

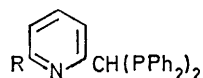
New, Ready Degradation Reactions of Bisphosphines

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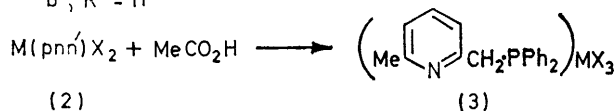
2-Bis(diphenylphosphino)methyl-6-methylpyridine (1a) and 2-bis(diphenylphosphino)methylpyridine (1b) undergo ready degradation to monophosphine derivatives on aerial oxidation, quaternisation, reaction with bromine, or warming with acetic acid. Similar reactions take place with the corresponding palladium(II) complexes. Oxidation with manganese dioxide and reaction with sulphur lead to bisphosphine oxides and sulphides, respectively. Bis(diphenylphosphino)methane (13b), 1,1-bis(diphenylphosphino)ethane (13a), and $\alpha\alpha$ -bis(diphenylphosphino)toluene (13c) generally do not undergo a similar loss of phosphorus, although treatment of (13c) with methyl iodide under more vigorous conditions gave benzylmethyl-diphenylphosphonium iodide.

A mechanism involving an increase in co-ordination at one phosphorus atom, followed by nucleophilic attack at the other is suggested, and the importance of the stability of the leaving carbanion is discussed.

THE 2-pyridyl-substituted bisphosphine (1a) (ppn') is an excellent chelating ligand exhibiting two types of bidentate behaviour.^{1,2} During investigations of the sites

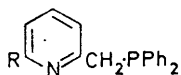


(1) a ; R = Me
b ; R = H

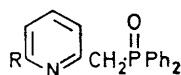


M = Co^{II} or Ni^{II}
X = Cl, Br, or I

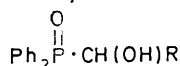
of co-ordination in (1a), neutral complexes of type (2) were treated with glacial acetic acid and gave² a new series of complexes (3). The breaking of carbon-phosphorus bonds, especially in phosphines, generally requires vigorous conditions and/or transition metal complex formation.³ In view of this it seemed likely that the novel degradation of (2) under such mild conditions was assisted by co-ordination to the metal ion. We report a study of this reaction which shows that the presence of metal ions is not a necessary condition for degradation. A number of other degradation reactions are described, the common factor throughout being the unprecedented ease of phosphorus-carbon bond breaking.



(4) a ; R = Me
b ; R = H



(5) a ; R = Me
b ; R = H



(6) R = Ph, PhCH_2 , or $p\text{-MeC}_6\text{H}_4$

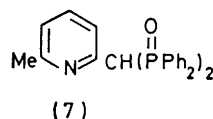
The bisphosphine (1a) reacted with a variety of reagents to give, in most cases, derivatives of 2-diphenylphosphinomethyl-6-methylpyridine (4a). Refluxing a

¹ W. V. Dahloff, T. R. Dick, G. H. Ford, W. S. J. Kelly, and S. M. Nelson, *J. Chem. Soc. (A)*, 1971, 3495.

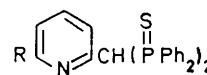
² W. V. Dahloff, T. R. Dick, and S. M. Nelson, *J. Chem. Soc. (A)*, 1969, 2919.

methanolic solution of (1a) in air gave the monophosphine oxide (5a) and diphenylphosphine oxide; the presence of the secondary phosphine oxide had been suggested by the isolation of α -hydroxy-phosphine oxides (6) from the reaction of (1a) with various aldehydes. The bisphosphine dioxide (7) could be obtained from (1a) by reaction with manganese dioxide in anhydrous methanol and was stable to refluxing in methanol in the presence of oxygen.

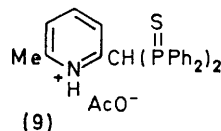
A stable disulphide (8a) could be prepared by treatment of (1a) with sulphur in carbon disulphide; in no case was any evidence found for monophosphine derivatives. The disulphide (8a) did not react with manganese dioxide and, more surprisingly, was recovered unchanged from attempted reduction with lithium



(7)



(8) a ; R = Me
b ; R = H



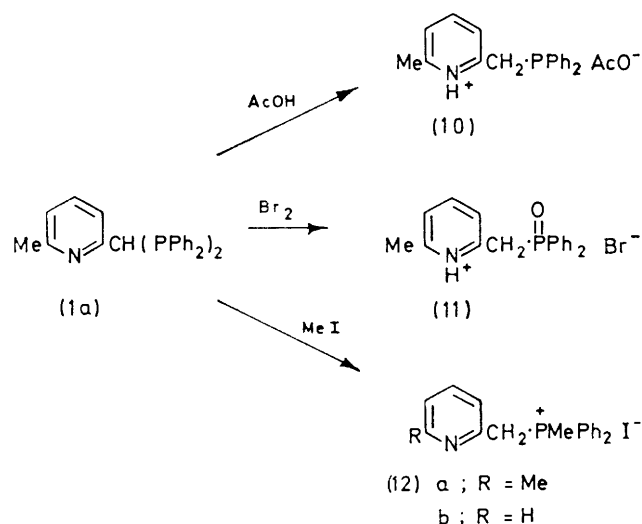
(9)

aluminium hydride. Recrystallisation from glacial acetic acid gave the pyridinium acetate (9). However reactions of (1a) with acetic acid, bromine, and methyl iodide, under various conditions, gave, respectively, compounds (10), (11), and (12a), indicating the loss of one phosphinyl group in each case. Protonation at N rather than P in (10) is supported by the strong absorption at 2500 cm^{-1} . The structures (5a) and (12a) were confirmed by synthesis from 2-diphenylphosphino-methyl-6-methylpyridine (4a). No evidence was obtained for either degradation or deuterium exchange after prolonged refluxing of (1a) in methan[²H]ol or in deuterium oxide.

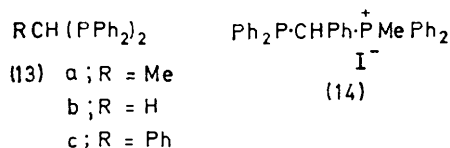
2-Bis(diphenylphosphino)methylpyridine (1b) reacted

³ G. van Koten and J. G. Noltes, *J.C.S. Chem. Comm.*, 1972, 452; W. C. Kasba, D. K. Mitchell, R. F. Reichelderfer, and W. D. Korte, *J. Amer. Chem. Soc.*, 1974, **96**, 2847; J. R. Blickensderfer and H. D. Kalsz, *ibid.*, 1975, **97**, 2681, and references therein.

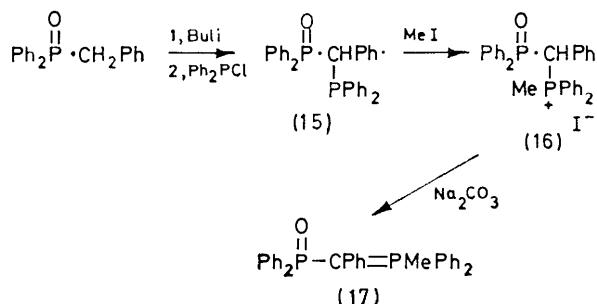
in a similar way with oxygen, methyl iodide, and sulphur to give compounds (5b), (12b), and (8b) respectively.



Analogous reactions with the bisphosphines (13a and b) did not involve loss of phosphorus, and dioxides, disulphides, and diphosphonium salts were obtained. The



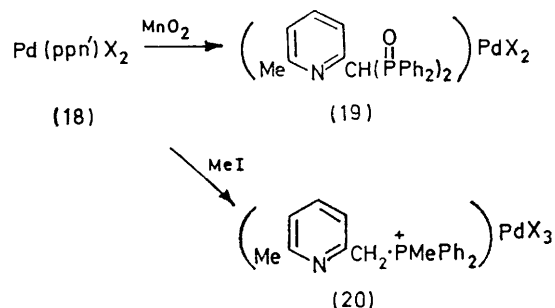
phenyl-substituted diphosphine (13c) also formed a diphosphine dioxide (the m.p. of our sample differs considerably from that previously reported) and a disulphide, and refluxing in benzene with 1 mol. equiv. of methyl iodide for 15 min gave the phosphonium salt (14), identified on the basis of its n.m.r. spectrum. The structure (14) was confirmed by oxidation to (α -diphenylphosphinoylbenzyl)methyl-diphenylphosphonium iodide (16), which in turn was prepared from benzyldiphenylphosphine oxide by phosphinoylation to give (15), followed by quaternisation with methyl iodide. The salt (16) was



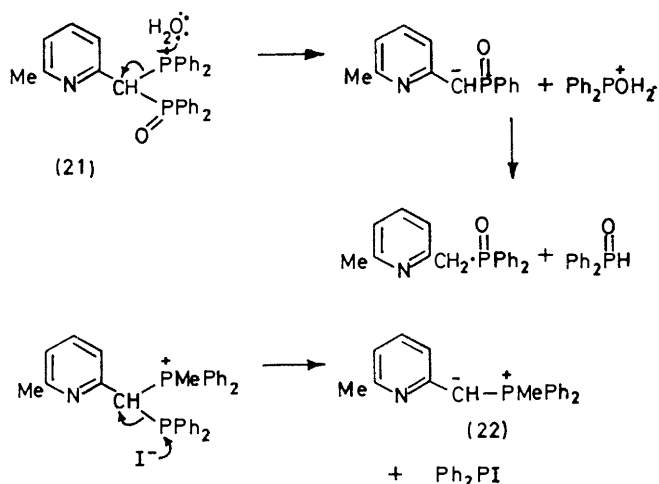
recovered unchanged from refluxing in methanol, methyl iodide, or acetic acid; however, treatment with sodium carbonate gave the corresponding phosphonium ylide (17). Loss of phosphorus from (13c) to give benzyl-

methyldiphenylphosphonium iodide did occur on refluxing with an excess of methyl iodide.

Reactions with the palladium(II) complex (18) of ppn' (1a) generally gave results similar to those obtained with the free ligand. On the basis of analysis and mass spectra, oxidation with manganese dioxide under anhydrous conditions probably gives the bisphosphine dioxide complex (19) rather than the mono-oxide complex, and refluxing in an excess of methyl iodide gave the degraded monophosphoniopalladium(II) complex (20). However, $\text{Pd(ppn}')\text{X}_2$ was recovered unchanged from treatment with 1 mol. equiv. of methyl iodide, and no product could be isolated from reaction with glacial acetic acid.



The presence of water in the reaction mixture appeared to be crucial for degradation to take place during oxidations of (1a) and (1b). The dioxide (7) is not an intermediate in the degradation since it is recovered unchanged from refluxing in absolute methanol. However, degradation

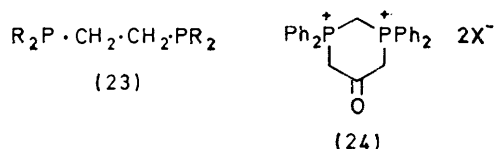


SCHEME

does not precede oxidation since the bisphosphine (1a) is also stable in refluxing methanol in the absence of oxygen. In view of this a reasonable mechanism for oxidative degradation involves the bisphosphine mono-oxide (21). The second stage of the reaction is presumably hydrolysis of (21) and here attack at trivalent phosphorus is preferred since (a) diphenylphosphine oxide is an isolated product, while no significant amount

of phosphinic acid was detected, (b) phosphites are generally hydrolysed much faster than the corresponding pentavalent analogues,^{4,5} and (c) tetrahedral pentavalent phosphorus is more effective than trivalent phosphorus at stabilising adjacent negative charge. An analogous mechanism, involving iodide as nucleophile (see Scheme), can be written for degradative methylation. No evidence for the phosphonium ylide (22) was found, although diphenylphosphine oxide was obtained after the addition of water.

The importance of the stability of the leaving carbanion is further evidenced by the absence of degradation of (13a and b). The case of (13c) is presumably intermediate, since a full positive charge on phosphorus and forcing conditions are required for degradation. In view of this the reported stability of the bisphosphines (23)⁶ and bisphosphonium salts (24)⁷ to mild degradative conditions is predictable. The degradations of (1a and b) in



acetic acid presumably rely on stabilisation of the carbanion by the pyridinium system, since the phosphine (10) is the isolated product.

The absence of degradation during sulphurisation is more difficult to explain, but may be due to inferior carbanion stabilisation in the sulphur case. Alternatively, the addition of a second sulphur atom, to give the stable disulphide (8), may be fast.

EXPERIMENTAL

I.r., mass, and n.m.r. spectra were obtained with a Perkin-Elmer 457, an A.E.I. MS902, and a Varian HA-100 spectrometer (tetramethylsilane as internal reference), respectively, unless otherwise stated. All experiments involving phosphines, and other air-sensitive compounds, were carried out under dry, oxygen-free, nitrogen, unless otherwise stated.

Preparation of Bisphosphines.—2-Bis(diphenylphosphino)methyl-6-methylpyridine (1a), m.p. 78—80°, τ (CDCl₃) 2.4—2.9 (21 H, m), 3.26 (1 H, d, J_{HH} 4.0 Hz), 3.40 (1 H, d, J_{HH} 3.8 Hz), 5.22 (1 H, t, J_{PH} 2.2 Hz), and 7.77 (3 H, s), was prepared from 2,6-lutidine by the method previously described.¹ A similar procedure starting from α -picoline gave 2-bis(diphenylphosphino)methylpyridine (1b), ν_{max} (KBr) 1 585 and 1 570 cm⁻¹ (Found: C, 77.8; H, 5.2; N, 2.9. C₃₀H₂₅NP₂ requires C, 78.1; H, 5.4; N, 3.0%). 2-Diphenylphosphinomethyl-6-methylpyridine (4a),² ν_{max} (CHCl₃) 1 586 and 1 572 cm⁻¹ (the absence of appreciable phosphine oxide impurities was confirmed by the lack of a strong absorption at 1 180 cm⁻¹); m/e 291 (M^+); τ (CDCl₃) 2.4—2.9 (11 H, m), 3.22 (1 H, d, J_{HH} 4.0 Hz), 3.40 (1 H, d, J_{HH} 3.9 Hz), 6.40 (2 H, d, J_{PH} 0.5 Hz), and 7.59 (3 H, s), was prepared from

2,6-lutidine by using a 1 : 1 molar ratio of butyl-lithium and chlorodiphenylphosphine.

α -Bis(diphenylphosphino)toluene (13c). 2*M*-Butyl-lithium (10 ml, 0.02 mol) was added to benzyldiphenylphosphine (5.4 g, 0.02 mol) in ether (200 ml). After stirring for 4 h, chlorodiphenylphosphine (4.4 g, 0.02 mol) in ether (30 ml) was added and stirring was continued for 30 min, during which time the mixture became colourless. An equal volume of water was added and the organic layer was separated, dried, and evaporated to give α -bis(diphenylphosphino)toluene (5.6 g, 62%), m.p. 93—95°; ν_{max} (KBr) 1 496, 1 482, 1 456, and 1 436 cm⁻¹; τ (CDCl₃) 2.0—2.8 (25 H, m) and 5.57 (1 H, t, J_{PH} 3.5 Hz) (Found: C, 80.6; H, 5.7. C₃₁H₂₆P₂ requires C, 80.9; H, 5.7%).

1,1-Bis(diphenylphosphino)ethane (13a) was prepared from 1,1-dichloroethane by a modification of the general method of Issleib⁸ to give crystals, m.p. (from ethanol) 106—108°; τ (CDCl₃) 2.4—2.8 (20 H, m), 6.81 (1 H, q, J_{HH} 7 Hz), and 9.02 (3 H, dt, $^2J_{\text{HH}}$ 7, $^3J_{\text{PH}}$ 10.5 Hz) (Found: C, 78.7; H, 5.8. C₂₆H₂₄P₂ requires C, 78.4; H, 6.1%).

Reactions of 2-Bis(diphenylphosphino)methyl-6-methylpyridine (1a).—(i) **Oxidation.** (i) The phosphine (1a) (4.75 g, 0.01 mol) was refluxed in benzene (25 ml) in air for 30 min. On cooling a white precipitate formed, m.p. 52°, identical with an authentic sample of diphenylphosphine oxide.⁹ The filtrate was evaporated to give (6-methyl-2-pyridylmethyl)diphenylphosphine oxide (5a) (2.5 g, 82%) as a pale yellow oil, ν_{max} (film) 1 180 cm⁻¹; m/e 307 (M^+); τ (CDCl₃) 2.9—3.4 (13 H, m), 6.25 (2 H, d, J_{PH} 12.0 Hz), and 7.68 (3 H, s) (Found: C, 74.6; H, 6.2; P, 4.8. C₁₉H₁₈NOP requires C, 74.3; H, 5.9; N, 4.6%).

(ii) The phosphine (1a) (0.47 g, 0.001 mol) and manganese dioxide (0.53 g, 0.006 mol) in dry tetrahydrofuran (30 ml) were refluxed under nitrogen for 12 h. The white precipitate which formed upon cooling was filtered off and vacuum dried at room temperature to give 6-bis(diphenylphosphino)methyl-2-methylpyridine PP'-dioxide (7) (0.34 g, 60%), m.p. 213—214°; ν_{max} (KBr) 1 205 cm⁻¹; τ (CDCl₃) 2.5—3.5 (23 H, m), 4.76 (1 H, t, J_{PH} 13.0 Hz), and 7.76 (3 H, s) (Found: C, 73.0; H, 4.9; N, 2.6. C₃₁H₂₇N₂O₂P₂ requires C, 73.3; H, 5.3; N, 2.8%). The dioxide (7) was unchanged after refluxing for 1 h in oxygenated methanol.

(b) **With bromine.** Bromine (0.16 g) in chloroform (10 ml) was added to the phosphine (1a) (0.5 g) in chloroform (10 ml) and the mixture stirred at room temperature for 2 h. The solvent was removed under vacuum and the residue taken up in hot benzene. Cooling gave (6-methyl-2-pyridylmethyl)diphenylphosphine oxide hydrobromide (11) (0.15 g, 40%), m.p. 184—185°; ν_{max} (KBr) 2 500br, 1 620, 1 608, and 1 180 cm⁻¹; τ (CDCl₃) 1.7—2.7 (14 H, m), 5.26 (2 H, d, J_{PH} 14 Hz), and 7.24 (3 H, s) (Found: C, 58.1; H, 4.9; Br, 20.6. C₁₉H₁₉BrNOP requires C, 58.7; H, 4.9; Br, 20.6%).

(c) **With methyl iodide.** (i) The phosphine (1a) (1.1 g) and methyl iodide (25 ml) were refluxed for 30 min under nitrogen. The excess of methyl iodide was distilled off and the oily residue taken up in ethanol. Careful addition of ether gave (6-methyl-2-pyridylmethyl)methylidiphenylphosphonium iodide (12a) (0.4 g), m.p. 193—195°; m/e 306; τ (CDCl₃) 2.0—2.5 (11 H, m), 2.80 (1 H, d, J_{HH} 3.8 Hz), 2.88

⁶ R. B. King and P. R. Heckley, *Phosphorus*, 1974, **4**, 209.

⁷ T. A. Mastryukova, Kh. A. Suerbaev, P. V. Petrovskii, E. I. Fedin, and M. I. Kabachnik, *Zhur. obshechi Khim.*, 1974, **44**, 2398 (*Chem. Abs.*, 1975, **82**, 98057q).

⁸ K. Issleib and D. Muller, *Chem. Ber.*, 1959, **92**, 3175.

⁹ R. C. Miller, *J. Org. Chem.*, 1959, **24**, 2013.

⁴ J. Michalski and T. Modro, *Bull. Acad. polon. Sci., Sér. Sci. chim.*, 1962, **10**, 327; M. Lepawy, J. Michalski, and J. Zabrocki, *Chem. and Ind.*, 1964, 835.

⁵ G. Aksnes and D. Aksnes, *Acta Chem. Scand.*, 1964, **18**, 1623; D. S. Noyce and J. A. Virglio, *J. Org. Chem.*, 1972, **37**, 1052.

(1 H, d, J_{HH} 3.7 Hz), 5.12 (2 H, d, J_{PH} 16.0 Hz), 7.19 (3 H, d, J_{PH} 14 Hz), and 7.70 (3 H, s) (Found: C, 54.9; H, 4.8; I, 29.0. $\text{C}_{20}\text{H}_{21}\text{INP}$ requires C, 55.5; H, 4.8; I, 29.3%). The filtrate was evaporated to give diphenylphosphine oxide, identical with an authentic sample.

(ii) The phosphine (1a) (2.4 g, 0.005 mol) in benzene (30 ml) was added to methyl iodide (0.7 g, 0.005 mol) and the mixture was refluxed for 1 h. Cooling and addition of ether gave a precipitate of (6-methyl-2-pyridylmethyl)methyl-diphenylphosphonium iodide (12a).

(d) *With acetic acid.* The phosphine (4.8 g, 0.01 mol) in deoxygenated glacial acetic acid (25 ml) was refluxed for 15 min. The excess of acetic acid was removed under vacuum and the residue dissolved in methanol. Addition of water gave 2-(diphenylphosphinomethyl)-6-methylpyridinium acetate (10) as a yellow oil, ν_{max} (KBr) 2 560, 1 720, 1 600, 1 580, and 1 250 cm^{-1} ; m/e 292 (Found: C, 72.0; H, 6.4; N, 3.8. $\text{C}_{21}\text{H}_{22}\text{NO}_2\text{P}$ requires C, 71.8; H, 6.3; N, 4.0%). The acetate (10) (3.51 g, 0.01 mol) in deoxygenated ethanol (50 ml) was added to a filtered solution of nickel(II) bromide trihydrate (1.93 g, 0.01 mol) in ethanol (25 ml). The solution was refluxed for 5 min and cooled to give blue-green crystals of the pyridinonickel(II) tribromide,² m.p. 208—210°, identical with an authentic sample (i.r.).

(e) *With sulphur.* The phosphine (4.8 g, 0.01 mol) was added to a deoxygenated solution of sulphur (0.96 g, 0.03 mol) in carbon disulphide (50 ml). The solution was refluxed for 16 h and filtered hot. Cooling gave 2-bis(diphenylphosphino)methyl-6-methylpyridine PP'-disulphide (8a) (3.5 g, 62%), m.p. 211—213°; ν_{max} (KBr) 625 cm^{-1} ; m/e 539; τ (CDCl_3) 1.9—2.9 (21 H, m), 3.28 (1 H, d, J_{HH} 2.0 Hz), 3.36 (1 H, d, J_{HH} 2.0 Hz), 4.10 (1 H, t, J_{PH} 13.0 Hz), and 7.78 (3 H, s) (Found: C, 68.5; H, 5.0; N, 2.4. $\text{C}_{31}\text{H}_{27}\text{NP}_2\text{S}_2$ requires C, 69.0; H, 5.0; N, 2.6%).

(f) *With aldehydes.* (i) The phosphine (4.8 g, 0.01 mol) was added to a solution of benzaldehyde (2.12 g, 0.02 mol) in acetic anhydride (50 ml). The solution was refluxed for 24 h and cooled to give α -hydroxybenzyl-diphenylphosphine oxide, m.p. 174—176° (lit.,¹⁰ 178—179.5°); ν_{max} (KBr) 3 410, 1 625, and 1 165 cm^{-1} .

(ii) Phenylacetaldehyde gave, under similar conditions, 1-hydroxy-2-phenylethyl-diphenylphosphine oxide, m.p. 164—166°, ν_{max} (KBr) 3 410, 1 610, and 1 152 cm^{-1} (Found: C, 74.15; H, 5.7. $\text{C}_{20}\text{H}_{16}\text{O}_2\text{P}$ requires C, 74.55; H, 5.9%).

(iii) *p*-Tolualdehyde gave, under similar conditions, α -hydroxy-*p*-methylbenzyl-diphenylphosphine oxide, m.p. 149—150° (lit.,¹¹ 152—155°).

(g) *Attempted deuteration.* The phosphine (10% solution in CDCl_3) was shaken with an equal volume of deuterium oxide for $\frac{1}{2}$ h; the n.m.r. spectrum of the resulting solution was identical with that of an untreated sample. The n.m.r. spectrum of a solution of the phosphine in methan[^2H]ol suggested that no deuterium exchange had occurred even after several days.

Reactions of 2-Bis(diphenylphosphino)methyl-6-methylpyridine PP'-Disulphide (8a).—(a) *Reduction.* (i) The disulphide (5.4 g, 0.01 mol) was added to a solution of lithium aluminium hydride (1.9 g, 0.05 mol) in dry tetrahydrofuran (150 ml) and the mixture was refluxed for 24 h. The product was filtered through kieselguhr and evaporated to give unchanged disulphide (8a) (84%), m.p. 211—213°.

(ii) The disulphide (5.4 g, 0.01 mol) was added to a sus-

pension of copper powder (6.4 g, 0.1 mol) in dry ethanol (300 ml) and the mixture was refluxed for 2 days. The product was filtered through kieselguhr and evaporated to give unchanged disulphide (8a) (89%), m.p. 211—213°.

(b) *Oxidation.* The disulphide (0.54 g, 0.001 mol) was added to a suspension of manganese dioxide (0.44 g, 0.005 mol) in ethanol (150 ml). The mixture was refluxed with stirring for 2 days and filtered through kieselguhr. Evaporation of the resulting solution gave unchanged disulphide (92%), m.p. 211—213°.

(c) *With acetic acid.* A solution of the disulphide (0.54 g, 0.001 mol) in deoxygenated acetic acid (50 ml) was refluxed for 2 h; it was then evaporated to ca. 20 ml and slowly deposited crystals of 2-bis(diphenylphosphino)methyl-6-methylpyridinium PP'-disulphide acetate (9) (80%); ν_{max} (KBr) 2 560, 1 708, 1 601, 1 580, and 1 275 cm^{-1} ; m/e 540; τ (CDCl_3) 1.8—3.3 (24 H, m), 4.03 (1 H, t), 7.80 (3 H, s), and 7.88 (3 H, s) (Found: C, 65.9; H, 5.1; S, 10.2. $\text{C}_{33}\text{H}_{31}\text{NO}_2\text{P}_2\text{S}_2$ requires C, 66.1; H, 5.2; S, 10.7%).

Reactions of 2-(Diphenylphosphinomethyl)-6-methylpyridine (4a).—(a) *Oxidation.* The corresponding oxide (5a) was obtained by refluxing the phosphine (0.5 g) in unpurified methanol (25 ml) for 10 min.

(b) *With sulphur.* The phosphine (2.91 g, 0.01 mol) was added to a solution of sulphur (0.32 g, 0.01 mol) in oxygen-free benzene (25 ml) and the mixture was refluxed for 12 h. Filtration and evaporation gave 2-(diphenylphosphino)methyl-6-methylpyridine P-sulphide (2.4 g, 74%); ν_{max} (KBr) 620 cm^{-1} ; m/e 323; τ (CDCl_3) 2.0—3.2 (13 H, m), 5.89 (2 H, d, J_{PH} 14.0 Hz), and 7.69 (3 H, s) (Found: C, 70.4; H, 5.5; N, 4.2; S, 9.6. $\text{C}_{19}\text{H}_{18}\text{NPS}$ requires C, 70.6; H, 5.6; N, 4.3; S, 9.9%).

(c) *With methyl iodide.* The phosphine (0.58 g, 0.002 mol) and methyl iodide (25 ml) were refluxed for $\frac{1}{2}$ h. Evaporation and crystallisation of the resulting oil from ethanol-ether gave 2-(diphenylphosphino)methyl-6-methylpyridine methiodide (0.5 g), m.p. 193—195°.

Reactions of 2-Bis(diphenylphosphino)methylpyridine.—(a) *Oxidation.* The phosphine (0.46 g, 0.001 mol) in methanol (25 ml) was refluxed in air for 10 min. Cooling and dropwise addition of water gave diphenyl-2-pyridylmethylphosphine oxide (5b), ν_{max} (KBr) 1 185 cm^{-1} ; m/e 293; τ (CDCl_3) 2.3—3.3 (14 H, m) and 6.12 (2 H, d, J_{PH} 13.0 Hz) (Found: C, 73.3; H, 5.1. $\text{C}_{15}\text{H}_{16}\text{NOP}$ requires C, 73.7; H, 5.4%).

(b) *With methyl iodide.* The phosphine (0.46 g, 0.001 mol) in methyl iodide (25 ml) was refluxed for $\frac{1}{2}$ h. The methyl iodide was removed under reduced pressure to leave an oil which was dissolved in ethanol. Addition of ether gave methyl-diphenyl-(2-pyridylmethyl)phosphonium iodide (12b) (0.3 g), m.p. 162—164°; τ (CDCl_3) 1.8—2.9 (14 H, m), 4.88 (2 H, d, J_{PH} 14.0 Hz), and 7.06 (3 H, d, J_{PH} 14.0 Hz) (Found: C, 54.0; H, 4.3; I, 29.9. $\text{C}_{19}\text{H}_{19}\text{INP}$ requires C, 54.4; H, 4.5; I, 30.3%).

(c) *With sulphur.* The phosphine (4.6 g, 0.01 mol) was added to a solution of sulphur (0.32 g, 0.01 mol) in oxygen-free carbon disulphide (25 ml) and the mixture refluxed for 12 h. Filtration and evaporation under reduced pressure gave 2-bis(diphenylphosphino)methylpyridine PP'-disulphide (8b) (82%), m.p. 215—216°; ν_{max} (KBr) 620 cm^{-1} ; τ (CDCl_3) 1.7—3.2 (24 H, m) and 4.06 (1 H, t, J_{PH} 13.0 Hz) (Found: C, 68.3; H, 4.4. $\text{C}_{30}\text{H}_{25}\text{NP}_2\text{S}_2$ requires C, 68.6; H, 4.8%).

Reactions of 1,1-Bis(diphenylphosphino)ethane.—(a) *Oxidation.* The phosphine (3.98 g, 0.01 mol) in methanol (50 ml)

¹⁰ R. C. Miller, W. Rogers, L. A. Hamilton, and C. D. Miller, *J. Amer. Chem. Soc.*, 1957, **79**, 424.

¹¹ D. S. Marmor and D. Seyferth, *J. Org. Chem.*, 1969, **34**, 748.

was added to manganese dioxide (0.1 mol). The mixture was refluxed for 12 h, allowed to cool, and filtered through kieselguhr, and the filtrate was evaporated to ca. 15 ml. This solution slowly deposited crystals of 1,1-bis(diphenylphosphino)ethane PP'-dioxide (78%), m.p. 178—180°; ν_{\max} (KBr) 1180 cm^{-1} (Found: C, 73.0; H, 5.9; P, 14.1). $\text{C}_{26}\text{H}_{24}\text{O}_2\text{P}_2$ requires C, 72.6; H, 5.6; P, 14.4%. The corresponding mono-oxide¹² could be converted into 1,1-bis(diphenylphosphino)ethane PP'-dioxide by treatment with hydrogen peroxide.

(b) *With sulphur*. The phosphine (3.98 g, 0.01 mol) was added to sulphur (0.96 g, 0.03 mol) in deoxygenated carbon disulphide (40 ml). The solution was refluxed for 12 h, then filtered hot through kieselguhr and cooled to give crystals of 1,1-bis(diphenylphosphino)ethane PP'-disulphide (3.8 g), m.p. 182—184°; ν_{\max} (KBr) 579 cm^{-1} ; m/e 462; τ (CDCl_3) 1.8—2.8 (20 H, m), 5.87 (1 H, dq, $^2J_{\text{HH}}$ 7.0, $^2J_{\text{HP}}$ 14.0 Hz), and 8.61 (3 H, dt, $^2J_{\text{HH}}$ 7, $^2J_{\text{PH}}$ 17 Hz) (Found: C, 67.4; H, 5.0; S, 13.6). $\text{C}_{26}\text{H}_{24}\text{P}_2\text{S}_2$ requires C, 67.5; H, 5.2; S, 13.9%.

(c) *With methyl iodide*. The phosphine (3.98 g, 0.01 mol) in methyl iodide (25 ml) was refluxed for 0.5 h. The excess of methyl iodide was removed under reduced pressure and the residual oil recrystallised from ethanol-ether to give 1,1-bis(diphenylphosphino)ethane bismethiodide (4.2 g), m.p. 248—250°; m/e 428; τ [$(\text{CD}_3)_2\text{SO}$] 1.5—2.8 (20 H, m), 4.04br (1 H, s), 6.87 (6 H, d, $^2J_{\text{PH}}$ 13 Hz), and 8.34 (3 H, dt, $^2J_{\text{HH}}$ 7.0, $^2J_{\text{PH}}$ 16 Hz) (Found: C, 49.0; H, 4.4; I, 36.8). $\text{C}_{28}\text{H}_{30}\text{I}_2\text{P}_2$ requires C, 49.3; H, 4.4; I, 37.2%.

(d) *With acetic acid*. The phosphine was unchanged after refluxing for 5 h in glacial acetic acid.

Reactions of α -Bis(diphenylphosphino)toluene (13c).

(a) *Oxidation*. The phosphine (4.6 g, 0.01 mol), added to ethanol (25 ml), was refluxed in air until all the solid had dissolved. Filtration and cooling gave white crystals of α -bis(diphenylphosphino)toluene PP'-dioxide (3 g), m.p. 211—213° (lit.,¹³ 306—307°); ν_{\max} (KBr) 1180 cm^{-1} ; m/e 492; τ (CDCl_3) 2.0—3.0 (25 H, m) and 5.02 (1 H, t, $^2J_{\text{PH}}$ 16 Hz) (Found: C, 75.6; H, 5.6). $\text{C}_{31}\text{H}_{28}\text{O}_2\text{P}_2$ requires C, 75.6; H, 5.3%.

(b) *With sulphur*. The phosphine (2.3 g, 0.005 mol) was added to sulphur (0.32 g, 0.01 mol) dissolved in deoxygenated carbon disulphide (50 ml). The solution was refluxed for 24 h, filtered, and evaporated under reduced pressure to give α -bis(diphenylphosphino)toluene PP'-disulphide (2.4 g), m.p. (from ethanol) 196—199°; ν_{\max} (KBr) 604 cm^{-1} ; τ (CDCl_3) 1.8—3.2 (25 H, m) and 4.68 (1 H, t, $^2J_{\text{PH}}$ 14 Hz) (Found: C, 70.7; H, 5.2; S, 11.9). $\text{C}_{31}\text{H}_{28}\text{P}_2\text{S}_2$ requires C, 71.0; H, 5.0; S, 12.2%.

(c) *With acetic acid*. The phosphine was unchanged after refluxing for 10 h in glacial acetic acid.

(d) *With methyl iodide*. (i) The phosphine (1 g) in methyl iodide (25 ml) was refluxed for 0.5 h. The excess of methyl iodide was removed under reduced pressure and the residual oil was crystallised from ether-ethanol to give benzylmethyl-diphenylphosphonium iodide (0.5 g), m.p. 241—244° (lit.,¹⁴ 243—245°); τ [$(\text{CD}_3)_2\text{SO}$] 2.2—3.0 (15 H, m), 5.40 (2 H, d, $^2J_{\text{PH}}$ 15.7), and 7.51 (3 H, d, $^2J_{\text{PH}}$ 13.5 Hz) (Found: C, 57.2;

H, 4.7; I, 30.0). $\text{C}_{20}\text{H}_{20}\text{IP}$ requires C, 57.4; H, 4.8; I, 30.4%.

(ii) The phosphine (4.6 g, 0.01 mol) was added to methyl iodide (1.4 g, 0.01 mol) in benzene (30 ml) and the mixture was refluxed for 10 min. Careful addition of ether to the cooled mixture gave (α -diphenylphosphinobenzyl)methyl-diphenylphosphonium iodide (14), m.p. 107—109°; τ [$(\text{CD}_3)_2\text{SO}$] 2.2—3.0 (25 H, m), 3.77 (1 H, q, $^2J_{\text{PH}}$ 16.0, $^2J_{\text{PH}}$ 1.0 Hz), and 7.48 (3 H, d, $^2J_{\text{PH}}$ 14 Hz) (Found: C, 63.7; H, 4.6; I, 22.0). $\text{C}_{32}\text{H}_{29}\text{IP}_2$ requires C, 63.8; H, 4.8; I, 21.2%.

Reactions of 2-Bis(diphenylphosphino)methyl-6-methylpyridinepalladium Dihalides (18).—(a) *Oxidation*. The complex $\text{Pd}(\text{ppn}')\text{Br}_2$ (18; X = Br) was refluxed in dichloroethane for 1 h with a five-fold excess of manganese dioxide. The mixture was filtered through kieselguhr and on cooling gave a brown precipitate of the PP'-dioxide (19; X = Br); m/e 507 (low intensity) (Found: C, 48.5; H, 3.7; N, 1.7; Br, 21.2). $\text{C}_{31}\text{H}_{27}\text{Br}_2\text{NO}_2\text{P}_2\text{Pd}$ requires C, 48.75; H, 3.5; N, 1.8; Br, 20.95%. The corresponding dichloride (X = Cl) and di-iodide (X = I) were obtained under similar conditions.

(b) *With methyl iodide*. The complex $\text{Pd}(\text{ppn}')\text{I}_2$ (18; X = I) in a 10-fold molar excess of methyl iodide was refluxed for 1 h. The methyl iodide was removed under reduced pressure and the residue was dissolved in hot dichloroethane. This solution gave on cooling orange crystals of methyl-(6-methyl-2-pyridylmethyl)diphenylphosphoniopalladium tri-iodide (20; X = I) (Found: C, 30.9; H, 2.6; N, 1.3; I, 47.7). $\text{C}_{20}\text{H}_{21}\text{I}_3\text{NPPd}$ requires C, 30.3; H, 2.6; N, 1.7; I, 48.0%.

α -(Diphenylphosphino)benzylidiphenylphosphine Oxide (15).—2*M*-Butyl-lithium (10 ml, 0.02 mol) was added to a stirred solution of benzylidiphenylphosphine oxide (5.84 g, 0.02 mol) in ether (250 ml). After 4 h chlorodiphenylphosphine (4.4 g, 0.02 mol) in ether (40 ml) was added and stirring was continued for 2 h. An equal volume of water was added and the organic layer was separated, dried, and evaporated to give the phosphine oxide (15) (5.8 g), m.p. 135—138°.

α -Diphenylphosphino)benzylidene(methyl)diphenylphosphorane (17).— α -(Diphenylphosphino)benzylidiphenylphosphine oxide (4.76 g, 0.01 mol) and methyl iodide (1.42 g, 0.01 mol) in benzene (40 ml) were refluxed for 1 h. Cooling gave white crystals of α -diphenylphosphino)benzyl(methyl)diphenylphosphonium iodide (16) (4.5 g), m.p. 204—206°; ν_{\max} (KBr) 1160 cm^{-1} ; τ [$(\text{CD}_3)_2\text{SO}$] 2.0—3.1 (25 H, m), 3.60 (1 H, q, $^2J_{\text{PH}}$ 15, $^2J_{\text{PH}}$ 17 Hz), and 7.01 (3 H, d, $^2J_{\text{PH}}$ 14 Hz) (Found: C, 61.9; H, 4.6; P, 9.7). $\text{C}_{32}\text{H}_{28}\text{IOP}_2$ requires C, 62.1; H, 4.7; P, 10.0%. The phosphonium salt (16) (3.1 g, 0.005 mol) in ethanol (100 ml) was treated with *m*-sodium carbonate (5 ml; 0.005 mol). The resulting solution slowly precipitated α -diphenylphosphino)benzylidene(methyl)diphenylphosphorane (3.9 g), m.p. 189—191°; ν_{\max} (KBr) 1180 cm^{-1} ; τ (CDCl_3) 2.15—3.0 (25 H, m) and 6.34 (3 H, d, $^2J_{\text{PH}}$ 14 Hz) (Found: C, 78.0; H, 5.6; P, 12.4). $\text{C}_{32}\text{H}_{28}\text{OP}_2$ requires C, 78.3; H, 5.7; P, 12.7%.

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¹³ M. I. Kabachnik, T. Ya. Medved, Yu. M. Polikarpov, and K. S. Yudina, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1967, 591 (*Chem. Abs.*, 1968, 68, 39743y).

¹⁴ S. Trippett, *J. Chem. Soc.*, 1961, 2813.

¹² S. O. Grim, L. C. Satek, C. A. Tolman, and J. P. Jesson, *Inorg. Chem.*, 1975, 14, 656.