# Regioselectivity and Control in Alkene Formation from a Carbonium Ion after Diphenylphosphinoyl Migration [1]

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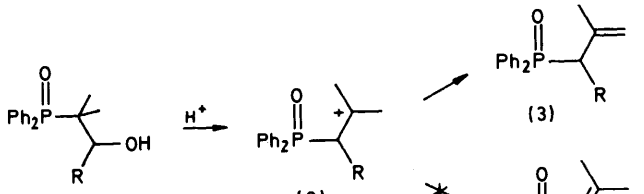
Conversion of 2-hydroxyalkyldiphenylphosphine oxides into allylphosphine oxides by acid-catalysed diphenylphosphinoyl migration shows complete regioselectivity in favour of the more substituted olefin when the migration origin is unsymmetrical. The other, less substituted olefin is formed exclusively when a trimethylsilyl group is present on the appropriate carbon atom as it both increases the rate of the rearrangement and is lost in preference to a proton. The allylphosphine oxides are used in diene synthesis.

ONE common fate of a carbonium ion is alkene formation by loss of a proton. The reaction is used synthetically, particularly when tertiary alcohols are dehydrated by acids, but it usually gives mixtures of olefins if the cation carries two or three different alkyl substituents, and each olefin is often a mixture of *E*- and *Z*-isomers.[2] We have



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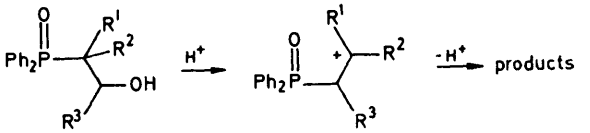
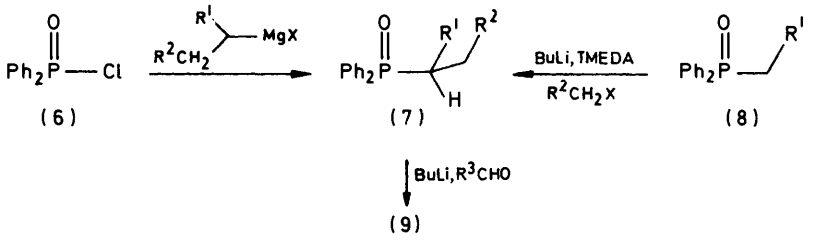


(5)

described [3,4] how tertiary cations (2), formed by diphenylphosphinoyl migration from secondary alcohols (1), cleanly give allyl- (3) and not vinyl- (4) phosphine oxides. We have now extended this work to the situation where the alkyl group (9; $R^1$ = Me, $R^2$ = Me or Bu$^n$). These compounds could be made either by adding the entire aliphatic portion as a Grignard reagent, (6) ⟶ (7) (from s-butyl bromide, for $R^1$ = $R^2$ = Me), or by alkylating the anion of the primary alkylphosphine oxide (8; $R^1$ = Me or n-butyl) ⟶ (7) with ethyl iodide and methyl iodide, respectively. The alkylation gives high yields when the complexing agent tetramethylethylenediamine (TMEDA) is present. In both cases the secondary alkylphosphine oxides (7; $R^1$ = Me, $R^2$ = Me or Bu$^n$) could be added to aldehydes [$R^3$ = Me or Ph (for $R^2$ = Me)] to give the alcohols (9).

Rearrangement of these alcohols (9) with toluene-*p*-sulphonic acid (TsOH) in benzene under reflux ($R^3$ = Me), or in trifluoroacetic acid (TFA) at room temperature ($R^3$ = Ph) gave in each case a regiospecific rearrangement: only the allylphosphine oxides (11; $R^1$ = Me) with the more substituted double bond were formed (Table 1). Each was mainly the *E*-isomer, but contained up to 10% of the *Z*-isomer. The same products [*E*- and *Z*-(11; $R^1$ = $R^3$ = Me)] were also formed by the TFA-catalysed dehydration of the tertiary alcohols (13; $R^1$ = $R^3$ = Me) formed by adding the appropriate ketone to ethyldiphenylphosphine oxide (12; $R^3$ = Me). This is the higher yielding route to (11; $R^1$ = $R^2$ = $R^3$ = Me) as the acetaldehyde addition to the anion of (7; $R^1$ = Me, $R^2$ = Me) gave only a 66% yield, in contrast to the



(6) (7) (8) (9)

two substituents $R^1$ and $R^2$ in (5) are different and we have found that the reaction is remarkably regioselective and can also be controlled to give the less favoured product by having a trimethylsilyl group at the appropriate site.

*Rearrangement of Alcohols* (5) *with an Unsymmetrical Tertiary Migration Origin.*—We first examined the simplest situation, with one methyl and one primary benzaldehyde addition which gives (9; $R^1$ = $R^2$ = Me, $R^3$ = Ph) in 85% yield.

Every combination of phosphorus-stabilised anion and carbonyl compound in these sequences [(7) ⟶ (9), (12) ⟶ (13)] gives a mixture of diastereoisomers. These can usually be separated by t.l.c. but this is not necessary as we showed that either diastereoisomer of (9; $R^1$ = $R^2$ = $R^3$ = Me) gave the same mixture of *E*- and *Z*-isomers of (11; $R^1$ = $R^2$ = $R^3$ = Me). Since

[1] Preliminary communications, A. H. Davidson and S. Warren, *J.C.S. Chem. Comm.*, 1976, 181; I. Fleming, A. Pearce, and R. L. Snowden, *ibid.*, p. 182.

[2] R. Askani in 'Alkene, Cycloalkene, Arylalkene,' Methoden der Organischen Chemie (Houben–Weyl), Thieme, Stuttgart, 1972, vol. V/1b, pp. 85—104.

[3] D. Howells and S. Warren, *J.C.S. Perkin II*, 1973, 1472.

[4] A. H. Davidson and S. Warren, *J.C.S. Chem. Comm.*, 1975, 148; *J.C.S. Perkin I*, 1976, 639; A. H. Davidson, P. K. G. Hodgson, D. Howells, and S. Warren, *Chem. and Ind.*, 1975, 455.

this is also the same mixture formed from the tertiary alcohols (13; $R^1 = R^2 = R^3 = Me$), the cation (10) is presumably an intermediate in all the dehydration reactions with or without diphenylphosphinoyl migration, and deprotonation evidently occurs mostly at the more substituted carbon atom.

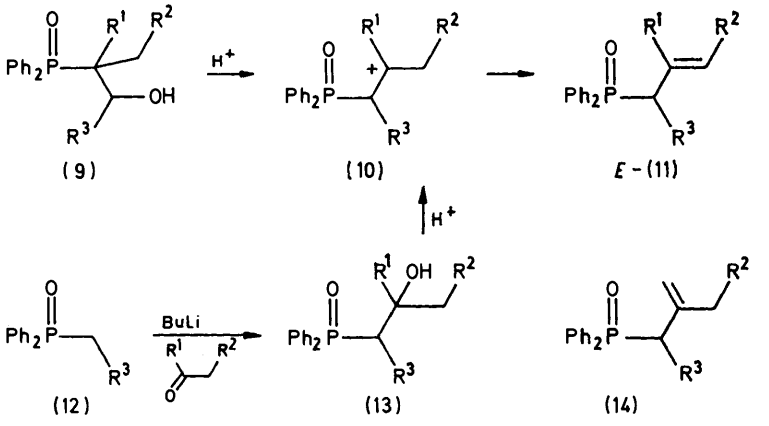
Me, $R^2 = H$) of s-butyldiphenylphosphine oxide (15; $R^1 = Me$) or the butan-2-one adduct (16; $R^1 = H$, $R^2 = Me$) of isopropyldiphenylphosphine oxide (15; $R^1 = H$). Both reactions in TFA give as the only product the *E*-isomer of the more substituted allyl compound (19; $R^1 = Me$, $R^2 = H$).

TABLE 1

Regio- and stereo-selectivity in allylphosphine oxide formation by dehydration of alcohols

| | | | | | | Products | | |
|---|---|---|---|---|---|---|---|---|
| Alcohol | $R^1$ | $R^2$ | $R^3$ | Catalyst [a] | Time (h) | *E*- (11) | *Z*- (11) | (14) |
| (9) | Me | Me | Ph | TsOH | 4 | 60 | 0 | 30 |
| (9) | Me | Me | Ph | TsOH | 24 | 90 | 0 | 0 |
| (9) | Me | Me | Ph | TFA [b] | 12 | 90 | 0 | 0 |
| (9) | $Me_3Si{\cdot}CH_2$ | Me | Ph | TFA | 0.5 | 0 | 0 | 95 |
| (9) | $Me_3Si{\cdot}CH_2$ | Me | Ph | TFA [b] | 0.5 | 90 | 0 | 0 |
| (9) | Me | Me | Me | TsOH | 6 | 80 | 12 | 0 |
| (9) | Me | $Bu^n$ | Me | TsOH | 12 | 90 | 5 | 0 |
| (13) | Me | Me | Me | TFA | 0.5 | 80 | 12 | 0 |
| (13) | Me | $Bu^n$ | Me | TFA | 0.5 | 90 | 5 | 0 |
| 25; R = Me) | | | | TsOH | 6 | 24 | | 55 |
| 25; R = Me) | | | | TsOH | 30 | 90 | | 0 |
| 25; R = Ph) | | | | TsOH | 6 | 0 | | 85 |

TsOH refers to toluene-*p*-sulphonic acid in benzene under reflux; TFA to trifluoroacetic acid at room temperature. [b] At 75 °C.



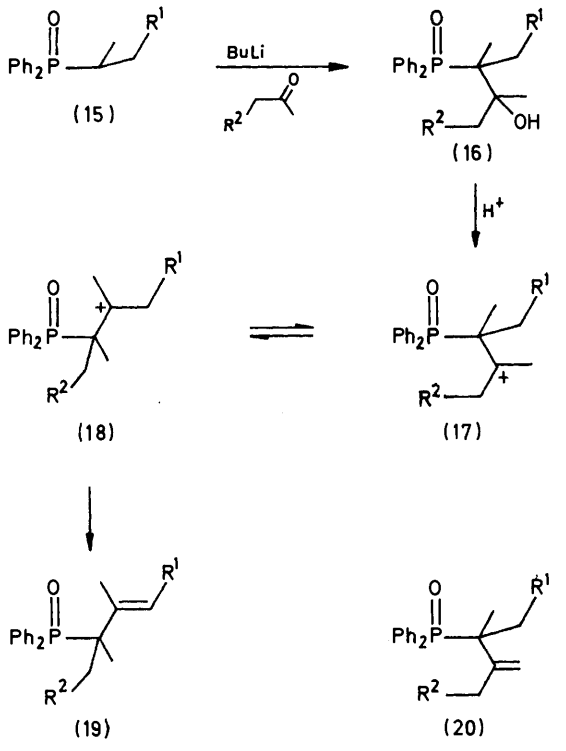

The reason for this is presumably the greater stability of the trisubstituted olefin (11) over the methylene compound (14). We have used this factor to drive a diphenylphosphinoyl migration from a tertiary migration origin to a tertiary migration terminus. We have already shown [3] by deuterium labelling that diphenylphosphinoyl migration between the two degenerate cations (17) and (18) ($R^1 = R^2 = H$) is faster than the dehydration of the symmetrical alcohol (16; $R^1 = R^2 = H$) and that a bromine atom makes the cation (17; $R^1 = H$, $R^2 = Br$) less stable than the rearranged cation (18; $R^1 = H$, $R^2 = Br$). When the substituent is a methyl group, both the cation (18; $R^1 = Me$, $R^2 = H$) and the allylphosphine oxide (19; $R^1 = Me$, $R^2 = H$) should be more stable than the alternatives (17) and (20) ($R^1 = Me$, $R^2 = H$), respectively. This system can be entered by the dehydration of either the acetone adduct (16; $R^1 =$

[5] A. S. Dreiding and R. J. Pratt, *J. Amer. Chem. Soc.*, 1954, **76**, 1902; C. E. Berkoff, R. C. Cookson, J. Hudek, D. W. Jones, and R. O. Williams, *J. Chem. Soc.*, 1965, 194; R. Criegee and K. Noll, *Annalen*, 1959, **627**, 1; R. Criegee, D. Seebach, R. E. Winter, B. Börretzen, and H.-A. Bruner, *Chem. Ber.*, 1965, **98**, 2339; D. Ben-Ishai, I.Gillon, and A. Warshansky, *J. Heterocyclic Chem.*, 1973, **10**, 149; D. B. Denny, and W. R. Davis, *J. Organometallic Chem.*, 1970, **24**, 537.

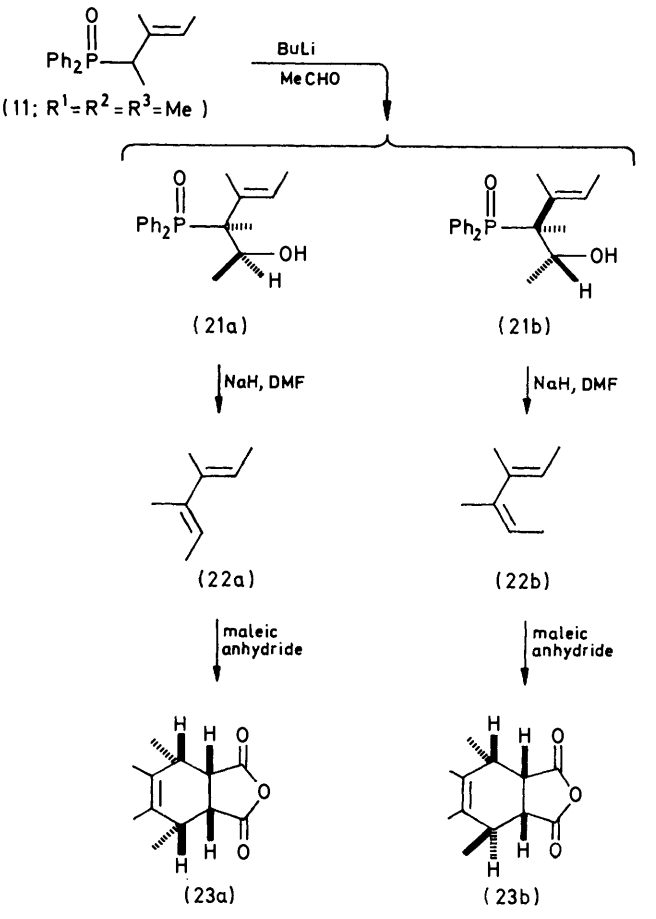
Though the *E*-isomer of the allyl compounds (11) and (19) is expected to be preferred in a stereoselective reaction, we decided to determine the configuration of the major product in one case, the trimethylallyl compound (11; $R^1 = R^2 = R^3 = Me$). We therefore carried through the diene synthesis [4] on this compound as outlined in Scheme 1. The allylphosphine oxide (11; $R^1 = R^2 = R^3 = Me$), still containing a trace of the minor isomer, was added to acetaldehyde to give two diastereoisomeric alcohols (21a and b). These were separated by t.l.c. and recrystallised. The n.m.r. spectra now showed that each was a single compound free from any trace of other geometrical isomers. Completion of the Wittig–Horner reaction gave two isomers of 3,4-dimethylhexa-2,4-diene (22a and b), which were added at once to maleic anhydride to give the two crystalline adducts (23a and b). These dienes and their Diels–Alder adducts have been the subject of some confusing and even contradictory reports,[5] but our physical data and i.r., u.v., and n.m.r. spectra all agree with those in two recent publications.[6] The two dienes are the *E,E*- (22a) and

[6] G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Amer. Chem. Soc.*, 1971, **93**, 1379; W. Reeve and D. M. Reichel, *J. Org. Chem.*, 1972, **37**, 68.

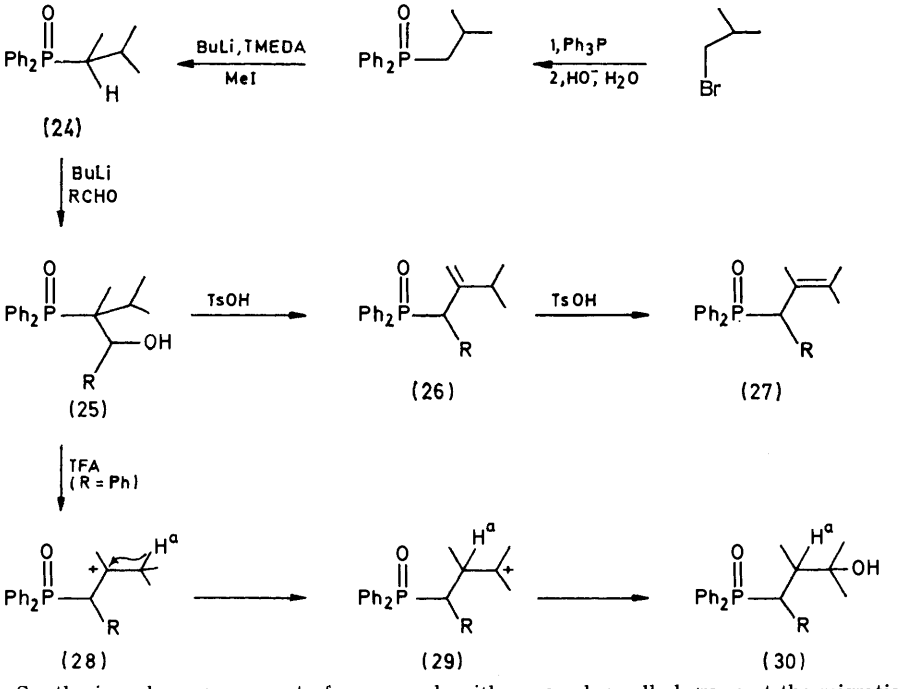
the *E,Z*- (22b) isomers, and the configuration of the original double bond, common to both isomers, is therefore *E*.




The rearrangement of the secondary benzyl alcohol (9; $R^1 = R^2 = Me$, $R^3 = Ph$) in TsOH for a short time gave a mixture of the methylene compound (14; $R^2 = Me$, $R^3 = Ph$) with the trisubstituted olefin (11; $R^1 =$




SCHEME 1 Diene synthesis from the allylphosphine oxide *E*-(11; $R^1 = R^2 = R^3 = Me$)



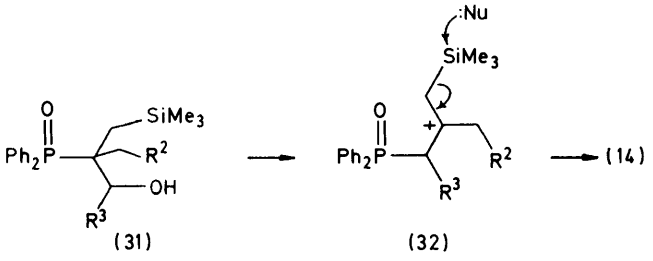

SCHEME 2 Synthesis and rearrangement of compounds with a secondary alkyl group at the migration origin

$R^2 = R^3 = Me$); the latter is the only product after further treatment under the same conditions, or after treatment of the alcohol with TFA. It is possible that the methylene compound (14; $R^2 = Me$, $R^3 = Me$) is also formed in the rearrangement of the alcohol (9; $R^1 = R^2 = R^3 = Me$) but that under the more vigorous conditions needed for the rearrangement, it isomerises to the trimethylallyl compound (11; $R^1 = R^2 = R^3 = Me$).

The kinetic advantage of the methylene compound (14) is more marked when one of the substituents at the migration origin is a secondary alkyl group. Both the acetaldehyde adduct (25; R = Me) and the benzaldehyde adduct (25; R = Ph) of the branched phosphine oxide (24) rearranged with TsOH in benzene to the methylene compound (26) (Scheme 2). Further treatment of the methylene compound (26; R = Me) under the same conditions slowly gave the tetrasubstituted olefin (27; R = Me). We normally use TFA for the rearrangement of secondary benzyl alcohols such as (25; R = Ph), but an interesting double rearrangement occurred in this case, the first-formed cation (28) undergoing a hydride shift to give a tertiary alkyl cation (29) with the electron-withdrawing diphenylphosphinoyl group one atom further away from the positive charge. On aqueous work-up this cation or its trifluoroacetate gave the alcohol (30).

We believe that this double migration occurs by a hydride shift and not by dehydration to the olefin (27; R = Ph) and reprotonation to give the cation (29), because the olefin (27; R = Ph) can be formed in trifluoroacetic acid from (26; R = Ph) without conversion into (30), and when the rearrangement of (25; R = Ph) was conducted in [$^2$H]TFA, the signal for $H^a$ was still present in the n.m.r. spectrum of the product (30).

*Control by Silicon.*—We reasoned that replacement of a methyl group in the alcohol (9) by a trimethylsilyl group (31) would have two effects: the rearranged cation (32) would be stabilised by the β-trimethylsilyl group,[7]




and this same group would be removed, in preference to a proton,[8] by nucleophilic attack of water or TsOH. Thus the methylene compound (14) might be formed under conditions mild enough to prevent its isomerisation to (13).

The synthesis of the silylated alcohol (31; $R^2 = Me$, $R^3 = Ph$) proved rather difficult (Scheme 3). Alkylation of neither of the ketones (34) or (35) was succesful, an *O*-alkylation product being obtained in one case. The silylated phosphine oxide (33), with a primary alkyl group next to phosphorus and silicon, was metallated next to phosphorus as expected, diphenylphosphinoyl being a much more powerful anion-stabilising group than trimethylsilyl. But the silylated phosphine oxide (36), with a secondary alkyl group next to the phosphorus atom, surprisingly was metallated next to silicon, as shown by work-up with deuterium oxide. The reaction with benzaldehyde gave a mixture of compounds, tentatively identified by n.m.r. as the *E*- and *Z*-allylphosphine oxides (38) formed by the Peterson reaction.[9] Presumably a chelate with the phosphinoyl group (37) is responsible for this large increase in kinetic acidity next to silicon; tetramethylsilane, for example, is metallated only after 3—4 days at room temperature with butyllithium and TMEDA,[10] whereas the silane (36) was metallated in 8 min at −50 °C without TMEDA. However, the silicon atom is still playing a significant part, for diphenyl-t-butylphosphine oxide was not cleanly metallated under these or more vigorous conditions.

Metallation next to silicon was a kinetic, and not a thermodynamic process: addition of TMEDA caused the lithium derivative (37) to rearrange slowly to its isomer (39). Addition of benzaldehyde now gave the adduct (40). A lithium base is normally used in the Wittig–Horner reaction [11] to prevent decomposition of the intermediate (40), but TMEDA, by chelating with the lithium, makes the intermediate decompose to the allylsilane (41) unless it is rapidly neutralised. By careful adjustment of the conditions we were eventually able to get 32% of the alcohol (42).

Rearrangement of the silylated alcohol (42) occurred in 0.5 h at room temperature in TFA: the analogue (9; $R^1 = R^2 = Me$, $R^3 = Ph$) without the trimethylsilyl group is little affected by these conditions. The only product was indeed the methylene compound (14; $R^2 = Me$, $R^3 = Ph$). On treatment with TFA under reflux, the silylated alcohol (42) did give instead the trisubstituted olefin (9; $R^1 = R^2 = Me$, $R^3 = Ph$), so it appears that both effects of the trimethylsilyl group are necessary: exclusive formation of the less substituted product, and a more rapid reaction under milder conditions to prevent its isomerisation to the more substituted alternative. We estimate the increase in rate in this case to be about tenfold.

*Diphenylphosphinoyl Migration between Secondary Centres.*—Another way to use these effects would be to drive forward diphenylphosphinoyl migrations which do not normally occur. The adducts (44) between primary alkylphosphine oxides (43) and aldehydes undergo dehydration in TsOH without diphenylphosphinoyl migration (Table 2). The propionaldehyde adduct (44; $R^1 = R^2 = Me$) gave only the allylphosphine oxide

[7] C. Eaborn, *J.C.S. Chem. Comm.*, 1972, 1255, and references therein.

[8] C. Eaborn and R. W. Bott in ' Organometallic Compounds of the Group IV Elements,' vol. 1, part 1, ed. A. G. MacDiarmid, Dekker, New York, 1968, p. 359.

[9] D. J. Peterson, *J. Org. Chem.*, 1968, **33**, 780.

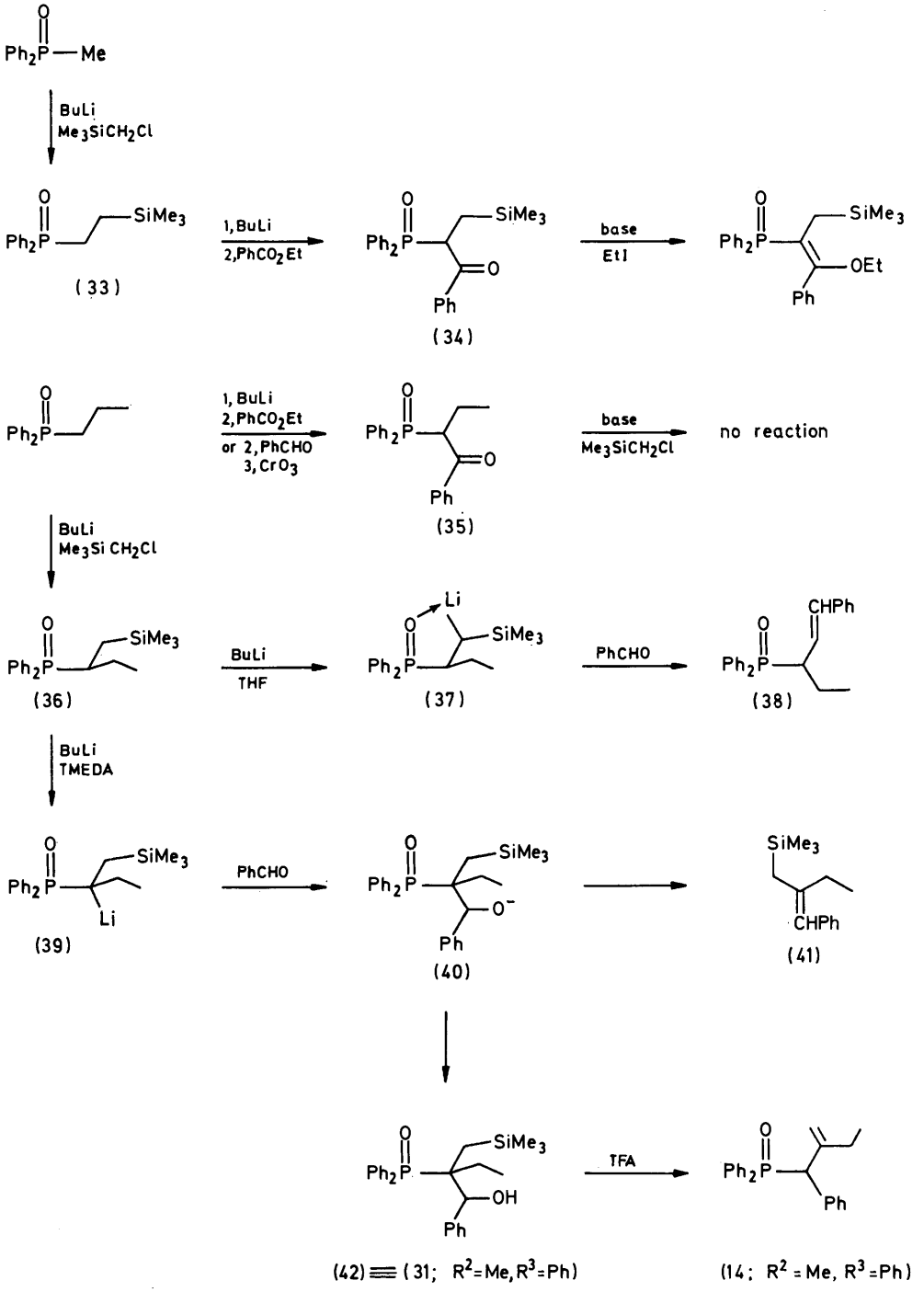
[10] D. J. Peterson, *J. Organometallic Chem.*, 1967, **9**, 373.

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

(46; $R^1 = R^2 = Me$), but the acetaldehyde adduct (44; $R^1 = Et$, $R^2 = H$), the allylphosphine oxide from which would be a monosubstituted olefin (46; $R^1 = Et$, $R^2 = H$), gave a mixture of this and the vinyl compound (45; $R^1 = Et$, $R^2 = H$).

pletion of the Wittig–Horner reaction gave only (*Z*)-1-phenylpropene. This alcohol (47) was dehydrated in TFA to give the vinylphosphine oxide (48).*

The silylated analogues (49; R = Me, Et, or Ph) were made by adding aldehydes to the 2-trimethylsilylethyl-




SCHEME 3 Synthesis of the silylated alcohol (31; $R^2 = Me$, $R^3 = Ph$)

The addition of benzaldehyde to ethyldiphenylphosphine oxide is very stereoselective giving a single diastereoisomer of the adduct (47) in 74% yield. The configuration of this adduct proved to be that shown, as com-

phosphine oxide (33), a high-yielding reaction lacking the problems associated with the silylated phosphine oxide (36). The acetaldehyde (49; R = Me) and benz-

* Probably *E*; see Experimental section.

aldehyde (49; R = Ph) adducts on treatment with acid (TsOH and TFA, respectively), rearranged cleanly to the stable β-silyl cation, which lost the trimethylsilyl group to give the monosubstituted olefins (51; R = Me or Ph). Only in the reaction of the propionaldehyde adduct (49; R = Et), where the unrearranged allylphosphine oxide (52) is a 1,2-disubstituted olefin, did the reaction give a mixture of this and the rearranged product (51; R = Et), in a 1 : 2 ratio.

The limit is finally reached with the cyclohexanone adduct (53), a tertiary alcohol with the diphenylphosphinoyl group on a secondary carbon atom. Even the trimethylsilyl group cannot push this rearrangement uphill and the allylphosphine oxide (54) is formed in TFA without the loss of the trimethylsilyl group and without diphenylphosphinoyl migration.

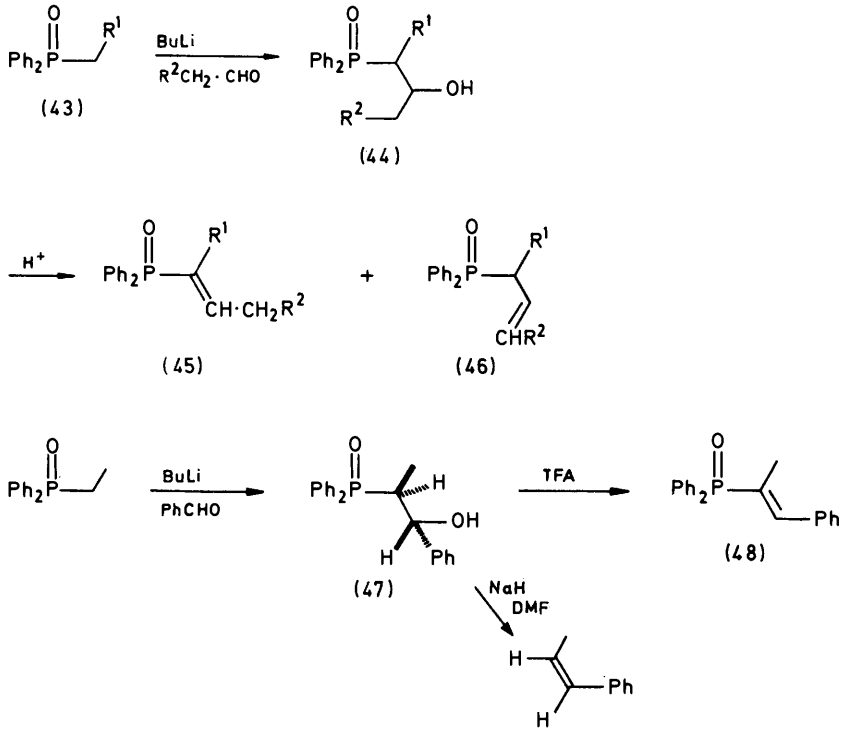
In the diphenylphosphinoyl migrations from one secondary centre to another [*e.g.* in (44)] or from one tertiary centre to another [*e.g.* in (16)], the usual driving force for rearrangement, the formation of a more stable cation,[3,12] is absent (unless a trimethylsilyl group makes one of the cations more stable). In the migrations between tertiary centres, the energy barrier for migration is low enough for both cations [*e.g.* (17) and (18)] to be present so that either may go through to whatever is the more stable product. This clearly does not happen with two secondary centres as no rearranged product is formed even when the same driving force [as in (44; $R^1$ = Et, $R^2$ = H)] is present, as was successful in the all-tertiary system (16) ⟶ (19) ($R^1$ = Me, $R^2$ = H).

TABLE 2

Products of attempted rearrangements from a secondary migration origin to a secondary migration terminus

| | | | Products | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | Rearranged Allyl | | Unrearranged | | | |
| | | | | | Allyl | | Vinyl | |
| Compound | Conditions | Time | Cpd. | % | Cpd. | % | Cpd. | % |
| (44) $R^1$ = Et, $R^2$ = H | TsOH [a] | 3 days | | | (46) | 38 | (45) | 40 |
| (44) $R^1$ = $R^2$ = Me | TsOH [a] | 3 days | | | (46) | 80 | (45) | 0 |
| (47) | TFA [b] | 16 h | | | | | (48) | 85 |
| (49) R = Ph | TFA [c] | 1.5 h | (51) | 90 | | | | |
| (49) R = Me | TsOH [a] | 24 h | (51) | 85 | | | | |
| (49) R = Et | TsOH [a] | 23 h | (51) | 55 | (52) | 31 | | |

[a] In toluene under reflux. [b] Under reflux. [c] At room temperature.




*Origins of the Regioselectivity.*—Two types of regioselectivity occur in the formation of olefins from cation (55); (*a*) selectivity between vinyl (56) and allyl [(57) + (58)] products, and (*b*) selectivity between the two allyl products (57) and (58). We have not previously commented on the possibility of vinylphosphine oxide formation as the compounds described in this paper are not transformed into vinyl compounds even after prolonged treatment with acid. Only when the allyl

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

compound is a 1,1-disubstituted olefin [*i.e.* (55; $R^1 = R^2 = X = H$, $R^3 = H$,[13] Me,[4] or Ph[4])] is the vinyl compound (56; $R^1 = R^2 = H$) the thermodynamic product. In carbonyl compounds (59) the vinyl compound (60) is nearly always thermodynamically more stable than the allyl compound (61) because of conjugation: dehydration of aldol products [14] and ethoxycarbonyl rearrangement [15] [to give (59; $R^1$ = EtO, $R^2$ = Ph)] both give only the vinyl compound (60) after equilibration. The diphenylphosphinoyl group does not conjugate except weakly by $3p_\pi$–$2p_\pi$ overlap and may even, as is the case with sulphones and sulphoxides, actually prefer not to be ' conjugated ' with the double bond.[16]

Whatever the thermodynamic situation, the primary selection against the vinyl compound is kinetic. While carbonyl compounds may enolise in acid, no such process is possible in phosphine oxides, and loss of $H^a$ from (55) would probably put an unfavourable partial positive charge on the carbon atom next to phosphorus in the transition state.

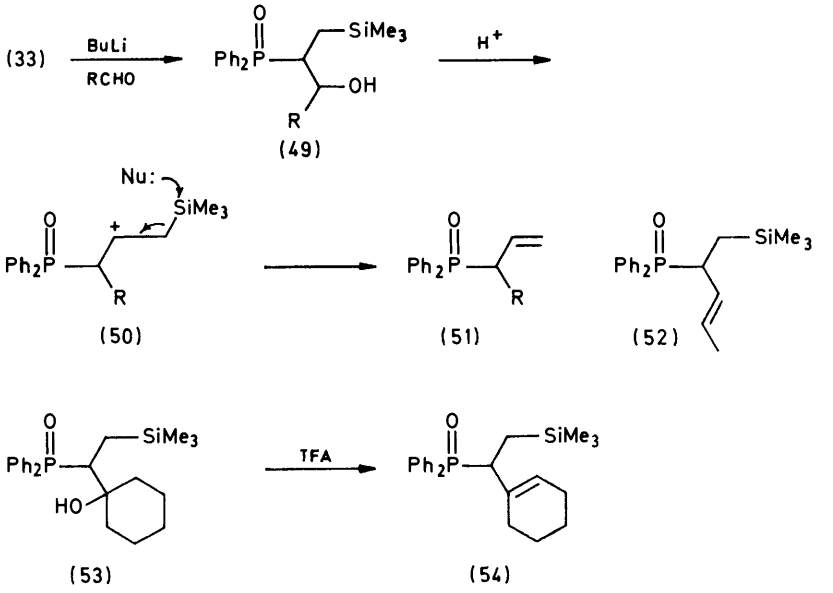
The high selectivity between the two allyl products is more surprising. The loss of X from (55) seems to be kinetically favoured whether X is a proton or a trimethylsilyl group but the more substituted compound (56) is the thermodynamic product. This distinction is found also in simple alkyl cations [2] but the selectivity is rarely complete, and it does not seem to be possible to select in favour of one isomer by virtue of a single methyl group, as it is with the phosphine oxides [*e.g.* (58; $R^1$ = Me, $R^2$ = H)].

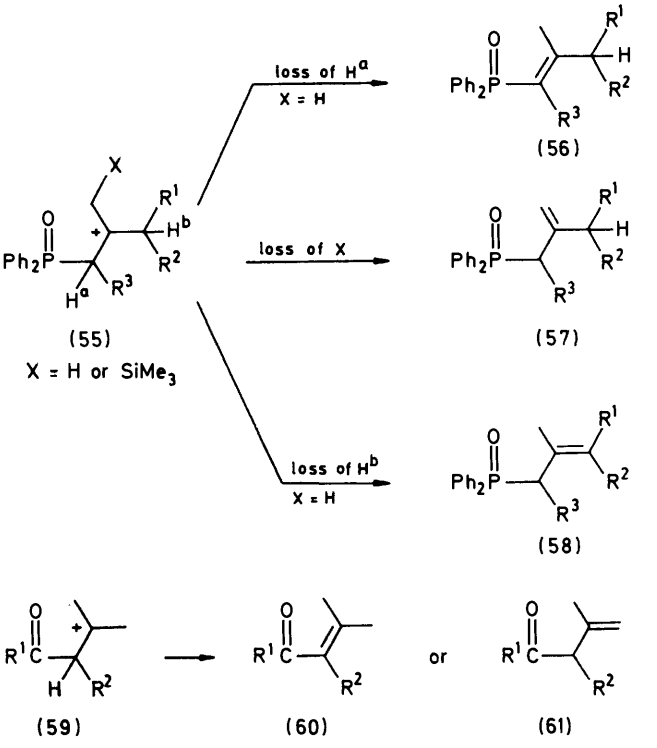
Whatever the origin of this selectivity, it must also apply to the corresponding phenylthio compounds,[17] and also to the 'second ' diphenylphosphinoyl migration,[1] and cannot therefore involve the selective removal of protons by the oxygen atom of the phosphinoyl group.

[13] P. F. Cann, D. Howells, and S. Warren, *J.C.S. Perkin II*, 1972, 304.

[14] H. O. House, ' Modern Synthetic Reactions,' Benjamin, Menlo Park, 1972, 2nd edn., pp. 629—733.

It seems that the diphenylphosphinoyl group enhances not only kinetic preference for the less substituted compound [*e.g.* in compound (25)], a not surprising result considering its bulk, but also the thermodynamic preference for the more substituted compound, when this is a trisubstituted olefin. This may also be a steric effect as it may be preferable to have the larger substituent planar [*e.g.* (58)] when it is close to the large tetrahedral diphenylphosphinoyl group.



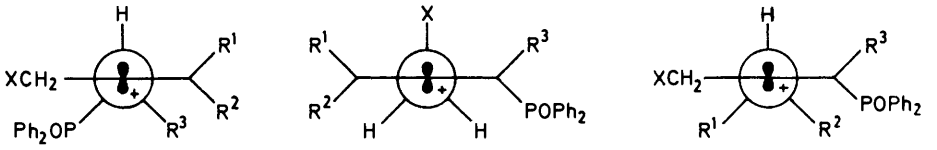




[15] T. H. Phan and H. Dahn, *Helv. Chim. Acta*, 1976, **59**, 335.

[16] E. A. Fehnel, *J. Amer. Chem. Soc.*, 1952, **74**, 1569; D. E. O'Connor and W. I. Lyness, *ibid.*, 1963, **85**, 3045.

[17] P. Brownbridge and S. Warren, *J.C.S. Perkin I*, in the press.

Another and probably more important factor which influences both the selectivity between allyl and vinyl products and the selectivity between alternative allyl products is that the conformation (A) required for vinylphosphine oxide (56) formation from cation (55) and that (C) required for the formation of the allylphosphine oxide (58) with three substituents on the double bond have two large groups close together and will be less populated than that (B) for formation of the methylene compound (57). This problem does not arise in the formation of the more substituted allyl compound (58)




when $R^2$ = H, as conformation (C) then has no very large groups close together. This conformation (C; $R^2$ = H) also leads to the *E*-isomer of (58). Similar arguments have been used to explain the selectivity observed in the dehydration of aryl-substituted tertiary alcohols under the same conditions.[18] When X = $SiMe_3$, conformation (B) will be preferred as it is only in this conformation that the $SiMe_3$ group can stabilise the cation.

We have already described [4] how allylphosphine oxides may be used in diene synthesis, though we have not previously been able to control either the position or the stereochemistry of the double bond. The sequence (11) ⟶ (23) ($R^1$ = $R^2$ = $R^3$ = Me) illustrates how our compounds may be used to make single isomers of dienes in which each atom of the diene framework is derived from a different electrophilic source and each double bond has a specific and known configuration.

## EXPERIMENTAL

I.r. spectra were taken for solutions in chloroform unless otherwise stated on a Perkin-Elmer 257, n.m.r. spectra on a Perkin-Elmer R12B, Hitachi–Perkin-Elmer R24A, or Varian HA100D, and mass spectra on an A.E.I. MS9, MS30, or MS902 instrument. N.m.r. signals marked with an asterisk belong to diastereotopic groups of protons. T.l.c. was run on silica gel GF 254; $R_F$ values are quoted for development in ethyl acetate unless otherwise stated. Column chromatography was run on B.D.H. silica (100—200 mesh). M.p.s were taken on a Kofler hot-stage apparatus. TsOH refers to toluene-*p*-sulphonic acid monohydrate, TFA to trifluoroacetic acid, THF to tetrahydrofuran, DMF to dimethylformamide and petrol to light petroleum (b.p. 60—80 °C).

*Diphenylpropylphosphine Oxide* [19].—Triphenylphosphine (25 g) was heated under reflux in n-propyl bromide (100 ml) for 36 h. The white solid formed was filtered off, washed with ether, and then heated with sodium hydroxide solution (100 ml; 30%) while benzene distilled out. After all the benzene had been distilled off, the mixture was cooled and extracted with chloroform (3 × 50 ml). The extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the phosphine oxide (16 g, 80%), m.p. 98—100 °C (from EtOAc) (lit.,[20] 100—101 °C).

*Diphenyl-s-butylphosphine Oxide* (7; $R^1$ = Me, $R^2$ = Et).—Diphenylphosphinic acid [21] (10 g) was heated under reflux with thionyl chloride (20 ml) in dry toluene (100 ml) for 1 h. The toluene was then evaporated off under reduced pressure and the remaining oil dissolved in dry benzene (20 ml) and added dropwise over 1.5 h to s-butylmagnesium bromide [from s-butyl bromide (40 ml) and magnesium (8 g) in ether (100 ml)]. The solution was heated under reflux for 2 h and cooled to 0 °C, and ice (50 g) and hydrochloric acid (10%; 100 ml) were added. The aqueous layer was extracted with ether (3 × 50 ml) and the combined ethereal layers were dried ($MgSO_4$) and evaporated under reduced pressure; the product was collected and recrystallised from ethyl acetate to give the *phosphine oxide* (7; $R^1$ = Me, $R^2$ = Et) (9 g, 75%), m.p. 102—105 °C, $R_F$ 0.4, $\nu_{max.}$ 1 440 (PPh) and 1 180 $cm^{-1}$ (P=O), τ ($CDCl_3$) 2.0—2.6 (10 H, m, $Ph_2PO$), 7.7 (1 H, m, PC*H*Me), 8.0—8.6 (2 H, m, $CH_2$Me), 8.8 (3 H, dd, $J_{PH}$ 17, $J_{HH}$ 7 Hz, PCH*Me*), and 9.05 (3 H, t, $J_{HH}$ 7 Hz), *m/e* ($M^+$, 50%), 230 ($Ph_2POEt$, 40), and 201 ($Ph_2PO$, 100) (Found: C, 74.6; H, 7.5; P, 11.9. $C_{16}H_{19}OP$ requires C, 74.4; H, 7.35; P, 12.0%).

*Preparation of Diphenyl-s-butylphosphine Oxide* (7; $R^1$ = Me, $R^2$ = Et) *by Alkylation*.—Ethyldiphenylphosphine oxide (1.5 g) was stirred in dry ether (50 ml) under nitrogen with n-butyl-lithium (4 ml; 1.5M in hexane) for 0.5 h. Ethyl iodide (1 g) was added and the mixture stirred for 10 min, then water (100 ml) was added. The aqueous layer was separated and extracted with chloroform (3 × 25 ml). The combined organic layers were washed with sodium thiosulphate solution (2 × 25 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give an oil, containing starting material and the phosphine oxide (7; $R^1$ = Me, $R^2$ = Et) (0.5 g, 40%) which were separated by column chromatography (elution with 4 : 1 ethyl acetate–petrol).

*3-Diphenylphosphinoyl-3-methylpentan-2-ol* (9; $R^1$ = $R^2$ = $R^3$ = Me).—Diphenyl-s-butylphosphine oxide (1 g) in dry ether (50 ml) was stirred at 0 °C under nitrogen with n-butyl-lithium (2.5 ml; 1.5M in hexane) for 0.5 h. The red solution was cooled to −78 °C and a solution of acetaldehyde in dry ether saturated with anhydrous lithium bromide was added until the red colour was discharged. The solution was allowed to reach room temperature and water (50 ml) 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 the two diastereoisomers of the alcohol (9; $R^1$ = $R^2$ = $R^3$ = Me) which were separated by column chromatography (elution with 4 : 1 ethyl acetate–petrol) to give the high $R_F$ *diastereoisomer* (350 mg, 33%),

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m.p. 147—148 °C (from EtOAc–$Pr^i_2O$), $R_F$ 0.5, $\nu_{max.}$ 3 300 (OH), 1 435 (PPh), and 1 150 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 1.8—2.5 (1 OH, m, $Ph_2PO$), 5.0 (1 H, s, OH), 5.85 (1 H, overlapping dq, $J_{PH}$ 14, $J_{HH}$ 6 Hz, C*H*OH), 8.1 (2 H, overlapping dq, $J_{PH}$ 15, $J_{HH}$ 7 Hz, $CH_2$Me), 8.8 (3 H, d, $J_{PH}$ 17 Hz, PCMe), 8.85 (3 H, d, $J_{HH}$ 6 Hz, *Me*CHOH), and 9.2 (3 H, t, $J_{HH}$ 7 Hz, $CH_2$*Me*), *m/e* 302 ($M^+$, 6%), 258 ($M$ − MeCHO, 100), 243 (80), and 201 ($Ph_2PO$, 80) (Found: C, 71.7; H, 7.8; P, 10.2. $C_{18}H_{23}O_2P$ requires C, 71.6; H, 7.6; P, 10.3%), and the low $R_F$ *diastereoisomer* (320 mg, 30%), m.p. 174—176 °C (from EtOAc), $R_F$ 0.4, $\nu_{max.}$ 3 300 (OH), 1 435 (PPh), and 1 150 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 1.8—2.6 (1 OH, m, $Ph_2PO$), 5.0 (1 H, s, OH), 5.9 (1 H, dq, $J_{PH}$ 17, $J_{HH}$ 7 Hz, C*H*OH), 7.9—8.3 (2 H, m, $CH_2$Me), 8.7 (3 H, d, $J_{PH}$ 17 Hz, PCMe), 8.9 (3 H, d, $J_{HH}$ 7 Hz, *Me*CHOH), and 9.2 (3 H, t, $J_{HH}$ 7 Hz, $CH_2$*Me*), *m/e* 302 ($M^+$, 5%), 258 ($M$ − MeCHO, 90), 243 (90), and 201 ($Ph_2PO$, 100) (Found: C, 71.6; H, 7.8; P, 10.6. $C_{18}H_{23}O_2P$ requires C, 71.6; H, 7.6; P, 10.3%).

*Treatment of the Alcohol* (9; $R^1 = R^2 = R^3$ = Me) *with TsOH in Benzene*.—A mixture of the two diastereoisomers of the alcohol (9; $R^1 = R^2 = R^3$ = Me) (50 mg) in benzene (25 ml) was heated under reflux in a Dean–Stark apparatus with TsOH (70 mg) for 6 h. The solution was cooled, poured into ether (100 ml), washed with saturated sodium hydrogen carbonate solution (3 × 25 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give *4-diphenylphosphinoyl-3-methylpent-2-ene* (11; $R^1 = R^2 = R^3$ = Me) (44 mg, 90%). The n.m.r. spectrum of the crude material showed that there was less than 12% of the *Z*-isomer and over 80% of the *E*-isomer. Recrystallization from ethyl gave the E-*isomer*, m.p. 113—116 °C, $\nu_{max.}$ 1 435 (PPh), and 1 170 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 2.0—2.7 (10 H, m, $Ph_2PO$), 4.7 (1 H, broad quint, $J_{PH} = J_{HH}$ = 6 Hz, CH=C), 6.95 (1 H, quint, $J_{PH} = J_{HH}$ = 7 Hz, PC*H*Me), 8.4 (3 H, broad s, HC=CMe), 8.6 (3 H, t, $J_{PH} = J_{HH}$ 6 Hz, C=CH*Me*), 8.7 (3 H, q, $J_{PH}$ 16, $J_{HH}$ 7 Hz, PCH*Me*), *m/e* 284 ($M^+$, 50%) and 201 ($Ph_2PO$, 100) (Found: C, 76.0; H, 7.65; P, 10.6. $C_{18}H_{21}OP$ requires C, 76.1; H, 7.6; P, 10.9%).

*Preparation of the Allylphosphine Oxide* (11; $R^1 = R^2 = R^3$ = Me) via *the Tertiary Alcohol* (13; $R^1 = R^2$ = Me).—Ethyldiphenylphosphine oxide (3 g) in dry ether (100 ml) under nitrogen was stirred with n-butyl-lithium (8 ml; 1.5M in hexane) for 0.5 h and cooled to −78 °C. Ethyl methyl ketone (720 mg) in dry ether (50 ml) was added, the solution was allowed to warm to room temperature, and water (100 ml) was added. The aqueous layer was separated and extracted with chloroform (3 × 50 ml), and the combined organic layers were dried ($MgSO_4$) and evaporated to leave a white crystalline solid. N.m.r. showed this to be a mixture of the two diastereoisomers of the tertiary alcohol (13; $R^1 = R^2$ = Me). The mixture was not purified but stirred in TFA (50 ml) at 70 °C for 25 min. The solution was then poured into water (100 ml) and extracted with chloroform (3 × 50 ml). The extracts were washed with sodium hydrogen carbonate solution (3 × 50 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give the allylphosphine oxide (11; $R^1 = R^2$ = Me) (3 g, 80%).

*2-Diphenylphosphinoyl-2-methyl-1-phenylbutan-1-ol* (9; $R^1 = R^2$ = Me, $R^3$ = Ph).—Diphenyl-s-butylphosphine oxide (0.5 g) was stirred under nitrogen in dry ether (50 ml) with n-butyl-lithium (1.5 ml; 1.2M in hexane) at 0 °C for 0.5 h. The solution was cooled at −78 °C and benzaldehyde (200 mg) in dry ether (25 ml) was added. The solution was allowed to warm to room temperature and water (50 ml) was added. The aqueous layer was extracted with chloroform (3 × 50 ml) and the combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure. The white solid obtained contained both diastereoisomers of the *alcohol* (9; $R^1 = R^2$ = Me, $R^3$ = Ph), which were separated by fractional recrystallization from ethyl acetate. The high $R_F$ *diastereoisomer* (250 mg, 35%) had m.p. 200—203 °C (from EtOAc), $R_F$ 0.6, $\nu_{max.}$ 3 300 (OH), 1 430 (PPh), and 1 150 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 1.8—2.6 (10 H, m, $Ph_2PO$), 2.85 (5 H, s, Ph), 4.25 (1 H, d, $J_{HH}$ 3 Hz, OH), 5.0 (1 H, dd, $J_{PH}$ 11, $J_{HH}$ 3 Hz, PhC*H*OH), 8.4 (2 H, m, $CH_2$Me), 8.8 (3 H, d, $J_{PH}$ 16 Hz, PCMe), and 9.6 (3 H, t, $J_{HH}$ 7 Hz, $CH_2$*Me*), *m/e* 364 ($M^+$, 12%), 258 ($M$ − PhCHO, 75), 243 (100), and 201 ($Ph_2PO$, 20) (Found: C, 75.6; H, 6.7; P, 8.4. $C_{23}H_{25}O_2P$ requires C, 75.8; H, 6.85; P, 8.5%). The low $R_F$ *diastereoisomer* (350 mg, 50%) had m.p. 215—216 °C (from EtOAc), $R_F$ 0.5, $\nu_{max.}$ 3 300 (OH), 1 430 (PPh), and 1 150 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 1.8—2.6 (10 H, m, $Ph_2PO$), 2.8 (5 H, s, Ph), 4.2 (1 H, d, $J_{HH}$ 2 Hz, OH), 5.3 (1 H, dd, $J_{PH}$ 11, $J_{HH}$ 2 Hz, PhC*H*OH), 8.3 (2 H, m, $CH_2$Me), 9.0 (3 H, d, $J_{PH}$ 16 Hz, PCMe), and 9.4 (3 H, t, $J_{HH}$ 7 Hz, $CH_2$*Me*), *m/e* 364 ($M^+$, 5%), 258 ($M$ − PhCHO, 50), 243 (75), and 201 ($Ph_2PO$, 100) (Found: C, 75.5; H, 7.1; P, 8.4. $C_{23}H_{25}O_2P$ requires C, 75.8; H, 6.85; P, 8.5%).

*Trifluoroacetolysis of the Alcohol* (9; $R^1 = R^2$ = Me, $R^3$ = Ph).—A mixture of diastereoisomers of the alcohol (9; $R^1 = R^2$ = Me, $R^3$ = Ph) (35 mg) was kept at 70 °C in TFA (0.4 ml) for 12 h. The solution was poured into water (50 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 *4-diphenylphosphinoyl-3-methyl-4-phenylbut-2-ene* (11; $R^1 = R^2$ = Me, $R^3$ = Ph) (30 mg, 90%), m.p. 254—255 °C, $R_F$ 0.7, $\nu_{max.}$ 1 440 (PPh) and 1 180 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 2.0—3.0 (15 H, m, $Ph_2PO$ and Ph), 4.2 (1 H, m, CH=C), 5.9 (1 H, d, $J_{PH}$ 8 Hz, PCH), 8.3 (3 H, s, CH=C*Me*), 8.6 (3 H, broad d, $J_{HH}$ 5 Hz, C=CH*Me*), *m/e* 346 ($M^+$, 50%) and 201 ($Ph_2PO$, 100) (Found: C, 79.7; H, 6.7; P, 9.2. $C_{23}H_{23}OP$ requires C, 79.8; H, 6.65; P, 9.0%).

*Treatment of the Alcohol* (9; $R^1 = R^2$ = Me, $R^3$ = Ph) *with TsOH*.—A mixture of the diastereoisomers of the alcohol (100 mg) was heated under reflux in benzene (25 ml) in a Dean–Stark apparatus with TsOH (40 mg) for 4 h. The solution was then poured into ether (100 ml) and washed with saturated sodium hydrogen carbonate solution (3 × 25 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The white solid was a mixture of the allylphosphine oxide (14; $R^2$ = Me, $R^3$ = Ph) (see below), and the allylphosphine oxide (11; $R^1 = R^2$ = Me, $R^3$ = Ph) (see above) in the ratio 1 : 2. Further treatment of the mixture under the same conditions gave exclusively the allylphosphine oxide (11; $R^1 = R^2$ = Me, $R^3$ = Ph).

*(1-Methylhexyl)diphenylphosphine Oxide* (7; $R^1$ = Me, $R^2 = Bu^n$).—Hexyldiphenylphosphine oxide (3 g) in dry ether was stirred with tetramethylethylenediamine (1.2 ml) at room temperature under nitrogen for 5 min. n-Butyl-lithium (6 ml; 1.5M in hexane) was added and the mixture stirred for a further 25 min. Then methyl iodide (0.35 ml) was added, discharging the red colour. More n-butyl-lithium (4 ml) was added and the solution stirred for 10 min; methyl iodide (0.35 ml) was then added, followed by water (50 ml). The aqueous layer was extracted with chloroform (3 × 25 ml) and the combined organic layers were washed with sodium thiosulphate solution (3 × 25 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give the

*phosphine oxide* (7; $R^1$ = Me, $R^2$ = $Bu^n$) (2.5 g, 80%), m.p. 78—80 °C (from petrol), $R_F$ 0.5, $\nu_{max.}$ 1 435 (PPh) and 1 170 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 2.1—2.6 (10 H, m, $Ph_2PO$), 7.7 (1 H, m, PCH), 8.2—9.0 (8 H, m, $[CH_2]_4$), 8.8 (3 H, dd, $J_{PH}$ 16, $J_{HH}$ 7 Hz, PCH*Me*), and 9.2 (3 H, t, $J_{HH}$ 5 Hz, $CH_2$*Me*), *m/e* 300 ($M^+$, 12%), 230 ($M - C_5H_{11}$, 100), and 201 ($Ph_2PO$, 100) (Found: $M^+$, 300.164 1. $C_{19}H_{25}OP$ requires *M*, 300.164 2).

3-*Diphenylphosphinoyl*-3-*methyloctan*-2-*ol* (9; $R^1$ = Me, $R^2$ = $Bu^n$, $R^3$ = Me).—The procedure was the same as that for the alcohol (9; $R^1$ = $R^2$ = $R^3$ = Me). (1-Methylhexyl)diphenylphosphine oxide (500 mg), n-butyl-lithium (1.1 ml; 1.5 M in hexane), and acetaldehyde in ether (25 ml), saturated with anhydrous lithium bromide, gave an oil, which crystallised, containing both diastereoisomers of the *alcohol* (9; $R^1$ = $R^3$ = Me, $R^2$ = $Bu^n$), which were not separated (350 mg, 70%); m.p. 90—110 °C, $R_F$ 0.5 and 0.6, $\nu_{max.}$ 3 320 (OH), 1 440 (PPh), and 1 150 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 1.8—2.6 (10 H, m, $Ph_2PO$), 5.4 (1 H, broad s, OH), 5.6—6.1 (1 H, m, C*H*OH), 8.4—9.0 (8 H, m, $[CH_2]_4$), 8.7 (3 H, 2 × d, $J_{PH}$ 16 Hz, PCMe), and 8.8 (3 H, 2 × d, $J_{HH}$ 6 Hz, *Me*CHOH), *m/e* 344 ($M^+$, 5%), 300 ($M$ — MeCHO, 50), and 201 ($Ph_2PO$, 100) (Found: $M^+$, 344.187 1. $C_{21}H_{29}O_2P$ requires *M*, 344.185 9).

*Treatment of the Alcohol* (9; $R^1$ = $R^3$ = Me, $R^2$ = $Bu^n$) *with TsOH in Benzene*.—The procedure used was the same as that for the alcohol (9; $R^1$ = $R^2$ = $R^3$ = Me). The alcohol (9; $R^1$ = $R^3$ = Me, $R^2$ = $Bu^n$) (150 mg) and TsOH (100 mg) in benzene (25 ml) gave, after 12 h, (E)-2-*diphenylphosphinoyl*-3-*methyloct*-3-*ene* (11; $R^1$ = $R^3$ = Me, $R^2$ = $Bu^n$) (130 mg, 90%), m.p. 89—90 °C (from EtOAc–$Pr^i_2O$), $R_F$ 0.6, $\nu_{max.}$ 1 440 (PPh) and 1 170 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 2.0—2.8 (10 H, m, $Ph_2PO$), 4.8 (1 H, m, C=CH), 6.95 (1 H, quint, $J_{PH}$ = $J_{HH}$ = 8 Hz, PC*H*Me), 8.1 (2 H, m, C=CHC*H*$_2$), 8.3 (3 H, s, CH=C*Me*), 8.65 (3 H, dd, $J_{PH}$ 16, $J_{HH}$ 8 Hz, PCH*Me*), 8.9 (6 H, m, $[CH_2]_3$), and 9.2 (3 H, t, $J_{HH}$ 5 Hz, $CH_2$*Me*), *m/e* 326 ($M^+$, 60%) and 201 ($Ph_2PO$, 100) (Found: C, 77.5; H, 8.2; P, 9.7. $C_{21}H_{27}OP$ requires C, 77.3; H, 8.3; P, 9.5%). No trace of the *Z*-isomer was found.

*Preparation of the Allylphosphine Oxide* (11; $R^1$ = $R^3$ = Me, $R^2$ = $Bu^n$) via *the Tertiary Alcohol* (13; $R^1$ = $R^3$ = Me, $R^2$ = $Bu^n$).—The procedure used was the same as that for the allylphosphine oxide (11; $R^1$ = $R^2$ = $R^3$ = Me). Ethyldiphenylphosphine oxide (5 g) in dry ether (200 ml), n-butyl-lithium (16 ml; 1.5 M in hexane) and heptan-2-one (2.5 g) in dry ether (50 ml) gave the tertiary alcohol, which was dehydrated with TFA (50 ml) to give the allylphosphine oxide (11; $R^1$ = $R^3$ = Me, $R^2$ = $Bu^n$) (6 g, 80%).

3-*Diphenylphosphinoyl*-2,3-*dimethylpentan*-2-*ol* (16; $R^1$ = Me, $R^2$ = H).—Diphenyl-s-butylphosphine oxide (1 g) in dry ether (100 ml) was stirred at 0 °C under nitrogen with n-butyl-lithium (2.5 ml; 1.5 M in hexane) for 0.5 h. The red solution was cooled to −78 °C and acetone (500 mg) in dry ether (50 ml) was added over 10 min. The solution was allowed to warm to room temperature and the procedure repeated. Water (100 ml) was then added, and the aqueous layer separated and extracted with chloroform (3 × 25 ml). The combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure to give an oil which crystallized; the solid was recrystallized from ethyl acetate–petrol to give the *alcohol* (16; $R^1$ = Me, $R^2$ = H) (750 mg, 60%), m.p. 155—156 °C (from EtOAc), $R_F$ 0.5, $\nu_{max.}$ 3 320 (OH), 1 435 (PPh) and 1 150 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 2.0—2.6 (10 H, m, $Ph_2PO$), 4.5 (1 H, s, OH), 7.7—8.3 (2 H, m, C$H_2$Me), 8.6 (3 H, d, $J_{PH}$ 17 Hz, PCMe), 8.8 (6 H, s, $CMe_2$), and 9.2 (3 H, t, $J_{HH}$ 7 Hz, $CH_2$*Me*), *m/e* 316 ($M^+$, 2%), 258 ($M$ — $Me_2CO$, 70), and 201 ($Ph_2PO$, 100) (Found: C, 72.2; H, 8.0; P, 10.0. $C_{19}H_{25}O_2P$ requires C, 72.1; H, 7.9; P, 9.8%).

4-*Diphenylphosphinoyl*-3,4-*dimethylpentan*-3-*ol* (16; $R^1$ = H, $R^2$ = Me).—The procedure was the same as that for the alcohol (16; $R^1$ = Me, $R^2$ = H). Isopropyldiphenylphosphine oxide (1 g) and n-butyl-lithium (2 ml; 2 M in hexane) and ethyl methyl ketone (500 mg) gave an oil which crystallized; the solid was recrystallized from ethyl acetate–petrol to give the *alcohol* (16; $R^1$ = H, $R^2$ = Me) (900 mg, 70%), m.p. 124—125 °C, $R_F$ 0.5, $\nu_{max.}$ 3 320 (OH), 1 435 (PPh), and 1 150 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 1.9—2.5 (10 H, m, $Ph_2PO$), 5.5 (1 H, s, OH), 8.2 (2 H, m, C$H_2$Me), 8.7 and 8.75 (each 3 H, d, $J_{PH}$ 16 Hz, PC$Me_2$*), 8.85 [3 H, s, C(OH)Me], and 9.1 (3 H, t, $J_{HH}$ 7 Hz, $CH_2$*Me*), *m/e* 316 ($M^+$, 3%), 244 ($M$ — MeCOEt, 90), and 201 ($Ph_2PO$, 100) (Found: C, 72.2; H, 7.9; P, 10.1. $C_{19}H_{25}O_2P$ requires C, 72.2; H, 7.9; P, 9.8%).

*Trifluoroacetolysis of the Alcohol* (16; $R^1$ = Me, $R^2$ = H).—The alcohol (16; $R^1$ = Me, $R^2$ = H) (100 mg) was kept at 70 °C for 3 h in TFA (0.4 ml). The solution was then poured into water (100 ml) and extracted with chloroform (3 × 25 ml), and the extracts were washed with saturated sodium hydrogen carbonate solution (3 × 25 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was recrystallized from ethyl acetate–petrol to give 4-*diphenylphosphinoyl*-3,4-*dimethylpent*-2-*ene* (19; $R^1$ = Me, $R^2$ = H) (90 mg, 89%), m.p. 98—100 °C, $R_F$ 0.6, $\nu_{max.}$ 1 430 (PPh) and 1 170 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 2.0—2.6 (10 H, m, $Ph_2PO$), 4.7 (1 H, $J_{PH}$ = $J_{HH}$ = 6 Hz, MeC=CH*Me*), 8.5 (3 H, s, *Me*C=CH), 8.55 (3 H, t, $J_{PH}$ = $J_{HH}$ = 6 Hz, MeC=CH*Me*), and 8.6 (6 H, d, $J_{PH}$ 15 Hz, PC$Me_2$), *m/e* 298 ($M^+$, 50%) and 201 ($Ph_2PO$, 100) (Found: C, 76.3; H, 8.0; P, 10.6. $C_{19}H_{23}OP$ requires C, 76.5; H, 7.7; P, 10.4%). The alcohol (16; $R^1$ = H, $R^2$ = Me) under the same conditions also gave the allylphosphine oxide (19; $R^1$ = Me, $R^2$ = H) in high yield.

3-*Diphenylphosphinoyl*-3,4-*dimethylhex*-4-*en*-2-*ol* (21).—The allylphosphine oxide (11; $R^1$ = $R^2$ = $R^3$ = Me) (3 g) in dry ether (100 ml) was stirred with n-butyl-lithium (7 ml; 1.5 M in hexane) at 0 °C under nitrogen for 0.5 h. The solution was cooled to −78 °C and a solution of acetaldehyde in ether, saturated with lithium bromide, was added until the red colour was discharged. The solution was allowed to reach 0 °C and water (100 ml) added. The aqueous layer was separated and extracted with chloroform (3 × 50 ml), and the combined organic layers were dried ($MgSO_4$) and evaporated under reduced pressure. The residue contained the two diastereoisomers of the *alcohol* (21) which were separated by column chromatography (elution with 4 : 1 EtOAc–petrol), and small amounts of γ-adducts. The (2RS,3SR)-*alcohol* (21b) (780 mg, 25%) was an oil, characterised as the 3,5-dinitrobenzoate (see below), $R_F$ 0.6, $\nu_{max.}$ 3 300 (OH), 1 440 (PPh), and 1 160 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 2.0—2.6 (10 H, m, $Ph_2PO$), 4.3 (1 H, broad quint, $J_{PH}$ = $J_{HH}$ = 6 Hz, C=C*H*Me), 4.6 (1 H, broad m, OH), 5.7 (1 H, quint, $J_{PH}$ = $J_{HH}$ = 6 Hz, C*H*OH), 8.2 (3 H, broad s, CH=C*Me*), 8.5 (3 H, broad t, $J_{PH}$ = $J_{HH}$ = 6 Hz, C=CH*Me*), 8.9 (3 H, d, $J_{PH}$ 17 Hz, PCMe), and 8.95 (3 H, d, $J_{HH}$ 6 Hz, *Me*CHOH), *m/e* 328 ($M^+$, 3%), 284 ($M$ — MeCHO, 100) and 201 ($Ph_2PO$, 90). The alcohol (21b) was converted [22] into its 3,5-*dinitrobenzoate*, m.p. 247—249 °C, $R_F$ 0.7, $\nu_{max.}$ 1 730 (ester), 1 540, 1 350 ($NO_2$), 1 440 (PPh), 1 280

[22] Method of A. Vogel, 'A Textbook of Practical Organic Chemistry,' Longmans, London, 1959, 3rd edn., p. 682.

(ester), and 1 180 $cm^{-1}$ (P=O), τ ($CDCl_3$) 0.85 (1 H, m, ArH), 1.05 (2 H, d, $J_{HH}$ 2 Hz, ArH), 2.0—2.8 (10 H, m, $Ph_2PO$), 4.1 (1 H, overlapping d q, $J_{PH}$ 4, $J_{HH}$ 6 Hz, CHOCO), 4.4 (1 H, broad quint, $J_{PH} = J_{HH} = 6$ Hz, C=C*H*Me), 8.3 (3 H, s, *Me*C=CHMe), 8.4 (3 H, t, $J_{PH} = J_{HH} = 6$ Hz, C=CH*Me*), 8.5 (3 H, d, $J_{PH}$ 17 Hz, PCMe), and 8.55 (3 H, d, $J_{HH}$ 6 Hz, *Me*CHO), *m/e* 522 ($M^+$, 5%), 310 ($M$ − OCOMe, 80), 283 (85), and 201 ($Ph_2PO$, 100) (Found: C, 61.9; H, 5.1; N, 5.1; P, 5.9. $C_{27}H_{27}N_2O_7P$ requires C, 62.1; H, 5.2; N, 5.4; P, 5.9%). The (2RS,3SR)-*alcohol* (21a) (1 g, 33%) had m.p. 147—149 °C (from EtOAc), $R_F$ 0.5, $\nu_{max.}$ 3 300 (OH), 1 440 (PPh), and 1 160 $cm^{-1}$ (P=O), τ ($CDCl_3$) 2.0—2.6 (10 H, m, $Ph_2PO$), 4.7 (1 H, quint, $J_{PH} = J_{HH} = 6$ Hz, C=C*H*Me), 4.9 (1 H, s, OH), 5.2 (1 H, overlapping dq, $J_{PH}$ 8, $J_{HH}$ 6 Hz, C*H*OH), 8.4 (3 H, t, $J_{PH} = J_{HH} = 6$ Hz, C=CH*Me*), 8.7 (3 H, d, $J_{PH}$ 16 Hz, PCMe), 8.8 (3 H, s, *Me*C=CHMe), and 9.0 (3 H, d, $J_{HH}$ 6 Hz, *Me*CHOH), *m/e* 328 ($M^+$, 2%), 284 ($M$ − MeCHO, 100), and 201 ($Ph_2PO$, 90) (Found: C, 73.3; H, 7.75; P, 9.4. $C_{20}H_{25}O_2P$ requires C, 73.2; H, 7.6; P, 9.4%).

*Conversion of the Alcohols* (21) *into Dienes* (22) *and their Diels–Alder Adducts with Maleic Anhydride* (23).—Each alcohol (21) (300 mg) in dimethylformamide (20 ml) was added to sodium hydride (60 mg of 60% dispersion in oil; washed with petrol) under nitrogen, and the mixture stirred at room temperature for 1 h. Water (20 ml) was added slowly and the solution extracted with light petroleum (b.p. 30—40 °C) (3 × 25 ml). The extracts were washed with water (6 × 25 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give the dienes (21). Each diene (50 mg) was heated under reflux in dry benzene (10 ml) with maleic anhydride (60 mg) for 10 h or until the reaction was complete.

(*E,E*)-3,4-Dimethylhexa-2,4-diene [6] (22a) (80 mg, 80%) had $\nu_{max.}$ 3 000—2 900, 2 860, 1 445, and 1 380 $cm^{-1}$ (CH), τ ($CDCl_3$) 4.5 (2 H, q, *J* 6 Hz, C=C*H*Me), 8.3 [6 H, s, CC(Me)=C(Me)C], and 8.35 (6 H, d, *J* 6 Hz, C=CH*Me*). The maleic anhydride adduct (23a) had m.p. 112—114 °C (lit.,[23] 113—114 °C), $\nu_{max.}$ 1 845 and 1 775 $cm^{-1}$ (anhydride), τ ($CDCl_3$) 6.8 (2 H, dd, *J* 2 and 4 Hz, HC·CO), 7.5 (2 H, m, C*H*Me), 8.3 (6 H, s, Me=CMe), and 8.6 (6 H, d, *J* 7 Hz, CH*Me*), *m/e* 208 ($M^+$, 50%), 136 (60), and 131 (100).

(*E,Z*)-3,4-Dimethylhexa-2,4-diene [6] (22b) (70 mg, 70%) had $\nu_{max.}$ 3 000—2 900, 2 850, 1 450, and 1 370 $cm^{-1}$ (CH), τ ($CDCl_3$) 4.8 (2 H, broad, *J* 6 Hz, C=C*H*Me), 8.3 (3 H, d, *J* 6 Hz, C=CH*Me*), 8.35 [6 H, s, CC(Me)=C(Me)C], and 8.4 (3 H, d, *J* 6 Hz, C=CH*Me*). The maleic anhydride adduct (23b) had m.p. 67—68 °C (lit.,[23] 68—69 °C), $\nu_{max.}$ 1 845 and 1 775 $cm^{-1}$ (anhydride), τ ($CDCl_3$) 6.7 (1 H, dd, *J* 9 and 6 Hz, HC·CO), 7.0 (1 H, dd, *J* 9 and 3 Hz), 7.3 (2 H, m, MeC*H*), 8.3 (6 H, s, *Me*C=C*Me*), 8.8 (3 H, d, *J* 7 Hz, CH*Me*), and 8.85 (3 H, d, *J* 7 Hz, CH*Me*), *m/e* 208 ($M^+$, 40%), 180 ($M$ − CO, 60), and 136 (100).

2-*Diphenylphosphinoyl*-3-*methylbutane* (24).—1-Diphenylphosphinoyl-2-methylpropane (3 g) in dry ether (100 ml) was stirred with tetramethylethylenediamine (1.3 g) for 10 min under nitrogen. The solution was cooled to 0 °C, n-butyl-lithium (7 ml; 2M in hexane) was added, and the bright orange solution was stirred for 25 min. Methyl iodide (0.75 ml) was added, followed by water (100 ml). The aqueous layer was extracted with chloroform (3 × 25 ml), and the combined organic layers were washed with sodium thiosulphate solution (2 × 25 ml), dried ($MgSO_4$), and evaporated under reduced pressure. The residue was recrystallised from ethyl acetate to give the *phosphine oxide* (24) (2.5 g, 80%), m.p. 156—158 °C, $R_F$ 0.4, $\nu_{max.}$ 1 435 (PPh) and 1 170 $cm^{-1}$ (P=O), τ ($CDCl_3$) 2.0—2.6 (10 H, m, $Ph_2PO$), 7.7 (2 H, m, PC*H*C*H*Me), 8.9 (3 H, dd, $J_{PH}$ 16, $J_{HH}$ 7 Hz, PCH*Me*), and 8.9 and 8.95 (each 3 H, d, $J_{PH}$ 6 Hz, $CMe_2$*), *m/e* 272 ($M^+$, 30%), 230 ($M - C_3H_6$, 50), and 201 ($Ph_2PO$, 100) (Found: C, 74.9; H, 8.75; P, 11.5. $C_{17}H_{21}OP$ requires C, 75.0; H, 7.70; P, 11.5%).

3-*Diphenylphosphinoyl*-3,4-*dimethylpentan*-2-*ol* (25; R = Me).—The procedure used was the same as that for the alcohol (9; $R^1 = R^2 = R^3$ = Me). The phosphine oxide (24) (1.5 g) in dry ether (50 ml), n-butyl-lithium (3.5 ml; 2M in hexane), and acetaldehyde in ether, saturated with anhydrous lithium bromide, gave an oil which crystallised, containing both diastereoisomers of the *alcohol* (25; R = Me). Fractional recrystallisation from ethyl acetate gave the high $R_F$ *diastereoisomer* (600 mg, 40%), m.p. 184—186 °C (from EtOAc–petrol), $R_F$ 0.7, $\nu_{max.}$ 3 300 (OH), 1 435 (PPh), and 1 150 $cm^{-1}$ (P=O), τ ($CDCl_3$) 1.8—2.6 (10 H, m, $Ph_2PO$), 4.6 (1 H, broad s, OH), 5.8 (1 H, overlapping dq, $J_{PH}$ 14, $J_{HH}$ 7 Hz, C*H*OH), 7.4—7.9 (1 H, overlapping double septet, $J_{PH}$ 7, $J_{HH}$ 6 Hz, PCC*H*$Me_2$), 8.7 (3 H, d, $J_{PH}$ 18 Hz, PCMe) 8.8 (3 H, d, $J_{HH}$ 7 Hz, CH*Me*OH), and 9.0 (each 3 H, d, $J_{HH}$ 6 Hz, CHMe*), *m/e* 316 ($M^+$, 5%), 272 ($M$ − MeCHO, 80), and 201 ($Ph_2PO$, 100) (Found: C, 71.9; H, 7.9; P, 9.9. $C_{19}H_{25}O_2P$ requires C, 72.1; H, 7.9; P, 9.8%). The low $R_F$ *isomer* (400 mg, 26%) had m.p. 177—179 °C, $R_F$ 0.6, $\nu_{max.}$ 3 300 (OH), 1 435 (PPh), and 1 150 $cm^{-1}$ (P=O), τ ($CDCl_3$) 1.8—2.6 (10 H, m, $Ph_2PO$), 4.7 (1 H, s, OH), 5.8 (1 H, dq, $J_{PH}$ 19, $J_{HH}$ 6 Hz, C*H*OH), 7.7 (1 H, oct, $J_{PH} = J_{HH}$ 7 H =z, C*H*$Me_2$), 8.7 (3 H, d, $J_{PH}$ 18 Hz, PCMe), 8.8 (3 H, d, $J_{HH}$ 6 Hz, *Me*CHOH), and 9.0 and 9.05 (each 3 H, d, $J_{HH}$ 7 Hz, $CHMe_2$*), *m/e* 316 ($M^+$, 3%), 272 ($M$ − MeCHO, 80), and 201 ($Ph_2PO$, 100) (Found: C, 71.9; H, 8.1; P, 9.5. $C_{19}H_{25}O_2P$ requires C, 72.1; H, 7.9; P, 9.8%).

*Treatment of the Alcohol* (25; R = Me) *with TsOH in Benzene*.—The procedure used was the same as that for the alcohol (9; $R^1 = R^2 = R^3$ = Me). A mixture of diastereoisomers of the alcohol (25; R = Me) (100 mg) and TsOH (70 mg) in benzene (25 ml) gave, after 6 h, a mixture of three compounds: starting alcohol (15 mg, 15%), the allylphosphine oxide (27; R = Me) (25 mg, 24%) (see below), and 2-*isopropyl*-3-*diphenylphosphinoylbut*-1-*ene* (26; R = Me), purified by recrystallisation from ethyl acetate (56 mg, 55%); m.p. 112—115 °C, $R_F$ 0.7, $\nu_{max.}$ 1 435 (PPh) and 1 170 $cm^{-1}$ (P=O), τ ($CDCl_3$) 1.8—2.8 (10 H, m, $Ph_2PO$), 4.6 (1 H, d, $J_{PH}$ 4 Hz, $CH_2$=C), 4.95 (1 H, d, $J_{HH}$ 3.5 Hz, $CH_2$=C), 7.0 (1 H, quint, $J_{PH} = J_{HH} = 7$ Hz, PC*H*Me), 8.1 (1 H, m, C*H*$Me_2$), 8.6 (3 H, dd, $J_{PH}$ 16, $J_{HH}$ 7 Hz, PCH*Me*), and 9.1 and 9.2 (each 3 H, d, $J_{HH}$ 7 Hz, $CHMe_2$*), *m/e* 298 ($M^+$, 25%) and 201 ($Ph_2PO$, 100) (Found: $M^+$, 298.148 4. $C_{19}H_{23}OP$ requires $M$, 298.1485).

*Treatment of the Alcohol* (25; R = Me) *with TsOH in Toluene*.—The procedure used was the same as that for the alcohol (9; $R^1 = R^2 = R^3$ = Me). A mixture of diastereoisomers of the alcohol (25; R = Me) (100 mg) and TsOH (100 mg) was heated under reflux in toluene (25 ml) for 30 h and gave 4-*diphenylphosphinoyl*-2,3-*dimethylpent*-2-*ene* (27; R = Me) (91 mg, 90%), m.p. 130—132 °C (from EtOAc), $R_F$ 0.7, $\nu_{max.}$ 1 435 (PPh) and 1 170 $cm^{-1}$ (P=O), τ ($CDCl_3$) 2.0—2.8 (10 H, m, $Ph_2PO$), 6.5 (1 H, quint, $J_{PH} = J_{HH}$ = 7 Hz, PC*H*Me), 8.2 (3 H, broad s, *Me*C=C$Me_2$), 8.5 (3 H, d, $J_{PH}$ 5 Hz, MeC=C$Me_2$), 8.6 (3 H, broad s, MeC=C$Me_2$), and 8.7 (3 H, dd, $J_{PH}$ 16, $J_{HH}$ 7 Hz, PCH*Me*), *m/e* 298 ($M^+$, 35%) and 201 ($Ph_2PO$, 100) (Found: C, 76.3; H, 7.8; P, 10.5. $C_{19}H_{23}OP$ requires C, 76.5; H, 7.7; P, 10.4%).

[23] R. Criegee and K. Noll, *Annalen*, 1959, **627**, 1.

*2-Diphenylphosphinoyl-2,3-dimethyl-1-phenylbutan-1-ol* (25; R = Ph).—The procedure was the same as that for the alcohol (9; $R^1 = R^2 = Me$, $R^3 = Ph$). 2-Diphenylphosphinoyl-3-methylbutane (1.4 g), n-butyl-lithium (4 ml; 1.5M in hexane), and benzaldehyde (600 mg) gave a solid mixture of the two diastereoisomers of the *alcohol* (25; R = Ph), separated by fractional recrystallisation from ethyl acetate. The higher $R_F$ *isomer* (800 mg, 40%) had m.p. 214—215 °C (from methanol), $R_F$ 0.8, $\nu_{max.}$ 3 300 (OH), 1 430 (PPh), and 1 140 $cm^{-1}$ (P=O), τ ($CDCl_3$) 1.7—2.5 (10 H, m, $Ph_2PO$), 2.7 (5 H, broad s, Ph), 3.3 (1 H, s, OH), 4.9 (1 H, d, $J_{PH}$ 9 Hz, PhC*H*OH), 7.5—8.2 (1 H, oct, $J_{PH} = J_{HH} = 7$ Hz, C*H*$Me_2$), 8.65 (3 H, d, $J_{HH}$ 7 Hz, CH*Me*$_2$*), 8.8 (3 H, d, $J_{PH}$ 17 Hz, PC*Me*), and 9.3 (3 H, d, $J_{PH}$ 7 Hz, CH*Me*$_2$*), *m/e* 378 ($M^+$, 3%), 272 ($M$ − PhCHO, 100). and 201 ($Ph_2PO$, 50) (Found: C, 75.9; H, 7.3; P, 8.0. $C_{24}H_{27}O_2P$ requires C, 76.2; H, 7.15; P, 8.2%). The lower $R_F$ *isomer* (400 mg, 20%) had m.p. 248—250 °C (from methanol), $R_F$ 0.7, $\nu_{max.}$ 3 300 (OH), 1 430 (PPh), and 1 150 $cm^{-1}$ (P=O), τ ($CDCl_3$; the compound is not very soluble) 1.7—2.7 (10 H, m, $Ph_2PO$), 2.7 (5 H, s, Ph), 7.4 (1 H, broad s, OH), 5.7 (1 H, d, $J_{PH}$ 6 Hz, PhC*H*OH), 7.7—8.1 (1 H, m, C*H*$Me_2$), 8.6 (3 H, d, $J_{PH}$ 17 Hz, PCMe), and 8.95 and 9.05 (each 3 H, d, $J_{HH}$ 7 Hz, CH*Me*$_2$*), *m/e* 378 ($M^+$, 5%), 272 ($M$ − PhCHO, 100), and 201 ($Ph_2PO$, 80) (Found: C, 75.8; H, 7.3; P, 8.1. $C_{24}H_{27}O_2P$ requires C, 76.2; H, 7.15; P, 8.2%).

*Trifluoroacetolysis of the Alcohol* (25; R = Ph).—A mixture of diastereoisomers of the alcohol (25; R = Ph) (100 mg) was heated under reflux in TFA (10 ml) for 4 h. The solution was poured into water (100 ml) and extracted with chloroform (3 × 25 ml). The extract was then washed with saturated sodium hydrogen carbonate solution (3 × 25 ml), dried ($MgSO_4$), and evaporated under reduced pressure to give *4-diphenylphosphinoyl-3,4-dimethyl-4-phenylbutan-2-ol* (30; R = Ph) (90 mg, 90%), m.p. 196—198 °C (from methanol), $R_F$ 0.7, $\nu_{max.}$ 3 300 (OH), 1 440 (PPh), and 1 175 $cm^{-1}$ (P=O), τ ($CDCl_3$) 1.9—3.0 (15 H, m, $Ph_2PO$ and Ph), 5.6 (1 H, dd, $J_{PH} = J_{HH} = 2$ Hz, PC*H*Ph), 7.6 (1 H, two overlapping quartets of doublets, $J_{PH}$ 15, $J_{HH}$ 7 and 2 Hz, PCHC*H*Me), 8.2 (1 H, broad s, OH), 8.75 (3 H, d, $J_{HH}$ 7 Hz, CH*Me*), and 8.95 and 9.05 (each 3 H, d, C*Me*$_2$*OH), *m/e* 378 ($M^+$, 3%), 360 ($M$ − $H_2O$, 6). 291 ($Ph_2POCHPh^+$, 16), and 201 ($Ph_2PO$, 100) (Found: C, 76.2; H, 7.1; P, 8.5. $C_{24}H_{27}O_2P$ requires C, 76.2; H, 7.15; P, 8.2%). Only one diastereoisomer was isolated.

*Treatment of the Alcohol* (25; R = Ph) *with TsOH in Benzene*.—The procedure was the same as that for the alcohol (9; $R^1 = R^2 = R^3 = Me$). A mixture of diastereoisomers of the alcohol (25; R = Ph) (120 mg) heated under reflux with TsOH (60 mg) in benzene (25 ml) for 6 h gave *2-(α-diphenylphosphinoylbenzyl)-3-methylbut-1-ene* (26; R = Ph) (100 mg, 85%), m.p. 173—175 °C (from EtOAc), $R_F$ 0.7, $\nu_{max.}$ 1 440 (PPh) and 1 175 $cm^{-1}$ (P=O), τ ($CDCl_3$) 2.0—3.0 (15 H, m, $Ph_2PO$ and Ph), 4.1 (1 H, d, $J_{PH}$ 2 Hz, C=C*H*$_2$), 4.9 (1 H, s, C=C*H*$_2$), 5.9 (1 H, d, $J_{PH}$ 9 Hz, PC*H*Ph), 7.9 (1 H, m, C*H*$Me_2$). and 9.1 and 9.2 (each 3 H, d, $J_{HH}$ 7 Hz, CH*Me*$_2$*), *m/e* 360 ($M^+$, 30%) and 201 ($Ph_2PO$, 100) (Found: $M^+$, 360.162 8. $C_{24}H_{25}OP$ requires $M$, 360.164 2).

*Diphenyl-2-trimethylsilylethylphosphine Oxide*. (33).—n-Butyl-lithium (13.3 ml; 1.5M in hexane) was added dropwise to a stirred solution of methyldiphenylphosphine oxide (4.32 g) in dry THF (100 ml) under nitrogen at 25 °C. After 15 min, trimethylsilylmethyl chloride[24] (3 g) was added dropwise. The mixture was kept for 17 h at 25 °C, poured into water, and extracted with chloroform: the extract was dried ($MgSO_4$) and evaporated *in vacuo* to give the *phosphine oxide* (33) (4.1 g, 68%), m.p. 116—117 °C (from hexane) (Found: C, 67.75; H, 7.7. $C_{17}H_{23}OPSi$ requires C, 67.55; H, 7.6%), $\nu_{max.}$ (Nujol) 1 440 (P–Ph), 1 252 (SiMe), and 1 152 $cm^{-1}$ (P=O), τ ($CDCl_3$) 2.15—2.8 (10 H, m, $Ph_2PO$), 7.72—8.01 (2 H, 9 lines, $PCH_2$) 9.12—9.45 (2 H, 9 lines, $CH_2Si$), and 10.05 (9 H, s, $SiMe_3$).

*2-Diphenylphosphinoyl-3-trimethylsilylpropiophenone* (34).—n-Butyl-lithium (7 ml; 1.5M in hexane) was added dropwise to a stirred solution of the phosphine oxide (33) (3.2 g) in dry THF (40 ml) under nitrogen at 0 °C. After 20 min, ethyl benzoate (1.65 g) in dry THF (2 ml) was added dropwise and the temperature raised to 25 °C over 30 min. The mixture was then poured into water and extracted with chloroform. The extract was washed with sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaported *in vacuo* to give the *ketone* (34) (2.9 g, 67%), m.p. 170—172 °C (from $CHCl_3$–hexane) (Found: C, 71.0; H, 6.75. $C_{24}H_{27}O_2PSi$ requires C, 70.9; H, 6.65%), $R_F$ ($Et_2O$) 0.25, $\nu_{max.}$ (Nujol) 1 673 (C=O), 1 439 (Ph–P), and 1 194 $cm^{-1}$ (P=O), τ ($CDCl_3$) 1.9—2.9 (15 H, m, $Ph_2PO$ and Ph), 5.39 (1 H, ddd, $J$ 2, 12, and 16.5 Hz, PCH), 8.39 (1 H, ddd, $J$ 5.5, 12, and 14.5 Hz, $CH_AH_BSi$), 8.92 (1 H, dt, $J$ 2, 14.5, and 14.5 Hz, $CH_AH_BSi$), and 10.14 (9 H, s, $SiMe_3$).

*Ethyl 2-Diphenylphosphinoyl-1-ethoxy-1-phenyl-3-trimethylsilylpropene*.—Sodium hydride (120 mg) was added to a stirred solution of the phosphine oxide (34) (1.15 g) in dry THF (25 ml) under nitrogen at 25 °C, and the mixture kept for 90 min. Ethyl iodide (470 mg; freshly distilled) was added dropwise at 25 °C and the mixture was heated under reflux for 1 h, poured into cold water and extracted with chloroform. The extract was washed with sodium hydrogen carbonate solution and with water, dried ($MgSO_4$), and evaporated *in vacuo* to give an oil, which was purified by column chromatography on silica (200 g; made up in and eluted with ether) to give the *O-ethyl derivative* (1.0 g, 81%), $R_F$ (EtOAc) 0.41, τ ($CCl_4$) 2.10—2.94 (15 H, m, $Ph_2PO$ and Ph), 7.35 (2 H, q, $J$ 7 Hz, OC*H*$_2$CH$_3$), 8.14 (2 H, d, $J$ 17 Hz, $CH_2Si$), 9.63 (3 H, t, $J$ 7 Hz, OCH$_2$C*H*$_3$), and 10.38 (9 H, s, $SiMe_3$) (Found: $M^+$, 434.181 9. $C_{26}H_{31}O_2PSi$ requires $M$, 434.183 0), *m/e* 434 (13%) and 419 (100).

*2-Diphenylphosphinoyl-1-phenylbutan-1-ol*.— n-Butyl-lithium (6.6 ml; 1.5M in hexane) was added dropwise to a stirred slurry of diphenylpropylphosphine oxide (2.44 g) in dry ether (40 ml) under nitrogen at 25 °C. After 20 min, benzaldehyde (1.2 g) in dry ether (6 ml) was added dropwise at 25 °C. The mixture was kept for 17 h, poured into water, and extracted with chloroform. The extract was washed with sodium hydrogen carbonate solution and with water, dried ($MgSO_4$), and evaporated *in vacuo* to give a pale yellow oil (3.5 g, 104%), which was a mixture of two diastereoisomeric alcohols. Some of the mixture was purified by t.l.c. (silica; eluted with EtOAc). The *major isomer* (200 mg) had m.p. 154—157 °C (from $CHCl_3$–hexane) (Found: C, 73.1; H, 6.6. $C_{22}H_{23}O_2P$ requires C, 73.4; H, 6.6%), $R_F$ (EtOAc) 0.40, τ ($CDCl_3$) 1.9—2.9 (15 H, m, $Ph_2PO$ and Ph), 4.75 (1 H, d, $J$ 10 Hz, C*H*OH), 5.28 (1 H, s, OH), 7.64 (1 H, m, PCH), 8.18 (2 H, m, C*H*$_2$CH$_3$), and 9.62 (3 H, t, $J$ 7 Hz, CH$_2$C*H*$_3$), $\nu_{max.}$ (Nujol) 3 240 (OH), 1 440 (P–Ph), and 1 158 $cm^{-1}$ (P=O), *m/e* 350 (30%, $M^+$) and 244 (100). The *minor isomer* (45 mg) had m.p. 135—138° (from $CHCl_3$–hexane) (Found: C, 73.0; H, 6.35%), $R_F$ (EtOAc)

[24] J. D. Roberts and S. Dev, *J. Amer. Chem. Soc.*, 1951, **73**, 1879.

0.29, τ ($CDCl_3$) 2.0—3.0 (15 H, m, $Ph_2PO$ and Ph), 4.50 (1 H, s, OH), 4.97 (1 H, d, *J* 18 Hz, C*H*OH), 7.42 (1 H, m, PCH), 8.50 (2 H, m, $CH_2CH_3$), and 9.36 (3 H, t, *J* 7 Hz, $CH_2CH_3$), *m/e* 350 (2%, $M^+$) and 244 (100).

*2-Diphenylphosphinoylbutyrophenone* (35).—*Method A*. Sodium dichromate (3 g) in aqueous sulphuric acid (50 ml; 1N) was added dropwise over 30 min to a stirred solution of the mixture of diastereoisomeric alcohols (above) (3.1 g) in acetone (100 ml) at 25 °C. The mixture was kept for 30 min, then water (200 ml) was added, and chloroform (50 ml). The chloroform layer was washed with sodium hydrogen carbonate solution and with water, dried ($MgSO_4$), and evaporated *in vacuo*, and the residue purified by chromatography on a column of silica (200 g) (elution with ethyl acetate), to give the *ketone* (35) (1.85 g, 60%), m.p. 156—159 °C (from $CHCl_3$–hexane) (Found: C, 75.7; H, 6.1. $C_{22}H_{21}OP$ requires C, 75.9; H, 6.0%), $R_F$ (EtOAc) 0.31, $\nu_{max.}$ (Nujol) 1 672 (PhCO), 1 440 (Ph–P), and 1 173 $cm^{-1}$ (P=O), τ ($CDCl_3$) 1.95—2.81 (15 H, m, $Ph_2PO$ and Ph), 5.53 (1 H, ddd, *J* 3.5, 10.5, and 16.5 Hz, PCH), 7.5—8.2 (2 H, m, $CH_2CH_3$), and 9.10 (3 H, t, *J* 7 Hz, $CH_2CH_3$), *m/e* 348 (33%, $M^+$) and 202 (100).

*Method B*. n-Butyl-lithium (6.6 ml; 1.5M in hexane) was added dropwise to a stirred slurry of diphenylpropylphosphine oxide (2.44 g) in dry ether (25 ml) under nitrogen at 25 °C. After 15 min, ethyl benzoate (1.65 g) in dry ether (5 ml) was added dropwise at 25 °C; the mixture was kept for 1 h, poured into water, and extracted with chloroform. The extract was washed with sodium hydrogen carbonate solution and with water, dried ($MgSO_4$), and evaporated *in vacuo* to give the same ketone (1.9 g, 57% after recrystallisation from $CHCl_3$–hexane).

*Diphenyl-1-(trimethylsilylmethyl)propylphosphine Oxide* (36).—n-Butyl-lithium (13.3 ml; 1.5M in hexane) was added dropwise to a stirred solution of diphenylpropylphosphine oxide (4.88 g) in dry THF (70 ml) under nitrogen at 25 °C. After 15 min, trimethylsilylmethyl chloride [24] (3 g) was added dropwise. The mixture was kept for 17 h at 25 °C, poured into water, and extracted with chloroform. The extract was washed with sodium hydrogen carbonate solution and with water, dried ($MgSO_4$), and evaporated *in vacuo* to give the *phosphine oxide* (36) (4.5 g, 68%), m.p. 119—121 °C (from $CHCl_3$–hexane) (Found: C, 69.35; H, 8.2. $C_{19}H_{27}OPSi$ requires C, 69.1; H, 8.2%), $\nu_{max.}$ (Nujol) 1 440 (Ph–P), 1 252 (SiMe), and 1 180 $cm^{-1}$ (P=O), τ ($CCl_4$) 1.9—2.7 (10 H, m, $Ph_2PO$), 7.78 (1 H, m, PCH), 8.47 (2 H, m, $CH_2CH_3$), 9.1—9.4 (5 H, t and m, $CH_2CH_3$ and $CH_2SiMe_3$), and 10.12 (9 H, s, $SiMe_3$), *m/e* 330 (24%, $M^+$), 329 (5%), and 274 (100).

*Metallation of Diphenyl-1-(trimethylsilylmethyl)propylphosphine Oxide* (36).—n-Butyl-lithium (0.66 ml; 1.5M in hexane) was added dropwise to a stirred solution of the phosphine oxide (36) (0.33 g) in dry THF (15 ml) under nitrogen at −50 °C. After 8 min, deuterium oxide (1 ml) was added and the mixture stirred for 12 h, as the temperature rose to room temperature. The mixture was poured into water and extracted with chloroform, and the chloroform layer was washed with sodium hydrogen carbonate solution and with water, dried ($MgSO_4$), and evaporated *in vacuo* to give the deuteriated starting material (0.25 g), m.p. 118—120 °C (from hexane), τ ($CDCl_3$) 7.68 (1 H, m, PCH), 8.40 (2 H, m, $CH_2CH_3$), 9.0—9.3 (4 H, t and m, $CH_2CH_3$ and C*H*D$SiMe_3$), and 10.05 (9 H, s, $SiMe_3$), *m/e* 331 (22%, $M^+$), 330 (7), and 275 (100). Evidently, metallation took place next to silicon to give (37) and thence the deuteriated compound (37; D for Li). A closely similar reaction was carried out, but benzaldehyde (1 equiv.) was added in place of the deuterium oxide. The mixture was worked up after 2 h and the major component, which still appeared to be a mixture, was separated by t.l.c. (silica; eluted with $Et_2O$). Some crystals separated, double m.p. 207—208 and 221—222 °C (from $CHCl_3$–hexane), τ ($CDCl_3$) 1.9—3.0 (15 H, m, $Ph_2PO$ and Ph), 3.45 (1 H, d, *J* 6 Hz, PhC*H*=C), 5.08 (1 H, dd, *J* 6 and 19 Hz, PCH–C*H*=CHPh), 7.6—8.8 (3 H, m, PC*H*C$H_2$CH$_3$), and 8.86 (3 H, t, *J* 7 Hz, $CH_2CH_3$). This compound appeared to be the *Z*-isomer (38).

*(2-Ethyl-3-phenylallyl)trimethylsilane* (41).—n-Butyl-lithium (3.3 ml; 1.5M in hexane) was added dropwise to a stirred solution of the phosphine oxide (36) (1.65 g) in dry THF (25 ml) containing TMEDA (1 ml) under nitrogen at 30 °C. After 1 h, benzaldehyde (580 mg) in dry THF (1 ml) was added at 30 °C. The mixture was kept for 17 h, poured into water, and extracted with chloroform. The extract was washed with sodium hydrogen carbonate solution and with water, dried ($MgSO_4$), and evaporated *in vacuo* to leave a pale yellow oil. This was chromatographed on silica (100 g), (elution with hexane) to give a 1 : 1 mixture of the *allylsilanes* (41) as an oil (610 mg, 56%), $R_F$ (hexane) 0.37, $R_F$ (EtOAc) 0.71, τ ($CCl_4$) 2.87 (5 H, m, Ph), 4.87 and 4.86 (1 H, two s, C=C*H*Ph), 7.68 and 7.76 (2 H, two q, *J* 7 Hz, $CH_2CH_3$), 8.03 and 8.24 (2 H, two s, $CH_2SiMe_3$), 8.77 and 8.83 (3 H, two t, *J* 7 Hz, $CH_2CH_3$), and 9.82 and 9.93 (9 H, two s, $SiMe_3$) (Found: $M^+$, 218.150 7. $C_{14}H_{22}Si$ requires *M*, 218.149 0), *m/e* 218 (100%) and 105 (55).

*2-Diphenylphosphinoyl-1-phenyl-2-trimethylsilylmethylbutan-1-ol* (42).—Diphenyl-1-(trimethylsilylmethyl)propylphosphine oxide (36) (3.30 g) and TMEDA (3 ml) in dry THF (100 ml) were stirred with n-butyl-lithium (7.0 ml; 1.6M in hexane) at room temperature under nitrogen for 1 h. Benzaldehyde was added dropwise with stirring at room temperature until the deep red colour was discharged. The solution was immediately poured into water (100 ml) and extracted with chloroform (3 × 100 ml). The combined extracts were washed successively with dilute hydrochloric acid (100 ml), sodium hydrogen carbonate solution (100 ml; saturated), and sodium chloride solution (100 ml; saturated), dried ($Na_2SO_4$), and evaporated *in vacuo*. Crystallisation of the oil from ethyl acetate–hexane gave the *alcohol* (42) as a 1 : 1 mixture of diastereoisomers (1.36 g, 32%). These were separated by preparative t.l.c. ($Et_2O$) to give one *diastereoisomer*, m.p. 204—205 °C (from EtOAc) (Found: C, 71.5; H, 7.8; P, 7.15. $C_{26}H_{33}O_2PSi$ requires C, 71.6; H, 7.6; P, 7.1%), $\nu_{max.}$ 3 150 (OH), 1 435 (PPh), 1 248 ($SiMe_3$), and 1 160 $cm^{-1}$ (P=O), τ ($CDCl_3$) 1.8—2.7 (15 H, m, $Ph_2PO$ and Ph), 3.50 (1 H, d, *J* 7 Hz, OH), 5.10 (1 H, dd, *J* 7 and 18 Hz, C*H*OH), 8.0—9.0 (total 7 H, m overlain by triplet, *J* 6 Hz, at 8.83, $CH_2CH_3$ and $CH_2Si$) and 9.90 (9 H, s, $SiMe_3$), *m/e* 436 (0.3%, $M^+$), 421 (13, *M* − Me), 346 (6, *M* − $Me_3SiOH$), 330 (42, *M* − PhCHO), 274 (29, $Ph_2POSiMe_3$), 257 (100), 202 (54, $Ph_2POH$), and 201 ($Ph_2PO$), and the other *diastereoisomer*, m.p. 223—224 °C (from EtOAc) (Found: C, 71.4; H, 7.6; P, 6.8. $C_{26}H_{33}O_2PSi$ requires C, 71.6; H, 7.6; P, 7.1%), $R_F$ 0.4, $\nu_{max.}$ 3 150 (OH), 1 435 (PPh), 1 248 ($SiMe_3$) and 1 160 $cm^{-1}$ (P=O), τ ($CDCl_3$) 1.9—2.8 (15 H, m, $Ph_2PO$ and Ph), 4.60 (1 H, s, OH), 4.70 (1 H, d, *J* 12 Hz, C*H*OH), 8.0—9.3 (total 7 H, m overlain by triplet, *J* 6 Hz, at 9.20, $CH_2CH_3$ and $CH_2Si$), and 10.18 (9 H, s, $SiMe_3$), *m/e* 436 (0.4%, $M^+$), 421 (13, *M* − Me), 346 (18, *M* − $Me_3SiOH$), 330 (40, *M* − PhCHO), 274 (29, $Ph_2POSiMe_3$), 257 (100), 202 (50, $Ph_2POH$), and 201 (50, $Ph_2PO$).

2-(α-*Diphenylphosphinoylbenzyl*)*but*-1-*ene* (14; $R^2$ = Me, $R^3$ = Ph).— 2-Diphenylphosphinoyl-1-phenyl-2-trimethylsilylmethylbutan-1-ol (42) (186 mg; diastereoisomeric mixture) was stirred with TFA (3 ml) for 30 min at room temperature. The mixture was diluted with chloroform (30 ml) and stirred with sodium hydrogen carbonate solution (50 ml; saturated). The aqueous layer was extracted with chloroform (2 × 20 ml). The combined extracts were dried ($Na_2SO_4$) and evaporated *in vacuo* to give the *olefin* (14; $R^2$ = Me, $R^3$ = Ph) (140 mg, 95%), m.p. 231—232 °C (from EtOAc–hexane) (Found: C, 79.9; H, 6.8; P, 8.8. $C_{23}H_{23}OP$ requires C, 79.8; H, 6.7; P, 8.9%), $R_F$ 0.3 ($Et_2O$), $\nu_{max.}$ 1 640 (C=C), 1 440 (PPh), and 1 180 $cm^{-1}$ (P=O), τ ($CDCl_3$) 2.0—2.9 (15 H, m, Ph and $Ph_2PO$), 4.30—4.40 (1 H, broad s, C=C$H_A$), 4.96—5.06 (1 H, broad s, C=C$H_B$), 5.90 (1 H, d, *J* 8 Hz, PC*H*Ph), 7.8—8.1 (2 H, m, $CH_2$), and 9.12 (3 H, t, *J* 8 Hz, $CH_3$), *m/e* 346 (28%, $M^+$), 202 (88, $Ph_2POH$), and 201 (100, $Ph_2PO$).

4-*Diphenylphosphinoyl*-3-*methyl*-4-*phenylbut*-2-*ene* (11; $R^1$ = $R^2$ = Me, $R^3$ = Ph) *from the Alcohol* (42).—The alcohol (42) (109 mg; diastereoisomeric mixture) was heated under reflux in TFA (2 ml) for 30 min. The mixture was diluted with chloroform (20 ml) and stirred with sodium hydrogen carbonate solution (50 ml; saturated). The aqueous layer was extracted with chloroform (2 × 10 ml); the combined extracts were dried ($Na_2SO_4$) and evaporated *in vacuo*, to give the olefin (11; $R^1$ = $R^2$ = Me, $R^3$ = Ph), m.p. and mixed m.p. 254—255 °C, identical (i.r., n.m.r.) with an authentic sample (described above).

3-*Diphenylphosphinoylpentan*-2-*ol* (44; $R^1$ = Et, $R^2$ = H).—The procedure was the same as for the alcohol (9; $R^1$ = $R^2$ = $R^3$ = Me). Diphenylpropylphosphine oxide (1 g) in dry ether (50 ml), n-butyl-lithium (2.5 ml; 1.8M in hexane), and a solution of acetaldehyde in ether, saturated with anhydrous lithium bromide, gave an oil containing the two diastereoisomers of the *alcohol* (44; $R^1$ = Et, $R^2$ = H), which were separated by p.l.c. The high $R_F$ *isomer* (280 mg, 27%) had m.p. 124—126 °C (from EtOAc), $R_F$ 0.6, $\nu_{max.}$ 3 350 (OH), 1 440 (PPh), and 1 160 $cm^{-1}$ (P=O), τ ($CDCl_3$) 2.0—2.6 (10 H, m, $Ph_2PO$), 5.6 (1 H, overlapping dq, $J_{PH}$ 12, $J_{HH}$ 6 Hz, C*H*OH), 5.65 (1 H, s, OH), 7.7—8.5 (3 H, m, PC*H*C$H_2$Me), 8.7 [3 H, d, $J_{HH}$ 6 Hz, CH(OH)*Me*], and 9.1 (3 H, t, $J_{HH}$ 7 Hz, $CH_2$*Me*), *m/e* 288 ($M^+$, 6%), 244 (*M* — MeCHO, 60), 230 (100), and 201 ($Ph_2PO$, 80) (Found: C, 70.6; H, 7.5; P, 10.5. $C_{17}H_{21}O_2P$ requires C, 70.8; H, 7.3; P, 10.5%). The low $R_F$ *isomer* (260 mg, 25%) had m.p. 185—186 °C (from EtOAc), $R_F$ 0.5, $\nu_{max.}$ 3 350 (OH), 1 440 (PPh), and 1 160 $cm^{-1}$ (P=O), τ ($CDCl_3$) 2.0—2.6 (10 H, m, $Ph_2PO$), 5.6 (1 H, s, OH), 5.8 (1 H, m, C*H*OH), 7.6 (1 H, m, PCH), 8.4 (2 H, m, C$H_2$Me), 8.7 [3 H, d, $J_{HH}$ 6 Hz, CH(OH)*Me*], and 9.1 (3 H, t, $J_{HH}$ 7 Hz, $CH_2$*Me*), *m/e* 288 ($M^+$, 6%), 244 (*M* — MeCHO, 60), 230 (100), and 201 ($Ph_2PO$, 80) (Found: C, 70.7; H, 7.4; P. 10.5. $C_{17}H_{21}O_2P$ requires C, 70.8; H, 7.3; P, 10.8%).

*Treatment of the Alcohol* (44; $R^1$ = Et, $R^2$ = H) *with TsOH in Toluene*.—The procedure was the same as for the alcohol (9; $R^1$ = $R^2$ = $R^3$ = Me). A mixture of diastereoisomers of the alcohol (44; $R^1$ = Et, $R^2$ = H) (100 mg) was heated under reflux in toluene (25 ml) with TsOH (150 mg) for 3 days. The residue was separated by p.l.c. to give 3-diphenylphosphinoylpent-1-ene (51; R = Et) (40 mg, 38%) (see above) and 3-*diphenylphosphinoylpent*-2-*ene* (45; $R^1$ = Et, $R^2$ = H) (42 mg, 40%), m.p. 88—89 °C (from EtOAc–petrol), $\nu_{max.}$ 1 435 PPh) and 1 170 $cm^{-1}$ (P=O), τ ($CDCl_3$) 2.2—2.6 (10 H, m, $Ph_2PO$), 3.8 (1 H, dq, $J_{PH}$ 21, $J_{HH}$ 7 Hz, PC=CH), 7.6 (2 H, overlapping dq, $J_{PH}$ 17, $J_{HH}$ 8 Hz, C$H_2$Me), 8.1 (3 H, dd, $J_{PH}$ 2, $J_{HH}$ 7 Hz, C=CH*Me*), and 9.1 (3 H, t, $J_{HH}$ 8 Hz, $CH_2$*Me*), *m/e* 270 ($M^+$, 100) and 201 ($Ph_2PO$, 60) (Found: $M^+$, 270.116 9. $C_{17}H_{19}OP$ requires *M*, 270.117 2).

2-*Diphenylphosphinoylpentan*-3-*ol* (44; $R^1$ = $R^2$ = Me).—The procedure was the same as described for the alcohol (9; $R^1$ = $R^2$ = $R^3$ = Me). Ethyldiphenylphosphine oxide (2 g) in dry ether (100 ml), n-butyl-lithium (2 ml; 1.5M in hexane), and a solution of propionaldehyde in dry ether, saturated with anhydrous lithium bromide, gave an oil containing the two diastereoisomers of the *alcohol* (44; $R^1$ = $R^2$ = Me), which were separated by p.l.c. The high $R_F$ *isomer* (600 mg, 30%) had m.p. 105—107 °C (from EtOAc–petrol), $R_F$ 0.6, $\nu_{max.}$ 3 350 (OH), 1 435 (PPh), and 1 160 $cm^{-1}$ (P=O), τ ($CDCl_3$) 2.0—2.6 (10 H, m, $Ph_2PO$), 5.9 (1 H, s, OH), 6.1 (1 H, m, C*H*OH), 7.6 (1 H, quint, $J_{PH}$ = $J_{HH}$ = 7 Hz, PCH*Me*), 8.1—8.6 (2 H, m, C$H_2$Me), 8.8 (3 H, dd, $J_{PH}$ 17, $J_{HH}$ 7 Hz, PC*H*Me), and 9.1 (3 H, t, $J_{HH}$ 7 Hz, $CH_2$*Me*), *m/e* 288 ($M^+$, 2%), 259 (60), 230 (*M* — MeCHO, 100), and 201 ($Ph_2PO$, 80) (Found: C, 70.8; H, 7.4; P, 10.8. $C_{17}H_{21}O_2P$ requires C, 70.8; H, 7.3; P, 10.8%). The low $R_F$ *isomer* (600 mg, 30%) had m.p. 150—152 °C, $R_F$ 0.5, $\nu_{max.}$ 3 350 (OH), 1 435 (PPh), and 1 160 $cm^{-1}$ (P=O), τ ($CDCl_3$) 2.1—2.5 (10 H, m, $Ph_2PO$), 5.9 (1 H, s, OH), 6.2 (1 H, m, C*H*OH), 7.3 (1 H, m, PC*H*Me), 8.5 (2 H, m, C$H_2$Me), 9.0 (3 H, dd, $J_{PH}$ 17, $J_{HH}$ 7 Hz, PCH*Me*), and 9.05 (3 H, t, $J_{HH}$ 7 Hz, $CH_2$*Me*), *m/e* 288 ($M^+$, 2%), 230 (*M* — MeCHO, 100), and 201 ($Ph_2PO$, 80) (Found: C, 70.8; H, 7.3; P, 10.5. $C_{17}H_{21}O_2P$ requires C, 70.8; H, 7.3; P, 10.8%).

*Treatment of the Alcohol* (44; $R^1$ = $R^2$ = Me) *with TsOH in Toluene*.—The procedure used was the same as for the alcohol (9; $R^1$ = $R^2$, $R^3$ = Me). A mixture of diastereoisomers of the alcohol (44; $R^1$ = Me, $R^2$ = Me) (150 mg) was heated under reflux in toluene (25 ml) with TsOH (150 mg) for 3 days. The residue was an oil whose n.m.r. spectrum showed it to be mainly one geometric isomer of 4-*diphenylphosphinoylpent*-2-*ene* (46; $R^1$ = $R^2$ = Me) (120 mg, 80%), $R_F$ 0.5, $\nu_{max.}$ 1 435 (PPh) and 1 170 $cm^{-1}$ (P=O), τ ($CDCl_3$) 1.9—2.5 (10 H, m, $Ph_2PO$), 4.4 (2 H, m, C*H*=CH), 6.57—7.0 (1 H, m, PCH*Me*), 8.3 (3 H, t, $J_{PH}$ = $J_{HH}$ = 5 Hz, C=CH*Me*), and 8.7 (3 H, dd, $J_{PH}$ 16, $J_{HH}$ 7 Hz, PCH*Me*), *m/e* 270 ($M^+$, 20%) and 201 ($Ph_2PO$, 100) (Found: $M^+$, 270.116 4. $C_{17}H_{19}OP$ requires *M*, 270.117 2).

(1RS,2SR)-2-*Diphenylphosphinoyl*-1-*phenylpropan*-1-*ol* (47).—Ethyldiphenylphosphine oxide (5 g) in dry THF (120 ml) was stirred at 0 °C under nitrogen with n-butyl-lithium (16 ml; 1.5M in hexane) for 0.3 h. The red anion colour was quenched with benzaldehyde (2.5 g). The pale yellow solution was allowed to warm to room temperature, water (25 ml) was added, and the solution was evaporated. The yellow solid was dissolved in water (50 ml) and chloroform (100 ml); the layers were separated, and the aqueous layer was washed with chloroform (3 × 25 ml). The organic layers were dried ($MgSO_4$) and evaporated. Recrystallisation from light petroleum (b.p. 100—120 °C) gave the (1RS,2SR)-*alcohol* (47) as white needles (5.3 g, 74%), m.p. 169—171 °C (decomp.), $R_F$ (10% MeOH in EtOAc) 0.55, $\nu_{max.}$ 3 400 (OH), 1 440 (PPh), and 1 170 $cm^{-1}$ (P=O), τ ($CDCl_3$) 2.5 (10 H, m, $Ph_2PO$), 2.75 (5 H, s, PhC), 4.73 (1 H, dd, $J_{HP}$ 9, $J_{HH}$ 1 Hz, PCHC*H*OH), 5.3 (1 H, s, broad, OH), 7.4 [1 H, double quint, $J_{MeH}$ = $J_{PH}$ = 8, $J_{HH}$ 1 Hz, MeC*H*(P)CHOH], and 8.98 (3 H, dd, $J_{PMe}$ 16, $J_{MeH}$ 8 Hz, C$H_3$CHP), *m/e* 230 ($Ph_2POEt^+$, 100%), 202 ($Ph_2POH^+$,

40%), and 105 ($PhCO^+$, 37%) (Found: C, 74.8; H, 6.4; P, 9.5. $C_{21}H_{21}O_2P$ requires C, 74.9; H, 6.3; P, 9.2%).

*Completion of the Wittig–Horner Reaction of the Alcohol* (47).—The alcohol (47) (200 mg) was stirred with sodium hydride [1 g; 50% dispersion in oil, washed with petrol (3 × 20 ml)] in dry DMF at room temperature under nitrogen for 18 h. Water (50 ml) was added to the yellow suspension, and the solution filtered. The filtrate was extracted with carbon tetrachloride (3 × 20 ml); the combined organic layers were dried ($MgSO_4$) and evaporated to give the olefin as a pale yellow oil. Preparative t.l.c. with 10% MeOH in EtOAc as eluant gave (*Z*)-1-phenylpropene ($R_F$ 0.75), τ ($CCl_4$) 2.88 (5 H, m, Ph), 3.65 (1 H, double q, $J_{HH}$ 12, $J_{HMe}$ 1.5 Hz, PhC*H*=CHMe), 4.30 (1 H, double q, $J_{HH}$ 12, $J_{HMe}$ 6 Hz, CH=C*H*Me), and 8.2 (3 H, dd, $J_{MeH}$ 6, $J_{MeH}$ 1.5 Hz, CH=CH*Me*).[25] (*E*)-1-Phenylpropene, prepared from (*E*)-cinnamyl alcohol,[26] had a different and appropriate n.m.r. spectrum.[25]

2-*Diphenylphosphinoyl*-1-*phenylpropene* (48).—The alcohol (47) (2 g) was dissolved in TFA (15 ml) and heated under reflux under nitrogen for 16 h. The solution was poured into water (50 ml) and extracted with chloroform (3 × 25 ml). The extracts were washed with saturated sodium hydrogen carbonate solution (2 × 15 ml), dried ($MgSO_4$), and evaporated to an oil. This was distilled to give the *olefin* (48) as a pale yellow viscous oil (1.65 g, 85%), b.p. 220 °C (bath temp.) at 0.07 mmHg. The olefin slowly crystallised and was obtained with difficulty as white crystals from light petroleum (b.p. 100—120 °C); m.p. 55—57 °C, $R_F$ (10% MeOH in EtOAc) 0.5, $\nu_{max.}$ 1 620 (C=C), 1 440 (PPh), and 1 170 $cm^{-1}$ (P=O), τ ($CDCl_3$) 2.5 (10 H, m, $Ph_2PO$), 2.66 (5 H, s, PhC), 2.89 (0.5 H, d, $J_{HH}$ 1.5 Hz, PC=C*H*, half of widely split doublet, other half masked by phenyl signal), and 7.89 [3 H, dd, $J_{MeP}$ 14, $J_{MeH}$ 1.5 Hz, $CH_3C(P)$=CHPh], *m/e* 318 ($M^+$, 84%) and 202 ($Ph_2POH^+$, 100%) (Found: $M^+$, 318.117 0. $C_{21}H_{19}OP$ requires *M*, 318.117 2). The corresponding ethyl compound, $Ph_2PO$·CEt=CHPh, formed under the same conditions, showed the complete doublet, $J_{HH}$ 22 Hz,[27] for the vinyl proton, and is therefore the *E*-isomer.[28]

3-*Diphenylphosphinoyl*-4-*trimethylsilylbutan*-2-*ol* (49; R = Me).—Diphenyl-2-trimethylsilylethylphosphine oxide (33) (3.02 g) in dry THF (20 ml) was stirred with n-butyllithium (7.0 ml; 1.6M in hexane) at room temperature under nitrogen for 0.5 h. The solution was cooled to −78 °C and a solution of acetaldehyde (*ca.* 6 ml) in dry THF (10 ml) saturated with anhydrous lithium bromide was added until the red colour was discharged. The solution was allowed to reach room temperature, poured into water (100 ml), and extracted with chloroform (3 × 30 ml). The combined extracts were washed with sodium chloride solution (100 ml; saturated), dried ($Na_2SO_4$), and evaporated *in vacuo*. The resulting white solid was recrystallised from ethyl acetate to give the *alcohol* (49; R = Me) as a 1 : 1 mixture of diastereoisomers (2.88 g, 83%), m.p. 179 °C (from EtOAc) (Found: C, 65.8; H, 7.8; P, 9.1. $C_{19}H_{27}O_2PSi$ requires C, 65.9; H, 7.85; P, 8.9%), $R_F$ 0.4 (EtOAc), $\nu_{max.}$ (Nujol) 3 340 (OH), 1 140 (PPh), 1 252 ($SiMe_3$), and 1 160 $cm^{-1}$ (P=O), τ ($CDCl_3$) 2.0—2.7 (10 H, m, $Ph_2PO$), 5.5—5.9 (1 H, m, MeC*H*OH), 6.28 (1 H, s, OH), 7.2—7.6 (1 H, m, PC*H*$CH_2$·$SiMe_3$), 8.6—9.4 (5 H, m overlain by doublets at 8.78 and 8.84, *J* 2 Hz, $CH_2$ and $CH_3$), and 9.97 and 10.02 (9 H, two s, $SiMe_3$), *m/e* 346 (0.7%, $M^+$), 331 (70, *M* − Me), 302 (51, *M* − MeCHO), 274 (48, $Ph_2POSiMe_3$), 202 (100, $Ph_2POH$), and 201 (49, $Ph_2PO$).

2-*Diphenylphosphinoyl*-1-*trimethylsilylpentan*-3-*ol* (49; R = Et).—In a closely analogous preparation, the *alcohol* (49; R = Et) was obtained (87%) from diphenyl-2-trimethylsilylethylphosphine oxide (33) and propionaldehyde as a mixture of diastereoisomers, m.p. 183—185 °C (from EtOAc–hexane) (Found: C, 66.7; H, 8.2; P, 8.3. $C_{20}H_{29}O_2PSi$ requires C, 66.6; H, 8.1; P, 8.6%), $R_F$ 0.6 (EtOAc), $\nu_{max.}$ (Nujol) 3 280 (OH), 1 438 (PPh), 1 252 ($SiMe_3$), and 1 160 $cm^{-1}$ (P=O), τ ($CDCl_3$) 2.0—2.8 (10 H, m, $Ph_2PO$), 5.78 (1 H, d, *J* 8 Hz, OH), 6.0—6.5 (1 H, m, C*H*OH), 7.25—7.50 (1 H, m, PC*H*$CH_2$), 8.4—9.3 (7 H, m overlain by quartet, *J* 7 Hz, at 8.60 and by triplet, *J* 7 Hz, at 9.16, $CH_2CH_3$ and $CH_2Si$), and 9.99 and 10.05 (9 H, two s, $SiMe_3$), *m/e* 360 (1%, $M^+$), 345 (21, *M* − Me), 331 (20, *M* − Et), 302 (31, *M* − EtCHO), 274 (43, $Ph_2POSiMe_3$), 202 (100, $Ph_2POH$), and 201 (92, $Ph_2PO$).

1-*Diphenylphosphinoyl*-1-*phenyl*-3-*trimethylsilylpropan*-1-*ol* (49; R = Ph).—Diphenyl-2-trimethylsilylethylphosphine oxide (33) (3.02 g) in dry THF (20 ml) was stirred with n-butyl-lithium (7.0 ml; 1.6M in hexane) under nitrogen at room temperature for 0.5 h. The solution was cooled to −78 °C, and benzaldehyde was added dropwise until the red colour was discharged. The solution was allowed to reach room temperature, poured into water (100 ml), and extracted with chloroform (3 × 50 ml). The combined organic layers were washed with sodium chloride solution (100 ml; saturated), dried ($Na_2SO_4$), and evaporated *in vacuo*. The resulting oil was chromatographed on silica gel; elution with ether gave the *alcohol* (49; R = Ph) as essentially one diastereoisomer (2.57 g, 63%), m.p. 140—141 °C (from EtOAc–hexane) (Found: C, 70.7; H, 7.2; P, 7.3. $C_{24}H_{29}O_2PSi$ requires C, 70.5; H, 7.15; P, 7.6%), $R_F$ 0.5 ($Et_2O$), $\nu_{max.}$ (Nujol) 3 200 (OH), 1 435 (PPh), 1 250 ($SiMe_3$), and 1 150 $cm^{-1}$ (P=O), τ ($CDCl_3$) 1.9—2.9 (15 H, m, $Ph_2PO$ and Ph), 4.75 (1 H, d, *J* 10 Hz, C*H*OH), 5.20 (1 H, s, OH), 7.37 (1 H, q, *J* 6 Hz, PC*H*$CH_2$), 8.73 (1 H, ddd, *J* 6, 8, and 16 Hz, $CH_AH_B$), 9.24 (1 H, ddd, *J* 6, 16, and 24 Hz, $CH_AH_B$), and 10.68 (9 H, s, $SiMe_3$), *m/e* 408 (0.6%, $M^+$), 393 (13, *M* − Me), 302 (59, *M* − PhCHO), 274 (6, $Ph_2POSiMe_3$), 229 (100), 202 (28, $Ph_2POH$), and 201 (16, $Ph_2PO$).

3-*Diphenylphosphinoylbut*-1-*ene* (51; R = Me).—3-Diphenylphosphinoyl-4-trimethylsilylbutan-2-ol (49; R = Me) (246 mg; diastereoisomer mixture) was heated under reflux in dry toluene (15 ml) with TsOH (600 mg) for 23 h. The solution was poured into sodium hydrogen carbonate solution (50 ml; saturated) and extracted with ether (3 × 30 ml). The combined extracts were washed with water (50 ml), dried ($Na_2SO_4$), and evaporated *in vacuo*. Preparative t.l.c. (EtOAc) gave 3-diphenylphosphinoylbut-1-ene (51; R = Me) (156 mg, 85%), m.p. 90—92 °C (from hexane), (lit.,[29] 91—92 °C), $R_F$ (EtOAc) 0.3, $\nu_{max.}$ 1 640 (C=C), 1 448 (PPh), and 1 180 $cm^{-1}$ (P=O), τ ($CDCl_3$) 2.1—2.6 (10 H, m, $Ph_2PO$), 3.88—4.33 (1 H, m, C*H*=$CH_2$), 4.80—5.07 (2 H, m, CH=C*H*$_2$), 6.5—7.0 (1 H, m, PC*H*Me), and 8.68 (3 H, dd, *J* 8 and 16 Hz, Me).

*Rearrangement of* 2-*Diphenylphosphinoyl*-1-*trimethylsilylpentan*-3-*ol* (49; R = Et).—The alcohol (49; R = Et) (360 mg; diastereoisomeric mixture) was heated under

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reflux in dry toluene (10 ml) with TsOH (400 mg) for 23 h. The solution was poured into sodium hydrogen carbonate solution (50 ml; saturated) and extracted with ether (3 × 30 ml). The combined extracts were washed with water (50 ml), dried ($Na_2SO_4$), and evaporated *in vacuo*. Preparative t.l.c. (EtOAc) gave *4-diphenylphosphinoyl-5-trimethylsilylpent-2-ene* (52) (105 mg, 31%) as a mixture of *cis*- and *trans*-isomers, m.p. 160—161 °C (from hexane) (Found: C, 70.0; H, 7.8; P, 8.8. $C_{20}H_{27}OPSi$ requires C, 70.1; H, 7.9; P, 9.0%), $R_F$ (EtOAc) 0.5, $\nu_{max.}$ 1 440 (PPh), 1 250 ($SiMe_3$), and 1 170 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 2.0—2.8 (10 H, m, $Ph_2PO$), 4.4—4.8 (2 H, m, vinylic), 6.6—7.1 (1 H, m, PC*H*$CH_2$), 8.44 and 8.76 (total 3 H, t, *J* 4 Hz, *cis*- and *trans*-$CH_3$), 8.9—9.2 (2 H, m, $CH_2Si$), and 9.98 (9 H, s, $SiMe_3$), *m/e* 342 (12%, $M^+$), 327 (21, $M - CH_3$), 274 (100, $Ph_2POSiMe_3$), 202 (56, $Ph_2POH$), and 201 (39, $Ph_2PO$), and *3-diphenylphosphinoylpent-1-ene* (51; R = Et) (149 mg, 55%), m.p. 123—124 °C (from hexane) (Found: C, 75.2; H, 6.95; P, 11.2. $C_{17}H_{19}OP$ requires C, 75.5; H, 7.1; P, 11.4%) $R_F$ (EtOAc) 0.4, $\nu_{max.}$ 1 642 (C=C), 1 450 (PPh), and 1 180 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 2.1—2.7 (10 H, m, $Ph_2PO$), 4.07—4.40 (1 H, m, C*H*=$CH_2$), 4.78—5.12 (2 H, m, CH=C*H*$_2$), 7.10 (1 H, 8 lines, *J* 4, 8, and 18 Hz, PC*H*$CH_2$), 8.0—8.5 (2 H, m, $CH_2$), and 9.05 (3 H, t, *J* 6 Hz, C*H*$_3$), *m/e* 270 (16%, $M^+$), 255 (3, $M - CH_3$), 241 (3, $M - CH_2CH_3$), 202 (58, $Ph_2POH$), and 201 (100, $Ph_2PO$).

*3-Diphenylphosphinoyl-3-phenylpropene* (51; R = Ph).—1-Diphenylphosphinoyl-1-phenyl-3-trimethylsilylpropan-1-ol (49; R = Ph) (408 mg) was stirred with TFA (2 ml) at room temperature for 2 h. The mixture was diluted with chloroform (50 ml) and stirred with sodium hydrogen carbonate solution (100 ml; saturated). The aqueous layer was extracted with chloroform (2 × 20 ml) and the combined extracts were dried ($Na_2SO_4$) and evaporated *in vacuo*. Crystallisation of the resulting solid gave the olefin (51; R = Ph) (286 mg, 90%), m.p. 191.5—192.5 °C (lit.,[29] 193—193.5 °C) (from ethyl acetate–hexane), $R_F$ 0.3 ($Et_2O$), $\nu_{max.}$ 1 635 (C=C), 1 440 (PPh), and 1 180 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 2.0—2.9 (15 H, m, Ph, $Ph_2PO$), 3.52—3.94 (1 H, m, C*H*=$CH_2$), 4.72—5.10 (2 H, m, CH=C*H*$_2$), and 5.74 (1 H, t, *J* 8 Hz, PC*H*Ph), *m/e* 318 (20%, $M^+$), 202 (45, $Ph_2POH$), and 201 (100, $Ph_2PO$).

*1-(1-Diphenylphosphinoyl-2-trimethylsilylethyl)cyclohexanol* (53).—n-Butyl-lithium (4 ml; 1.5M in hexane) was added dropwise to a stirred solution of the phosphine oxide (33) (1.81 g) in dry THF (20 ml) under nitrogen at 25 °C. After 15 min, cyclohexanone (627 mg; freshly distilled) was added dropwise and the mixture kept at 25 °C for 17 h. It was poured into water and extracted with chloroform, and the extract was washed with sodium hydrogen carbonate solution and with water, dried ($MgSO_4$), and evaporated *in vacuo* to give the *alcohol* (53) (1.65 g, 69%), m.p. 195—198 °C (from $CHCl_3$–hexane) (Found: C, 68.9; H, 8.5. $C_{23}H_{33}O_2PSi$ requires C, 69.0; H, 8.25%), $\nu_{max.}$ (Nujol) 3 335 (OH), 1 438 (P–Ph), 1 250 (SiMe), and 1 160 or 1 152 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 2.2—2.9 (10 H, m, $Ph_2PO$), 6.35 (1 H, s, OH), 7.47 (1 H, dt, *J* 4, 6.5, and 6.5 Hz, PCH), 8.0—9.5 (12 H, m, C*H*$_2SiMe_3$ and ring $CH_2$s), and 10.22 (9 H, s, $SiMe_3$), *m/e* 400 (19%, $M^+$) and 274 (100).

*1-(1-Diphenylphosphinoyl-2-trimethylsilylethyl)cyclohexene* (54).—The alcohol (53) (500 mg) was stirred with TFA (10 ml) for 12 h at room temperature. The solution was then 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. The residue was recrystallised from ethyl acetate to give the *allylphosphine oxide* (54) (420 mg, 85%), m.p. 190—192 °C, $R_F$ 0.6, $\nu_{max.}$ 1 430 (PPh), 1 252 ($SiMe_3$), and 1 170 $cm^{-1}$ (P=O), $\tau$ ($CDCl_3$) 1.9—2.6 (10 H, m, $Ph_2PO$), 4.5 (1 H, broad s, C=CH), 7.0—7.3 (1 H, m, PCH), 8.1 (4 H, m, $CH_2C=CH_2$), 8.6 (4 H, m, $CH_2CH_2$), 8.7—9.1 (2 H, m, C*H*$_2SiMe_3$), and 9.9 (9 H, s, $SiMe_3$), *m/e* 387 ($M^+$, 50%), 274 (100), and 201 ($Ph_2PO$, 15) (Found: C, 72.2; H, 8.2; P, 8.2. $C_{23}H_{31}OPSi$ requires C, 72.3; H, 8.1; P, 8.1%).

[6/1473 *Received*, 27*th July*, 1976]