The Reactions of Tetraphenyldiphosphine with Aliphatic Carboxylic Acids and with Aldehydes

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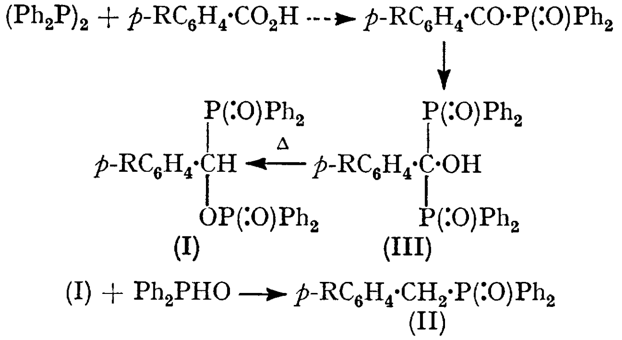
Tetraphenyldiphosphine and aliphatic carboxylic acids at 180° give 1-hydroxy-1,1-bisdiphenylphosphinylalkanes which slowly rearrange to 1-diphenylphosphinyloxyalkyldiphenylphosphine oxides. The acids $Ph{\cdot}X{\cdot}CH_2{\cdot}CO_2H$ (X = O or S) also give the esters $Ph_2P(\colon O)XPh$. Di- and tri-phenylacetic acids give only di- and tri-phenylmethanes with the formation of carbon monoxide.

Tetraphenyldiphosphine and aldehydes at 180° give 1-hydroxyalkyldiphenylphosphines and 1-acyloxyalkyldiphenylphosphines isolated as their oxides. With aromatic aldehydes having a *para*-substitutent capable of electron supply, these are further reduced to benzyldiphenylphosphine oxides.

We previously showed[1] that aromatic carboxylic acids on heating with tetraphenyldiphosphine give phosphinyloxyphosphine oxides (I) when R is electron attractive, or benzylphosphine oxides (II) when R is capable of electron supply. These reactions were shown to involve formation of aroyldiphenylphosphines and/or their oxides, followed by addition to the carbonyls of diphenylphosphine oxide and rearrangement of the α-hydroxydiphosphine dioxides (III) to the phosphinyloxyphosphine oxides (I) which are further reduced by diphenylphosphine oxide to the oxides (II) when R is capable of electron supply. At that time experiments with aliphatic carboxylic acids seemed to be pursuing a different course and difficulty was experienced in isolating pure products. We have now shown that this difficulty was due to the relatively slow rearrangement of the α-hydroxydiphosphine dioxides (IV) which in some cases can be isolated.



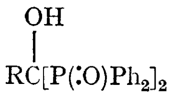
$$(Ph_2P)_2 + p\text{-}RC_6H_4{\cdot}CO_2H \dashrightarrow p\text{-}RC_6H_4{\cdot}CO{\cdot}P(\colon O)Ph_2$$

$$p\text{-}RC_6H_4{\cdot}\underset{OP(\colon O)Ph_2}{\overset{P(\colon O)Ph_2}{CH}} \xleftarrow{\Delta} p\text{-}RC_6H_4{\cdot}\underset{P(\colon O)Ph_2}{\overset{P(\colon O)Ph_2}{C}}{\cdot}OH$$

(I) (III)

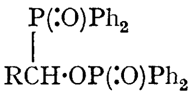
$$(I) + Ph_2PHO \longrightarrow p\text{-}RC_6H_4{\cdot}CH_2{\cdot}P(\colon O)Ph_2$$

(II)



$$R\overset{OH}{C}[P(\colon O)Ph_2]_2$$

(IV)



$$RCH{\cdot}\overset{P(\colon O)Ph_2}{}OP(\colon O)Ph_2$$

(V)

3-Phenylpropionic acid and tetraphenyldiphosphine at 180—200° for 4 hr. gave two isomeric compounds, $C_{33}H_{30}O_3P_2$, whose formulae were confirmed by mass spectrometry. The first showed absorption in the i.r. characteristic of phosphine oxides (1180 cm.$^{-1}$) and of hydrogen-bonded hydroxy (3200 cm.$^{-1}$, broad) and is therefore the α-hydroxydiphosphine dioxide (IV; $R = PhCH_2{\cdot}CH_2$). On keeping at 200° for 15 hr. it gave the second compound which showed no hydroxy-absorption but had absorption characteristic of phosphine oxides and of phosphinates [1230 (P:O) and a doublet centred on 1000 cm.$^{-1}$ (P·O·C)]. The mass spectrum of the second isomer contained the fragment *m/e* 217 (Ph_2PO_2) and the compound is therefore the phosphine oxide–phosphinate (V; $R = PhCH_2{\cdot}CH_2$). The slow rearrangement of the α-hydroxydiphosphine dioxide (IV; $R = PhCH_2{\cdot}CH_2$) relative to the dioxides (III), which were never detected in the reactions of tetraphenyldiphosphine with aromatic carboxylic acids, agrees with mechanism for the rearrangement in which the α-carbon developes carbanion character.

The α-hydroxydiphosphine dioxide (IV; R = Me) was obtained from acetic anhydride and two mol. of diphenylphosphine oxide at 100°. The ^1H n.m.r. spectrum showed the methyl as a 1 : 2 : 1 triplet at τ 8·55 (J_{PH} 14·5 c./sec.). At 200° the dioxide rearranged to the oxide–phosphinate (V; R = Me); the ^1H n.m.r. spectrum now showed the methyl as a quartet at τ 8·45 (J_{HH} 7 c./sec., J_{PH} 14 c./sec.).

Acetyldiphenylphosphine was prepared by Isslieb and Priebe[2] from sodium diphenylphosphide and acetyl chloride. We obtained it from acetic anhydride and one mol. equivalent of diphenylphosphine at 100°. Isslieb oxidised the phosphine with pure oxygen to give " acetyldiphenylphosphine oxide ", m.p. 158—159°. In our hands the oxidation has given only the α-hydroxydiphosphine dioxide (IV; R = Me), m.p. 159—160°, presumably formed by the addition of diphenylphosphine oxide (formed from adventitious water) to the highly reactive acetyldiphenylphosphine oxide. More recently Isslieb and Löw[3] reported the preparation, from acetyl chloride and the potassium salt of dibutylphosphine oxide, of acetyldibutylphosphine oxide having the unexpectedly high b.p. of 224—247°/8—10 mm. Similar reactions in our hands have given complex mixtures of high-boiling compounds probably formed by further addition to the acetylphosphine oxides.

Phosphinyloxyphosphine oxides (V) were also obtained from tetraphenyldiphosphine and phenylacetic, isovaleric, and phenoxyacetic acids. In the reaction with phenylacetic acid, toluene (21%) was also formed.

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[1] R. S. Davidson, R. A. Sheldon, and S. Trippett, *J. Chem. Soc.* (*C*), 1967, 1547.

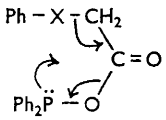
[2] K. Isslieb and E. Priebe, *Chem. Ber.*, 1959, **92**, 3183.

[3] K. Isslieb and O. Löw, *Z. anorg. Chem.*, 1966, **346**, 241.

With diphenylacetic and triphenylacetic acids no oxides corresponding to (V) were formed but diphenylmethane (27%) and triphenylmethane (46%) were isolated. The acids did not decarboxylate when heated alone at 200° and in the reaction with diphenylacetic acid carbon monoxide, but not carbon dioxide, was detected. The hydrocarbons probably result from the homolytic decomposition of acyl or acyloxyphosphine oxides to give acyl radicals which decarbonylate.

$$Ph_2P{\cdot}O{\cdot}COR \longrightarrow Ph_2PO^{\bullet} + RCO^{\bullet}$$
$$RCO^{\bullet} \longrightarrow R^{\bullet} + CO$$

In the reaction of tetraphenyldiphosphine with phenoxyacetic acid, phenyl diphenylphosphinate was formed in addition to the phosphinyloxyphosphine oxide (V; R = PhO·CH$_2$) and similarly (phenylthio)-acetic acid gave *S*-phenyl diphenylphosphinothioate. The origin of these phosphinates is obscure: they are not formed by an intramolecular elimination of ketene from the acyloxyphosphines (VI) which were obtained independently from chlorodiphenylphosphine and the sodium salts of the acids. Acetoxydiphenylphosphine was also prepared by this route. Like benzoyloxydiphenylphosphine[1] it gave the acid anhydride and tetraphenyldiphosphine monoxide on heating.



(VI)

Reactions of Tetraphenyldiphosphine with Aldehydes.—Tetraphenyldiphosphine and an excess of benzaldehyde at 180° gave α-hydroxybenzyldiphenylphosphine oxide (VII; R = Ph) and its benzoate (VIII; R = Ph). Oxidation must have occurred during the isolation and indeed treatment of the reaction mixture with methyl iodide gave the methiodide of α-hydroxybenzyldiphenylphosphine. *p*-Isopropylbenzaldehyde similarly gave analogous oxides together with *p*-isopropylbenzyldiphenylphosphine oxide. Nicotinaldehyde behaved similarly. Anisaldehyde gave only *p*-methoxybenzyldiphenylphosphine oxide while *p*-cyanobenzaldehyde gave only α-hydroxy-*p*-cyanobenzyldiphenylphosphine oxide in low yield.

It was originally thought that these were radical reactions involving diphenylphosphinyl and aroyl radicals, but in the reaction of tetraphenyldiphosphine with 2-phenylpropionaldehyde, giving 1-hydroxy-3-phenylpropyldiphenylphosphine oxide, no ethylbenzene could be detected and the acyl radical cannot therefore be involved. An ionic mechanism in which the first stage is the formation of diphenylphosphine and acyldiphenylphosphine is possible. The diphenylphosphine would then add to the aldehyde to give an α-hydroxybenzyldiphenylphosphine (VII) which would be acylated by the acyldiphenylphosphine.[3] With a *para*-substituent capable of electron supply the phosphine (IX) would be further reduced by diphenylphosphine to a benzyldiphenylphosphine in a reaction analogous to the reduction of the corresponding α-phosphinyloxy-compounds.[1]

$$(Ph_2P)_2 + RCHO \longrightarrow Ph_2PH + RCO{\cdot}PPh_2$$
$$Ph_2PH + RCHO \longrightarrow \underset{\text{(VII)}}{RCH(OH)PPh_2}$$

$$RCH(OH)PPh_2 + RCO{\cdot}PPH_2 \longrightarrow \underset{\text{(VIII)}}{RCH(O{\cdot}COR)PPh_2} + Ph_2PH$$

$$\underset{\text{(IX)}}{ArCH(O{\cdot}COAr)PPh_2} + Ph_2PH \longrightarrow ArCH_2{\cdot}PPh_2 + Ph_2P{\cdot}O{\cdot}COAr$$

EXPERIMENTAL

All experiments were carried out under oxygen-free nitrogen. Light petroleum had b.p. 60—80°. ^{1}H N.m.r. spectra were recorded for solutions in deuteriochloroform on a Varian A-60 spectrometer. Mass spectra were determined on an A.E.I. MS 9 instrument; in each case the mass peak is given first followed by those of structural significance.

Reaction of Tetraphenyldiphosphine with 3-*Phenylpropionic Acid.*—The diphosphine (3 g.) and 3-phenylpropionic acid (1·25 g.) were kept at 180—200° for 3 hr. The mixture was dissolved in chloroform, washed with dilute aqueous sodium hydroxide and water, and dried. Evaporation and trituration of the residue with ether gave 1,1-*bisdiphenylphosphinyl*-3-*phenylpropan*-1-*ol* (1·2 g.), m.p. 155—156° (from benzene), $\nu_{max.}$ 1180 and 3200 cm.$^{-1}$, *m/e* 536, 335, and 201 (Found: C, 74·3; H, 5·6; P, 11·8. $C_{33}H_{30}O_3P_2$ requires C, 73·9; H, 5·6; P, 11·6%). Evaporation of the ether gave an oil which was dissolved in chloroform, washed with alkaline hydrogen peroxide solution and water, and dried. Evaporation and trituration with ether gave 1-*diphenylphosphinyl*-1-*diphenylphosphinyloxy*-3-*phenylpropane* (1·4 g.), m.p. 147—148° (from ethyl acetate), $\nu_{max.}$ 960, 1030, 1205, and 1230 cm.$^{-1}$, *m/e* 536, 335, 319, 217, and 201 (Found: C, 74·1; H, 5·8; P, 11·7. $C_{33}H_{30}O_3P_2$ requires C, 73·9; H, 5·6; P, 11·6%). The 1,1-bisdiphenylphosphinyl-3-phenylpropan-1-ol was kept at 180—200° for 15 hr. Crystallisation from ethyl acetate gave 1-diphenylphosphinyl-1-diphenylphosphinyloxy-3-phenylpropane, m.p. and mixed m.p. 147—148° (from ethyl acetate).

Reaction of Acetic Anhydride with Diphenylphosphine Oxide.—Acetic anhydride (0·6 g.) and diphenylphosphine oxide (2·02 g.) were kept at 100° for 6 hr. The reaction mixture was dissolved in chloroform, washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated. Evaporation and trituration with ether gave 1,1-*bisdiphenylphosphinylethanol* (0·9 g.), m.p. 159—160° (from benzene–ether), $\nu_{max.}$ 1110 and 1180 cm.$^{-1}$, triplet at τ 8·5 (3H, J_{PH} 15 c./sec.) (Found: C, 69·8; H, 5·2; P, 14·1. $C_{26}H_{24}O_3P_2$ requires C, 70·0; H, 5·4; P, 13·9%). This oxide was kept at 180—200° for 3 hr. and distilled to give 1-diphenylphosphinyl-1-diphenylphosphinyloxyethane, b.p. 280—290°/0·2 mm., $\nu_{max.}$ 950, 1060, and 1230 cm.$^{-1}$, quadruplet at τ 8·45 (3H, J_{HH} 7 c./sec., J_{PH} 14 c./sec.), complex multiplet at τ 3·5 (1H), *m/e* 446, 217, and 201.

Reaction of Acetic Anhydride with Diphenylphosphine.—Acetic anhydride (4·5 g.) and diphenylphosphine (7·5 g.) were kept at 100° for 3 hr. Distillation gave acetyldiphenylphosphine (7·5 g.), b.p. 137—140°/0·8 mm. (lit.,[2] 143—146°/2—5 mm.), $\nu_{\text{max.}}$ 1670 cm.$^{-1}$.

Oxidation of Acetyldiphenylphosphine.—Pure, dry oxygen was bubbled through a solution of acetyldiphenylphosphine (1·0 g.) in benzene (50 ml.) for 1 hr. Evaporation and trituration with ether gave 1,1-bisdiphenylphosphinylethanol (0·7 g.), m.p. and mixed m.p. 159—160° (from benzene–ether).

Reaction of Tetraphenyldiphosphine with Phenylacetic Acid.—The diphosphine (3 g.) and the acid (1·2 g.) were kept at 180—200° for 3 hr. The mixture was dissolved in chloroform, washed with dilute aqueous sodium hydroxide and water, and dried. G.l.c. analysis (2 m. silicone gum rubber column at 70°) of the solution showed that toluene (21%) had been produced. Evaporation of the chloroform gave an oil which crystallised slowly from ether–ethyl acetate to give 1-*diphenylphosphinyl*-1-*diphenylphosphinyloxy*-2-*phenylethane* (0·9 g.), m.p. 83—84° (from ether–ethyl acetate), $\nu_{\text{max.}}$ 995, 1010, 1040, 1190, and 1230 cm.$^{-1}$ (Found: C, 72·9; H, 5·4; P, 11·7. $C_{38}H_{28}O_3P_2$ requires C, 73·5; H, 5·4; P, 11·9%).

1-*Diphenylphosphinyl*-1-*diphenylphosphinyloxy*-2-*phenylethane.*—Phenylacetic anhydride (2·54 g.) and diphenylphosphine oxide (4·02 g.) were kept at 100° for 2 hr. The mixture was dissolved in chloroform, washed with aqueous sodium hydrogen carbonate and water, and dried. Evaporation left an oil which slowly crystallised from ether to give 1-diphenylphosphinyl-1-diphenylphosphinyloxy-2-phenylethane (2·6 g.), m.p. and mixed m.p. 83—84° (from ether–ethyl acetate).

Reaction of Tetraphenyldiphosphine with Diphenylacetic Acid.—The diphosphine (3·0 g.) and diphenylacetic acid (1·8 g.) were kept at 180—200° for 3 hr. An i.r. spectrum of the gases evolved showed carbon monoxide and not carbon dioxide was produced. The reaction mixture was dissolved in chloroform, washed with alkaline hydrogen peroxide and water, and dried. Acidification of the alkaline extract gave diphenylphosphinic acid (2·7 g.), m.p. and mixed m.p. 192—193° (from aqueous ethanol). Evaporation of the chloroform left an oil which was placed on a column of silica gel. Elution with benzene gave diphenylmethane (0·36 g.), identified by i.r. spectroscopy. Elution with ether gave (diphenylmethyl)diphenylphosphine oxide (0·04 g.), m.p. and mixed m.p. 304—305° (from methanol).

Reaction of Tetraphenyldiphosphine with Triphenylacetic Acid.—The diphosphine (3·7 g.) and triphenylacetic acid (2·3 g.) were kept at 180—200° for 3 hr. and then dissolved in chloroform, washed with alkaline hydrogen peroxide and water, and dried. Acidification of the alkaline extract gave diphenylphosphinic acid (3·3 g.), m.p. an mixed m.p. 192—193° (from aqueous ethanol). Evaporation of the chloroform gave an oil which crystallised from aqueous ethanol to give triphenylmethane (0·9 g.), m.p. and mixed m.p. 91—92° (from ethanol).

Reaction of Tetraphenyldiphosphine with Isovaleric Acid.—The diphosphine (3·0 g.) and isovaleric acid (0·9 g.) were kept at 180—200° for 3 hr. The mixture was dissolved in chloroform, washed with dilute aqueous sodium hydroxide and water, and dried. Evaporation gave an oil which on trituration with ether gave 1-*diphenylphosphinyl*-1-*diphenylphosphinyloxy*-3-*methylbutane* (1·1 g.), m.p. 143—144° (from ethyl acetate–ether), $\nu_{\text{max.}}$ 990, 1045, 1200, and 1225 cm.$^{-1}$ (Found: C, 71·1; H, 6·1; P, 12·9. $C_{29}H_{30}O_3P_2$ requires C, 71·3; H, 6·1; P, 12·7%).

Reaction of Tetraphenyldiphosphine with Phenoxyacetic Acid.—The diphosphine (3·0 g.) and phenoxyacetic acid (1·3 g.) were kept at 180—200° for 3 hr. The reaction mixture was dissolved in chloroform, washed with dilute aqueous sodium hydroxide and water, and dried. Evaporation of the solvent left an oil which was placed on a column of silica gel. Elution with ether gave phenyl diphenylphosphinate (0·45 g.), m.p. and mixed m.p. 134—136° (from ether). Elution with ether–methanol (9 : 1) gave an oil (1·7 g.) which could not be crystallised, $\nu_{\text{max.}}$ 950, 1060, 1200, and 1230 cm.$^{-1}$.

Diphenylphosphine oxide (4·02 g.) and phenoxyacetic anhydride (2·86 g.) were kept at 100° for 3 hr. The reaction mixture was dissolved in chloroform, washed with dilute aqueous sodium hydroxide and water, and dried. Evaporation of the solvent left an oil (3·4 g.) which had an i.r. spectrum identical to that of the ether–methanol eluate above.

Reaction of Tetraphenyldiphosphine with (*Phenylthio*)-*acetic acid.*—The diphosphine (3·0 g.) and the acid (1·4 g.) were kept at 180—200° for 3 hr. The reaction mixture was chromatographed on silica gel. Elution with benzene gave S-*phenyl phenylthiothioacetate* (0·22 g.), m.p. 66—67° (from light petroleum), $\nu_{\text{max.}}$ 1050 and 1690 cm.$^{-1}$, singlet at τ 6·15 (2H), *m*/*e* 260, 151, 123, and 109 (Found: C, 64·4; H, 4·6; S, 24·5. $C_{14}H_{12}OS_2$ requires C, 64·6; H, 4·6; S, 24·6%). Elution with ether gave *S*-phenyl diphenylphosphinothioate (0·3 g.), m.p. and mixed m.p. 88—89° (from light petroleum).

Acetoxydiphenylphosphine.—A mixture of anhydrous sodium acetate (0·9 g.), diphenylphosphinous chloride (2·29 g.), and ether (50 ml.) was heated under reflux for 15 hr., cooled, and filtered. Evaporation of the ether gave acetoxydiphenylphosphine (2·3 g.) $\nu_{\text{max.}}$ 1750 cm.$^{-1}$ (lit.,[4] 1750 cm.$^{-1}$). The product could not be distilled without change. After heating at 160° for 1 hr., trituration with ether gave tetraphenyldiphosphine monoxide (1·4 g.) m.p. and mixed m.p. 155—157°.

Reaction of Tetraphenyldiphosphine with Benzaldehyde.—A mixture of the diphosphine (1·0 g.) and benzaldehyde (10 ml.) was heated under reflux for 3 hr. Removal of the excess of benzaldehyde by distillation under reduced pressure left a residue which on trituration with benzene gave α-hydroxybenzyldiphenylphosphine oxide (0·65 g.) m.p. and mixed m.p. 171—174° (from benzene). Evaporation of the benzene and trituration of the residue with ether gave α-*benzoyloxybenzyldiphenylphosphine oxide* (0·75 g.) m.p. 188—189° (from aqueous methanol), $\nu_{\text{max.}}$ 1180 and 1730 cm.$^{-1}$ (Found: C, 75·4; H, 5·3; P, 7·4. $C_{26}H_{21}O_3P$ requires C, 75·7; H, 5·1; P, 7·5%).

A mixture of the diphosphine (0·85 g.) and benzaldehyde (10 ml.) was heated under reflux for 3 hr. Methyl iodide (1 ml.) was added to the cooled solution and the mixture set aside at room temperature for 12 hr. Filtration gave α-hydroxybenzylmethyldiphenylphosphonium iodide (0·25 g.), m.p. and mixed m.p. 157—158°.

α-*Benzoyloxybenzyldiphenylphosphine oxide.*—Benzoyl chloride (0·4 ml.) was added to a solution of α-hydroxybenzyldiphenylphosphine oxide (1·0 g.) in pyridine (10 ml.) and the solution was set aside at room temperature for 1 hr. Chloroform was added and the mixture was washed with

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

aqueous dilute hydrochloric acid and aqueous sodium hydrogen carbonate and dried. Evaporation and trituration of the residue with ether gave α-benzoyloxybenzyldiphenylphosphine oxide (0·8 g.), m.p. and mixed m.p. 188—189° (from aqueous methanol).

Reaction of Tetraphenyldiphosphine with p-*Isopropylbenzaldehyde*.—A mixture of the diphosphine (3·0 g.) and *p*-isopropylbenzaldehyde (10 ml.) was kept at 180—200° for 3 hr. Removal of the excess of aldehyde by distillation under reduced pressure left a residue which on trituration with benzene gave α-hydroxy-*p*-isopropylbenzyldiphenylphosphine oxide (1·4 g.), m.p. and mixed m.p. 168—169° (from benzene). The benzene was evaporated and the residue chromatographed on alumina. Elution with ether gave *p*-isopropylbenzyldiphenylphosphine oxide (0·13 g.), m.p. and mixed m.p. 190·5—191·5° (from ethyl acetate). Elution with ether–ethyl acetate (4 : 1) gave (α-p-*isopropylbenzoyloxy*-p-*isopropylbenzyl*)*diphenylphosphine oxide* (1·9 g.) m.p. 191—192° (from benzene–light petroleum), $\nu_{max.}$ 1180 and 1730 cm.$^{-1}$, *m*/*e* 496, 349, 201, and 147, two doublets at τ 8·7 (6H) and 8·9 (6H) (Found: C, 77·1; H, 6·7; P, 6·4. $C_{32}H_{33}O_3P$ requires C, 77·4; H, 6·7; P, 6·3%).

Reaction of Tetraphenyldiphosphine with p-*Methoxybenzaldehyde*.—A mixture of the diphosphine (2·9 g.) and the aldehyde (10 ml.) was kept at 180—200° for 3 hr. Removal of the excess of aldehyde under reduced pressure and trituration of the residue with ether gave *p*-methoxybenzyldiphenylphosphine oxide (2·2 g.), m.p. and mixed m.p. 228—229° (from benzene).

Reaction of Tetraphenyldiphosphine with Nicotinaldehyde.—A mixture of the diphosphine (2·5 g.) and the aldehyde (10 ml.) was kept at 180—200° for 1 hr. The reaction mixture became very dark. Removal of the excess of aldehyde under reduced pressure left a black tar. A hot solution of the tar in benzene was treated with charcoal and filtered. Evaporation of the benzene and trituration of the residue with ether gave a white solid (0·5 g.). Crystallisation of the solid from benzene gave 3-*pyridylmethyldiphenylphosphine oxide*, m.p. and mixed m.p. 220—221° (from ethyl acetate) [an authentic sample from 3-hydroxymethylpyridine and dimethylaminodiphenylphosphine at 130° for 4 hr. showed m.p. 220—221° (from ethyl acetate)], $\nu_{max.}$ 1160 and 1180 cm.$^{-1}$, *m*/*e* 293, 201, and 92 (Found: C, 73·9; H, 5·5; N, 4·7; P, 10·7. $C_{18}H_{16}NOP$ requires C, 73·7; H, 5·5; N, 4·8; P, 10·6%). Concentration of the benzene solution gave α-hydroxy-3-pyridylmethyldiphenylphosphinic oxide, m.p. and mixed m.p. 198—199° (from benzene).

Reaction of Tetraphenyldiphosphine with p-*Cyanobenzaldehyde*.—A mixture of the phosphine (3·0 g.) and the aldehyde (5 g.) was kept at 180—200° for 3 hr. Trituration of the cold reaction mixture with benzene gave α-hydroxy-*p*-cyanobenzyldiphenylphosphine oxide (1·1 g.), m.p. and mixed m.p. (from ethyl acetate) 207—208°. Evaporation of the benzene gave an oil which was placed on a column of alumina. Elution with ethyl acetate gave p-*cyanobenzyldiphenylphosphine oxide* (0·16 g.), m.p. 195—196° (from ethyl acetate), $\nu_{max.}$ 1180 and 2250 cm.$^{-1}$, doublet at τ 4·4 (2H, (J_{PH} 15 c./sec.) (Found: C, 75·3; H, 4·9; N, 4·3; P, 10·1. $C_{20}H_{16}NOP$ requires C, 75·7; H, 5·0; N, 4·4; P, 9·8%).

Reaction of Tetraphenyldiphosphine with 3-*Phenylpropionaldehyde*.—A mixture of the diphosphine (3·0 g.) and the aldehyde (10 ml.) was kept at 180—200° for 3 hr. Ethylbenzene could not be detected in the reaction mixture by g.l.c. analysis (2 m. silicone gum rubber column at 160°). Removal of the excess of aldehyde under reduced pressure and trituration of the residue with ether gave 1-hydroxy-3-phenylpropyldiphenylphosphine oxide (2·5 g.), m.p. and mixed m.p. 187—188° (from benzene).

α-*Hydroxybenzyldiphenylphosphine Oxides*.—Authentic samples of these compounds were prepared in appropriate cases, by reaction of the aldehyde with diphenylphosphine in the presence of a trace of acid, followed by oxidation with hydrogen peroxide.

α-(*Hydroxy*)-p-*isopropylbenzyldiphenylphosphine oxide* has m.p. 168—169° (from benzene), $\nu_{max.}$ 1170 and 3300br cm.$^{-1}$ (Found: C, 75·3; H, 6·4; P, 9·0. $C_{22}H_{23}O_2P$ requires C, 75·4; H, 6·6; P, 8·9%). α-*Hydroxy*-3-*pyridylmethyldiphenylphosphine oxide* has m.p. 198—199° (from benzene), $\nu_{max.}$ 1160 and 3200br cm.$^{-1}$ (Found: C, 69·9; H, 5·2; N, 4·6; P, 10·0. $C_{18}H_{16}NO_2P$ requires C, 69·9; H, 5·2; N, 4·5; P, 10·0%).

α-*Hydroxy*-p-*cyanobenzyldiphenylphosphine oxide* has m.p. 207—208° (from ethyl acetate), $\nu_{max.}$ 1170, 2250, and 3200br cm.$^{-1}$ (Found: C, 72·0; H, 4·8; N, 4·4; P, 9·4. $C_{20}H_{16}NO_2P$ requires C, 72·1; H, 4·8; N, 4·2; P, 9·3%).

1-*Hydroxy*-3-*phenylpropyldiphenylphosphine oxide* has m.p. 187—188° (from benzene), $\nu_{max.}$ 1110, 1180, and 3200 cm.$^{-1}$ (Found: C, 75·2; H, 6·2; P, 9·3. $C_{21}H_{21}O_2P$ requires C, 75·0; H, 6·25; P, 9·2%).

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