

Synthesis of Phosphindoline Oxides, Tetrahydrophosphinoline Oxides, and Related Compounds by Cyclisation of Allyl- and Vinyl-phosphine Oxides

By J. Ian Grayson, Howard K. Norrish, and Stuart Warren,* University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

The acid-catalysed dehydration of β -hydroxyalkylphosphine oxides gives initially allyl- or vinyl-phosphine oxides, which cyclise to give five- or six-membered rings in which the alkyl chain forms a new carbon-carbon bond to either an aryl or another unsaturated alkyl chain. These reactions offer a general synthesis of the title compounds. A series of these compounds is described, including 4,5-dihydro-1,1,5,5-tetramethyl-3*H*-2a-phospha-acenaphthene 2a-oxide(18). Attempted 1,3-anionic cycloadditions of vinylphosphine oxide anions were not successful.

β -HYDROXYALKYLPHOSPHINE OXIDES (1) give olefins in basic solution by the Wittig-Horner reaction.¹ In acidic solution, when the substitution pattern is right (*e.g.* R¹, R², R³ = alkyl, R⁴ = H) we have shown that they react by diphenylphosphinoyl migration to give allylphosphine oxides,²⁻⁶ but that with other substitution patterns (*e.g.* R¹ = R³ = H) dehydration to a vinyl- or an allyl-phosphine oxide occurs without rearrangement.⁶ We now report that protonation of allyl or vinyl phosphine oxides in strong acid gives cations which are captured by other π -systems within the molecule to give cyclic phosphine oxides.

Cyclic phosphine oxides are usually made by ring closure involving the formation of one or two phosphorus-carbon bonds.^{7,8} Methods related to the Friedel-Crafts reaction, such as the cyclisation of arylphosphinic acids, have proved awkward in the past⁹ and it is only

recently that phosphindoline oxides¹⁰ (3) and tetrahydrophosphinoline oxides¹¹ (5) have been synthesised *via* the Friedel-Crafts cyclisation of chlorophosphines. Many successful syntheses^{12,13} of these compounds have followed the alternative logic of forming a carbon-carbon bond in the cyclisation step, but here again Friedel-Crafts methods¹³ have sometimes been troublesome.

One of the reasons for the difficulty of these reactions [*e.g.* (2) and (4)] is that a phosphinoyl substituent deactivates the benzene ring towards electrophilic attack: arylphosphine oxides undergo nitration in the *meta*-position, and other reactions of this type are virtually unknown.¹⁴ To make the reaction possible, very favourable conditions must therefore be chosen, such as an intramolecular reaction with a long-lived cation [*e.g.* (2) or (4), R², R³ = alkyl]. We chose to try forcing conditions [polyphosphoric acid (PPA) at 170 °C] †

† Since the completion of this work, the cyclisation of allylphosphine oxides, including the preparation of compound (10), has been reported by Berlin and his group,^{15a} who had previously used PPA for the cyclisation of allylphosphonium salts.^{15b}

¹ L. Horner, H. Hoffmann, H. G. Wippel, and G. Klahre, *Chem. Ber.*, 1959, **92**, 2499; A. J. Bridges and G. H. Whitham, *J.C.S. Chem. Comm.*, 1974, 142; A. W. Johnson, 'Ylid Chemistry,' Academic Press, New York, 1966, pp. 192-203.

² P. F. Cann, D. Howells, and S. Warren, *J.C.S. Perkin II*, 1972, 304.

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

⁴ D. Howells and S. Warren, *J.C.S. Perkin II*, 1973, 1645.

⁵ A. H. Davidson and S. Warren, *J.C.S. Chem. Comm.*, 1975, 148; 1976, 181; *J.C.S. Perkin I*, 1976, 639.

⁶ A. H. Davidson, I. Fleming, J. I. Grayson, A. Pearce, R. L. Snowden, and S. Warren, submitted to *J.C.S. Perkin I*.

⁷ K. D. Berlin and D. M. Hellwege, *Topics Phosphorus Chem.*, 1969, **6**, 1; 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; F. G. Mann, 'The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, and Bismuth,' Wiley, New York, 1970; L. D. Quin, J. P. Gratz, and T. P. Barket, *J. Org. Chem.*, 1968, **33**, 1034.

⁸ R. B. Wetzel and G. L. Kenyon, *J. Amer. Chem. Soc.*, 1974, **96**, 5189.

⁹ G. O. Doak, L. D. Freedman, and J. B. Levy, *J. Org. Chem.*, 1964, **29**, 2382; C. H. Chen and K. D. Berlin, *ibid.*, 1971, **36**, 2791; I. G. M. Campbell and J. K. Way, *J. Chem. Soc.*, 1961, 2133; E. R. Lynch, *ibid.*, 1962, 3729; B.P. 933,800 (*Chem. Abs.*, 1964, **60**, 1796).

¹⁰ D. J. Collins, L. E. Rowley, and J. M. Swan, *Austral. J. Chem.*, 1974, **27**, 831.

¹¹ L. E. Rowley and J. M. Swan, *Austral. J. Chem.*, 1974, **27**, 801.

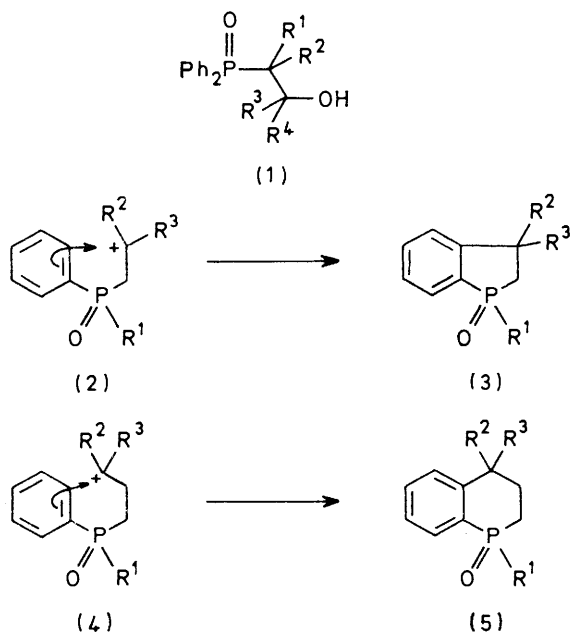
¹² T. H. Chan and L. T. C. Wong, *Canad. J. Chem.*, 1971, **49**, 530; G. Märkl and D. Matthes, *Tetrahedron Letters*, 1974, 4385.

¹³ R. C. Hinton, F. G. Mann, and D. Todd, *J. Chem. Soc.*, 1961, 5454; M. J. Gallagher, E. C. Kirby, and F. G. Mann, *ibid.*, 1963, 4846; Y. Segall, I. Granoth, and A. Kalir, *J.C.S. Chem. Comm.*, 1974, 501. See also H. G. Henning, *Z. Chem.*, 1965, **5**, 417; H. G. de Graaf and E. Bickelhaupt, *Tetrahedron*, 1975, **31**, 1097.

¹⁴ K. D. Berlin and G. B. Butler, *Chem. Rev.*, 1960, **60**, 251.

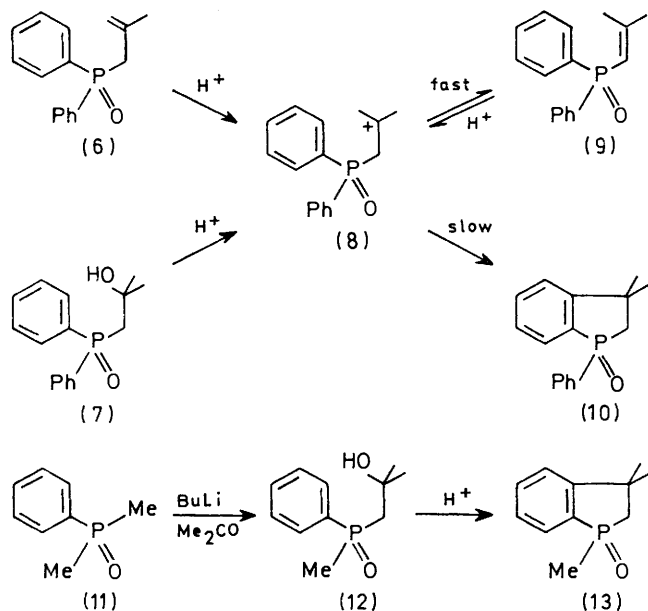
¹⁵ (a) M. El-Deek, G. D. Macdonnell, S. D. Venkataramu, and K. D. Berlin, *J. Org. Chem.*, 1976, **41**, 1403; (b) G. A. Dilbeck, D. L. Morris, and K. D. Berlin, *J. Org. Chem.*, 1975, **40**, 1150; W. R. Purdum, G. A. Dilbeck, and K. D. Berlin, *ibid.*, p. 3763.

on the cation (8), as we had already shown² that it is an intermediate in reactions under milder conditions [e.g. (6) or (7) \rightarrow (9)]. Either the allyl- (6) or the hydroxyalkyl- (7) phosphine oxide did indeed give the



cyclic compound (10) in high yield under these forcing conditions.

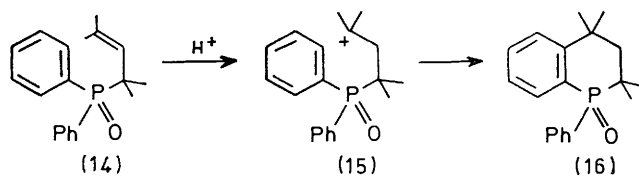
The alcohols [e.g. (12)] are the more accessible starting materials as they can be made from an alkylphosphine



oxide [e.g. (11)] and a ketone.^{1,4,5} Since both (6) and (7) give the vinylphosphine oxide (9) under milder acidic conditions,² we assume that both cyclisations to

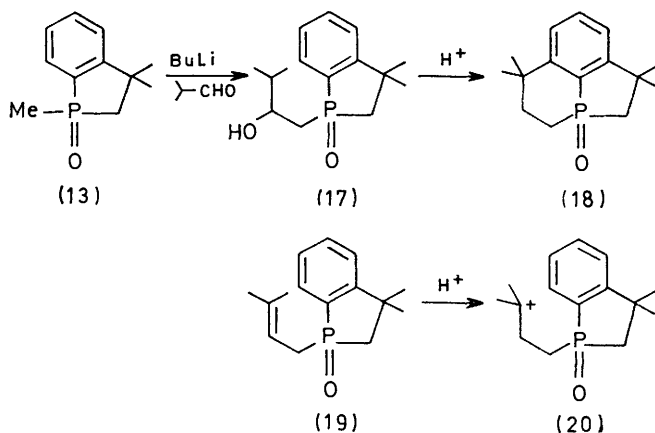
give (10) and (13) in fact occur by reprotonation and cyclisation of a vinylphosphine oxide intermediate.

In cases [e.g. the allylphosphine oxide (14)] where isomerisation in acid to a vinylphosphine oxide cannot occur, protonation might give a cation (15), which could cyclise to the six-member heterocycle (16). Treatment of the allyl compound (14)⁴ with 98% phosphoric acid, again at 170 °C, gave the tetrahydrophosphinolene (16) in 86% yield. In making the six-membered ring it is not necessary to block the α -position to prevent vinylphosphine oxide formation. Dehydration of alcohols such as (17) under mild conditions gives the allyl compound if it is a more highly substituted olefin than the vinyl compound, as there is



virtually no conjugation between the C=C and P=O bonds to encourage the formation of the vinyl compound.⁶

We have used this method to build the bicyclic structure (18). Metallation of the previously cyclised product (13) occurred exclusively on the methyl group, and gave the isobutyraldehyde adduct (17). Treatment of this with phosphoric acid presumably gives the allyl compound (19), protonation then gives the stable tertiary cation (20). The yield is relatively low (48%), presumably because of the strain built into the bicyclic system.⁸

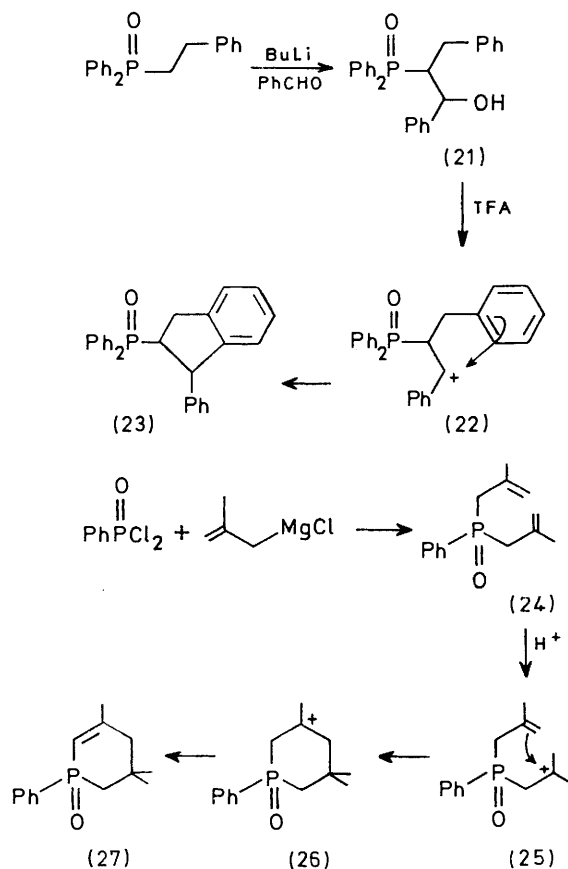


There is no doubt that these cyclisations are occurring reluctantly with a deactivated ring since another benzene ring in the molecule preferentially captures the cation. The benzaldehyde adduct (21) cyclises under much milder conditions [trifluoroacetic acid (TFA) at 45 °C] to form only the indane (23), presumably *via* the cation (22). Even an isolated double bond reacts in preference to the deactivated benzene ring on the

phosphinoyl group since the bismethylallylphosphine oxide (24) gives the tetrahydrophosphorin oxide (27) via the cations (25) and (26). The conditions are again mild (TFA; 70 °C).

Some of these compounds, particularly the hygroscopic dialkylphosphine oxides (13) and (27), are difficult to crystallise, and the structures of many of the new cyclic phosphine oxides were difficult to determine from simple spectra. We therefore carried out n.m.r. shift reagent experiments with $\text{Eu}(\text{dpm})_3$ and measured the induced shift as a function of the molar ratio of

with nitrogen to stabilise the anion. We used the vinylphosphine oxides (28; $\text{R}^1 = \text{R}^2 = \text{H}$),²⁰ (28; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Ph}$),⁶ and (28; $\text{R}^1 = \text{R}^2 = \text{Ph}$), which we prepared from the benzaldehyde adduct (21) by elimination with thionyl chloride in pyridine.



$\text{Eu}(\text{dpm})_3$ to substrate giving an l.i.s. value for each observable set of protons.^{8,16,*} These values are summarised in the Table, and agree well with the proposed structures, if we assume that the europium atom binds to the phosphinoyl oxygen atom.

Attempted Base-catalysed Cycloadditions.—We have attempted to carry out the 1,3-cycloaddition (28) \rightarrow (31) in which the driving force would be the stabilisation of the carbanion (31) by phosphorus and the formation of two new carbon-carbon single bonds. This type of reaction has been investigated by Kauffmann,¹⁹ chiefly

* These relative l.i.s. values are useful only for comparisons with very similar substrates as the binding constants are ignored in their determination.^{17,18}

¹⁶ B. C. Mayo, *Chem. Soc. Rev.*, 1973, 2, 49.

¹⁷ D. R. Kelsey, *J. Amer. Chem. Soc.*, 1972, 94, 1764.

Lanthanide-induced shift values in the n.m.r. spectra of cyclic phosphine oxides

Compound	L.i.s. values for protons ¹⁶			
	α to phosphorus		others	
	cis to O	trans	cis to O	trans
	H ^a 6.3 *	H ^b 4.6 *	H ^c 2.0 *	
	H ^a 5.6	H ^b 4.4	Me ^c 1.7	Me ^d 0.9
	H ^a 5.4	H ^b 2.8	Me ^c 2.2	Me ^d 1.9
	H ^a 7.6 *	H ^b 4.0 *	Not recorded *	
			Me ^a 4.1	Me ^b 3.3
			H ^c 3.4	H ^d 2.9
			Me ^e 1.0	Me ^f 0.8
	H ^a 6.5	H ^b 4.2	Me ^c 1.9	Me ^d 1.3
	H ^b 5.0	H ^e 2.5		H ^f 2.0
			Me ^g 1.2	

* Values from ref. 8. See also D. D. Cuddy, K. Treen, and B. J. Walker, *Tetrahedron Letters*, 1971, 4433.

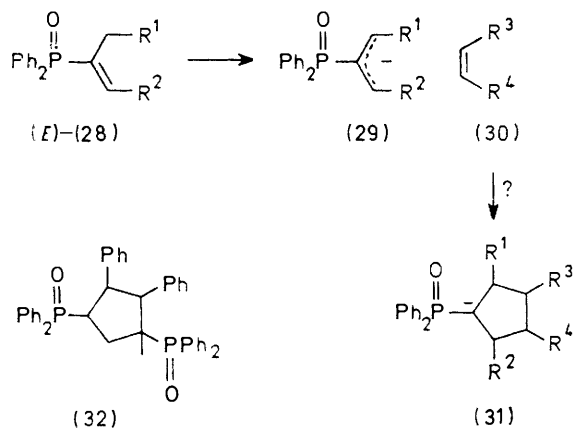
Attempted formation of the unsubstituted anion (29; $\text{R}^1 = \text{R}^2 = \text{H}$) with butyl-lithium or lithium di-isopropylamide led only to polymerisation. We were able to make the phenyl-substituted anions (29; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Ph}$) and (29; $\text{R}^1 = \text{R}^2 = \text{Ph}$) with either base at -78 °C: quenching with D_2O gave deuteriated starting materials. However, no reaction occurred between either anion and various olefins (30) (stilbene, acenaphthylene, acrylonitrile, maleic anhydride). Treatment of (28; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Ph}$) with butyl-lithium at

¹⁸ I. Armitage, G. Dunsmore, L. D. Hall, and A. G. Marshall, *Chem. Comm.*, 1971, 1281.

¹⁹ T. Kauffmann, *Angew. Chem. Internat. Edn.*, 1974, 13, 627.

²⁰ F. J. Welch and H. J. Paxton, *J. Polymer Sci. (A)*, 1965, 3427, 3439.

0 °C gave a crystalline compound, M^+ 636, which we tentatively identify from its n.m.r. spectrum as one of the regioisomers of (32). Though this product would be the result of a 1,3-anionic cycloaddition, we do not feel that the reaction promises to be a useful way to make five-membered rings. We have since been able



to make substituted cyclopentylidiphosphine oxides by other routes.²¹

EXPERIMENTAL

I.r. spectra were taken on Pye-Unicam SP 1000 and Perkin-Elmer 257, n.m.r. spectra on Varian HA 100, Perkin-Elmer R12B, and Hitachi-Perkin-Elmer R24B, and mass spectra on A.E.I. MS9 and MS30 instruments; u.v. spectra were obtained with a Unicam SP 800B machine. T.l.c. was run on Merck silica gel 60 F₂₅₄. Petrol refers to light petroleum (b.p. 60–80 °C). N.m.r. peaks marked with an asterisk belong to diastereoisotopic groups of protons. Solvents were purified by drying and distilling in the usual way. Tetrahydrofuran (THF) was freshly distilled from lithium aluminium hydride. Reactions with butyl-lithium were carried out under nitrogen.

3,3-Dimethyl-1-phenylphosphindoline 1-Oxide (10).—Methylallyldiphenyl phosphine oxide² (6) (3 g) was heated at 170 °C with polyphosphoric acid (60 ml) for 4 h. The mixture was cooled to 100 °C and poured carefully into ice-water (350 ml). The product was extracted with dichloromethane (5 × 50 ml); the extracts were washed with 10% sodium hydrogen carbonate solution (50 ml) and water (50 ml), and dried (MgSO₄). Evaporation and trituration with petrol gave the *phosphindoline oxide* (10) (2.6 g, 87%), m.p. 92–94 °C (from benzene-petrol), R_F (EtOAc) 0.3, ν_{\max} (CHCl₃) 1 440 (P-Ph) and 1 190 cm⁻¹ (P=O), τ (CDCl₃) 2.1–2.7 (9 H, m, Ar), 7.4–7.9 (2 H, ABP system, $J_{AB} = J_{AP} = 16$ Hz, $J_{BP} = 10$ Hz, PCH₂*), and 8.44 and 8.58 (each 3 H, s, CMe₂*) (shift reagent experiments confirmed these assignments; see below), m/e 256 (M^+ , 100%) and 241 ($M - Me$, 88) (Found: C, 75.2; H, 6.9; P, 12.0. C₁₆H₁₇OP requires C, 75.0; H, 7.0; P, 12.2%).

1-Diphenylphosphinoyl-2-methylpropan-2-ol (7).—Diphenylmethylphosphine oxide (2.16 g; made by the action of methylmagnesium iodide on diphenylphosphinoyl chlor-

ide^{5,6,22}) in dry tetrahydrofuran (THF) (50 ml) under nitrogen was treated with *n*-butyl-lithium (7.4 ml; 15% in hexane) at room temperature for 30 min. The orange solution was cooled to –78 °C and a 20% solution of acetone in THF was added until no colour remained. The mixture was allowed to reach room temperature, and aqueous ammonium chloride solution (100 ml) was added. The layers were separated, and the aqueous layer was extracted with dichloromethane (3 × 50 ml). The combined organic layers were dried (MgSO₄) and evaporated. Column chromatography (elution with ethyl acetate) gave the alcohol (7) (2 g, 72%), m.p. 104–106 °C (lit.,² 106–108 °C) (from benzene-petrol), R_F (9:1 EtOAc-MeOH) 0.52; spectra agree with those reported.²

This alcohol (7) (5 g) was converted into the phosphindoline oxide (10) (82%) under the same conditions but with 98% phosphoric acid (100 ml).

1-Methylphenylphosphinoyl-2-methylpropan-2-ol (12).—Dimethylphenylphosphine oxide²³ (11) (1.54 g) in THF (50 ml) was treated with *n*-butyl-lithium (7.4 ml; 15% in hexane) at room temperature; the orange solution was cooled to –78 °C, and a 20% solution of acetone in THF saturated with lithium bromide was added until no colour remained. After 30 min, ammonium chloride solution (100 ml) was added, and the aqueous layer was separated and extracted with chloroform (3 × 50 ml). The combined organic layers were dried (MgSO₄) and evaporated, and the residue was recrystallised from ethyl acetate-petrol to give the alcohol (12) (1.42 g, 67%), m.p. 85–87 °C, R_F 9:1 EtOAc-MeOH) 0.22, ν_{\max} (CHCl₃) 3 380 (OH), 1 442 (P-Ph), and 1 170 cm⁻¹ (P=O), τ (CDCl₃) 2.1–2.6 (5 H, m, PPh), 5.48 (1 H, s, OH), 7.74 (2 H, d, J_{PH} 10 Hz, PCH₂), 8.26 (3 H, d, J_{PH} 13 Hz, PMe), and 8.64 and 8.76 (each 3 H, s, CMe₂*), m/e 212 (M^+ , 25%), 197 ($M - Me$, 61), 154 ($M - acetone$, 64), and 77 (100) (Found: C, 62.0; H, 8.1; P, 14.35. C₁₁H₁₇O₂P requires C, 62.3; H, 8.1; P, 14.6%).

1,3,3-Trimethylphosphindoline 1-Oxide (13).—The alcohol (12) (5 g) was stirred at 170 °C with 98% phosphoric acid for 4 h. The mixture was cooled to below 100 °C and poured into ice-water (400 ml). The solution was extracted with dichloromethane (5 × 50 ml), and the extracts were dried (MgSO₄) and evaporated. Distillation gave the *phosphindoline oxide* (13) (3.7 g, 81%), b.p. 115–120 °C at 0.1 mmHg, which crystallised in the receiver but could not be isolated as crystals because it is very hygroscopic, R_F (9:1 EtOAc-MeOH) 0.2, ν_{\max} 1 439 (PPh) and 1 195 cm⁻¹ (P=O), λ_{\max} (EtOH) 269 (ϵ 840) and 276 nm (794), τ (CDCl₃) 2.1–2.7 (4 H, m, ArH), 7.3–8.0 (2 H, ABP system, $J_{AB} = J_{AP} = 17$, $J_{BP} = 6$ Hz, PCH₂*), 8.18 (3 H, d, $J_{HP} = 13$ Hz, PMe), and 8.48 and 8.58 (each 3 H, s, CMe₂*) (shift reagent experiments confirmed these assignments; see below), m/e 194 (M^+ , 55%) and 179 ($M - Me$, 100). The compound was too hygroscopic for analysis (Found: M^+ , 194.0859. C₁₁H₁₅OP requires M , 194.0860).

3,3-Dimethyl-1-(2-hydroxy-3-methylbutyl)phosphindoline 1-Oxide (17).—The phosphindoline oxide (13) (1 g) was treated in THF (50 ml) with *n*-butyl-lithium (3.8 ml; 15% in hexane) at room temperature. After 30 min, freshly distilled isobutyraldehyde (0.38 ml) in THF (10 ml) was added at –78 °C. The solution was allowed to come to room temperature, and saturated aqueous ammonium chloride (50 ml) was added. The aqueous layer was separated and extracted with chloroform (3 × 50 ml), and the combined

²¹ A. H. Davidson, C. G. Earnshaw, J. I. Grayson, and S. Warren, submitted to *J.C.S. Perkin I*.

²² D. C. Morrison, *J. Amer. Chem. Soc.*, 1950, **72**, 4820.

²³ F. Allen, O. Kennard, L. Nassimbeni, R. Shepherd, and S. Warren, *J.C.S. Perkin II*, 1974, 1530.

organic layers were dried (MgSO_4) and evaporated. Recrystallisation from benzene-petrol gave the *alcohol* (17) as a mixture of diastereoisomers (1.2 g, 86%), R_F (9 : 1 EtOAc-MeOH) 0.37 (major) and 0.47 (minor). This mixture was used in the preparation of the bicyclic compound (18), but a small amount was fractionally recrystallised from benzene-petrol to give the *major diastereoisomer*, m.p. 154–156 °C R_F (9 : 1 EtOAc-MeOH) 0.37, ν_{max} (CHCl_3) 3 310 (OH), 1 438 (PPh), and 1 185 cm^{-1} (P=O), τ (CDCl_3) 2.1–2.8 (4 H, m, ArH), 5.7br (1 H, s, OH), 5.98 [1 H, ddt, J 10, 10, 5, and 2 Hz, $\text{PCH}_2\text{CH}(\text{OH})\text{CH}$], 7.5–8.0 (2 H, ABP system, $J_{AB} = J_{AP} = 17$, J_{BP} 9 Hz, PCH_2^*), 7.9–8.4 [3 H, m, $\text{PCH}_2\text{CH}(\text{OH})\text{CHMe}_2$], 8.51 and 8.62 (each 3 H, s, CMe_2^*), and 9.07 and 9.09 (each 3 H, d, J_{HH} 7 Hz, CHMe_2^*), m/e 266 (M^+ , 10%), 265 (47), 223 ($M - \text{CHMe}_2$, 50), 194 (92), and 180 (100) (Found: C, 67.7; H, 9.0; P, 11.5. $\text{C}_{15}\text{H}_{23}\text{O}_2\text{P}$ requires C, 67.6; H, 8.7; P, 11.6%).

4,5-Dihydro-1,1,5,5-tetramethyl-3H-2a-phospha-acenaphthene 2a-Oxide (18).—The mixture of diastereoisomers of the *alcohol* (17) (1.5 g) was heated at 170 °C in 98% phosphoric acid (40 ml) for 6 h, cooled to below 100 °C, and poured into ice-water (300 ml). The aqueous solution was extracted with chloroform (3 × 100 ml); the extracts were washed with sodium hydrogen carbonate solution (50 ml; 10%) and water (50 ml), dried (MgSO_4), and evaporated. Preparative t.l.c. gave the *phosphine oxide* (18) (0.7 g, 48%), R_F (9 : 1 EtOAc-MeOH) 0.46, m.p. 150–165 °C, ν_{max} (CHCl_3) 1 438 (PPh) and 1 205 cm^{-1} (P=O), τ (CDCl_3) 2.62 (1 H, t, J_{HH} 8 Hz, ArH *para* to P), 2.88 (2 H, dd, J_{HH} 8, J_{PH} 6 Hz, ArH *meta* to P), 7.3–8.3 (6 H, m, CH_2), 8.40 and 8.48 (each 3 H, s, CMe_2^* in five-membered ring), and 8.60 and 8.79 (each 3 H, s, CMe_2^* in six-membered ring), m/e 248 (M^+ , 100%) and 233 ($M - \text{Me}$, 9) (Found: M^+ , 248.1308. $\text{C}_{15}\text{H}_{21}\text{OP}$ requires M , 248.1330).

1,2,3,4-Tetrahydro-2,2,4,4-tetramethyl-1-phenylphosphinoline 1-Oxide (16).—2,4-Dimethyl-4-diphenylphosphinoyl-pent-2-ene⁴ (14) (0.56 g) and 98% phosphoric acid (20 ml) were heated at 170 °C for 4 h. The mixture was cooled to below 100 °C and poured into ice-water (100 ml). The solution was extracted with chloroform (3 × 30 ml) and the extracts were washed with sodium hydrogen carbonate solution (40 ml) and water (40 ml), dried (MgSO_4), and evaporated. The resulting oil slowly crystallised, and was recrystallised from benzene-petrol to give the *phosphine oxide* (16) (0.48 g, 86%), m.p. 112–115 °C, R_F (9 : 1 EtOAc-MeOH) 0.39, ν_{max} (CHCl_3) 1 438 (PPh) and 1 165 cm^{-1} (P=O), τ (CDCl_3) 2.1–2.8 (9 H, m, ArH), 8.14 and 8.17 (2 H, ABP system, J_{AB} 14, J_{AP} 22, J_{BP} 19 Hz, $\text{PC}\cdot\text{CH}_2^*$), 8.52 and 8.59 (each 3 H, s, CMe_2^*), 8.62 (3 H, d, J_{PH} 14 Hz, PCMe^*), and 8.95 (3 H, d, J_{PH} 15 Hz, PCMe^*) (shift reagent experiments confirm these assignments; see below), m/e 298 (M^+ , 77%), 283 ($M - \text{Me}$, 100), 255 (45), and 241 (51) (Found: M^+ , 298.1467. $\text{C}_{19}\text{H}_{23}\text{OP}$ requires M , 298.1485).

(*Phenethyl*)*diphenylphosphine Oxide*.²⁴—This was prepared by the phosphonium salt route.^{6,25} Triphenylphosphine (20 g, 0.08 mol) and phenethyl bromide (29.5 g, 0.16 mol) were heated together at 100 °C for 18 h. The resulting gum was heated under reflux with 30% sodium hydroxide solution (150 ml) for 0.5 h, and the benzene formed was removed by distillation. After cooling, the residue was extracted with chloroform (3 × 50 ml). The organic extracts were

dried (MgSO_4) and evaporated under reduced pressure to give a gummy solid. Recrystallisation from cyclohexane gave the *phosphine oxide* (21.8 g, 90%), m.p. 99–101 °C (lit.,²⁴ 102–103 °C), R_F (9 : 1 EtOAc-MeOH) 0.45, ν_{max} (CHCl_3) 1 440 (P-Ph) and 1 175 cm^{-1} (P=O), τ (CDCl_3) 2.5 (10 H, m, Ph_2PO), 2.8 (5 H, m, Ph), and 6.9–7.6 (4 H, m, AA'BB'P system, $\text{CH}_2\cdot\text{CH}_2\cdot\text{P}$), m/e 306 (M^+ , 5%) and 202 (Ph_2POH , 100).

1,3-Diphenyl-2-diphenylphosphinoylpropan-1-ol (21).—(Phenethyl)diphenylphosphine oxide (2 g, 6.5 mmol) was dissolved in dry THF (60 ml) at 0 °C and the deep red anion was formed with *n*-butyl-lithium (2.9 ml; 2.4M in hexane). After stirring for 0.2 h at 0 °C the anion was quenched with benzaldehyde (0.7 ml, 7 mmol) and the mixture allowed to warm to room temperature. Water (60 ml) was added, the layers were separated, and the aqueous layer was extracted with chloroform (3 × 30 ml). The combined organic extracts were dried (MgSO_4) and evaporated under reduced pressure to give a pale brown solid. Recrystallisation from ethyl acetate-petrol gave the *alcohol* (21) as a mixture of diastereoisomers (1.88 g, 71%), m.p. 187–189 °C, R_F (9 : 1 EtOAc-MeOH) 0.6, ν_{max} (CHCl_3) 3 360 (OH), 1 455 (Ph-P), and 1 170 cm^{-1} (P=O), τ (CDCl_3) 2.5 (10 H, m, Ph_2P), 2.7 (5 H, m, PhC), 3.2 (5 H, m, PhC), 3.9 (0.5 H, dd, J_{PH} 7, J_{HH} 1.5 Hz, P-CH-CH-OH), 4.65 (0.5 H, d, J_{PH} 10 Hz, P-C-CH-OH), 5.06 (1 H, s, OH), and 6.7–7.3 (3 H, m, AA'BP system, $\text{CH}_2\cdot\text{CH}\cdot\text{P}$), m/e 412 (M^+ , 2%), 306 ($M - \text{PhCHO}$, 38), and 202 (Ph_2POH , 100) (Found: C, 78.3; H, 6.2; P, 7.8. $\text{C}_{27}\text{H}_{25}\text{O}_2\text{P}$ requires C, 78.6; H, 6.1; P, 7.5%).

2-Diphenylphosphinoyl-1-phenylindane (23).—The *alcohol* (21) (1 g) was heated with trifluoroacetic acid (15 ml), at 45 °C for 4 h. The solution was poured into water (50 ml), neutralised with sodium hydrogen carbonate solution, and extracted with chloroform (3 × 25 ml). The extracts were dried (MgSO_4) and evaporated under reduced pressure to give a pale yellow oil. Crystallisation from ethyl acetate-petrol gave a single diastereoisomer of the *indane* (23) (0.53 g, 57%), m.p. 227–228 °C, R_F (9 : 1 EtOAc-MeOH) 0.6, ν_{max} (CHCl_3) 1 440 (P-Ph) and 1 180 cm^{-1} (P=O), τ (CDCl_3) 2.6 (10 H, m, Ph_2P), 3.0–3.2 (9 H, m, Ph and indane ring), 5.18 (1 H, dd, J_{HP} 16, J_{HH} 8 Hz, P-CH-CHPh), and 6.6 (3 H, m, ABCP system, P-CH- CH_2), m/e 394 (M^+ , 8%), 202 (Ph_2POH , 100), and 192 ($M - \text{Ph}_2\text{POH}$, 19) (Found: C, 82.05; H, 6.0; P, 7.5. $\text{C}_{27}\text{H}_{23}\text{OP}$ requires C, 82.2; H, 5.9; P, 7.85%).

Dimethylallylphenylphosphine Oxide (24).—Methylallyl-magnesium chloride [from methylallyl chloride (9.8 ml) and magnesium (2 g) in THF (100 ml)] was added slowly to phenylphosphonic dichloride^{23,26} (8.75 g) under nitrogen during 1 h. The solution was stirred for 30 min and saturated aqueous ammonium chloride (100 ml) was added. The layers were separated, the aqueous layer was extracted with dichloromethane (3 × 100 ml), and the organic layers were dried (MgSO_4) and evaporated. Column chromatography of the residue (elution with 3 : 1 dichloromethane-petrol) gave a fraction which was recrystallised from petrol to give the *phosphine oxide* (24) (5.7 g, 54%), m.p. 68–70 °C (lit.,²⁷ 67–69 °C), R_F (EtOAc) 0.4, ν_{max} (CHCl_3) 1 635 (C=C), 1 440 (PPh), and 1 190 (P=O) cm^{-1} , τ (CDCl_3) 2.2–2.6 (5 H, m, PhP), 5.13 (1 H, m, C=CH), 5.30 (1 H, d, J_{HH} 4 Hz, with further fine splitting, C=CH), 7.12 and 7.28 (4 H, ABP system, $J_{AB} = J_{AP} = 15$, J_{BP} 14 Hz, PCH_2), and 8.24 (6 H,

²⁴ A. M. Aguiar and D. Daigle, *J. Org. Chem.*, 1965, **30**, 2826.

²⁵ K. Sasse in Houben-Weyl, 'Methoden der Organischen Chemie,' Thieme, Stuttgart, 1963, vol. 12/1, pp. 144–150.

²⁶ A. Michaelis, *Annalen*, 1876, **181**, 265.

²⁷ K. D. Berlin and G. B. Butler, *J. Amer. Chem. Soc.*, 1960, **82**, 2712.

s, with fine splitting, Me), *m/e* 234 (M^+ , 100%), 219 ($M - \text{Me}$, 64), 179 ($M - \text{methylallyl}$, 100), and 140 (61).

1,2,3,4-Tetrahydro-3,3,5-trimethyl-1-phenylphosphorin 1-Oxide (27).—Dimethylallylphosphine oxide (24) (1 g) was heated with 98% phosphoric acid at 170 °C for 4 h. The product was cooled to below 100 °C and poured into ice-water (100 ml). The aqueous solution was extracted with chloroform (5 × 25 ml) and the extracts were washed with sodium hydrogen carbonate (5%, 20 ml) and water (20 ml), dried (MgSO_4), and evaporated. Recrystallisation from light petroleum (b.p. 80–100 °C) gave the tetrahydrophosphorin (27) (0.73 g, 73%), m.p. 84–86 °C, R_F (EtOAc) 0.27, ν_{max} (CHCl_3) 1 630 (C=C), 1 442 (PhP), and 1 165 cm^{-1} (P=O), τ (CDCl_3) 2.2–2.6 (5 H, m, PPh), 4.08 (1 H, d, J_{PH} 14 Hz, with further fine splitting, PCH=C), 7.5–8.4 (4 H, m, CH_2), 8.0 (3 H, s, MeC=C), 8.67 (3 H, s, CMe*), and 8.94 (3 H, d, J_{PH} 2 Hz, CMe*), shift reagent experiments confirmed these assignments (see below), *m/e* 234 (M^+ , 100%) 219 ($M - \text{Me}$, 61), 179 (75), and 150 (43) (the compound was too hygroscopic for a good analysis) (Found: M^+ , 234.1169. $\text{C}_{14}\text{H}_{19}\text{OP}$ requires M , 234.1173). The tetrahydrophosphorin was also made by treatment of dimethylallylphenyl phosphine oxide with (a) cold concentrated sulphuric acid for a few minutes, or (b) TFA at 70 °C for 4 h.

Experiments with the N.m.r. Shift Reagent $\text{Eu}(\text{dpm})_3$.—In each case, n.m.r. spectra were run on a Varian HA100 machine with trisdipivaloylmethanatoeuropium(III) [$\text{Eu}(\text{dpm})_3$] in CDCl_3 solution. The shift reagent was added so that the molar ratio of shift reagent to substrate increased from zero to 1.0 in steps of 0.2. The observed chemical shift of each proton or group of protons was plotted against this ratio, giving good straight lines in all cases except for some curvature near shift reagent–substrate ratios of 1.0 for compound (16). The slopes of these lines (the i.s. values^{17,18}) are given in the Table.

(E)-2-Diphenylphosphinoyl-1,3-diphenylpropene (28; $R^1 = R^2 = \text{Ph}$).—The alcohol (21) (1.5 g, 3.6 mmol) was heated under reflux with thionyl chloride (0.75 ml, 0.01 mol) in dry pyridine (20 ml) for 0.2 h. The red solution was neutralised with dilute hydrochloric acid and the product extracted with chloroform (3 × 30 ml). The extracts were dried (MgSO_4) and evaporated under reduced pressure to give a yellow oil. Column chromatography (9 : 1 CHCl_3 –MeOH as eluant) gave the olefin (E) - (28; $R^1 = R^2 = \text{Ph}$) * (1.1 g, 77%) as a pale yellow gum, R_F (9 : 1 EtOAc–MeOH) 0.6, ν_{max} 1 600, 1 490 (Ph), 1 435 (P–Ph), and 1 170 cm^{-1} (P=O), τ (CDCl_3) 2.4–2.8 (16 H, m, Ph_2P , Ph, and vinyl H), 3.01 (5 H, s, Ph), and 6.01 (2 H, d, J_{HP} 18 Hz, P·C· CH_2), *m/e* 394 (M^+ , 100%), 303 ($M - \text{PhCH}_2$, 10), and 202 (Ph_2POH , 97) (the compound was too hygroscopic for a good analysis) (Found: M^+ , 394.1472. $\text{C}_{27}\text{H}_{23}\text{OP}$ requires 394.1485).

Reaction of n-Butyl-lithium with Isopropenyldiphenylphosphine Oxide.—The phosphine oxide (28; $R^1 = R^2 = \text{H}$)²⁰ (65 mg) in dry THF (7 ml) was treated with n-butyl-lithium (0.17 ml; 1.5M in hexane) at 20 °C. The deep red solution was quenched after 0.2 h with deuterium oxide (0.05 ml) and evaporated under reduced pressure. The residue was washed with chloroform and the washings were evaporated under reduced pressure to give a pale yellow solid, a polymer of unknown structure, R_F (EtOAc) 0.0.

* Assumed to have the E-configuration by comparison with (E) - (28; $R^1 = \text{Me}$, $R^2 = \text{Ph}$) and (E) - (28; $R^1 = \text{H}$, $R^2 = \text{Ph}$).

A similar polymer was the only product when the anion was formed at –78 °C with n-butyl-lithium and then quenched with deuterium oxide, or when the anion was formed with lithium di-isopropylamide at 0 °C in the presence of *trans*-stilbene and then quenched with water.

Reaction of n-Butyl-lithium with 2-Diphenylphosphinoyl-1-phenylpropene.—The olefin (E) - (28; $R^1 = \text{H}$, $R^2 = \text{Ph}$)⁶ (59 mg, 0.18 mmol) was treated with n-butyl-lithium (0.08 ml; 1.8M in hexane) at –78 °C in dry THF (13 ml). A deep red-yellow anion was formed which was quenched after 0.2 h with deuterium oxide (0.1 ml) to give a pale yellow solution. The solution was evaporated under reduced pressure and the residue was purified by preparative t.l.c. (9 : 1 EtOAc–MeOH) to give the [^3H]propene as a pale yellow oil (30 mg, 51% recovery), R_F (9 : 1 EtOAc–MeOH) 0.55, *m/e* 319 ($\text{C}_{21}\text{H}_{18}\text{DOP}$, 60%), 318 ($\text{C}_{21}\text{H}_{19}\text{OP}$, 37), and 202 (Ph_2POH , 100); n.m.r. showed partial deuteration of the methyl group. The olefin was also recovered when the anion was formed in the presence of *trans*-stilbene at –78 °C, or when the anion was formed with lithium di-isopropylamide at –78 °C, and subsequently quenched with water. When the olefin (E) - (28; $R^1 = \text{H}$, $R^2 = \text{Ph}$) (108 mg) was treated with n-butyl-lithium (0.25 ml; 2.4M in hexane) in dry THF (20 ml) at 0 °C, a deep red colour formed. After 0.2 h, water (50 ml) was added, and the product extracted with chloroform (3 × 25 ml). The extracts were dried (MgSO_4) and evaporated under reduced pressure to give a white solid. Preparative t.l.c. (9 : 1 EtOAc–MeOH) gave as the major product, a crystalline solid (62 mg), m.p. 325–330 °C, tentatively identified as one of the regioisomers of structure (32), R_F (9 : 1 EtOAc–MeOH) 0.3, τ (CDCl_3) 2.5 (20 H, m, Ph_2P), 3.04 (5 H, s, Ph), 3.37 (5 H, s, Ph), 5.5 (1 H, m, CHPh), 5.88 (1 H, q, $J_{\text{HH}} = J_{\text{HP}} = 11$ Hz, P·C· $\text{CH}\cdot\text{CH}_2$), 6.65 (1 H, m, PCH), 7.6br (2 H, m), and 8.54 (3 H, d, J_{HP} 16 Hz, MeC·P), *m/e* 636 (M^+ , 3%), 559 ($M - \text{Ph}$, 6), 435 ($M - \text{Ph}_2\text{PO}$, 38), 318 ($\text{Ph}_2\text{PO}\cdot\text{CMe}\cdot\text{CHPh}$, 22), 233 (98), 201 (Ph_2PO , 99), and 77 (Ph, 100).

Reaction of n-Butyl-lithium with 2-Diphenylphosphinoyl-1,3-diphenylpropene.—The olefin (E) - (28; $R^1 = R^2 = \text{Ph}$) (87 mg, 0.22 mmol) was treated with n-butyl-lithium (0.1 ml, 2.4M in hexane) at –78 °C in dry THF (20 ml). The intensely purple-red anion was quenched after 0.2 h with deuterium oxide (0.1 ml). The solvent was evaporated off and the pale yellow residue was dissolved in water (20 ml) and extracted with dichloromethane (2 × 10 ml). The extracts were dried (MgSO_4) and evaporated under reduced pressure to give a pale yellow oil. Preparative t.l.c. (9 : 1 EtOAc–MeOH) gave 2-diphenylphosphinoyl-1,3-diphenyl-[^2H]propene as the only identifiable product (69 mg, 80%), R_F (9 : 1 EtOAc–MeOH) 0.6, τ (CDCl_3) 2.4–2.8 (16 H, m, Ph_2P , Ph, and vinyl H), 3.01 (5 H, s, Ph), and 6.01 (1 H, d, J_{HP} 18 Hz, P·C· CHDPh), *m/e* 395 (M^+ 74%), 303 ($M - \text{Ph}\cdot\text{CHD}$, 10), and 202 (Ph_2POH , 100). Formation of the anion with lithium di-isopropylamide at –78 °C and subsequent quenching with deuterium oxide also gave the deuterated olefin in 91% yield.

Attempted 1,3-Anionic Cycloaddition of the Anion (29; $R^1 = R^2 = \text{Ph}$).—The anion was formed by treating the olefin (E) - (28; $R^1 = R^2 = \text{Ph}$) (104 mg, 0.26 mmol) with n-butyl-lithium (0.12 ml; 2.4M in hexane) in dry THF (20 ml) at –78 °C. After 0.2 h, a solution of *trans*-stilbene (60 mg, 0.33 mmol) in THF was added, and the solution stirred for 48 h at room temperature without colour change. Quenching with water (1 ml) and evaporation gave a pale

brown solid, which was purified by preparative t.l.c. (9 : 1 EtOAc-MeOH). The upper band (R_F 0.8) was identified as *trans*-stilbene, which was totally recovered. The lower band (R_F 0.6) (87 mg, 80% recovery) was identified as the olefin (28; $R^1 = R^2 = Ph$). When lithium di-isopropylamide was used as base, and *trans*-stilbene as the anionophile, the same result was obtained. Similarly, acenaph-

thylene was recovered along with unchanged olefin under similar conditions. With maleic anhydride or acrylonitrile as anionophile, the anionophile was decomposed by the anion without cycloaddition and the other starting material was recovered unchanged (the anion catalysed the polymerisation of acrylonitrile).

[6/1020 Received, 27th May, 1976]
