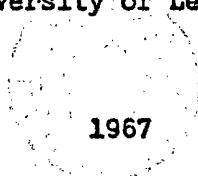


SOME REACTIONS
OF
TETRAPHENYLDIPHOSPHINE

By
ROGER ARTHUR SHELDON

A Thesis submitted for the degree of Doctor of Philosophy
of the
University of Leicester



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STATEMENT

The work described in this thesis was carried out by the author in the Department of Chemistry of the University of Leicester, under the supervision of Dr. R. S. Davidson and Dr. S. Trippett. No part of it is concurrently being submitted for any other degree.

October 1964 - May 1967

Signed *R.A. Sheldon*
(R. A. Sheldon)

ACKNOWLEDGEMENTS.

The author would like to record his sincere thanks to Dr. R. S. Davidson and Dr. S. Trippett for their supervision and constant encouragement, to Albright and Wilson Manufacturing Company Limited for a Maintenance Grant and to Miss R. E. O'Neill for the typing involved.

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SUMMARY

Both the methods of preparation, and the reactions, of diphosphines are reviewed briefly.

Both the photolytic and thermal reactions of tetraphenyl-diphosphine with alcohols have been studied. The reaction probably proceeds via a combination of ionic and free radical mechanisms. The mechanistic postulations are supported by the results of the reaction of tetraphenyldiphosphine with ditertiarybutyl peroxide.

The reactions of tetraphenyldiphosphine with both aromatic and aliphatic carboxylic acids have been studied. The results have been rationalized into a general mechanism which involves the rearrangement of an α -hydroxy phosphine oxide to a phosphinate. This type of rearrangement may be extended to include all α -hydroxy phosphine oxides which contain a group capable of stabilising a carbanion in the α -position to both the phosphine oxide and the hydroxyl group.

The reactions of tetraphenyldiphosphine with aldehydes have been studied briefly and a mechanism has been postulated to account for the products which are formed.

INTRODUCTION

Silicon and sulphur, which are situated to the left and right of phosphorus in the periodic table, form numerous chain and cyclic structures, but it is only recently that an interest in compounds containing phosphorus-phosphorus bonds has developed. The chemistry of the phosphorus-phosphorus bond has been reviewed by Cowley.¹ The subject has been briefly summarized by Huheey,² and monographs by Maier,³ Paddock⁴ and Sasse⁵ contain sections that deal with certain aspects of polyphosphine chemistry. The trifluoroalkyl derivatives have been discussed by Banks and Haszeldine.⁶

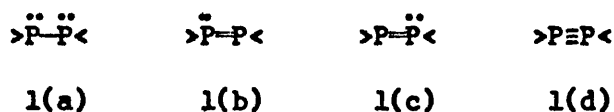
The name "diphosphine" rather than "biphosphine" for P_2H_4 and its derivatives conforms to the latest I.U.P.A.C. report on inorganic nomenclature.

1. The nature of the phosphorus-phosphorus linkage.

The P-P bond displays a number of peculiarities. Not the least of these is the existence of 60° angles in the P_4 tetrahedron of white phosphorus. Another interesting feature of the P-P bond is the essential consistency of its length.¹ With the possible exception of P_4S_7 the P-P bond length appears to be insensitive to the electronic characteristics of the substituents or to changes in oxidation state.

Like other second row elements, phosphorus prefers catenation to multiple bonding, due to increased inner shell repulsions and less effective π -bonding utilising 3p orbitals. The P-P bond is comparable in strength to the Si-Si^{9,77} and the S-S bond⁹ but stronger than the N-N single bond.⁶⁸ Elemental phosphorus (P₄) has a P-P bond energy in the range 44-48 kcal.^{7,8,9} Various estimates of the steric strain in the P₄ molecule have been used to derive an unstrained P-P single bond energy between 47.2 and 54.5 kcal.^{8,9,10,11,12} Thus^{the} P-P single bond is stronger than the N-N single bond which has a bond energy of 37 kcal.⁶⁸

In a diphosphine the two phosphorus atoms are joined by a σ -bond and a lone pair of electrons remains on each atom [I(a)].



Evidence for the contribution of structures 1(b), 1(c) and 1(d), which involve $p_{\pi}\text{--}d_{\pi}$ bonding, comes from the intense ultraviolet absorption spectra of diphosphines compared with monophosphines.^{13,14} The marked chromophoric effect of the P-P bond is shown by the ultraviolet absorption spectrum of tetrakis(trifluoromethyl)diphosphine¹³ ($\lambda_{\text{max.}}$ 216 m μ ; ϵ ca. 4000) compared with that of tris(trifluoromethyl)phosphine which shows only end absorption in the ultraviolet. Replacement of CF₃ by CH₃

moves the spectrum towards higher wavelengths as is shown by the spectra of $(\text{CF}_3)_2\text{P}-\text{P}(\text{CH}_3)_2$ ($\lambda_{\text{max.}}$ 233 m μ ; ϵ 4520) and $(\text{CH}_3)_4\text{P}_2$ ($\lambda_{\text{max.}}$ 242 m μ ; ϵ 4000).¹⁴ This is interpreted as closer spacing of energy levels for less electronegative phosphorus. Various polyphosphines, such as $(\text{CF}_3\text{P})_4$ and $(\text{CF}_3\text{P})_5$ ⁶⁶ also show intense ultraviolet absorption spectra. This chromophoric effect of the P-P bond is attributed to the π -acceptor bonding power of the P_{3d} orbitals of phosphorus.

II. Preparation of diphosphines.

Diphosphine (P_2H_4) has been known for many years and several methods of preparation are known. The first organo-substituted diphosphine was synthesized over 70 years ago by the reaction of diphenylphosphine with diphenylphosphinous chloride.¹⁵ The same method was used by Kuchen and Buchwald³⁶ to prepare tetraphenyldiphosphine in 80% yield. More recently this method has been extended to tetraalkyl diphosphines¹⁶ and unsymmetrical diphosphines.^{14,17}

A well known method of preparing diphosphines is by coupling of phosphinous chlorides using active metals such as lithium,¹⁸ sodium,^{19,20,21,22,23} potassium,^{20,21} and magnesium.^{20,24} Alkali metal coupling probably proceeds via the metal organophosphide since diphosphines have been produced from the second step of the reaction.²³

4.



R = alkyl or aryl M = Li, Na, K or Mg.

One of the most interesting diphosphine syntheses depends on Burg's recognition that the P-P bond can form two π -bonds whereas the P-N bond can form only one.¹⁶ This, together with the higher bond energy of the N-H bond compared to the P-H bond, is the reason why dimethylphosphine will displace dimethylamine from dimethylaminodiphenylphosphine.



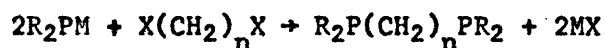
Tetraphenyldiphosphine can also be prepared by this²⁵ method.

Certain Grignard reagents react anomalously with thiophosphoryl chloride ($PSCl_3$) to produce diphosphine disulphides rather than the expected tertiary phosphine sulphide. When a diphosphine disulphide is readily available in this manner, desulphurization represents a convenient synthesis of the diphosphine. Many reducing agents will effect this desulphurization and metals such as copper, cadmium and lead²¹ have been used. Trivalent phosphorus compounds such as triethylphosphite⁶¹ and tributylphosphine⁶⁵ also effect the desulphurization.

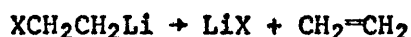
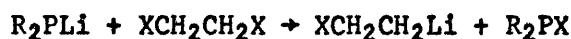
The reaction of a metal organophosphide with an organic dihalide has been used in the synthesis of some interesting

5.

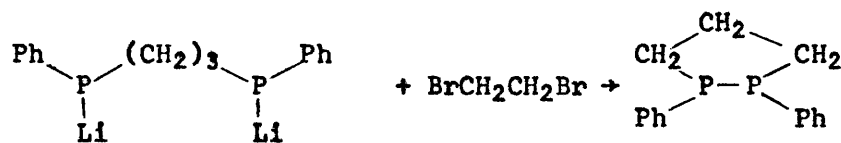
ditertiary phosphines.²⁶ However, when $n=2$, $X=Cl$ or Br , $M=Li$ and $R=C_2H_5$ or C_6H_{11} , it is not possible to isolate the expected ditertiary phosphine.²⁷ Instead lithium-halogen interconversion



takes place, resulting in ethylene evolution and the formation of the diphosphine.

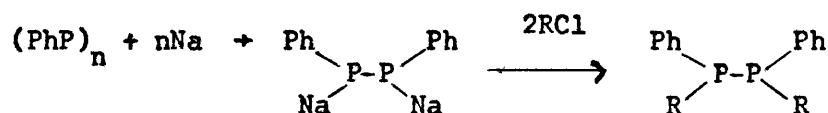


Metal-halogen exchange has also made available some diphosphines that would be inaccessible by other routes, such as 1,2-diphenyldiphosphine²⁸ and the novel heterocycle diphosphine²⁹.



2.

Unsymmetrical diphosphines may also be prepared from 1,2-disodio-1,2-diphenyldiphosphide which can be isolated under carefully controlled conditions from the reaction of sodium with the cyclopolyphosphine $(C_6H_5P)_n$.³⁰



Burg has used the CF_3 - substituted cyclopolyphosphines as a source of several unusual compounds. Reaction of these compounds with tertiaryphosphines⁶⁹ results in interesting polar isomers of diphosphines, $\text{R}_3\text{P}^+\text{PCF}_3^-$, which consist of phosphonium and phosphide ions in the same molecule.

III. Reactions of diphosphines.

A. Disproportionation.

The thermal stability of diphosphine itself is so low that it disproportionates rapidly above 0° . Complete substitution of the hydrogen atoms of P_2H_4 by alkyl or aryl groups raises the thermal stability considerably and tetraphenyldiphosphine may be distilled in vacuo above 200° without change. However, above 350° tetraphenyldiphosphine decomposes giving triphenylphosphine and phosphorus.³⁶ The unsymmetrical diphosphines are noticeably¹⁴ less thermally stable than their symmetrical analogues.¹⁴ In these cases decomposition is probably facilitated by the formation of intermolecular P-P bonds between the relatively basic and acidic phosphorus atoms.

B. Phosphonium salt formation.

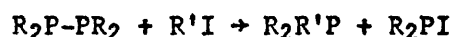
A characteristic reaction of a tertiary phosphine is phosphonium salt formation. Even though two trivalent phosphorus atoms are available in a diphosphine it is possible to quaternize only one of them. Apparently the positive charge on the adjacent phosphorus atom diminishes the basicity of the second site¹⁹ since

7.



bisphosphonium salt formation only becomes possible when interaction between the phosphorus atoms is reduced by methylene group insertion.¹⁸

Cleavage, rather than quaternization, takes place when the P-P bond is weakened by electron withdrawing substituents^{31,32,33} or when the alkyl groups are replaced by bulkier C_6H_{11} groups.¹⁹



The tetraalkyldiphosphines require a temperature of 200° to effect such a decomposition.³⁴ The cleavage reaction probably involves an intermediate complex rather than a free-radical mechanism since the reaction proceeds in the dark.³¹

Diphosphines which have sites of differing basicity, such as $(CF_3)_2P-P(CH_3)_2$, undergo disproportionation with methyl iodide, possibly involving an unstable monophosphonium salt as the first step.¹⁴

c. Donor and acceptor properties of diphosphines.

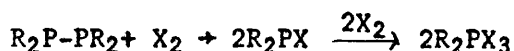
By reason of their lone pairs diphosphine and substituted diphosphines will form complexes with Lewis acids. The reactivity towards acceptors depends on the basicity of the phosphorus atoms. Diphosphine itself forms diadducts with BF_3 and the BH_3 group.³⁵ When the diphosphine substituents are mildly electron withdrawing, it is possible to isolate only monoadducts, such as $(C_6H_5)_4P_2 \cdot BF_3$.³⁶

Protic acids cause P-P bond cleavage and again the reactivity of the diphosphine appears to depend on base action by at least one of the phosphorus atoms. $(\text{CF}_3)_4\text{P}_2$ is inert towards HCl up to 300° ¹⁴ but other diphosphines are cleaved to a secondary phosphine and a phosphinous chloride.

In recent years there has been considerable interest in the reactions of various transition metal compounds with phosphine ligands. Burg and Mahler³⁸ first observed that $(\text{CF}_3)_4\text{P}_2$ reacts with nickel carbonyl and since then a considerable number of diphosphine complexes have been studied.

D. Cleavage of the P-P bond.

It has been mentioned above that diphosphines are cleaved by protic acids and that certain diphosphines are cleaved by alkyl halides. Equimolar amounts of the halogens, usually in inert solvents at room temperature, cause essentially quantitative P-P bond cleavage of both symmetrical^{19,32,36} and unsymmetrical diphosphines.^{39,40} If the halogen is in excess this is followed by conversion of the phosphinous halide to the corresponding phosphorane.

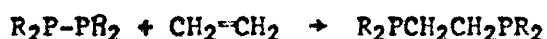


Diphosphines react slowly with water at room temperature and are rapidly hydrolysed by boiling water to the corresponding secondary phosphine and the secondary phosphine oxide. Most of the



hydrolysis experiments with diphosphines have been done with trifluoromethyl substituted diphosphines.³⁷

One of the most elegant concepts in polyphosphine chemistry is Burg's "pseudo halogen" concept whereby the R_2P moiety of a diphosphine is likened to a halogen atom. Thus $(CF_3)_4P_2$ or $(CH_3)_4P_2$ will add across ethylenic or acetylenic multiple bonds in much the same way as a halogen molecule.¹⁶



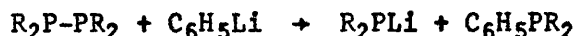
A similar approach has been used to obtain small yields of o-phenylenebisdiethylphosphine by adding $(C_2H_5)_4P_2$ across the triple bond of benzyne.⁶⁷

Diphosphines readily undergo cleavage by alkali metals and this is analogous to the homolytic cleavage of tetraphenylhydrazine and hexaphenylethane by alkali metals. Homolytic cleavage of the P-P bond is a useful source of reactive monophosphorus compounds.^{18,20,21,41,42,43,44,45}

The ease of cleavage varies with the substituents and decreases in the order

$C_6H_5 > CH_3 > C_2H_5 > n-C_3H_7 > n-C_4H_9$; hence the best combination of solvent and metal depends on the particular diphosphine. As expected, replacement of alkyl by aryl groups weakens the P-P bond because of the electron withdrawing effect of the aryl groups and the stabilization of the anion R_2P^- by delocalization of the negative charge onto the benzene rings. Recently it has been shown²⁹

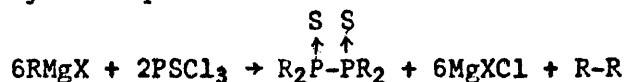
that certain organometallic reagents will also cleave diphosphines.



The relative ease of cleavage closely resembles that for the alkali metals and the reactivity of the organometallic reagents follows the sequence $LiC_6H_5 > LiC_2H_5 > Mg(C_2H_5)_2 > Al(C_2H_5)_3 > Pb(C_2H_5)_4$.

IV. Diphosphine oxides and sulphides.

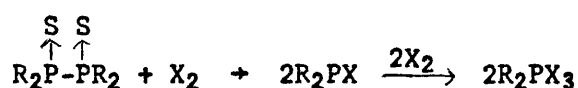
It has been mentioned earlier in connection with the preparation of diphosphines that certain Grignard reagents react with thiophosphoryl chloride ($PSCl_3$) to give the diphosphine disulphide instead of the expected tertiaryphosphine sulphide. Kabachnik and Shepeleva⁵⁶ found that the reaction of CH_3MgI with $PSCl_3$ gave tetramethyldiphosphine disulphide rather than the expected trimethylphosphine sulphide $(CH_3)_3P(S)$. Since then a considerable number of diphosphine disulphides have been prepared by this method. The course of this novel reaction is usually expressed by the equation:-



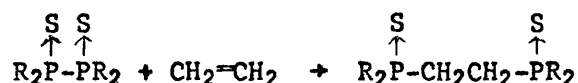
This equation is undoubtedly an oversimplification, particularly with respect to the formation of the hydrocarbon $R-R$. Although the appropriate hydrocarbons have been isolated in some instances, it has been shown⁵⁷ that the gaseous products formed during the preparation of tetraethyldiphosphine disulphide, $(C_2H_5)_4P_2S_2$, are ethane and ethylene and not the expected butane. The yield of diphosphine disulphide depends on many factors,^{21,58}

such as temperature, rate of reaction and the steric and electronic characteristics of the group on the Grignard reagent. Aromatic Grignard reagents lead exclusively to the tertiary phosphine sulphide, $R_3P(S)^{21}$ and give none of the anomalous product.

Diphosphine disulphides may be cleaved by halogens, in the same way that diphosphines are cleaved, by addition of the theoretical quantity of halogen.^{59,60} An excess of halogen causes halogenation of both P-P and P-S bonds.



Diphosphinedisulphides, like the diphosphines, also undergo the ethylene insertion reaction.^{61,62}

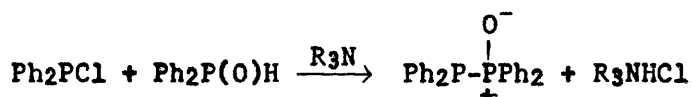
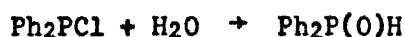


Diphosphine monosulphides may be prepared by removal of one sulphur atom from a diphosphine disulphide³⁹ or by addition of the appropriate quantity of sulphur to a diphosphine.⁶³ The remaining lone pair makes diphosphine monosulphides sensitive to oxidation, and, as expected, the P-P bond may be cleaved by halogens.³⁹

Diphosphine dioxides are generally prepared^{19,22,36} by controlled oxidation of a diphosphine. Quin and Anderson claimed to have prepared tetraphenyldiphosphine dioxide by exposing to air an ethereal solution of diphenylphosphinous chloride and a

tertiary amine in the presence of small quantities of water.⁶⁴

However, McKechnie et al.⁷⁰ showed that the product was tetraphenyl-diphosphine monoxide and not the dioxide. The monoxide is completely stable in air for short periods; on long standing in air it becomes sticky and diphenylphosphinic acid is formed.



The monoxide and dioxide have very similar physical properties.

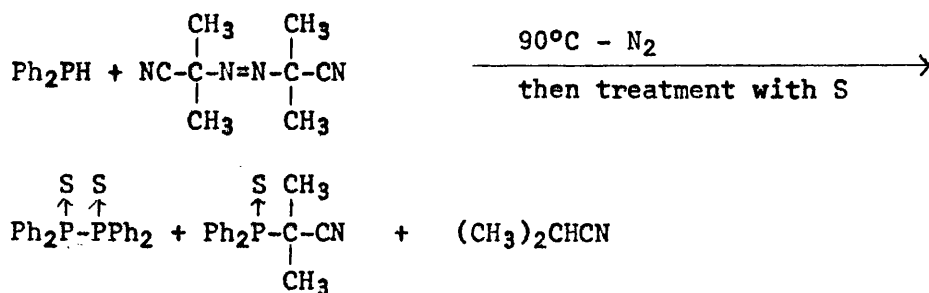
V. Preparation and reactions of the diphenylphosphorus radical.

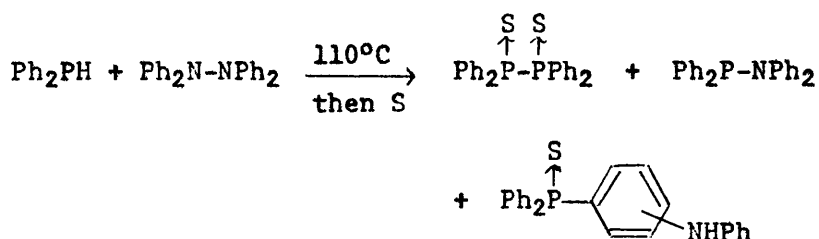
Tetraphenyldiphosphine may be considered as the organophosphorus analogue of hexaphenylethane and consequently may be expected to dissociate, thermally or photolytically, to give the diphenylphosphorus radical analogous to the triphenylmethyl radical. Hexaphenylethane is known to dissociate, in solution at room temperature, into triphenylmethyl radicals. Tetraphenylhydrazine is known to dissociate into diphenylnitrogen radicals on heating to about 70° in a solvent. However the P-P bond is significantly stronger than the N-N bond (see P.2) and tetraphenyldiphosphine would not be expected to dissociate so freely as tetraphenylhydrazine. Schmidt et al.,⁴⁶ using the same practical methods which led to the isolation of the phenylsulphur radical,⁴⁷ succeeded in isolating the diphenylphosphorus radical. When

evaporating tetraphenyldiphosphine was irradiated with short wave ultraviolet light at 0.01 m.m. Hg and the vapour condensed immediately behind the zone of irradiation on a cold finger cooled with liquid nitrogen, the diphenylphosphorus radical condensed as a faintly pink transparent film which lost its colour only after 30 minutes at 170°K. It was concluded that the diphenylphosphorus radical is equal in thermal stability to the phenylsulphur radical. In the same way photolytic cleavage of the P-H bond in diphenyl phosphine yields the diphenylphosphorus radical. Electron paramagnetic resonance measurements at 77°K showed a strong signal with a weakly anisotropic g factor ($g = 2.009$). This seems to indicate that the odd electron is localized on the phosphorus atom to a large extent.

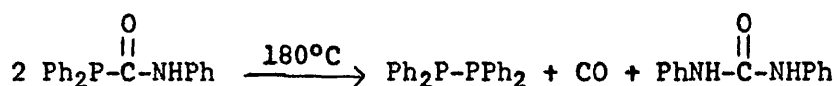
The free radical addition of phosphines to olefins has been studied extensively⁴⁸ and a close analogy between phosphines and thiols has been established.⁴⁹

The diphenylphosphorus radical is presumably an intermediate in the thermal reaction of diphenylphosphine with bisazo-⁵⁰isobutyronitrile and with tetraphenylhydrazine.





It has also been postulated as an intermediate in the thermal decomposition of diphenylphenylcarbamoylphosphine.⁵¹



Evidence for the existence of the diphenylphosphorus radical as an intermediate was provided by trapping with phenyl-sulphur radicals. The reaction was carried out in the presence of diphenyl disulphide at elevated temperatures and phenyl diphenylthiophosphinite ($\text{Ph}_2\text{P-SPh}$) was isolated in 80% yield.

The diphenylphosphorus radical has been proposed as an intermediate in photolytic reactions of triphenylphosphine. The development of a pink colour on exposure of triphenylphosphine (in vacuo) to light has been attributed to the presence of the triphenylphosphinium cation radical $\text{Ph}_3\text{P}^{\cdot+}$. Likewise, the deep red colour, attended by the development of paramagnetic resonance absorption, which results when chloranil and triphenylphosphine are mixed, is attributed to this radical cation.

However, higher energy irradiation with ultraviolet light results in scission of the phenyl-phosphorus bond. Photolysis of

triphenylphosphine in benzene solution has been studied by Griffin⁵⁵ and shown to result in the formation of diphenyl and diphenylphosphine. Initial formation of a phenyl radical and a diphenylphosphorus radical, by scission of the phenyl-phosphorus bond, was postulated. Presumably this was followed by attack on the solvent.

Horner⁵⁴ has studied the photolysis of triphenylphosphine in alcohol solutions. He proposed that excitation involved a $n-\sigma^*$ transition, followed by scission of the phenyl-phosphorus bond. The subsequent reactions were rather complex (see P. 22).

Reaction of Tetraphenyldiphosphine with Alcohols.

1. The ultraviolet absorption spectrum of tetraphenyldiphosphine.

In general, a central atom with an unshared electron pair, when bound to one or more phenyl groups, is responsible for a considerable perturbation of the benzene spectrum⁷¹. The spectra of the triphenyl derivatives of the Group V elements all show a single major band (see table I).

Table 1

	Ph ₃ N	Ph ₃ P	Ph ₃ As	Ph ₃ Sb	Ph ₃ Bi
$\lambda(\text{m}\mu)$	297	261	248	256	248
$\epsilon \times 10^{-4}$	2.21	1.10	1.23	1.17	1.29

As might have been anticipated from the generally known greater conjugating ability of first row elements, triphenylamine absorbs at the longest wavelength and has the highest intensity. The bands for the rest of the series occur quite close together. This perturbation of the benzene spectrum is caused by conjugation of the lone pair of electrons on the group V element with the benzene rings. The spectra of the phenyl derivatives in which the central atom has no lone pair of electrons are completely different. The benzenoid spectra are only mildly perturbed. Thus the band of triphenylphosphine is of much greater intensity than the bands in the same region shown by triphenylphosphine oxide (see fig. 1),

which are similar to the corresponding bands of benzene and show the fine structure clearly. The relatively small effect of the P-O group suggests that no resonance occurs between the P-O group and the aromatic nucleus. Therefore, it is probable that the phosphorus atom of this group has no π orbitals which can interact with the π electrons of the benzene ring. This conclusion is consistent with the view that the P-O bond has no appreciable double bond character.

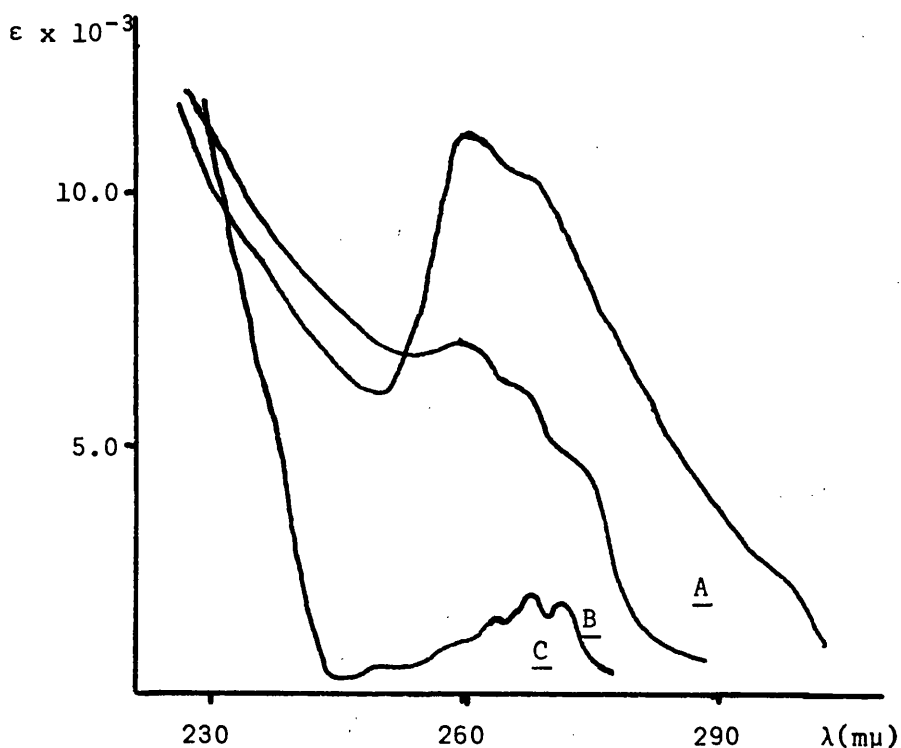


Fig. 1

The ultraviolet absorption spectrum of A triphenylphosphine, B tetraphenyldiphosphine and C triphenylphosphine oxide.

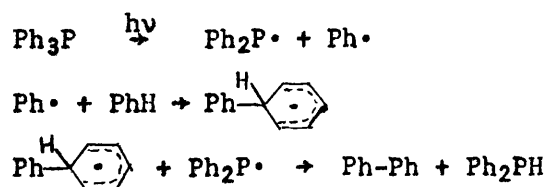
(The spectra were recorded in ethanol solution).

The spectrum of tetraphenyldiphosphine seems to be intermediate between a typical phosphine and a typical phosphine oxide spectrum. However, the spectrum of tetraphenyldiphosphine monoxide is very similar to that of the diphosphine, and considering the ease of air oxidation of the diphosphine to the monoxide in very dilute solutions, the spectrum of the diphosphine may not be entirely reliable. The extent of conjugation of the lone pair with the benzene rings might be expected to be reduced somewhat because of involvement of the lone pair electrons in $p\pi-d\pi$ bonding between the two phosphorus atoms. Moreover, a significant difference between the diphosphine and its monoxide may not necessarily be expected, as the monoxide still contains one trivalent phosphorus atom bearing a lone pair of electrons.

II. Attempted trapping of diphenylphosphorus radicals.

Griffin⁵⁵ studied the photolysis of triphenylphosphine in benzene solution and reported the formation of diphenyl and diphenylphosphine. A solution of tetraphenyldiphosphine in dry benzene was irradiated for 12 hours⁷² in a quartz apparatus. No diphenylphosphine could be detected by gas-liquid chromatography and only a trace of diphenyl could be detected (<1%). The photolysis of triphenylphosphine was repeated and diphenyl and diphenylphosphine were detected by gas-liquid chromatography but in much reduced yields from those reported (c.a. 3% instead of 20%).

The formation of diphenyl and diphenylphosphine when triphenylphosphine is irradiated in benzene solution may be explained by initial scission of a phenyl-phosphorus bond to give a phenyl radical and a diphenyl-phosphorus radical. The reactive phenyl radical would then attack the solvent to give a phenylcyclohexadienyl radical. The longer lived diphenylphosphorus radical may then abstract a hydrogen atom from the phenylcyclohexadienyl radical to give diphenyl and diphenylphosphine.

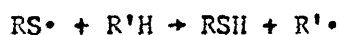


In the case of the diphosphine, irradiation would presumably cause scission of the P-P bond to give two diphenylphosphorus radicals. Hence there is no reactive phenyl radical to attack the solvent and it appears that the most favourable pathway open to the diphenylphosphorus radicals is recombination.

A solution of tetraphenyldiphosphine in dry toluene was irradiated for 12 hours but no dibenzyl could be detected by gas-liquid chromatography. However, irradiation of a solution of tetraphenyldiphosphine in dry cumene for 24 hours resulted in the formation of diphenylphosphine and a small amount of dicumene was isolated (3%). Tetraphenyldiphosphine in refluxing cumene for 15 hours gave no dicumene. Hence it appears that tetraphenyldiphosphine

is dissociated into diphenylphosphorus radicals under the photolysis conditions but the most favourable reaction is recombination.

Substantial yields of dicumene are obtained from the irradiation of solutions of disulphides in cumene.⁷³ The RS-H bond dissociation energy of n-alkylmercaptans is approximately 86 kcal.⁷⁴ If the C-H bond dissociation energy in cumene is assumed to be the same as in toluene, 77.5 kcal,⁷ then one concludes, even taking into account the appreciable error in bond dissociation energies, that hydrogen abstraction from cumene by a thiyl radical, RS•, should be an exothermic process.



However, the P-H bond dissociation energy is less than the S-H bond dissociation energy (approx. 77 kcal in PH₃).⁷⁵ Hydrogen abstraction from cumene by a diphenylphosphorus radical would, therefore, be expected to be much less favourable than by a thiyl radical.

A well known reaction of disulphides is dehydrogenation of hydroaromatic compounds.⁷⁶ However, irradiation of a solution of tetraphenyldiphosphine and tetralin in benzene for three days gave no naphthalene. Similarly, no naphthalene was obtained by heating tetraphenyldiphosphine and tetralin at 180° for five hours.

III. Irradiation of triphenylphosphine in alcohol solutions.

⁵⁴Horner has studied the photolysis of triphenylphosphine in alcohol solutions. Products were isolated as their oxidised derivatives and the results are shown in table 2.

Table 2

	A	B	C
Ph ₃ PO	5.8 m.mole	1.59 m.mole	5.30 m.mole
Ph ₂ PO ₂ H	1.8 m.mole	trace	3.70 m.mole
PhPO ₃ H ₂	0.1 m.mole	3.48 m.mole	trace
Ph ₄ P ⁺	1.9 m.mole	trace	0.04 m.mole

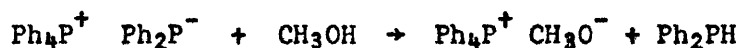
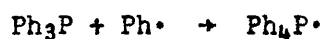
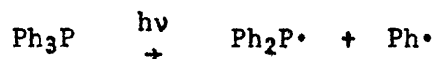
A = 0.006 molar solution of 10 m.mole Ph₃P in methanol

B = 0.003 molar solution of 5 m.mole Ph₃P in methanol

C = 0.006 molar solution of 10 m.mole Ph₃P in isopropanol

Thus apart from the different results in different alcohols, there is a significant change in product ratio when the concentration is altered for a particular alcohol. Benzene and diphenyl were detected qualitatively by gas chromatography. In the case of isopropanol, acetone was detected qualitatively by gas chromatography.

Horner explains the formation of the tetraphenylphosphonium cation by the following sequence.



The phenylphosphine (isolated as PhPO_3H_2), is presumably, produced by further reaction of the diphenylphosphine. The benzene is obviously the result of attack by phenyl radicals on the solvent and/or diphenylphosphine. The formation of diphenyl may be explained by attack of phenyl radicals on the benzene, although this would be expected to be very unfavourable considering the minute concentration of benzene in the solution. However, good yields of diphenyl (and phenylcyclohexadiene) have been reported⁹⁶ in the irradiation of sodium tetraphenylboron in dilute aqueous and alcoholic solutions. The irradiation of triphenylphosphine in methanol has been repeated and the results are shown for the irradiation of a 0.006 molar (A) and a 0.003 molar solution (B) in table 3.

Table 3

Compound	% yield		method of estimation
	A	B	
benzene	20	15	G.L.C.
diphenyl	2	1	G.L.C.
diphenylphosphine	23	none	G.L.C.
phenylphosphine	none	9	G.L.C.
Ph_4P^+	36	none	precipitation as $\text{Ph}_4\text{P}^+ \text{Ph}_4\text{B}^-$
$\text{Ph}_2\text{P}(\text{O})\text{OCH}_3$	10	14	P.M.R.

The only major difference from Horner's results is the isolation of methyl diphenylphosphinate [$\text{Ph}_2\text{P}(\text{O})\text{OCH}_3$] in both cases, which Horner did not report. An authentic sample of tetraphenylphosphonium methoxide was prepared from tetraphenylphosphonium chloride and sodium methoxide. Irradiation of a 0.003M solution of this in methanol for 18 hr. resulted in complete decomposition. This drastic change in the stability to irradiation of the phosphonium methoxide, which is a result of merely halving the concentration, is inexplicable.

The formation of methyl diphenylphosphinate is interesting as it may have been formed by attack of diphenylphosphorus radicals on the solvent (methanol). If this was so it would be very unusual as free radical attack on alcohols does not usually occur at the O-H bond.

IV. Irradiation of tetraphenyldiphosphine in alcohol solutions.⁸¹

As scission of the P-P bond in tetraphenyldiphosphine produces two identical radicals, this should facilitate the interpretation of subsequent reactions. A solution of the diphosphine in the anhydrous alcohol was irradiated for 18 hr., at room temperature, in a pyrex tube (with rigorous exclusion of air). This resulted in the formation, in good yield, of diphenylphosphine and the corresponding alkyl diphenylphosphinate (see table 4.). In the absence of ultraviolet light there was no reaction between tetraphenyldiphosphine and an alcohol at room temperature.

Table 4

ROH	RH	Ph ₂ PH	Ph ₂ P(O)OR	
	%	%(a)	%(b)	%(c)
MeOH		93	91	58
EtOH		79	73	
Pr ⁱ OH		86	88	72
Bu ^t OH		91	0	0
2-C ₈ H ₁₇ OH		75		58
PhCH ₂ OH	80	74	75	46

(a) gas chromatography (b) P.m.r. spectroscopy (c) isolated

The intermediacy of free radicals was shown in the reaction of the diphosphine with benzyl alcohol. The expected products, diphenylphosphine and benzyl diphenylphosphinate were obtained, together with a high yield of toluene and a small amount of dibenzyl.

The two outstanding features of the reaction are (a) the apparent abstraction of a hydrogen atom from an O-H bond (D 108 kcal.mole⁻¹) when more favourable hydrogen atoms bonded to carbon (D ~90 kcal.mole⁻¹) are available; and (b) the formation of alkyl diphenylphosphinate [$\text{Ph}_2\text{P}(\text{O})\text{OR}$] and not the phosphinite (Ph_2POR).

Although abstraction of the hydrogen atom from the O-H bond of an alcohol is unusual it has been reported by Glockling¹⁰¹ for the case of the isobutenyl radical ($(\text{CH}_3)_2\text{C}=\text{CH}\cdot$) in ethanol solution. To ensure that the oxidation step implied in (b) was a genuine feature of the reaction a number of experiments were carried out. To check that the diphosphine was not being oxidised by air, prior to reaction, a solution of tetraphenyl-diphosphine monoxide in methanol was irradiated for 18 hr. No phosphinate was formed and the monoxide was recovered unchanged. A solution of methyl diphenylphosphinite in methanol was irradiated for 18 hr. and the phosphinite recovered unchanged. A solution of methyl diphenylphosphinite plus a small amount of the diphosphine in methanol was irradiated for 18 hr. At the end of this time,

in addition to a small amount of diphenylphosphine, the mixture consisted of methyl diphenylphosphinite and the phosphinate. The amount of phosphinate was too much to have come from the diposphine alone.

V. Irradiation of other trivalent phosphorus compounds in
alcohol solution.⁷⁸

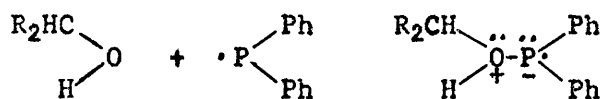
Another mode of formation of the diphenylphosphorus radical in solution is by abstraction of the hydrogen atom from the P-H bond of diphenylphosphine by a suitable radical. This can be achieved by use of bisazoisobutyronitrile.⁵⁰ A solution of diphenylphosphine and excess bisazoisobutyronitrile in methanol was irradiated for 18 hr. in pyrex apparatus. The only phosphorus compound isolated was tetraphenyldiphosphine monoxide. This result indicates that the reaction of tetraphenyldiphosphine with alcohols, although obviously involving free radicals, may not be straightforward attack by diphenylphosphorus radicals on the solvent. However, when a solution of diphenylphosphine, methyl diphenylphosphinite and bisazoisobutyronitrile in methanol was irradiated for 18 hr. in pyrex apparatus the result was that 50% of the phosphinite was oxidised to the phosphinate. When a blank was run with no diphenylphosphine present no oxidation occurred. A limitation of using bisazoisobutyronitrile as the radical initiator is that side reactions cause reductions in yields and

large amounts of material are unaccounted for. Thus when biszobutyronitrile was added to a solution of tetraphenyl-diphosphine in methanol and the solution photolysed, the yield of methyl diphenylphosphinate was much reduced.

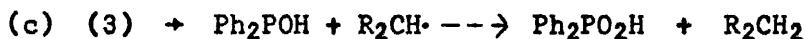
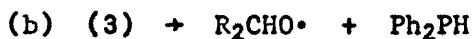
Photolysis of a methanol solution of dimethylamino-diphenylphosphine ($\text{Ph}_2\text{PN}(\text{CH}_3)_2$), in pyrex apparatus, gave methyl diphenylphosphinite in good yield. However, if isopropanol was used as the solvent no isopropyl diphenylphosphinite was formed using the same conditions. When quartz apparatus was used (using isopropanol as solvent) the only isolable product was tetraphenyldiphosphine monoxide. Irradiation of a benzyl alcohol solution of dimethylaminodiphenylphosphine in quartz apparatus gave a mixture of tetraphenyldiphosphine monoxide and benzyl diphenylphosphinate. Considering the drastic change produced by changing the solvent from methanol to isopropanol it is doubtful whether these reactions are free radical processes when carried out in pyrex apparatus.

VI. Discussion of results.

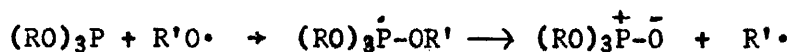
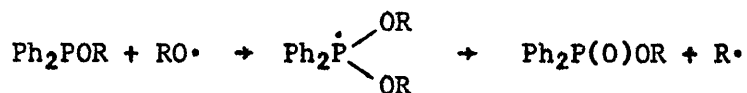
It was first thought that the results could be explained by attack of diphenylphosphorus radicals on the oxygen atom of the alcohol. The intermediate (3) could then break down in several ways.



(3)



Intermolecular hydrogen abstraction by a diphenylphosphorus radical (a) would lead to diphenylphosphine and the alkyl diphenylphosphinite. Intramolecular hydrogen abstraction (b) gives diphenylphosphine and an alkoxyl radical. The oxidation of phosphinite to phosphinate is then brought about by attack of alkoxyl radicals on the phosphinite by analogy with the oxidation of phosphites to phosphates by alkoxyl radicals.⁷⁹ The alkyl

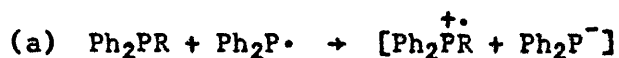


radicals (R·) could then form the alkane by hydrogen abstraction from diphenylphosphine or from the solvent. Although present in only small amounts compared to the solvent, hydrogen abstraction from the P-H bond of diphenylphosphine is very favourable as diphenylphosphine has been shown to be an extremely good hydrogen donor to radicals.⁸⁰ The absence of acetone in irradiations

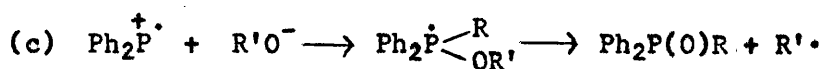
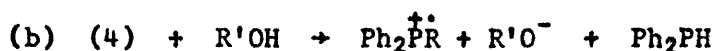
carried out in isopropanol supports the observation of Walling and Rabinowitz⁷⁹ that the reaction of alkoxyl radicals with tervalent phosphorus compounds is extremely rapid.

Irradiation of the diphosphine in t-butyl alcohol gave diphenylphosphine, diphenylphosphinic acid, and a trace of acetone. This may be due to the formation of water (which occurs when t-butyl alcohol is irradiated) and subsequent reaction with the diphosphine, or to decomposition of intermediate (3) by pathway (c). t-Butyl diphenylphosphinate was prepared and photolysed in t-butyl alcohol solution after which it was recovered unchanged.

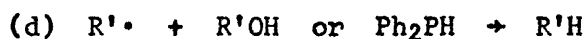
The irradiations with diphenylphosphine and bisazoisobutyronitrile in alcohol solutions, however, suggest that the products from the photolysis of tetraphenyldiphosphine in alcohols are not formed simply by attack of diphenylphosphorus radicals on the alcohol. Nevertheless, production of diphenylphosphorus radicals in the presence of tervalent phosphorus compounds (in alcohol solutions) definitely results in oxidation. This can be accounted for by the following sequence:-



(4)

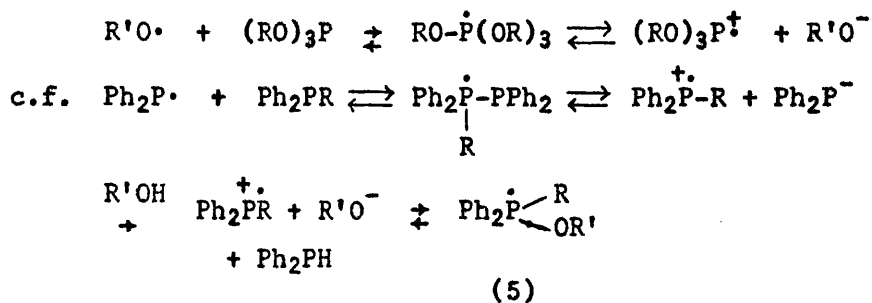


(5)



Where R=Ph, OR, NR₂

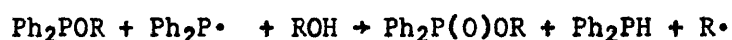
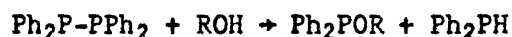
The radical cation (4) is analogous to the triphenylphosphinium cation radical previously proposed as an intermediate in some reactions of triphenylphosphine.^{52,53} Formation of substantial amounts of triphenylphosphine oxide in the irradiation of triphenylphosphine in alcohol solutions may be explained in this manner. When $R=RO$, intermediate (5) becomes the same as that postulated on P.29. for attack of alkoxyl radicals on a phosphinite. Thus the same intermediate may be arrived at without ever invoking an alkoxyl radical. Decomposition of the phosphoranyl radical (5) is exactly analogous to the decomposition of phosphoranyl radicals produced by the attack of alkoxyl radicals on phosphites. As Walling has pointed out⁷⁹ in the reaction of alkoxyl and thiyl radicals with phosphites, since these are very strongly electron-accepting radicals it is plausible that the reaction derives considerable driving force from the contribution of polar structures to the transition state, especially in a polar solvent:-



Subsequent breakdown of the phosphoranyl radical (5) in turn must derive its driving force from the very strong $\overset{+}{\text{P}}-\overset{-}{\text{O}}$ bond in the product.

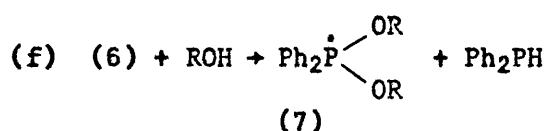
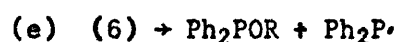
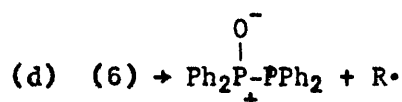
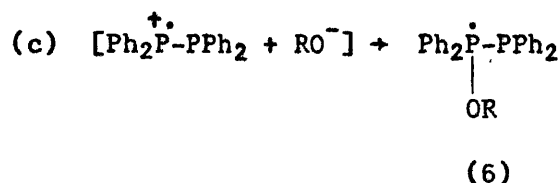
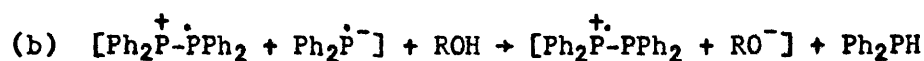
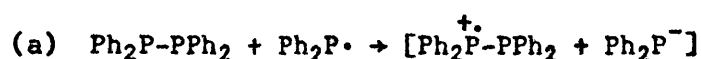
Generation of thiyl radicals in the presence of tervalent phosphorus compounds, in alcohol solutions, does not exhibit this solvent participation.⁷⁸ This may be explained by the fact that the relative acid strengths of thiols, alcohols, and phosphines decrease in the order $\text{RSH} > \text{ROH} > \text{R}_2\text{PH}$. Step (b) in the sequence shown, obviously depends on the fact that $\text{R}'\text{OH}$ is a stronger acid than Ph_2PH . In the case of thiyl radicals, ROH is not a stronger acid than RSH , and therefore the reaction would not be expected to proceed via step (b).

Considering that the photolysis of dimethylamino-diphenylphosphine in methanol gives methyl diphenylphosphinite apparently by an ionic mechanism, the photolysis of tetraphenyl-diphosphine in alcohol solutions may involve a combination of ionic and free radical mechanisms. Thus the first step may be formation of methyl diphenylphosphinite by an ionic mechanism. At the same time, diphenylphosphorus radicals may be formed by homolytic cleavage of the P-P bond, and these in turn may oxidise the methyl diphenylphosphinite by the mechanism outlined on P.30.



Theoretically, if all the alkane was produced as a result of hydrogen abstraction from the diphenylphosphine, then only a catalytic amount of diphenylphosphorus radicals need be present in solution to effect complete oxidation of the phosphinite. In practice some of the alkane is probably produced by attack on the solvent. Obviously this would depend on the stability of $R\cdot$.

A further possible mechanism is via attack of diphenylphosphorus radicals on the tetraphenyldiphosphine as shown:-



As is shown there are three possible modes of decomposition of the intermediate (6). Pathway (d) leads to tetraphenyldiphosphine monoxide which is not formed in any significant amount in these reactions. Pathway (e) leads to phosphinite and diphenylphosphorus radicals which is exactly the same state of affairs proposed in the previous mechanism. Pathway (f) invokes the formation of the same phosphoranyl radical as in the previous mechanism which then decomposes to phosphinate and an alkyl radical $R\cdot$. In principle, the intermediate (6) could be prepared by the reaction of a peroxide with tetraphenyldiphosphine (see P.40 for the reaction of ditertiarybutyl peroxide with tetraphenyldiphosphine).

VII. Photolysis of tetraphenyldiphosphine in optically active octan-2-ol.⁸⁵

Evidence to support the postulate that no α -C-H bond was broken during the formation of the phosphinates was gained from the photolysis of tetraphenyldiphosphine in optically active octan-2-ol.

Octan-2-ol was resolved using the normal procedure.⁸⁴ Irradiation of a 40% solution of tetraphenyldiphosphine in (-)-octan-2-ol, $[\alpha]_D^{20} -9.44^\circ$, at 100° (because of low solubility) gave a mixture of (-)-octan-2-yl diphenylphosphinite and the phosphinate, air oxidation of which gave the phosphinate $[\alpha]^{20} -4.98^\circ$ (589m μ),

-5.22° (578 mμ), -5.80° (546 mμ), -9.30° (436 mμ), -12.9° (365 mμ in hexane). Authentic (-)-octan-2-yl diphenylphosphinate, obtained by oxidation of the (-)-phosphinite prepared from (-)-octan-2-ol and dimethylaminodiphenyl phosphine at 125° for 15 hr., had $[\alpha]^{20}_D$ -5.63° (589 mμ), -5.91° (578 mμ), -6.64° (546 mμ), -10.51° (436 mμ), -14.44° (365 mμ in hexane). The high degree of retention of configuration shows clearly that at no part in the reaction is the α-C-H bond broken.

VIII. Irradiation of tetraphenyldiphosphine in a benzene solution containing phenol.

A solution of tetraphenyldiphosphine and excess phenol in dry benzene was irradiated for 18 hr. in a pyrex apparatus. As with the irradiations in alcohol solutions the products were diphenylphosphine and the corresponding phosphinate, in this case, phenyl diphenylphosphinate.

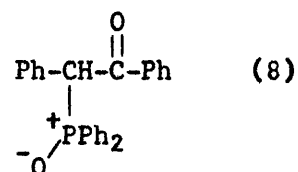
IX. The thermal reaction of tetraphenyldiphosphine with alcohols. ⁸¹

As it seemed likely that tetraphenyldiphosphine would be dissociated into diphenylphosphorus radicals at high temperatures, the thermal reaction of tetraphenyldiphosphine with alcohols has been studied. A mixture of the diphosphine and the alcohol was kept at 180°-200° for 3-4 hours. The results were different to those of the irradiation experiments. In the thermal reactions with ROH, when R was a benzylic group ($R = CH_2Ph$, $CHPh_2$, CPh_3 or

CHPh•COPh) the corresponding phosphine oxide, $\text{Ph}_2\text{P}(\text{O})\text{R}$, was formed instead of the phosphinate, $\text{Ph}_2\text{P}(\text{O})\text{OR}$. When R was not a benzylic group ($\text{R} = 2\text{-C}_8\text{H}_{17}$) the phosphinate was formed, as in the irradiation experiments. The thermal reaction of tetraphenyl-diphosphine with phenol also gave the phosphinate, in this case phenyl diphenylphosphinate, $\text{Ph}_2\text{P}(\text{O})\text{OPh}$.

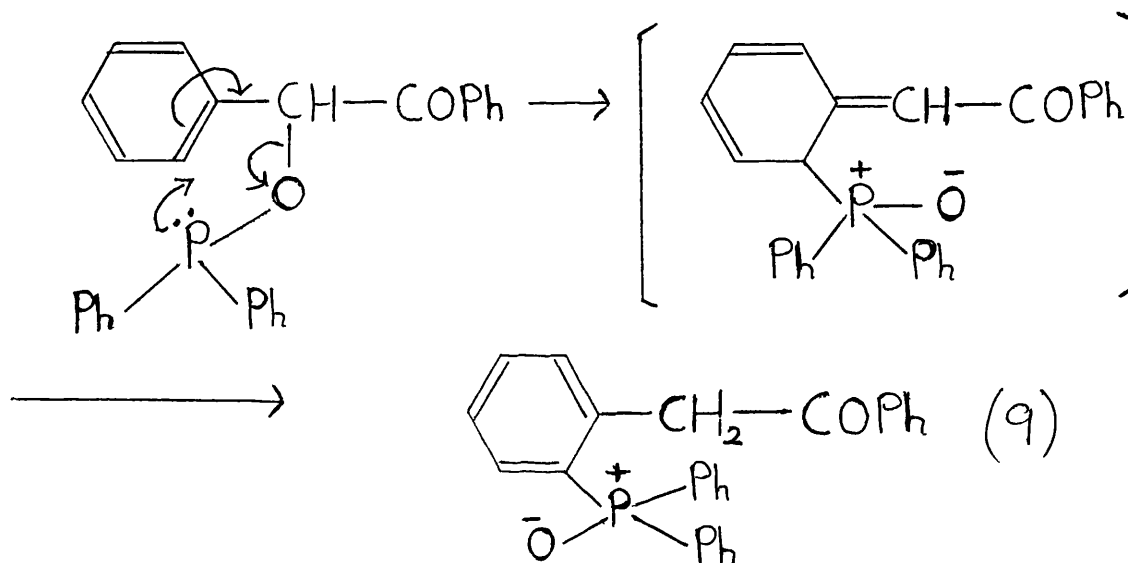
The reaction with benzyl alcohol gave diphenylphosphine and benzyldiphenylphosphine oxide in good yield but no toluene was formed. Diphenylmethanol gave, in addition to diphenylphosphine, benzophenone (32%) and (diphenylmethyl)-diphenylphosphine oxide (30%). Triphenylmethanol gave triphenylmethane (73%) and diphenylphosphinic acid, together with a small amount (7%) of diphenyl(triphenylmethyl)phosphine oxide.

The reaction of tetraphenyldiphosphine with benzoin gave a number of products. In addition to the expected (α -benzoylbenzyl) diphenylphosphine oxide (8), deoxybenzoin and diphenylphosphinic acid were also isolated together with a phosphine oxide isomeric with (8). A proton magnetic resonance spectrum of this



unknown phosphine oxide showed the presence of a CH_2 group (singlet $\tau 5.7$) and a mass spectrum had peaks at m/e 396 (molecular ion),

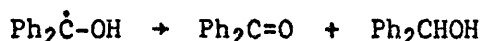
291 $[\text{Ph}_2\text{P}(\text{O})\text{C}_6\text{H}_4\text{CH}_2^+]$, 201 $(\text{Ph}_2\text{P}^+-\text{O})$ and 105 $(\text{PhC}^+=\text{O})$. These facts suggested that the compound was 2-diphenylphosphinylbenzyl phenyl ketone (9). Confirmation that the structure was correct was obtained by its oxidation to o-diphenylphosphinylbenzoic acid with alkaline potassium permanganate. An authentic sample of the acid was obtained by oxidation of diphenyl-o-tolylphosphine oxide with alkaline potassium permanganate. The phosphine oxide



is probably formed by an allylic rearrangement of the intermediate phosphinite. Other reactions in which this type of rearrangement occur have been encountered.⁸²

The formation of benzophenone in good yield in the reaction of diphenylmethanol indicates the presence of free radicals. The hydrogen of the α -C-H bond is very readily abstracted by free radicals to give the α -hydroxydiphenylmethyl radical (10) which readily disproportionates to give benzophenone

and diphenylmethanol. Likewise, the isolation of alkanes in good



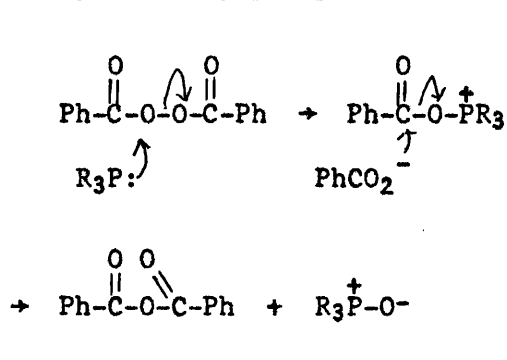
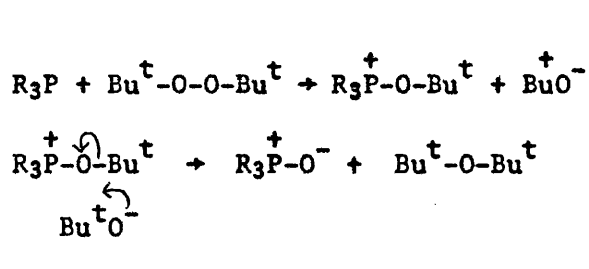
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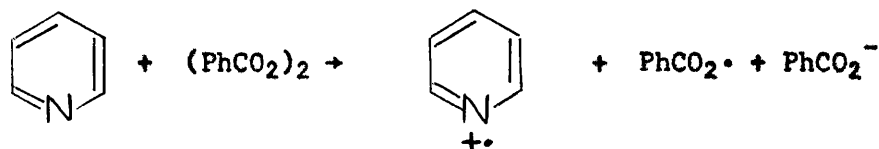
yields from the reaction with triphenylmethanol and benzoin also point to a radical mechanism. The formation of phosphine oxides and not phosphinates may be accounted for by the ease of thermal rearrangement of benzylic phosphinites.⁸³ As was suggested with the irradiation experiments the thermal reactions may involve a combination of ionic and radical mechanisms.

As with the irradiation experiments, the thermal reaction of tetraphenyldiphosphine with optically active octan-2-ol was studied to demonstrate that the α -C-H bond was not broken during the reaction.

(+)-Octan-2-ol, $[\alpha]_{\text{D}}^{20} + 9.45^\circ$, on heating with tetraphenyldiphosphine to 180° - 200° for 4 hours gave octan-2-yl diphenylphosphinite having $[\alpha]_{\text{D}}^{20} + 26.9^\circ$ (benzene) which on oxidation gave the phosphinate having $[\alpha]_{\text{D}}^{20} + 1.9^\circ$ (20% solution in CCl_4). Authentic phosphinite obtained from (+)-octan-2-ol and diphenylphosphinous chloride had $[\alpha]_{\text{D}}^{20} + 28.1^\circ$ (benzene). Authentic phosphinate obtained from (+)-octan-2-ol and diphenylphosphinic chloride had $[\alpha]_{\text{D}}^{20} + 1.85^\circ$ (20% solution in CCl_4). The high degree of retention of configuration clearly shows, as with the photolysis in optically active octan-2-ol, that at no part in

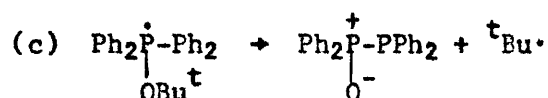
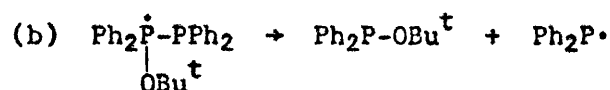
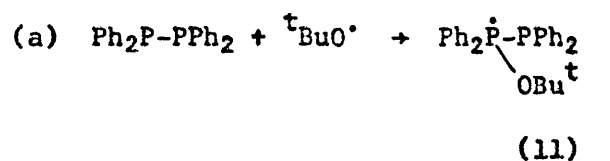
peroxide.





The reaction between tetraphenyldiphosphine and ditertiarybutyl peroxide has been studied at 130° because it was hoped that as the half-life of ditertiarybutyl peroxide is fairly short at this temperature then a free radical reaction with the diphosphine would be more likely than at room temperature.

Attack by tertiarybutoxyl radicals on tetraphenyldiphosphine would give the intermediate (11) which is exactly analogous to the intermediate (6) proposed on P. 33 as a possible intermediate in the photolysis of tetraphenyldiphosphine in alcohol solutions. As shown there are then two possibilities for breakdown



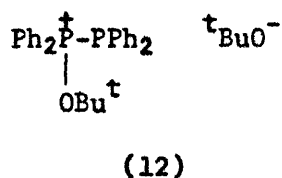
of (11). Pathway (b) leads to exactly the same state of affairs cited in the photolysis reactions in alcohol solution which lead to oxidation of the phosphinite.

Ditertiarybutyl peroxide was added to tetraphenyldiphosphine in chlorobenzene at 130° [in the molar ratio 2(Ph_2P)₂:1(${}^t\text{BuO}$)₂].

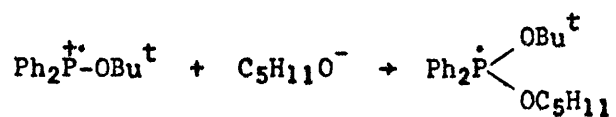
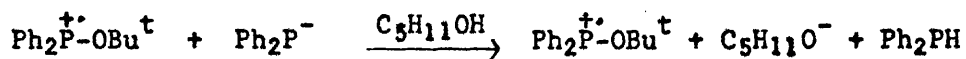
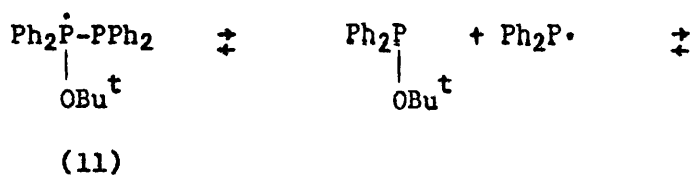
The solution was kept at 130° for 15 hours and then evaporation of the solvent gave a good yield of tetraphenyldiphosphine monoxide. This was as predicted by pathway (c) above. If an excess of peroxide was used this resulted in complete oxidation of the diphosphine to diphenylphosphinic anhydride.

Assuming the reaction was proceeding via (11) then if it was carried out in alcohol solution the products should be the same as in the alcohol reactions with tetraphenyldiphosphine. There was virtually no reaction between tetraphenyldiphosphine and pentan-2-ol at 130°C so the reaction was carried out using pentan-2-ol as solvent. The products isolated were pentan-2-yl diphenylphosphinate and diphenylphosphine oxide (isolated as condensation product with acetone). The reaction between the diphosphine and the peroxide is undoubtedly much faster than with the solvent under these conditions, even though the solvent is present in large excess. Additional evidence against the reaction proceeding via initial reaction with the solvent was provided by using benzyl alcohol as solvent. The products were benzyl diphenylphosphinate and diphenylphosphine oxide; no benzyl-diphenylphosphine oxide was detected. If the reaction with the solvent was faster than reaction with the peroxide the benzyl diphenylphosphinite so produced would undoubtedly rearrange to benzyldiphenylphosphine oxide extremely rapidly under these conditions. Furthermore, no ethers could be found in any of

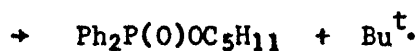
these reactions, thus implying that the reaction was not proceeding via an ionic mechanism. Indeed it is difficult to see how the observed products could be derived from the expected ionic intermediate (12), although a mechanism can be written via a



pentacovalent intermediate. From these results, therefore, it seems likely that the reaction is proceeding via a free radical mechanism involving the intermediate (11) shown on P. 40.



(13)



The formation of pentan-2-yl diphenylphosphinate and not tertiarybutyl diphenylphosphinate from intermediate (13) is not unexpected as the formation of the tertiarybutyl radical is

much more favourable than formation of the pentan-2-yl radical. Moreover, intermediate (13) may eventually consist of two pentan-2-yloxy groups via dissociation and exchange with solvent.

Summary

From the experimental evidence two alternative mechanisms are proposed to account for the results of irradiations of tetraphenyldiphosphine in alcohol solutions. These are (a) initial formation of diphenylphosphine and alkyl diphenylphosphinite by alcoholysis of the diphosphine followed by oxidation of the phosphinite via attack of diphenylphosphorus radicals on the phosphinite and anion exchange with the solvent, and (b) attack of diphenylphosphorus radicals on the diphosphine to give a radical cation and a diphenylphosphide anion which proceed to products via anion exchange with the solvent. From the experimental evidence it is impossible to distinguish between these two alternative mechanisms. Similarly the thermal reaction of alcohols with tetraphenyldiphosphine may be a combination of ionic and free radical mechanisms.

From the experimental evidence it seems likely that the thermal reaction of tetraphenyldiphosphine with ditertiarybutyl peroxide is a free radical reaction and the results substantiate some of the mechanistic postulates concerning the alcohol reactions.

EXPERIMENTAL

All experiments were carried out under oxygen-free nitrogen. Light petroleum refers to the fraction b.p. 60-80°. P.m.r. spectra were recorded for solutions in carbon tetrachloride or deuteriochloroform using a Varian A-60 spectrometer. Irradiation of tetraphenyldiphosphine in cumene (isopropylbenzene).

Tetraphenyldiphosphine (1.0 g.) was dissolved in pure dry cumene (10 ml.) (purified by the method of Bartlett et al;⁹⁴ warming was necessary to effect dissolution) and the solution irradiated for 30 hours in quartz apparatus. After removal of the excess cumene in vacuo the residue was taken up in chloroform and washed thoroughly with alkaline hydrogen peroxide, then with water, and dried. Removal of the chloroform left a small amount of an oily residue which, on trituration with a small amount of ethanol, solidified. The solid was dicumene (25 mg.), m.p. and mixed m.p. 116-117° (lit.⁷³ 117-118°).

Irradiation of triphenylphosphine in methanol (I).

A solution of triphenylphosphine (1.57 g.; 0.006 mole) in dry methanol (100 ml; distilled under nitrogen) was irradiated for 8 hr. Benzene, diphenyl and diphenylphosphine were determined by gas chromatography (2m apiezon column at 40°, and 2m silicone gum rubber column at 170° and 200° respectively). Tetraphenyl-

phosphonium methoxide was determined by precipitation; excess ethanolic sodium tetraphenylboron was added to the solution and the precipitate of tetraphenylphosphonium tetraphenylboron, washed well with water, ethanol, then ether, and finally dried (wt. 0.71 g.), m.p. and mixed m.p. 263-4°. The mother liquors left after precipitation of the phosphonium salt were evaporated to dryness and the last traces of methanol removed in vacuo. Methyl diphenylphosphinate was determined in the residue by quantitative p.m.r. spectroscopy using toluene as an internal standard. A small amount of pure methyldiphenylphosphinate, m.p. and mixed m.p. (light petroleum) 61-62° was obtained by distillation of the residue under reduced pressure. Authentic tetraphenylphosphonium tetraphenylboron was prepared by adding an ethanolic solution of sodium tetraphenylboron to an ethanolic solution of tetraphenylphosphonium iodide. The precipitate was washed with water, ethanol, ether and dried to give tetraphenylphosphonium tetraphenylboron (91%) m.p. 263-4°.

In another experiment, using exactly the same conditions, aliquots were taken from the solution every hour and the amount of benzene determined by gas chromatography. The formation of benzene had reached a maximum after four hours and then decreased slightly in the next four hours.

Irradiation of triphenylphosphine in methanol (II).

A solution of triphenylphosphine (0.79 g; 0.003 mole)

in dry methanol (100 ml; distilled under nitrogen) was irradiated for 8 hr. Benzene and diphenyl were determined by gas chromatography as before. No diphenylphosphine was detected by gas chromatography. Similarly no precipitate formed on the addition of an ethanolic solution of sodium tetraphenylboron. Phenylphosphine was determined by gas chromatography (2m. silicone gum rubber column at 100°). The solution was evaporated to leave an oily residue, the infrared spectrum of which indicated that it contained a lot of triphenylphosphine oxide. P.m.r. spectroscopy showed that the residue contained some methyl diphenylphosphinate. The residue was chromatographed on basic alumina (10 g; Spence type H). Elution with ether gave methyl diphenylphosphinate (0.11 g.) m.p. and mixed m.p. (from light petroleum) 61-62°. Elution with acetone gave triphenylphosphine oxide (0.29 g.), m.p. and mixed m.p. (from ether) 152-153°.

Preparation and irradiation of tetraphenylphosphonium methoxide.

A solution of tetraphenylphosphonium chloride (0.467 g; 0.00125 mole) in dry methanol (50 ml.) was added to 50 ml. of a 0.025M solution of sodium methoxide in methanol. The solution was then irradiated for 18 hr., after which time the solution gave no precipitate when treated with sodium tetraphenylboron. Evaporation of the solution gave an oily residue, the infrared spectrum of which indicated that it was a complex mixture.

Irradiation of tetraphenyldiphosphine in alcoholic solutions.

A solution of the diphosphine (0.5 g.) in the anhydrous alcohol (15 ml; distilled under nitrogen) was irradiated for 18 hr. at room temperature. Diphenylphosphine and toluene were determined by gas chromatography (2m. silicone gum rubber column at 200° and 70° respectively). Alkyl diphenylphosphinates were determined, after removal of the excess alcohol, by quantitative p.m.r. spectroscopy using toluene as an internal standard. The results are given in the table on P. 25. The residues, after removal of the excess alcohol, could in some cases be crystallized. If not, acidic impurities were removed by washing a solution in chloroform with aqueous sodium hydrogen carbonate and the residue was then crystallized.

The following phosphinates were obtained: methyl (0.18 g.), m.p. and mixed m.p. (from light petroleum) 61-62°; ethyl (0.2 g.), b.p. 162-165°/0.8 mm. (lit., ⁹⁰ 173-175°/1.5mm.), quintet at τ 5.9 (J_{PH} 7 c.p.s.), triplet at τ 8.7 (J_{HH} 6 c.p.s.); isopropyl (0.26 g.), m.p. and mixed m.p. (from ether) 96-97° (lit., ⁹¹ 95-96°); octan-2-yl (0.26 g.), b.p. 178-182°/0.3 mm., infrared spectrum identical with that of an authentic sample; benzyl (0.19 g.), m.p. and mixed m.p. (from ether) 77-78°.

The reaction mixture after irradiation in t-butyl alcohol contained acetone and volatile hydrocarbons (50 m. polypropylene glycol column at room temperature). The residue, after evaporation

crystallized from ether to give diphenylphosphinic acid (0.2 g.), m.p. and mixed m.p. (from aqueous ethanol) 190-192°.

Authentic samples of the phosphinates were prepared by the following general method. Diphenylphosphinic chloride (1.2 g.) was added to a solution of the alcohol (slight excess) in dry pyridine (10 ml.). The solution was allowed to stand at room temperature for 30 min. and then poured into excess dilute hydrochloric acid (2N). The mixture was extracted with chloroform and the chloroform extract washed with aqueous sodium hydrogen carbonate, then with water, and dried. Removal of the chloroform left a residue which crystallized in most cases. If not, the residue was purified by chromatography on basic alumina (Spence type H) or by distillation. The phosphinates had the following properties: methyl m.p. (from light petroleum) 61-62°, doublet at τ 6.4 (J_{PH} 11 c.p.s.); ethyl, b.p. 163-165°/0.8 mm. (lit., ⁹⁰ 173-175°/1.5mm.), n_D^{25} 1.5636 (lit., ⁹² 1.5632); isopropyl, m.p. (from ether) 95-96°, doublet at τ 8.7 (J_{HH} 7 c.p.s.); octan-2-yl, b.p. 180-182°/0.3 mm. (Found: C, 72.6; H, 8.1; P, 9.3. $C_{20}H_{27}O_2P$ requires C, 72.75; H, 8.2; P, 9.4%); benzyl, m.p. (from benzene-light petroleum) 78-78.5°, doublet at τ 4.95 (J_{PH} 7 c.p.s.), (Found: C, 73.8; H, 5.4; P, 10.0. $C_{19}H_{17}O_2P$ requires C, 74.0; H, 5.5; P, 10.0%); phenyl m.p. (from aqueous ethanol) 137-138° (lit., ⁹³ 135-136°).

t-Butyl diphenylphosphinate was obtained by treating t-butyl alcohol (5 ml.) in pyridine (10 ml.) with diphenylphosphinous chloride (4.4 g.) for 1 hr. After filtration, air was drawn through the reaction mixture for 10 min. The mixture was poured into sulphuric acid (30 ml; 2N), extracted with chloroform, and the extract washed with aqueous sodium hydroxide and water, and dried. Removal of the chloroform in vacuo left an oil which, on dissolution in ether and cooling to -40° , gave t-butyl diphenylphosphinate (2.0 g.), m.p. (from light petroleum b.p. $80-100^{\circ}$) $114.5-115^{\circ}$ (Found: C, 69.4; H, 7.0; P, 11.35. $C_{16}H_{19}O_2P$ requires C, 70.1; H, 6.95; P, 11.3%). After irradiation of the t-butyl diphenylphosphinate for 18 hr. in t-butanol it could be recovered unchanged by evaporation of the solvent.

Irradiation of tetraphenyldiphosphine in a benzene solution containing phenol.

The diphosphine (0.5 g.) and phenol (2.5 g.) were dissolved in benzene (15 ml.) and irradiated for 18 hr. Benzene (35 ml.) was added, and the solution washed with aqueous sodium hydroxide and water and then dried. Methyl iodide (2 ml.) was added, and the solution heated under reflux for 1 hr; dimethyldiphenylphosphonium iodide (0.33 g.) separated, m.p. and mixed m.p. (from chloroform/ethyl acetate) $256-257^{\circ}$. The mother liquors were evaporated and the residue recrystallized from ether, to give phenyl diphenylphosphinate (0.25 g.) m.p. and mixed m.p.

(from ether) 135-136°.

Irradiation of tetraphenyldiphosphine in (-)-octan-2-ol.

A solution of tetraphenyldiphosphine (2.2 g.) in pure, dry (-)-octan-2-ol (5 ml.; $[\alpha]_D^{20}$ -9.44°; it was necessary to maintain the solution at 100° by passing steam through a tube immersed in the pyrex reaction vessel) was irradiated for 18 hr. The reaction mixture was then distilled under reduced pressure. The first fraction collected (b.p. 90-120°/0.3 mm.) consisted mainly of diphenylphosphine. A further three fractions were taken over the boiling range 144-188°/0.3 mm. The optical rotations and infrared spectra of these fractions indicated that they were mixtures of (-)-octan-2-yl diphenylphosphinate and phosphinate, the high boiling fraction being almost pure phosphinate. The fractions were combined (combined wt. 0.55 g.) and dissolved in benzene (20 ml.). Air was drawn through the solution for 1 hr. after which time the solution was chromatographed on basic alumina (10 g; Spence type H). (-)-octan-2-yl diphenylphosphinate was eluted with ether (0.32 g.), infrared spectrum identical with authentic sample, $[\alpha]^{20}$ -4.98° (589 mμ), -5.22° (578 mμ), -5.80° (546 mμ), -9.30° (436 mμ), -12.9° (365 mμ).

Authentic (-)-octan-2-yl diphenylphosphinite was prepared by heating dimethylaminodiphenylphosphine (2.3 g.) and (-)-octan-2-ol (2 ml.) at 125° for 15 hr. The product was distilled under reduced pressure, b.p. 145-146°/0.3mm.,

$[\alpha]^{20}$ -28.42° (589 mμ), -29.49° (578 mμ), -32.96° (546 mμ), -57.35 (436 mμ), -92.87 (365 mμ in benzene). Authentic (-)-octan-2-yl diphenylphosphinate was prepared by the following method. (-)-Octan-2-ol (1.3 g.) was added to a solution of diphenylphosphinic chloride (2.37 g.) in pyridine (10 ml.) and the solution allowed to stand for 2 days. The solution was poured into excess dilute sulphuric acid (2N) and extracted with ether. The ether extract was washed with aqueous sodium hydrogen carbonate, then with water, and dried. After removal of the ether the residue was distilled under reduced pressure b.p. 186-187°/0.6 mm., $[\alpha]^{20}$ -5.63° (589 mμ), -5.91° (578 mμ), -6.64° (546 mμ), -10.51° (436 mμ), -14.44° (365 mμ in hexane).

The thermal reaction of tetraphenyldiphosphine with benzyl alcohol

A mixture of the diphosphine (1.0 g.) and benzyl alcohol (5 ml.) was heated under reflux for 7 hr. The excess of alcohol was removed by distillation in vacuo, and the residue triturated with ether, to give benzyldiphenylphosphine oxide (0.8 g.), m.p. and mixed m.p. (from ethanol) 192-193° (lit.,⁸³ 192-193°).

The thermal reaction of tetraphenyldiphosphine with octan-2-ol.

A mixture of the diphosphine (1.0 g.) and octan-2-ol (5 ml.) was heated under reflux for 3 hr. The mixture was distilled in vacuo. The following fractions were obtained: b.p. 48-55°/0.8 mm., unchanged octan-2-ol; b.p. 101-110°/0.8 mm.

(0.36 g.), diphenylphosphine; b.p. 178-186° (0.65 g.), octan-2-yl diphenylphosphinate, infrared spectrum identical with an authentic sample (see P. 47).

The thermal reaction of tetraphenyldiphosphine with phenol.

A mixture of the diphosphine (0.5 g.) and phenol (5 g.) was kept at 190-200° for 4 hours. The reaction mixture was dissolved in benzene, washed with aqueous sodium hydroxide and water, and dried. Methyl iodide (5 ml.) was added and the solution heated under reflux for 1 hr., to give dimethyldiphenylphosphonium iodide (0.31 g.), m.p. and mixed m.p. (from chloroform/ethylacetate) 256-257°. Evaporation of the mother liquors gave an oil which crystallized from ether to give phenyl diphenylphosphinate (0.22 g.), m.p. and mixed m.p. (from ether) 134-136°.

The thermal reaction of tetraphenyldiphosphine with diphenylmethanol

A mixture of the diphosphine (0.5 g.) and diphenylmethanol (0.25 g.) was kept at 190-200° for 3 hr. Chromatography of the reaction products on alumina (10 g; Spence type H) and elution with benzene gave benzophenone (0.09 g.), identified by infrared spectroscopy; elution with benzene-ether (1:1) gave (diphenylmethyl)diphenylphosphine oxide (0.19 g.) m.p. and mixed m.p. (from methanol) 304-305° (lit., ⁹⁷ 303°). An authentic sample of (diphenylmethyl)diphenylphosphine oxide was prepared from diphenylphosphinous chloride and diphenylmethanol m.p. 304-305°

(from methanol) (lit., ⁹⁷ 303°).

The thermal reaction of tetraphenyldiphosphine with triphenylmethanol.

A mixture of the diphosphine (0.74 g.) and the alcohol (0.52 g.) was kept at 180-200° for 3 hr. Methyl iodide (5 ml.) and benzene (10 ml.) were added, and the mixture was heated under reflux for 1 hr., to give dimethyldiphenylphosphonium iodide (0.15 g.), m.p. and mixed m.p. (from ethyl acetate/chloroform) 255-257°. Concentration of the mother liquors gave further crops of material: diphenylphosphinic acid (0.40 g.), m.p. and mixed m.p. (from aqueous ethanol) 190-192°; triphenylmethane (0.36 g.), m.p. and mixed m.p. (from ethanol) 91-92°; and diphenyl(triphenylmethyl)phosphine oxide (0.06 g.) m.p. and mixed m.p. (from ethanol) 227-228° (lit., ⁸³ 227-229°). An authentic sample of diphenyl(triphenylmethyl)phosphine oxide was prepared from triphenylmethyl chloride and methyl diphenylphosphinite in benzene, m.p. 227-228°.

The thermal reaction of tetraphenyldiphosphine with benzoin.

A mixture of the diphosphine (5.55 g.) and benzoin (3.18 g.) was kept at 180-200° for 4 hr. Trituration of the reaction mixture gave a solid. This was dissolved in chloroform and the solution washed with aqueous sodium hydroxide. Acidification of the alkaline washings gave diphenylphosphinic acid

(3.2 g.), m.p. and mixed m.p. (from aqueous ethanol) 190-192°. Evaporation of the dried chloroform solution gave (α -benzoylbenzyl)diphenylphosphine oxide (0.7 g.), m.p. and mixed m.p. (from aqueous methanol) 234-235° (lit.,⁹⁸ 235-236°). Evaporation of the ethereal solution gave a gum which was chromatographed on alumina (20 g; Spence type H). Elution with benzene gave deoxybenzoin (1.1 g.), m.p. and mixed m.p. (from light petroleum, b.p. 80-100°) 59-60°; elution with benzene/ether (1:1 v/v) gave 2-diphenylphosphinylbenzyl phenyl ketone (0.4 g.) m.p. (from aqueous ethanol) 137.5-138.5° (Found: C, 78.7; H, 5.4; P, 8.0. $C_{26}H_{21}O_2P$ requires C, 78.8; H, 5.35; P, 7.8%), and benzyldiphenylphosphine oxide (0.06 g.), m.p. and mixed m.p. (from ethanol) 192-193°; elution with ether gave diphenylphosphine oxide (0.03 g.), identified by infrared spectroscopy.

Preparation of o-diphenylphosphinylbenzoic acid.

Diphenyl-o-tolyl-phosphine oxide (2.92 g.) was suspended in aqueous sodium hydroxide (0.2 N; 100 ml.) Potassium permanganate (10 g.) was added, and the mixture heated under reflux for 5 hr., filtered, and acidified. The precipitated o-diphenylphosphinylbenzoic acid (3.3 g.) was filtered off, m.p. (from aqueous ethanol) 254-255° (found: C, 70.7; H, 4.65; P, 9.5. $C_{19}H_{15}O_3P$ requires C, 70.8; H, 4.7; P, 9.6%).

Oxidation of 2-diphenylphosphinylbenzyl phenyl ketone.

The phosphine oxide (0.1 g.) was suspended in aqueous

sodium hydroxide (0.2 N; 10 ml.), and potassium permanganate (0.25 g.) added. The mixture was heated under reflux for 5 hr. The excess of potassium permanganate was destroyed by the addition of ethanol. The reaction mixture was filtered and the filtrate acidified. The precipitated o-diphenylphosphinylbenzoic acid (0.05 g.) was filtered off, m.p. and mixed m.p. (from aqueous ethanol) 249-251°. The aqueous mother liquors were extracted with chloroform, and the chloroform solution dried and evaporated gave a small amount (~10 mg.) of benzoic acid, m.p. and mixed m.p. (from water) 119-121°. An attempted synthesis of o-diphenylphosphinylbenzyl phenyl ketone from diphenyl-o-tolyl-diphenylphosphine oxide, butyllithium and benzoyl chloride was a failure.

The thermal reaction of tetraphenyldiphosphine with (+)-octan-2-ol.

A mixture of tetraphenyldiphosphine (3.7 g.) and (+)-octan-2-ol (5 ml; $[\alpha]_D^{20} + 9.45$) was boiled under reflux for 4 hr. The solution was then distilled in vacuo and gave the following fractions: b.p. 60-70°/2 mm., unchanged (+)-octan-2-ol; b.p. 95-105°/0.5 mm. (1.45 g.), diphenylphosphine; b.p. 161-162°/1.2 mm. (1.3 g.), (+)-octan-2-yl diphenylphosphinite; >162°/1.2 mm., mixture of octan-2-yl diphenylphosphinite and phosphinate. The fraction b.p. 161-162°/1.2 mm. had an infrared spectrum identical with authentic octan-2-yl diphenylphosphinite and $[\alpha]_D^{20} + 26.9^\circ$ (10% in benzene). Air oxidation gave

(+)-octan-2-yl diphenylphosphinate having $[\alpha]_D^{20} + 1.9^\circ$ (20% solution in CCl_4). Authentic (+)-octan-2-yl diphenylphosphinite was obtained by heating dimethylaminodiphenylphosphine and (+)-octan-2-ol at 125° for 15 hours and had b.p. $174-175^\circ/1 \text{ mm.}$, $[\alpha]_D^{20} + 28.1^\circ$ (10% in benzene). Authentic (+)-octan-2-yl diphenylphosphinate was prepared from (+)-octan-2-ol and diphenylphosphinic chloride in pyridine and had b.p. $178-179^\circ/0.5 \text{ mm. Hg}$, $[\alpha]_D^{20} + 1.85^\circ$ (20% solution in CCl_4).

The thermal reaction of tetraphenyldiphosphine with ditertiarybutyl peroxide in chlorobenzene.

Ditertiarybutyl peroxide (0.1 ml.) was added to a solution of tetraphenyldiphosphine (0.5 g.) in dry chlorobenzene (10 ml.) at 130° and the solution then kept at 130° for 15 hr. On removing the chlorobenzene in vacuo the residue solidified and was washed with ether and collected. This gave tetraphenyldiphosphine monoxide (0.42 g.) m.p. and mixed m.p. $154-156^\circ$. Authentic tetraphenyldiphosphine monoxide was prepared by the method of McKechnie et al⁷⁰ and had m.p. $155-157^\circ$ (from benzene/ether). In a second experiment ditertiarybutyl peroxide (0.2 ml.) was added to a solution of tetraphenyldiphosphine (0.45 g.) in dry chlorobenzene (10 ml.) at 130° and the solution kept at 130° for 15 hr. Evaporation of the solution gave diphenylphosphinic anhydride m.p. and mixed m.p. (from benzene/ether) $149-150^\circ$.

Authentic diphenylphosphinic anhydride was prepared by the method of Moedritzer⁹⁹ and had m.p. 149-150° (lit. 143°).

The thermal reaction of tetraphenyldiphosphine with ditertiary-butyl peroxide in pentan-2-ol.

Ditertiarybutyl peroxide (0.1 ml.) was added to a solution of tetraphenyldiphosphine (0.5 g.) in dry pentan-2-ol (10 ml: distilled under nitrogen) at 130° and the solution kept at 130° for 15 hr. Removal of the solvent in vacuo left an oily residue, the infrared spectrum of which indicated that it contained diphenylphosphine oxide together with a phosphinate. The oil was dissolved in acetone (10 ml.) and one drop of pyridine added. On standing, colourless crystals separated and were filtered off and washed with ether and dried to give (α -hydroxyisopropyl)diphenylphosphine oxide (0.34 g.), m.p. and mixed m.p. 151-152° (d), (lit.,¹⁰⁰ 152° (d)). Evaporation of the mother liquors in vacuo gave an oil (0.25 g.) which was pentan-2-yl diphenylphosphinate (identified by infrared and p.m.r. spectroscopy).

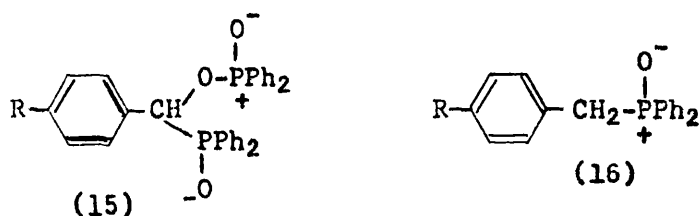
The thermal reaction of tetraphenyldiphosphine with ditertiary-butyl peroxide in benzyl alcohol.

Ditertiarybutyl peroxide (0.1 ml.) was added to a solution of tetraphenyldiphosphine (0.5 g.) in dry benzyl alcohol

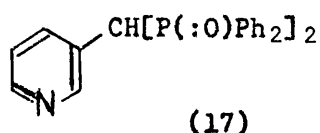
(10 ml; distilled under nitrogen) at 130° and kept at 130° for 15 hr. After removal of the solvent in vacuo the oily residue was taken up in acetone (10 ml.) and one drop of pyridine added. Crystals of (α -hydroxyisopropyl)diphenylphosphine oxide (0.39 g.) separated, m.p. and mixed m.p. 151-152°. The mother liquors were evaporated and the residue chromatographed on alumina (Spence type H). Elution with ether gave benzyl diphenylphosphinate (0.27 g.) m.p. and mixed m.p. 76-78° (from benzene/light petroleum). Neither dibenzyl ether nor benzyltertiarybutyl ether were detected in the reaction mixture.

Benzoic acid and tetraphenyldiphosphine at 180-200° for

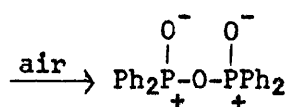
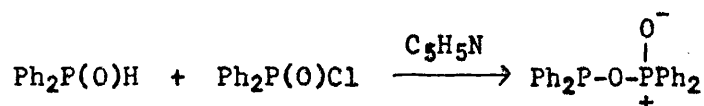
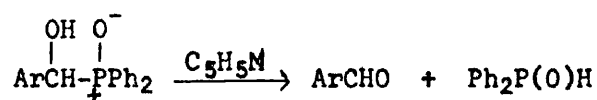
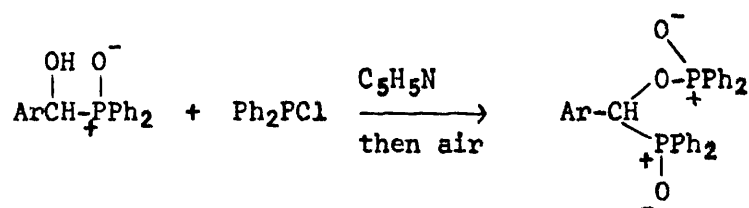
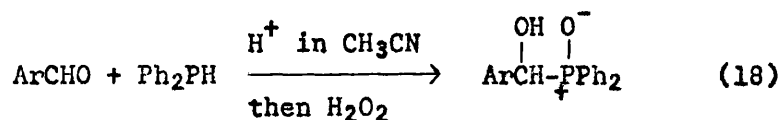
4 hr. gave a compound whose molecular formula, $C_{31}H_{26}O_3P_2$, was confirmed by mass spectrometry. Significant peaks besides the parent at m/e 508 included m/e 201 (Ph_2PO), 217 (Ph_2PO_2), and 291 ($Ph_2PO.CHPh$). The infrared spectrum included absorption characteristic of phosphine oxides (1203 cm^{-1}) and phosphinates [1220 cm^{-1} ($P:O$) and a doublet centred on 1000 cm^{-1} ($P\cdot O\cdot C$)] and the compound was therefore α -(diphenylphosphinyloxy) benzyldiphenylphosphine oxide (15; $R=H$).



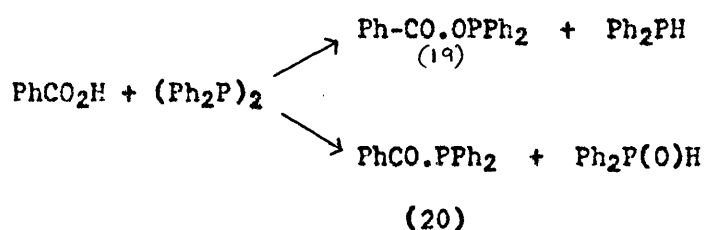
On the other hand, under the same conditions anisic acid and tetraphenyldiphosphine gave *p*-methoxybenzyldiphenyl phosphine oxide (16; $R=OMe$). In general, aromatic acids containing electron attracting substituents gave phosphine oxides (15) analogous to that from benzoic acid while those acids having substituents capable of electron-supply gave substituted benzyl-phosphine oxides (16). *p*-Isopropylbenzoic acid gave a mixture of the oxides (15 + 16; $R=Me_2CH$) while nicotinic acid gave, besides an oxide analogous to (15), the ditertiaryphosphine dioxide (17).



The oxides (15) were unambiguously synthesized from the corresponding α -hydroxybenzylidiphenylphosphine oxides (18) by the action of chlorodiphenylphosphine and pyridine followed by oxidation with air. The direct route with diphenylphosphinic chloride and pyridine gave largely diphenylphosphinic anhydride, probably formed via the base catalysed dissociation of the oxides (18) to give diphenylphosphine oxide. α -Hydroxybenzylidiphenylphosphine oxides are easily prepared from the corresponding aldehyde as shown.¹⁰³



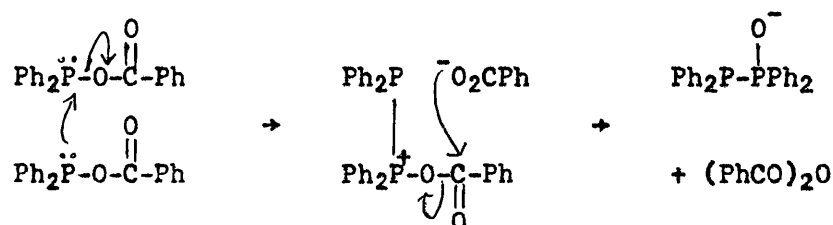
Two routes have been considered for the formation, from tetraphenyldiphosphine, of the phosphine oxide (15; R=H) involving as first steps the formation of benzoyloxydiphenylphosphine (19) and benzoyldiphenylphosphine (20) respectively. The latter reaction is analogous to the formation of amides and diphenylphosphine oxide in the reactions of carboxylic acids with dialkylaminodiphenylphosphines (102). The preparation and properties of (19) and (20) have therefore been studied together



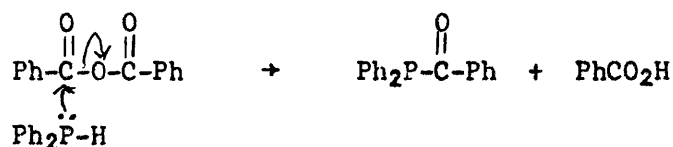
with those of benzoyldiphenylphosphine oxide which could conceivably be formed by rearrangement of (19). It has been shown (see P. 70) that the oxides (15) are intermediates in those reactions which lead to the benzylphosphine oxides (16).

Acyloxyphosphines^{82,121,122} and the analogous dialkyl acyl phosphites^{123,124,125} have been reported. Benzoyloxydiphenylphosphine (19) was obtained (a) from benzoic anhydride and diethylaminodiphenylphosphine, (b) from triethylammonium benzoate and diphenylphosphinous chloride in methylene chloride at room temperature, and (c) from sodium benzoate and diphenylphosphinous chloride in refluxing ether. When heated with diphenylphosphine at 100° it gave tetraphenyldiphosphine and benzoic acid. Alone

at 140° it gave, not the expected benzoyldiphenylphosphine oxide, but benzoic anhydride and tetraphenyldiphosphine monoxide. It therefore seems improbable that the reaction of tetraphenyl-diphosphine with benzoic acid proceeds via benzoyloxydiphenylphosphine.



Benzoyldiphenylphosphine has been prepared by Issleib and Priebe¹⁰⁴ from sodium diphenylphosphide and benzoyl chloride. It may also be prepared by heating benzoic anhydride and diphenylphosphine at 100°. Heating the resulting mixture of benzoyldiphenylphosphine and benzoic acid with diphenylphosphine oxide

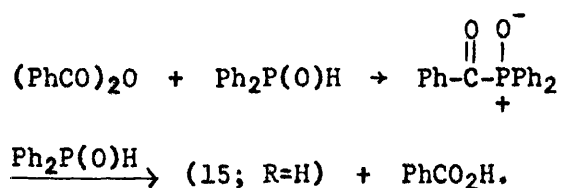


gave, after working up in air,* a high yield of the phosphine

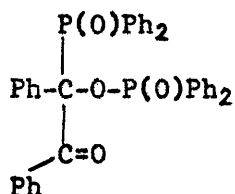
* The stoichiometry of this and of several of the other reactions described in this paper demands that oxidation by air occurs during the isolation of the product.

oxide (15; R=H) obtained from tetraphenyldiphosphine and benzoic acid. The latter reaction probably involves the intermediate formation of benzoyldiphenylphosphine and diphenylphosphine oxide.

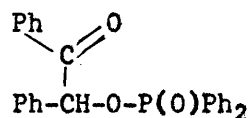
Issleib and Priebe¹⁰⁴ reported that benzoyldiphenylphosphine could not be oxidised to its oxide. Several possible routes to this oxide have been investigated but the oxide appears to be so susceptible to nucleophilic addition that only products of further reactions have been isolated. The corresponding dialkyl benzoylphosphonates are known¹⁰⁵ to be extremely reactive carbonyl compounds. When equimolar amounts of benzoic anhydride and diphenylphosphine oxide were heated together, half of the anhydride was consumed and the oxide (15; R=H) was isolated. Two molar equivalents of diphenylphosphine oxide gave a quantitative yield of the oxide (15; R=H).



When the sodium salt of diphenylphosphine oxide was treated with benzoyl chloride in tetrahydrofuran at 0°, two compounds were isolated. One was the oxide (15; R=H) and the other has been assigned structure (21). Acidic hydrolysis of (21) gave the oxide (15; R=H), benzoic and diphenylphosphinic acids and the ester (22) of benzoin and diphenylphosphinic acid. The oxide (15; R=H) is unaffected by refluxing concentrated hydrochloric acid. Alkaline

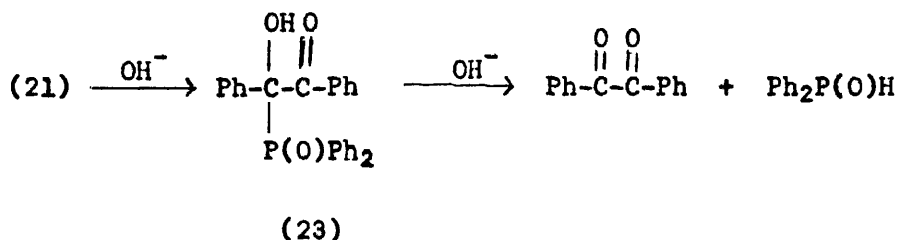


(21)



(22)

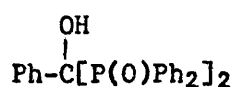
hydrolysis gave benzoic, benzilic, and diphenylphosphinic acids, and benzyldiphenylphosphine oxide. Inadvertent chromatography of the oxide (21) on basic alumina gave benzil which presumably is the source of the above benzilic acid and is formed by base-catalysed dissociation of the hydroxy-phosphine oxide (23).



An attempted preparation of benzoyldiphenylphosphine oxide by an Arbuzov reaction using methyl diphenylphosphinite and benzoyl chloride gave a crude product, the infrared spectrum of which showed a small carbonyl peak. However, the only isolable product was the oxide (15; R=H) which must have been formed via partial hydrolysis of the benzoyldiphenylphosphine oxide by moist air and subsequent addition of the so formed diphenylphosphine oxide to the benzoyldiphenylphosphine oxide.

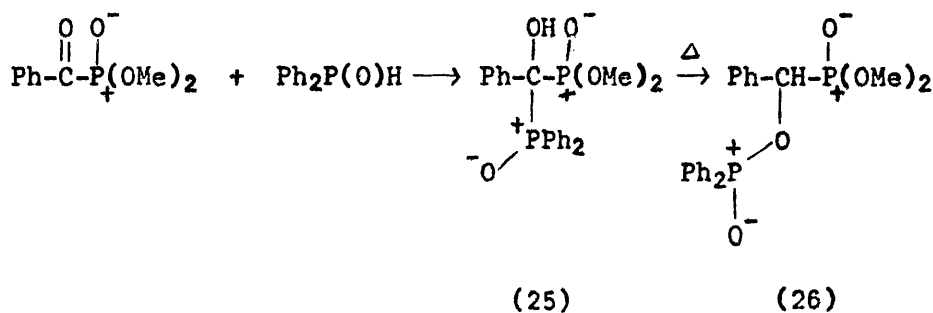
Nucleophilic addition of diphenylphosphine oxide to benzoyldiphenylphosphine oxide would be expected to give, not the

oxide (15; 2=H), but the hydroxy-phosphine oxide (24). Indeed the addition of diphenylphosphine oxide to dimethyl benzoylphosphonate gave the expected oxide (25) which, however, on heating

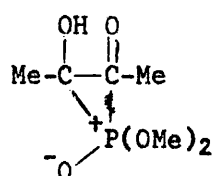


(24)

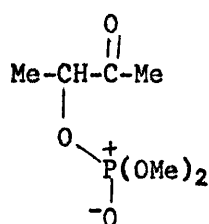
to 160° for one hour rearranged to the phosphinate (26). Likewise, dimethyl phosphite with dimethyl benzoylphosphonate gave a



rearranged product. A similar rearrangement was reported by Kukatin, Abramov, and Orekhova¹⁰⁶ in the reaction of dimethyl phosphite with diacetyl. Below 100° the product was the phosphonate (27) but above 100° the phosphate (28) was formed. A further rearrangement of this type in the formation of phosphinate

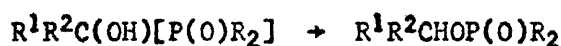


(27)

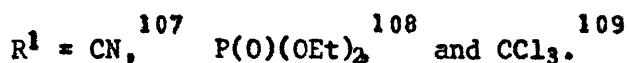


(28)

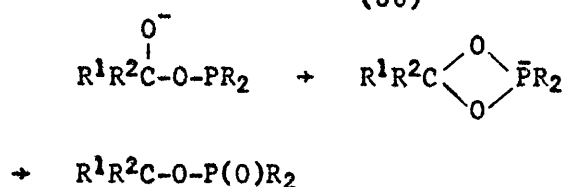
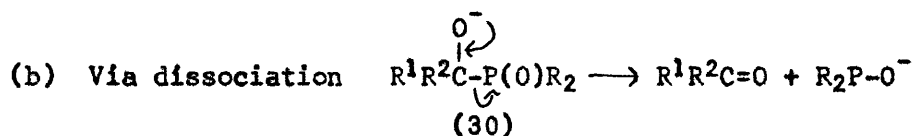
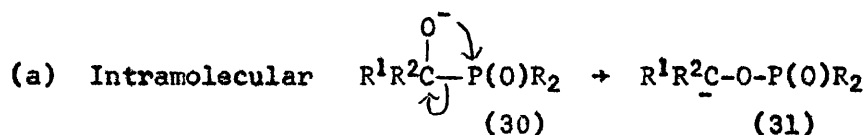
(22) from diphenylphosphine oxide and benzil. The rearrangement may be generalised as follows, where R^1 is a group capable of stabilising an adjacent carbanion. Examples include rearrangement of (29) when



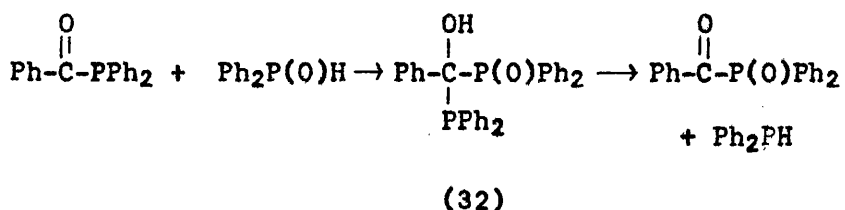
(29)



The rearrangement may be intramolecular¹¹⁰ or may involve dissociation of the anion (30) to ketone and secondary phosphine oxide anion, followed by nucleophilic attack of the latter with oxygen. The ambident nature of the secondary phosphine oxide anion has been shown by Quin and Anderson.¹¹¹ Subsequent reactions as shown would then give the phosphinate via the stabilised carbanion (31). Alternatively this carbanion could be formed directly by attack of the phosphine oxide anion on the oxygen of the ketone.



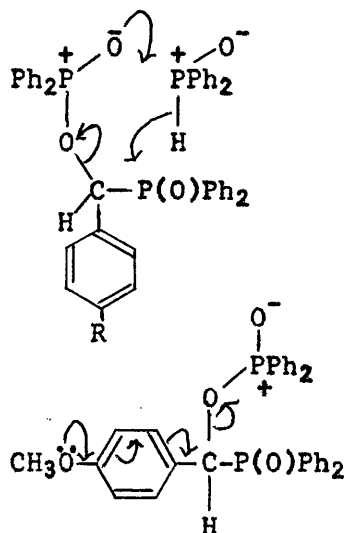
The several reactions described above which lead to the oxide (15; R=H) are therefore envisaged as proceeding by the addition of diphenylphosphine oxide to either benzoyldiphenylphosphine or its oxide. It has not been established that the intermediate (32), formed by the addition to the phosphine, does in fact rearrange but the diphenylphosphino group is known to stabilise adjacent carbanions.¹¹² In any case, the phosphine and its oxide will be involved in the following equilibria and further reaction may be entirely via the oxide. In the reaction



of benzoyl chloride with the sodium salt of diphenylphosphine oxide, the anion [31; R, R¹=Ph; R²=P(O)Ph₂] reacts further with benzoyl chloride to give the oxide (21). The ditertiaryphosphine dioxide obtained from nicotinic acid is probably formed from the intermediate analogous to (32) by the known rearrangement of α-hydroxyalkylphosphines to alkylphosphine oxides.¹¹³

The phosphine oxides (15) having a substituent R capable of electron-supply are further reduced by diphenylphosphine oxide to the benzylphosphine oxides (16). The oxide (15; R=MeO) was obtained either from the reaction of two molar equivalents of diphenylphosphine oxide with anisic anhydride or from the reaction

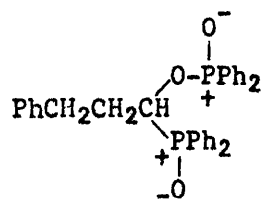
of diphenylphosphine oxide with anisoyldiphenylphosphine oxide. On heating with one molar equivalent of diphenylphosphine oxide at 180° it gave an almost quantitative yield of *p*-methoxybenzyl-diphenylphosphine oxide (16; R=OMe). The oxide (15; R=H) was unaffected under these conditions. The proposed mechanism for this reaction, which is shown below, will obviously be facilitated by a strongly electron releasing group R because this will be able to neutralise the accumulation of positive charge at the oxygen bearing carbon atom.



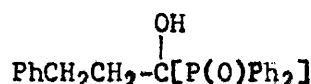
II. The reaction of tetraphenyldiphosphine with aliphatic carboxylic acids.

It has been shown that tetraphenyldiphosphine reacts with aliphatic carboxylic acids in analogous manner to its reaction with aromatic carboxylic acids. Thus tetraphenyldiphosphine

reacted with phenylacetic, 2-phenylpropionic, isovaleric, phenoxyacetic and phenylthioacetic acids at 180-200° to give oxides analogous to (15). In the case of 2-phenylpropionic acid, in addition to the oxide (33), the hydroxy-phosphine oxide (34) was also isolated.



(33)

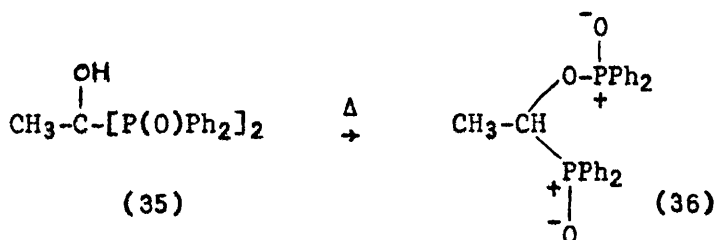


(34)

The hydroxy-phosphine oxide (34) is analogous to the oxide (24) postulated as an intermediate in the reaction of tetraphenyldiphosphine with benzoic. On prolonged heating at 180-200° (34) was converted to (33). Furthermore, it has been shown that the rearrangement of (29) is less favourable when an aryl group is replaced by an alkyl group. Thus when R² was aryl it was impossible to isolate the intermediate [29; R = P(O)Ph₂]. This is to be expected as replacement of an aryl group by an alkyl group results in less effective stabilisation of the intermediate carbanion.

Acetic anhydride plus two molar equivalents of diphenylphosphine oxide gave a compound whose molecular formula, C₂₆H₂₄O₃P₂, was confirmed by mass spectrometry which showed a parent peak at m/e 446 and other peaks at m/e 201 (Ph₂PO) and m/e 245. An infrared spectrum included absorption characteristic of a phosphine

oxide (1180 cm.^{-1}) and of a hydroxyl group (3100 cm.^{-1} , broad). A p.m.r. spectrum showed the presence of a methyl group (triplet $\tau 8.55$). From this evidence the compound was assigned the structure (35). Heating at $180\text{--}200^\circ$ for three hours gave a different compound

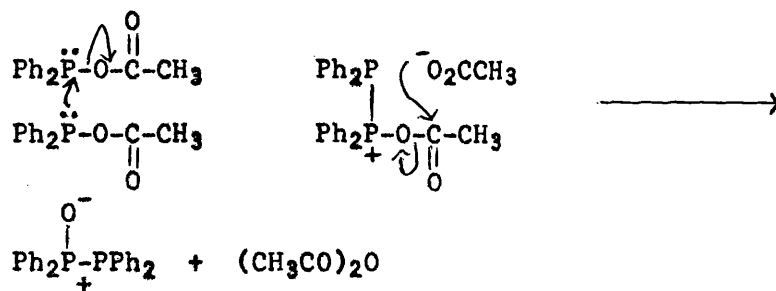


which was an isomer of (35). The infrared spectrum of this compound included absorption characteristic of a phosphine oxide (1205 cm.^{-1}) and of a phosphinate [1230 cm.^{-1} (P:O) and 950 cm.^{-1} , 1060 cm.^{-1} (P·O·C)]. The mass spectrum showed a parent peak at m/e 446 and other significant peaks at m/e 217 (Ph_2PO_2) and m/e 201 (Ph_2PO). A p.m.r. spectrum showed the presence of a methyl group (quadruplet; $\tau 8.45$) and also a complex multiplet (1H) at $\tau 3.5$. From this evidence the compound was assigned the structure (36).

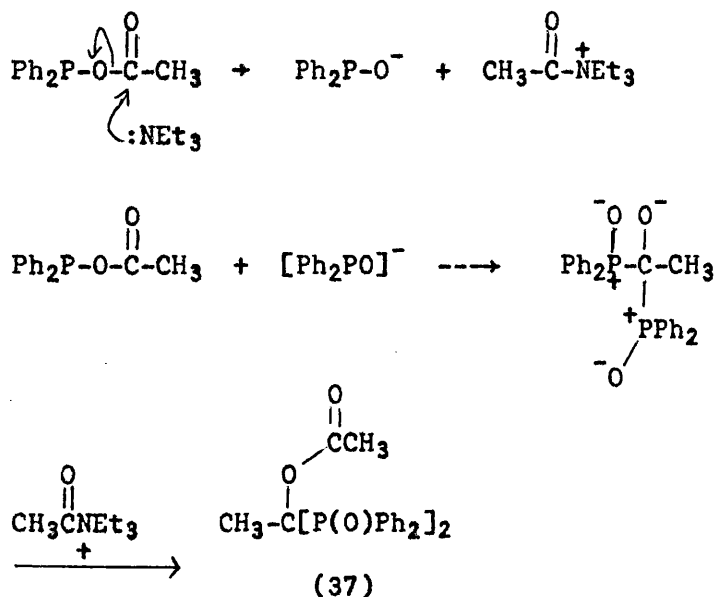
Acetyldiphenylphosphine has been prepared by Issleib¹⁰⁴ and Priebe¹⁰⁴ from sodium diphenylphosphide and acetyl chloride. It may also be prepared by heating acetic anhydride and diphenylphosphine at 100° followed by distillation in vacuo. Acetyldiphenylphosphine and diphenylphosphine oxide heated at 100° gave (35).¹⁰⁴ Issleib and Priebe reported the preparation of acetyldiphenyl-

phosphine oxide from the oxidation of acetyldiphenylphosphine by pure oxygen. However, this preparation has been repeated and the only isolable product was (35). The oxide (35) is a white crystalline solid m.p. 159-160° and the reported m.p. of acetyldiphenylphosphine oxide¹⁰⁴ is 158-159°. Obviously (35) must be formed via partial hydrolysis of acetyldiphenylphosphine oxide by moist air in the isolation.

Acetoxydiphenylphosphine has also been prepared by the same methods used for the preparation of benzoyloxydiphenylphosphine. Like benzoyloxydiphenylphosphine, on heating at 140° acetoxydiphenylphosphine gave tetraphenyldiphosphine monoxide as shown.



Another interesting reaction of acetoxydiphenylphosphine has been found.⁷⁸ On treating acetoxydiphenylphosphine with triethylamine at room temperature the oxide (37) was formed in good yield, presumably by the mechanism shown. This reaction seems to be peculiar to acetoxydiphenylphosphine as benzoyloxydiphenylphosphine and phenylacetoxydiphenylphosphine when treated with triethylamine at room temperature merely gave tetraphenyldiphosphine monoxide

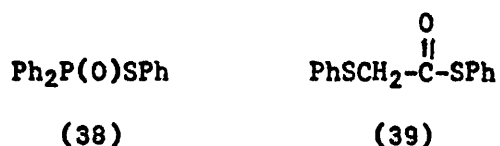


and the acid anhydride as in the thermal reaction.

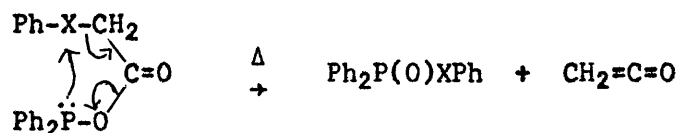
In the reaction of tetraphenyldiphosphine with phenylacetic acid toluene (21%) was determined in the reaction mixture by gas chromatography. When tetraphenyldiphosphine was allowed to react with diphenylacetic or triphenylacetic acid at 180-200° no product corresponding to (15) was formed. Diphenylmethane and triphenylmethane were formed in 27 and 46% yield respectively. In both cases virtually all the phosphorus was accounted for by isolation as diphenylphosphinic acid from washing the reaction mixture with aqueous sodium hydroxide. If the reaction mixture was recrystallised from benzene/ether, instead of washing with aqueous sodium hydroxide, it was possible to isolate diphenylphosphinic anhydride. The acids did not decarboxylate to any

extent when heated alone at 180-200° so it seems likely that the alkanes are formed by the free radical decomposition of some intermediate in the reaction. This decomposition is obviously facilitated by heavily substituting the α -position of the carboxylic acid with bulky substituents. It is not certain which intermediate is responsible for the formation of alkane. It may be due to the acylphosphine, acyloxyphosphine or the acylphosphine oxide, and may be analogous to the free radical decomposition of diphenylphenylcarbamoylphosphine⁵¹ or that proposed in the reaction of an alkali metal phosphide with phosgene.¹⁰⁴

In the reaction of tetraphenyldiphosphine with phenoxyacetic acid, in addition to the expected product analogous to (15), phenyl diphenylphosphinate was formed. Similarly in the reaction with phenylthioacetic acid S-phenyl diphenylthiophosphinate (38) was formed together with the thioester (39). The mode of



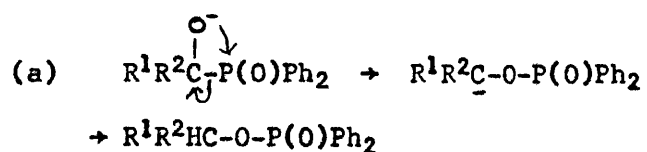
formation of these compounds is not known. It was first thought that the phosphinate (or thiophosphinate) may have been formed by an intramolecular elimination of ketene as shown. However, phenoxyacetoxydiphenylphosphine has been prepared and shown not to undergo this reaction.



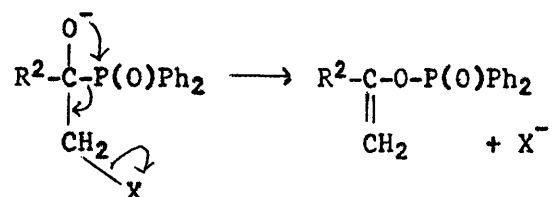
where X = O or S

III. Reactions of some α -hydroxyphosphine oxides

The rearrangement of the α -hydroxy-phosphine oxides encountered in the carboxylic acid reactions may be just one example of a whole range of rearrangements of α -hydroxy-phosphine oxides. Thus if there was a group capable of leaving as an anion situated at a suitable point in the molecule then the outcome of the reaction may be quite different. The possibilities are shown in the following examples.

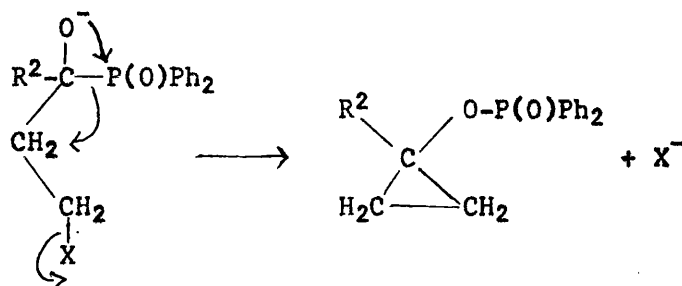


(b) where R^1 or $\text{R}^2 = \text{CH}_2\text{X}$ where X is a group capable of leaving as an anion e.g. Cl, Br etc.

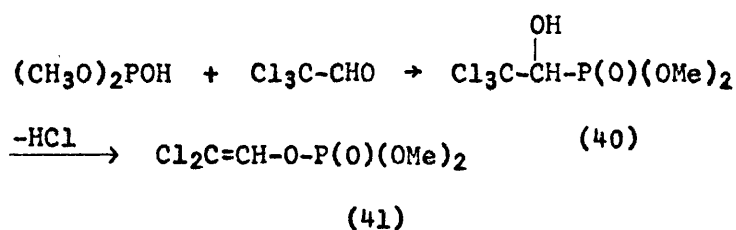


(c) where R^1 or $\text{R}^2 = (\text{CH}_2)_n\text{X}$ where X is a group capable of leaving as an anion and $n > 1$.

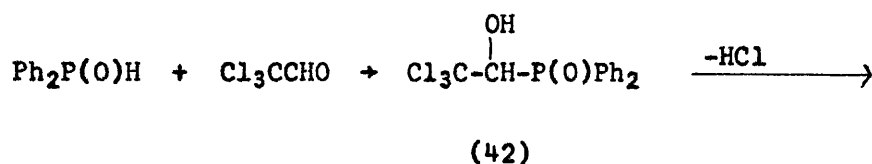
e.g. when $n=2$; $X=\text{Cl}$, Br etc.

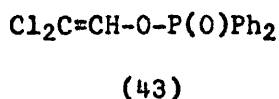


The reaction (b) is analogous to the Perkow reaction of trialkyl phosphites with α -halocarbonyl compounds. Moreover, dimethylphosphite is known to react with chloral¹⁰⁹ to give the phosphonate (40) which on treatment with aqueous alkali gave the vinyl phosphate (41). Chloral reacted with diphenylphosphine

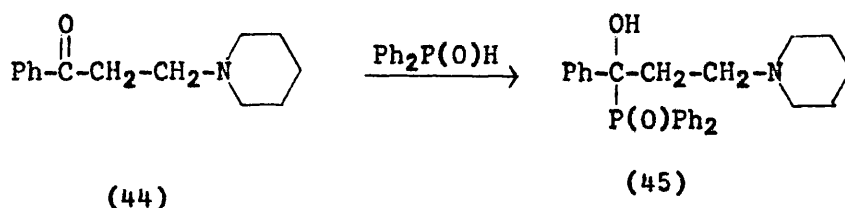


oxide, in benzene solution, exothermically at room temperature to give (42). When (42) was heated to 150° hydrogen chloride was given off. In the presence of a base (42) could be decomposed at much lower temperatures to give a compound which from infrared data was assigned the structure (43).

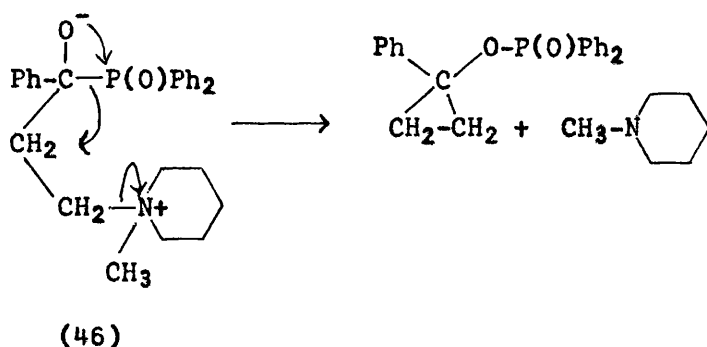




To ascertain whether a reaction of the type (c) was possible, diphenylphosphine oxide was allowed to react with the Mannich base (44) to give the α -hydroxy-phosphine oxide (45). Quaternization of (45) with methyl iodide should give (46) which



contains a good leaving group in the correct position for the formation of a cyclopropane ring as shown.



However, treatment of (45) with methyl iodide gave the methiodide of the Mannich base (44) and diphenylphosphine oxide. This is probably because (45) is a base and is therefore able to catalyse its own decomposition. Hence in solution (45) is probably dissociated to a small extent into diphenylphosphine oxide and the Mannich base.

The addition of methyl iodide obviously removes the Mannich base and forces the equilibrium over to complete dissociation.

Experimental

All experiments were carried out under oxygen-free nitrogen. Light petroleum refers to the fraction of b.p. 60-80°. P.m.r. spectra were recorded for solutions in deuteriochloroform using a Varian A-60 spectrometer. Mass spectra were determined using an A.E.I. MS-9 instrument; in each case the mass peak is given first followed by those of structural significance.

The reaction of tetraphenyldiphosphine with benzoic acid. -

A mixture of the diphosphine (5 g.) and benzoic acid (1.7 g.) was kept at 180-200° for 4 hr. The reaction mixture was dissolved in chloroform, washed with dilute aqueous sodium hydroxide and water, and dried. Evaporation and trituration with ether gave α -(diphenylphosphinyloxy)benzyldiphenylphosphine oxide (3.8 g.), m.p. (from ethyl acetate) 190-191°, quadruplet at τ 3.7 (J_{PH} 2 and 11 c.p.s.) equivalent to one proton, (Found: C, 72.8; H, 5.2; P, 12.3. $\text{C}_{31}\text{H}_{26}\text{O}_3\text{P}_2$ requires C, 73.2; H, 5.1; P, 12.2%). Using benzonitrile as solvent under reflux gave a 79% yield of the same product.

In a similar way p-cyanobenzoic acid gave p-cyano- α -(diphenylphosphinyloxy)benzyldiphenylphosphine oxide (63%), m.p. (from ethyl acetate) 180-181°, ν_{max} 984, 1180, 1229 cm^{-1} (Found: C, 71.9; H, 4.7; N, 2.8; P, 11.8. $\text{C}_{32}\text{H}_{25}\text{NO}_3\text{P}_2$ requires C, 72.0; H, 4.7; N, 2.6; P, 11.6%), and terephthalic acid gave α, α' -bis(diphenylphosphinyl)- α, α' -bis(diphenylphosphinyloxy)-p-xylene

(48%), m.p. (from ethyl acetate) 295-296°, ν_{max} , 993, 1010, 1203, 1220 cm^{-1} (Found: C, 71.5; H, 4.9; P, 13.45. $\text{C}_{56}\text{H}_{46}\text{O}_6\text{P}_4$ requires C, 71.6; H, 4.9; P, 13.2%).

The reaction of tetraphenyldiphosphine with nicotinic acid. -

A mixture of the diphosphine (1.1 g.) and nicotinic acid (0.4 g.) was kept at 180-200° for 4 hr. and then dissolved in benzene and placed on a column of basic alumina (20 g; Spence type H). Elution with ethyl acetate gave α -diphenyl-phosphinyl- α -diphenylphosphinyloxy- β -picoline (0.53 g.), m.p. (from ethyl acetate) 186-187°, ν_{max} , 982, 1180, 1229 cm^{-1} , $\underline{m/e}$ 509, 292, 217, 201 (Found: C, 70.8; H, 5.1; N, 2.9; P, 12.3. $\text{C}_{30}\text{H}_{25}\text{NO}_3\text{P}_2$ requires C, 70.7; H, 4.9; N, 2.75; P, 12.2%). Elution with ethyl acetate containing methanol (1%) gave α,α -bis(diphenylphosphinyl)- β -picoline (0.35 g.), m.p. 214-215° (from ethyl acetate), ν_{max} , 1180 cm^{-1} , $\underline{m/e}$ 495, 292, 201 (Found: C, 72.8; H, 5.3; N, 2.9; P, 12.5. $\text{C}_{30}\text{H}_{25}\text{NO}_2\text{P}_2$ requires C, 73.0; H, 5.1; N, 2.85; P, 12.6%).

The reaction of tetraphenyldiphosphine with p-dimethylaminobenzoic acid.

A mixture of the diphosphine (0.74 g.) and p-dimethylaminobenzoic acid (0.33 g.) was kept at 180-200° for 4 hr. The reaction mixture was dissolved in chloroform, washed with dilute aqueous sodium hydroxide and water, and dried. After removal of solvent the residue, in benzene, was placed on a column of alumina (20 g; Spence type H). Elution with ether containing

methanol (1%) gave p-dimethylaminobenzyldiphenylphosphine oxide (0.34 g.), m.p. (from ethyl acetate) 212-213°, ν_{max} 1180 cm^{-1} , doublet at τ 6.5 (J_{PH} 13 c.p.s.) equivalent to two protons, m/e 335, 201, 134. (Found: C, 75.2; H, 6.5; N, 4.1; P, 9.5. $\text{C}_{21}\text{H}_{22}\text{NOP}$ requires C, 75.2; H, 6.6; N, 4.2; P, 9.25%).

In a similar way anisic acid gave p-methoxybenzyl-diphenylphosphine oxide (40%), m.p. (from benzene) and mixed m.p. 228-229°. An authentic sample was obtained from dimethylaminodiphenylphosphine and anisyl alcohol at 130° for 15 hr. and had m.p. (from benzene) 228-229°. ν_{max} 1180 cm^{-1} , m/e 322, 201, 121. (Found: C, 74.4; H, 6.0; P, 9.4. $\text{C}_{20}\text{H}_{19}\text{O}_2\text{P}$ requires C, 74.5; H, 5.9; P, 9.6%).

The reaction of tetraphenyldiposphine with p-isopropylbenzoic acid.

A mixture of the diphosphine (1.1 g.) and p-isopropylbenzoic acid (0.55 g.) was kept at 180-200° for 3 hr. and then placed, in benzene, on a column of alumina (20 g; Spence type H). Elution with ether gave p-isopropylbenzyldiphenylphosphine oxide (20 mg.), m.p. (from ethyl acetate) and mixed m.p. 189-191°. An authentic sample was obtained from dimethylaminodiphenylphosphine and p-isopropylbenzyl alcohol at 130° for 4 hr. and showed m.p. (from ethyl acetate) 190.5-191.5°, ν_{max} 1180 cm^{-1} , m/e 334, 201, 133. (Found: C, 78.9; H, 6.9; P, 9.4. $\text{C}_{22}\text{H}_{23}\text{OP}$ requires C, 79.05; H, 6.9; P, 9.3%). Elution with ether containing methanol (5%) gave α -(diphenylphosphinyloxy)-p-isopropylbenzyldiphenylphosphine oxide

(0.62 g.), m.p. (from ethyl acetate) 181-182°, ν_{max} , 1010, 1020, 1195, 1221 cm^{-1} , m/e 550, 333, 217, 201 (Found: C, 73.9; H, 5.7; P, 11.3. $\text{C}_{34}\text{H}_{32}\text{O}_3\text{P}_2$ requires C, 74.2; H, 5.8; P, 11.3%).

α -(Diphenylphosphinyloxy)benzyldiphenylphosphine oxide.

Diphenylphosphinous chloride (0.5 g.) was added to α -hydroxybenzyldiphenylphosphine oxide (0.62 g.; prepared by the method of Buckler and Epstein)¹⁰³ in pyridine (10 ml.), the solution set aside at room temperature for $\frac{1}{2}$ hr., and then air bubbled through for $\frac{1}{2}$ hr. The solution, in chloroform, was then washed with dilute hydrochloric acid, with sodium hydrogen carbonate solution, and with water, dried, and evaporated. Crystallisation of the residue from ethyl acetate gave α -(diphenylphosphinyloxy)benzyldiphenylphosphine oxide (0.45 g.), m.p. 190-191°.

Diphenylphosphinic chloride (0.45 g.) was added to α -hydroxybenzyldiphenylphosphine oxide (0.62 g.) and pyridine (0.2 g.) in benzene (50 ml.) and the solution heated under reflux for 1 hr. and filtered. The filtrate was washed with water and evaporated. Crystallisation of the residue from benzene-ether gave diphenylphosphinic anhydride, m.p. and mixed m.p. 149-150°. An authentic sample of diphenylphosphinic anhydride was prepared by the method of Moedritzer⁹⁹ and had m.p. 149-150° (lit. 142-143°).

α -(Diphenylphosphinyloxy)-p-isopropylbenzyldiphenylphosphine oxide. -

p-Isopropylbenzaldehyde (1.58 g.) was added to a solution of diphenylphosphine (1.86 g.) in acetonitrile (10 ml.) containing

concentrated hydrochloric acid (0.25 ml.), the solution set aside for 10 min. and then hydrogen peroxide (1.15 g. of 100 volume) added with cooling. Ether (25 ml.) was added and the solution set aside at room temperature overnight. Filtration gave α -hydroxy-p-isopropylbenzyldiphenylphosphine oxide (2.6 g.), m.p. (from benzene) 168-169° (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%).

This oxide was treated with diphenylphosphinous chloride in pyridine as described above to give α -(diphenylphosphinyloxy)-p-isopropylbenzyldiphenylphosphine oxide (52%), m.p. and mixed m.p. with the product from the reaction of tetraphenyldiphosphine with p-isopropylbenzoic acid, 179-180°.

Benzoyloxydiphenylphosphine.

(a) A mixture of benzoic anhydride (2.26 g.) and diethylaminodiphenylphosphine (2.57 g.) was kept at 100° for 1 hr. when the infrared spectrum showed the disappearance of starting materials and new carbonyl absorptions at 1630 and 1700 cm^{-1} . Distillation from an oil-bath at 110° gave N,N-diethylbenzamide, b.p. 72°/0.1 mm., ν_{max} 1630 cm^{-1} . The residue of benzoyloxydiphenylphosphine could not be distilled without change. After heating at 140° for 1 hr., trituration with ether gave tetraphenyldiphosphine monoxide (1.6 g.), m.p. and mixed m.p. 153-156°, having an infrared spectrum identical with that of an authentic sample. Evaporation of the ether gave benzoic anhydride having

an infrared spectrum identical with that of an authentic sample.

(b) Diphenylphosphinous chloride (4.6 g.) was added to a solution of benzoic acid (2.44 g.) and triethylamine (2.1 g.) in methylene chloride (50 ml.) and the solution set aside at room temperature for 15 hr. The solvent was removed under reduced pressure and the residue extracted with benzene. Evaporation gave an oil (6.1 g.), $\nu_{\text{max.}}$ 1700 cm^{-1} , which could not be distilled without change.

(c) A suspension of anhydrous sodium benzoate (1.6 g.) in ether (50 ml.) containing diphenylphosphinous chloride (2.3 g.) was heated under reflux for 15 hr., cooled, and filtered. Evaporation of the ether gave an oil (3.0 g.) having an infrared spectrum identical with that of the product obtained in (b).

Reaction of benzoyloxydiphenylphosphine with diphenylphosphine.

A mixture of benzoic anhydride (2.26 g.) and diethylaminodiphenylphosphine (2.57 g.) was kept at 100° for 1 hr. Diphenylphosphine (1.86 g.) was then added and the mixture kept at 100° for a further hour. Trituration with ether gave a solid which absorbed oxygen exothermically from the air to give tetraphenyldiphosphine monoxide (3.75 g.), m.p. 153-156°, having an infrared spectrum identical with that of an authentic sample. The ether solution was extracted with aqueous sodium hydrogen carbonate. Acidification of the extract gave benzoic acid (1.1 g.), m.p. and mixed m.p. 121°. Evaporation of the ether gave N,N-diethylbenzamide (1.6 g.).

Reaction of benzoyldiphenylphosphine with diphenylphosphine oxide.

A mixture of diphenylphosphine (0.93 g.) and benzoic anhydride (1.13 g.) was kept at 100° for 3 hr. when infrared absorption showed the absence of reactants and the formation of benzoyldiphenylphosphine ($\nu_{\text{max.}}$ 1650 cm.^{-1}). Diphenylphosphine oxide (1.01 g.) was then added and the mixture kept at 100° for a further 3 hr. It was then dissolved in chloroform and the solution washed with aqueous sodium hydrogen carbonate and with water, dried, and evaporated. Trituration of the residue with ether gave α -(diphenylphosphinyloxy)benzyldiphenylphosphine oxide (1.8 g.), m.p. (from ethyl acetate) and mixed m.p. 190-191°.

Reaction of benzoic anhydride with diphenylphosphine oxide.

A mixture of diphenylphosphine oxide (2.02 g.) and benzoic anhydride (2.26 g.) was kept at 100° for 3 hr., when infrared absorption showed that all of the oxide had been used but much anhydride remained. Diphenylphosphine oxide (2.02 g.) was added and the mixture kept at 100° for 15 hr. It was then dissolved in chloroform and the solution washed with aqueous sodium hydrogen carbonate and with water, dried and evaporated. Trituration of the residue with ether gave α -(diphenylphosphinyloxy)benzyldiphenylphosphine oxide (4.5 g.), m.p. (from ethyl acetate) and mixed m.p. 190-191°.

Reaction of benzoyl chloride with sodium diphenylphosphinoate.

Water (3 ml.) was added to a solution of diphenylphosphinous chloride (8.8 g.) in benzene (50 ml.) and the suspension heated under reflux for 1 hr. when benzene and excess water were removed by distillation at atmospheric pressure. The residue was dissolved in tetrahydrofuran (50 ml.) and the solution heated under reflux with a large excess of sodium wire for 1 hr. After cooling, the excess of sodium was removed and the solution added slowly to a solution of benzoyl chloride (7 g.) in tetrahydrofuran (50 ml.) cooled in ice. Solvent was then evaporated and the residue dissolved in chloroform. The solution was washed with water, dried, and evaporated. The residue, in benzene, was placed on a column of basic alumina. Elution with benzene gave α -benzoyl- α -(diphenylphosphinyloxy)-benzyldiphenylphosphine oxide (21; 3.7 g.), m.p. (from benzene) 207-208°, ν_{max} complex pattern 1000-1040, 1182, 1240, 1680 cm^{-1} , m/e 612, 507, 395, 217, 201 (Found: C, 74.6; H, 5.0; P, 10.1. $\text{C}_{38}\text{H}_{30}\text{O}_4\text{P}_2$ requires C, 74.5; H, 4.9; P, 10.1%). Elution with ether containing methanol (5%) gave α -(diphenylphosphinyloxy)benzyldiphenylphosphine oxide (2.4 g.), m.p. and mixed m.p. 190-191°.

Acidic hydrolysis of the oxide (21).

The oxide (0.31 g.) was heated under reflux for 8 hr. with ethanol (25 ml.) and 2N-hydrochloric acid (25 ml.) and the solution then evaporated to dryness. The residue was dissolved in chloroform and the solution washed with dilute aqueous sodium

hydroxide and with water, dried and evaporated. Trituration of the residue with ether gave α -(diphenylphosphinyloxy)benzyl-diphenylphosphine oxide (90 mg.), m.p. (from ethyl acetate) and mixed m.p. 190-191°. Evaporation of the ether and crystallisation of the residue from benzene-light petroleum gave α -benzoylbenzyl diphenylphosphinate (35 mg.), m.p. and mixed m.p. 139-140°.

The alkaline extract was acidified and extracted with chloroform. The solution was washed with water, dried and evaporated, and the residue extracted with hot light petroleum leaving diphenylphosphinic acid (80 mg.) m.p. and mixed m.p. 192-193. Evaporation of the light petroleum gave benzoic acid (30 mg.), m.p. and mixed m.p. 121-122°.

Alkaline hydrolysis of the oxide (21).

The oxide (310 mg.) was heated under reflux for 15 hr. with 2N-sodium hydroxide (50 ml.). Filtration then gave benzyl-diphenylphosphine oxide (50 mg.), m.p. and mixed m.p. 190-192°. Acidification of the filtrate gave diphenylphosphinic acid (0.18 g.), m.p. and mixed m.p. 191-193°. The mother liquors were extracted with chloroform, the solvent evaporated, and the residue (40 mg.) extracted with hot light petroleum leaving benzilic acid m.p. and mixed m.p. 149-150°. Evaporation of the light petroleum gave benzoic acid m.p. and mixed m.p. 121-122°.

Reaction of benzoyl chloride with methyl diphenylphosphinite.

A solution of benzoyl chloride (0.7 g.) and methyl

diphenylphosphinite (1.08 g.) in benzene (50 ml.) was heated under reflux for 1 hr. Evaporation of the solution gave a yellow solid which showed infrared absorption at 1650 cm.^{-1} . Trituration with ether gave α -(diphenylphosphinyloxy)benzyl-diphenylphosphine oxide (0.9 g.), m.p. and mixed m.p. (from ethyl acetate) $190-191^\circ$. No other product could be crystallised from the mother liquors.

Reaction of diphenylphosphine oxide with dimethyl benzoylphosphonate.

Dimethylbenzoylphosphonate (4.28 g.) in benzene (50 ml.) was added to diphenylphosphine oxide (4.04 g.) in benzene (50 ml.) and the solution set aside at room temperature overnight. Filtration gave dimethyl- α -(diphenylphosphinyl)- α -hydroxybenzylphosphonate (7.6 g.), m.p. (from benzene) $120-121^\circ$ (Found: C, 61.1; H, 5.4; P, 14.9. $\text{C}_{21}\text{H}_{22}\text{O}_5\text{P}_2$ requires C, 60.6; H, 5.3; P, 14.9%). The compound showed no absorption in the infrared due to carbonyl but had strong, broad, absorption at 3000 cm.^{-1} due to hydrogen-bonded hydroxyl.

The above phosphonate (2.5 g.) was kept at 160° for 1 hr. and distilled to give dimethyl- α -(diphenylphosphinyloxy)-benzylphosphonate (1.5 g.), b.p. $192-194^\circ/0.3\text{ mm.}$, m/e 416, 217 (Ph_2PO_2), 199 [PhCHP(O)(OMe)_2], (Found: C, 60.6; H, 5.5; P, 14.65. $\text{C}_{21}\text{H}_{22}\text{O}_5\text{P}_2$ requires C, 60.6; H, 5.3; P, 14.9). The compound showed no absorption in the infrared due to hydroxyl or carbonyl.

α -Benzoylbenzyl diphenylphosphinate.

Diphenylphosphinic chloride (2.37 g.) was added slowly to a solution of benzoin (2.12 g.) in pyridine (10 ml.) and the solution set aside at room temperature for 1 hr. and then poured into an excess of dilute hydrochloric acid. Isolation of the neutral fraction in chloroform and removal of solvent gave an oil which on trituration with ether gave α -benzoylbenzyl diphenylphosphinate (3.2 g.), m.p. (from aqueous ethanol) 139-140° (Found: C, 75.6; H, 5.2; P, 7.6. $C_{26}H_{21}O_3P$ requires C, 75.7; H, 5.1; P, 7.5%).

Reaction of benzil with diphenylphosphine oxide.

A mixture of benzil (2.1 g.) and diphenylphosphine oxide (2.02 g.) was kept at 100° for 15 hr. Crystallisation from benzene-light petroleum gave α -benzoylbenzyl diphenylphosphinate (3.4 g.), m.p. and mixed m.p. 138-140°.

Reaction of dimethylphosphite with dimethyl benzoylphosphonate.

A mixture of dimethyl phosphite (2.2 g.) and dimethyl benzoylphosphonate (4.28 g.) was kept at 100° for 4 hr. Distillation then gave dimethyl- α -(dimethoxyphosphinyloxy)-benzylphosphonate (4.2 g.), b.p. 179-180°/0.2 m.m., m/e 324, 215, 109 (Found: C, 40.0; H, 5.7; P, 19.2. $C_{11}H_{18}O_7P_2$ requires C, 40.75; H, 5.6; P, 19.1%). The compound showed no absorption in the infrared due to hydroxyl or carbonyl. Dimethylphosphite with benzoic anhydride at 100° for 4 hr. gave none of the product

above but gave methyl benzoate in good yield.

α -(Diphenylphosphinyloxy)-p-methoxybenzyldiphenyl phosphine
oxide

(a) A mixture of anisic anhydride (2.86 g.) and diphenylphosphine oxide (4.02 g.) was kept at 100° for 15 hr. A solution of the product in chloroform was washed with aqueous sodium hydrogen carbonate and with water, dried, and evaporated. Trituration of the residue with ether gave α -(diphenylphosphinyloxy)-p-methoxybenzyldiphenylphosphine oxide (2.9 g.), m.p. (from ethyl acetate) 205.5-206.5°, $\nu_{\text{max.}}$ 1208, 1080, 990 cm.^{-1} , $\underline{m/e}$ 538, 337, 321, 217, 201 (Found: C, 70.3; H, 5.2; P, 12.1. $\text{C}_{32}\text{H}_{28}\text{O}_4\text{P}_2$ requires C, 71.2; H, 5.2; P, 11.5%).

(b) A mixture of diphenylphosphine (1.86 g.) and anisic anhydride (2.86 g.) was kept at 100° for 3 hr. Infrared absorption then indicated the absence of starting materials and the formation of anisoyldiphenylphosphine ($\nu_{\text{max.}}$ 1655 cm.^{-1}). Diphenylphosphine oxide (2.02 g.) was added and the mixture kept at 100° for 15 hr. A solution of the product in chloroform was washed with aqueous sodium hydrogen carbonate and with water, dried and evaporated. Crystallisation of the residue from ethyl acetate gave the above oxide, m.p. and mixed m.p. 205.5-206.5°.

A mixture of this oxide (0.54 g.) and diphenylphosphine oxide (0.25 g.) was kept at 180-200° for 3 hr. A solution of the product in chloroform was extracted with dilute sodium hydroxide solution. Acidification of the extract gave

diphenylphosphinic acid (0.35 g.), m.p. and mixed m.p. 192-193°.

The chloroform solution was washed with water, dried and evaporated. Trituration of the residue with ether gave *p*-methoxybenzyldiphenylphosphine oxide (0.29 g.) m.p. and mixed m.p. (from benzene) 228-229°.

Reaction of tetraphenyldiphosphine with isovaleric acid.

A mixture of tetraphenyldiphosphine (3.0 g.) and isovaleric acid (0.9 g.) was 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 gave an oil which on trituration with ether and standing gave α -(diphenylphosphinyloxy)isovaleryldiphenylphosphine oxide (1.1 g.), m.p. (from ethyl acetate-ether) 143-144°, ν_{max} . 990, 1045, 1200, 1225 cm^{-1} (Found: C, 71.1; H, 6.1; P, 12.9. $\text{C}_{29}\text{H}_{30}\text{O}_3\text{P}_2$ requires C, 71.3; H, 6.1; P, 12.7%).

Reaction of tetraphenyldiphosphine with β -phenylpropionic acid.

A mixture of tetraphenyldiphosphine (3.0 g.) and β -phenylpropionic acid (1.25 g.) was 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 and trituration with ether gave α -hydroxy- α,α -bis(diphenylphosphinyl)-3-phenylpropane (34; 1.2 g.), m.p. (from benzene) 155-156°, m/e 536, 335, 201 (Found: C, 74.3; H, 5.6; P, 11.8. $\text{C}_{33}\text{H}_{30}\text{O}_3\text{P}_2$ requires C, 73.9; H, 5.6; P, 11.6%).

The infrared spectrum included absorption characteristic of a phosphine oxide (1180 cm^{-1}) and of a hydrogen-bonded hydroxyl (3200 cm^{-1} , broad). Evaporation of the mother liquors gave an oil which was dissolved in chloroform and washed with alkaline hydrogen peroxide to remove traces of diphenylphosphine oxide. The chloroform solution was then washed with water, dried and evaporated. Trituration of the residue with ether gave α -(diphenylphosphinyloxy)-3-phenylpropyl-diphenylphosphine oxide (1.4 g.), m.p. (from ethyl acetate) $147-148^\circ$, m/e 536, 335, 319, 217, 201, $\nu_{\text{max.}}$ 960, 1030, 1205, 1230 cm^{-1} (Found: C, 74.1; H, 5.8; P, 11.7. $\text{C}_{33}\text{H}_{30}\text{O}_3\text{P}_2$ requires C, 73.9; H, 5.6; P, 11.6%). Heating the oxide (34) for 15 hours at $180-200^\circ$ gave α -(diphenylphosphinyloxy)-3-phenylpropyldiphenylphosphine oxide.

Reaction of tetraphenyldiphosphine with phenylacetic acid.

A mixture of tetraphenyldiphosphine (3.0 g.) and phenylacetic acid (1.2 g.) was kept at $180-200^\circ$ for 3 hr. The reaction mixture was dissolved in chloroform and the solution washed with dilute aqueous sodium hydroxide and water, and dried. Toluene was determined in the solution by gas chromatography (2 m. silicone gum rubber column at 70°). Evaporation of the solution gave an oil which crystallised slowly from ether-ethyl acetate to give α -(diphenylphosphinyloxy)- β -phenylethyldiphenylphosphine oxide (0.9 g.), m.p. (from ethyl acetate-ether) $83-84^\circ$, $\nu_{\text{max.}}$ 995, 1010, 1040, 1190, 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%).

α -(diphenylphosphinyloxy)- β -phenylethyldiphenylphosphine oxide.

A mixture of phenylacetic anhydride (2.54 g.) and diphenylphosphine oxide (4.02 g.) was kept at 100° for 2 hr. The reaction mixture was dissolved in chloroform and washed with aqueous sodium hydrogen carbonate and water, and dried. Evaporation gave an oil which crystallised slowly from ether to give α -(diphenylphosphinyloxy)- β -phenylethyldiphenylphosphine oxide (2.6 g.), m.p. and mixed m.p. with the product from tetraphenyldiphosphine and phenylacetic acid 83-84°.

Reaction of tetraphenyldiphosphine with diphenylacetic acid.

A mixture of tetraphenyldiphosphine (3.0 g.) and diphenylacetic acid (1.8 g.) was kept at 180-200° for 3 hr. The reaction mixture was dissolved in chloroform and washed with alkaline hydrogen peroxide. Acidification of the alkaline extract gave diphenylphosphinic acid (2.7 g.), m.p. and mixed m.p. (from aqueous ethanol) 192-193°. The chloroform layer was washed with water, dried and evaporated. The residue was chromatographed on a silica gel column. Elution with benzene gave diphenylmethane (0.36 g.), infrared spectrum identical with an authentic sample. Elution with ether gave (diphenylmethyl)-diphenylphosphine oxide (40 mg.), m.p. and mixed m.p. (from methanol) 304-305°.

In a similar way triphenylacetic acid and tetraphenyldiphosphine gave diphenylphosphinic acid (80%) and triphenyl-

methane (46%), m.p. and mixed m.p. (from ethanol) 93-94°.

Reaction of tetraphenyldiphosphine with phenoxyacetic acid.

A mixture of the diphosphine (3.0 g.) and phenoxyacetic acid (1.3 g.) was kept at 180-200° for 180-200° for 3 hr. The reaction mixture was dissolved in chloroform, washed with aqueous sodium hydroxide and water, and dried. Evaporation gave an oily residue which was chromatographed on a silica gel column. Elution with ether gave phenyl(diphenylphosphinate) (0.45 g.), m.p. and mixed m.p. (from petroleum ether b.p. 80-100°) 135-136°. Elution with ether containing methanol (10%) gave an oil (1.7 g.) which could not be crystallised. The infrared spectrum showed absorption characteristic of a phosphine oxide (1200 cm^{-1}) and of a phosphinate [1230 cm^{-1} (P:O) and $950, 1060\text{ cm}^{-1}$ (P-O-C)]. Phenoxyacetic anhydride with diphenylphosphine oxide at 100° for 3 hr. gave an oil with an identical infrared spectrum to the product above.

A suspension of anhydrous sodium phenoxyacetate (2.0 g.) and diphenylphosphinous chloride (2.29 g.) in ether (50 ml.) was heated under reflux for 15 hr. Filtration and evaporation gave an oil which showed infrared absorption (1750 cm^{-1}) characteristic of an acyloxyphosphine. The oil was then kept at 180-200° for 3 hr. after which time no phenyl diphenylphosphinate was detected in the reaction mixture. Indeed no pure material could be isolated. Similarly, dimethylaminodiphenylphosphine and

phenoxyacetic anhydride at 100° for 2 hr. followed by pyrolysis at 180-200° for 3 hr. gave no phenyl diphenylphosphinate.

Reaction of tetraphenyldiphosphine with phenylthio-acetic acid.

A mixture of tetraphenyldiphosphine (3.0 g.) and phenylthio-acetic acid (1.4 g.) was kept at 180-200° for 3 hr. The reaction mixture was then chromatographed on silica gel. Elution with benzene gave S-phenyl- α -phenylthiothioacetate (39; 220 mg.), m.p. (from petroleum spirit) 66-67°, m/e 260, 151, 123, 109; singlet at 6.15 τ corresponding to two protons (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 thiodiphenylphosphinate (300 mg.), m.p. (from petroleum spirit) and mixed m.p. 88-89°. Elution with ether containing methanol (10%) gave an oil (1.8 g.) which could not be crystallised. The infrared spectrum of the oil was very similar to that of the oil obtained from the phenoxyacetic acid reaction.

Reaction of diphenylphosphine oxide with acetic anhydride..

A mixture of diphenylphosphine oxide (2.02 g.) and acetic anhydride (0.6 g.) was kept at 100° for 6 hr. The reaction mixture was dissolved in chloroform, washed with aqueous sodium hydrogen carbonate and water, and dried. Evaporation and trituration with ether gave α -hydroxy- α , α -bis(diphenylphosphinyl) ethane (0.9 g.), m.p. (from benzene-ether) 159-160°; (Found: C, 69.8; H, 5.2; P, 14.1. $C_{25}H_{24}O_3P_2$ requires C, 70.0; H, 5.4; P, 13.9%).

The product above was kept at 180-200° for 3 hr. and distilled to give α -(diphenylphosphinyoxy)ethyldiphenylphosphine oxide, b.p. 280-290°/0.2 m.m., m/e 446, 217, 201; quadruplet at τ 8.45 (J_{CH} 7 c.p.s. and J_{PH} 4 c.p.s.), equivalent to three protons, complex multiplet (1H) at 3.5.

Acetyldiphenylphosphine.

A mixture of diphenylphosphine (7.5 g.) and acetic anhydride (4.5 g.) was kept at 100° for 3 hr. followed by distillation to give acetyldiphenylphosphine (7.5 g.), b.p. 137-140°/0.8 m.m. (lit. ¹⁰⁴, 143-146°/2.5 m.m.), ν_{max} 1670 cm.⁻¹

Pure, dry oxygen was bubbled slowly through a solution of acetyldiphenylphosphine (1.0 g.) in dry benzene (50 ml.) for 1 hr. Evaporation and trituration with ether gave α -hydroxy- α,α -bis(diphenylphosphinyl)ethane (0.7 g.), m.p. and mixed m.p. (from benzene-ether) 159-160°.

Acetoxydiphenylphosphine.

A suspension of anhydrous sodium acetate (0.9 g.) and diphenylphosphinous chloride (2.29 g.) in ether (50 ml.) was heated under reflux for 15 hr. Filtration and evaporation gave acetoxydiphenylphosphine (2.3 g.) ν_{max} 1750 cm.⁻¹ (lit. ⁸² 1750 cm.⁻¹). The product could not be distilled and on heating at 160° for 1 hr. gave tetraphenyldiphosphine monoxide, m.p. and mixed m.p. 155-157°. Phenylacetoxydiphenylphosphine could be prepared by the same method.

Reaction of chloral with diphenylphosphine oxide.

A solution of diphenylphosphine oxide (4.04 g.) in benzene (50 ml.) was added to anhydrous chloral (3.0 g.) in benzene (50 ml.) at room temperature. An exothermic reaction ensued, followed by crystallisation of α -hydroxy- β,β,β -trichloro-ethyldiphenylphosphine oxide (7 g.), m.p. (from benzene) 163-164° (Found: C, 48.2; H, 3.5; Cl, 30.3; P, 9.0. $C_{14}H_{12}Cl_3O_2P$ requires C, 48.1; H, 3.4; Cl, 30.5; P, 8.9%). The infrared spectrum showed no absorption due to a carbonyl but had strong, broad absorption at 3100 cm^{-1} due to hydrogen-bonded hydroxyl.

On heating a small amount of the product to 150° hydrogen chloride was given off. A suspension of the product (1 g.) and excess calcium carbonate in toluene (50 ml.) was heated under reflux, with vigorous stirring for 3 hr. Filtration and evaporation gave a colourless oil, m/e 313, 217 (Ph_2PO_2), 96. The infrared spectrum showed no absorption due to a carbonyl or a hydroxyl but showed absorption characteristic of a phosphinate [1230 cm^{-1} (P:O) and 970 cm^{-1} (P-O-C)] and of a carbon-carbon double bond (1630 cm^{-1} weak; 800 cm^{-1} strong). On this evidence it was concluded that the oil was β,β -dichlorovinyl diphenylphosphinate. The product could not be distilled without decomposition.

Reaction of diphenylphosphine oxide with β -(1-piperidyl)propiophenone.

β -(1-piperidyl)propiophenone was prepared by a Mannich reaction using acetophenone, paraformaldehyde and piperidine

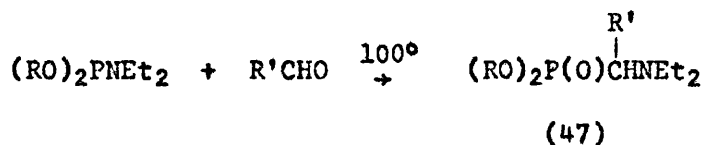
hydrochloride. Diphenylphosphine oxide (2.02 g.) and β -(1-piperidyl)propiophenone (2.17 g.) were mixed together at room temperature. An exothermic reaction ensued and when the reaction had subsided the mixture was kept at 100° for 10 min. to complete the reaction. Trituration with ether gave α -hydroxy- α -diphenylphosphinyl- γ -(1-piperidyl)-3-phenylpropane (2.5 g.), m.p. (from benzene-light petroleum) 97-98° (Found: C, 74.2; H, 7.3; N, 3.4; P, 7.5. $C_{26}H_{30}NO_2P$ requires C, 74.4; H, 7.2; N, 3.4; P, 7.4%). An infrared spectrum showed no absorption due to a carbonyl but showed absorption characteristic of a phosphine oxide (1180 $cm.^{-1}$). The product (1.0 g.) was dissolved in benzene (25 ml.) and excess methyl iodide added. On standing N-methyl-piperidinium iodide (0.6 g.) crystallised out, m.p. (from ethanol) 177-178° (Found: C, 50.0; H, 6.0; N, 4.0. $C_{15}H_{22}INO$ requires C, 50.1; H, 6.1; N, 3.9%). An attempted reaction of diphenylphosphine oxide with the hydrochloride of the Mannich base gave no addition product.

Chapter 4.

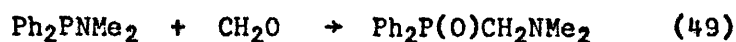
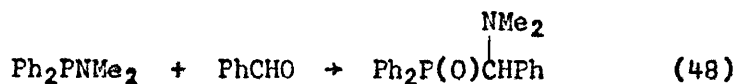
The reaction of tetraphenyldiphosphine with aldehydes.

The reactions of aldehydes with a large number of tervalent phosphorus compounds have been studied. Kabachnik and Shepeleva^{114,115} have studied the reactions of aldehydes with phosphorustrichloride. The reactions of trialkyl phosphites with aldehydes have been studied extensively by Ramirez and co-workers.¹²⁰

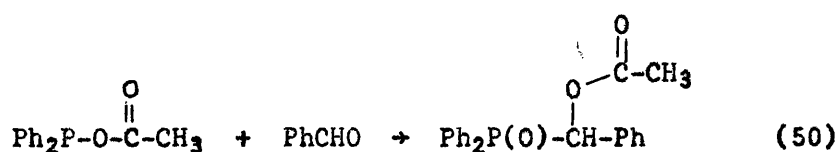
Aminophosponites have been shown to react with aldehydes at 100° to give the phosphonates (47).¹¹⁶



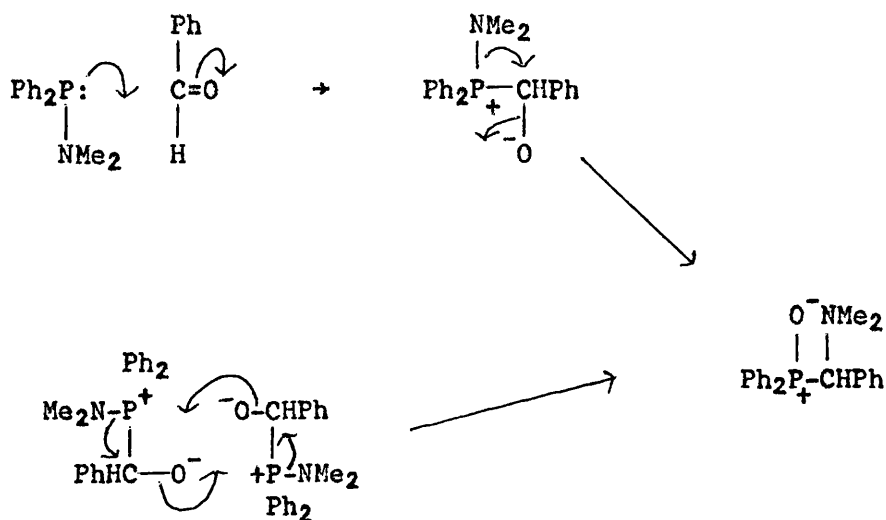
Dimethylaminodiphenylphosphine has been shown to react with aldehydes in a similar manner. Thus dimethylaminodiphenylphosphine and benzaldehyde at 120° gave the phosphine oxide (48). Similarly, paraformaldehyde with dimethylaminodiphenylphosphine gave the oxide (49).



A similar rearrangement occurred in the reaction of acetoxydiphenylphosphine with benzaldehyde which gave the oxide (50).⁸²



The mechanisms of these rearrangements are uncertain and they may be inter or intramolecular as shown.



Benzoyldiphenylphosphine reacted with aromatic aldehydes at 190° to give the benzyl-phosphine oxide as shown. 118
 The mechanism of this reaction is not known but the benzyl group

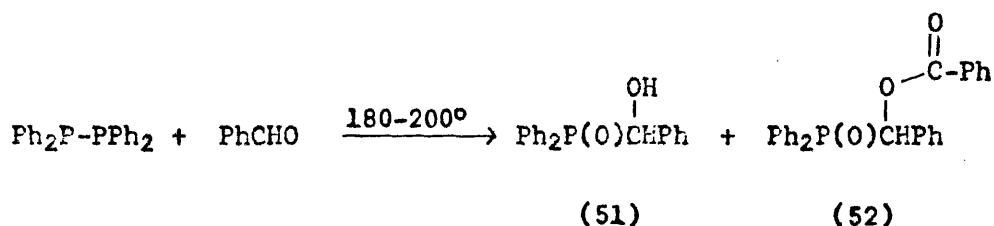


has been shown to come from the aldehyde and not from the benzoyl group of the starting phosphine.

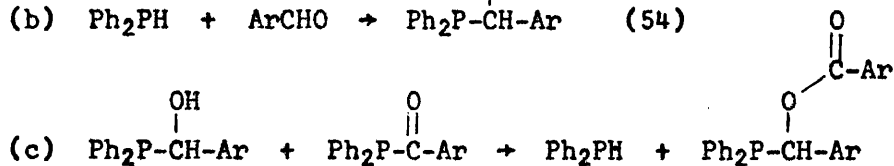
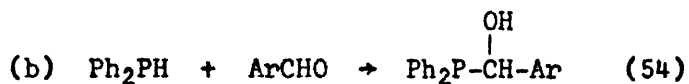
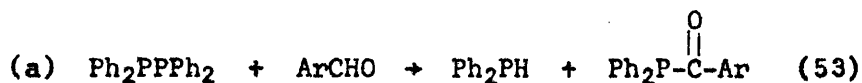
The thermal reaction of tetraphenyldiphosphine has been studied as it was originally thought that the hydrogen atom of

the aldehyde group might be readily abstracted by a diphenylphosphorus radical. However, experimental evidence suggests that the reaction of the diphosphine with aldehydes proceeds via an ionic mechanism.

Tetraphenyldiphosphine and excess benzaldehyde at 180-200° for 3 hr., followed by isolation in air, gave a mixture of α -hydroxybenzylidiphenylphosphine oxide (51) and its benzoylated derivative (52) as shown. When p-isopropylbenzaldehyde was used



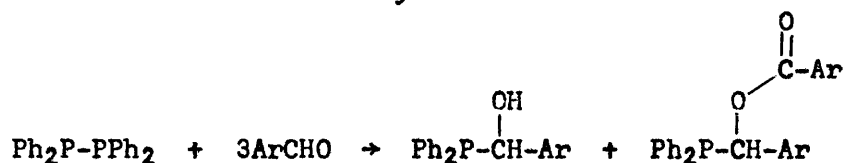
the analogous products were formed, together with a small amount of p-isopropylbenzylidiphenylphosphine oxide. These results may be rationalized in the following manner.



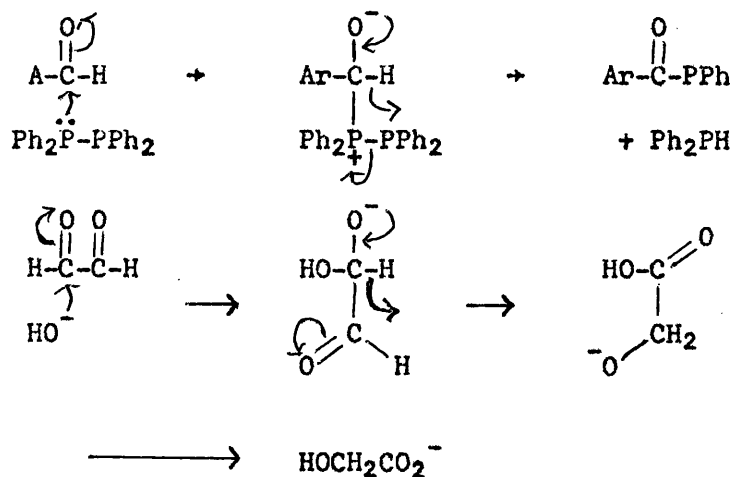
Presumably the phosphines were oxidised by air to the corresponding oxide during their isolation. Indeed if methyl

iodide was added at the end of the reaction, the methiodide of (54) could be isolated. The condensation of diphenylphosphine with benzaldehyde to give α -hydroxybenzylidiphenylphosphine occurs very readily under these conditions. Issleib and Low¹¹⁹ have shown that acylphosphines (53) are good acylating agents and readily acylate alcohols, amines etc. Hence the α -hydroxy-phosphine (54) would be readily acylated by the acylphosphine (53).

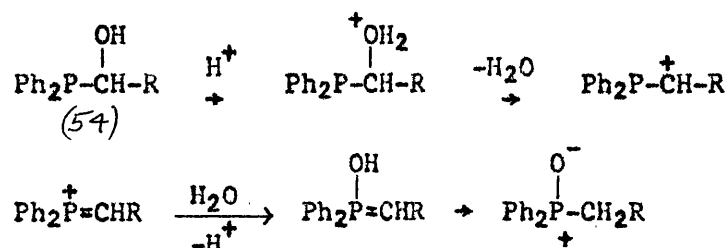
The overall stoichiometry of the reaction is



Step (a) is an unusual reaction and the mechanism of this step is uncertain. One possible mechanism, involving a hydride shift, is shown below. This is somewhat analogous to an intramolecular Cannizzaro reaction.



The formation of a small amount of *p*-isopropylbenzyl-diphenylphosphine oxide in the reaction with *p*-isopropylbenzaldehyde may be explained by the rearrangement of the α -hydroxyphosphine (54). This is a known reaction¹¹³ and usually occurs in the presence of strong acid, proceeding via an intermediate carbonium ion as shown.



In the aldehyde reactions there is almost certainly a small amount of the corresponding carboxylic acid present as an impurity in the aldehyde. This small quantity of acid may be sufficient to effect rearrangement of some of the α -hydroxyphosphine at the temperature of the reaction. Indeed when *p*-isopropylbenzaldehyde (which purposely had not been redistilled) was treated with diphenylphosphine at 180-200° for 15 hr., a significant amount of *p*-isopropylbenzyl-diphenylphosphine oxide was formed, together with the α -hydroxy-phosphine. Obviously, considering the mechanisms shown above, the rearrangement of the α -hydroxy-phosphine will be facilitated by electron-releasing substituents which are capable of stabilising the intermediate carbonium ion. Thus when tetraphenyldiphosphine was allowed to

react with p-anisaldehyde at 180-200° the only product isolated was p-methoxy-benzylidiphenylphosphine oxide. Similarly, when p-anisaldehyde was treated with diphenylphosphine at 180-200° for 15 hr., p-methoxybenzylidiphenylphosphine oxide was formed in good yield and no α -hydroxyphosphine was found. However, assuming that in the reaction of the diphosphine with p-anisaldehyde all the α -hydroxy-phosphine undergoes isomerism, there should still be one molar equivalent of the p-anisoyldiphenylphosphine present in the reaction mixture. The absence of this in the reaction mixture may be explained by the known reaction of aroyldiphenylphosphines with aromatic aldehydes to give a benzylphosphine oxide.

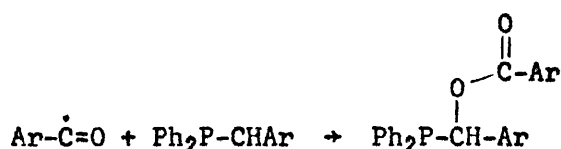
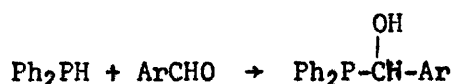
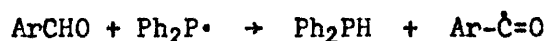
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Nicotinic aldehyde and the diphosphine at 180-200° gave a black tar, from which it was possible to isolate small amounts of the α -hydroxy-phosphine oxide and the rearrangement product, β -picolinylidiphenylphosphine oxide. No acylation product was found.

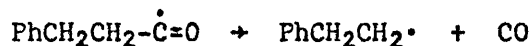
p-Cyanobenzaldehyde with the diphosphine gave a good yield of α -hydroxy-p-cyanobenzylidiphenylphosphine oxide and small amounts of two unidentified phosphine oxides. No product of acylation of the α -hydroxy-phosphine was found.

An alternative explanation for the results of the aldehyde reactions is one involving free radicals. Thus if the first step involved hydrogen abstraction by a diphenylphosphorus radical to give diphenylphosphine and an aroyl radical ($\text{Ph}-\dot{\text{C}}=\text{O}$),

then this aroyl radical could subsequently effect acylation of the α -hydroxy-phosphine. Acylation by aroyl radicals is a known reaction.



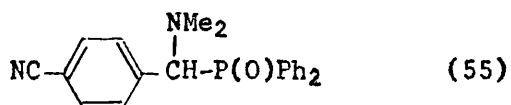
As a test for this alternative mechanism the diphosphine was allowed to react with β -phenylpropionaldehyde at 180-200°. If acyl radicals were formed in the reaction then in this case they would readily decarbonylate to give the alkyl radical and carbon monoxide as shown.



This is a known reaction of acyl radicals $\text{R}-\dot{\text{C}}=\text{O}$ where R is alkyl. The alkyl radical so formed would then, presumably, abstract a hydrogen atom from the aldehyde or from diphenylphosphine to give ethylbenzene. However, no ethylbenzene was detected in the reaction mixture by gas chromatography. The only product isolated was α -hydroxy- γ -phenylpropyldiphenylphosphine oxide. No acylation product was found. Hence it has been

assumed that the reaction of aldehydes with tetraphenyldiphosphine proceeds via an ionic mechanism.

Finally, another interesting reaction of the α -hydroxy-phosphine oxides, formed from an aldehyde and diphenylphosphine followed by oxidation, may be mentioned. α -Hydroxy-p-cyanobenzoyldiphenylphosphine oxide with dimethylaminodiphenylphosphine gave the oxide (55). This oxide is probably formed via dissociation of the α -hydroxy-phosphine to the aldehyde and diphenylphosphine oxide, followed by reaction of the aldehyde with the dimethylaminodiphenylphosphine. Dissociation of α -hydroxy-phosphine oxides is known to occur in the presence of base and dimethylaminodiphenylphosphine is probably a strong enough base to effect this dissociation. Aromatic aldehydes are known to react with dimethylaminodiphenylphosphine to give oxides analogous to (55).



Experimental

All experiments were carried out under oxygen-free nitrogen. Light petroleum refers to the fraction of b.p. 60-80°. P.m.r. spectra were recorded for solutions in deuteriochloroform using a Varian A-60 spectrometer. Mass spectra were determined using an A.E.I. MS-9 instrument; in each case the mass peak is given first followed by those of structural significance.

A mixture of tetraphenyldiphosphine (1.0 g.) and benzaldehyde (10 ml.) was kept at 180-200° for 3 hr. The excess benzaldehyde was removed by distillation in vacuo and the residue triturated with benzene to give α -hydroxy-benzoyldiphenylphosphine oxide (0.65 g.), m.p. and mixed m.p. (from benzene) 171-174°. Evaporation of the mother liquors and trituration with ether gave α -benzoyloxybenzoyldiphenylphosphine oxide (0.75 g.), m.p. (from aqueous methanol) 188-189°.

α -benzoyloxybenzoyldiphenylphosphine oxide

Benzoyl chloride (0.4 ml.) was added to a solution of α -hydroxybenzoyldiphenylphosphine oxide (1.0 g.) in pyridine (10 ml.) and the solution set aside at room temperature for one hour. The reaction mixture, in chloroform was washed with 2N hydrochloric acid, then with aqueous sodium hydrogen carbonate, and dried. Evaporation and trituration with ether gave

α -benzoyloxybenzyldiphenylphosphine oxide (0.8 g.), m.p. and mixed m.p. with product from tetraphenyldiphosphine with benzaldehyde (from aqueous methanol) 189-189.5°, ν_{max} 1730, 1180 cm^{-1} (Found: C, 75.4; H, 5.3; P, 7.4. $\text{C}_{26}\text{H}_{21}\text{O}_3\text{P}$ requires C, 75.7; H, 5.1; P, 7.5%).

Reaction of tetraphenyldiphosphine with p-isopropylbenzaldehyde.

A mixture of the tetraphenyldiphosphine (3.0 g.) and p-isopropylbenzaldehyde (10 ml.) was kept at 180-200° for 3 hr. The excess aldehyde was removed in vacuo and trituration of the residue with benzene gave α -hydroxy-p-isopropylbenzyldiphenylphosphine oxide (1.4 g.) m.p. and mixed m.p. (from benzene) 168-169°. The mother liquors were evaporated and the residue chromatographed on a neutral alumina column. Elution with ether gave p-isopropylbenzyldiphenylphosphine oxide (0.13 g.) m.p. and mixed m.p. (from ethyl acetate) 190.5-191.5°. Elution with ether containing ethyl acetate (20%) gave α -(p-isopropylbenzoyloxy) benzyldiphenylphosphine oxide (1.9 g.) m.p. (from benzene-light petroleum) 191-192°, ν_{max} 1730 and 1180 cm^{-1} , m/e 496, 349, 201, 147 (Found: C, 77.1; H, 6.7; P, 6.4. $\text{C}_{32}\text{H}_{33}\text{O}_3\text{P}$ requires C, 77.4; H, 6.7; P, 6.3%). A p.m.r. spectrum showed two doublets very close to each other at τ 8.7-8.9; equivalent to six hydrogen atoms each.

A mixture of diphenylphosphine (1.0 g.) and p-isopropylbenzaldehyde was kept at 180-200° for 15 hr. The excess aldehyde was removed in vacuo and the residue triturated with ether to give a mixture of α -hydroxy-p-isopropylbenzyl-diphenylphosphine oxide and p-isopropylbenzyl-diphenylphosphine oxide. Crystallisation from benzene gave α -hydroxy-p-isopropylbenzyl-diphenylphosphine oxide (0.65 g.), m.p. and mixed m.p. 168-169°. Evaporation of the benzene mother liquors and crystallisation from ethyl acetate gave p-isopropylbenzyl-diphenylphosphine oxide (0.38 g.) m.p. and mixed m.p. 190-191°.

Reaction of tetraphenyldiphosphine with p-anisaldehyde.

A mixture of tetraphenyldiphosphine (2.9 g.) and p-anisaldehyde (10 ml.) was kept at 180-200° for 3 hr. Removal of the excess aldehyde in vacuo and trituration of the residue with ether gave p-methoxybenzyl-diphenylphosphine oxide (2.2 g.) m.p. and mixed m.p. (from benzene) 228-229°.

A mixture of diphenylphosphine (1.0 g.) and p-anisaldehyde (10 ml.) was kept at 180-200° for 15 hr. Removal of the excess aldehyde in vacuo and trituration with ether gave p-methoxybenzyl-diphenylphosphine oxide (12. g.), m.p. and mixed m.p. (from benzene) 228-229°.

Reaction of tetraphenyldiphosphine with nicotinic aldehyde.

A mixture of tetraphenyldiphosphine (2.5 g.) and nicotinic aldehyde (10 ml.) was kept at 180-200° for one hour

after which time the reaction mixture had darkened in colour considerably. Removal of excess aldehyde in vacuo gave a black tar. A solution of the residue in benzene was treated with charcoal and filtered. Evaporation and trituration with ether gave a mixture (0.5 g.) of β -picolinylidiphenylphosphine oxide and α -hydroxy- β -picolinyl-diphenylphosphine oxide. These were separated by crystallisation from benzene.

β -picolinylidiphenylphosphine oxide.

A mixture of 3-hydroxymethylpyridine (0.33 g.) and dimethylaminodiphenylphosphine (0.69 g.) was kept at 130° for 4 hr. Trituration with ether gave β -picolinylidiphenylphosphine oxide (0.5 g.), m.p. and mixed m.p. with product from nicotinic aldehyde with tetraphenyldiphosphine (from ethyl acetate) 220-221°, m/e 293, 201, 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%).

α -hydroxy- β -picolinylidiphenylphosphine oxide

Pyridine-3-carboxaldehyde (1.07 g.) was added to a solution of diphenylphosphine (1.86 g.) in acetonitrile (10 ml.) containing concentrated hydrochloric acid (0.25 ml.), and the solution set aside at room temperature for 10 min. Hydrogen peroxide (1.15 g.; 100 volume) was added dropwise with cooling, and shaking. The solution was then diluted with ether (10 ml.) and set aside at room temperature overnight. Filtration gave α -hydroxy- β -picolinylidiphenylphosphine oxide (2.2 g.) m.p. and

mixed m.p. with product from nicotinic aldehyde and tetraphenyl-diphosphine (from benzene plus a small amount of methanol)

198-199° (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%).

Reaction of tetraphenyldiphosphine with *p*-cyanobenzaldehyde

A mixture of tetraphenyldiphosphine (3.0 g.) and *p*-cyanobenzaldehyde (5 g.) was kept at 180-200° for 3 hr.

Trituration with benzene gave α -hydroxy-*p*-cyanobenzoyldiphenylphosphine oxide (1.1 g.), m.p. 207-208° (from ethyl acetate).

The benzene mother liquors were evaporated and chromatographed on neutral alumina. Elution with ethyl acetate gave *p*-cyano-benzoyldiphenylphosphine oxide (0.16 g.), m.p. (from ethyl acetate)

195-196°, ν_{\max} . 1180 (P=O), 2250 (C \equiv N) cm^{-1} , doublet at τ 4.4

(J_{PH} 15 c.p.s.) equivalent to two protons (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%) together with an unknown phosphorus compound

(0.25 g.), m.p. (from ethyl acetate-light petroleum) 176-177°.

An infrared spectrum of the unknown showed absorption characteristic of a cyanide (2250 cm^{-1}) and of a phosphinate [1220 cm^{-1} (P=O) and 1000 cm^{-1} P=O-C]. However, the compound was not simply *p*-cyanobenzyl diphenylphosphinate as a p.m.r. spectrum showed the absence of a CH_2 group.

α -hydroxy-*p*-cyanobenzoyldiphenylphosphine oxide

p-Cyanobenzaldehyde (2.6 g.) was added to a solution of

diphenylphosphine (3.72 g.) in acetonitrile (20 ml.) containing concentrated hydrochloric acid (0.5 ml.) and the solution set aside for 10 min. Hydrogen peroxide (2.3 g; 100 volume) was added slowly with cooling. The solution was diluted with ether (60 ml.). Filtration gave α -hydroxy-p-cyanobenzoyldiphenylphosphine oxide (5.8 g.), m.p. and mixed m.p. with product from p-cyano-benzaldehyde with tetraphenyldiphosphine (from ethyl acetate) 207-208° (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%).

The product above and dimethylaminodiphenylphosphine at 130° for 4 hr. gave α -dimethylamino-p-cyanobenzoyldiphenylphosphine oxide (40%), m.p. (from benzene) 162-162.5°, (Found: C, 73.4; H, 5.8; N, 8.0; P, 8.8. $C_{22}H_{21}N_2OP$ requires C, 73.4; H, 5.8; N, 7.8; P, 8.6%). An infrared spectrum included absorption characteristic of a cyanide (2250 cm.^{-1}), a dimethylamino group (2800 cm.^{-1}) and of a phosphine oxide (1180 cm.^{-1}).

Reaction of tetraphenyldiphosphine with β -phenylpropion-aldehyde.

A mixture of tetraphenyldiphosphine (3.0 g.) and β -phenylpropionaldehyde (10 ml.) was kept at 180-200° for 3 hr. No ethyl benzene could be detected in the reaction mixture by gas chromatography (2m. silicone gum rubber column at 160°). Removal of the excess aldehyde in vacuo and trituration of the residue with ether gave α -hydroxy- γ -phenylpropyldiphenylphosphine oxide (2.5 g.), m.p. (from benzene) 187-188°. No other product could be crystallised from the mother liquors. Authentic

114.

α -hydroxy- β -phenylpropyldiphenylphosphine oxide was prepared by the usual method and had m.p. and mixed m.p. with the product above (from benzene) 187-188° (Found: C, 75.2; H, 6.2; P, 9.3. $C_{21}H_{21}O_2P$ requires C, 75.0; H, 6.25; P, 9.23%).

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