

Allylic Phosphine Oxides as Precursors of Conjugated Dienes of Defined Geometry

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Methods are described for the preparation in geometrically homogeneous form of allylic diphenylphosphine oxides. These compounds can be used in Horner reactions with carbonyl compounds to provide a convenient one-step synthesis of conjugated dienes in which the geometry present in the original allyl system is preserved. The method is exemplified by the preparation of the homogeneous *Z*- and *E*-forms of but-2-enylidenecyclohexane and of 3-methylpent-2-enylidenecyclohexane.

THE observation that allylic phosphonium bromides of *Z*-geometry can be used in Wittig reactions to give conjugated dienes in which the original *Z*-geometry is retained was first made¹ during the synthesis of dienes and trienes related to vitamin D. Although the method has since been used successfully in other fields of synthesis,² examples³ have been recorded of failure to prepare the geometrically homogeneous phosphonium halides which are necessary intermediates. Such difficulties may be partly due to the physical properties of the phosphonium compounds, which are unfavourable to purification from geometrical isomers. Difficulties also result from the relatively weak nucleophilic character of triphenylphosphine, which makes S_N2 reaction with an allyl chloride slow at room temperature; the use of heat

during the quaternisation can cause geometric change. Allyl bromides, which react satisfactorily at room temperature, are less stable and more difficult to obtain in the geometrically homogeneous state than the chlorides. Although such difficulties can usually be overcome by a proper choice of reaction conditions they can detract from the convenience of the method. It seemed likely to us that they could be avoided by working, not with triphenylphosphonium halides, but with allylic diphenylphosphine oxides, which could then be used in Horner⁴ olefination reactions; these possibilities were examined in the work now reported.

At the outset, only one allylic diphenylphosphine oxide had been used in the Horner method; diphenyl-(5-phenylpentadienyl)phosphine oxide, metallated by using the sodio-derivative of dimethyl sulphoxide, reacted

¹ I. T. Harrison and B. Lythgoe, *J. Chem. Soc.*, 1958, 843.

² E. Truscheit and K. Eiter, *Annalen*, 1962, **658**, 65; F. Näf, R. Decorzant, W. Thommen, B. Willhalm, and G. Ohloff, *Helv. Chim. Acta*, 1975, **58**, 1016.

³ G. Pattenden and B. C. L. Weedon, *J. Chem. Soc. (C)*, 1968, 1984; R. Bausch, B. Bogdanowicz, H. Dreeskamp, and J. B. Koster, *Annalen*, 1974, 1625.

⁴ L. Horner, H. Hoffmann, and H. G. Wippel, *Chem. Ber.*, 1958, **91**, 61, 64; 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.

with benzaldehyde to give 1,6-diphenylhexatriene in 45% yield.⁵ Such metallations are more conveniently effected with *n*-butyl-lithium; but for ordinary alkyl-diphenylphosphine oxides it is then necessary to isolate an intermediate β -hydroxy-phosphine oxide and carry out its decomposition in a separate step, for example, with sodium hydride in dimethylformamide.⁶ This two-step procedure was used in a recently recorded example⁷ of a Horner reaction between a secondary allylic diphenylphosphine oxide and benzaldehyde. Our own preliminary experiments showed that when allylic diphenylphosphine oxides are metallated with butyl-lithium, and then brought into reaction with, for example, cyclohexanone, the lithio-derivative of the β -hydroxy-phosphine oxide, which is formed rapidly, undergoes elimination of lithium diphenylphosphinate completely within 2 h at 25 °C, so that the whole olefination can conveniently be carried out in one step without isolation of intermediates. The solubility of lithium diphenylphosphinate in water facilitates the isolation of the product. Thus (2-cyclohexylidene-ethyl)diphenylphosphine oxide and cyclohexanone gave 1,2-dicyclohexylidene-ethane⁸ directly in 80% yield, and 3-methylbut-2-enyldiphenylphosphine oxide similarly gave 3-methylbut-2-enylidencyclohexane. These results, and the others described below, also reassured us as to another aspect of the reaction. Some allylic phosphorus compounds,⁹ when metallated, react with a carbonyl compound not only at C_{α} , but also at C_{γ} , the latter reaction giving compounds which are valueless for the formation of the olefin. As our main concern was with allylic diphenylphosphine oxides unsubstituted at C_{α} , and bearing one of two substituents at C_{γ} , it was expected that reaction at C_{γ} would be unimportant, and the present results show that this view is correct.

Primary alkyl halides react with the sodio-¹⁰ or lithio-^{11,*} derivatives of dialkyl- or diaryl-phosphines, giving tertiary phosphines which can be oxidised with hydrogen peroxide¹² to give the phosphine oxides. We have used this method to prepare allylic diphenylphosphine oxides from allylic chlorides; convenient methods are available¹³ for the preparation of geometrically homogeneous allylic chlorides from the corresponding alcohols, and an unambiguous S_N2 reaction of the chlorides at or below 0 °C is ensured by the powerfully nucleophilic character of the diphenylphosphide ion, so that the original allyl geometry is retained. Tosylates, generated *in situ*^{13a} from the allyl alcohol, can also be used instead of the chlorides. Finally, we have found

* In the present work, lithium diphenylphosphide solutions were prepared by treatment of diphenylphosphine (D. Wittenberg and H. Gilman, *J. Org. Chem.*, 1958, **23**, 1063) in dry tetrahydrofuran at 0 °C under nitrogen with 1 equiv. of *n*-butyl-lithium in light petroleum.

† The (*Z*)-alcohol was obtained by reduction with $LiAlH_4$ (K. H. Dahm, B. M. Trost, and H. Röller, *J. Amer. Chem. Soc.*, 1967, **89**, 5191) of ethyl (*Z*)-3-methylpent-2-enoate (J. B. Siddall, M. Biskup, and J. H. Fried, *ibid.*, 1969, **91**, 1853); the (*E*)-alcohol was obtained similarly from methyl (*E*)-3-methylpent-2-enoate, prepared by the reaction of the pure acid (G. A. R. Kon, R. P. Linstead, and J. M. Wright, *J. Chem. Soc.*, 1934, 599) with diazomethane.

that pure allylic diphenylphosphine oxides can be prepared conveniently with retention of the allyl geometry from the corresponding 2,6-dichlorobenzoates,¹⁴ by reaction with lithium diphenylphosphide between -40 and 0 °C. The 2,6-dichlorobenzoates, which can be purified by chromatography, and are stable, are readily obtained by interaction of the alcohol and the acid in the presence of dimethylformamide dineopentyl acetal.¹⁵

By using the dichlorobenzoate method, geometrically homogeneous (*Z*)-but-2-enyldiphenylphosphine oxide (1) was prepared in 65% yield from (*Z*)-but-2-en-1-ol,¹⁶ and the corresponding homogeneous (*E*)-phosphine oxide (2) was obtained in 78% yield from (*E*)-but-2-en-1-ol.¹⁶ Each of these phosphine oxides showed characteristic i.r. bands which would have allowed any significant contamination with the other isomer to be detected. Moreover, the $CH_3C=^1H$ n.m.r. signal of the *Z*-isomer lies between τ 8.4 and 8.6, and that of the *E*-isomer between τ 8.28 and 8.45, and inspection of the relevant regions in each spectrum provided further proof of geometrical homogeneity.

In a similar manner, geometrically homogeneous (*Z*)-3-methylpent-2-enyldiphenylphosphine oxide (5) and its (*E*)-isomer (6) were prepared from the corresponding alcohols † *via* the 2,6-dichlorobenzoates. The $CH_3C=$ signal of the *Z*-isomer was found to lie between τ 8.26 and 8.39, and that of the *E*-isomer between τ 8.48 and 8.61, so that any contamination of either isomer with the other would be easily detected. It is of interest that in the isomeric pair (5) and (6), as in the pair (1) and (2), the diphenylphosphine oxide group exercises a shielding effect upon a methyl group which is situated on the same side of the double bond.

Geometry was best maintained in the olefination reaction when the phosphine oxide was metallated, and the carbonyl compound added, at *ca.* -70 °C; the mixture was then allowed to warm slowly to 25 °C. In this way, the (*Z*)-phosphine oxide (1) and cyclohexanone gave in 72% yield (*Z*)-but-2-enylidencyclohexane (3) containing (g.l.c.) not more than 2% of the (*E*)-isomer

⁵ M. P. Savage and S. Trippett, *J. Chem. Soc. (C)*, 1966, 1842.

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

⁷ A. H. Davidson and S. Warren, *J.C.S. Chem. Comm.*, 1975, 148.

⁸ I. T. Harrison, B. Lythgoe, and S. Trippett, *J. Chem. Soc.*, 1955, 4016.

⁹ E. J. Corey and D. E. Cane, *J. Org. Chem.*, 1969, **34**, 3053.

¹⁰ W. Kuchen and H. Buchwald, *Chem. Ber.*, 1959, **92**, 227.

¹¹ K. Issleib and A. Tschach, *Chem. Ber.*, 1959, **92**, 1118.

¹² K. Sasse in 'Houben-Weyl, Methoden der Organischen Chemie,' 4th edn., Thieme Verlag, Stuttgart, 1963, vol. 12/1, p. 140.

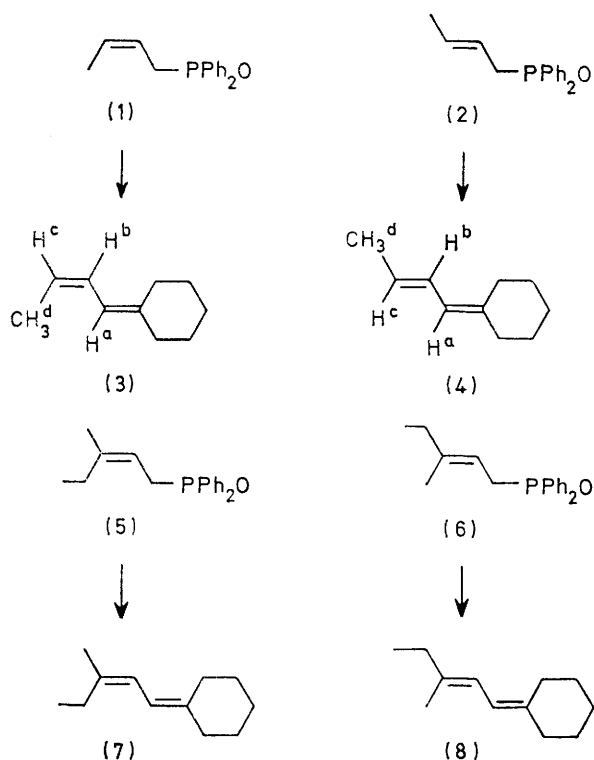
¹³ (a) G. Stork, P. A. Grieco, and M. Gregson, *Tetrahedron Letters*, 1969, 1393; (b) E. J. Corey, C. U. Kim, and M. Takeda, *ibid.*, 1972, 4399; (c) E. W. Collington and A. I. Meyers, *J. Org. Chem.*, 1971, **36**, 3044; (d) J. B. Lee and T. J. Nolan, *Canad. J. Chem.*, 1966, **44**, 1331.

¹⁴ G. Stork and W. N. White, *J. Amer. Chem. Soc.*, 1956, **78**, 4609.

¹⁵ H. Brechbühler, H. Büchi, E. Hartz, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, 1965, **48**, 1746.

¹⁶ L. F. Hatch and S. S. Nesbitt, *J. Amer. Chem. Soc.*, 1950, **72**, 729.

(4); the (*E*)-isomer, as similarly obtained from the (*E*)-phosphine oxide (2), contained not more than 3% of the (*Z*)-isomer. The dienes (3) and (4) have not previously



been described separately, although a mixture containing about equal parts of each has been obtained.¹⁷ They are distinguished by the higher ϵ value of the *E*-isomer, by their i.r. spectra, each of which shows bands which would allow its presence as a contaminant in the other to be detected (see Experimental section), and by their ¹H n.m.r. spectra (see Table).

Isomeric but-2-enylidencyclohexanes: n.m.r. data (solvent CDCl_3 ; τ values; J in Hz) obtained at 90 MHz with the aid of spin-decoupling experiments

| Compd. | H^a | H^b | H^c | H^d |
|--------|-------------------------|---|-------------------------------------|---------------------------------------|
| (3) | 3.96 (d, J_{ab} 12) | 3.8 (dd of q, J_{ab} 12, J_{bc} 10, J_{bd} 1.5) | 4.6 (dq, J_{bc} 10, J_{cd} 7) | 8.25 (dd, J_{cd} 7, J_{bd} 1.5) |
| (4) | 4.25 (d, J_{ab} 10.5) | 3.7 (dd of q, J_{ab} 10.5, J_{bc} 15, J_{bd} 1.5) | 4.4 (dq, J_{bc} 15, J_{cd} 6.5) | 8.23 (dd, J_{cd} 6.5, J_{bd} 1.5) |

The isomeric phosphine oxides (5) and (6) were used in reactions with cyclohexanone to give, respectively, the *Z*- and *E*-isomers of 3-methylpent-2-enylidencyclohexane. The *Z*-isomer (7) contained (g.l.c.) *ca.* 2% of the *E*-isomer as a contaminant. The *E*-isomer (8) was prepared from a solution of the metallated phosphine oxide which had been generated at 0 °C, and allowed to reach 20 °C, and the fact that it contained *ca.* 4.5% of the *Z*-isomer illustrates the need to keep low temperatures during generation of the ylide, and while the initial reaction with the carbonyl compound is in progress. The i.r. spectrum of each of the dienes (7) and (8) shows

¹⁷ O. Grummit and Z. Mandel, *J. Amer. Chem. Soc.*, 1956, **78**, 1054; K. J. Crowley, *Tetrahedron*, 1965, **21**, 1001.

¹⁸ Some of these results have appeared in preliminary form: B. Lythgoe, T. A. Moran, M. E. N. Nambudiry, S. Ruston, J. Tideswell, and P. W. Wright, *Tetrahedron Letters*, 1975, 3863.

bands which enable its detection as a contaminant in the other. The differences between the n.m.r. data for the two isomers, though noticeable, are small.

The above experiments show that geometrically homogeneous allylic diphenylphosphine oxides can be prepared readily from the corresponding alcohols, and can be used in Horner reactions to provide an efficient and convenient synthesis of conjugated dienes of defined geometry.^{18,19} The application of these methods to synthesis in the vitamin D field will be described in another paper.

EXPERIMENTAL

Unless otherwise specified, u.v. data relate to solutions in EtOH and n.m.r. data to solutions in CDCl_3 ; light petroleum unless further qualified refers to the fraction of b.p. 40–60 °C. T.l.c. was carried out with Kieselgel GF₂₅₄.

3-Methylbut-2-enyldiphenylphosphine Oxide.—3-Methylbut-2-enyl chloride (1.04 g) in dry tetrahydrofuran (5 cm³) was added with stirring (15 min) to a solution of lithium diphenylphosphide (16 cm³; 0.63M) at 0 °C. The red colour was discharged; the solution was evaporated under reduced pressure, and the residue was dissolved in chloroform and shaken successively with aqueous 5% hydrogen peroxide, aqueous sodium sulphite, dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water, and was then dried and evaporated. Crystallisation from cyclohexane–light petroleum gave the phosphine oxide (2.3 g, 85%), m.p. 122–124° (lit.,⁶ 124–125°), τ 2.0–2.6 (10 H, m, ArH), 4.7 (1 H, distorted q, =CH), 6.9 (2 H, dd, J_{vic} 7.5, $J_{H,P}$ 14.5 Hz, $\text{CH}_2\cdot\text{P}$), 8.3 (3 H, dd, J 4.5 and 1 Hz, =C·CH₃), and 8.52 (3 H, dd, J 3 and 1 Hz, =C·CH₃).

(2-Cyclohexylidene-ethyl)diphenylphosphine Oxide.—2.35M-Butyl-lithium in light petroleum (2.13 cm³) was added dropwise to a stirred solution of 2-cyclohexylidene-ethanol (630 mg) in tetrahydrofuran (20 cm³) at 0 °C under nitrogen; stirring and cooling were then continued while toluene-*p*-sulphonyl chloride (0.95 g) in tetrahydrofuran (5 cm³) was added slowly. The mixture was then added slowly under

nitrogen to a stirred solution of lithium diphenylphosphide (1.19M; 4.2 cm³) at 0 °C; after a further 0.5 h water (5 cm³) was added and the solvents were removed under reduced pressure. The residue, dissolved in chloroform, was worked up as in the preceding experiment. The resulting phosphine oxide (1.1 g, 65%), m.p. 160–162° (from acetone), gave on recrystallisation material of m.p. 164–165° (lit.,⁶ 166–167°), ν_{max} (CHCl_3) 1173 and 1120 cm⁻¹, τ 2.0–2.7 (10 H, m, ArH), 4.8 (1 H, distorted q, =CH), 6.9 (2 H, dd, J_{vic} 8, $J_{H,P}$ 15 Hz, $\text{CH}_2\cdot\text{P}$), *ca.* 8.1 (4 H, m, $\text{CH}_2\cdot\text{C}=\text{C}$), and 8.62 (6 H, m, CH_2) (Found: C, 77.2; H, 7.85; P, 9.9. Calc. for $\text{C}_{20}\text{H}_{23}\text{OP}$: C, 77.4; H, 7.5; P, 10.0%).

(E)-But-2-enyldiphenylphosphine Oxide (2).—(*E*)-But-2-en-1-ol (1.44 g) containing less than 2% of the *Z*-isomer, 2,6-dichlorobenzoic acid (4.2 g), dimethylformamide di-

¹⁹ Similar findings have since been described independently in preliminary form: M. Schlosser and H. B. Tuong, *Chimia (Switz.)*, 1976, **30**, 197.

neopentyl acetal (6.0 g), and benzene (50 cm³) were heated under reflux for 1 h. The cooled solution was diluted with ether, washed with aqueous sodium hydrogen carbonate and then with water, dried, and evaporated. Distillation gave the 2,6-dichlorobenzoate (4.3 g, 88%), b.p. 114–116° at 0.1 mmHg, which crystallised from light petroleum at –40 °C and then had m.p. 38°, ν_{\max} (film) 1 740, 1 430, 1 270, and 1 140 (all vs) cm⁻¹ (Found: C, 53.85; H, 4.2; Cl, 29.1. Calc. for C₁₁H₁₀Cl₂O₂: C, 53.9; H, 4.1; Cl, 28.9%).

To a stirred solution of the ester (1.71 g) in tetrahydrofuran at –40 °C under nitrogen, lithium diphenylphosphide solution (from 1.63 g of diphenylphosphine) was added during $\frac{1}{2}$ h; the temperature was then allowed to rise to –25 °C and after $\frac{3}{4}$ h more to 25 °C. After a further 1 h water (1 cm³) was added, solvents were removed under reduced pressure, and the residue, dissolved in chloroform, was worked up with hydrogen peroxide as described for the other phosphine oxides. Crystallisation of the product from cyclohexane gave crude phosphine oxide (1.40 g), m.p. 116–118°; more (204 mg; total 89%) was obtained by p.l.c. (CHCl₃), which also gave some of the starting 2,6-dichlorobenzoate (62 mg), and a compound (80 mg), m.p. 151–152° (from benzene–light petroleum), formed by replacement of one of the chlorine atoms of the starting ester by a PPh₂O group (Found: C, 67.0; H, 4.9; Cl, 8.5; P, 7.7. C₂₃H₂₀ClO₃P requires C, 67.1; H, 4.9; Cl, 8.6; P, 7.6%). Pure (*E*)-but-2-enyldiphenylphosphine oxide had m.p. 118–119°, ν_{\max} (Nujol) 1 855, 1 122m, 974m, 845m, 740m, 723s, and 694s cm⁻¹ [the italicized bands are absent from the spectrum of the *Z*-isomer (*q.v.*)], τ 2.1–2.6 (10 H, m, ArH), 4.5 (2 H, m, *W* $\frac{1}{2}$ 12 Hz, =CH), 6.9 (2 H, dd, *J*_{vic} 6, *J*_{H,P} 14 Hz, CH₂·P), and 8.37 (3 H, apparent t, CH₃·C=) (Found: C, 74.9; H, 6.55; P, 12.1. C₁₈H₁₇OP requires C, 75.0; H, 6.7; P, 12.1%).

(*Z*)-But-2-enyldiphenylphosphine Oxide (1).—(*Z*)-But-2-en-1-ol (1.64 g), containing less than 2% of the *E*-isomer was converted, as described for the *E*-isomer, into the 2,6-dichlorobenzoate (4.35 g, 78%) (purified by chromatography on neutral alumina with benzene–light petroleum), ν_{\max} (film) 1 740, 1 433, 1 270, and 1 142 (all vs) cm⁻¹, τ (CCl₄) 2.73 (3 H, s, ArH), *ca.* 4.3 (2 H, m, =CH), 5.13br (2 H, d, *J* 5.5 Hz, CH₂·O), and 8.23 (3 H, d, *J* 5.5 Hz, CH₃·C=) (Found: C, 54.3; H, 4.4; Cl, 29.2. C₁₁H₁₀Cl₂O₂ requires C, 53.9; H, 4.1; Cl, 28.9%).

A portion of the above ester (1.77 g) was converted into the phosphine oxide essentially as described for the *E*-isomer. (*Z*)-But-2-enyldiphenylphosphine oxide (1.4 g, 76%) separated from cyclohexane, m.p. 111–112.5°, ν_{\max} (Nujol) 1 184vs, 1 160m, 1 119m, 994w, 834m, 748s, 720vs, 702vs, and 667s cm⁻¹ (the italicized bands are not shown by the *E*-isomer), τ 2.1–2.6 (10 H, m, ArH), 4.42 (2 H, m, =CH), 6.85 (2 H, dd, *J*_{vic} 7, *J*_{H,P} 15 Hz, CH₂·P), and 8.52 (3 H, apparent t, CH₃·C=) (Found: C, 74.85; H, 6.75; P, 12.05. C₁₈H₁₇OP requires C, 75.0; H, 6.7; P, 12.1%).

(*E*)-3-Methylpent-2-enyldiphenylphosphine Oxide (6).—(*E*)-3-Methylpent-2-en-1-ol (2.0 g) containing less than 1% of the *Z*-isomer was converted, as described for the but-2-en-1-ols into the 2,6-dichlorobenzoate; after chromatography on silica gel with benzene–light petroleum it was obtained as a liquid (4.69 g, 86%), ν_{\max} (film) 1 740, 1 432, 1 271, and 1 140 (all vs) cm⁻¹, τ 2.7 (3 H, s, ArH), 4.5 (1 H, t with fine splitting, *J*_{vic} 7 Hz, =CH), 5.07 (2 H, d, *J* 7 Hz, O·CH₂), 7.9 (2 H, q, *J* 7 Hz, CH₂·Me), 8.22br (3 H, s, CH₃·C=), and 8.97 (3 H, t, *J* 7 Hz, CH₂·CH₃) (Found: C, 56.8; H, 5.4; Cl, 25.8. C₁₃H₁₄Cl₂O₂ requires C, 57.2; H, 5.1; Cl, 25.95%).

The ester (2.4 g) was converted into the phosphine oxide as described for the corresponding but-2-enyl esters, and the product was chromatographed on silica gel with 2% methanol in chloroform. Some starting ester (220 mg) was recovered, and the (*E*)-3-methylpent-2-enyldiphenylphosphine oxide (1.95 g, 78%) was obtained as crystals, m.p. 118–119° (from cyclohexane), τ 2.1–2.7 (10 H, m, ArH), 4.74 (1 H, distorted q, *J*_{vic} 7.5, *J*_{H,P} *ca.* 6–8 Hz, =CH), 6.89 (2 H, dd, *J*_{vic} 7.5, *J*_{H,P} 15 Hz, CH₂·P), *ca.* 8.05 (2 H, m, CH₂·C=), 8.55 (3 H, d, *J* 2 Hz, CH₃·C=), and 9.11 (3 H, t, *J* 7 Hz, CH₃·CH₂) (Found: C, 76.0; H, 7.5; P, 11.4. C₁₈H₂₁OP requires C, 76.1; H, 7.5; P, 10.9%).

(*Z*)-3-Methylpent-2-enyldiphenylphosphine Oxide (5).—(*Z*)-3-Methylpent-2-en-1-ol, containing less than 3% of the *E*-isomer, was converted in the usual way into the 2,6-dichlorobenzoate (75%), ν_{\max} (film) 1 740, 1 435, 1 275, and 1 142 (all vs) cm⁻¹, τ 2.7 (3 H, s, ArH), 4.52 (1 H, t, *J* 7 Hz, =CH), 5.09 (2 H, d, *J* 7 Hz, CH₂·O), 7.77 (2 H, q, *J* 7 Hz, CH₂·Me), 8.19 (3 H, s, CH₃·C=), and 8.94 (3 H, t, *J* 7 Hz, CH₃·CH₂) (Found: C, 57.2; H, 5.25; Cl, 26.05. C₁₃H₁₄Cl₂O₂ requires C, 57.15; H, 5.2; Cl, 25.95%).

The ester was converted in the usual way into the phosphine oxide (72%), m.p. 116–117° (from light petroleum), τ 2.1–2.7 (10 H, m, ArH), 4.8 (1 H, distorted q, *J*_{vic} 7.2, *J*_{H,P} *ca.* 6–8 Hz, =CH), 6.89 (2 H, dd, *J*_{vic} 7.2, *J*_{H,P} 15 Hz, CH₂·P), 8.07 (2 H, q, *J* 7 Hz, CH₂·Me), 8.33 (3 H, d, *J* 3 Hz, CH₃·C=), and 9.18 (3 H, t, *J* 7 Hz, CH₃·CH₂) (Found: C, 75.9; H, 7.4; P, 11.3. C₁₈H₂₁OP requires C, 76.1; H, 7.5; P, 10.9%).

3-Methylbut-2-enyldiphenylphosphine Oxide.—To a stirred solution of 3-methylbut-2-enyldiphenylphosphine oxide (405 mg) in tetrahydrofuran at 0 °C under nitrogen was added 2.35m-n-butyl-lithium in light petroleum (0.64 cm³). After a further 15 min cyclohexanone (147 mg) in tetrahydrofuran (1 cm³) was added dropwise at 0 °C, discharging the red colour. After being left overnight at 25 °C the solution was diluted with chloroform, washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated. The oily residue, chromatographed (p.l.c.) with light petroleum, gave first the diene (165 mg) and then (CHCl₃) the starting phosphine oxide (90 mg). 3-Methylbut-2-enyldiphenylphosphine oxide had λ_{\max} 239, 247, and 255 nm (ϵ 18 000, 20 300, and 15 500), ν_{\max} (film) 1 622m, 983s, and 845vs cm⁻¹, τ 3.97 (2 H, q, *J* 12.5 Hz, =CH), 7.8 (4 H, m, CH₂·C=), 8.2br (6 H, s, =CMe₂), and 8.43 (6 H, m, CH₂) (Found: *M*⁺, 150.140 89. C₁₁H₁₈ requires *M*, 150.140 84).

1,2-Dicyclohexylidene-ethane.—Prepared from (2-cyclohexylidene-ethyl)diphenylphosphine oxide (620 mg) and cyclohexanone (215 mg) in essentially the same way as described above, the crude product was separated (p.l.c.; light petroleum, then CHCl₃) giving 1,2-dicyclohexylidene-ethane (310 mg, 81%), m.p. 44–45° (from light petroleum) (lit.⁸ 45–47°), λ_{\max} 241.5, 250, and 259 nm (ϵ 31 700, 38 000, and 26 300), and unchanged phosphine oxide (88 mg).

(*E*)-But-2-enyldiphenylphosphine Oxide (4).—A solution of the phosphine oxide (2) (512 mg) in tetrahydrofuran (10 cm³) at –78 °C under nitrogen was stirred during dropwise addition of 1.43m-n-butyl-lithium (1.4 cm³). After a further $\frac{1}{2}$ h a solution of cyclohexanone (215 mg) in tetrahydrofuran (2 cm³) was added dropwise at –78 °C; after some time the red colour was discharged. The solution was then allowed to attain 25 °C, and after a further 2 h it was diluted with ether, washed in turn with dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water, and dried. The solvent was removed by using a column packed with glass

beads. The residue was separated by p.l.c. (light petroleum, then CHCl_3) into two fractions: the slower-moving gave the starting phosphine oxide (130 mg) and the faster-moving (131 mg, 48%) was the (*E*)-diene (4); on g.l.c. (75 ft column of 1.5% TCEPE, 79 °C) 97% had retention time 14.5 min; ca. 3% (*Z*-isomer) showed retention time 15 min. The diene had λ_{max} 233 and 240 (ϵ 28 800 and 32 000), and 247sh nm, ν_{max} (film) 1 659w, 1 622m, 1 342s, 1 229m, 980s, 960vs, 928s, and 850s cm^{-1} ; the italicized bands are not shown by the *Z*-isomer (3) (Found: M^+ , 136.124 66. $\text{C}_{10}\text{H}_{16}$ requires M , 136.125 19).

(*Z*)-But-2-enylidenecyclohexane (3).—The (*Z*)-phosphine oxide (1) (900 mg), metallated with *n*-butyl-lithium, and cyclohexanone (450 mg) were treated as in the preparation of the diene (4) to give a crude product which was purified as before. The (*Z*)-diene (3) (346 mg, 72%) showed on g.l.c. (75 ft column of 1.5% TCEPE; 78 °C) <2% *E*-isomer, retention time 15.7 min, and >98% *Z*-isomer, retention time 16.6 min. It had λ_{max} 241 (ϵ 27 700) and 234sh and 249sh nm, ν_{max} (film) 1 649m, 1 608w, 1 340s, 1 229m, 980s, 850s, and 718vs cm^{-1} (the italicized bands are not shown by the *E*-isomer) (Found: M^+ , 136.124 93. $\text{C}_{10}\text{H}_{16}$ requires M , 136.125 19).

(*E*)-3-Methylpent-2-enylidenecyclohexane (8).—Metallation of the phosphine oxide (6) (568 mg) between 0 and 20 °C and reaction at 0 °C with cyclohexanone (215 mg) in a way similar to that described for the preparation of the diene (3) gave a crude product which was separated by p.l.c., giving unchanged phosphine oxide (6) (105 mg) and (*E*)-3-methylpent-2-enylidenecyclohexane (170 mg, 52%); g.l.c. (75 ft

column of 1.5% TCEPE; 80 °C) showed ca. 4.5% *Z*-isomer, retention time 28.8 min, and ca. 95.5% *E*-isomer, retention time 33 min. It had λ_{max} 240.5, 248, and 257 nm (ϵ 26 800, 30 600, and 23 000), ν_{max} (film) 1 620m, 982m, 859s, and 673m cm^{-1} (but unlike the *Z*-isomer, no absorption at 1 000 cm^{-1}), τ 4.01 (2 H, incipient q, J 13 Hz, =CH), ca. 7.8 (6 H, m, $\text{CH}_2\cdot\text{C}=\text{}$), 8.25 (3 H, s, $\text{CH}_3\cdot\text{C}=\text{}$), 8.44br (6 H, s, CH_2), and 8.79 (3 H, t, J 7.5 Hz, CH_3) (Found: M^+ , 164.156 66. $\text{C}_{12}\text{H}_{20}$ requires M , 164.156 49).

(*Z*)-3-Methylpent-2-enylidenecyclohexane (7).—The (*Z*)-phosphine oxide (5) (426 mg) was metallated at -78 °C, and the reaction with cyclohexanone (147 mg) was carried out at the same temperature. After 1 h at 20 °C the mixture was worked up in the usual way, and separated by p.l.c., giving unchanged phosphine oxide (5) (30 mg) and the (*Z*)-diene (7) (160 mg, 67%); g.l.c. (75 ft column of 1.5% TCEPE; 76 °C) showed the presence of 98% *Z*-isomer, retention time 28 min, and ca. 2% *E*-isomer, retention time 31.5 min. The (*Z*)-diene showed λ_{max} 240.5, 248, and 257 nm (ϵ 26 100, 29 200, and 21 400), ν_{max} (film) 1 620m, 1 020w, 1 000w, 985w, and 852s cm^{-1} (unlike the *E*-isomer, no absorption at 859 and 673 cm^{-1}) τ 4.03 (2 H, incipient q, J 12.5 Hz, =CH), ca. 7.8 (6 H, m, $\text{CH}_2\cdot\text{C}=\text{}$), 8.22 (3 H, s, $\text{CH}_3\cdot\text{C}=\text{}$), 8.44br (6 H, s, CH_2), and 8.99 (3 H, t, J 7.5 Hz, $\text{CH}_3\cdot\text{CH}_2$) (Found: M^+ , 164.155 89. $\text{C}_{12}\text{H}_{20}$ requires M , 164.156 49).

We thank the S.R.C. for a Studentship (to S. R.).

[6/964 Received, 20th May, 1976]