Electrophilic Substitution at Phosphorus: Reactions of Diphenylphosphinyl Systems with Carbonyl Compounds

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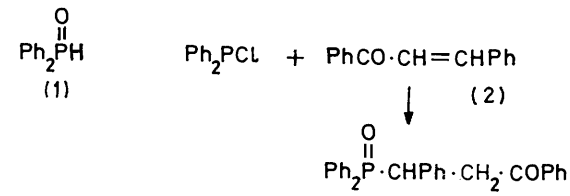
Methods of making adducts of diphenylphosphine oxide include the addition of its anion, either as a Grignard reagent or as the sodium salt, to carbonyl compounds. With acetone, the Grignard method gave a substantial yield of a phorone (2,6-dimethylhepta-2,5-dien-4-one) bis-adduct, and with enones addition occurred either to the carbonyl group or to the double bond. A new reaction is described in which a nucleophilic Ph_2PO group is released, by the debenzylation and decarboxylation of benzyl diphenylphosphinylformate, to react with carbonyl compounds or iodine. The debenzylation can be separated kinetically from the rest of the reaction.

DIPHENYLPHOSPHINE OXIDE (1) was first prepared in 1957 when Hunt and Saunders [1] hydrolysed the magnesium complex formed from phenylmagnesium bromide and diethyl phosphite. The first adduct of diphenylphosphine oxide and an electrophilic π-system was however prepared as long ago as 1923 by Conant,[2] who added chloro(diphenyl)phosphine to the enone (2) in the presence of acetic acid.

Since that date diphenylphosphine oxide adducts have been prepared from the Grignard reagent $Ph_2POMgBr$,[3,4] sodium diphenylphosphinite,[5] by oxidation [6] or rearrangement [7] of diphenylphosphine adducts, and by the



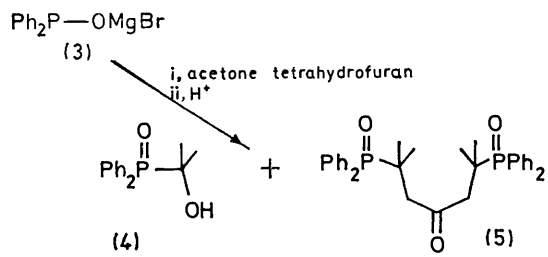
catalysed [8,9] or uncatalysed [10] addition of diphenylphosphine oxide to electrophilic π-systems.

[1] B. B. Hunt and B. C. Saunders, *J. Chem. Soc.*, 1957, 2413.
[2] J. B. Conant, J. B. S. Bravermann, and R. E. Hussey, *J. Amer. Chem. Soc.*, 1923, **45**, 165.
[3] L. Horner, P. Beck, and V. G. Toscano, *Chem. Ber.*, 1961, **94**, 1317.
[4] R. C. Miller, C. D. Miller, W. Rogers, and L. A. Hamilton, *J. Amer. Chem. Soc.*, 1957, **79**, 424.
[5] L. Horner, P. Beck, and V. G. Toscano, *Chem. Ber.*, 1961, **94**, 1323.
[6] H. Hellermann, J. Bader, H. Birkener, and O. Schumacher, *Annalen*, 1962, **659**, 49.
[7] S. Trippett, *J. Chem. Soc.*, 1961, 2813.
[8] L. Horner, H. Hoffmann, H. G. Wippel, and G. Klahre, *Chem. Ber.*, 1954, **92**, 2499.
[9] J. A. Miller, *Tetrahedron Letters*, 1969, 4335; A. J. Floyd, K. C. Symes, G. I. Fray, G. F. Gymer, and A. W. Oppenheimer, *Tetrahedron Letters*, 1970, 1735.
[10] U.K.A.E.A., Fr.P., 1314706/1963 (*Chem. Abs.*, 1963, **59**, 1682); I. G. M. Campbell and I. D. R. Stevens, *Chem. Comm.*, 1966, 505; R. C. Miller, *J. Org. Chem.*, 1959, **24**, 2013; N. Kreutzkamp and H. Storck, *Naturwiss.*, 1960, **47**, 497.

Each of these reactions involves an electrophilic substitution at phosphorus [11] in which the leaving group is a proton or a metal atom and the electrophile a carbonyl compound. We report a new reaction of this kind [12] in which the leaving group is carbon dioxide and describe new adducts formed by this and other reactions.

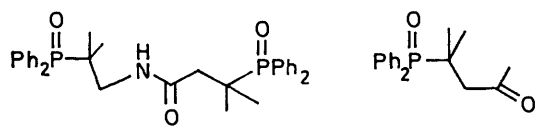
RESULTS

Additions of the Grignard Reagent.—The Grignard reagent from diphenylphosphine oxide [which is in fact [13] the magnesium ester (3)] is most conveniently prepared from diethyl phosphite and 3 mol. equiv. of phenylmagnesium bromide in tetrahydrofuran. Treatment of this solution with acetone, however, gave only 41% of the adduct (4),* and evaporation of the mother liquors revealed 22% of the symmetrical bisdiphenylphosphinyl ketone (5), presumably formed by the addition of the Grignard reagent (3) to phorone, itself formed by base-catalysed trimerisation of acetone. The base involved

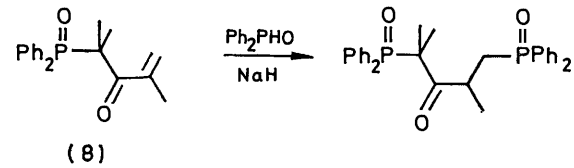


is ethoxide ion, released in the reaction of phenylmagnesium bromide with diethyl phosphite; when the Grignard reagent (3) was prepared directly from diphenylphosphine oxide and methylmagnesium iodide in the absence of any other base the acetone adduct (4) was isolated in 92% yield.

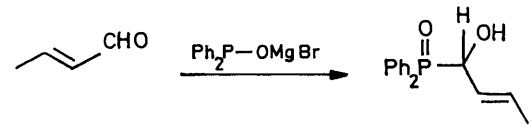
The ketone (5) reacts readily with hydroxylamine to give an oxime, and this rearranges in the usual way with phosphorus pentachloride to the amide (6), but neither base nor acid under the most vigorous conditions hydrolysed the amide. This is presumably a steric effect, though it is curious that oxime formation should not be more inhibited.



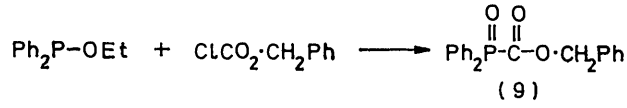
Additions to Enones.—We have already reported [14] that the addition of diphenylphosphine oxide to mesityl oxide to give the 3-oxo-phosphine oxide (7) is best accomplished with sodium hydride catalysis in tetrahydrofuran; addition in the Michael sense also occurs [15] with the very crowded ketone (8). However, crotonaldehyde gives a 1-hydroxyphosphine oxide, the product



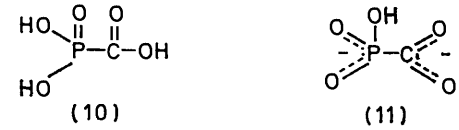
of direct addition to the carbonyl group, on treatment with either the Grignard reagent (3) or diphenylphosphine oxide and sodium hydride. Addition of the Grignard reagent (3) even gave the 1-hydroxyphosphine oxide in the presence of copper(I) iodide, and we have so far been unable to prepare the 1,4-adduct.



Benzyl Diphenylphosphinylformate.—The Arbuzow reaction with diphenylethoxyphosphine is the best way of making diphenylphosphinyl compounds providing that the correct halide is available; benzyl chloroformate gives a good yield of benzyl diphenylphosphinylformate (9) by this method. We have already described [16] the decarboxylation of phosphonoformic acid (10) in acid



solution. The carboxylate salt of this compound (11) does not decarboxylate since the first pK_a of the phosphonate group is lower (0·49) than that of the carboxylic acid (3·41) and there is little tendency to lose $HO{\cdot}PO_2^{-2}$ as a leaving group.



However, the diphenylphosphinylformate anion is not subject to this restraint, and the decarboxylation is so rapid that we have been unable to prepare either the free acid or a carboxylate salt in this series. One attempt, by the debenzylation of the ester (9) with sodium iodide in acetone, gave instead a strongly basic

* Previously prepared by other methods.[8]

[11] S. G. Warren, *Angew. Chem. Internat. Edn.*, 1968, **7**, 606.
[12] Preliminary communication, S. Warren and M. R. Williams, *Chem. Comm.*, 1969, 180.
[13] H. R. Hays, *J. Org. Chem.*, 1968, **33**, 3690; *J. Amer. Chem. Soc.*, 1969, **91**, 2736.
[14] P. F. Cann, D. Howells, and S. Warren, *J.C.S. Perkin II*, 1972, 304.
[15] D. Howells and S. Warren, unpublished observations.
[16] S. Warren and M. R. Williams, *J. Chem. Soc.* (*B*), 1971, 618.

solution from which the acetone adduct (4) precipitated on addition of water. This reaction proved to be an excellent method for preparing other 1-hydroxyalkyldiphenylphosphine oxides (12) either in the carbonyl compound as solvent or in dimethoxyethane. In the latter case, addition of 1 mol. equiv. of acetic acid gave higher yields (Table 1).

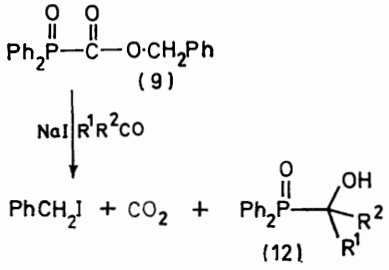
TABLE 1

Conversion of the diphenylphosphinylformate (9) into the adduct (12)

R^1	R^2	Solvent *	Yield of adduct (12) (%)
H	Me	MeCHO	55
Me	Me	Me_2CO	66
Me	Ph	PhCOMe	50
H	4-$O_2N{\cdot}C_6H_4$	DME [a]	83
H	2,4-$(NO_2)_2C_6H_4$	DME [b]	40

[a] With 1 equiv. of HOAc. [b] Containing 5% water.
* DME = Dimethoxyethane.

One advantage of this method is that it avoids altogether the troublesome preparation of diphenylphosphine oxide. All preparations of this secondary phosphine oxide seem to give a product contaminated with diphenylphosphinic acid, though this contaminant can be removed by dissolving the phosphine oxide in dry tetrahydrofuran and filtering off the insoluble acid. This serves another purpose, since the peroxides invariably present in anhydrous tetrahydrofuran oxidise diphenylphosphine oxide to more insoluble acid, and filtration gives a clean solution.



Mechanism.—The structures of the products reveal that three processes must occur in this reaction: (i) nucleophilic attack by I^- on the methylene group with cleavage of the C–O bond; (ii) decarboxylation; and (iii) formation of the new P–C bond. When the reaction was run with *p*-nitrobenzaldehyde in dimethoxyethane it was possible to follow the first stage by observing the 100 MHz n.m.r. spectrum at suitable intervals. The singlet at τ 4·71, corresponding to the methylene group, disappeared in a pseudo-first-order reaction and at a different rate from that of the disappearance of the aldehyde proton signal (τ 0·14) or the AB quartet of the aldehyde aromatic protons (τ 1·77). Variation of iodide concentration and temperature showed that the debenzylation was in fact a second-order reaction (Table 2), $\Delta S^{\ddagger} = -30{\cdot}7$ cal mol^{-1} K^{-1} at 30°.

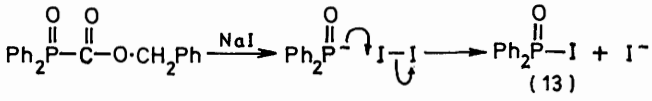
TABLE 2

Second-order rate constants for the debenzylation of benzyl diphenylphosphinylformate

T/°C	$10^5 k_2$/l mol^{-1} s^{-1}
30	2·25
42	7·02
50	11·51

$\Delta H^{\ddagger} = 15{\cdot}5$ kcal mol^{-1}. $\Delta S^{\ddagger} = -30{\cdot}7$ cal mol^{-1} K^{-1}

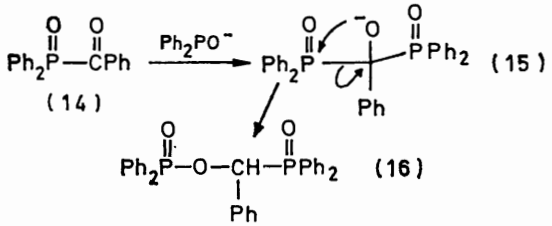
In a competition experiment, the ester was debenzylated in the presence of equimolecular amounts of acetone and *p*-nitrobenzaldehyde: only the aldehyde adduct was formed. Other electrophiles than carbonyl groups gave the expected results: iodine (only a catalytic quantity of sodium iodide was needed) in 50% aqueous dimethoxyethane gave a 94% yield of diphenylphosphinic acid, presumably by hydrolysis of the intermediate (13). In methanol as solvent iodine and sodium iodide gave



methyl diphenylphosphinite, as expected from the methanolysis of the intermediate (13), together with a considerable amount of diphenylphosphinic acid.

Reaction with benzoyl chloride should first produce the acylphosphine oxide (14). Compounds of this class are notoriously difficult to prepare, as the carbonyl group is extremely electrophilic,[17] and in fact the compound isolated from this reaction was the phosphinite ester (16), previously prepared [18] by the reaction of benzoic acid with tetraphenyldiphosphine. Presumably diphenylphosphinyl anion adds to the arylphosphine oxide (14) to give the anion (15), which undergoes a three-centre rearrangement known to occur with this type of compound.[17,19]

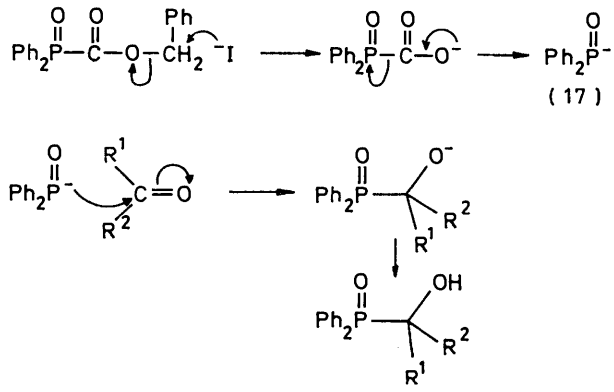
Conclusions.—The reaction begins with the bimolecular attack of iodide ion, a soft nucleophile, on the CH_2



group, a soft electrophilic centre. We expect the decarboxylation to be fast, and it is reasonable then to

[17] Organophosphorus Chemistry, vol. 2, Chem. Soc. Special. Rev. Report, 1971, pp. 56—58.
[18] R. S. Davidson, R. A. Sheldon, and S. Trippett, *J. Chem. Soc.* (*C*), 1967, 1547.
[19] A. N. Pudovik, I. V. Gur'yanova, M. G. Zimin, and A. V. Durneva, *Zhur. obshchei Khim.*, 1969, **39**, 1018.

postulate the anion (17) as an intermediate. Its reaction with the carbonyl group is then that of a hard nucleophile with a hard electrophile. The decarboxylation may be concerted with the addition to the carboxy-group.



(17)

Although there are many cases of *intra*molecular S_EP reactions involving the making and breaking of P–C bonds (phosphorus migrations [17]) the decarboxylation reaction is an unusual if not unique example of an *inter*molecular reaction of this kind.

EXPERIMENTAL

1-*Hydroxy*-1-*methylethyl*(*diphenyl*)*phosphine Oxide* (4) *by the Grignard Method.*—Diphenylphosphine oxide [1] (5·05 g, 25 mmol) in tetrahydrofuran (50 ml) was treated with a solution of methylmagnesium iodide [from methyl iodide (2·84 g, 20 mmol) and magnesium (0·5 g, 20 mmol)] in tetrahydrofuran (10 ml), and acetone (1·2 g, 20 mmol) was added to the resulting solution. Bromine was dripped in to remove excess diphenylphosphine oxide until a faint brown colour remained. The solvent was removed under reduced pressure and the residue taken up in dichloromethane (25 ml). This solution was washed with sodium hydrogen carbonate solution (10 ml) to remove diphenylphosphinic acid, then with water (10 ml), dried ($MgSO_4$), and evaporated to give the phosphine oxide (4) (2·4 g, 92%), m.p. 144—145° (decomp.) [lit.,[8] 152° (decomp.)]. Horner [8] prepared this compound by the addition of diphenylphosphine oxide to acetone, but characterised it only by m.p. and C and H analysis. It has $\nu_{max.}$ (Nujol) 3170 (OH), 1440 (P–Ph), and 1135 (P=O) cm^{-1}, τ ($CDCl_3$) 1·9—2·6 (10H, m, Ph_2PO), 7·15 (1H, s, OH), and 8·55 (6H, d, J_{PH} 13 Hz, $PCMe_2$); the mass spectrum shows no M^+, but has *m/e* 202 ($Ph_2\dot{P}HO$, 100%) (Found: C, 69·4; H, 6·9; P, 11·5. Calc. for $C_{15}H_{17}O_2P$: C, 69·4; H, 6·8; P, 11·9%).

Bis-(2-*methyl*-2-*diphenylphosphinylpropyl*) *Ketone* (5).—Bromobenzene (314 g, 2 mol) in tetrahydrofuran (300 ml) was added dropwise and with stirring to magnesium turnings (48 g, 2 mol) under tetrahydrofuran (300 ml). When almost all the magnesium had dissolved, the solution was cooled, and redistilled diethyl phosphite (92 g, 0·66 mol) in tetrahydrofuran (300 ml) was added slowly. The solution was refluxed for 0·5 h and cooled, and acetone (58 g, 1 mol) was added. The white precipitate which appeared was removed and treated with dil. hydrochloric acid to give 1-hydroxy-1-methylethyl(diphenyl)phosphine oxide (70 g, 41%). Evaporation of the mother liquors, treatment with dil. hydrochloric acid, extraction with ether (3 × 100 ml), and evaporation of the extract gave the *ketone* (5) (39 g, 22), m.p. 181—182° (from ethyl acetate), $\nu_{max.}$ (Nujol) 1710 (ketone C=O), 1446 (P–Ph), and 1180 cm^{-1} (P=O), τ ($CDCl_3$) 1·8—2·6 (20H, m, $POPh_2$), 7·36 (4H, d, J_{HP} 8 Hz, $PCMe_2$·CH_2), and 8·64 (12H, d, J_{PH} 15·5 Hz, $PCMe_2$), *m/e* 542 (M^+, 5%) and 202 ($Ph_2PHO^{+\cdot}$, 100%).

Bis-(2-*methyl*-2-*diphenylphosphinylpropyl*) *Ketone Oxime.*—Hydroxylamine hydrochloride (5·6 g, 0·08 mol), the ketone (5) (21·7 g, 0·04 mol), and triethylamine (5 ml), were dissolved in absolute ethanol (30 ml) and refluxed for 22 h. The solution was poured into ice–water (200 ml), conc. hydrochloric acid (5 ml), and dichloromethane (50 ml), and the precipitate was filtered off. Recrystallisation from aqueous ethanol gave the *oxime* (17·5 g, 77%), m.p. 218—219°, $\nu_{max.}$ 3400, 3200 (OH), 1650 (C=N), 1446 (PPh), and 1175 (P=O) cm^{-1}; τ 1·9—2·7 (20H, m, $POPh_2$), 7·34 (2H, d, J_{PH} 7·5 Hz, 2H, CH_2·C=NOH), 7·50 (2H, d, J_{PH} 7·5 Hz, CH_2·C=NOH), and 8·82 (12H, d, J_{PH} 15·5 Hz, $PCMe_2$).

3-*Methyl*-N-(2-*methyl*-2-*diphenylphosphinylpropyl*)-3-*diphenylphosphinylbutyramide* (6).—To the foregoing oxime (0·279 g) suspended in tetrahydrofuran (10 ml) at 0° was added phosphorus pentachloride (0·5 g) with stirring. The oxime gradually dissolved. After 30 min, the solution was poured into water (100 ml) and extracted with dichloromethane (4 × 25 ml). The extracts were dried ($MgSO_4$) and evaporated to give an oil which crystallised on trituration with tetrahydrofuran (5 ml) and gave the *amide* (6) (0·26 g, 93%), m.p. 142—144° (from aqueous ethanol), $\nu_{max.}$ 3220 (NH), 1655 (amide I), 1550 (amide II), 1440 (PPh), and 1170 (P=O) cm^{-1}, τ 1·9—2·7 (20H, m, Ph_2PO), 2·25 (1H, t, J_{HH} 7 Hz, NHCO), 6·55 (2H, dd, J_{HH} 7, J_{PH} 16 Hz, CH_2·NH·CO), 8·52 (2H, d, J_{PH} 9 Hz, CH_2·CO·NH), 8·60 (6H, d, J_{PH} 16 Hz, CMe_2·CH_2·CO), and 8·78 (6H, d, J_{PH} 16 Hz, CMe_2·CH_2·NH).

Additions to Crotonaldehyde.—(a) *Grignard method.* Diphenylphosphine oxide (5·0 g) in tetrahydrofuran (20 ml) was added slowly to a solution of methylmagnesium iodide [from methyl iodide (3·5 g) and magnesium (0·6 g)] in tetrahydrofuran (10 ml). The mixture was heated under reflux for 30 min, and cooled to 0°, and crotonaldehyde (1·75 g) in tetrahydrofuran (20 ml) also at 0° was added slowly. The mixture was stirred at 0° for 1 h, then poured into aqueous ammonia–ammonium chloride buffer (pH 8; 20 ml). The aqueous layer was extracted with tetrahydrofuran (20 ml) and the combined organic layers were dried ($MgSO_4$) and evaporated. The residue was dissolved in chloroform (50 ml) and washed with aqueous sodium hydrogen carbonate solution (2 × 20 ml). The chloroform was removed and the residue dissolved in the minimum amount of ethyl acetate. Cooling this solution to −60° produced white crystals of 1-*hydroxybut*-2-*enyl*(*diphenyl*)*phosphine oxide* (4 g), m.p. 122—125°, $\nu_{max.}$ (Nujol) 3200br (OH), 1665 (C=C), 1440 (PPh), and 1175 (P=O) cm^{-1}, τ ($CDCl_3$) 2·1—2·6 (10H, m, Ph_2PO), 4·40 (2H, m, HC=CH), 5·00 (1H, s, OH), 5·10 (1H, m, C*H*·OH), and 8·23 (3H, m, CH_3), *m/e* 272 (M^+, <1%), 201 (Ph_2PO, 100%), 71 (M − Ph_2PO, 4%), 70 (M − Ph_2POH, 18%), and 69 (CH_3·CH=CH·CO^+, 19%).

(b) *Grignard method with copper*(I) *iodide.* The Grignard reagent was prepared as in method (a) but copper(I) iodide (0·48 g) was added before the crotonaldehyde. The mixture was worked up in the same way to give the same product.

(c) *Anion method.* Sodium hydride (50% dispersion in oil; 0·004 g) was added to a solution of diphenylphosphine oxide (3 g) in tetrahydrofuran (25 ml), and crotonaldehyde (1·05 g) in tetrahydrofuran (25 ml) was slowly added to the stirred mixture. After 1 h the mixture was worked up as under (a) to give the same product.

Benzyl diphenylphosphinylformate (9).—Benzyl chloroformate (23 g, 0·135 mol) was added dropwise during 30 min to ethoxy(diphenyl)phosphine (30·6 g, 0·133 mol) at 110°. The mixture was stirred at this temperature for a further 30 min then taken up in ether (200 ml); the mixture was filtered to give a solid which was recrystallised from benzene and identified as benzyldiphenylphosphine oxide [20] (13·6 g) from its n.m.r. and mass spectra. The filtrate was evaporated and the residue recrystallised from 1 : 1 ether–petroleum and then from carbon tetrachloride to give the *ester* (9) (13·7 g, 31%), m.p. 96—97°, $\nu_{max.}$ (Nujol) 1695 (ester C=O), 1435 (P–Ph), and 1240 (P=O) cm^{-1}, τ ($CDCl_3$) 2·1—2·8 (15H, m, aromatic) and 4·76 (2H, s, $PhCH_2{\cdot}O$), *m/e* 336 (M^+, 1%) (Found: C, 71·4; H, 5·1; P, 8·9. $C_{20}H_{17}O_3P$ requires C, 71·4; H, 5·1; P, 9·2%).

Reactions of Benzyl Diphenylphosphinylformate with Carbonyl Compounds.—(i) *Acetone.* The benzyl ester (9) (3·36 g, 10 mmol) was dissolved in acetone (50 ml) containing sodium iodide (1·5 g, 10 mmol) and the mixture refluxed for 17 h. The solution was filtered from a white solid (350 mg; the sodium salt of the product) and evaporated to a gum; this was extracted with chloroform (3 × 20 ml), leaving sodium iodide (820 mg) undissolved. The chloroform solution was evaporated to a gum and triturated with ether to give 1-hydroxy-1-methylethyl(diphenyl)phosphine oxide, m.p. 145—146° (decomp.) (from chloroform) [lit.,[8] 152° (decomp.)] (1·2 g, 54%).

(ii) *Acetaldehyde.* The same method with benzyl diphenylphosphinylformate (336 mg) and sodium iodide (150 mg) in acetaldehyde (2 ml) gave 1-*hydroxyethyl(diphenyl)phosphine oxide* (135 mg, 55%), m.p. 129—129·9 (from acetonitrile), $\nu_{max.}$ (Nujol) 3130 (OH), 1440 (P–Ph), and 1150 (P=O) cm^{-1}, τ ($CDCl_3$) 1·9—2·7 (10H, m, Ph_2PO), 5·40 (1H, dq, J_{PH} 1·0, J_{HH} 7·0 Hz, CH), 5·92 (1H, s, OH), and 8·57 (3H, dd, J_{PH} 15·0, J_{HH} 7·0 Hz, CMe), *m/e* (no M^+) 202 (base peak, $M - CH_3CHO$) (Found: C, 66·8; H, 6·1; P, 13·7. $C_{14}H_{15}O_2P$ requires C, 68·3; H, 6·15, P, 12·6%).

(iii) *Acetophenone.* The same method with benzyl diphenylphosphinylformate (336 mg), sodium iodide (150 mg), and acetophenone (5 ml) gave 1-*hydroxy*-1-*phenylethyl(diphenyl)phosphine oxide* (162 mg, 50%), m.p. 109—111° (from aqueous ethanol and ether), $\nu_{max.}$ (Nujol) 3610 and 3320 (OH), 1430 (P–Ph), and 1150 (P=O) cm^{-1}, τ [$(CD_3)_2SO$] 1·8—3·1 (15H, m, aromatic) and 8·36 (3H, d, J_{PH} 14·0 Hz, CMe).

(iv) 4-*Nitrobenzaldehyde.* Benzyl diphenylphosphinylformate (6·72 g, 20 mmol) was dissolved in dry, peroxide-free dimethoxyethane (100 ml). To this were added 4-nitrobenzaldehyde (3·02 g, 20 mmol), sodium iodide (6·0 g, 40 mmol), and glacial acetic acid (1·14 ml, 20 mmol). After 24 h at room temperature white crystals had separated; heating at 100° for 5 min completed the reaction (t.l.c.). Water (3 × 300 ml) was added and the crystals were collected, washed with ether to remove benzyl iodide, and recrystallised from aqueous ethanol to give α-hydroxy-4-nitrobenzyl(diphenyl)phosphine oxide, m.p. 186·5—188·5° (lit.,[21] 191·5—193·0), $\nu_{max.}$ (Nujol) 3150 (OH), 1535 and 1365 (Ar–NO_2), 1440 (P–Ph), and 1165 (P=O) cm^{-1}, τ [$(CD_3)_2SO$] 1·8—2·7 (14H, m, aromatic), 3·17 (1H, dd, J_{PH} 17·0, J_{HH} 6·0 Hz, OH), and 4·20 (1H, dd, J_{PH} 10·0, J_{HH} 6·0 Hz, CH).

(v) 2,4-*Dinitrobenzaldehyde.* Benzyl diphenylphosphinylformate (672 mg, 2 mmol), sodium iodide (600 mg, 4 mmol), and 2,4-dinitrobenzaldehyde (392 mg, 2 mmol) were dissolved in dimethoxyethane (9·5 ml) and water (0·5 ml). The solution was left at room temperature for 24 h, water (30 ml) was added, and the product was recrystallised from aqueous ethanol to give α-*hydroxy*-2,4-*dinitrobenzyl(diphenyl)phosphine oxide* as pale yellow needles (246 mg, 31%), m.p. 173—174°, $\nu_{max.}$ (Nujol) 3120 (OH), 1540 and 1350 (Ar–NO_2), 1440 (P–Ph), and 1150 (P=O) cm^{-1}, τ [$(CD_3)_2SO$] 1·3—2·8 (13H, m, aromatic), 3·25 (1H, dd, J_{PH} 12, J_{HH} 6 Hz, CH), and 3·05 (1H, dd, J_{PH} 4, J_{HH} 6 Hz, OH) (Found: C, 56·6; H, 3·8; P, 8·6; N, 6·8. $C_{19}H_{15}N_2O_6P$ requires C, 57·3; H, 3·9; P, 7·8; N, 7·0%).

(vi) *Mixed carbonyl compounds.* Benzyl diphenylphosphinylformate (672 mg, 2 mmol) and sodium iodide were dissolved in dimethoxyethane (10 ml). Acetone (0·147 ml, 2 mmol), 4-nitrobenzaldehyde (302 mg, 2 mmol), and acetic acid (0·114 ml, 2 mmol) were added and the solution was left at room temperature for 2 days. Water (30 ml) was added; the precipitate was collected, washed with ether, and dried to give α-hydroxy-4-nitrobenzyl(diphenyl)-phosphine oxide (610 mg, 86·5%). The mother liquors showed no trace of the acetone adduct (4) (t.l.c.).

(vi) *Benzoyl chloride.* Benzyl diphenylphosphinylformate (3·36 g, 10 mmol), sodium iodide (3·0 g, 20 mmol), and benzoyl chloride (1·4 g, 10 mmol) were dissolved in dimethoxyethane (100 ml). A white precipitate (NaCl) formed at once. After 0·5 h more sodium iodide was added (1·5 g, 10 mmol) and the mixture left at room temperature for 4 days. The precipitate was removed, the solvent evaporated off, and the residue taken up in chloroform, leaving the excess of sodium iodide undissolved. The solution was evaporated to an oil and triturated with light petroleum to give white crystals which were recrystallised from ethyl acetate and then from acetone to give α-(diphenylphosphinyloxy)benzyl(diphenyl)phosphine oxide (1·2 g, 47%), softens 190—191°, decomp. 216—218° (lit.,[18] m.p. 190—191°), i.r. and n.m.r. spectra identical with those reported by Trippett.[18]

Reaction of Benzyl Diphenylphosphinylformate with Iodine.—(i) *In aqueous solution.* Benzyl diphenylphosphinylformate (336 mg, 1 mmol), iodine (245 mg, 1 mmol), and sodium iodide (15 mg, 0·1 mmol) were dissolved in 1 : 1 aqueous dimethoxyethane (5 ml). The mixture was refluxed for 16 h, the solvent was removed under vacuum, water (10 ml) was added, and the precipitate (205 mg, 94%) was collected. Recrystallisation from chloroform gave diphenylphosphinic acid, identical with an authentic sample.

(ii) *In methanolic solution.* Benzyl diphenylphosphinylformate (336 mg, 1 mmol) was dissolved in methanol (5 ml), and sodium iodide (150 mg, 1 mmol) and iodine (234 mg, 1 mmol) were added. The solution was refluxed for 16 h, the methanol was removed under reduced pressure, and the residue was taken up in chloroform and washed with sodium thiosulphate solution to remove iodine. The chloroform was evaporated off, the residue was dissolved in benzene and the solution was filtered to give diphenylphosphinic acid (150 mg). Evaporation of the benzene filtrate gave methyl diphenylphosphinite (80 mg), τ ($CDCl_3$) 2·2—2·8 (10H,

[20] A. Michaelis and W. La Coste, *Ber.*, 1885, **18**, 2109.
[21] R. S. Marmor and D. Seyferth, *J. Org. Chem.*, 1969, **34**, 847.

Ph_2PO), and 6·4 (3H, d, J_{PH} 14·0 Hz, POMe), identical with an authentic specimen.

Rate of Debenzylation of Benzyl Diphenylphosphinylformate.—Dimethoxyethane was distilled from lithium aluminium hydride to remove peroxides. The reaction mixture was made up from benzyl diphenylphosphinylformate (2·0 ml of 0·5M-solution in dimethoxyethane containing 10% water), 4-nitrobenzaldehyde (2·0 ml of 0·5M-solution in the same solvent), acetic acid (0·114 ml), and trichloroethylene (0·1 ml, as a reference standard), and the reaction was started by the addition of sodium iodide (4·0 ml, 1M in the same solvent): the total volume of solution was 10 ml. A sample of this solution was transferred to an n.m.r. tube and the n.m.r. spectrum was recorded at intervals. The constant temperature bath and the n.m.r. probe were kept at the same temperature (±0·5°). Each spectrum was integrated seven times. The machine was locked on the dimethoxyethane signal (MeO protons) instead of tetramethylsilane.

The concentration of benzyl diphenylphosphinylformate was measured from the integral of the methylene protons of the benzyl group (signal from trichloroethylene as standard).

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