*The Preparation and Properties of 2-Phenyl*iso*phosphindoline. A New Class of Co-ordinated Metallic Compounds.*

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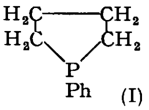
Two syntheses are described which furnish respectively the above *iso*phosphindoline and its quaternary salts. 2-Phenyl*iso*phosphindoline has many of the normal properties of a tertiary phosphine but is unique in that with palladium dichloride and dibromide it gives crystalline derivatives of composition $[(C_{14}H_{13}P)_2PdCl]$ and $[(C_{14}H_{13}P)_2PdBr]$ respectively. These compounds associate in solution but otherwise are stable derivatives of univalent palladium, and represent an entirely novel class of complex metallic compound.

ONLY two types of compound having a ring-system consisting of four carbon atoms and one phosphorus atom have hitherto been recorded, namely, 1-phenyltetramethylenephosphine (I) (Grüttner and Krause, *Ber.*, 1916, **49**, 438) and 1-ethylphosphindoline (II) (Mann and Millar, *J.*, 1951, 2205). We have now investigated the synthesis of 2-phenyl*iso*phosphindoline (III).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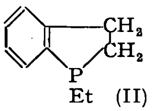
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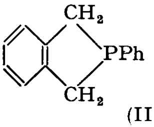
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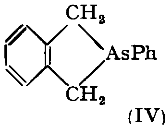
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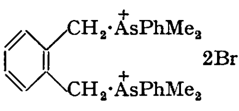
The arsenic analogue of (III), *i.e.*, 2-phenyl*iso*arsindoline (IV), can be prepared by the interaction of *o*-xylylene dibromide, phenyldichloroarsine, and sodium, the reaction being catalysed by ethyl acetate (Lyon and Mann, *J.*, 1945, 30). A similar experiment, using phenyldichlorophosphine, yielded however only a trace of the crude *iso*phosphindoline (III); this result was not unexpected, as Holliman and Mann (*J.*, 1943, 547) have shown that, although *o*-2-bromoethylbenzyl bromide, $C_6H_4(CH_2Br)\cdot C_2H_4Br$, condenses with phenyldichloroarsine and sodium to give 2-phenyl-1 : 2 : 3 : 4-tetrahydro*iso*arsinoline in good yield, with phenyldichlorophosphine under similar conditions it gives only a minute yield of the tetrahydro*iso*phosphinoline.

2-Phenyl*iso*arsindoline (IV) is, however, most readily prepared by the interaction of *o*-xylylene dibromide and phenyldimethylarsine to give a crude product which contains the diquaternary bromide (V) as the main component and on thermal decomposition gives the arsine (IV) in 57% yield (Lyon, Mann, and Cookson, *J.*, 1947, 662). Experiments, for which we are greatly indebted to Dr. Joan A. Reid, indicate that similar diquaternary salts

(VI) are formed by the interaction of the dibromide with phenyldimethyl- and phenyldiethyl-phosphine, but these salts when heated in a vacuum gave no detectable 2-substituted *iso*phosphindolines.

o-Xylylene dibromide in ether–benzene reacted readily with phenylphosphinebis(magnesium bromide), $Ph{\cdot}P(MgBr)_2$, but the organic product consisted almost exclusively of an amorphous insoluble powder, apparently produced by extensive linear condensation of the dibromide with the magnesium derivative. However this amorphous material decomposed when heated in a vacuum, with the production of the crude *iso*phosphindoline in 4% yield: redistillation gave the pure phenyl*iso*phosphindoline as a colourless liquid which has an unpleasant odour and readily undergoes oxidation on exposure to the air.

The formation of amorphous products in this type of reaction is not novel. Job, Reich, and Vergnaud (*Bull. Soc. chim.*, 1924, **35**, 1404) showed that phenylarsinebis(magnesium bromide), $Ph{\cdot}As(MgBr)_2$, and 2 : 2′-dichlorodiethyl sulphide formed a resinous material from which tetrahydro-4-phenylthiarsine (VII) could be extracted in only 7% yield. Beeby and Mann (*J.*, 1951, 886) found that this Grignard reagent reacted similarly with 2 : 2′-dibromodiethyl ether to give an insoluble product which on strong heating decomposed to tetrahydro-4-phenyloxarsine (as VII), and reacted with *NN*-bis-2-bromoethylaniline to give a resinous material and the crystalline hexahydro-1 : 4-diphenyl-1 : 4-azarsine (VIII). In all these cases, the production of insoluble amorphous products is probably the result of extensive—and presumably linear—condensation.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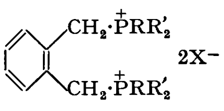
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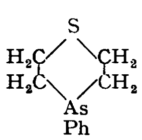
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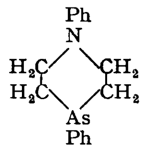
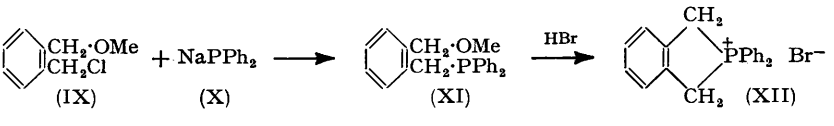

(VIII)

In view of the low yield of the *iso*phosphindoline (III) by the above method, other synthetic routes were investigated, particularly those which would avoid the use of the unpleasant phenylphosphine. Interaction of ethereal *o*-xylylene dichloride and magnesium in the presence, or with the subsequent addition, of phenyldichlorophosphine gave solely the polymeric *o*-xylylene, $(C_8H_8)_x$ (see previous paper). A mixture of the dichloride and the dichlorophosphine in boiling di-*n*-butyl ether, when treated with zinc, gave the same product.

It has been shown by Mann and Smith (*J.*, 1952, 4544) that when phenylarsine in liquid ammonia solution is treated in turn with two equivalents of sodium and of ethyl bromide, a good yield of phenyldiethylarsine results. In a model experiment, phenylarsine was similarly treated with two equivalents of sodium and one of *o*-xylylene dibromide, but no phenyl*iso*arsindoline (IV) was formed and only arsenobenzene, PhAs:AsPh, could be isolated. In view of this result, parallel experiments with phenylphosphine and the dibromide or dichloride were not undertaken.

It is possibly significant however that, although Mann and Smith (*loc. cit.*) found that simple alkyl groups could thus be introduced into phenylarsine, no cyclic derivatives could be similarly obtained by using ethylene dibromide or trimethylene dibromide, arsenobenzene being formed in each case. In view of this difficulty, in another model experiment diphenylphosphine and sodium, each in liquid ammonia solution, were mixed, and the resultant diphenylsodiophosphine (X) then treated with *o*-methoxymethylbenzyl chloride (IX) (cf. pp. 2819, 2829), with the formation of *o*-methoxymethylbenzyldiphenylphosphine (XI), a viscous oil characterised as its crystalline methiodide. This phosphine, when treated in boiling aqueous acetic acid with a stream of hydrogen bromide, underwent conversion into the *o*-bromomethyl derivative, which at once cyclised to 2 : 2-diphenyl*iso*-



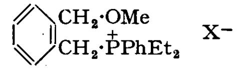
phosphindolinium bromide (XII), which in turn was characterised as its highly crystalline picrate.

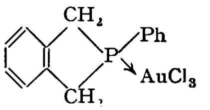
This synthesis has the advantage that the yields were good even on the small scale on which we were working, and would probably be excellent on a larger scale. On the other hand, it is highly improbable that a diphenylphosphonium salt such as (XII) could be converted into the tertiary 2-phenyl*iso*phosphindoline (III) by thermal decomposition. Such a conversion undoubtedly could be achieved by the use of the sodium derivative of a suitable alkylarylphosphine such as ethylphenylphosphine in place of (X). There is at present however no satisfactory method for the preparation of pure alkylarylphosphines, and no authentic examples of such compounds have been recorded. We have attempted to convert phenyldichlorophosphine by the action of diethylcadmium into phenylethylchlorophosphine, EtPhPCl, but the separation of this chloride from unchanged dichloride. or from phenyldiethylphosphine, proved very difficult, and the reduction of the crude chloride to the phosphine, EtPhPH, by the method employed for diphenylphosphine (Mann and Millar, *J.*, 1952, 3039) completely failed.

A brief examination was made of a possible alternative use of the chloride (IX), which was combined with phenyldiethylphosphine to give diethyl-*o*-methoxymethylbenzylphenylphosphonium chloride (XIII; X = Cl). There was a remote chance that this salt on thermal decomposition might lose ethylene and hydrogen chloride to form the ethylphenyl analogue of the phosphine (XI): actually, this decomposition regenerated the phenyldiethylphosphine, a result which was not unexpected in view of the lability of benzyl groups in phosphonium salts.

2-Phenyl*iso*phosphindoline (III) has, with one striking exception, the normal properties of a tertiary phosphine. It readily gives a crystalline methiodide, and with auric chloride under appropriate conditions gives the colourless crystalline monochloro-(2-phenyl*iso*phosphindoline)gold (XIV), the molecular weight of which shows that the phosphine has the simple " monomeric " structure (III). The stability of the ring system in the tertiary phosphine is shown by the fact that the quaternary methiodide, when heated to *ca.* 250°, decomposes to a mixture of the phosphine (III) and its hydriodide: simple quaternary phosphonium halides which contain both a benzyl and a methyl group, on the other hand, tend on heating to lose the benzyl rather than the methyl group (cf. Meisenheimer, Casper, Höring, Lauter, Lichtenstadt, and Samuel, *Annalen*, 1926, **449**, 213).

(XIII)





(XIV)

The remarkable feature in the chemistry of 2-phenyl*iso*phosphindoline is its reaction with palladous halides. Tertiary phosphines normally react with potassium palladochloride to give, according to the proportions used, either the simple compounds $[(R_3P)_2PdCl_2]$ which are usually bright yellow, or the " bridged " $[(R_3P)_2(PdCl_2)_2]$ which are orange; the bromo-analogues are usually orange and reddish-brown respectively (Mann and Purdie, *J.*, 1935, 1549; 1936, 873). The addition of a hot aqueous-ethanolic solution of potassium palladochloride to a slight excess of the *iso*phosphindoline (III) gives, however, colourless crystals of composition $[(C_{14}H_{13}P)_2PdCl]$, which melt at 177—178° to a clear scarlet liquid. This compound, monochlorobis-(2-phenyl*iso*phosphindoline)palladium, is dimorphic, and gives a second crystalline form, also colourless, melting at 129—131° also to a scarlet liquid: a mixture of the two forms melts however at 177—178°. The *iso*phosphindoline reacts similarly with potassium palladobromide to give scarlet crystals, m. p. 196—198° (decomp.), of composition $[(C_{14}H_{13}P)_2PdBr]$.

However, under appropriate conditions, the *iso*phosphindoline reacts normally with potassium palladochloride to form dichlorobis-(2-phenyl*iso*phosphindoline)palladium, $[(C_{14}H_{13}P)_2PdCl_2]$, yellow crystals, m. p. 256—260° (decomp. with severe darkening), which, unlike the monochloro-derivative, are almost insoluble in boiling ethanol and acetone. The crimson di-iodo-analogue, $[(C_{14}H_{13}P)_2PdI_2]$, has also been isolated.

It is significant that the colourless crystals of the monochloro-compound, when heated at 60°/0·1 mm. for 2 hours, become pale yellow but on cooling slowly lose this colour. Moreover, solutions of these crystals in warm ethanol, aqueous ethanol, or acetone are bright yellow and on boiling become bright red : on cooling these changes are reversed and (at suitable concentrations) the colourless compound crystallises again. This deepening in colour in solution with increasing temperature (a process which apparently goes to completion when the crystals are melted) would normally be indicative of dissociation : in fact, however, molecular-weight determinations in boiling ethanol and acetone agree closely with six-fold association, *i.e.*, with a formula $[(C_{14}H_{13}P)_2PdCl]_6$.

The red colour of a warm ethanolic solution of the monobromo-compound similarly becomes deep red as the solution is more strongly heated, this change reversing as the solution cools. The molecular weight of the monobromo-compound in solution has not yet been determined, however, owing to insufficient material.

This chloride and bromide are thus apparently co-ordinated derivatives of univalent palladium possessing considerable stability (apart from the factor of physical association) and they represent an entirely new type of co-ordinated metallic compound, of particular interest because authentic and stable derivatives of univalent palladium have not previously been isolated (cf. Sidgwick, " Chemical Elements and their Compounds," Oxford Univ. Press, 1950, p. 1557). Their complete structure cannot be investigated until we have larger supplies. It may be noted, however, that the univalent palladium atom in the simple unit $[(C_{14}H_{13}P)_2PdCl]$ should have an unshared electron, and unless association produces a structure in which this electron becomes shared, the compound should be paramagnetic. Dr. C. M. French of Queen Mary College in a preliminary investigation finds however that the chloride has a diamagnetic susceptibility of *ca.* $-0{\cdot}1 \times 10^{-5}$.

Although the complex palladous halide derivatives of numerous tertiary phosphines have been investigated in the past, 2-phenyl*iso*phosphindoline is the only one known to give these abnormal derivatives, and the very interesting point arises as to what is the particular factor in the structure of this phosphine which determines this behaviour. It is clear that, in the formation of these two compounds, the palladium dichloride and dibromide must undergo reduction to the monohalide which is immediately stabilised by co-ordination with the phosphine, although whether co-ordination precedes or follows reduction is not at present known. This type of reaction is however normal for tertiary phosphines treated in aqueous ethanol with potassium chloroaurate : a transient orange or brown auric compound may separate, but when the solution is warmed reduction and complete decolorisation occur and the aurous chloride is stabilised by formation of the compound $[R_3P{\rightarrow}AuCl]$. Some of these compounds are so stable that they can be distilled unchanged in a vacuum (Mann, Wells, and Purdie, *J.*, 1937, 1828). It is remarkable that, although the *iso*phosphindoline (III) shows this " normal " behaviour with auric chloride, it is the only known tertiary phosphine which will similarly reduce palladium dihalides to the monohalides under the mild conditions usually employed for these preparations.

We have sought other compounds having structural similarity to the phosphine (III)—and more accessible—to determine whether they also show this behaviour with palladous dihalides. 1-Ethylphosphindoline gives a normal palladous dibromide compound $[(C_{10}H_{13}P)_2PdBr_2]$ (Mann and Millar, *J.*, 1951, 2205), and 1-ethyltetrahydrophosphinoline and 2-ethyltetrahydro*iso*phosphinoline do likewise (Beeby and Mann, *J.*, 1951, 411); we now find that 2-phenyl*iso*arsindoline (IV) similarly gives the yellowish-orange crystalline derivative $[(C_{14}H_{13}As)_2PdBr_2]$.

We have also investigated dibenzylphenylphosphine, which bears a marked structural resemblance to the phosphine (III). Pure dibenzylphenylphosphine has not hitherto been recorded. Michaelis and Gleichmann (*Ber.*, 1882, **15**, 1961) attempted to prepare it by the interaction of benzyl chloride, phenyldichlorophosphine, and zinc, and obtained colourless crystals, m. p. 169—170°, which would not combine with alkyl iodides : it was in fact the phosphine oxide. Meisenheimer *et al.* (*loc. cit.*) and Kamai (*J. Gen. Chem. Russia*, 1932, **2**, 524) prepared the phosphine by the thermal decomposition of benzyldiethylphenylphosphonium chloride, and the former workers also by the interaction of benzylmagnesium chloride and phenyldichlorophosphine; Kamai described the phosphine as a liquid, b. p. >170°/10 mm., but all these workers characterised it solely as derivatives. We find that the phosphine is very readily oxidised even in solution, but, when prepared by Meisenheimer's second method in an atmosphere of nitrogen, and purified by distillation in a vacuum, it very readily forms colourless crystals, m. p. 71—72°. Treatment of this phosphine with potassium pallado-chloride and -bromide readily gave however the "normal" compounds of composition $[(C_{20}H_{19}P)_2PdCl_2]$ and $[(C_{20}H_{19}P)_2PdBr_2]$ respectively.

Apart from metallic derivatives, it is of interest to compare the properties of 2-phenyl*iso*indoline, 2-phenyl*iso*phosphindoline (III), and 2-phenyl*iso*arsindoline (IV) and their derivatives. The Table is noteworthy for the almost complete lack of regularity, but the fact that the amine is a solid of reasonably high m. p., whilst the phosphine and arsine are liquid, is particularly striking. Scholtz (*Ber.*, 1898, **31**, 414, 628) prepared the amine by the interaction of *o*-xylylene dibromide and aniline in ethanol or chloroform solution, but did not determine its molecular weight, which however we now find to be normal. To form the methiodide, the amine requires heating with methanolic methyl iodide at 100° for several hours: the phosphine and arsine however readily combine with methyl iodide.

	$C_{14}H_{13}N$	$C_{14}H_{13}P$ (III)	$C_{14}H_{13}As$ (IV)
"Base"	M. p. 170°	B. p. 110—112°/0·2 mm.	B. p. 136—138°/0·3 mm.
Methiodide	,, 177	M. p. 207—209°	M. p. 189—191°
Methopicrate	,, 140	,, 88—90	,, 122—123

We are now further investigating the above and other syntheses of the *iso*phosphindoline (III), and the reactions of such phosphines with the halides of palladium and of various other metals.

EXPERIMENTAL

2-*Phenyl*iso*phosphindoline* (III).—This preparation was performed in a flask fitted with a sealed stirrer, reflux condenser, and dropping-funnel, and through which nitrogen was passed throughout the experiment. A stirred solution of phenylmagnesium bromide, prepared by the action of bromobenzene (55·3 g., 2·2 mols.) on magnesium (8·94 g., 2·3 atoms) under ether (270 c.c.), was cooled in ice-water whilst phenylphosphine (17·6 g.) in benzene (100 c.c.) was added during 15 min. The mixture was boiled under reflux for 2·5 hr., then cooled again whilst *o*-xylylene dibromide (38·0 g., 0·9 mol.) in benzene (100 c.c.) was added during 30 min., much solid material meanwhile separating. The complete mixture was again boiled for 2·5 hr., cooled, and hydrolysed by the addition of ammonium chloride (17·5 g.) dissolved in air-free chilled water (200 c.c.). The aqueous layer was then siphoned off under reduced pressure.

The organic layer contained much suspended solid, which was collected, washed with benzene and water, and dried under nitrogen.

The combined organic extracts, when dried and evaporated, gave a syrupy amber residue (15 g.), which on distillation in nitrogen at 0·1 mm. gave the fractions: (*a*) b. p. 110—130° (mainly *o*-xylylene dibromide); (*b*) b. p. 130—185° [a mixture of the dibromide and the phosphine (III) identified as the methiodide, m. p. 202—204° (alone and mixed with authentic sample described below)]; and (*c*) b. p. 185—210° (a syrup which did not crystallise or form a crystalline derivative).

The above solid product when dried formed an ivory-coloured translucent glass (30 g.), soluble in ethanol but insoluble in water, benzene, or ether. A portion (25 g.) was powdered and then heated with a "brush" flame in a distillation apparatus in a stream of nitrogen at 0·3 mm. The powder at first decrepitated vigorously, then partly fused, and finally decomposed with darkening as the temperature approached a low red heat; meanwhile a mobile distillate (2·5 g.) collected, followed ultimately by a viscous syrup (*ca.* 1 g.). A considerable dark friable residue was formed.

The distillate on redistillation at 0·2 mm. gave the colourless fractions: (i) b. p. 80—110°, 0·7 g.; (ii) b. p. 110—112°, 0·3 g.; (iii) b. p. 112—130°, 0·4 g.; and an amber residue. Fraction (ii) was pure 2-*phenyl*iso*phosphindoline* (III) (Found: C, 79·4; H, 6·2. $C_{14}H_{13}P$ requires C, 79·2; H, 6·2%); fractions (i) and (iii) were crude samples pure enough for the preparation of certain derivatives.

It is noteworthy that in the above experiment using *o*-xylylene dibromide (0·9 mol.) a small proportion of this dibromide remained unchanged; when however 0·8 mol. of the dibromide was used, no unchanged dibromide could subsequently be detected, but the final reaction mixture contained some unchanged di-Grignard reagent, which evolved phenylphosphine during the hydrolysis.

The phosphine possesses a powerful odour resembling that of phenyldiethylphosphine: its ethanolic solution rapidly becomes turbid on exposure to air. The phosphine readily gave a *methiodide* (*i.e.*, *2-methyl-2-phenyl*iso*phosphindolinium iodide*), colourless crystals (from ethanol), m. p. 207—209° (decomp.) (Found: C, 50·8; H, 4·3. $C_{15}H_{16}IP$ requires C, 50·85; H, 4·55%): this gave a *methopicrate*, yellow crystals, m. p. 88—90°, from ethanol (Found: C, 55·65; H, 4·4; N, 9·5. $C_{21}H_{18}O_7N_3P$ requires C, 55·4; H, 4·0; N, 9·25%). The pure methiodide, when heated in nitrogen at 20 mm. decomposed above 250°, giving a dark residue and (in small yield) a viscous distillate consisting of the phosphine (III) and its hydriodide. This distillate when basified gave a mobile oil which, when extracted with ether and treated with methyl iodide, re-formed the above methiodide, m. p. 194—198° (decomp.) (alone and mixed) when once recrystallised from ethanol.

The addition of a small excess of the phosphine in ethanol to a warm aqueous solution of chloroauric acid deposited initially a yellow solid, which redissolved when the solution was boiled: heavy colourless crystals of *monochloro-(2-phenyl*iso*phosphindoline)gold* (XIV) then separated, m. p. 193° after recrystallisation from ethanol (Found: C, 38·0; H, 3·1%; *M*, ebullioscopic in 0·974% acetone solution, 441. $C_{14}H_{13}ClPAu$ requires C, 37·8; H, 2·95%; *M*, 445).

o-*Xylylene Dibromide and Phenyldichlorophosphine.*—Fine sodium wire (36·8 g., 8 atom-equivs.) was added to a solution of the dibromide (52·8 g.) and the chlorophosphine (35·8 g., 1 mol.) in ether (500 c.c.), which was then boiled under reflux in nitrogen for 11 hr., ethyl acetate (5, 2·5, 2·5 c.c.) being added after 0·5, 3, and 7 hours' boiling. The solution was then filtered through sintered glass under nitrogen pressure and evaporated and the residue distilled at 0·2 mm., giving the fractions: (*a*) b. p. 60—108° (2·5 g.), mainly unchanged dichlorophosphine; (*b*) b. p. 108—134° (2 g.), a colourless liquid; (*c*) b. p. 134—170° (3·5 g.), a pale amber oil; and (*d*) a dark residue (0·5 g.) which did not boil <360°/0·2 mm. and could not be crystallised.

Fraction (*b*) on redistillation gave several indefinite fractions, none of which gave a methiodide. Fraction (*c*), redistilled at 0·5 mm., gave the fractions: (i) b. p. <98° (0·2 g.); (ii) b. p. 98—102° (0·3 g.); (iii) b. p. 118—124° (0·2 g.); (iv) b. p. 130—150° (0·3 g.). Fraction (iii) consisted of the crude phosphindoline (III) (yield, 0·5%), for it readily gave the methiodide, which, once recrystallised from ethanol, had m. p. 190—195° (decomp.), mixed m. p. 200—205° (decomp.).

The solid material in the original ethereal mixture consisted almost entirely of unchanged sodium and its chloride and bromide.

o-*Xylylene Dibromide and Tertiary Phosphines.*—(*a*) A benzene solution of the dibromide and of phenyldimethylphosphine (1 mol.) was boiled under reflux for 2 hr., and the benzene then evaporated under reduced pressure. The glassy residue did not recrystallise. A portion was extracted with cold water, and the extract, after filtration to remove residual unchanged dibromide, was treated with aqueous sodium picrate. The precipitated o-*xylylenebis(phenyldimethylphosphonium) dipicrate* (VI; R = Ph, R′ = Me, X = $C_6H_2O_7N_3$), when thoroughly washed with water and recrystallised from ethanol containing a trace of acetone, formed yellow crystals, m. p. 180·5—181·5° (Found: C, 52·1; H, 3·85; N, 10·1. $C_{36}H_{34}O_{14}N_6P_2$ requires C, 51·7; H, 4·1; N, 10·1%). The original residue, obtained in several such experiments, was heated under various conditions, without evidence of cyclisation: at 260—280°/0·3 mm. and also at 320—360°/0·3 mm., the main component of the distillate was unchanged dibromide, and an aqueous extract of the very dark residue again gave the above dipicrate. Replacement of benzene by chloroform in the initial reaction gave the same results.

(*b*) The condensation was repeated, using however phenyldiethylphosphine, in benzene and in chloroform. A portion of the glassy residue, treated as before, gave o-*xylylenebis(phenyldiethylphosphonium) dipicrate* (VI; R = Ph, R′ = Et, X = $C_6H_2O_7N_3$), yellow crystals, m. p. 159—160°, from acetone–ethanol (Found: C, 53·9; H, 4·4; N, 9·3. $C_{40}H_{42}O_{14}N_6P_2$ requires C, 53·8; H, 4·75; N, 9·4%). The residue, when heated at 340°/0·5 mm., gave a small distillate of phenyldiethylphosphine, identified by conversion into *dibromobis(phenyldiethylphosphine)-palladium*, yellow crystals, m. p. 135° (from ethanol) (Found: C, 40·3; H, 4·95. $C_{20}H_{30}Br_2P_2Pd$ requires C, 40·1; H, 5·1%).

Partheil and Gronover (*Ber.*, 1900, **33**, 606) using triethylphosphine (2 mols.) obtained the dibromide (VI; R = R′ = Et, X = Br), m. p. 250—250·5°; its behaviour on heating was not examined.

o-*Methoxymethylbenzyldiphenylphosphine* (XI).—A solution of diphenylphosphine (3·5 g.) in ether (20 c.c.) was added with stirring to one of sodium (0·5 g., 1 atom-equiv.) in liquid ammonia (70 c.c.), the deep blue colour of which changed to deep brown. A solution of *o*-methoxymethylbenzyl chloride (IX) (3·5 g., 1 mol.) in ether (10 c.c.) was then slowly added, the solution becoming orange and depositing a white solid. The ammonia was allowed to evaporate spontaneously and the residual ethereal solution was boiled under reflux in nitrogen for 2 hr. The cooled, filtered solution on distillation gave a colourless unidentified fraction, b. p. *ca.* 100°/0·15 mm., and then the phosphine (XI), b. p. 180—196°/0·15 mm., as an extremely viscous greenish oil (1·6 g., 30%), which was not further purified (Found : 76·5; H, 6·5. Calc. for $C_{21}H_{21}OP$: C, 78·7; H, 6·5%). It was characterised as its *methiodide*, colourless crystals, m. p. 130—131°, from methanolic ether (Found : C, 56·8; H, 5·3. $C_{22}H_{24}OIP$ requires C, 57·1; H, 5·3%).

2 : 2-*Diphenyl*iso*phosphindolinium Bromide* (XII).—A solution of the phosphine (XI) (1·6 g.) in acetic acid (70 c.c.) diluted with hydrobromic acid of constant b. p. (70 c.c.) was boiled under reflux for 2·5 hr. whilst hydrogen bromide was passed through. The solvents were then removed in a vacuum, giving a glassy residue of the crude bromide (XII). This was extracted with cold water (leaving a liquid constituent of pleasant odour), and the filtered extract again evaporated. The bromide was obtained as a semicrystalline highly hygroscopic residue which could not be readily purified. A portion, treated with sodium picrate, each in aqueous solution, deposited the *picrate* (as XII), beautiful lemon-yellow needles, m. p. 180—181°, from ethyl acetate (Found: C, 60·1; H, 4·1; N, 8·2. $C_{26}H_{20}O_7N_3P$ requires C, 60·3; H, 3·8; N, 8·1%

Diethyl-o-*methoxymethylbenzylphenylphosphonium Salts* (XIII).—A mixture of the chloride (IX) (2·5 g.) and phenyldiethylphosphine (2·3 g., 1 mol.) was gently warmed under nitrogen at atmospheric pressure; a vigorous reaction occurred, giving on cooling a thick almost solid syrup. This was the crude phosphonium chloride (XIII; X = Cl), for it was freely soluble in water and when treated with aqueous potassium iodide gave the *iodide* (XIII; X = I), colourless crystals, m. p. 113—114°, from ethanol–ether (Found: C, 53·0; H, 6·0. $C_{19}H_{26}OIP$ requires C, 53·2; H, 6·0%).

This iodide was also prepared by the interaction of *o*-methoxymethylbenzyl iodide (cf. p. 2820) with phenyldiethylphosphine (1 mol.) in acetone; addition of ether precipitated the iodide, m. p. 113—114° (alone and mixed) when crystallised as before.

The crude chloride, when heated in a vacuum under nitrogen ultimately to *ca.* 350°, underwent much charring whilst yielding a semicrystalline distillate, which when basified and extracted with benzene gave on distillation a main fraction of phenyldiethylphosphine, b. p. 104—106°/17 mm., and then a very small fraction, b. p. 170—180°/16 mm., a yellow oil which did not combine with methyl iodide and was apparently not a phosphine.

Palladium Derivatives of the Phosphine (III).—(A) *Monochlorobis*-(2-*phenyl*iso*phosphindoline*)*palladium*. A hot concentrated aqueous solution of potassium palladochloride was added to an excess of a hot ethanolic solution of the phosphine (III) and the mixture then gently boiled. The clear solution thus obtained was cautiously diluted with water and allowed to cool, pale yellow crystals separating. These were recrystallised from aqueous ethanol, and the solution on slow cooling deposited fine colourless crystals of the *monochloro*-derivative, m. p. 177—178° (Found : C, 59·35; H, 4·9; Pd, 18·0%; *M*, ebullioscopic in 0·481% ethanolic solution, 3310; in 1·595% acetone solution, 3410. $C_{28}H_{26}ClP_2Pd$ requires C, 59·35; H, 4·65; Pd, 18·0%; *M*, 566·4). The material used in each of the molecular-weight determinations was subsequently recovered unchanged.

When this material was again recrystallised from aqueous ethanol, the solution being however rapidly cooled and scratched, the *monochloro*-derivative separated as colourless crystals, m.p. 129—131° (Found : C, 59·3; H, 5·0%).

Dr. French reports : " The quantity of substance available (40 mg.) was insufficient to measure by the normal Gouy method, but a Faraday-type method was improvised and measurements were made in this way. These measurements indicated that the substance had a very small diamagnetic susceptibility of the order of $-0·1 \times 10^{-6}$. However, on account of the comparative insensitivity of the method, the possibility of a very feeble paramagnetism could not unfortunately be entirely dismissed. Nevertheless, a compound of molecular weight approximately 500 with one unpaired electron would be expected to show a paramagnetic susceptibility of the order of 2×10^{-6}, and this possibility can, I think, be ruled out. Our general conclusion is that the substance is diamagnetic, the very low susceptibility being due to either (1) the presence of very small traces of a ferromagnetic impurity, or (2) a temperature-independent paramagnetism such as occurs in $KMnO_4$."

An acetone solution of a crude unrecrystallised sample of the monochloro-compound was gently evaporated during 2 hr., the process being twice interrupted for cooling and collection of a crop of the monochloro-compound; the final clear orange solution, when set aside, slowly deposited brilliant yellow crystals of *dichlorobis-(2-phenyl*iso*phosphindoline)palladium*, m. p. 256—260° (decomp.) (Found : C, 56·0; H, 4·8. $C_{28}H_{26}Cl_2P_2Pd$ requires C, 55·85; H, 4·4%), which then appeared to be almost completely insoluble in boiling ethanol and acetone. The precise conditions determining the formation of this compound are at present unknown. It does not arise by the decomposition of the monochloro-compound, for an acetone solution of a pure sample of the latter was similarly boiled for 4 hr., and when evaporated to dryness yielded a residue of unchanged material, m. p. 176—178°. The dichloro-compound appears to be reasonably soluble in the initial crude aqueous-ethanolic solution, but, when once crystallised in the pure condition, to be almost insoluble in the usual organic solvents.

Similarly, another crude unrecrystallised sample of the monochloro-compound, when treated in dilute aqueous-ethanolic solution with aqueous potassium iodide, deposited *diiodobis(2-phenyl*iso*phosphindoline)palladium*, deep crimson crystals, m. p. 246—248° after washing with boiling water and ethanol (Found : C, 43·3; H, 3·55. $C_{28}H_{26}I_2P_2Pd$ requires C, 42·8; H, 3·35%).

(B) *Monobromobis-(2-phenyl*iso*phosphindoline)palladium*. This was prepared as the monochloro-compound but with potassium palladobromide; dilution and cooling of the clear solution deposited scarlet crystals of the *monobromo*-compound, m. p. 196—198° (decomp.) after recrystallisation from aqueous ethanol (Found : C, 54·9; H, 4·5; Pd, 17·2. $C_{28}H_{26}BrP_2Pd$ requires C, 55·0; H, 4·3; Pd, 17·45%).

*Dibromobis-(2-phenyl*iso*arsindoline)palladium*.—This *compound*, prepared in the usual way by heating an aqueous-ethanolic solution of potassium palladobromide and the arsine (2 mols.), formed orange-yellow crystals, m. p. 248—249° (decomp.) from acetone (Found : C, 43·4; H, 3·1. $C_{28}H_{26}Br_2As_2Pd$ requires C, 43·2; H, 3·4%).

Dibenzylphenylphosphine.—This preparation was performed under pure nitrogen throughout. A solution of benzylmagnesium chloride was prepared by the addition of benzyl chloride (50·4 g., 4 mols.) during 2 hr. to magnesium (10·2 g., 4·2 atom-equivs.) under ether (200 c.c.), the mixture being then stirred for a further 2 hr. It was then cooled in ice-water and vigorously stirred whilst a solution of phenyldichlorophosphine (17·9 g., 1 mol.) in benzene (100 c.c.) was added during 30 min., a vigorous reaction ensuing. The mixture was heated under reflux for 30 min., cooled, and hydrolysed with aqueous ammonium chloride, the organic layer then syphoned off and dried (Na_2SO_4) and the solvent removed, the residual dibenzylphenylphosphine readily crystallising on cooling.

Distillation under nitrogen gave the pure *phosphine* (24 g., 83%), b. p. 176—177°/0·3 mm., m. p. 71—72° (Found : C, 82·2; H, 6·4. $C_{20}H_{19}P$ requires C, 82·7; H, 6·6%). The m. p. was not increased by redistillation, sublimation, or recrystallisation from ethanol or benzene under nitrogen.

Even a cold ethanolic solution on exposure to the air rapidly deposited the oxide, m. p. 174° (Found : C, 78·3; H, 6·2. Calc. for $C_{20}H_{19}OP$: C, 78·4; H, 6·25%) : the infra-red absorption spectrum shows a band at 8·45 μ, confirming the P–O linkage.

The phosphine was further characterised by formation of the methiodide, m. p. 206—208° after crystallisation from ethanol. Meisenheimer *et al.* (*loc. cit.*) give m. p. 208°.

The phosphine under the usual conditions gives *dichlorobis(dibenzylphenylphosphine)-palladium*, yellow crystals, m. p. 230—231° (decomp.) (Found : C, 63·2; H, 5·3. $C_{40}H_{38}Cl_2P_2Pd$ requires C, 63·35; H, 5·1%), and the *dibromo*-analogue, pale yellow crystals, m. p. 240—242° (decomp.) (Found : C, 56·4; H, 4·2. $C_{40}H_{38}Br_2P_2Pd$ requires C, 56·7; H, 4·5%).

*2-Phenyl*iso*indoline Methopicrate*.—The *iso*indoline was converted into the methiodide, m. p. 177° (Scholtz and Wolfrum, *Ber.*, 1910, **43**, 2304), which in turn gave the *methopicrate*, yellow crystals, m. p. 140—141°, from water (Found : N, 13·0. $C_{21}H_{18}O_7N_4$ requires N, 12·8%).

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