1175. *The Mechanism of the Reduction of Diphenylphosphinic Acid and Its Ethyl Ester by Lithium Aluminium Hydride.*

By K. B. Mallion and Frederick. G. Mann.

A considerable investigation of the reduction of diphenylphosphinic acid, its aluminium salt, and its ethyl ester by lithium aluminium hydride in tetrahydrofuran to diphenylphosphine has given evidence for the main stages of the reduction through diphenylphosphine oxide to the secondary phosphine, although the detailed mechanism of certain stages has not been fully elucidated. The main driving force of the reductions is ascribed to the intermediate formation of P–O–Al groups: these reductions cannot be achieved by lithium hydride.

The direct interaction of lithium diphenylphosphide and tetrahydrofuran on prolonged boiling to form 4-hydroxybutyldiphenylphosphine is described.

The reduction of *o*-, *m*- and *p*-methoxyphenylphenylphosphinic acids (I), by lithium aluminium hydride in tetrahydrofuran has been investigated by Mann, Tong, and Wystrach,[1] who showed that each acid gave a mixture of the secondary phosphine (II), and the tertiary methylphosphine (III), and much amorphous aluminium-containing material, which on hydrolysis gave the free phosphinic acid. It was shown that *o*-methoxyphenylphenylphosphine (II), when treated in tetrahydrofuran with lithium aluminium hydride, gave the *o*-methoxyphenylmethylphenylphosphine (III) and that that active reagent promoting the formation of the methylphosphine (III) was almost certainly the phosphide ion derived from the secondary phosphine (II).

$MeO{\cdot}C_6H_4PhP(O)OH$	$MeO{\cdot}C_6H_4PhPH$	$MeO{\cdot}C_6H_4PhPMe$
(I)	(II)	(III)

This was supported by the action of the diphenylphosphide ion, Ph_2P^-, on anisole in tetrahydrofuran, which gave methyldiphenylphosphine and phenol; repetition of this experiment has given each product in *ca.* 75% yield.[2]

We have therefore studied the mechanism of the reduction of the unsubstituted diphenylphosphinic acid (IV) and that of the methyl-group migration in methoxyarylphosphinic acids as separate investigations. Apart from the above work, the only recorded reduction of a phosphinic acid with lithium aluminium hydride is that of the acid (IV) in dioxan.[3]

It should be noted that two main mechanisms for the general reducing action of the hydride have been suggested. Trevoy and Brown[4] considered that reduction did not proceed by direct hydride-ion attack but through a series of complex Al–H ions of type AlX_nH_{4-n}, which acted as hydride carriers. Paddock[5] considered that free hydride ions arose from the equilibrium $LiAlH_4 \rightleftarrows Li^+H^- + AlH_3$, and that the function of the ethereal solvent was to co-ordinate with the aluminium hydride and thus promote the forward reaction.

On the basis of the earlier work,[1] it appeared probable that the reduction of diphenylphosphinic acid (IV) to the secondary phosphine in tetrahydrofuran followed four main stages. (*i*) The interaction of the acid with the hydride to give a Trevoy–Brown type of complex (V), with evolution of hydrogen. (*ii*) The complex then reacts by (*a*) hydride-ion transfer or (*b*) by direct attack of hydride ion, to give diphenylphosphine oxide (VI). (*iii*) The weakly acidic phosphine oxide (VI) in the alkaline solution loses a proton, giving hydrogen and the complex (VII), which isomerises to the more stable form (VIII); this is a known reaction of metal derivatives of such oxides.[6] (*iv*) The phosphinite form (VIII) then

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[1] F. G. Mann, B. P. Tong, and V. P. Wystrach, *J.*, 1963, 1155.

[2] K. B. Mallion and F. G. Mann, *Chem. and Ind.*, 1963, 654.

[3] F. Hein, K. Issleib, and H. Rabold, *Z. anorg. Chem.*, 1956, **287**, 208.

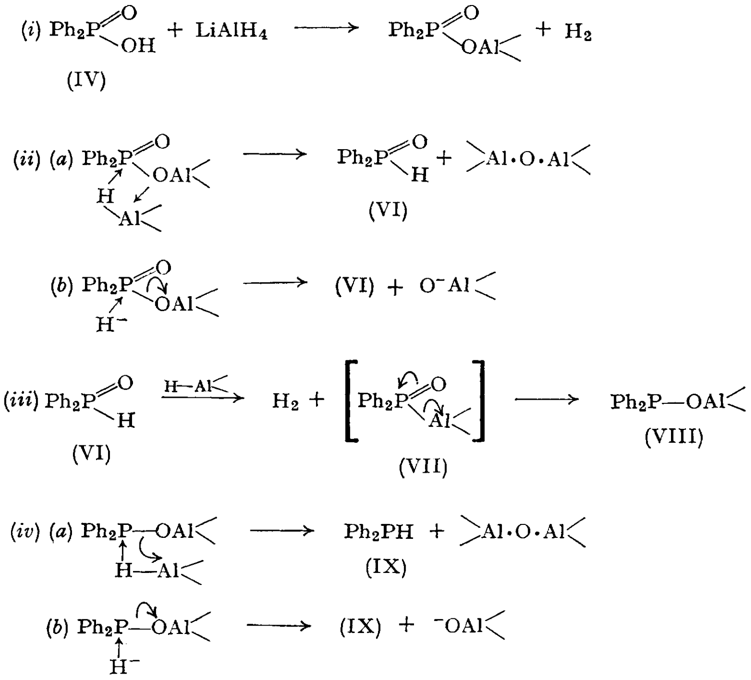
[4] L. W. Trevoy and W. G. Brown, *J. Amer. Chem. Soc.*, 1949, **71**, 1675.

[5] N. L. Paddock, *Nature*, 1951, **167**, 1070.

[6] B. B. Hunt and B. C. Saunders, *J.*, 1957, 2413; see also K. Moedritzer, *J. Inorg. Nuclear Chem.*, 1961, **22**, 19; L. W. Daasch, *J. Amer. Chem. Soc.*, 1958, **80**, 5301.

by (*a*) hydride transfer or (*b*) direct hydride attack gives the secondary phosphine, which will be present as the phosphide ion.

There is little doubt that the oxide (VI) is an intermediate in the reduction, for *o*-chlorophenylphenylphosphine oxide has been obtained by the reduction of the corresponding phosphinic acid under virtually identical conditions.[7]

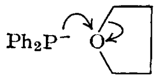


A secondary reaction of the lithium aluminium hydride on the solvent must be noted first. When the powdered hydride (1 mol. equiv.) was added to diphenylphosphinic acid in tetrahydrofuran, a vigorous evolution of hydrogen occurred. The mixture, when boiled, soon developed the orange colour of the Ph_2P^- ion, which almost disappeared after 75 min. After 4 hr. boiling, the concentrated, cooled mixture was extracted with ether and hydrolysed by aqueous potassium sodium tartrate solution. The ethereal layer on distillation gave (1) diphenylphosphine (IX) (13%); (2) 4-hydroxybutyldiphenylphosphine (X) (9%, calculated on the phosphinic acid), the total yield of the phosphine (IX) allowing for fraction (2), being 22%. The aqueous layer and residue on oxidation and acidification gave the purified acid (IV) in 20% yield. Repetition of this experiment, with 10 hr. boiling, gave the

$Ph_2P(O)OH$ (IV)

Ph_2PH (IX)

$Ph_2P\cdot(CH_2)_4OH$ (X)



(XI)

phosphine (IX) (10%), the hydroxy-phosphine (X) (14%), the total yield of the phosphine (IX), based on both fractions, being 24%: the acid (IV) (21%) was recovered.

The phosphine (X) has been identified by analysis, its infrared spectrum, and the preparation of various derivatives.[2] Garner and Tedeschi[8] obtained the same phosphine by the action of magnesium or lithium on cold diphenylphosphinous chloride in tetrahydrofuran, and suggested the transient formation of a cyclic intermediate having chlorine and metal atoms

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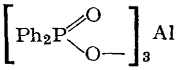
[7] M. J. Gallagher, E. C. Kirby, and F. G. Mann, *J.*, 1963, 4846.

[8] A. Y. Garner and A. A. Tedeschi, *J. Amer. Chem. Soc.*, 1962, **84**, 4734.

in the ring. In our experiments, this phosphine undoubtedly arises from the direct attack (XI) of the phosphide ion on the solvent. This was confirmed by boiling a tetrahydrofuran solution of the phosphine (IX) with butyl-n-lithium (1 mol. equiv.) for 7 hr., when the phosphine (X) was obtained in 22% yield.[9] The production of the phosphine (X) is therefore not a specific property of lithium aluminium hydride in this type of reduction.

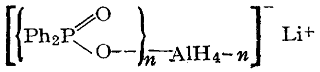
It was repetition of the above experiment, with the addition of anisole (1 equivalent), that gave phenol and methyldiphenylphosphine, each in *ca.* 75% yield, and no phosphine (X).[1,2] Clearly the Ph_2P^- ion reacts far more readily with the methoxyl group than with the furan; this is confirmed by the fact that in all the reductions of *o*-, *m*-, and *p*-methoxyphenylphenylphosphinic acids,[1] no formation of a methoxyphenylphenyl analogue of the phosphine (X) was detected. Further, the similar reduction of 3,5-dimethylphenylphenylphosphinic acid, in which methyl-group migration cannot occur, gave the 3,5-dimethyl homologues of both the phosphine (IX) and the hydroxyphosphine (X).[2,7]

Stage (*ii*) of the proposed mechanism of the reduction involves a fission of an $-OAl<$ group from a phosphorus atom by lithium aluminium hydride. To test this possibility, the hydride was added to the pure aluminium phosphinate (XII) in tetrahydrofuran, which after 10 hr. boiling furnished the phosphine (IX) in 35% yield (allowing for the hydroxyphosphine (X) also formed), and 12% of the unchanged aluminium salt was recovered as the free acid.



$[Ph_2P(=O)O-]_3Al$

(XII)



$[\{Ph_2P(=O)O-\}_n AlH_{4-n}]^- Li^+$

(XIII)

$Ph_2P(O)OEt$

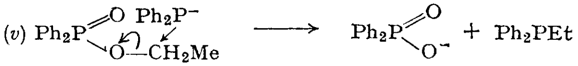
(XIV)

The experiment demonstrated the following points: (i) the $P-OAl<$ group can be cleaved at the P–O link by the hydride: (ii) the initial addition of the hydride caused the mixture to become warm, but without effervescence; this confirms that the vigorous effervescence that occurs when the free phosphinic acid is used is a normal acid–base reaction: (iii) since most of the aluminium salt went into solution early in the reaction, the final mixture was not pasty, unlike that resulting from the free acid. It is clear therefore that, in the reduction of the acid (IV), the insoluble aluminium derivative initially formed is not the simple salt (XII), but very probably a complex salt of type (XIII): (iv) the orange colour of the Ph_2P^- ion appeared earlier in the reduction of the salt (XII) than in that of the acid (IV); this, however, may be a solubility effect and not necessarily an indication of the relative speeds of the reduction.

When, however, the powdered hydride was added to a tetrahydrofuran solution of the ethyl ester (XIV), a steady effervescence occurred long before the appearance of the orange colour; if in these early stages the hydride was added without stirring, the local vigorous effervescence was accompanied by the production of the deep-yellow colour, which, however, was rapidly discharged (not dispersed) when stirring was started. The final mixture, after 10 hr. boiling, gave the phosphine (IX) in 65% yield, allowing for the hydroxyphosphine (X) also formed.

In contrast to these results, when the ester (XIV) was added slowly to an equimolecular solution of lithium diphenylphosphide in tetrahydrofuran–petroleum, the usual working-up gave ethyldiphenylphosphine in 79% yield from the organic layer, and the acid (IV) also in 79% yield from the acidified aqueous layer. The reverse addition of the lithium phosphide to the ester gave the same result.

It is clear that this reaction (*v*) involves nucleophilic attack of the Ph_2P^- ion on the ester group:



$(v)\quad Ph_2P(=O)O-CH_2Me + Ph_2P^- \longrightarrow Ph_2P(=O)O^- + Ph_2PEt$

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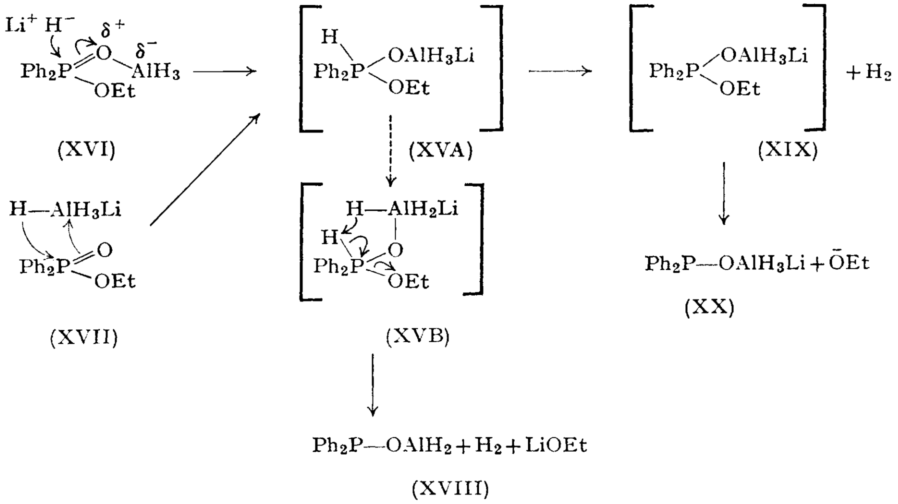
[9] K. B. Mallion and F. G. Mann, *Chem. and Ind.*, 1963, 1558.

The gas evolved during the reduction of the ester with lithium aluminium hydride did not condense when passed through a U-tube packed with glass wool and immersed in liquid nitrogen; it was therefore almost certainly hydrogen. These results indicate that in the reduction of the ester by lithium aluminium hydride (*a*) all the ester had reacted before any Ph_2P^- ion had formed, for no ethyldiphenylphosphine was detected; (*b*) the initial fast reaction must have produced an intermediate containing an acidic hydrogen atom; (*c*) the hydride or $HAl<$ ion did not attack the ethyl group, for this would have liberated ethane.

It is highly probable that the first stage in the reduction of the ester is the rapid formation of the complex (XVA) by the reaction (XVI) or (XVII). The latter, of the Trevoy–Brown type, involves the unlikely interaction between the AlH_4^- ion and the negative end of the P=O dipole, whereas the reaction (XVI), of the Paddock type, is free from this objection. [The formation of the complex (XVA) would not be unexpected. Jørgensen[10] has shown that the rapidly produced primary product in the reduction of cinnamic aldehyde is the complex $PhCH{:}CH{\cdot}CH_2{\cdot}OAlH_3Li$, and Hein, Plust, and Pohleman[11] have stressed the many similar reactions of the P=O and C=O groups.]

The complex (XVA) could react in the form (XVB) and thus generate the phosphinite complex (XVIII); alternatively, the complex (XVA) in the alkaline solution could give the complex (XIX), which in turn would give the phosphinite complex (XX). Hydrolysis of the complexes (XVIII) or (XX) would generate the diphenylphosphine oxide (VI).

Supporting evidence is the fact that, although reduction of the ethyl ester by lithium aluminium hydride with 10 hr. boiling gave no trace of this oxide, reduction at 0° with the hydride (0·66 mol. equiv.) with rapid working-up gave the oxide (VI) and the phosphine (IX); the use of the hydride (1·0 mol. equiv.) at 0° decreased the yield of the oxide and increased that of the phosphine.



It is noteworthy that lithium hydride would not reduce diphenylphosphinic acid (IV), its aluminium salt (XII), or its ethyl ester (XIV). This failure is not due simply to the lithium hydride being an insufficiently powerful H^- donor: sodium hydride, normally a more powerful donor, did not reduce the secondary phosphine oxide. This shows that the $P{-}O{-}Al<$ group strongly facilitates H^- transfer in the last of these reduction stages, and probably in them all.

The process of reduction of the oxide (VI) was shown when an excess of sodium hydride was added to the oxide in cold tetrahydrofuran, causing a vigorous evolution of hydrogen, but the reaction mixture remained colourless; hence, the sodium salt of the oxide had been

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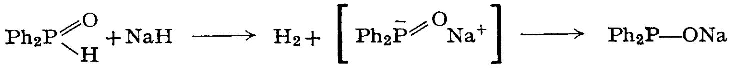
[10] M. J. Jørgensen, *Tetrahedron Letters*, 1963, 559.

[11] F. Hein, H. Plust, and H. Pohleman, *Z. anorg. Chem.*, 1953 **272**, 25.

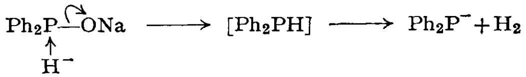
formed and no reduction had occurred (reaction *vi*). When lithium aluminium hydride was now added, a further effervescence occurred and the mixture became yellowish-orange. The mixture was worked up at once, and during the removal of the solvent the solution frothed vigorously and became deep-orange. This corresponded to reaction (*vii*), the sodium salt having been reduced to diphenylphosphine, which then reacted with more hydride to give the diphenylphosphide ion and more hydrogen. The lithium salt of the oxide (VI) similarly gave reaction (*vii*).

(*vi*)



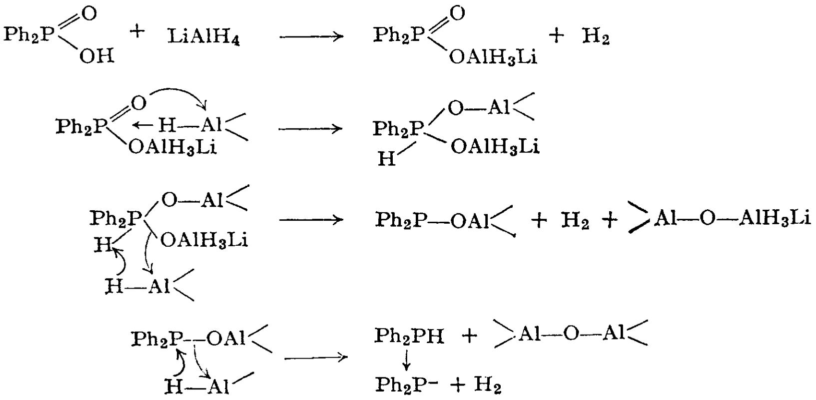
$$Ph_2P\overset{O}{\underset{H}{<}} + NaH \longrightarrow H_2 + \left[Ph_2\bar{P}\overset{O}{\diagup}\ Na^+\right] \longrightarrow Ph_2P—ONa$$

(*vii*)



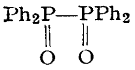
$$\underset{\uparrow \atop H^-}{Ph_2P}—ONa \longrightarrow [Ph_2PH] \longrightarrow Ph_2P^- + H_2$$

The mechanism of the reduction of diphenylphosphinic acid is probably very similar to that of the ester, with the exception of the first stage; the P–O–Al< group again plays an important part in facilitating H^- transfer, but the particular alumino-hydride complexes that transfer H^- to the phosphorus atom and remove it as a proton, are unknown. They are denoted as H–Al< in the following outline of the probable main steps in the reduction of the acid.



Essentially this differs from our earlier projected mechanism (p. 6122) only in the method of formation of the diphenylphosphinite intermediate.

One unexpected feature appears in the reduction of the ethyl phosphinate under certain conditions: it has been noted that this ester when treated in tetrahydrofuran at 0° with the hydride, and rapidly worked up, gives the oxide (VI) and the phosphine, Ph_2PH; when, however, this experiment was repeated at room temperature and the reaction mixture stirred for 2½ hr., working-up afforded the phosphine, Ph_2PH, and a solid that, after repeated

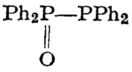


$$\underset{O}{\underset{\|}{Ph_2P}}—\underset{O}{\underset{\|}{PPh_2}}$$

(XXI)

$Ph_2P—PPh_2$

(XXII)



$$Ph_2\underset{O}{\underset{\|}{P}}—PPh_2$$

(XXIII)

recrystallisation, afforded the pure tetraphenyldiphosphine dioxide (XXI). The origin of this compound is uncertain. Its solution in tetrahydrofuran, when treated with the hydride, gave an effervescence and an orange colour, therefore the dioxide (XXI) was not a true reduction product. The precursor of the dioxide might have been the diphosphine (XXII) or the diphosphine monoxide (XXIII), steady atmospheric oxidation of which necessitated the repeated recrystallisation. Since, however, the diphenylphosphide ion does not attack the phosphorus of the ester and, in the course of the reduction, this ion is not formed whilst any free ester remains, the initial crude solid could not have been the monoxide (XXIII); further, the monoxide would have been cleaved by the hydride,[12] and could not remain in the reduction mixture. The diphosphine (XXII), however, would not be cleaved in this way,[12] yet it was not found in our experiments in which the reduction mixture was boiled for 4 or 10 hr. The conditions under which the diphosphine (XXII) is formed indicate a reaction between the Ph_2P^- ion and complexes such as $PhP_2{-}OAlH_2$ or $Ph_2P{-}OAlH_3Li$. The probable explanation of these results is that in our normal reductions, where the reaction mixture was boiled under reflux immediately after the addition of the hydride, the H^- transfer is a much more rapid process than the formation of the diphosphine (XXII), which is therefore produced only under the special conditions described.

We have repeated the earlier reduction of *o*-chlorophenylphenylphosphinic acid,[7] but using 1·30 instead of 1·0 mol. equivalents of the hydride. The yield of the phosphine oxide was almost unchanged, but that of the mixture of phenyl- and *o*-chlorophenyl-phenylphosphines was increased; formation of the *o*-chloro-analogue of the tertiary phosphine (X) was not detected.

The resistance of the *o*-chlorophenylphenylphosphine oxide to reduction is unlikely to be steric, since reduction in the *o*-methoxyphenylphenyl series proceeded smoothly. If this resistance were due to the inductive effect of the chloro-group, it should be shown also in the *p*-chloro-series, but *p*-chlorophenylphenylphosphinic acid on reduction gave the secondary phosphine in yield comparable with that from the unsubstituted acid (IV) and no phosphine oxide (as VI) was obtained.

It is clear that the *o*-chloro-group must decelerate markedly the final stages of the reduction of the phosphine oxide to the secondary phosphine, (possibly because the inductive effect of the *o*-chloro-group may not markedly weaken the co-ordinating power of the oxygen in the highly polarisable P=O group in the early stages of the reduction), but does weaken that of the feebly polarisable oxygen of the P–O–Al group at the phosphinite stage. The absence of the *o*-chloro-phosphine (as X) indicates that the *o*-chlorophenylphenylphosphide ion has considerably weaker nucleophilic power than that of the unsubstituted Ph_2P^- ion.

EXPERIMENTAL

All operations involving secondary or tertiary phosphines were conducted under "pure" nitrogen, which had in addition been passed through alkaline pyrogallol, then Feiser's solution, and finally dried.

Certain compounds gave consistent melting points only when they were heated in a sealed tube, denoted as (S.T.). Refractive indices (n_D) were measured with a Bellingham and Stanley Abbé refractometer, at 23° unless otherwise stated. The term "petroleum" refers throughout to light petroleum, b. p. 60—80°.

Diphenylphosphinic Acid (IV).—This was prepared by two methods: (1) diethyl phosphite[13] was converted by phenylmagnesium bromide into diphenylphosphine oxide,[6] which was then oxidised by hydrogen peroxide to the acid; (2) phenyldiazonium fluoroborate was converted by the Doak–Freedman reaction with phenylphosphonous dichloride and cuprous bromide in ethyl acetate into the acid, and the precautions previously described[1,14] were taken. For moderately large-scale work, method (2) was quicker and less expensive. The crude acid, when prepared by method (2), was triturated with ice-cold acetone to remove a brown impurity and after recrystallisation from ethanol (charcoal) had m. p. 194—196°.

Reduction of the Acid (IV).—These reductions were usually carried out with 4 or 10 hr. boiling of the reaction mixture. Details are given for one experiment with 10 hr. heating, to illustrate the isolation of the 4-hydroxybutyl phosphine (X).

Powdered lithium aluminium hydride (10 g., 1·15 mol.) was added in portions to a cold stirred

[12] K. Issleib and A. Tzschach, *Chem. Ber.*, 1959, **92**, 704, 1118.
[13] H. McCombie, B. C. Saunders, and G. T. Stacey, *J.*, 1945, 380.
[14] R. C. Hinton, F. G. Mann, and D. Todd, *J.*, 1962, 945.

suspension of the powdered acid (IV) (50 g.) in tetrahydrofuran (300 ml.), hydrogen being vigorously evolved. The mixture was boiled under reflux for 10 hr., becoming very pasty; a yellow colour was perceptible after 75 min. heating, and became bright orange after 4 hr. The solvent was removed at atmospheric pressure, and the cooled, pasty orange residue was treated with wet ether (300 ml.) followed by 20% aqueous Rochelle salt (200 ml.) which caused hydrogen evolution.

The ether layer was blown under nitrogen into a separating funnel, and the residue extracted with ether (100 ml.), which was similarly collected; removal of the solvent from the combined dried extracts gave an oil (17 g.), which on distillation at 0·3 mm. gave the fractions: (1), b. p. rising to 110° (4·3 g.); (2) b. p. 165—175° (8·6 g.). Fraction (1), crude diphenylphosphine (IX) (10%), on refractionation gave the pure phosphine, b. p. 85—90°/0·15 mm., n_D1·6274 (3·2 g., 7·5%). Fraction (2) was the crude phosphine (X) (14%) equivalent to 6·17 g. of the phosphine (IX); total effective yield calculated as (IX), 24%. Fraction (2) on refractionation gave the pure phosphine (X) (4·4 g.), b. p. 160—163°/0·3 mm. (lit.,[8] 170°/0·16 mm.), n_D 1·6101 (Found: C, 74·75; H, 7·4; P, 12·1. Calc. for $C_{16}H_{19}OP$: C, 74·4; H, 7·4; P, 12·0%).

The pure phosphine (X) gave a *methiodide*, m. p. 164·5—166° (from ethanol) (Found: C, 51·0; H, 5·8; P, 8·1. $C_{17}H_{22}IOP$ requires C, 51·0; H, 5·55; P, 7·7%). The infrared spectrum of the phosphine showed an OH peak; that of the methiodide also showed this peak, and an intense peak at 900 cm.$^{-1}$ due to P–Me group.[15] The phosphine gave the yellow *bis-(4-hydroxybutyldiphenylphosphine)dibromopalladium*, m. p. 169—172° (decomp.) from ethyl acetate–petroleum (Found: C, 48·3; H, 4·7. $C_{32}H_{38}Br_2O_2P_2Pd$ requires C, 49·1; H, 4·9%); it separated initially as a gum and crystallisation was difficult. The phosphine, when oxidised with aqueous permanganate,[8] furnished 3-carboxypropyldiphenylphosphine oxide, m. p. 162—164° (lit.,[8] 162·5—163°) from water (Found: C, 66·4; H, 5·7. Calc. for $C_{16}H_{17}O_3P$: C, 66·6; H, 5·6%).

The aqueous layer from the ether extraction was treated with sodium hydroxide (10 g.) in water (150 ml.) and with "100 vol." hydrogen peroxide (25 ml.) in water (25 ml.) and then boiled (charcoal), filtered, cooled and acidified, giving the acid (IV) (10·5 g. after purification, 21%), m. p. 194—196°.

When the reduction of the acid (IV) was carried out as above, but with only 4 hr. boiling, the ether extract gave a crude oil (13·2 g.), which on slow distillation at 0·3 mm., gave the following fractions: (1) b. p. below 110° (5·6 g., 13%), n_D 1·6265, the almost pure phosphine (IX); (2) b. p. 110—148° (0·3 g.); (3) b. p. 148—165° (5·1 g., 9%), the phosphine (X). Excluding fraction (2), a mixture of the two phosphines, the effective yield of the "phosphide ion" was 22%. The pure recovered acid (IV) (9·5 g., 19%) had m. p. 194—196°.

Attempted Reduction with Lithium Hydride.—The above experiment was repeated, the acid (50 g.) being treated, however, with lithium hydride (10 g., 5·5 mol.) for 15 min. with steady effervescence. The mixture was boiled for 4 hr., and the pasty product diluted with more solvent (150 ml.), but no colour could be detected.

The product was worked up as before, but the ethereal layer and extract gave no residue on evaporation. The aqueous layer, which contained a fluffy white solid, (which almost was certainly the lithium phosphinate), was heated with additional water to give a clear solution, which when boiled (charcoal), filtered, cooled, and acidified with concentrated hydrochloric acid deposited the acid (IV), 42·3 g., (85%), m. p. 193—195°.

Direct Preparation of the Phosphine (X).—A stirred solution of diphenylphosphine (IX) (7·9 g.) in tetrahydrofuran (100 ml.) was treated under nitrogen with butyl-lithium (1 mol.) in petroleum (37 ml.), and the orange solution was boiled under reflux for 7 hr., cooled, and ether (100 ml.) and water (50 ml.) then added. Evaporation of the dried ethereal layer gave an oil (8·2 g.) which on fractionation at 0·3 mm. gave the phosphine (IX) (4·7 g.) and the phosphine (X) (2·4 g., 22%). The phosphine (X) was identified by its infrared spectrum and by conversion into its methiodide, m. p. and mixed m. p. 164—166°.

Aluminium Diphenylphosphinate.—Preparation and reduction. Anhydrous sodium carbonate (2·432 g., 1 mol.) in water (30 ml.) was added to a suspension of the acid (IV) (10·0 g., 2 mol.) in water (25 ml.). The mixture was warmed as carbon dioxide was evolved, giving a clear solution, pH 6·5—7·0. This solution was cooled and added with shaking to an ice-cold solution of aluminium sulphate ($16H_2O$) (4·82 g., 0·33 mol.) in water (30 ml.). The *aluminium phosphinate* (9·84 g.) separated immediately, and was collected, washed thoroughly with water, and dried at 160°/14 mm. for 5 hr. (Found: C, 63·1; H, 5·0. $C_{36}H_{30}AlO_6P_3$ requires C, 63·8; H, 4·5%).

A stirred suspension of this powdered salt (51·3 g.) in tetrahydrofuran (300 ml.), when treated

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[15] K. B. Mallion, F. G. Mann, B. P. Tong, and V. P. Wystrach, *J.*, 1963, 1327.

with lithium aluminium hydride (10 g., 1·15 mol.), became warm without effervescence. The mixture was boiled under reflux for 10 hr.: after 30 min. most of the solid had dissolved and the mixture was pale yellow, after 2 hr. it was bright yellow and after 10 hr. yellow-orange. The solvent (190 ml.) was distilled off, and the product worked up as described for the acid, except that the aqueous layer was twice extracted with ether (2 × 100 ml.).

The crude oil from the ether layer, distilled at 0·18 mm., gave the following fractions: (1) b. p. 84—101° (10·4 g.); (2) b. p. 147—168° (0·5 g.); (3) b. p. 168—173° (5·9 g.). Fraction (1) was crude diphenylphosphine (IX) (25%), and on refractionation gave the pure phosphine, b. p. 83—87°/0·30 mm. (8·5 g., 20%). Fraction (3) was the viscous phosphine (X), identified by its infrared spectrum and its methiodide, m. p. and mixed m. p. 164—166° (from ethanol). This fraction was equivalent to 4·25 g. of the phosphine (IX), and the total yield of the "phosphide ion" was 14·65 g. (35%).

The aqueous layer, treated with hydrogen peroxide as before, gave the acid (IV), 6·0 g., m. p. 194—196°.

A similar treatment of the aluminium salt (48·4 g.) with lithium hydride (10 g., 5 mol.) gave no apparent reaction. After 4 hr. boiling, the product was worked as before. The ethereal layer gave no residue. The aqueous layer, when boiled with sodium carbonate (12 g.) (charcoal), filtered, cooled, and acidified, deposited a white solid (38·5 g.), m. p. > 360°, apparently unhydrolysed aluminium salt.

Ethyl Diphenylphosphinate (XIV).—*Preparation.* A stirred suspension of the acid (73 g.) in dry benzene (150 ml.), contained in a 3-necked flask fitted with stirrer and reflux condenser, was treated in turn with phosphorus trichloride (100 ml.) and pentachloride (70·5 g., 1 mol.). The warm clear solution was boiled for 2½ hr., and the benzene and unchanged chlorides were removed at 120°/14 mm. The residual crude diphenylphosphinic chloride was cooled in ice, and treated in turn with pyridine (31·1 g., 1·2 mol.) and ethanol (20·2 g., 1·2 mol.), each dissolved in benzene (75 ml.). The precipitated pyridine hydrochloride was collected, and the filtrate left overnight at 3°, filtered again, and distilled, giving the ethyl phosphinate, b. p. 148—148·5°/0·35 mm., n_D^{20} 1·5720 (43·3 g., 53%).

Reduction. (1) A stirred solution of the ester (45·3 g.) in tetrahydrofuran (300 ml.) was cooled in ice whilst lithium aluminium hydride (9 g., 1·28 mol.) was added in portions, producing a steady effervescence. A permanent yellow colour was not produced until the hydride (6 g.) had been added, and was not intensified during the subsequent 10 hr. boiling. The product was worked up as before. The residue from the ether layer, on distillation, gave the following fractions: (1) b. p. 94—110°/0·25 mm. (mainly at 94—96°), the almost pure phosphine (IX) (12·9 g., 38%); (2) b. p. 110—180°/0·30 mm. (mainly 170—180°), largely the phosphine (X) (13·0 g.). Fraction (2) is equivalent to the phosphine (IX) (9·4 g.), and the total yield of the crude (IX) is 65%. Fraction (1) on refractionation gave the pure phosphine (IX) (11·1 g., 33%), b. p. 97—98°/0·3 mm., $n_D^{21·0}$ 1·6279. Fraction (2) similarly gave the pure phosphine (X) (9·7 g.), b. p. 170—173°/0·3 mm., n_D 1·6096, identified by its infrared spectrum and its methiodide.

(2) The ester (10 g.) in ice-cold tetrahydrofuran (60 ml.) was now treated with the hydride (1·02 g., 0·66 mol.) over 20 min., and the product at once worked up. The aqueous layer was extracted with ether (3 × 30 ml.) and the united ether layers gave a clear oil (7·7 g.), which on fractionation gave the phosphine (IX) (2·6 g., 34%) and a fraction, b. p. 155—163°/0·2 mm. (2·6 g.) which slowly solidified: recrystallisation from ether with cooling with acetone–carbon dioxide gave the pure diphenylphosphine oxide, (VI), (1·23 g.), m. p. 52·5—55° (S.T.) (lit.,[6] 53—56°). Its infrared spectrum was identical with that of an authentic sample, and on oxidation it gave the acid (IV) (97%), m. p. and mixed m. p. 193—195°. The ethereal filtrate from the recrystallisation was rapidly treated with methyl iodide, and the crude deposited iodide was converted into dimethyldiphenylphosphonium picrate, m. p. and mixed m. p. 117—118·5°. The fraction of b. p. 155—163°/0·2 mm. therefore contained some phosphine (IX), arising from the thermal decomposition of a portion of the oxide (VI).

A solution of the undistilled residue (from the initial ether layer) in aqueous sodium carbonate, when filtered and acidified, furnished the acid (IV), m. p. and mixed m. p. 193—195·5°.

(3) Repetition of (2), but with 1 mol. of the hydride, afforded the crude phosphine (IX) (45%) and a fraction, (1·1 g.), b. p. 145°/0·2 mm. from which the crystalline oxide (VI), m. p. 49—53° (S.T.) was isolated. The undistilled residue again furnished the acid (IV).

(4) Experiment (3) was repeated, but the reaction mixture was stirred at room temperature for 2½ hr. and then worked up as before. Evaporation of the ether layer gave a mixture of a white solid and an oil. The oil was taken up in a small quantity of ether and identified as the phosphine

(IX), for with methyl iodide it gave dimethyldiphenylphosphonium iodide, m. p. and mixed m. p. 247·5—251°, which in turn gave the picrate, m. p. 113—115°.

The residual white solid (2·1 g.) had no marked phosphine smell, was not quaternised by methyl iodide and had an infrared spectrum identical with that of diphenylphosphine oxide, except that the P=O band was missing. The material, recrystallised once from toluene, had m. p. 145—163°, increased to 172—179° by five more recrystallisations: three further recrystallisations from aqueous acetone gave tetraphenyldiphosphine dioxide (XXI), m. p. 179·5—181·5° (lit.,[16] 167°) [Found: C, 71·7; H, 4·8; P, 15·6%; *M* (in boiling benzene), 400. Calc. for $C_{24}H_{20}O_2P_2$: C, 71·6; H, 5·0; P, 15·4%; *M*, 402]. The dioxide, when oxidised in boiling acetone with hydrogen peroxide gave the acid (IV), m. p. and mixed m. p. 193—195°: the infrared spectrum was identical with that of the authentic acid.

(5) The ester (XIV) (10 g.) in tetrahydrofuran (60 ml.) was stirred at room temperature whilst lithium hydride (1·293 g., 4 mol.) was added, and the product was boiled for 4 hr. and then worked up as before, a violent effervescence occurring on the addition of wet ether and water. The ether layer and extracts, on evaporation, gave an oil (8·5 g.) having an infrared spectrum identical with that of the ester (XIV), and giving on distillation the pure ester (7·1 g.), b. p. 144—146°/0·25 mm. n_D^{22} 1·5700. The aqueous layer on acidification gave the acid (IV) (39 mg.), m. p. 193·5—195° after crystallisation from ethanol. No reduction of the ester had occurred.

Action of lithium diphenylphosphide on the ester (XIV). An orange solution of lithium diphenylphosphide was prepared by the addition of lithium butyl (1 mol.) in petroleum (35 ml.)[17] to a solution of diphenylphosphine (7·1 g., 1 mol.) in tetrahydrofuran (70 ml.). To this chilled, stirred solution, the ester (9·4 g., 1 mol.) in the furan (50 ml.) was added dropwise, a dark brown colour being at first produced and then replaced by a white deposit. After removal of the solvent, the cooled, very pale yellow residue was shaken with ether (130 ml.) and water (50 ml.).

The dried ether layer on evaporation afforded a residue (8·3 g.) of crude ethyldiphenylphosphine. A portion with methyl iodide gave ethylmethyldiphenylphosphonium iodide, m. p. and mixed m. p. 186·5—188° (lit.,[18] 186—187°) from ethanol, and the picrate, m. p. and mixed m. p. 99·5—102° (lit.,[18] 100·5—102°). The remainder (7·8 g.) required careful fractionation to eliminate traces of diphenylphosphine and give the ethyl phosphine (5·9 g., 79%), b. p. 114—116°/0·3 mm., n_D 1·6096; an authentic sample had n_D 1·6118. The undistilled residue (1·9 g.) from the fractionation did not react with nitric acid and was probably unchanged ester.

The aqueous layer on acidification gave the acid (IV), (6·6 g., 79%), m. p. and mixed m. p. 193—195°.

This experiment was repeated, with the lithium diphenylphosphide solution being added to that of the ester (XIV); the yields of the acid and the crude ethyl phosphine were again 79%.

Diphenylphosphine Oxide (VI).—This oxide (94%) was prepared by passing air through an isopropanol solution of the phosphine (IX)[19] and recrystallisation from ether cooled in acetone–carbon dioxide. The oxide is hygroscopic, and only a rapidly recorded infrared spectrum of the thoroughly dried material, showed no OH band.

Reduction. (1) A stirred, cooled solution of the oxide (7·7 g.) in tetrahydrofuran (60 ml.) was treated with lithium aluminium hydride (1·430 g., 1 mol.) with vigorous hydrogen evolution. The mixture was boiled for 30 min. and worked up as before. The ether layer and extracts gave an oil (6·1 g.), which on distillation at 0·15 mm. gave the following fractions: (1) b. p. 88—90° (3·1 g.), the phosphine (IX) (44%); (2) b. p. 90—145° (mainly 135—145°) (1·9 g.), unreduced oxide (VI). Fraction (1) was identified by its infrared spectrum and by conversion to the methopicrate, m. p. and mixed m. p. 116·5—118°, and fraction (2) by its spectrum and recrystallisation to the pure oxide.

(2) A solution of the oxide (10 g.) in tetrahydrofuran (60 ml.) was treated with sodium hydride (3·5 g., 3 mol.), again with hydrogen evolution. The mixture was boiled for 4 hr. and when worked up in the usual way afforded only the oxide (VI): the phosphine (IX) could not be detected.

The first stage of this experiment was repeated with 1·2 mol. of sodium hydride to form the sodium salt, with boiling for 30 min. The cooled stirred product was then treated with lithium aluminium hydride (1·88 g., 1 mol.) over 15 min., with more effervescence and the production of a yellow colour. The solution was then concentrated and worked up as before. The ethereal portion

[16] W. Kuchen and H. Buchwald, *Angew. Chem.*, 1957, **69**, 307.
[17] H. Gilman, W. Langham, and F. W. Moore, *J. Amer. Chem. Soc.*, 1940, **62**, 2327.
[18] K. B. Mallion and F. G. Mann, *J.*, 1964, 5716.
[19] M. M. Rauhut and H. A. Currier, *J. Org. Chem.*, 1961, **26**, 4626.

gave an oil (8·7 g.), which on distillation at 0·2 mm. gave the phosphine (IX) (1·8 g., 20%): the undistilled residue was the oxide (VI) (5 g.).

When this experiment was repeated with the addition of lithium hydride only, no reduction of the oxide occurred; subsequent addition of lithium aluminium hydride (as above) gave the phosphine (IX).

When the oxide in tetrahydrofuran was converted into the lithium salt with butyl-lithium, subsequent reduction with lithium aluminium hydride (1 mol.), with boiling for 50 min., gave the phosphine (IX) and a low yield of the phosphine (X).

Reduction of o-*Chlorophenylphenylphosphinic Acid.*—A suspension of the acid (24·9 g.) in tetrahydrofuran (150 ml.) was treated with lithium aluminium hydride (4·85 g., 1·3 mol.) for 10 min., and then boiled for 4 hr. After working-up as before, the ethereal solution on evaporation gave a mobile oil, which when distilled at 0·2 mm. gave the following fractions: (1) b. p. below 140° (mainly 110—120°), (4·3 g.), a mixture of diphenyl- and *o*-chlorophenylphenyl-phosphine; (2) b. p. 140—163° (mainly 162—163°), rapidly solidifying (2·8 g.), *o*-chlorophenylphenylphosphine oxide.

Fraction (1), when refractionated at 0·25 mm., gave the fractions: (*a*) b. p. $<$ 110° (1·5 g.); (*b*) b. p. 110—115° (0·5 g.); (*c*) b. p. 115—118° (1·0 g.). Fraction (*a*) gave a methiodide, m. p. 213·5—215·5° after one, and 236—238° after eight, recrystallisations from ethanol. This salt was now the reasonably pure dimethyldiphenylphosphonium iodide, shown by m. p. and mixed m. p., and by almost identical infrared spectra, except that that of the salt showed a peak at 1050 cm.$^{-1}$, which is very strong in that of the *o*-chlorophenyl analogue. Fractions (*b*) and (*c*) were the pure *o*-chlorophenylphenylphosphine [Found: for fraction (*c*); P, 13·7. Calc. for $C_{12}H_{10}ClP$: P, 14·0%]: both fractions readily gave the pure *o*-chlorophenyldimethylphenylphosphonium iodide, having identical m. p. and infrared spectra with those of the authentic iodide. No *o*-chlorophenyl-4-hydroxybutylphenylphosphine could be detected.

p-*Chlorophenylphenylphosphinic Acid.*—This was also prepared by the Doak–Freedman method, an induction period of 0·75—1 hr. preceding the violent reaction of the *p*-chlorophenyldiazonium fluoroborate with the phenylphosphonous dichloride in ethyl acetate to give the acid (47%), m. p. 154—156° (lit.,[20] 158·5—159·5°) from aqueous ethanol.

The acid was converted as before into the *ethyl ester* (60%), b. p. 168—170°/0·3 mm., $n_D^{20·5}$ 1·5740 (Found: P, 11·2. $C_{14}H_{14}ClO_2P$ requires P, 11·0%).

The ester was reduced precisely as was the ester (XIV), and gave p-*chlorophenylphenylphosphine* (crude, 45%), pure, b. p. 115—120°/0·25 mm., n_D 1·6307 (Found: P, 13·6. $C_{12}H_{10}ClP$ requires P, 14·0%). With boiling methyl iodide it gave an iodide, which furnished p-*chlorophenyldimethylphenylphosphonium picrate*, m. p. 134—136° (ethanol) (Found: C, 50·4; H, 3·5; N, 8·6. $C_{20}H_{17}ClN_3O_7P$ requires C, 50·25; H, 3·6; N, 8·8%). No higher fraction corresponding to the phosphine oxide could be obtained.

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[20] L. D. Quin and R. E. Montgomery, *J. Org. Chem.*, 1962, **27**, 4120.