# Organic Synthesis using Diphenylphosphinoyl as a Migrating Functional Group: Diene Synthesis [1]

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Allyldiphenylphosphine oxides can be made from a carbonyl compound, an alkyl halide, and a diphenylphosphinoyl reagent by two routes, one involving migration of the diphenylphosphinoyl group. Lithium derivatives of these allylphosphine oxides add stereoselectively to aldehydes and the products undergo elimination of diphenylphosphinic acid stereospecifically to give single geometrical isomers of substituted dienes.

DIENES (3) can be synthesised by the Wittig reaction between allylphosphonium ylides (2) and carbonyl compounds.[2] The two most serious problems to be faced along this route are that the ylide (2) may react through either the α- or the γ-carbon atom, and that all four geometrical isomers of the diene may well be formed.[3]
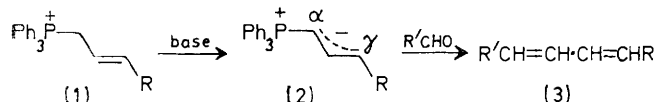

We report [4] that the Horner [5] variant of the Wittig reaction can be used to make single geometrical isomers of substituted dienes (6). The key intermediates are the allylphosphine oxides (4). In many cases these react with butyl-lithium and a carbonyl compound regiospecifically and stereoselectively to give the crystalline
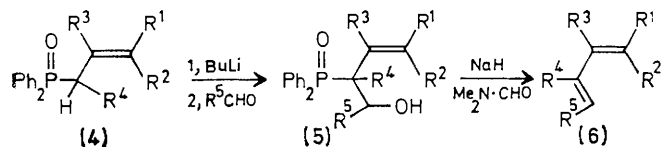

intermediates (5), which can be separated into diastereoisomers by chromatography and crystallisation. Elimination with a sodium base (e.g. NaH) then gives the dienes (6) stereospecifically, the other product being the easily extracted diphenylphosphinic acid.[6]

The allyldiphenylphosphine oxides (4) may be made by a number of methods [7] in which the complete allyl fragment is added to a suitable electrophilic [8] or nucleophilic [9] phosphorus reagent. We have found that these compounds can be made by the dehydration of tertiary alcohols [e.g. (7)] in acid. Brief treatment with trifluoroacetic acid gives the allyl compound (8); more prolonged treatment gives the vinyl compound (9). If

trifluoroacetic acid is used, the reaction is conveniently followed by n.m.r. Presumably the allyl compound is the kinetic, and the vinyl compound (9) the thermodynamic product.
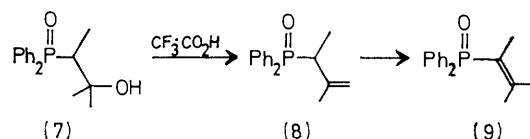
Where the substitution pattern is reversed so that the alcohol is secondary and the diphenylphosphinoyl group on a quaternary carbon [e.g. (10)] dehydration occurs *with rearrangement* to give the same allylphosphine oxide (8). We have previously reported [10] that this reaction occurs on solvolysis of derivatives (tosylate or mesylate) of the alcohol (10) but we have now found that it also occurs simply on heating the alcohol itself in benzene solution under reflux with toluene-*p*-sulphonic acid. Presumably the tertiary cation (11) is an intermediate in both reactions (7) ⟶ (8) and (10) ⟶ (8).
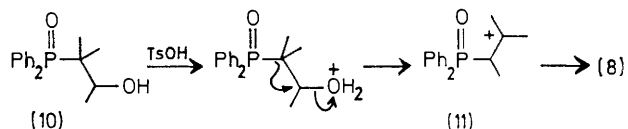
Both alcohols (7) and (10) may be made by the first stage of the Wittig–Horner reaction,[5] that is by treatment of a phosphine oxide (12) with butyl-lithium and a
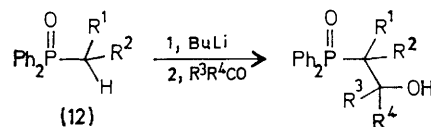
carbonyl compound. Primary alkylphosphine oxides (12; $R^2 = H$) are most economically made by quaternisation of triphenylphosphine and hydrolysis of the phosphonium salt [11] (13), the other product being benzene.

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

[2] H. von Brachel and U. Bahr, in Houben-Weyl, 'Methoden der Organischen Chemie,' Thieme, Stuttgart, 1970, vol 5/1c, pp. 590—601.

[3] E. J. Corey and B. W. Erikson, *J. Org. Chem.*, 1974, **39**, 821; E. Vedejs, J. P. Bershas, and P. L. Fuchs, *ibid.*, 1973, **38**, 3625; these papers refer to extensive earlier work.

[4] The thinking behind our work on synthesis is explained in A. H. Davidson, P. K. G. Hodgson, D. Howells, and S. Warren, *Chem. and Ind.*, 1975, 455.

[5] L. Horner, H. Hoffmann, and H. G. Wippel, *Chem. Ber.*, 1958, **91**, 61; L. Horner, H. Hoffmann, H. G. Wippel, and G. Klahre, *ibid.*, 1959, **92**, 2499; L. Horner, H. Hoffmann, W. Klink, H. Ertel, and V. G. Toscano, *ibid.*, 1962, **95**, 581; L. Horner, W. Klink, and H. Hoffmann, *ibid.*, 1963, **96**, 3133; L. Horner, *Fortschr. Chem. Forsch.*, 1966, **7**, 1.

[6] A. J. Bridges and G. H. Whitham, *J.C.S. Chem. Comm.*, 1974, 142.

[7] H. R. Hays and D. J. Peterson in 'Organic Phosphorus Compounds,' eds. G. M. Kosolapoff and L. Maier, Wiley, New York, 1972, vol. 3, pp. 341—500.

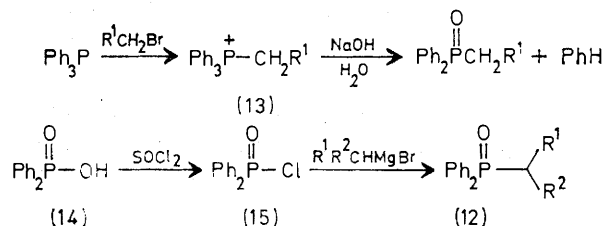[8] M. P. Savage and S. Trippett, *J. Chem. Soc. (C)*, 1966, 1842; 1967, 1998; 1968, 591.

[9] I. M. Downie and G. Morris, *J. Chem. Soc.*, 1965, 5771.

[10] D. Howells and S. Warren, *J.C.S. Perkin II*, 1973, 1472, 1645.

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

This reaction can also be used for secondary halides but the quaternisation is rather slow, and they may alternatively be converted into Grignard reagents and combined [12] with the acid chloride (15) made by recycling the 'waste product' of the Wittig–Horner reaction, diphenylphosphinic acid (14).

$$Ph_3P \xrightarrow{R^1CH_2Br} Ph_3\overset{+}{P}-CH_2R^1 \xrightarrow[H_2O]{NaOH} Ph_2\overset{O}{\underset{\|}{P}}CH_2R^1 + PhH$$

$$(13)$$

$$Ph_2\overset{O}{\underset{\|}{P}}-OH \xrightarrow{SOCl_2} Ph_2\overset{O}{\underset{\|}{P}}-Cl \xrightarrow{R^1R^2CHMgBr} Ph_2\overset{O}{\underset{\|}{P}}-\overset{R^1}{\underset{R^2}{\diagdown}}$$

$$(14) \qquad\qquad (15) \qquad\qquad\qquad (12)$$

These two routes to allylphosphine oxides (16) (Scheme 1) involve the same disconnection (17a or b) and, during retrosynthetic analysis,[13] the choice between them would depend on the availablity of the fragments as alkyl halides or as carbonyl compounds, since one electrophile of each type is used. Whether rearrangement is involved or not, the diphenylphosphinoyl group is used to link together a series of electrophilic molecules into the final diene structure (18) as it is derived from two carbonyl compounds and an alkyl halide. This requires umpolung [14] which arises because the phosphorus atom,
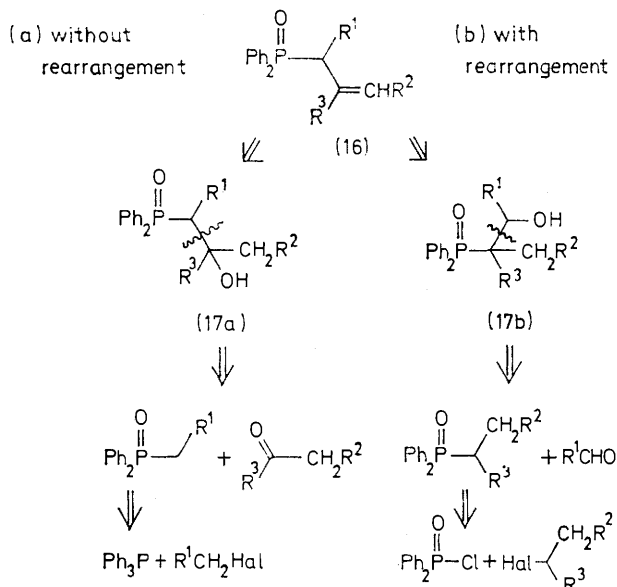
Scheme 1 Retrosynthetic analysis of allylphosphine oxide synthesis

whether in the initial P–C bond-forming reaction or during the rearrangement, becomes bonded to an electrophilic atom, but can then stabilise a negative charge or lithium derivative on that atom.

[12] D. C. Morrison, J. Amer. Chem. Soc., 1950, 72, 4820.
[13] I. Fleming, 'Selected Organic Syntheses,' Wiley, London, 1973, p. 3; see also E. J. Corey, R. D. Cramer, and W. J. Howe, J. Amer. Chem. Soc., 1972, 94, 440.
[14] D. Seebach, Chem. and Ind., 1974, 687.

So, starting with either cyclohexyl or ethyl-diphenylphosphine oxide (Scheme 2) we have synthesised the allylphosphine oxide (21) via the tertiary alcohol (19) or,

$$R^4CHO + R^3CH_2Hal + R^2CO\cdot CH_2R^1$$
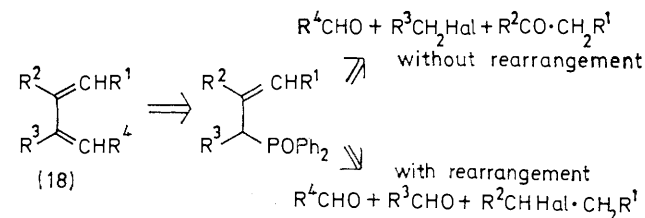
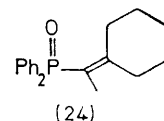with rearrangement of the diphenylphosphinoyl group, via the secondary alcohol (20). In the dehydration of
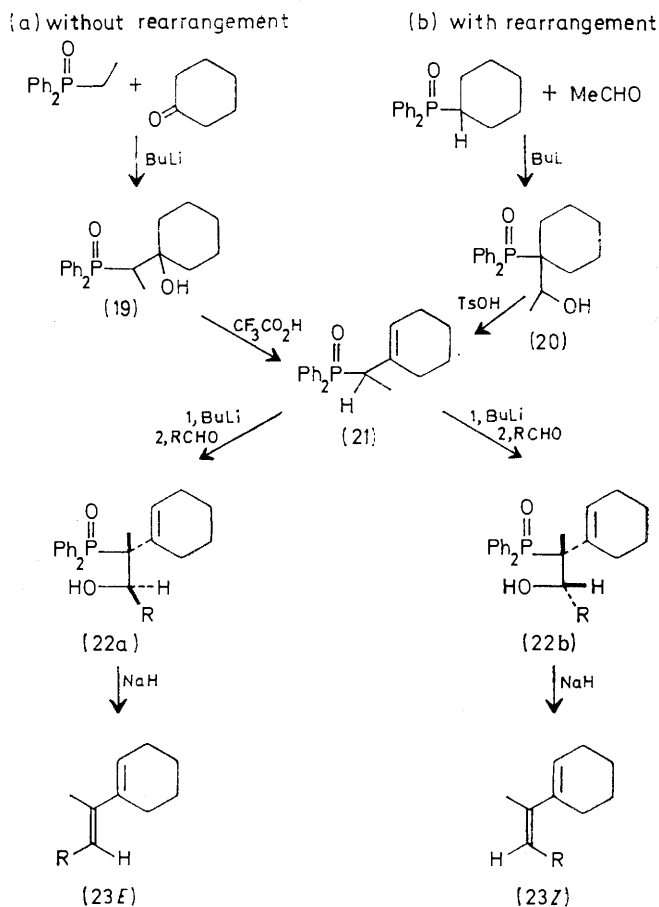
Scheme 2 Synthesis of dienes

the tertiary alcohol (19) in trifluoroacetic acid, the allylphosphine oxide (21) is not transformed into the vinyl-
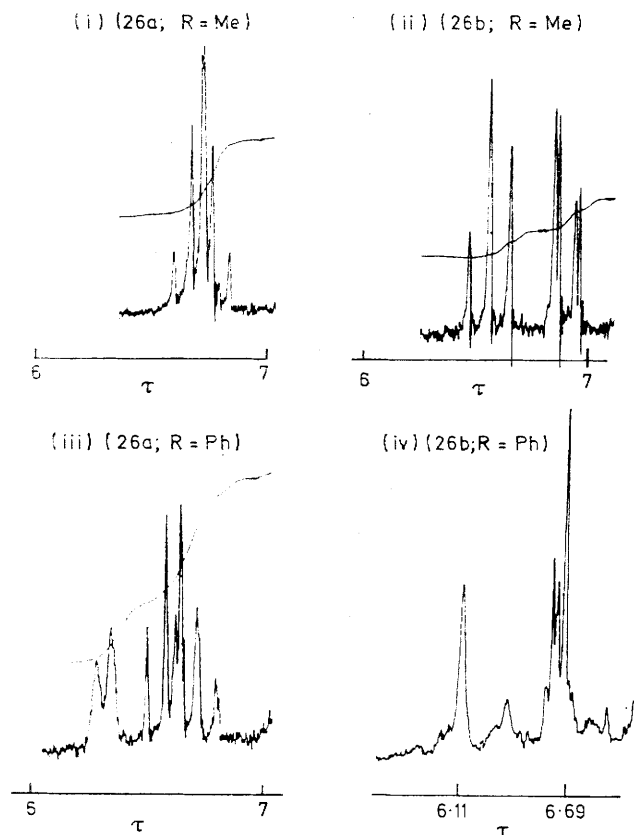
$$(24)$$

phosphine oxide (24) presumably because the weak p_π–d_π conjugation between C=C and P=O is outweighed by the disadvantage of an exocyclic double bond.

Treatment of the allylphosphine oxide (21) with butyl-lithium and acetaldehyde or benzaldehyde gave pairs of diastereoisomeric alcohols (22) in ratios [(a) : (b)] of 2 : 1

(25) → (26a) or (26b)
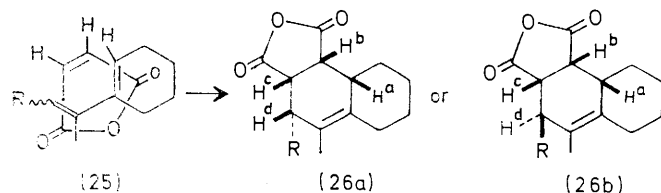
(for R = Me) or 1 : 3 (for R = Ph). In neither case was there any significant γ-addition. However, γ-addition to this allylphosphine oxide gives an unfavourable exocyclic double bond. The highly crystalline alcohols were separated and converted into the dienes (23) by sodium hydride in tetrahydrofuran or dimethylform-amide.[6] All diastereoisomers of the alcohols (22) and dienes (23) are easily distinguished by their n.m.r. spectra.
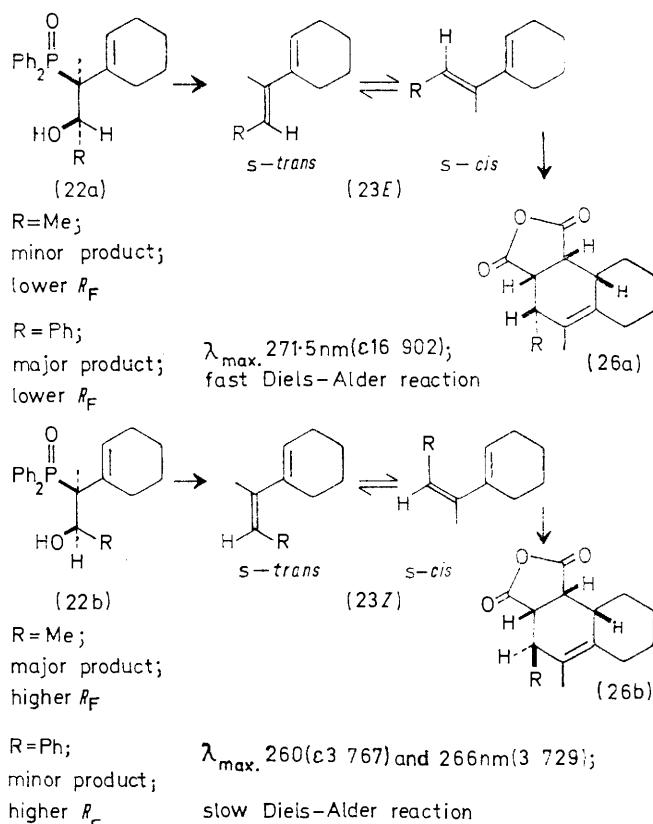
Addition of maleic anhydride to the dienes (23) gave the Diels–Alder adducts (26) whose n.m.r. spectra allowed us to make an unambiguous assignment of

bearing H^d in (26). The only protons whose n.m.r. signals emerge from the methylene envelope are H^b and H^c and, for R = Ph, H^d. These signals are shown in the Figure. In series (a) protons H^b and H^c give a symmetrical signal which, though not first-order, shows that all the coupling constants J_{ab}, J_{bc}, and J_{cd} are about the same (ca. 9 Hz). This is confirmed in the phenyl compound (26a; R = Ph) by the doublet for H^d (J 6 Hz). For (26b; R = Me) H^b and H^c give a first-order pattern of a triplet (J 9 Hz) and a double doublet (J 9 and 2 Hz), suggesting that $J_{ab} = J_{bc} = 9$ Hz, and $J_{cd} = 2$ Hz. For (26b; R = Ph) this signal is not first order but the signal for H^d is a broad singlet ($J_{cd} \leqslant 2$ Hz).

(22a) R=Me; minor product; lower R_F

R = Ph; major product; lower R_F

$\lambda_{max.}$ 271·5nm(ε16 902); fast Diels–Alder reaction

(22b) R = Me; major product; higher R_F

R = Ph; minor product; higher R_F

$\lambda_{max.}$ 260(ε3 767) and 266nm(3 729); slow Diels–Alder reaction

SCHEME 3 Configurations of alcohols (22), dienes (23), and Diels–Alder adducts (26)

(i) (26a; R = Me) (ii) (26b; R = Me)

(iii) (26a; R = Ph) (iv) (26b; R = Ph)

N.m.r. spectra of maleic anhydride adducts (26) at 100 MHz [except (iv) which is at 80 MHz] by Fourier transform

Models suggest that the conformation of the cyclo-hexene ring is boat-like with angles between the cis-substituents [e.g. H^a, H^b, H^c, and H^d in series (a)] of ca. 45°, and angles between the trans-substituents [e.g. H^c and H^d in series (b)] of ca. 75°. So we assign the sym-metrical signals with larger coupling to the all-cis-series and the smaller coupling to the only trans-protons, H^c and H^d in series (b). Since both the syn-elimination of diphenylphosphinic acid and the Diels–Alder reaction are stereospecific we can write the structures of alcohols (22) and dienes (23) as in Scheme 3. Additional evidence on the structure of the dienes (23; R = Ph) comes from the longer wavelength absorption of the E-isomer and the

configuration to series (a) and (b) (Scheme 3). Assuming endo-addition, the only chiral centre in question is that

reluctance with which the Z-isomer undergoes the Diels–Alder reaction because of its unfavourable s-cis-conformation. The stereoselectivity of the Horner reaction is different in that (22a) is favoured by 2 : 1 for R = Me but (22b) is favoured by 3 : 1 for R = Ph.

EXPERIMENTAL

General spectroscopic and chromatographic procedures have been described previously.[15] Petrol refers to light petroleum (b.p. 60—80°). R_F Values are quoted for development in ethyl acetate.

Cyclohexyldiphenylphosphine Oxide (method of ref. 12).—Diphenylphosphinic acid[16] (2 g) was heated under reflux in toluene with thionyl chloride (10 ml) for 1.5 h. The excess thionyl chloride was removed by evaporating most of the toluene under reduced pressure. The residue was diluted with dry benzene (50 ml) and added dropwise over 1.5 h to cyclohexylmagnesium bromide [from cyclohexyl bromide (15 ml) and magnesium (2 g)] in ether (100 ml). The solution was heated under reflux for 2 h, then cooled to 0 °C, and ice (25 g) and hydrochloric acid (10%; 50 ml) were added. The aqueous layer was extracted with ether (3 × 50 ml) and the combined ethereal layers were dried (MgSO₄) and evaporated; the product was collected and recrystallised from ethyl acetate to give the phosphine oxide (1.9 g, 65%), m.p. 164—166° (lit.,[17] 165°), R_F 0.25, $v_{max.}$ 1 440 (PPh) and 1 185 cm⁻¹ (P=O), τ (CDCl₃) 2.0—2.7 (10 H, m, Ph₂PO), 6.6—7.0 (1 H, m, PCH), and 8.0—8.8 (10 H, m, CH₂ envelope), m/e 284 (40%, M⁺) and 201 (100, Ph₂PO).

1-(1-Diphenylphosphinoylcylohexyl)ethanol (20).—Cyclohexyldiphenylphosphine oxide (350 mg) in dry ether (50 ml) was stirred at 0 °C under nitrogen with n-butyl-lithium (1 ml; 1.5M in hexane) for 0.5 h. The red solution was cooled to −78 °C and acetaldehyde (40 mg) in ether (4 ml) added over 5 min. The solution was allowed to warm up to 0 °C, the treatment with butyl-lithium and acetaldehyde was repeated, and water (50 ml) was added. The aqueous layer was extracted with chloroform (3 × 25 ml) and the combined organic layers were dried (MgSO₄) and evaporated under reduced pressure. The residue was recrystallised from ethyl acetate–di-isopropyl ether to give the *alcohol* (300 mg, 75%), m.p. 180—184°, R_F 0.33, $v_{max.}$ 3 350 (OH), 1 440 (PPh), and 1 170 cm⁻¹ (P=O), τ (CDCl₃) 1.8—2.8 (10 H, m, Ph₂PO), 5.6 (1 H, dq, J_{PH} 26, J_{HH} 6 Hz, PC·CHMe), 5.6 (1 H, s, OH), 7.3—8.7 (10 H, m, CH₂ envelope), and 8.85 (3 H, d, J_{HH} 6 Hz, CHMe), m/e 328 (8%, M⁺), 284 (90, M − MeCHO), and 201 (100, Ph₂PO) (Found: C, 73.2; H, 7.6; P, 9.0. C₂₀H₂₅O₂P requires C, 73.3; H, 7.6; P, 9.4%).

Preparation of Tosylates: 1-(1-*Diphenylphosphinoylcyclohexyl)ethyl Toluene-p-sulphonate.*—This procedure is typical. The alcohol (20) (400 mg) in dry tetrahydrofuran (50 ml) was stirred with n-butyl-lithium (1 ml; 1.5M in hexane) at 0 °C under nitrogen for 20 min. Toluene-p-sulphonyl chloride (400 mg) in dry tetrahydrofuran (10 ml) was added slowly and the solution stirred at room temperature for 0.5 h. Saturated sodium hydrogen carbonate solution (50 ml) was added and the organic layer was separated, washed with dilute hydrochloric acid (50 ml) and brine (50 ml), and dried (MgSO₄). Removal of solvent under reduced pressure and

recrystallisation of the residue from ethyl acetate gave the tosylate (400 mg, 55%), m.p. 117—120°, R_F 0.38, $v_{max.}$ 1 440 (PPh), 1 370, 1 180 (S=O), and 1 185 cm⁻¹ (P=O), τ (CDCl₃) 1.9—2.9 (14 H, m, Ar), 4.4—4.8 (1 H, dq, J_{HH} 6 Hz, PC·CHMe), 7.6 (3 H, s, MeAr), 7.7—8.7 (10 H, m, CH₂ envelope), and 8.5 (3 H, d, J_{HH} 6 Hz, CHMe).

Solvolysis of Tosylates: 1-(1-*Diphenylphosphinoylethyl)-cyclohexene* (21).—(a) *By trifluoroacetolysis.* The above tosylate (180 mg) in trifluoroacetic acid (10 ml) containing anhydrous sodium trifluoroacetate (40 mg) was kept at 70 °C for 8 h and 25 °C for 14 h. The solution was poured into water (50 ml) and extracted with ether (3 × 50 ml). The combined ether layers were washed with sodium hydrogen carbonate solution (2 × 50 ml) and water (50 ml), dried (MgSO₄), and evaporated. Recrystallisation of the residue from ethyl acetate–di-isopropyl ether gave the *olefin* (21) (100 mg, 85%), m.p. 145—147°, R_F 0.3, $v_{max.}$ 1 440 (PPh) and 1 180 cm⁻¹ (P=O), τ (CDCl₃) 2.0—2.8 (10 H, m, Ph₂PO), 4.5 (1 H, s, CH=C), 7.1 (1 H, quint, $J_{PH} = J_{HH} = 7$ Hz, P·CHMe), 7.8—8.8 (8 H, m, CH₂ envelope), and 8.7 (3 H, dd, J_{PH} 16, J_{HH} 7 Hz, PCHMe), m/e 310 (35%, M⁺), 228 (100, Ph₂PO·CH:CH₂), and 201 (50, Ph₂PO) (Found: C, 77.5; H, 7.65; P, 10.2. C₂₀H₂₃OP requires C, 77.4; H, 7.4; P, 10.0%).

(b) *By acetolysis.* The above tosylate (100 mg) was stirred in acetic acid (dried by distillation from acetic acid, acetic anhydride, and chromium trioxide;[18] 10 ml) and anhydrous sodium acetate (100 mg) for 24 h at 70 °C. The solution was poured into water and worked up in the same way as the trifluoroacetolysis product to give the same olefin (21) (63 mg, 96%).

Direct Conversion of the Alcohol (20) *into the Olefin* (21).—The alcohol (20) (50 mg) was heated under reflux in dry benzene (25 ml) and toluene-p-sulphonic acid (50 mg) in a Dean–Stark apparatus for 24 h. The solution was poured into saturated aqueous sodium hydrogen carbonate (50 ml) and extracted with chloroform (3 × 25 ml), the extracts were washed with water (25 ml) and dried (MgSO₄). Evaporation under reduced pressure and recrystallisation from ethyl acetate gave the olefin (21) (38 mg, 80%).

1-(1-Diphenylphosphinoylethyl)cyclohexanol (19)—Diphenylethylphosphine oxide (6 g) in dry ether (200 ml) under nitrogen was stirred with n-butyl-lithium (16 ml; 1.7M in hexane) for 0.5 h and cooled to −78 °C. Cyclohexanone (3 g) in dry ether (50 ml) was added, the solution was allowed to warm up to room temperature, and water (200 ml) was added. The crystalline *alcohol* (7 g, 80%) had m.p. 185—187° (from ethyl acetate–petrol), R_F 0.5, $v_{max.}$ 3 600 (OH), 1 440 (PPh), and 1 170 cm⁻¹ (P=O), τ (CDCl₃) 2.0—2.8 (10 H, m, Ph₂PO), 5.3 (1 H, s, OH), 7.4br (1 H, quint, $J_{PH} = J_{HH} = 8$ Hz, PCHMe), 8.0—9.0 (10 H, m, methylene envelope), and 8.85 (3 H, dd, J_{PH} 16, J_{HH} 8 Hz, PCHMe), m/e 328 (20%, M⁺), 310 (16, M − H₂O), 285 (42), 230 (62, Ph₂POEt), 202 (100, Ph₂POH), and 201 (80, Ph₂PO) (Found: C, 73.3; H, 7.5; P, 9.7. C₂₀H₂₅O₂P requires C, 73.2; H, 7.6; P, 9.45%).

1-(1-Diphenylphosphinoylethyl)cyclohexene (21) *from the Tertiary Alcohol* (19).—The alcohol (19) (5 g) was stirred in trifluoroacetic acid (25 ml) at 70° for 25 min and the solution poured into water (100 ml), and extracted with chloroform (3 × 50 ml). The extracts were washed with

[15] P. K. G. Hodgson and S. Warren, *J.C.S. Perkin II*, 1975, 372.

[16] G. M. Kosolapoff and R. F. Struck, *J. Chem. Soc.*, 1959, 3950.

[17] E. Muller and H. G. Padeken, *Chem. Ber.*, 1967, **100**, 521; L. Horner H. Hoffmann, and H. G. Wippel, *ibid.*, 1958, **91**, 61.

[18] D. D Perrin, W. L. F. Armarego, and R. H. Perrin, 'Purification of Laboratory Chemicals,' Pergamon, London, 1966.

aqueous sodium hydrogen carbonate (3 × 50 ml), dried (MgSO₄), and evaporated. The solid residue was recrystallised from ethyl acetate to give the olefin (21) (4.3 g, 86%, characterised above).

3-(Cyclohex-1-enyl)-3-diphenylphosphinoylbutan-2-ol (22; R = Me).—The olefin (21) (5 g) in dry ether (200 ml) was stirred with n-butyl-lithium (12 ml; 1.5M in hexane) under nitrogen for 0.5 h. The solution was cooled to −78 °C and a solution of acetaldehyde in ether saturated with anhydrous lithium bromide was added until the red colour was discharged.

Further additions of n-butyl-lithium at room temperature and acetaldehyde at −78° were made until the addition of n-butyl-lithium no longer produced a red colour. The solution was allowed to reach room temperature and water (200 ml) added; the aqueous layer was extracted with chloroform (3 × 50 ml) and the combined aqueous layers were dried (MgSO₄) and evaporated under reduced pressure. The resulting oil contained the two diastereoisomers of (22) and was separated by p.l.c. to give the (2RS,3RS)-*alcohol* (22a; R = Me) (2.4 g, 50%), m.p. 148—149° (from chloroform–petrol), R_F 0.6, $v_{max.}$ 3 300 (OH), 1 438 (PPh), and 1 150 cm⁻¹ (P=O), τ (CDCl₃) 2.0—2.8 (10 H, m, Ph₂PO), 4.2br (1 H, s, HC=C), 4.8 (1 H, m, OH), 5.7 (1 H, quint, $J_{PH} = J_{HH} = 6$ Hz, PC·CHMe), 7.6 (2 H, m, CH₂·C=C), 8.0 (2 H, m, CH₂·C=C), 8.6—9.0 (4 H, m, CH₂·CH₂), 8.95 (3 H, d, J_{PH} 18 Hz, PCMe), and 8.95 (3 H, d, J_{HH} 6 Hz,PC·CHMe), *m/e* 354 (10%, M⁺), 337 (5, M − OH), 309 (100, M − MeCHO), and 201 (90, Ph₂PO) (Found: C, 74.45; H, 7.85; P, 8.5. C₂₂H₂₇O₂P requires C, 74.6; H, 7.6; P, 8.7%), and the (2RS,3SR)-*alcohol* (22b; R = Me) (1.4 g, 29%), m.p. 189—191° (from chloroform–petrol), R_F 0.5, $v_{max.}$ 3 310 (OH), 1 440 (PPh), and 1 160 cm⁻¹ (P=O), τ (CDCl₃) 2.0—2.7 (10 H, m, Ph₂PO), 4.6br (1 H, s, HC=C), 6.3—6.6 (2H, m, OH and MeCH), 8.0 (2 H, m, CH₂·C=C), 8.3 (2 H, m, CH₂·C=C), 8.5—9.0 (4 H, m, CH₂·CH₂), 8.7 (3 H, d, J_{PH} 18 Hz, PCMe), and 8.95 (3 H, d, J_{HH} 6 Hz, MeCH), *m/e* 354 (8%, M⁺), 331 (5, M − OH), 310 (80, M − MeCHO), and 201 (100, Ph₂PO) (Found: C, 74.4; H, 7.8; P, 8.6. C₂₂H₂₇O₂P requires C, 74.6; H, 7.6; P, 8.7%).

2-(Cyclohex-1-enyl)-2-diphenylphosphinoyl-1-phenylpropan-1-ol (22; R = Ph).—The olefin (21) (2 g) was stirred under nitrogen in dry ether (100 ml) while butyl-lithium (6.5 ml; 1.5M in hexane) was added. The solution was cooled to −78 °C and benzaldehyde (700 mg) in dry ether (25 ml) was added, the red colour being discharged. The solution was allowed to reach room temperature, and water (100 ml) was added. The aqueous layer was extracted with chloroform (3 × 50 ml) and the combined organic layers were dried (MgSO₄) and evaporated under reduced pressure. The oily mixture of diastereoisomers was separated by column chromatography (elution with 1 : 1 ethyl acetate–petrol) to give the (2RS,3SR)-*alcohol* (22a; R = Ph) (300 mg, 12%), m.p. 144—147° (from ethyl acetate–di-isopropyl ether), R_F 0.75, $v_{max.}$ 3 300 (OH), 1 440 (PPh), and 1 150 cm⁻¹ (P=O), τ (CDCl₃) 2.0—2.6 (10 H, m, Ph₂PO), 2.7 (5 H, s, Ph), 3.9 (1 H, s, OH), 4.1 (1 H, m, HC=C), 4.9 (1 H, d, J_{PH} 6 Hz, PC·CH·OH), 8.0 (4 H, m, CH₂·C=CCH₂), 8.6 (4 H, m, CH₂·CH₂), and 9.1 (3 H, d, J_{PH} 18 Hz, PCMe), *m/e* 416 (2%, M⁺), 398 (3, M − H₂O), 310 (70, M − PhCHO), 202 (100, Ph₂POH), and 201 (95, Ph₂PO) (Found: C, 78.0; H, 7.2; P, 7.7. C₂₇H₂₉O₂P requires C, 77.9; H, 7.0; P, 7.4%), and the (2RS,3RS)-*alcohol* (22b; R = Ph) (1 g, 35%), m.p. 209—211° (from ethyl acetate–di-isopropyl ether), R_F 0.6, $v_{max.}$ 3 300 (OH), 1 440 (PPh), and 1 150 cm⁻¹ (P=O), τ

(CDCl₃) 2.0—2.6 (10 H, m, Ph₂PO), 2.8 (5 H, s, Ph), 4.4 (1 H, d, J_{PH} 6 Hz, PC·CH·OH), 4.7 (1 H, m, CH=C), 5.2 (1 H, m, OH), 8.1 (4 H, m, CH₂·C=C·CH₂), 8.6 (4 H, m, CH₂·CH₂), and 8.7 (3 H, d, J_{PH} 18 Hz, PCMe), *m/e* 416 (2%, M⁺), 415 (2, M − H), 398 (3, M − H₂O), 397 (6), 310 (100, Ph₂POEt), 202 (80, Ph₂POH), and 201 (80, Ph₂PO) (Found: C, 77.9; H, 6.9; P, 7.4. C₂₇H₂₉O₂P requires C, 77.9; H, 7.0; P, 7.4%).

Conversion of the Alcohols (22) *into Dienes* (23) *and their Diels–Alder Adducts with Maleic Anhydride.*—Each alcohol (22) (200 mg) in dimethylformamide (20 ml) was added to sodium hydride (50 mg of 60% dispersion in oil; washed with petrol) under nitrogen, and stirred at room temperature for 3 h. Water (20 ml) was added slowly and the solution extracted with petrol (3 × 25 ml). The extracts were washed with water (6 × 25 ml), dried (MgSO₄), and evaporated under reduced pressure to give the dienes (23). Each diene (40 mg) was heated under reflux in dry benzene (5 ml) with maleic anhydride (60 mg) for 60 h or until reaction was complete. The benzene was removed under reduced pressure, and the adducts were collected and recrystallised from toluene–petrol.

(*Z)-2-Cyclohex-1-enylbut-2-ene* (23 *Z*; R = Me) (64 mg, 80%) was an oil, R_F (petrol) 0.5, τ (CDCl₃) 4.6br (1 H, s, HC=C), 4.8br (1 H, q, *J* 7 Hz, MeCH=C), 8.0 (4 H, m, CH₂·C=C·CH₂), 8.3 br (3 H, s, MeC=C), 8.5 (3 H, d, *J* 7 Hz, MeCH=C). The maleic anhydride *adduct* (26a; R = Me) (50 mg, 70%) had m.p. 60—63°, R_F 0.8, $v_{max.}$ 1 858 and 1 780 cm⁻¹ (anhydride), τ * (CDCl₃) 6.4 (1 H, t, J_{HH} 9 Hz, HC·CO), 6.9 (1 H, dd, *J* 9 and 2 Hz, HC·CO), 7.4 (4 H, m, allylic CH₂), 8.3br (3 H, s, MeC=C), 8.5 (6 H, m, CH₂), and 8.8 (3 H, d, *J* 7 Hz, MeCH), *m/e* 234 (M⁺, 50%), 206 (60, M − CO), 161 (100, 206 − CO₂H) (Found: C, 71.5; H, 7.8. C₁₄H₁₈O₃ requires C, 71.8; H, 7.7%).

(*E)-2-Cyclohex-1-enylbut-2-ene* (23 *E*; R = Me) (64 mg, 80%) was an oil, R_F (petrol) 0.4, τ (CDCl₃) 4.2br (1 H, s, HC=C), 4.5 (1 H, q, *J* 7 Hz, MeCH=C), 7.8 (4 H, m, CH₂·C=C·CH₂), 8.35 (4 H, m, CH₂·CH₂), 8.3 (3 H, s, MeC=C), and 8.4 (3 H, d, *J* 7 Hz, MeCH=C). The maleic anhydride *adduct* (26b; R = Me) (4.6 mg, 66%) had m.p. 97—99°, R_F 0.8, $v_{max.}$ (CHCl₃) 1 855 and 1 780 cm⁻¹ (anhydride), τ * (CDCl₃) 6.7 (2 H, m, CH·CO), 7.9 (4 H, m, allylic CH₂), 8.3br (3 H, s, MeC=C), 8.5 (6 H, m, CH₂), and 8.7 (3 H, d, *J* 6 Hz MeCH), *m/e* 234 (50%, M⁺), 206 (60, M − CO), and 161 (100, 206 − CO₂H) (Found: C, 72.0; H, 7.9%).

(*Z)-2-Cyclohex-1-enyl-1-phenylprop-1-ene* (23 *Z*; R = Ph) (68 mg, 70%) was an oil, R_F (petrol) 0.5, $\lambda_{max.}$ 260 (ε 3 767) and 266 nm (3 729), τ (CDCl₃) 2.7br (5 H, s, Ph), 3.3br (1 H, s, PhCH), 4.0 (1 H, m, CH=C), 7.7 (4 H, m, CH₂·C=C·CH₂), 8.0 (3 H, s, MeC=C), and 8.3 (4 H, m, CH₂·CH₂), *m/e* 198 (100%, M⁺) and 183 (70, M − Me) (Found: M⁺, 198.140 7. C₁₅H₁₈ requires *M*, 198.140 8). The maleic anhydride adduct (26a; R = Ph) was formed very slowly and could be obtained in only tiny amounts. Its n.m.r. spectrum, recorded on the Fourier transform CFT-20 machine at 80 MHz, is described in the text.

(*E)-2-Cyclohex-1-enyl-1-phenylprop-1-ene* (23 *E*; R = Ph) (78 mg, 80%) had m.p. 44—47° R_F (petrol) 0.4, $\lambda_{max.}$ (95% EtOH) 271.5 nm (ε 16 902), τ (CDCl₃) 2.8 (5 H, m, Ph), 3.8 (1 H, m, PhCH=C), 4.4 (1 H, m, C=CH·CH), 8.0br (3 H, s, MeC=C), 8.0 (4 H, m, CH₂·C=C·CH₂), and 8.3 (4 H, m, CH₂·CH₂), *m/e* 198 (100%, M⁺), 183 (80, M − Me), 155 (80), and 141 (70) (Found: M⁺, 198.1400. C₁₅H₁₈ requires *M*, 198.1408). The maleic anhydride *adduct* (26a; R = Ph) (40 mg, 70%) had m.p. 128—130°, $v_{max.}$ (CHCl₃)

1 864 and 1 782 cm^{-1} (anhydride), τ * (CDCl$_3$) 2.7br (5 H, s, Ph), 4.3 (1 H, d, J 6 Hz, PhCH·CH·CO), 4.6 [2 H, overlapping ts, J 6 Hz, PhCH·CH(CO)·CH(CO)·CH], 6.7 (3 H, m, allylic CH), 7.7 (8 H, m, CH$_2$), and 7.6 (3 H, s, MeC=C),

m/e 296 (50%, M^+), 268 (70, M — CO), 224 (100, 268 — CO$_2$H), and 223 (80) (Found: C, 76.9; H, 6.8. C$_{19}$H$_{20}$O$_3$ requires C, 77.0; H, 6.7%).

* These n.m.r. spectra are described in the text.