

The Chemistry of Vinylphosphine Chalcogenides. Part 2.¹ Some Nucleophilic and Electrophilic Additions

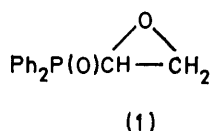
By S. Roderick Postle, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW
Gordon H. Whitham,* The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY

Diphenylvinylphosphine oxide (3) is inert to peroxy-acids, although it can be converted with *N*-bromoacetamide into 1-bromo-2-hydroxyethylidiphenylphosphine oxide (8). The reactions of the latter compound with bases are described. The phosphine oxide (3) with methanolic alkaline hydrogen peroxide gives a stable dialkyl peroxide (11). With aqueous alkaline methanol, the phosphine oxide (3) is converted into bis-1,2-(diphenylphosphinoyl)ethane (7), a compound also isolated from the reaction of 2-hydroxyethylidiphenylphosphine oxide (2) with butyl-lithium and bromine.

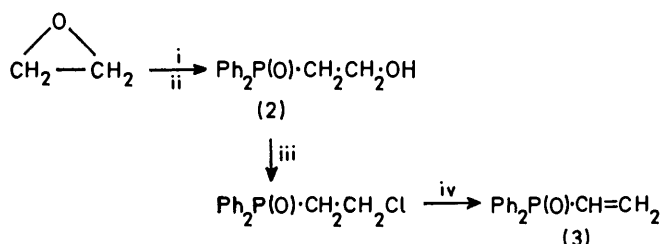
Diphenylvinylphosphine sulphide (5) does not react with hydroxide or hydroperoxide anion, but is converted in aqueous alkaline methanol into 2-methoxyethylidiphenylphosphine sulphide (13). The phosphine sulphide (5) also undergoes Michael-type addition of *t*-butoxide anion.

IN common with other electron-withdrawing groups, diphenylphosphinoyl and diphenylthiophosphinoyl groups activate an olefinic residue to nucleophilic (Michael-type) additions with simple nucleophilic species.^{2,3} As expected from such behaviour, both diphenylphosphinoyl and diphenylthiophosphinoyl groups display large σ^- values.⁴ A Hammett treatment has indicated that the diphenylphosphinoyl group is approximately equivalent to the ethoxycarbonyl group in mesomeric electron-withdrawing power.⁵

A study was undertaken of the reactions of peroxidic nucleophiles with diphenylvinylphosphine oxide (3) and diphenylvinylphosphine sulphide (5). One goal of this investigation was the synthesis of the potential two-carbon synthon, 2-diphenylphosphinoyloxiran (1). The reactions of the phosphine chalcogenides (3) and (5) with some electrophiles were also examined.



Syntheses.—The phosphine oxide (3) was prepared in an overall yield of nearly 50% *via* 2-hydroxyethylidiphenylphosphine oxide (2) (Scheme 1). This route



SCHEME 1 Reagents: i, LiPPh_2 -THF; ii, H_2O_2 -AcOH; iii, PCl_5 - C_6H_6 , reflux; iv, NET_3 - C_6H_6 , reflux

could not be extended to the preparation of the phosphine sulphide (5): the corresponding 2-chloroethyl-

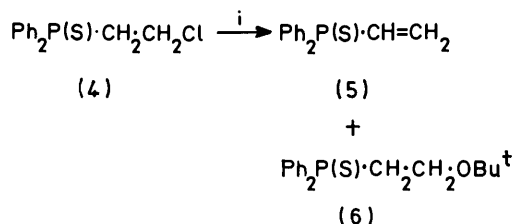
¹ Part 1, B. F. G. Johnson, J. Lewis, and S. R. Postle, *J. Organometallic Chem.*, 1976, **121**, C7.

² M. I. Kabachnik, T. Y. Medved, Y. M. Polikarpov, and K. S. Yudena, *Izvest. Akad., Nauk S.S.S.R., Otdel. khim. Nauk*, 1962, **9**, 1589.

³ D. Collins, L. Rowley, and J. Swan, *Austral. J. Chem.*, 1974, **27**, 841.

diphenylphosphine sulphide (4)⁷ was unchanged after treatment with triethylamine in benzene or toluene at reflux.

With potassium *t*-butoxide, dehydrohalogenation of the phosphine sulphide (4) to the phosphine sulphide (5) was accompanied by formation of 2-*t*-butoxyethylidiphenylphosphine sulphide (6), the two products being isolated in approximately equimolar amounts (Scheme 2).



SCHEME 2 Reagents: i, KO^-Bu^t -THF, reflux

Treatment of the phosphine sulphide (5) with an equimolar amount of potassium *t*-butoxide in refluxing tetrahydrofuran (THF) led to the isolation of the phosphine sulphides (5) and (6) in the ratio *ca.* 3:5. The phosphine sulphide (5) was prepared by the method of Collins *et al.*³

Reactions.—In contrast to diethyl vinylphosphonate,⁸ the phosphine oxide (3) was recovered quantitatively after treatment with peroxy-acids (for example 3-chloroperbenzoic acid in dichloroethane at reflux or trifluoroacetic acid in dichloromethane at reflux). The phosphine sulphide (5) reacted vigorously with 3-chloroperbenzoic acid in chloroform at 20 °C to yield the phosphine oxide (3) in high yield: no phosphinoyloxiran (1) was detected.

Attention was then turned to the synthesis of the oxiran (1) *via* (1-bromo-2-hydroxyethyl)diphenylphosphine oxide (8). It is known that treatment of 2-hydroxyethylidiphenylphosphine oxide (2) with 2 mol. equiv. of *n*-butyl-lithium in THF at -63 °C, followed by

⁴ E. N. T. Tsvetkov, D. O. Lobanov, M. M. Matchamatkhanov, and M. I. Kabachnik, *Tetrahedron*, 1969, **25**, 5623, and references therein.

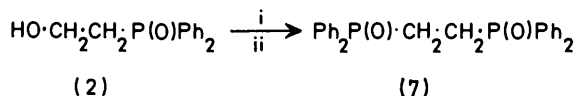
⁵ J. J. Monagle, J. V. Mengershauser, and D. A. Jones, *J. Org. Chem.*, 1967, **32**, 2477.

⁶ A. J. Bridges and G. H. Whitham, unpublished work.

⁷ S. R. Postle, *Phosphorus and Sulphur*, in the press.

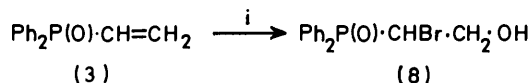
⁸ K. Hunger, *Chem. Ber.*, 1968, **101**, 3530.

quenching with iodomethane leads to (2-hydroxy-1-methylethyl)diphenylphosphine oxide (*ca.* 40%).⁶ Treatment of the phosphine oxide (2) with 2 mol. equiv. of *n*-butyl-lithium followed by quenching of the dianion with bromine did not, however, lead to the phosphine oxide (8). The only identified product, isolated in 19% yield, was 1,2-bis(diphenylphosphinoyl)ethane (7) (Scheme 3).



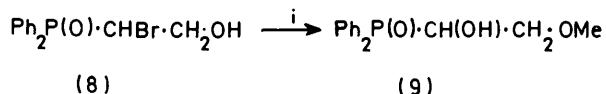
SCHEME 3 Reagents: i, BuⁿLi-THF, -63 °C; ii, Br₂

The phosphine oxide (3) was unchanged after treatment with either *N*-bromoacetamide or *N*-bromosuccinimide in a number of different solvents at 20 °C. It was also unaffected by *N*-bromoacetamide in water at 80 °C, conditions under which the similar phosphine oxide, 3-methyl-1-phenyl-Δ²-phospholen 1-oxide, is converted into the corresponding bromohydrin.⁹ The phosphine oxide (8) was prepared by treatment of the phosphine oxide (3) with these reagents at reflux, in 58% yield (Scheme 4). Assignment of the orientation of addition was based on the n.m.r. spectrum (see Experimental section).



SCHEME 4 Reagents: i, AcNHBr-H₂O, reflux

Attempts were made to convert the phosphine oxide (8) into the oxiran (1). The phosphine oxide (8) was unchanged after treatment with potassium acetate in refluxing acetone,⁹ and was also unaffected by aqueous potassium hydroxide at reflux. Treatment of the phosphine oxide (8) with methanolic sodium methoxide under reflux gave 1-hydroxy-2-methoxyethyldiphenylphosphine oxide (9) in 59% yield. The orientation of the hydroxy- and methoxy-groups was deduced from the n.m.r. spectrum (see Experimental section). It is suggested that the phosphine oxide (1) is an intermediate in the formation of (9) from (8) (Scheme 5). If this is the case, then epoxide formation is favoured over elimination *via* a Horner reaction¹⁰ under these conditions.



SCHEME 5 Reagents: i, NaOMe-MeOH, reflux

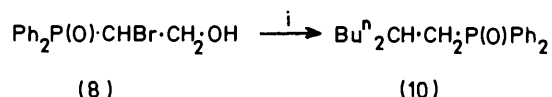
Treatment of the phosphine oxide (8) with sodium hydride-THF or potassium *t*-butoxide-THF, at reflux

⁹ D. G. Smith and D. J. H. Smith, *Tetrahedron Letters*, 1973, 1249.

¹⁰ A. J. Bridges and G. H. Whitham, *J.C.S. Chem. Comm.*, 1974, 142.

temperature, afforded diphenylphosphinic acid as the only phosphorus-containing product. Treatment of the phosphine oxide (8) with 1 equiv. of *n*-butyl-lithium in THF resulted in 5-(diphenylphosphinoylmethyl)nonane (10) (Scheme 6). It is suggested that this compound is formed *via* two elimination-addition sequences.

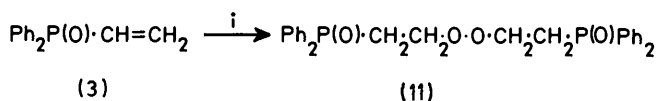
Attempts to prepare the phosphine oxide (1) *via* the nucleophilic addition of a peroxide nucleophile to the phosphine oxide (3) were unsuccessful. The phosphine oxide (3) was unchanged after treatment with *t*-butyl hydroperoxide in the presence of basic catalysts,¹¹ conditions under which the epoxidation of diethyl vinylphosphonate and similar vinylphosphonates is successful.¹² The phosphine oxide (3) was also unaffected by



SCHEME 6 Reagents: i, BuⁿLi-THF, reflux

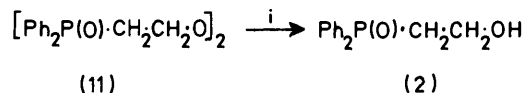
sodium 3-chloroperbenzoate. Treatment of (3) with aqueous methanolic sodium hydroxide and hydrogen peroxide at 20 °C led to bis-(2-diphenylphosphinoyl-ethyl) peroxide (11) in 79% yield (Scheme 7).

The peroxide (11) is remarkably stable, melting without decomposition at 267–268 °C. It gave analytical data compatible with a dihydrate. Its identification is based on chemical and spectroscopic evidence. It instantly liberates iodine from potassium iodide solution, and is cleanly reduced by lithium aluminium hydride in ether to give the phosphine oxide (2) in 84% yield of



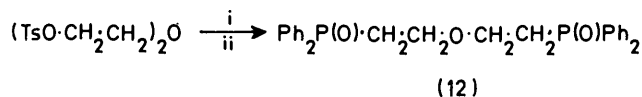
SCHEME 7 Reagents: i, NaOH-aq.MeOH-H₂O₂

isolated product (Scheme 8). Similar stable peroxides have recently been obtained by base-catalysed addition of hydrogen peroxide to vinyl sulphones.¹³



SCHEME 8 Reagents: i, LiAlH₄-Et₂O, 20 °C

In Tables 1 and 2 the peroxide (11) is compared with phosphine oxides (2) and (12) [for the preparation of the phosphine oxide (12) see Scheme 9].



SCHEME 9 Reagents: i, LiPPh₂-THF; ii, AcOH-H₂O₂

¹¹ G. B. Payne, *J. Org. Chem.*, 1960, **25**, 275; N. C. Yang and R. A. Finnegan, *J. Amer. Chem. Soc.*, 1958, **80**, 5845.

¹² C. E. Griffin and S. K. Kundu, *J. Org. Chem.*, 1969, **34**, 1532.

¹³ H. Kropf, M. Ball, and K. Hofmann, *Annalen*, 1976, 2316.

Treatment of the peroxide (11) with potassium *t*-butoxide–dimethyl sulphoxide at 20 °C gave the phosphine oxide (2) and an unidentified product, a phosphine oxide having no absorption in the ^1H n.m.r. spectrum above τ 3.5, but not the phosphine oxide (3). It was not further examined.

Treatment of the phosphine oxide (3) with dilute aqueous methanolic sodium hydroxide gave the phosphine oxide (7) in 96% yield (Scheme 10). A possible mechanism for this reaction involving the phosphine oxide (2) as an intermediate which undergoes fragmentation to oxiran and diphenylphosphinite was excluded

TABLE 1

^{13}C N.m.r. data for the aliphatic C(1) and C(2) in the phosphine oxides (2), (11), and (12) ^{a,b}

	$\delta_{\text{C}(1)}$	$J_{\text{P,C}(1)}$	$\delta_{\text{C}(2)}$	$J_{\text{P,C}(2)}$
$\text{Ph}_2\text{P}(\text{O})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ (2)	32.9	69.7	56.0	0
$[\text{Ph}_2\text{P}(\text{O})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}]_2$ (11)	29.1	70.7	69.7	0
$[\text{Ph}_2\text{P}(\text{O})\cdot\text{CH}_2\cdot\text{CH}_2]_2\text{O}$ (12)	30.5	70.8	64.1	0

^a C(1) is α to phosphorus. ^b δ Values in p.p.m. downfield from internal Me_4Si ; P, C-coupling constants in Hz.

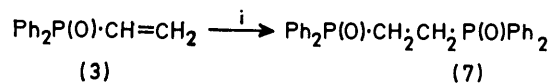
TABLE 2

^1H N.m.r. data (aliphatic protons only) for the phosphine oxides (2), (11), and (12) ^{a,b}

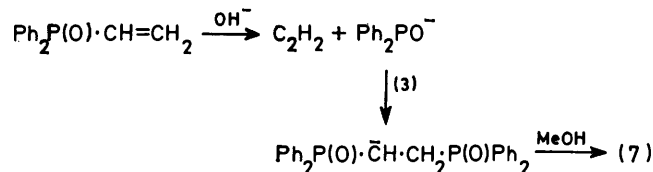
	$\tau_{\text{H}(1)}$	$J_{\text{P,H}(1)}$	$\tau_{\text{H}(2)}$	$J_{\text{P,H}(2)}$
$\text{Ph}_2\text{P}(\text{O})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ (2)	7.40	10	6.02	15
$[\text{Ph}_2\text{P}(\text{O})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}]_2$ (11)	7.27	14	5.75	12
$[\text{Ph}_2\text{P}(\text{O})\cdot\text{CH}_2\cdot\text{CH}_2]_2\text{O}$ (12)	7.54	13	6.33	12

^a H(1) is α to phosphorus. ^b Coupling constants in Hz, to the nearest integer; $J_{1,2}$ 8 Hz in each case.

since (2) was stable to the reaction conditions. It may be that diphenylphosphinite is formed by elimination from (3) and thus undergoes β -addition to more (3) (Scheme 11).



SCHEME 10 Reagents: *i*, NaOH–aq.MeOH, 20 °C

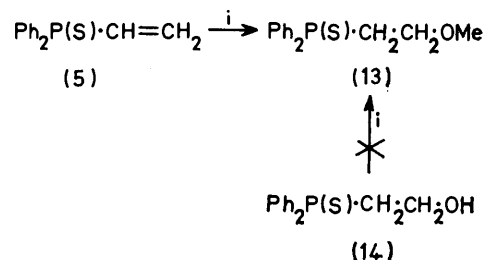


SCHEME 11

Treatment of the phosphine sulphide (5) with aqueous methanolic sodium hydroxide under reflux gave 2-methoxyethylidiphenylphosphine sulphide (13) in 93% yield (Scheme 12). 2-Hydroxyethylidiphenylphosphine sulphide (14) is stable to the reaction conditions.

Treatment of the phosphine sulphide (5) with aqueous

alkaline methanolic hydrogen peroxide under the same conditions as for the conversion of the phosphine oxide



SCHEME 12 Reagents: *i*, NaOH–aq.MeOH, reflux

(3) into the peroxide (11) gave only starting material and the phosphine sulphide (13) in *ca.* 15% yield. No phosphine oxides [(3) or (1)] were detected. The phosphine sulphide (5) was unchanged after treatment with potassium hydroxide–THF at reflux, or potassium hydroxide–dimethyl sulphoxide at 20 °C [if any phosphine sulphide (14) had been formed, it might have been expected to decompose to methyldiphenylphosphine sulphide and formaldehyde under the reaction conditions,¹⁴ but neither of these compounds was detected].

EXPERIMENTAL

I.r. spectra were recorded for solutions in CHCl_3 solution with a Perkin-Elmer 257 spectrophotometer; frequencies are given in cm^{-1} . ^1H N.m.r. spectra were recorded with a Perkin-Elmer R14 (100 MHz), a Perkin-Elmer R32 (90 MHz), or a Varian HA-100 (100 MHz) instrument, for solutions in $^2\text{HCCl}_3$. ^{13}C N.m.r. spectra were recorded with Bruker WH90 (22.63 MHz) and Varian XL-100-15 (25.2 MHz) instruments, for solutions in $^2\text{HCCl}_3$ solution. Chemical shifts are given in p.p.m. (δ_{C}) downfield from internal tetramethylsilane and coupling constants in Hz. Mass spectra were obtained with a Varian CH7 instrument (ionising voltage 70 eV) by direct insertion. Tetrahydrofuran was distilled from sodiobenzophenone prior to use. The drying agent used for organic solutions was anhydrous sodium sulphate.

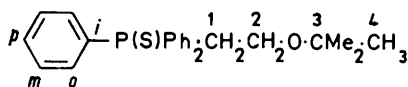
Diphenylvinylphosphine Oxide (3).—2-Chloroethylidiphenylphosphine oxide¹⁵ (59.5 g, 2.25×10^{-1} mol) was refluxed with triethylamine (38 ml, 2.8×10^{-1} mol) in benzene (220 ml) for 1.25 h. Filtration of the cooled solution and evaporation of the filtrate gave an oil (35.4 g), which deposited crystals. Recrystallisation from ethyl acetate, with re-working of the mother liquors, gave diphenylvinylphosphine oxide (33.8 g, 66%) as a powder, m.p. 117° (lit.,³ 117°).

*Reaction of Potassium *t*-Butoxide with Diphenylvinylphosphine Sulphide* (5).—Potassium *t*-butoxide (0.112 g, 10^{-3} mol) and diphenylvinylphosphine sulphide³ (0.244 g, 10^{-3} mol) were heated under reflux in THF (2 ml) for 2.5 h. The mixture was quenched with water (5 ml) and extracted with dichloromethane (2×5 ml). The extracts were dried and evaporated to yield a brown oil. Preparative layer chromatography (silica; ethyl acetate) gave starting material (61 mg) and an oil considered to be 2-*t*-butoxyethylidiphenylphosphine sulphide (135 mg), τ 2.1–2.4

¹⁴ S. R. Postle and G. H. Whitham, unpublished work.

¹⁵ J. Gloede, *J. prakt. Chem.*, 1972, **314**, 281.

(4 H), 2.5—2.7 (6 H), 6.25 (2 H, dt, $J_{P,H}$ 13, $J_{H,H}$ 7), 7.28 (2 H, dt, $J_{P,H}$ 11), 8.95 (9 H); δ_C 27.8 [$J_{P,C(4)}$ 0], 34.3 [$J_{P,C(1)}$ 56.4], 56.4 [$J_{P,C(2)}$ 0], 73.8 [$J_{P,C(3)}$ 0], 128.8 [$J_{P,C(m)}$ 11.8], 131.8 [$J_{P,C(p)}$ 3.3], 131.3 [$J_{P,C(o)}$ 10.3], and 133.4 [$J_{P,C(i)}$ 78.8].



Reaction of Butyl-lithium and Bromine with 2-Hydroxyethylidiphenylphosphine Oxide (2).—2-Hydroxyethylidiphenylphosphine oxide^{6,15} (2.46 g) was stirred at -63°C under nitrogen in THF, and to the mixture was added, over 20 min, butyl-lithium (2.0M; 10 ml, 2×10^{-2} mol). The mixture was stirred a further 40 min to give a deep red solution, then bromine (0.76 ml, 1.5×10^{-2} mol) was added, and the mixture was slowly warmed to 20°C and kept there for 20 h. Saturated aqueous sodium sulphite (25 ml) was added, and the ethereal layer separated. The aqueous portion was extracted with dichloromethane (2×20 ml), and the combined organic portions were washed with brine, dried, and evaporated to yield an orange oil (2.48 g). This was revealed by t.l.c. (alumina; ethyl acetate) to be a complex mixture; it was covered with ethyl acetate and set aside. Crystals (0.41 g) were deposited which were recrystallised twice from ethyl acetate to give 1,2-bis(diphenylphosphinoyl)ethane as needles, m.p. 268—269° (lit.,¹⁶ 268—270°), M^+ 430, τ 2.15—2.60 (10 H) and 7.48 (2 H, m).

1-Bromo-2-hydroxyethylidiphenylphosphine Oxide (8).—Diphenylvinylphosphine oxide (3.8 g, 1.67×10^{-2} mol) and *N*-bromoacetamide (2.32 g, 1.67×10^{-2} mol) were heated under reflux in water (40 ml) for 24 h. The mixture was cooled and extracted with dichloromethane (3×20 ml). The extracts were dried and evaporated to yield a clear glass (4.8 g). Recrystallisation from ethyl acetate gave 1-bromo-2-hydroxyethylidiphenylphosphine oxide (3.16 g, 58%), m.p. 130—131° (Found: C, 51.7; H, 4.35. $C_{14}H_{14}BrO_2P$ requires C, 51.5; H, 4.15%), ν 3 305, 1 470, 1 435, 1 370, and 1 175; τ 2.10—2.30 (4 H), 2.56 (6 H), 5.47 (1 H, dt, $J_{P,H}$ 8, $J_{H,H}$ 6), 5.80 (1 H, exchanged with $^2\text{H}_2\text{O}$), and 6.00 (2 H, dd, $J_{P,H}$ 11).

1-Hydroxy-2-methoxyethylidiphenylphosphine Oxide (9).—1-Bromo-2-hydroxyethylidiphenylphosphine oxide (1.37 g, 4.2×10^{-3} mol) was heated under reflux overnight with freshly prepared sodium methoxide [from sodium chips (97 mg)] in methanol (5 ml). The mixture was evaporated to dryness, treated with water (20 ml), and extracted with dichloromethane (3×10 ml). The extracts were washed with brine, dried, and evaporated to yield a glass (0.91 g). Chromatography (silica; methanol) gave 1-hydroxy-2-methoxyethylidiphenylphosphine oxide as an hygroscopic oil (0.72 g, 59%) (Found: C, 64.9; H, 6.0. $C_{15}H_{17}O_3P$ requires C, 65.2; H, 6.2%); ν 3 330, 1 470, 1 435, 1 178, 1 120, and 1 105; τ 2.0—2.15 (4 H), 2.5—2.6 (6 H), 4.84 (1 H, exchanged with $^2\text{H}_2\text{O}$), 5.31 (1 H, m; sharpens on addition of $^2\text{H}_2\text{O}$), 6.29 (2 H, m), and 6.79 (3 H, m).

5-(Diphenylphosphinoylmethyl)nonane (10).—1-Bromo-2-hydroxyethylidiphenylphosphine oxide (0.163 g, 5×10^{-4} mol) in THF (2 ml) under nitrogen was treated with butyl-lithium in hexane (1.5M; 0.33 ml); the mixture was then brought to reflux and heated for 5 h. The cooled mixture was treated with water (2 ml) and extracted with dichloromethane (3×2 ml). The extracts were washed with

brine, dried, and evaporated to give a brown oil (0.154 g). Preparative layer chromatography (alumina; methanol) gave 5-(diphenylphosphinoylmethyl)nonane (0.083 g, 49%) as an oil (Found: C, 77.45; H, 8.95. $C_{22}H_{31}OP$ requires C, 77.15; H, 9.1%); M^+ 342; τ 2.25 (4 H), 2.55 (6 H), 8.2—8.95 (15 H), and 9.13 (6 H, t, $J_{H,H}$ 7).

Bis-(2-diphenylphosphinoylethyl) Peroxide (11).—Diphenylvinylphosphine oxide (3.42 g, 1.5×10^{-2} mol) in methanol (25 ml) was stirred at 0°C and treated, sequentially, with 30% hydrogen peroxide (4 ml) and 2.5M-sodium hydroxide (aqueous) (6.0 ml, 1.5×10^{-2} mol), with the temperature kept below 10°C . The mixture was stirred at 20°C in the dark for 24 h, then treated with water (150 ml), and extracted with dichloromethane (3×40 ml). The extracts were washed with saturated aqueous sodium sulphite (100 ml), dried, and evaporated to give a white oil, which slowly furnished crystals. Recrystallisation from ethyl acetate-hexane gave bis-(2-diphenylphosphinoylethyl) peroxide (2.89 g, 79%), m.p. 267—268° (Found: C, 65.2; H, 6.35. $C_{28}H_{28}O_4P_2$ requires C, 70.9; H, 5.95%. $C_{28}H_{28}O_4P_2 \cdot 2H_2O$ requires C, 65.9; H, 6.3%). The compound decomposed to a red oil upon attempted recrystallisation from di-*n*-butyl ether; ν 3 130m, 1 440s, 1 230w, 1 155s, 1 115w, 1 095w, 1 070w, 1 030m, 1 014sh, 994w, 827w, 795w, 746m, 726m, and 694m; m/e 215 (100%), 201 (97), 216 (91), 77 (75), 202 (62), 227 (15), 244 (13), 243 (10), and 245 (4).

The peroxide (0.2 g) in acetic acid (5 ml) was treated with potassium iodide (0.2 g) in acetic acid (10 ml), and the liberated iodine was titrated against aqueous sodium thiosulphate (0.05M). In two concurrent runs the titres were 1.55 and 1.50 ml. This gives a mean molecular weight for the peroxide of 525: the dihydrate has M 526, and the anhydrous peroxide M 490.

Reduction of Bis-(2-diphenylphosphinoylethyl) Peroxide (11) with Lithium Aluminium Hydride.—Bis-(2-diphenylphosphinoylethyl) peroxide (0.368 g, 7.5×10^{-4} mol) and lithium aluminium hydride (0.019 g, 5×10^{-4} mol) were stirred in THF (5 ml) under nitrogen at ambient temperature for 30 min. Acetic acid (0.1 ml) in water (10 ml) was added, and the mixture extracted with dichloromethane (2×20 ml). The extracts were dried and evaporated to give an oil (0.342 g), which crystallised from ethyl acetate to give 2-hydroxyethylidiphenylphosphine oxide (0.310 g, 84%), m.p. 87—88° (lit.,⁶ 88.5—91.5°). No other phosphorus-containing compounds were isolated.

Bis-(2-diphenylphosphinoylethyl) Ether (12).—Lithium diphenylphosphide¹⁷ [1.5×10^{-2} mol in tetrahydrofuran (15 ml)] was added to diethylene glycol ditosylate (2.07 g, 5×10^{-3} mol), and the mixture was stirred under nitrogen overnight. Methanol (10 ml) was added, followed by 30% hydrogen peroxide (10 ml) in methanol (10 ml), over 15 min, the mixture being cooled to 0°C . Stirring was continued for 1 h, then water (50 ml) was added, and the mixture was extracted with dichloromethane (3×50 ml). The extracts were washed with 2M-sodium hydroxide and brine, dried, and evaporated to yield a yellow oil (3.15 g). Chromatography (alumina; methanol: alumina; ethyl acetate) gave an oil (2.68 g), which solidified. Recrystallisation from ethyl acetate afforded bis-(2-diphenylphosphinoylethyl) ether (2.23 g, 94%), m.p. 81—82°. The sample for analysis was recrystallised once more (Found: C, 68.5;

¹⁶ J. R. Shutt and S. Trippett, *Chem. Comm.*, 1969, 789.

¹⁷ A. M. Aguiar, J. Beisler, and A. Mills, *J. Org. Chem.*, 1963, 28, 3545.

H, 6.3. $C_{28}H_{28}O_3P_2 \cdot H_2O$ requires C, 68.3; H, 6.15%; *m/e* 228 (100%), 201 (100), 227 (68), 77 (66), 202 (60), 245 (15), and 18 (15).

Reaction of Diphenylvinylphosphine Oxide (3) with Alkali.

—Diphenylvinylphosphine oxide (1 g) was stirred with 2M-sodium hydroxide (aqueous; 20 ml) and methanol (20 ml) for 24 h. The mixture was evaporated to dryness, and the oily residue shaken with brine (40 ml) and extracted with dichloromethane (2×50 ml). The extracts were dried and evaporated to yield an oily solid (1.12 g), which furnished feathery crystals of 1,2-bis(diphenylphosphinoyl)ethane (0.92 g, 96%), m.p. 268—269° (lit.,¹⁸ 268—270°) (from benzene) (mixed m.p. 267—268°).

2-Methoxyethylidiphenylphosphine Sulphide (13).—Di-

phenylvinylphosphine sulphide (1 g) was stirred under reflux in methanol (20 ml) and aqueous 2M-sodium hydroxide (20 ml) for 24 h. The mixture was evaporated to small volume and extracted with dichloromethane (3×10 ml). The extracts were dried and evaporated to yield, as an oil (1.05 g) which was not crystallised, 2-methoxyethylidiphenylphosphine sulphide (Found: C, 64.95; H, 6.25. $C_{13}H_{17}OPS$ requires C, 65.2; H, 6.2%); τ 2.2—2.4 (4 H), 2.55—2.65 (6 H), 6.19 (2 H, dt, $J_{P,H}$ 11, $J_{H,H}$ 7), 6.74 (3 H), and 7.18 (2 H, dt, $J_{P,H}$ 12).

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