+, 58%) and 201 (Ph_2PO, 100) (Found: M^+, 296.1324. $C_{19}H_{21}OP$ requires M, 296.1329). The lower R_F isomer was 1-(1-*diphenylphosphinoylethylidene*)*cyclopentane* (24; R = Me) (65 mg, 20%), obtained as an oil, R_F 0.25, $\nu_{max.}$ ($CHCl_3$) 1 615 (C=C), 1 440 (P–Ph), and 1 160 cm^{-1} (P=O), τ ($CDCl_3$) 2.0—2.8 (10 H, m, Ph_2PO), 7.3—7.8 (4 H, m, allyl CH_2), and 8.2—8.5 (7 H, m, non-allylic CH_2 and MeCP), *m/e* 296 (M^+, 80%), 295 (M − H, 100), and 202 (Ph_2POH, 100) (Found: M^+, 296.1329. $C_{19}H_{21}OP$ requires M, 296.1329).

(1-*Diphenylphosphinoylcyclobutyl*)*phenylmethanol* (26).—Cyclobutyldiphenylphosphine oxide [13] (25) (0.6 g, 2.3 mmol) was stirred at −78 °C under nitrogen in dry THF (30 ml) with n-butyl-lithium (1.45 ml; 1.8M in hexane) for 0.2 h. The red anion was quenched with benzaldehyde (0.26 ml, 2.6 mmol); the mixture was stirred at −78 °C for a further 0.2 h and then poured into aqueous ammonium chloride (50 ml). The layers were separated, the aqueous layer was washed with chloroform (3 × 30 ml), and the combined organic layers were dried ($MgSO_4$) and evaporated to give the *alcohol* (0.4 g, 58%), m.p. 175—178° (from EtOAc–petrol), R_F 0.40, ν_{max} 3 350 (OH), 1 440 (P–Ph), and 1 150 cm^{-1} (P=O), τ ($CDCl_4$) 2.1—2.8 (15 H, m, Ph_2PO and PhC), 4.75 (1 H, d, J_{PH} 12 Hz, PCCH·O), 5.02 (1 H, s, OH), 7.1—8.2 (4 H, m, CH_2 next to P·C), and 8.92 (2 H, quintet, J_{HH} 8 Hz, other CH_2 in ring), *m/e* 362 (M^+, 1%), 255 (M − PhCHOH, 48), and 201 (Ph_2PO, 100) (Found: C, 76.1; H, 6.5; P, 8.2. $C_{23}H_{23}O_2P$ requires C, 76.2; H, 6.4; P, 8.5%).

1-(α-*Diphenylphosphinoylbenzyl*)*cyclobutene* (27).—The alcohol (26) (0.8 g) was heated under reflux in TFA (15 ml) for 0.4 h, and the product was poured into water (50 ml). The solution was extracted with chloroform (3 × 30 ml); the extracts were washed with aqueous sodium hydrogen carbonate (20 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give a cream-coloured solid. Recrystallisation from di-isopropyl ether gave the *cyclobutene* (300 mg, 40%), m.p. 193—197 °C, R_F 0.47, $\nu_{max.}$ ($CHCl_3$) 1 435 (P–Ph) and 1 175 cm^{-1} (P=O), τ ($CDCl_3$) 2.0—2.8 (15 H, m, Ph_2PO and PhC), 4.2 (1 H, d, J_{HP} 3 Hz, vinyl H), 5.67 (1 H, d, J_{PH} 10 Hz, CHP), and 7.4—7.8 (4 H, m, cyclobutene ring), *m/e* 344 (M^+, 35%) 299 ($Ph_2PO{\cdot}CH_2{\cdot}CH_2$, 45), and 201 ($Ph_2PO$, 100) (Found: C, 78.4; H, 6.2; P, 8.5%; M^+ 344.1333. $C_{23}H_{21}OP,0.5H_2O$ requires C, 78.2; H, 6.3; P, 8.75%. $C_{23}H_{21}OP$ requires M, 344.1329). The mother liquor contained mainly starting material and the vinylphosphine oxide (28).

1-(α-*Diphenylphosphinoylbenzylidene*)*cyclobutane* (28).—The alcohol (26) (100 mg) was heated under reflux with TFA (3 ml) for 18 h, and the product was poured into aqueous sodium hydrogen carbonate. The solution was extracted with chloroform (3 × 10 ml); the extracts were dried ($MgSO_4$) and evaporated to give a yellow oil. Preparative t.l.c. (ethyl acetate) gave the *cyclobutane* (28) (26 mg, 27%) as an oil, R_F 0.29, $\nu_{max.}$ ($CHCl_3$) 1 630 (C=C), 1 435 (P–Ph), and 1 165 cm^{-1} (P=O), τ ($CDCl_3$) 2.2—2.8 (10 H, m, Ph_2PO), 2.9 (5 H, m, PhC), 7.1—7.4 (4 H, m, allyl CH_2 in ring), and 8.06 (2 H, quintet, J_{HH} 7 Hz, non-allylic CH_2), *m/e* 344 (M^+, 83%) and 201 (Ph_2PO, 100) (Found: M^+, 344.1314. $C_{23}H_{21}OP$ requires M, 344.1329). None of the cyclobutene (27) was present, The only other identified product was a small amount of the diene (29).

4-(α-*Diphenylphosphinoylbenzyl*)*cyclohex-4-ene-1,2-dicarboxylic Anhydride* (30).—The cyclobutene (29) (250 mg) and maleic anhydride (108 mg) were heated together under reflux under nitrogen in xylene (15 ml) for 18 h. After removal of the solvent, recrystallisation of the residue (chloroform–petrol) gave the *maleic anhydride adduct* (30) (141 mg, 44%), m.p. 260—265 °C, R_F 0.05, $\nu_{max.}$ ($CHCl_3$) 1 845 and 1 780 (C=O), 1 440 (P–Ph), and 1 175 cm^{-1} (P=O), τ [$(CD_3)_2SO$] 2.0—3.0 (15 H, m, Ph_2PO and PhC), 3.7—3.9 (1 H, m, vinyl H), 5.28 (1 H, d, J_{HP} 9 Hz, PCH), 6.5—6.8 (4 H, m, allyl CH_2), and 7.6—7.9 (2 H, m, CH–C=O), *m/e* 442 (M^+, 19%), 344 (M − maleic anhydride, 9), 219 (56), and 201 (Ph_2PO, 100) (Found: M^+, 442.1336. $C_{27}H_{23}O_4P$ requires M, 442.1333).

3-*Diphenylphosphinoyl-2-methylbut-1-ene* (8; R = Me) via *the Tertiary Alcohol* (32; R^1 = H, R^2 = R^3 = Me).—Ethyldiphenylphosphine oxide (500 mg) in dry ether (50 ml) was stirred with n-butyl-lithium (2 ml; 1.5M in hexane) under nitrogen for 30 min. The solution was cooled to −78 °C and acetone (200 mg) in dry ether (25 ml) was added over 10 min. The solution was allowed to warm to room temperature, water (100 ml) was added, and the aqueous layer was extracted with chloroform (3 × 50 ml). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give a white solid (the tertiary alcohol) which was heated under reflux in TFA (20 ml) for 20 min. The solution was poured into water (100 ml) and extracted with chloroform (3 × 25 ml). The extracts were washed with saturated sodium hydrogen carbonate solution (3 × 25 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give the allylphosphine oxide (8; R = Me) (500 mg, 75%), m.p. 112—114 °C (lit.,[4] 113—114 °C).

3-*Diphenylphosphinoyl-2-methylpentan-2-ol* (33; R = Et).—Diphenylpropylphosphine oxide [22] (5 g, 0.021 mol) was stirred at −78 °C in dry THF with n-butyl-lithium (13 ml; 1.8M in hexane) for 0.2 h. The solution was quenched with acetone (1.73 ml, 0.023 mol) and after stirring at −78 °C for a further 0.2 h was poured into aqueous ammonium chloride. The layers were separated, and the aqueous

[22] S. Trippett, *J. Chem. Soc.*, 1961, 2813.

layer was extracted with chloroform (3 × 40 ml). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give the *alcohol* (33; R = Et) (5.0 g, 80%), m.p. 158—160 °C (from EtOAc), R_F 0.32, $\nu_{max.}$ ($CHCl_3$) 3 350 (OH), 1 435 (P–Ph), and 1 170 cm^{-1} (P=O), τ ($CDCl_3$) 2.0—2.5 (10 H, m, Ph_2PO), 5.04 (1 H, s, OH), 7.6 (1 H, m, PCH), 8.1—8.5 (2 H, m, CH_2CP), 8.66 and 8.72 (each 3 H, s, CMe_2*), and 9.2 (3 H, t, J_{HH} 7 Hz, $CH_3{\cdot}CH_2$), *m/e* 302 (M^+, 1%), 287 ($M - H_2O$, 20), 244 (Ph_2POPr, 48), 229 ($Ph_2PO{\cdot}CH_2{\cdot}CH_2$, 100), and 201 ($Ph_2PO$, 60) (Found: C, 71.5; H, 7.6; P, 10.0. $C_{18}H_{23}O_2P$ requires C, 71.5; H, 7.7; P, 10.2%).

3-*Diphenylphosphinoyl*-2-*methylpent*-1-*ene* (8; R = Et).—The alcohol (33; R = Et) (4.5 g) was heated under reflux in TFA (25 ml) for 0.3 h. The solution was poured into aqueous sodium hydrogen carbonate (100 ml) and extracted with chloroform (3 × 40 ml). The extracts were dried ($MgSO_4$) and evaporated to give the allylphosphine oxide (8; R = Et) (3.67 g, 87%) (from EtOAc–petrol).

1-(1-*Diphenylphosphinoylethyl*)*cyclopentanol* (34).—Ethyldiphenylphosphine oxide (5 g, 22 mmol) was stirred at −78 °C in dry THF (50 ml) with n-butyl-lithium (10 ml, 2.4M in hexane) for 0.2 h. The red anion was quenched with freshly distilled cyclopentanone (1.4 ml, 24 mmol), the mixture was allowed to warm to room temperature, and water (1 ml) was added. The solvent was removed under reduced pressure and the residue extracted from water (50 ml) with chloroform (3 × 40 ml). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the *alcohol* (34) (5.6 g, 82%), m.p. 165—166 °C (from EtOAc), R_F 0.48, $\nu_{max.}$ ($CHCl_3$) 3 360 (OH), 1 440 (P–Ph), and 1 160 cm^{-1} (P=O), τ ($CDCl_3$) 2.2—2.6 (10 H, m, Ph_2PO), 5.5 (1 H, s, OH), 7.6 (1 H, quintet, $J_{HP} = J_{HH} = 7$ Hz, PC*H*CH_3), 8.0—8.9 (8 H, m, cyclopentyl ring), and 8.80 (3 H, dd, J_{HP} 17, J_{HH} 7 Hz, PCH·C*H*$_3$), *m/e* 314 (M^+, 27%), 296 ($M - H_2O$, 15), 230 (Ph_2POEt, 60), and 202 (Ph_2POH, 100) (Found: C, 72.7; H, 7.3; P, 9.6. $C_{19}H_{23}O_2P$ requires C, 72.6; H, 7.4; P, 9.85%).

1-(1-*Diphenylphosphinoylethyl*)*cyclopentene* (23; R = Me).—The alcohol (34) (1 g) was heated under reflux in TFA (10 ml) for 0.2 h, and the product was poured into water and extracted with chloroform (3 × 20 ml). The extracts were washed with aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated under reduced pressure to give the allylphosphine oxide (23; R = Me) (0.86 g, 90%) (from cyclohexane).

4-*Diphenylphosphinoyl*-3-*methyl*-1,4-*diphenylbut*-3-*en*-1-*ol* (38).— 3-Diphenylphosphinoyl-3-phenyl-2-methylpropene (8; R = Ph) (250 mg) in dry ether (50 ml) was stirred with n-butyl-lithium (1 ml; 1.5M in hexane) under nitrogen for 0.5 h. The solution was cooled to −78 °C and benzaldehyde (80 mg) in dry ether (10 ml) was added over 10 min. The solution was allowed to warm to room temperature and water (50 ml) was added. The aqueous layer was extracted with chloroform (3 × 25 ml), and the combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give the *alcohol* (38) (180 mg, 55%), m.p. 154—157° (from EtOAc), R_F 0.7, $\nu_{max.}$ 3 250 (OH), 1 160 (C=C), 1 440 (PPh), and 1 150 cm^{-1} (P=O), τ ($CDCl_3$) 3.0—3.2 (20 H, m, Ar), 4.0 (1 H, s, OH), 5.0 (1 H, dd, J_{HH} 10, 3 Hz, PhC*H*OH), 6.2—6.5 (1 H, t, J_{AX} 10, J_{AB} 10 Hz, CH_AH_B-CH_XOH), 7.5 (1 H, dd, J_{BX} 3, J_{AB} 10 Hz, $CH_AH_BCH_X$OH), and 8.2br (3 H, s, *Me*CCH_2), *m/e* 438 (M^+, 6%), 421 (M − OH, 100), 331 (M − PhCHOH, 80), and 201 (Ph_2PO, 50) (Found: C, 79.6; H, 6.4; P, 6.9. $C_{29}H_{27}O_2P$ requires C, 79.5; H, 6.2; P, 7.1%).

Reaction of Benzaldehyde with the Allylphosphine Oxide (39; R^1 = Me).—The allylphosphine oxide (39; R^1 = Me) (475 mg) was stirred in dry ether (50 ml) with n-butyllithium (1.1 ml; 1.5M in hexane) under nitrogen for 0.5 h. The solution was cooled to −78 °C and benzaldehyde (160 mg) in dry ether (25 ml) was added, discharging the red colour. The solution was allowed to reach room temperature and water (50 ml) was added. The aqueous layer was extracted with chloroform (3 × 25 ml) and the combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure. The resulting oil contained four compounds which were separated by p.l.c. (ethyl acetate) to give the high R_F diastereoisomer of 2-*diphenylphosphinoyl*-2,3-*dimethyl*-1-*phenylpent*-3-*en*-1-*ol* (40; R^1 = Me, R^2 = Ph) (60 mg, 10%), an oil, R_F 0.8, $\nu_{max.}$ 3 300 (OH), 1 435 (PPh), and 1 150 cm^{-1} (P=O), τ ($CDCl_3$) 2.0—2.6 (10 H, m, Ph_2PO), 2.85 (5 H, s, Ph), 3.5 (1 H, s, OH), 4.5 (1 H, m, CH=C), 4.8 (1 H, d, J_{PH} 7 Hz, PhC*H*OH), 8.2 (3 H, s, *Me*C=CH), 8.5br (3 H, d, C=CH*Me*), and 9.0 (3 H, d, J_{HH} 18 Hz, PCMe), *m/e* 390 (M^+, 0.5%), 372 ($M - H_2O$, 5), 284 (M − PhCO, 100), and 201 (Ph_2PO, 50) (Found: M^+, 390,1743. $C_{25}H_{27}O_2P$ requires M, 390.1748); the low R_F diastereoisomer of 2-*diphenylphosphinoyl*-2,3-*dimethyl*-1-*phenylpent*-3-*en*-1-*ol* (40; R^1 = Me, R^2 = Ph) (160 mg, 25%), m.p. 195—197° (from EtOAc), R_F 0.7, $\nu_{max.}$ 3 300 (OH), 1 435 (PPh), and 1 150 cm^{-1} (P=O), τ ($CDCl_3$) 2.0—2.6 (10 H, m, Ph_2PO), 2.8 (5 H, s, Ph), 4.3 (1 H, d, J_{PH} 7 Hz, PC*H*OH), 4.8 (1 H, m, OH), 4.9br (1 H, quintet, $J_{PH} = J_{HH} = 6$ Hz, MeC*H*=C), 8.6 (3 H, t, $J_{PH} = J_{HH} = 6$ Hz, C=CH*Me*), 8.7 (3 H, s, HC=C*Me*), and 8.75 (3 H, d, J_{PH} 18 Hz, PCMe), *m/e* 390 (M^+, 0.3%), 372 ($M - H_2O$, 7), 284 (M − PhCHO, 100), and 201 (Ph_2PO, 50) (Found: C, 76.6; H, 7.0; P, 8.2. $C_{25}H_{27}O_2P$ requires C, 76.9; H, 6.9; P, 8.0%); the high R_F diastereoisomer of 4-*diphenylphosphinoyl*-2,3-*dimethyl*-1-*phenylpent*-3-*en*-1-*ol* (41; R^1 = Me, R^2 = Ph) (60 mg, 10%), m.p. 175—176° (from EtOAc), R_F 0.25, $\nu_{max.}$ 3 300 (OH), 1 440 (PPh), and 1 160 cm^{-1} (P=O), τ ($CDCl_3$) 2.2—2.6 (10 H, m, Ph_2PO), 2.65 (5 H, s, Ph), 5.45 (1 H, d, J_{HH} 9 Hz, PhC*H*OH), 6.8 (2 H, m, OH, and MeC*H*), 7.95br (3 H, s, PC=C*Me*), 8.3br (3 H, d, J_{PH} 14 Hz, PCMe), and 9.25 (3 H, d, J_{HH} 7 Hz, CH*Me*), *m/e* 390 (M^+, 12%), 372 ($M - H_2O$, 25), 284 (M − PhCHO, 100), and 201 (Ph_2PO, 100) (Found: M^+, 390,1747. $C_{25}H_{27}O_2P$ requires M 390.1748), and the low R_F diastereoisomer of 4-*diphenylphosphinoyl*-2,3-*dimethyl*-1-*phenylpent*-3-*en*-1-*ol* (41; R^1 = Me, R^2 = Ph) (70 mg, 12%), m.p. 164—166° (from EtOAc), R_F 0.12, $\nu_{max.}$ 3 300 (OH), 1 440 (PPh), and 1 160 cm^{-1} (P=O), τ ($CDCl_3$) 2.5—3.0 (10 H, m, Ph_2PO), 2.65 (5 H, s, Ph), 5.45 (1 H, d, J_{HH} 9 Hz, PhC*H*OH), 6.7 (1 H, overlapping d q, J_{HH} 9 and 7 Hz, MeC*H*), 8.1br (3 H, s, PC=CMe), 8.55br (1 H, d, J_{PH} 14 Hz, PCMe), and 8.75 (3 H, d, J_{HH} 7 Hz, CH*Me*), *m/e* 390 (M^+, 2%), 372 ($M - H_2O$, 10), 284 (M − PhCHO, 60), and 201 (Ph_2PO, 100) (Found: C, 77.1; H, 7.05; P, 7.9. $C_{25}H_{27}O_2P$ requires C, 76.9; H, 6.9; P, 8.0%).

5-*Diphenylphosphinoyl*-3,4-*dimethylhex*-4-*en*-2-*ol* (41; R^1 = R^2 = Me).—The preparation of 4-diphenylphosphinoyl-3-methylpent-2-ene (39; R^1 = Me), its addition to acetaldehyde, and the characterisation of the two α-adducts (40; R^1 = R^2 = Me) have already been reported.[6] Also formed was one diastereoisomer of the *γ-adduct* (41; R^1 = R^2 = Me) (350 mg, 12%), m.p. 150—152 °C (from EtOAc), R_F 0.2, $\nu_{max.}$ 3 300 (OH), 1 435 (PPh), and 1 160 cm^{-1} (P=O), τ ($CDCl_3$) 2.1—2.8 (10 H, m, Ph_2PO), 6.2 (1 H, overlapping dq, J_{HH} 8 and 6 Hz, C*H*OH), 7.3br (1 H,

quintet, J_{HH} 8 Hz, MeC*H*CHOH), 8.0br (3 H, s, PC=CMe), 8.3 (3 H, dd, J_{PH} 14, J_{HH} 1 Hz, PCMe), 8.75 (3 H, d, J_{HH} 6 Hz, CHOH*Me*), and 9.0 (3 H, d, J_{HH} 8 Hz, CH*Me*), *m/e* 328 (M^+, 60%), 284 (M − MeCHO), and 201 (Ph_2PO, 100) (Found: C, 72.9; H, 7.8; P, 9.4. $C_{20}H_{25}O_2P$ requires C, 73.2; H, 7.6; P, 9.45%).

(E)-2-(1-*Diphenylphosphinoylethylidene*)*cyclopentanecarboxylic Acid* (**43**).—The olefin (**23**; R = Me) (1 g, 3.4 mmol) was stirred at −78 °C in dry THF (40 ml) with n-butyl-lithium (2.1 ml, 1.8M in hexane) for 0.3 h. The deep red anion was quenched by bubbling an excess of dry carbon dioxide through the solution, and allowing to warm to room temperature in an atmosphere of carbon dioxide. After addition of water (2 ml), the solvent was removed under reduced pressure and the residue extracted with chloroform (3 × 30 ml) from dilute hydrochloric acid (30 ml). The organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the *acid* (**43**) (0.91 g, 81%), m.p. 196—200 °C (decomp.) (from chloroform–petrol), R_F (EtOH) 0.35, $\nu_{max.}$ ($CHCl_3$) 3 100–2 500 (OH), 1 705 (C=O), 1 620 (C=C), 1 440 (P–Ph), and 1 150 cm^{-1} (P=O), τ ($CF_3{\cdot}CO_2H$) 2.2—2.7 (10 H, m, Ph_2P), 6.0 (1 H, m, C*H*·CO_2H), 7.5—8.3 (6 H, m, ring protons), and 8.06 (3 H, d, J_{PH} 15 Hz, CH_3CP), *m/e* 340 (M^+, 13%), 322 (M − H_2O, 12), 296 (M − CO_2, 100), and 202 (Ph_2POH, 98) (Found: M^+, 340.1206. $C_{20}H_{21}O_3P$ requires M, 340.1227).

(E)-2-(1-*Diphenylphosphinoylethylidene*)*cyclopentyl*-(*phenyl*)*methanol* (**42**).—The olefin (**23**; R = Me) (0.5 g, 1.7 mmol) was stirred at −78 °C in dry THF (40 ml) with n-butyl-lithium (1.2 ml; 1.8M in hexane) for 0.3 h. The deep red anion was quenched with benzaldehyde (0.2 ml, 3 mmol), and the mixture was allowed to warm to room temperature. After addition of water (1 ml) the solvent was evaporated off under reduced pressure and the residue was extracted from water (30 ml) with chloroform (3 × 30 ml). The organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give a yellow oil, which crystallised on scratching with ethyl acetate to give the *alcohol* (**42**) (0.34 g, 50%) as a mixture of diastereoisomers, m.p. 205—210 °C (from toluene–petrol), R_F 0.21, $\nu_{max.}$ ($CHCl_3$) 3 300 (OH), 1 615 (C=C), 1 440 (P–Ph), and 1 160 cm^{-1} (P=O), τ ($CDCl_3$) 2.2—2.8 (15 H, m, Ph_2P and PhC), 5.05 and 5.36 (1 H, each d, J_{HH} 5 and 8 Hz, CH·C*H*Ph), 6.16 (1 H, s, OH), 6.7—6.9 (1 H, m, C*H*·CHPh), 7.2—8.7 (6 H, m, ring protons), and 8.15 and 8.6 (3 H, each d, J_{PH} 13 and 14 Hz, MeCP), *m/e* 402 (M^+, 7%), 384 (M − H_2O, 14), 296 (M − PhCHO, 100), and 202 (Ph_2POH, 87) (Found: C, 77.55; H, 6.9; P, 7.35. $C_{26}H_{27}O_2P$ requires C, 77.6; H, 6.8; P, 7.7).

(E)-1-(1-*Diphenylphosphinoylethylidene*)-2-*phenylthiocyclopentane*, *E*-(**44**).—The olefin (**23**; R = Me) (2 g, 6.8 mmol) was stirred at −78 °C in dry THF (30 ml) with n-butyl-lithium (4 ml; 1.8M in hexane) for 0.3 h. The deep red anion was added to diphenyl disulphide (1.62 g, 7.4 mmol) in dry THF (30 ml) at −78 °C, and the mixture was allowed to warm to room temperature and poured into aqueous sodium hydrogen carbonate. The layers were separated, and the aqueous layer was extracted with chloroform (3 × 30 ml). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the *allyl sulphide*, *E*-(**44**) (1.98 g, 73%), m.p. 116—117° (from cyclohexane), R_F (EtOAc) 0.24, $\nu_{max.}$ 1 620 (C=C), 1 440 (P − Ph), and 1 160 cm^{-1} (P=O), τ ($CDCl_3$) 2.2—2.8 (15 H, m, Ph_2P and PhS), 5.6 (1 H, m, SCH), 7.4 (2 H, m, CH_2·C=), 7.9—8.4 (4 H, m, other ring protons), and 8.17 (3 H, d, J_{HP} 15 Hz, MeCP), *m/e* 404 (M^+, 58%), 295 (M − PhS, 96), 201 (Ph_2PO, 66), and 185 (Ph_2P, 100) (Found: C, 74.4; H, 6.5; P, 7.25. $C_{25}H_{25}OPS$ requires C, 74.2; H, 6.2; P, 7.6%). Shift-reagent experiments confirmed the configuration as *E*. Trisdipivaloylmethanatoeuropium, $Eu(dpm)_3$, was added to a solution of (**44**) in $CDCl_3$ so that the ratio of shift reagent to substrate increased in steps of 0.25. The observed shifts of each set of protons were extrapolated to a molar ratio of 1.0 to give the lanthanide-induced shift (LIS) values shown in the Table. It is assumed that the europium atom binds to the phosphinoyl oxygen.[23]

Proton [in (**44**)]	Chemical shift (τ)	LIS value (p.p.m.)
H^a	5.6	2.4
H^b	7.4	4.0
PhS	2.7	0.4

2-*Diphenylphosphinoyl*-1-*phenyl*-2-(5-*phenylthiocyclopent*-1-*enyl*)*propan*-1-*ol* (**45**; R = Ph).—The allyl sulphide (**44**) (0.5 g, 1.25 mmol) was stirred in dry THF (30 ml) at −78 °C with n-butyl-lithium (0.8 ml; 1.8M in hexane) for 0.2 h. The orange anion was quenched with benzaldehyde (0.14 ml, 1.4 mmol) and, after stirring at −78 °C for 0.2 h, the mixture was poured into aqueous ammonium chloride and extracted with chloroform (3 × 30 ml). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give an oil, containing the alcohol (**45**; R = Ph) and the diene obtained by completion of the Wittig–Horner reaction. Crystallisation from ethyl acetate–petrol gave a single diastereoisomer of the *alcohol* (**45**; R = Ph) (130 mg, 21%), m.p. 195—197 °C, R_F (EtOAc) 0.51, $\nu_{max.}$ ($CHCl_3$) 3 350 (OH), 1 440 (P–Ph), and 1 165 cm^{-1} (P=O), τ ($CDCl_3$) 2.1—2.9 (20 H, m, Ph_2P, PhS, and PhC), 4.2 (1 H, m, vinyl H), 5.01 (1 H, d, J_{HP} 5 Hz, PCC*H*Ph), 6.7 (1 H, m, CHS), 7.6 (1 H, s, OH), 7.9—8.8 (4 H, m, ring protons), and 8.14 (3 H, d, J_{HP} 14 Hz, MeCCP), *m/e* 510 (M^+, 20%), 492 (M − H_2O, 50), 404 (M − PhCHO, 47), 383 (M − H_2O − PhS, 75), 294 (M − PhCHO − PhSH, 100), and 201 (Ph_2PO, 90) (Found: C, 75.6; H, 6.1; P, 6.1. $C_{32}H_{31}O_2PS$ requires C, 75.3; H, 6.1; P, 6.1%).

3-*Diphenylphosphinoyl*-3-(5-*phenylthiocyclopent*-1-*enyl*)-*butan*-2-*ol* (**45**; R = Me).—The allyl sulphide (**44**) (2 g, 5 mmol) was stirred in dry THF (50 ml) saturated with anhydrous lithium bromide at −78 °C with n-butyl-lithium (2.3 ml; 2.4M in hexane) for 0.3 h. The orange anion was quenched by titrating with a solution of acetaldehyde in dry THF, until the colour changed to pale yellow. The solution was poured into aqueous ammonium chloride (50 ml) and the layers were separated; the aqueous layer was extracted with chloroform (3 × 30 ml). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give an oil, from which a single diastereoisomer of the *alcohol* (**45**; R = Me) was crystallised with ethyl acetate–petrol (0.62 g, 28%), m.p. 165—166°, R_F (EtOAc) 0.41, $\nu_{max.}$ ($CHCl_3$) 3 300 (OH), 1 435 (P=Ph), and 1 160 cm^{-1} (P=O), τ ($CDCl_3$) 2.0—2.6 (10 H, m, Ph_2P), 2.78 (5 H, s, PhS), 4.26 (1 H, m, vinyl H), 4.82 (1 H, quintet, J_{HH} = J_{HP} = 6 Hz, MeC*H*CP), 5.25 (1 H, s, OH), 5.95 (1 H, d, J_{HH} 6 Hz, SC*H*CH_2), 7.3—8.8 (4 H, m, ring protons), 8.48 (3 H, d, J_{HP} 16 Hz, MeCP), and 8.87 (3 H, d, J_{HH} 6 Hz, CH_3CH), *m/e* 404 (M − CH_3CHO, 25%), 294 (M − CH_3CHO − PhSH, 100), and 201 (Ph_2PO, 100) (Found: C, 72.4; H, 6.6; P, 6.9. $C_{27}H_{29}O_2PS$ requires C, 72.3; H, 6.5; P, 6.9%).

2-(5-*Phenylthiocyclopent*-1-*enyl*)*but*-2-*ene* (**47**).—The

[23] R. B. Wetzel and G. L. Kenyon, *J. Amer. Chem. Soc.*, 1974, **96**, 5189; B. C. Mayo, *Chem. Soc. Rev.*, 1973, **2**, 49; J. I. Grayson, H. K. Norrish, and S. Warren, *J.C.S. Perkin I*, 1976, 2556.

alcohol (**45**; R = Me) (200 mg, 0.45 mmol) in dry dimethylformamide (20 ml) was added to sodium hydride [48 mg, 1 mmol of a 50% dispersion in oil, washed with light petroleum (b.p. 30—40 °C) and dried under nitrogen] and the mixture was stirred under nitrogen at room temperature for 18 h. The thick precipitate was dissolved in aqueous ammonium chloride (40 ml) and extracted with chloroform (3 × 30 ml). The extract was dried ($MgSO_4$) and the solvent removed under reduced pressure to give a pale yellow oil, which was purified by preparative t.l.c. (dichloromethane). The major band at R_F 0.83 was the *dienyl sulphide* (**47**) (82 mg, 80%), $\nu_{max.}$ 1 670 and 1 605 cm^{-1} (diene C=C), $\lambda_{max.}$ (EtOH) 230 nm (ε 22 000), τ (CCl_4) 2.6—2.9 (5 H, m, PhS), 4.1—4.4 (2 H, m, vinyl H), 5.7 (1 H, m, PhS·CH), 7.6—8.1 (4 H, m, ring protons), 8.22 (3 H, s, MeC=C), and 8.26 (3 H, d, J_{HH} 6 Hz, *Me*-CH=C), *m/e* 230 (M^+, 37%), 121 (M − PhS, 100), and 93 (C_7H_9, 57) (Found: M^+, 230.1127. $C_{15}H_{18}S$ requires M, 230.1128).

[6/2287 *Received*, 16*th December*, 1976]