XV.—*On Benzyl Phosphines and their Derivatives.* By Professor LETTS and R. F. BLAKE, Esq., Queen's College, Belfast. (With a Plate.)

(Read 20th May 1889.)

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PART I.—BENZYL PHOSPHINES.

INTRODUCTION.

The phosphines which have been obtained as yet are not very numerous, and with one or two exceptions their properties have not been exhaustively studied, a fact which is no doubt largely due to the difficulties encountered in preparing them in any quantity.

There are consequently a great many points in their history which require examination, and the object we had in view in the present investigation was chiefly to extend our knowledge of this interesting group of substances.

It may not be inadvisable, before describing the results of our experiments, to give a brief summary of the work done already by others.

We discuss the methods for obtaining phosphines in another part of this paper (p. 589), so that for the present we shall content ourselves with their properties and reactions.

General Properties of the Primary Phosphines.

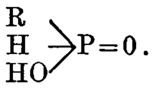
The following primary bases have been obtained :—

Name.	Condition.	Boiling Point.
Methyl phosphine (1), ...	Gas.	− 14
Ethyl " (2), ...	Liquid.	+ 25
Iso-propyl " (3), ...	"	+ 41
Iso-butyl " (4), ...	"	+ 62
Iso-amyl " (5), ...	"	+106
Octyl (normal) (6), ...	"	+184–187
Phenyl " (7), ...	"	+160–161
Benzyl " (8), ...	"	+180
p. Tolyl " (9), ...	Solid at + 4.	+178

(1) HOFMANN, *Berichte*, iv. (1871) p. 209.
(2) HOFMANN, *Berichte*, iv. (1871) p. 432.
(3) *Ibid.* *Ibid.* vi. (1873) p. 292.
(4) *Ibid.* *Ibid.* vi. (1873) p. 296.
(5) *Ibid.* *Ibid.* vi. (1873) p. 297.
(6) MOSLINGER, *Ibid.* ix. (1876) p. 1005.
(7) MICHAELIS, *Ibid.* vii. (1874) p. 6 and p. 1688.
(8) HOFMANN, *Ibid.* v. (1872) p. 100.
(9) MICHAELIS and PANEK, *Annalen*, 212, p. 233.

With the exception of methyl phosphine, which is a gas, and p. tolyl phosphine, which is a solid, the primary bases are liquids at ordinary temperatures, insoluble in water, but soluble in ether, &c. Exposed to the air they fume powerfully and grow very hot, their vapour igniting spontaneously at times. The products of this oxidation appear to have been investigated only in a few cases, and chiefly in the aromatic series.

Phenyl phosphine[*] and tolyl phosphine[†] both absorb a molecule of oxygen, and are converted into phosphinous acids, which are monobasic, and therefore probably have the constitution,



$$\left.\begin{matrix}R\\H\\HO\end{matrix}\right\rangle P=O.$$

These acids are readily decomposed by heat, giving the primary phosphine, and the corresponding phosphinic acid,

$$3RPH_2O_2=RPH_2+2RPH_2O_3,$$

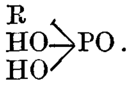
a reaction analogous to that which gives rise to phosphuretted hydrogen and phosphoric acid when hypophosphorous and phosphorous acids are heated.

MOSLINGER (*loc. cit.*) has in part investigated the products of the spontaneous oxidation of octyl phosphine, and believes that it also is converted into a phosphinous acid.

Submitted to the action of strong nitric acid, many of the primary phosphines (and probably all) absorb three atoms of oxygen, and are converted into phosphinic acids. This has been shown by HOFMANN[‡] to be the case in the methyl, ethyl, iso-propyl, iso-butyl, and iso-amyl series. The phosphinic acids are solid substances, which with the lower members of the fatty series can be distilled unchanged.[§] But in some other instances a different reaction occurs: thus phenyl phosphinic[||] acid, when heated slowly to 200° C., gives a pyro acid, while when rapidly heated to 250° C. it decomposes into benzol and meta-phosphoric acid,

$$C_6H_5PH_2O_3=C_6H_6+HPO_3.$$

The phosphinic acids are all dibasic, and no doubt have the structure—



$$\left.\begin{matrix}R\\HO\\HO\end{matrix}\right\rangle PO.$$

All the primary phosphines have distinct alkaline properties. They combine readily with hydracids, forming crystalline compounds which can as a rule be volatilised (with dissociation more or less complete), and which resemble the compounds of phosphuretted hydrogen in other respects, particularly in being instantly decomposed by water with liberation of the phosphine. The hydrochlorates combine with chloride of platinum to give chloroplatinates. The salts of the primary bases with oxyacids have been scarcely at all investigated.

The action of halogens on mono-phosphines has not been sufficiently investigated. Methyl and ethyl phosphine take fire when they come in contact with chlorine or bromine,[¶] but in other cases the action does not appear to have been studied.

[*] MICHAELIS, *Berichte*, x. (1877) p. 807.

[†] MICHAELIS and PANEK, *Annalen*, 212, p. 234.

[‡] HOFMANN, *Berichte*, v. (1873) p. 110.

[§] HOFMANN, *Berichte*, vi. (1873) p. 303.

[||] MICHAELIS, *Berichte*, vii. (1874) p. 1070.

[¶] HOFMANN, *Berichte*, iv. (1871) pp. 433 and 609.

Sulphur acts on the primary bases. With the methyl and ethyl derivatives, compounds have been obtained but not investigated.* With phenyl phosphine sulphur acts slowly in the cold, rapidly at a high temperature.† Two substances are produced, one, a thick liquid soluble in ether, having the composition $(C_6H_5)PH_2S$, the other a crystalline product to which MICHAELIS assigns the formula $(C_6H_5P)_3S$. The first of these bodies decomposes when heated in the following manner :—

$$2C_6H_5PH_2S = C_6H_5PS + C_6H_5PH_2 + H_2S\,.$$

In view of the analogies existing between nitrogen and phosphorus, considerable interest is attached to the action of carbonyl chloride and bisulphide of carbon on the primary phosphines. Bisulphide of carbon acts upon both methyl and ethyl phosphine,‡ but the products have not been investigated. MICHAELIS and DITTLER § have studied the action of both reagents on phenyl phosphine. When carbonyl chloride is passed slowly into that substance, an energetic reaction occurs in the following manner :—

$$2COCl_2 + C_6H_5PH_2 = C_6H_5PCl_2 + 2CO + 2HCl\,.$$

Phenyl phosphine and bisulphide of carbon act upon each other when heated in a sealed tube at 150°, and sulphuretted hydrogen is liberated. The product of the reaction is a resinous body $(C_6H_5PHCS)_2S$, and the reaction itself proceeds according to the equation,

$$2C_6H_5PH_2 + 2CS_2 = (C_6H_5PHCS)_2S + H_2S\,.$$

MICHAELIS and DITTLER were not successful in their attempts to prepare a phosphorised mustard oil from this compound.

They were equally unsuccessful in obtaining a phosphorised carbylamine by the action of chloroform and caustic potash on phenyl phosphine. It is true that a reaction occurs, but its course is completely different from that which takes place with an amine, viz.,

$$C_6H_5PH_2 + 4KHO + CHCl_3 = C_6H_5PHKO_2 + 3KCl + CH_3OH + H_2O.$$

It thus appears that, in their behaviour with carbonyl chloride and a mixture of caustic potash and chloroform, primary phosphines behave in an entirely different manner from the corresponding amines, though there is a certain degree of analogy as regards the action of both on bisulphide of carbon. This difference is no doubt due to the strong affinity of phosphorus for electronegative elements, such as the halogens, oxygen, and sulphur.

Primary phosphines readily combine with alkyl iodides to give hydriodates of secondary phosphines.

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* HOFMANN, *Berichte*, iv. (1871) pp. 433 and 610.

† MICHAELIS, *Berichte*, x. (1877) p. 810.

‡ HOFMANN, *Berichte*, iv. (1871) pp. 433 and 610.

§ MICHAELIS and DITTLER, *Berichte*, xii. (1879) p. 338.

General Properties of the Secondary Phosphines.

The following secondary phosphines have been obtained :—

Name.	Condition.	Boiling Point.
Dimethyl phosphine (1), ...	Liquid.	25
Di-ethyl „ (2), ...	„	85
Di-isopropyl „ (3), ...	„	118
Di-isobutyl „ (4,)	„	153
Di-isoamyl „ (5), ...	„	210–215
Di-phenyl „ (6), ...	„	280 (about)
Methyl-isopropyl „ (7), ...	„	78–80
Iso-propyl, isobutyl „ (8), ...	„	139–140
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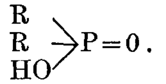
(1) HOFMANN, *Berichte*, iv. (1871) p. 610.
(2) HOFMANN, *Berichte*, iv. (1871) p. 433.
(3) *Ibid.* *Ibid.* vi. (1873) p. 294.
(4) *Ibid.* *Ibid.* vi. (1873) p. 296.
(5) *Ibid.* *Ibid.* vi. „ p. 298.
(6) MICHAELIS, *Ibid.* xv. (1882) p. 801A.
(7) *Ibid.* *Ibid.* vi. „ p. 295.
(8) HOFMANN, *Ibid.* vi. (1873) p. 300.

* Dibenzyl phosphine is not mentioned, for reasons which will become apparent in the body of the paper.

All the secondary phosphines obtained as yet are liquids, having a powerful odour. They are insoluble in water, but soluble in ether, &c.

They have as a rule a strong attraction for oxygen, fuming and growing hot on exposure to the air, and often inflaming spontaneously. In some cases they appear to have even a greater affinity for oxygen than the primary bases. This is so according to HOFMANN with all the secondary phosphines of the fatty series which he obtained. But apparently it is not the case with diphenyl phosphine. The products of this spontaneous oxidation do not appear to have been examined. But the products of their oxidation by nitric acid have been investigated, chiefly by HOFMANN.* They are in all cases phosphinic acids, R_2PHO_2, which are monobasic, and no doubt have the constitution,



$$\left.\begin{matrix}R\\R\\HO\end{matrix}\right\rangle P=O.$$

These acids are probably also produced when the chlorides R_2PCl are oxidised by nitric acid. Such is at least the case with $(C_6H_5)_2PCl$. Some of them can be distilled unchanged, *e.g.*, dimethyl phosphinic acid; others, *e.g.*, diphenyl phosphinic acid, lose water, and give pyro acids.

Secondary phosphines combine with acids, the resulting salts being far more stable than those of the primary bases. Thus in most cases they are not decomposed by water, though some are (*e.g.*, salts of diphenyl phosphine). Comparatively little is known regarding secondary phosphines, and very few of their compounds have been investigated.

Both sulphur and bisulphide of carbon act upon them, but the products have not

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* HOFMANN, *Berichte*, v. (1872) p. 104, and vi. (1873) p. 303.

been investigated. They readily combine with alkyl iodides, giving hydriodates of tertiary phosphines.

General Properties of Tertiary Phosphines.

The following tertiary bases have been obtained:—

Name.	Condition.	Boiling Point.
Trimethyl phosphine (1), . .	Liquid.	40–42
Tri-ethyl „ (2), . .	„	127
Tri-isopropyl „ (3), . .	„	?
Tri-isobutyl „ (4), . .	„	215
Tri-isoamyl „ (5), . .	„	about 300
Tri-phenyl „ (6), . .	Solid.	above 360
Ethyl-isopropyl-isobutyl „ (7), . .	Liquid.	about 190
Methyl-diphenyl „ (8), . .	„	284
Ethyl-diphenyl „ (9), . .	„	293
Di-ethyl-phenyl „ (10), . .	„	220
Di-methyl-ethyl „ (11), . .	„	83–85
Di-ethyl-methyl „ (12), . .	„	110–112
Di-ethyl-propyl „ (13), . .	„	146–149
Di-ethyl-isoamyl „ (14), . .	„	185–187
Di-ethyl-benzyl „ (15), . .	„	252–255
Ethyl-dibenzyl „ (16), . .	„	320–330
Dimethyl p. tolyl „ (17), . .	„	210
Di-ethyl p. tolyl „ (18), . .	„	240
Dimethyl xylyl „ (19), . .	„	230
Diethyl xylyl „ (20), . .	„	260

(1), (2) Hofmann and Cahours, *Ann. de Chim. und de Phys.*, 3, vol. li. p. 35.

(3), (4), (5) Hofmann, *Berichte*, vi. (1873) pp. 292 and 304.

(6) Michaelis, *Berichte*, xv. (1882) p. 801a.

(7) Hofmann, *Berichte*, vi. (1873) p. 304.

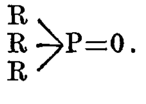
(8) *Ibid. Annalen*, 181, p. 345.

(9), (10) Michaelis and Link, *Annalen*, 107, p. 210.

(11), (12), (13), (14), (15), (16) Collie, *Chem. Soc. Jour.*, 1888, p. 714.

(17), (18), (19), (20) Czimatis, *Berichte*, xv. (1882) 2014.

The tertiary phosphines hitherto obtained are, with the exception of triphenyl phosphine, liquids at ordinary temperatures, having a powerful odour. They are insoluble in water, but soluble in ether, &c. As a rule, they oxidise rapidly in contact with the air, fuming and growing hot, and in some cases igniting spontaneously. The product of this oxidation is a tertiary phosphine oxide of the formula R_3PO, and no doubt of the constitution



$$\left.\begin{matrix}R\\R\\R\end{matrix}\right\rangle P{=}O.$$

The final products of the oxidation of phosphuretted hydrogen, and of primary, secondary, and tertiary phosphines are therefore respectively—

$$\begin{matrix}H_3PO_4\\RH_2PO_3\\R_2HPO_2\\R_3PO.\end{matrix}$$

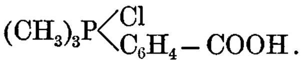
The amount of oxygen absorbed by the phosphine decreasing in a regular manner as the series is ascended.

The oxides of tertiary phosphines are solid substances of remarkable stability. They can in the majority of cases be distilled, and even boiled with nitric acid without change. By no means as yet discovered can they be reduced. Hydracids combine with them, and they give crystalline compounds, with a number of metallic salts, such as the chlorides of platinum, zinc, mercury, iron, cobalt, &c., also in some cases with chloride of acetyl, bromine, and sulphur.

Tertiary phosphines also combine with the elements of the sulphur group, forming compounds analogous to the oxides.

The salts of tertiary phosphines are readily obtained by dissolving the bases in acids. They are stable, and are not, as a rule, decomposed by water. Their compounds with hydracids have been chiefly studied; those containing oxyacids have not been investigated (with very few exceptions). The haloid salts dissociate to a greater or less extent on heating. Their hydrochlorates combine with chloride of platinum to give chloroplatinates of normal composition.

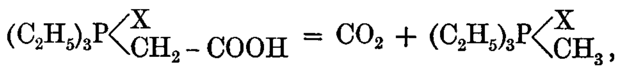
Some of the tertiary phosphines combine with chloracetic acid to give hydrochlorates of phosphorised betaines. At present only two or three of these substances have been obtained—tri-methyl phosphorus betaine by MEYER,* the corresponding ethyl derivative by HOFMANN,† and in addition to these two the closely allied compound, tri-methyl phosphorus benzo-betaine hydrochlorate, by MICHAELIS and CZIMATIS,‡



$$(CH_3)_3P\Big<\begin{matrix}Cl\\C_6H_4-COOH\end{matrix}.$$

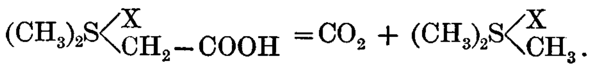
The compounds of these phosphorised betaines are stable and well-defined substances. One of us § has investigated the reactions and decompositions of the ethylated body, which are of some interest.

The hydrate and the salts of this betaine lose carbonic anhydride when heated, and give rise to the hydrate or salt of methyl-tri-ethyl-phosphonium,



$$(C_2H_5)_3P\Big<\begin{matrix}X\\CH_2-COOH\end{matrix} = CO_2 + (C_2H_5)_3P\Big<\begin{matrix}X\\CH_3\end{matrix},$$

a reaction which is entirely analogous to that occurring when the corresponding sulphur compounds (*thetines*) are heated,



$$(CH_3)_2S\Big<\begin{matrix}X\\CH_2-COOH\end{matrix} = CO_2 + (CH_3)_2S\Big<\begin{matrix}X\\CH_3\end{matrix}.$$

While it is perfectly different from that which the true (nitrogen) betaines experience, as they either dissociate into the original trialkyl-amine and the group $X-CH_2$—COOH (or the products of its decomposition), or distil unchanged.‖

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* MEYER, *Berichte*, iv. (1871) p. 734.

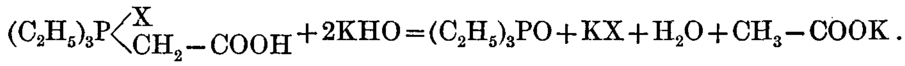
† HOFMANN, *Proc. Roy. Soc.*, xi. p. 530.

‡ MICHAELIS and CZIMATIS, *Berichte*, xv. (1882) p. 2018.

§ LETTS, these *Transactions*, xxx. part 1, p. 285.

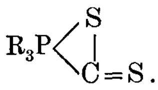
‖ BRÜHL, *Annalen*, 177, p. 214.

Treated with caustic potash, all the salts of tri-ethyl phosphorus betaine yield tri-ethyl phosphine oxide,



$$(C_2H_5)_3P{<}^{X}_{CH_2-COOH} + 2KHO = (C_2H_5)_3PO + KX + H_2O + CH_3-COOK .$$

Several of the tertiary phosphines combine directly and energetically with a molecule of bisulphide of carbon to give highly characteristic compounds, usually of a red colour, and possibly having the constitution,



So characteristic and so readily formed is this compound in the case of tri-ethyl phosphine, that its production may be employed as a test either for bisulphide of carbon or for the phosphine itself. As yet these (bisulphide) compounds have been obtained only with methyl, ethyl, and iso-propyl phosphine, and with those of the aromatic phosphines containing ethyl or methyl groups.

According to CZIMATIS,[*] these mixed phosphines combine very easily with bisulphide of carbon if they contain methyl, the readiness with which combination occurs diminishing however, in proportion to the molecular weight of the aromatic radical, while, if they contain ethyl, combination occurs only slowly and with difficulty. HOFMANN[†] has somewhat exhaustively studied the compound of tri-ethyl phosphine and the bisulphide, which forms with explosive violence. Among its properties are the following:—It is insoluble in water, difficultly soluble in ether, but easily dissolves in hot alcohol, from which it separates on cooling in red needles like chromic anhydride. From an ethereal solution it is deposited by spontaneous evaporation in large deep red monoclinic crystals exhibiting dichroism, which melt at 95° and volatilise at 100°. It is soluble in strong hydrochloric acid, and if the solution is mixed with platinic chloride, a yellow amorphous compound is produced, $2(C_2H_5)_3PCS_2,PtCl_4$. With silver oxide or nitrate, it is decomposed as follows:—

$$(C_2H_5)_3PCS_2 + 2Ag_2O = Ag_2S + Ag_2 + CO_2 + (C_2H_5)_3PS ,$$

and moist air produces a similar change. But if it is heated with water to 100° C., the following reaction occurs:—

$$4(C_2H_5)_3PCS_2 + 2H_2O = 2(C_2H_5)_3PS + (C_2H_5)_3PO + (C_2H_5)_3(CH_3)POH + 3CS_2 .$$

Heated with sulphuretted hydrogen, it suffers the following change—

$$3(C_2H_5)_3PCS_2 + H_2S = 2(C_2H_5)_3PS + (CH_2S)(C_2H_5)_3PCS_2 + CS_2 .$$

The action of halogens upon tertiary phosphines has not been very fully studied. Probably direct addition would occur in all cases. This has been proved to take place with tri-ethyl phosphine if the halogen is allowed to act very gradually upon it. The chloride $(C_2H_5)_3PCl_2$ thus obtained is crystalline, melting at 100° and volatilising readily,

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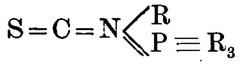
[*] CZIMATIS *Berichte*, xv. (1882) p. 2016

[†] HOFMANN, *Phil. Trans.*, 1860, p. 431.

though its boiling point is high. Similar compounds of bromine and iodine have been obtained.

Compounds of tri-methyl and tri-ethyl phosphine with mustard oils, are formed easily, and give crystalline hydrochlorates. They no doubt have the constitution,



$$S=C=N\begin{cases}R\\ P\equiv R_3\end{cases}$$

[*Note.*—Some of the aromatic tertiary phosphines, especially tri-phenyl phosphine, have properties which differ materially from those of other tertiary phosphines. Thus tri-phenyl phosphine is a crystalline solid having scarcely any odour, and it does not oxidise spontaneously. It is remarkably stable, and is not attacked by chlorine even when heated. The hydriodate and hydrochlorate are formed when it is dissolved in the warm concentrated hydracids, and are crystalline, but on adding water they dissociate. By treating the phosphine with bromine and an alkali, or by oxidising it with hydrochloric acid and chlorate of potash, the hydrate $(C_6H_5)_3P(OH)_2$ is obtained as a crystalline solid. This when heated to 100° readily loses water, and is converted into the oxide, a substance which is not acted upon by bromine, oxygen, sulphur, &c. By dissolving the phosphine in fuming nitric acid a nitrate of the formula $(C_6H_5)_3P(NO_3)_2$ is obtained.]

Tertiary phosphines, apparently without exception, unite with alkyl iodides to form phosphonium salts.

General Properties of Quaternary Compounds (Phosphonium Salts).

So many of these bodies have been obtained that a list appears inadvisable. It would include derivatives of the series C_nH_{2n+1} to the 5th term, one or two of the series C_nH_{2n-7}, and a large number of mixed phosphoniums containing various radicals, among which are vinyl, allyl, and ethylene.

The phosphonium salts are the most stable of all organic phosphorus compounds. None are decomposed by water, and most of them can be obtained readily in the crystalline state by evaporating their solutions.

As a rule, they are soluble in water and in alcohol. They are readily prepared from their iodides, either by double decomposition with a silver salt, or by first obtaining their hydrates (by the action of hydrate of silver), and subsequently neutralising the solution with the acid.

The hydrates R_4POH are solid substances, having a powerful alkaline reaction and many properties similar to those of an alkali. Indeed, in the case of tetrethyl phosphonium hydrate, the only remarkable point of difference between it and caustic potash (so far as its reactions with metallic salts, &c., are concerned) is that when added to a zinc or aluminum salt, the zinc or aluminum hydrate, which is at first precipitated, is insoluble in an excess. Phosphonium hydrates are decomposed when heated, and in some cases, when their solutions are boiled or at the moment of production, into a tertiary phosphine oxide and a hydro-carbon,

$$R_4POH=R_3PO+R-H.$$

The action of heat upon the salts of the phosphoniums has been investigated in a number of cases, partly by one of us* and N. Collie, and partly by the latter chemist alone.

As regards the haloid salts, the chlorides decompose almost quantitatively into a hydrocarbon and a tertiary phosphine hydrochlorate (Collie), furnishing an excellent method for "retrograding" from quaternary to tertiary bodies.

"When the phosphonium chloride contains several ethyl groups, then if more than one of the latter is present, ethylene is always formed, e.g.,

$$(C_2H_5)_3(C_7H_7)PCl = (C_2H_5)_2(C_7H_7)P.HCl + C_2H_4.$$

But when only one ethyl group is present, then, although ethylene is still formed, two decompositions occur, e.g.,

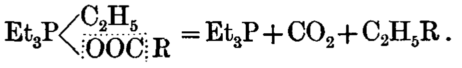
$$\begin{array}{ll} (1) & 2(C_2H_5)(CH_3)_3PCl = 2(C_2H_5)(CH_3)_2P.HCl + C_2H_4 \\ (2) & (C_2H_5)(CH_3)_3PCl = (CH_3)_3P.HCl \quad + \quad C_2H_4. \end{array}$$

If we compare the decomposition by heat of phosphonium chlorides with the decomposition of any of the compound ammonium salts, it must be with the hydroxides and not wth the corresponding chlorides" (Collie),† e.g.,

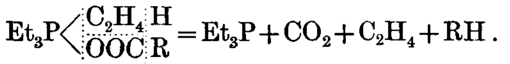
$$\begin{array}{l} (C_2H_5)_4PCl \quad = (C_2H_5)_3P.HCl + C_2H_4 \\ (C_2H_5)_4NOH = (C_2H_5)_3N \ + \ C_2H_4 + H_2O \end{array}$$

$$\begin{array}{l} (C_2H_5)_3(C_7H_7)P(OH) = (C_2H_5)_3PO + C_7H_8 \\ (C_2H_5)_3(CH_3)NCl \quad = (C_2H_5)_3N \ + CH_3Cl. \end{array}$$

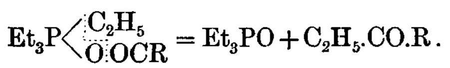
The effect of heat on phosphonium salts derived from oxy-acids is completely different. In the case of the ethyl series at all events, they suffer, as a rule, at least two and occasionally three different and distinct decompositions. In one of these the molecule splits up into three new groups, consisting respectively of carbonic anhydride, a (paraffin) hydrocarbon, and the tertiary phosphine. In the other, two hydrocarbons are formed, namely, an olefine and a paraffin, in addition to carbonic anhydride and the tertiary phosphine. Whilst in the third, a totally different change occurs, in which only two products are formed, namely, the oxide of the tertiary phosphine and a ketone,

(1) 

$$Et_3P\left\langle\begin{array}{l} C_2H_5 \\ OOC\,R \end{array}\right. = Et_3P + CO_2 + C_2H_5R.$$

(2) 

$$Et_3P\left\langle\begin{array}{l} C_2H_4\,H \\ OOC\,R \end{array}\right. = Et_3P + CO_2 + C_2H_4 + RH.$$

(3) 

$$Et_3P\left\langle\begin{array}{l} C_2H_5 \\ O\,OCR \end{array}\right. = Et_3PO + C_2H_5.CO.R.$$

It is possible, if not indeed probable, that the third reaction occurs subsequently to the first, and that it really depends upon the reducing action of the triethylphosphine

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* Letts and Collie, (1) these *Transactions*, xxx. part 1, p. 213; and (2) *Phil. Mag.*, August 1886.

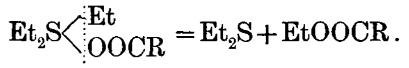
† Collie, (1) *Chem. Soc. Jour.*, 1888, p. 636; and (2) *Ibid.*, p. 714.

upon the carbonic anhydride, at the high temperature at which the decomposition usually occurs, whereby carbonic oxide is liberated, which combines with the hydrocarbon radical *in statu nascendi*, forming a ketone :—

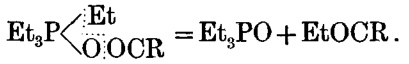
$$\mathrm{Et_3P+CO_2\ +(Et)+(R)=Et_3PO+EtCOR}$$
$$\mathrm{(or\ Et_3P+(OCO-R)\ +(Et)=Et_3PO+EtCOR)}.$$

If we merely consider the third kind of decomposition alone, it appears to be, to a certain extent, analogous to the decomposition which a sulphine compound suffers when heated, the difference depending on the greater attraction which phosphorus has for oxygen, compared with that of sulphur for the same element. In both cases a hydrocarbon group is detached from the molecule, and also the residue of the acid, but while with the sulphur compounds these two simply combine (forming a compound ether), and leave a hydrocarbon sulphide, in the case of the phosphonium salt the acid residue is reduced by the tertiary phosphine, and the group thus left combines with the hydrocarbon radical, forming a ketone.

Thus—



$$\mathrm{Et_2S}\left\langle\begin{matrix}\mathrm{Et}\\ \mathrm{OOCR}\end{matrix}\right.=\mathrm{Et_2S+EtOOCR}.$$

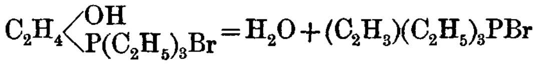


$$\mathrm{Et_3P}\left\langle\begin{matrix}\mathrm{Et}\\ \mathrm{O\,OCR}\end{matrix}\right.=\mathrm{Et_3PO+EtOCR}.$$

A result of this kind is in perfect harmony with the views already expressed by CRUM BROWN and LETTS* regarding the analogies and differences existing between phosphorus and sulphur and their compounds.

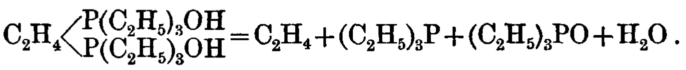
When the phosphonium salts contain ethylene they suffer a different decomposition under the influence of heat; at least this has been ascertained to be the case with the bromide of bromo-ethylene-triethylphosphonium, and the bromide of hydroxy-ethylene-triethyl phosphonium, which decompose as follows :†—

$$\mathrm{C_2H_4}\left\langle\begin{matrix}\mathrm{Br}\\ \mathrm{P(C_2H_5)_3Br}\end{matrix}\right.=\mathrm{HBr+(C_2H_3)(C_2H_5)_3PBr}$$



$$\mathrm{C_2H_4}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{P(C_2H_5)_3Br}\end{matrix}\right.=\mathrm{H_2O+(C_2H_3)(C_2H_5)_3PBr}$$

and also in that of the hydrate of ethylene-hexethyl diphosphonium, which decomposes according to the equation,



$$\mathrm{C_2H_4}\left\langle\begin{matrix}\mathrm{P(C_2H_5)_3OH}\\ \mathrm{P(C_2H_5)_3OH}\end{matrix}\right.=\mathrm{C_2H_4+(C_2H_5)_3P+(C_2H_5)_3PO+H_2O}.$$

MASSON and KIRKLAND ‡ have studied the action of bromine and chlorine on the salts of tetrethyl phosphonium, the results showing a very close similarity between the poly-haloid derivatives of tetrethyl phosphonium and those of trimethyl sulphine and of tetramethyl ammonium previously described by DOBBIN and MASSON.§ The tendency to form solid

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* CRUM BROWN and LETTS, these *Transactions*, xxviii. p. 371 ; LETTS, these *Transactions*, xxx. p. 285.

† HOFMANN.

‡ MASSON and KIRKLAND, *Chem. Soc. Jour.*, 1889 (*Trans.*), p. 126.

§ DOBBIN and MASSON, *Chem. Soc. Jour.*, 1885 (*Trans.*), p. 56, and 1886, p. 846.

poly-haloid compounds is, however, more marked. They give the following table, containing a list of the new substances, the methods of forming them, and their chief properties:—

No.	Substance.	Method of Formation.	Temperature of Formation.	Chief Properties.
1	PEt_4IBr_4 ?	Br_2 on iodide.	cold.	Bright red crystals, solid; unstable.
2	PEt_4IBr	Alcohol on I.	...	Orange crystals; stable.
3	PEt_4ICl_4	Cl_2 on iodide.	70°	Yellow crystal mass; unstable.
4	PEt_4ICl_2	Alcohol on 3.	...	Yellow crystals; stable.
5	PEt_4Br_7	Br_2 on bromide.	110	Yellow crystal mass; unstable.
6	PEt_4Br_3	Alcohol on 5 or 9.	...	Red crystals; stable.
7	PEt_4Cl_3	Cl_2 on chloride.	110	Yellow crystal mass; unstable.
8	$(PEt_4)_2SO_4Br_{22}$?	Br_2 on sulphate.	cold.	Red, liquid; unstable.
9	$(PEt_4)_2SO_4Br_{12}$	Br_2 on sulphate.	110	Red, solid; unstable.
10	$(PEt_4)_2SO_4Cl_4$	Cl_2 on sulphate.	130	Yellow, solid; unstable.

Organic Phosphorus Compounds which cannot be placed in any of the above Groups.

A phosphorised kakodyl $(CH_3)_4P_2$ (the methyl analogue of liquid phosphuretted hydrogen) was obtained by THENARD * by the action of chloride of methyl on phosphide of calcium, and is interesting not alone as being the sole representative (as yet prepared) of its class, but also as having been probably the first phosphine obtained. THENARD describes it as a colourless, highly refractive liquid, of an odour recalling that of kakodyl itself, insoluble in water, and boiling at about 250°. It inflames spontaneously in contact with air, but if oxidised slowly, gives a crystalline acid $(CH_3)_4P_2H_2O_4 = (CH_3)_2PHO_2$ (dimethyl phosphinic acid), analogous to kakodylic acid. Treated with an excess of hydrochloric acid, it is converted into trimethyl phosphine, and a solid yellow substance $(CH_3)_2P_4$ (which is also formed in the original reaction), and which THENARD regarded as the methyl analogue of solid phosphide of hydrogen.

MICHAELIS † obtained a substance, which he named *diphosphenyl*, or *phospho-benzol*, $C_6H_5-P=P-C_6H_5$ (corresponding to azobenzol), by the action of phenyl phosphorous chloride on monophenyl phosphine,

$$C_6H_5PCl_2 + C_6H_5PH_2 = (C_6H_5)_2P_2 + 2HCl.$$

It is a pale yellow powder, insoluble in water, alcohol, and ether, but readily soluble in hot benzol, and is slowly oxidised by the air to $(C_6H_5)_2P_2O$. Treated with chlorine, phenyl phosphorous chloride is regenerated. With nitric acid it is oxidised to phenyl phosphinous acid $C_6H_5PH_2O_2$, if the acid is dilute, but to phenyl phosphinic acid, $C_6H_5PH_2O_3$, if the acid is strong. Treated with hydrochloric acid, it reacts so as to regenerate the substances from which it is formed.

MICHAELIS ‡ also obtained a substance, which he called *di-phospho-benzene hydrate*, $C_6H_5-P=P-OH$, by the action of spontaneously inflammable phosphuretted hydrogen on phenyl phosphorous chloride. It is a yellow powder, soluble with ease in bisulphide of carbon, taking fire on exposure to air, and oxidised by nitric acid to phenyl phosphinic

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* THENARD, *Comptes Rendus*, xxi. p. 144, and xxv. p. 829.

† MICHAELIS, *Berichte*, x. p. 807.

‡ MICHAELIS, *Berichte*, vii. (1875) p. 499.

and phosphoric acids. In addition to the above, MICHAELIS[*] obtained a phenylated solid phosphide of hydrogen, $(C_6H_5)HP_4$, by treating phenyl phosphorous chloride with a quantity of water insufficient for complete decomposition (for instance, by keeping it in a badly-stoppered bottle). It is a dark yellow amorphous body, having a faint odour of phenyl phosphine, soluble in hot bisulphide of carbon, but insoluble in water, alcohol, and ether. Treated with chlorine, it reacts as follows :—

$$(C_6H_5)HP_4 + 6Cl_2 = 3PCl_3 + (C_6H_5)PCl_2 + HCl.$$

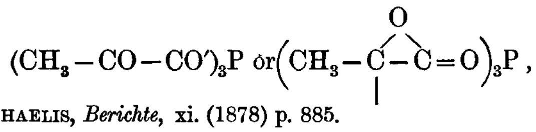
Nitric acid oxidises it to a mixture of phenyl phosphinic and phosphoric acids.

The action of phosphonium iodide on aldehydes has been studied by GIRARD,[†] while that of phosphuretted hydrogen and hydrochloric acid on the same bodies and on ketonic acids has been investigated by MESSINGER and ENGELS.[‡] GIRARD obtained products of addition containing four molecules of the aldehyde (valeric, propionic, salicylic, and benzoic) to one of phosphonium iodide.

MESSINGER and ENGELS obtained similar bodies by acting upon the aldehydes with hydrochloric acid and phosphuretted hydrogen. The compounds thus formed are for the greater part solid, crystalline, and fairly stable. By treatment with water, they are decomposed, and the aqueous solution gives the reactions of hydrochloric acid and phosphuretted hydrogen. Their constitution is probably represented by the formula $(R-CHOH)_4PCl$. Chloride of tetra-hydroxyethylidene phosphine $(C_2H_5O)_4PCl$, is decomposed by caustic potash into the free phosphine $(C_2H_5O)_3PC_2H_4O$, and the hydrate $(C_2H_5O)_4P(OH)$. Benzaldehyde and its mono-nitro derivative give compounds which differ from those obtained in the fatty series, in that they contain no hydracid.

MESSINGER and ENGELS have summarised the result of their researches as follows :— (1) Phosphuretted hydrogen does not act on an aldehyde alone, but is absorbed if at the same time a hydracid is present. The absorption occurs more completely if the aldehyde is largely diluted with ether. (2) The aldehydes of the fatty series combine with a molecule of phosphuretted hydrogen and a molecule of hydracid, while those of the aromatic series combine with phosphuretted hydrogen only, though in order that the compound shall be formed the presence of the hydracid is necessary. (With benzoic aldehyde the compound has the formula $(C_6H_5COH)_4PH_3$). (3) The phosphorised derivatives of the fatty series have an unpleasant smell, and are decomposed by water, while those of the aromatic series have no odour, and are nearly insoluble in water. All are soluble with difficulty in ether, and in some cases insoluble.

By the substitution of a ketonic acid for an aldehyde in the above reaction, compounds are produced in certain cases. Thus lævulinic acid gives an oil and pyruvic acid a solid compound either—



$$(CH_3-CO-CO')_3P \text{ or } \left(CH_3-\underset{|}{C}\overset{O}{\frown}C=O\right)_3P,$$

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[*] MICHAELIS, *Berichte*, xi. (1878) p. 885.

[†] GIRARD, *Ann. de Chim. und de Phys.* [vii.], ii. p. 50.

[‡] MESSINGER and ENGELS, *Berichte*, xxi. (1888) p. 328*a* and p. 2919*a*.

which is a well-defined crystalline body, having neither basic nor acid properties, soluble in alkalies with decomposition, and also decomposed when heated with acids. It dissolves, however, without change in glacial acetic acid, and crystallises out on cooling. Boiled with water, it is decomposed into the substances from which it was originally produced. It forms crystalline compounds with aniline, phenyl hydrazine, and toluene diamine.

On reading over the above, it will be seen that, although a fair amount of work has been done with the phosphines, they have by no means been exhaustively studied, and that many of their properties and reactions remain to be investigated. It was our wish to fill up some of these gaps in their history, and we chose the benzyl phosphines for investigation for several reasons, among which was the fact that the primary phosphine is a liquid at ordinary temperatures, also on account of the well-known chemical activity of the benzyl compounds, and partly because one of us and N. COLLIE had already studied somewhat exhaustively the compounds of tetrabenzyl phosphonium. HOFMANN[*] was the first to obtain monobenzyl phosphine, and as he believed dibenzyl phosphine also, by heating a mixture of chloride of benzyl, phosphonium iodide, and oxide of zinc in sealed tubes. He apparently submitted the two substances to a somewhat cursory examination, and only determined their leading properties. He mentions that bye products are formed, but these he did not investigate.

We have repeated HOFMANN'S experiments, and have submitted both the primary phosphine and also the substance which he regarded as the secondary derivative to a very careful examination. We have also isolated the other products and bye products of the reaction, and have determined their composition, and as far as possible their properties also. In the course of the research we incidentally discovered a method for preparing all the products of the oxidation of the benzyl phosphines. We describe this method, and also the properties of the oxidised substances.

MONOBENZYL PHOSPHINE AND ITS DERIVATIVES.

Preparation of Monobenzyl Phosphine.—HOFMANN recommends digestion during six hours at 160° C. of a mixture of 4 parts of oxide of zinc, 16 of iodide of phosphonium, and 12 of chloride of benzyl. Experiments conducted in this way with commercial chloride of benzyl from Kahlbaum gave in the tubes a viscous semicrystalline mass. To obtain a good result, thorough mixing of the materials in the sealed tubes by shaking before heating seemed to be necessary. On opening the tubes much phosphuretted hydrogen escaped, but on heating for a longer period or to a higher temperature, the escaping gas *seemed to consist of hydrochloric acid only.* It was soon found that at the temperature of 160° C., a great deal of hydrochloric acid is formed, and but little of the primary phosphine. The best results were obtained by a six hours' digestion of the

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[*] HOFMANN, *Berichte*, v. (1872) p. 100.

mixture at a temperature of 120° C. Experiments tried at 100° to 110° C. showed that but little of the primary phosphine is formed.

With the quantities HOFMANN recommends and a digestion for six hours at 120°, the tubes when cold contain a viscous semitransparent mass, sometimes of a brown colour sometimes red and opaque from the separation of free phosphorus. Above this a small quantity of a liquid usually floats, which at times is mobile, but at others thick and slightly fluorescent. A few crystals of undecomposed iodide of phosphonium are also frequently present. If pure chloride of benzyl is used there is usually no liquid floating on the surface of the product.

After opening the tubes, their contents were transferred to a flask, and submitted to the action of steam and water by means of the apparatus shown in figure 1 of the Plate.

A is a wide-mouthed flask provided with a large cork, with a large and somewhat conical hole, through which the inverted tube B passes.

C is a bent tube, which can be raised or lowered at will according to the length of B, so that its upper extremity may be near the closed end (of B). Through this tube steam from D, or carbonic acid from E, can be passed.

Two other tubes, F and G, pass through the same cork—one for blowing steam through the product, the other for carrying volatilised substances into the condenser H.

The apparatus was employed as follows:—After opening the tubes containing the product of the reaction, their tops were cut off with a file, and they were then placed in front of a strong fire to liquefy their contents and to drive off as much hydrochloric and hydriodic acids as possible. They were then allowed to cool in a nearly horizontal position, so that their contents solidified on one side of the tube, leaving a clear passage along their whole length. Next a stream of carbonic anhydride was passed through F into A until it was quite full of the gas. Steam was then passed through C, and one of the tubes B inverted over its open end, and rapidly pushed into the cork. Its contents almost immediately liquefied and dropped into A without coming in contact with the air. When the tube was completely washed out, it was removed and another one substituted. The contents of twelve tubes were usually worked up at one operation (each containing 4 grms. oxide of zinc, 16 grms. phosphonium iodide, and 12 grms. chloride of benzyl)—the last tube being left in the position shown in the figure. The tubes F and C were then interchanged, so that steam passed through F, while a gentle current of carbonic anhydride was passed through C.

By this means the product was submitted to the prolonged action of steam and water in a current of carbonic anhydride. The primary phosphine thus set free passed over along with the steam, and was condensed in H, and then flowed into the separating funnel I, which contained common salt to give greater density to the water, and thus cause the phosphine to rise to its surface, as its specific gravity is almost the same as that of water.

Without the above apparatus, we found it is almost impossible to separate the phosphine without considerable loss through oxidation.

Under favourable circumstances, from 60–70 grms. of crude monobenzyl phosphine were obtained from 360 grms. of benzyl chloride; or, in other words, each tube yielded a little over 2 grms., consequently the preparation of even the crude phosphine in any quantity is extremely tedious and troublesome.

The residue in the flask A always contained in addition to water, a brown viscous and insoluble liquid, which as a rule solidified on cooling. Both it and the water contained phosphorised benzyl derivatives. We shall first discuss the properties of the primary phosphine, and afterwards the nature of the various bye products, and the methods we employed for isolating them.

Monobenzyl Phosphine.—HOFMANN purified the crude phosphine by fractional distillation only. He states that after two rectifications in a stream of hydrogen it is obtained of the constant boiling point 180°.

Our own experiments, repeated again and again, and with the greatest care, have satisfied us that the pure phosphine cannot be readily obtained thus. We have at different times operated upon two to three hundred grams, and have invariably obtained the same results on fractionating it. The crude phosphine begins to boil at about 100°, the thermometer then rises rapidly to 160°, and from 160°–190° most passes over. The residue in the distilling flask decomposes if the distillation is pushed further, and red phosphorus separates. All the fractions contain the phosphine, for they all have its powerful and characteristic odour, and when mixed with fuming hydriodic acid they give its crystalline hydriodate. After repeated rectifications, the lower boiling fractions resolve themselves into a liquid, boiling at 110°–116°, which is no doubt toluol, while the high boiling fractions pass over from 175°–185°, the thermometer being fairly constant at 180°–183°.

We have investigated the high boiling residue (above 190°), and give the results on p. 585.

In view of the difficulty experienced in separating the primary phosphine by simple distillation, in a pure state, we decided to obtain the crystallised hydriodate from the crude product, and from it the phosphine, but, owing to the bulky nature of that compound (*i.e.*, the hydriodate) and its insolubility, we experienced considerable difficulty in effecting this. After several experiments, we found that either of the two following methods might be employed:—

(1) The crude phosphine was placed in a retort, and a stream of pure, dry, hydriodic acid gas was conducted by a long tube into the body of the retort. As soon as saturation appeared to be complete, the retort was heated gradually in an oil-bath to a temperature of 160°–180°, a slow current of hydriodic acid passing all the time. The hydriodate then sublimed in beautiful colourless scales, and when most had thus volatilised into the neck of the retort, the latter was allowed to cool, the hydriodate shaken out, and well washed with pure benzol.

(2) The crude product was mixed with about twenty times its volume of pure dry benzol, and the mixture saturated with dry hydriodic acid. It grew warm, and eventually

almost solid, from the separated hydriodate. The mass was thrown on to a linen filter and thoroughly squeezed, then pressed between filter paper, broken up, and washed with benzol, so long as the latter dissolved anything. The benzol was then removed as far as possible by pressure between filter paper, and the purified hydriodate dried *in vacuo.*

The hydriodate prepared by both these methods was snow white, and tolerably permanent in the air; but if not carefully prepared and thoroughly washed, it rapidly became brown. About 60 grms. of the hydriodate thus prepared were placed in a separate funnel, and caustic potash solution added until the funnel was nearly full; the mixture was then well shaken, when the hydriodate rapidly decomposed, and the phosphine separated as an oily layer, which floated on the watery liquid containing potash and potassium iodide. It was decanted, and submitted to fractional distillation in a stream of hydrogen. The thermometer rose rapidly to 178°, then slowly to 190°. It was fairly constant from 180°–182° when most distilled; only a little passed from 182°–190°. Fraction 178°–190° was redistilled. The thermometer rose at once to 177°, and from that temperature to 185° most distilled. The exact boiling point could not be fixed, but it is somewhere about 180°–183°. These experiments, conducted with the greatest possible care, and repeated two or three times, appear to indicate that the primary phosphine suffers a slight decomposition during distillation, but it is also possible that, in spite of the precautions adopted, the phosphine after all was not absolutely pure.

Properties.—Monobenzyl phosphine is a colourless, highly refractive liquid, possessing a very characteristic and penetrating odour. Its smell remains for days on the hands, and in one case it was observed on an instrument months after the latter had been handled by one of us, our fingers having been previously in contact with some of it.

Exposed to the air, it at once fumes very powerfully and grows hot. Its vapour indeed often inflames spontaneously on leaving a bottle containing it open for some time. The product of its oxidation is not a single substance, but contains no less than three different bodies.

Sulphur only acts upon it when the mixture is warmed. Torrents of sulphuretted hydrogen are then evolved, and a liquid product is formed.

It combines readily with hydriodic and hydrobromic acids, and also, though not so energetically, with hydrochloric acid. The resulting compounds are crystalline, and are very sparingly soluble in a saturated solution of the hydracid. They are volatile, with decomposition more or less complete—unless in a stream of gaseous hydracid, when the hydriodate and hydrobromate at all events sublime unchanged. They are immediately decomposed by water and alkalies. Halogens act violently upon the phosphine, and seize upon part (or all) of its hydrogen, the hydracid which is formed then combining with the rest of the phosphine to produce its haloid salt.

Bisulphide of carbon attacks it when the two are heated under pressure, sulphuretted hydrogen escapes, and two sulphurised products result.

Chloracetic and bromacetic acids also react with it—the first only when heated with the phosphine, the second at ordinary temperatures.

Chlorocarbonic ether also reacts with it at ordinary temperatures.

Monobenzyl Phosphine Hydriodate, $C_7H_7PH_2HI$.—This salt is easily formed, either by subliming the phosphine in dry hydriodic acid gas; by saturating a solution of the phosphine in benzol with dry hydriodic acid gas; or by dissolving the phosphine in warm fuming aqueous hydriodic acid.

By the first method it is obtained in snow-white scaly crystals like benzoic acid; by the second, as a seemingly amorphous bulky precipitate; while by the third it is also obtained in the crystalline state.

A specimen prepared by the first method was analysed.

Analysis.

0·6090 gave 0·5630 $AgI = \cdot3043015$ $I = 49\cdot97$ per cent.

	Obtained.	Calculated for $C_7H_7PH_2.HI$
Iodine, . . .	49·97	50·39

The hydriodate, when pure and dry, is permanent in dry air; but a trace of impurity causes it to become brown. It is rapidly decomposed by water, and instantly by caustic potash solution.

Monobenzyl Phosphine Hydrobromate, $C_7H_7PH_2HBr$.—HOFMANN could not obtain this compound in the crystalline state, but we found that it could be prepared with the greatest ease either by saturating a solution of the phosphine in benzol with gaseous hydrobromic acid, or by dissolving the phosphine in the fuming aqueous acid. It is also produced when bromine acts upon the phosphine in acetic acid solution, and is then precipitated as a colourless crystalline powder.

Analysis.

I. 0·3639 gave 0·3300 $AgBr = 0\cdot1404$ $Br = 38\cdot58$ per cent.

$$0\cdot448 \quad \text{gave} \begin{cases} 0\cdot2033\ H_2O = 0\cdot02258\ H = \ 5\cdot04 & \text{,,} \\ 0\cdot6799\ CO_2 = 0\cdot18542\ C = 41\cdot38 & \text{,,} \end{cases}$$

II. 0·8163 required 38·7 $c.c^{n}_{10}$ $AgNO_3 = 0\cdot3096$ $Br = 37\cdot90$ per cent.

	Obtained.		Calculated for $C_7H_7PH_2.HBr$
	I.	II.	
Bromine, . . .	38·58	37·90	39·02
Carbon, . . .	41·38	...	40·97
Hydrogen, . . .	5·04	...	4·88

I. Obtained by the action of bromine on the phosphine.

II. ,, ,, hydrobromic acid on the phosphine.

The salt is insoluble in benzol, and only very slightly soluble in warm fuming hydrobromic acid. Heated in a tube, it sublimes in glittering scales with slight decomposition. It is very deliquescent, and decomposes rapidly in contact with water and instantly with caustic potash.

Monobenzyl Phosphine Hydrochlorate, $C_7H_7PH_2HCl$.—We obtained this salt by similar methods to those which we employed for preparing the two compounds just described. On passing gaseous hydrochloric acid into a solution of the phosphine in benzol no effect is produced until saturation is complete, then colourless crystalline scales begin to form. On shaking the phosphine with a saturated aqueous solution of hydrochloric acid, a similar precipitate is produced. We have not analysed the compound, as we did not obtain it in sufficient quantity, but its composition cannot be doubted.

Chloroplatinate.—On mixing the phosphine with an aqueous or alcoholic solution of chloride of platinum, a light yellow bulky amorphous precipitate is produced. We did not analyse it.

Action of Air or Oxygen on Monobenzyl Phosphine.—As we have before mentioned, the phosphine attracts oxygen with great energy from the air, the temperature rises considerably, dense white vapours are produced which occasionally take fire spontaneously. The final product of the oxidation is a colourless viscous liquid which refuses to crystallise. It dissolves somewhat sparingly in water, and has a strong acid reaction.

On adding acetate of lead to its aqueous solution a white flocculent precipitate is produced which is by no means quite insoluble, so that its bulk diminishes considerably on washing. The following results were obtained on submitting it to analysis :—

Analysis.

I. 0·1060 gave 0·0925 $PbSO_4$ = ·06319 Pb = 59·60 per cent.
II. 0·4538 „ 0·4035 „ = ·275 Pb = 60·8 „

I. Prepared from the phosphine obtained from its hydriodate.
II. Prepared from the crude phosphine.

	Obtained.		Calculated for	
	I.	II.	$(C_7H_7HPO_2)_2Pb$	$(C_7H_7)PO_3Pb$
Lead, . .	59·6	60·8	39·92	54·97

It is obvious that the lead salt is neither the benzyl-phosphinite nor benzyl phosphinate. On the other hand, the percentage of lead does agree fairly well with that required for the formula $(C_7H_7)PO.Pb$—viz., 60·0, and this view of its composition, namely, that it is a derivative of an oxide $C_7H_7PH_2O$ in which the two atoms of hydrogen are replaced by one atom of lead, unlikely as it appeared, was supported by the increase in weight which a sample of the pure phosphine experienced on spontaneous oxidation—a rough experiment giving 14·1 per cent. increase in weight, instead of 12·9 per cent., the calculated amount.

At the time of our first experiments on this subject we were unacquainted with benzyl phosphinic acid, and hence knew nothing about the properties of its lead salt or of its other compounds. After it had been obtained, however, and its salts investigated, a simple means was at our disposal for ascertaining whether it was present in the product of oxidation of the primary phosphine, and for separating it if necessary from other substances. For benzyl phosphinate of barium is a highly characteristic salt, being much less soluble in boiling water than in cold, and is precipitated almost completely in the crystalline state on warming its cold solution, as it is only soluble to the extent of less than $\frac{1}{2}$ per cent. in a boiling solution.

Accordingly we oxidised a considerable quantity of the primary phosphine—dissolved the product in water and neutralised the solution with baryta, when a white flocculent precipitate was thrown down, which readily dissolved in acids, and gave a strong phosphoric acid reaction with molybdate of ammonia. There can be no doubt that it was phosphate of barium. The solution filtered from it was boiled to small volume, and gave a crystalline precipitate, which was purified by solution in cold water and reprecipitating by boiling. It had the appearance and properties of benzyl phosphinate of barium, and was proved by analysis to be that substance.

Analysis.

0·6367 lost at 110° C. 0·0630 $H_2O = 9·89$ per cent.
0·6367 gave 0·4296 $BaSO_4 = 0·25259$ Ba = 39·67 „

	Obtained.	Calculated for $C_7H_7PO_3Ba,2H_2O$
Water, . . .	9·89	10·49
Barium, . . .	39·67	39·94

The concentrated mother-liquors from this salt were syrupy and had a slight odour of the primary phosphine. After some time they became granular from the separation of a crystalline salt. The semisolid mass was dried for some time in a desiccator, then washed with alcohol (in which it was somewhat soluble), and dried *in vacuo*. A quantity of the salt thus purified was dried at 110° and analysed.

Analysis.

1·098 gave 0·5603 $BaSO_4 = 0·32944$ Ba = 30·00 per cent.

	Obtained.	Calculated for $(C_7H_7HPO_2)_2Ba$
Barium, . . .	30·00	30·64

In another experiment, the nature of the products of oxidation of the phosphine was proved in a similar manner, with this difference, that after separating the phosphate and phosphinate of barium, the remaining phosphinite was decomposed by sulphuric acid, and the liberated phosphinous acid extracted with ether. The ethereal extract left on evaporation a very viscous colourless liquid, which refused to crystallise. It was proved to be the phosphinous acid by the production of a number of salts which were analysed, and are described on pp. 610–611.

In a third experiment on the oxidation of the primary phosphine, the product was treated in a totally different manner, but with the same results.

In this experiment the oxidised product was dissolved in water as before, the solution boiled and acetate of zinc added. At first a precipitate was thrown down, which redissolved as fast as it was formed, but presently on adding more of the zinc salt a permanent precipitate was produced, which became pasty on boiling. It was filtered off, and the solution concentrated, when a totally different salt was thrown down. Analysis proved the first of these salts to be the phosphinate of zinc, the second the phosphinite.

Analysis of No. 1 Salt.

0·9037 gave 0·2839 ZnO = 0·2278 Zn = 25·20 per cent.

0·6028 gave $\begin{cases} 0·1914\ H_2O = 0·02126\ H = 3·52 & \text{,,} \\ 0·7442\ CO_2 = 0·20296\ C = 33·66 & \text{,,} \end{cases}$

	Obtained.	Calculated for $C_7H_7PO_3Zn,H_2O$
Zinc, ...	25·20	25·70
Carbon, . . .	33·66	33·20
Hydrogen, . . .	3·52	3·55

Analysis of No. 2 Salt.

I. 0·5145 gave 0·1133 ZnO = 0·0901 Zn = 17·66 per cent.
II. 0·8757 ,, 0·1946 ,, = 0·15616 ,, = 17·83 ,,

0·5273 gave $\begin{cases} 0·2021\ H_2O = 0·022455\ H = 4·25 & \text{,,} \\ 0·8417\ CO_2 = 0·229554\ C = 43·53 & \text{,,} \end{cases}$

	Obtained.		Calculated for $(C_7H_7HPO_2)_2Zn$
	I.	II.	
Zinc, . . .	17·66	17·85	17·33
Carbon, . . .	...	43·53	44·80
Hydrogen, . . .	...	4·25	4·26

The experiments described above prove conclusively that when monobenzyl phosphine oxidises spontaneously it gives rise to three different products, namely, phosphoric acid, benzyl phosphinous acid $(C_7H_7)H_2PO_2$, and benzyl phosphinic acid $(C_7H_7)H_2PO_3$. With regard to the relative quantities of the three substances, the phosphinous acid is produced in by far the largest proportion, and phosphoric acid in the smallest; the phosphinous acid is, in fact, the main product of the reaction. It is probable that phosphinous acids are always formed when primary phosphines are spontaneously oxidised.

H. Köhler and Michaelis* state that phenyl phosphine oxidises almost quantitatively in this manner, para-tolyl phosphine also gives rise to the corresponding phosphinous acid,† and Moslinger ‡ states that octyl phosphine is probably converted into a phosphinous acid by spontaneous oxidation. But, so far as we are aware, no other experiments have been made on this subject, which is one of some interest.

Action of Bromine on the Product of the Oxidation of the Primary Phosphine.—In some of our earlier experiments, before the nature of the products of the oxidation of the primary phosphine had been ascertained, one of us and W. Wheeler submitted these products to the action of bromine. We found that when bromine was added it was rapidly decolorised and the mixture grew hot, while hydrobromic acid was evolved, and the pungent odour of bromide of benzyl became manifest. Excess of bromine was added, and the mixture allowed to remain undisturbed for some time. A crop of crystals then separated, which dissolved both in water and ether, and were obtained colourless by recrystallisation. These crystals on analysis gave the following results :—

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* Köhler and Michaelis, *Berichte*, x. (1877) p. 810.

† Michaelis and Panek, *Annalen*, 212, p. 234.

‡ Moslinger, *Berichte*, ix. (1876) p. 1008.

Analysis.

0·221 gave 0·166 AgBr = 0·07065 Br = 31·9 per cent.

0·284 gave $\begin{cases} 0·6245\ CO_2 = 0·18735\ C = 48·9 \text{ ,,} \\ 0·1535\ H_2O = 0·01705\ H = 8·9 \text{ ,,} \end{cases}$

	Obtained.	Calculated for $(C_7H_7)_3P_2Br_2H_3O$
Carbon, . . .	48·9	49·0
Hydrogen, . . .	4·9	4·7
Bromine, . . .	31·9	31·1

In another experiment, conducted in a similar manner, we also obtained a solid crystalline substance, which, after crystallisation from water, consisted of scales with mother-o'-pearl lustre, and a melting point of 176° C. A bromine determination gave the following result:—

0·2423 gave 0·176 AgBr = 0·0849 Br = 30·9 per cent.

In a third experiment completely different results were obtained. In this experiment a quantity of the primary phosphine, which had been kept for some years in a loosely-corked flask, was treated with bromine, when, as in previous experiments, abundance of hydrobromic acid was evolved, and the mixture grew very hot. The product was heated for a considerable time on a water-bath to get rid of hydrobromic acid. The residue had an intolerable odour of bromide of benzyl. On treatment with water some of it dissolved, but an oily liquid remained, which solidified on cooling. The aqueous solution gave the reactions of benzyl phosphinic acid. The oily liquid had acid properties. It was dissolved in baryta water, the solution filtered, and precipitated by hydrochloric acid. The resulting crystalline precipitate was recrystallised from hot alcohol, in which it readily dissolved. Its corrected melting point was now found to be 176° C. Its analysis gave the following results:—

Analysis.

0·1671 gave $\begin{cases} 0·3920\ CO_2 = 0·106909\ C = 63·97 \text{ per cent.} \\ 0·1014\ H_2O = 0·011266\ H = 6·74 \text{ ,,} \\ 0·0732\ Mg_2P_2O_7 = 0·020443\ P = 12·23 \text{ ,,} \end{cases}$

	Obtained.	Calculated for $C_{28}H_{34}P_2O_5$
Carbon, ...	63·97	63·93
Hydrogen, . . .	6·74	6·96
Phosphorus, . . .	12·23	12·70

A quantity was converted into its barium salt, and the latter analysed.

Analysis.

0·3214 $\begin{cases} \text{lost at 110, } 0·0328 = 10·20 \text{ per cent. } H_2O \\ \text{gave } 0·1072\ BaSO_4 = 0·063031\ Ba = 19·61 \text{ per cent. Ba} \end{cases}$

	Obtained.	Calculated for $C_{26}H_{32}P_2O_5Ba,4H_2O$
Barium, ...	19·61	19·71
Water, ...	10·20	10·36

As we found that benzyl phosphinic acid is not attacked by bromine at ordinary temperatures, the substances which we obtained by the action of bromine on the oxidised phosphine are probably formed from benzyl phosphinous acid.

The experiments just described shows that the reaction is of a highly complex nature, and that it varies with the conditions of the experiment.

As the substances resulting from the reaction were obtained in very small quantity, barely sufficient for their analysis, we were unable to study their properties, and must remain in doubt regarding their exact nature.

Action of Sulphur on Monobenzyl Phosphine.—A preliminary experiment showed that no action occurs in the cold, but on warming the two bodies together the sulphur dissolves and abundance of sulphuretted hydrogen escapes.

About 4 grms. of the phosphine were placed in a test-tube full of carbonic anhydride, and heated by immersing the tube in a water-bath. Powdered sulphur was then added, and sulphuretted hydrogen was evolved in abundance—to such an extent, indeed, that at one time the liquid frothed over into the water-bath. Excess of sulphur was added to the liquid, which had thus frothed over (B), and the same was done with the liquid in the tube (A)—a very considerable quantity being required in both cases.

As soon as the evolution of sulphuretted hydrogen ceased, the liquid was allowed to cool. It was colourless and viscous. It was boiled with water, when sulphuretted hydrogen was again evolved—nearly the whole (of the viscous liquid) dissolved, forming a strongly acid solution. This was neutralised with baryta, and the solution heated, when a crystalline salt separated very much like benzyl phosphinate of barium, and was at first considered to be that substance.

The product B gave a similar salt. The two salts were purified by dissolving them in cold water and then heating the solution when they were deposited in the crystalline state.

Analysis of Barium Salt from A.

0·4710 gave 0·3184 $BaSO_4$ = 0·187213 Ba = 39·75 per cent.
0·4710 lost at 110° C. 0·0253 H_2O = 5·37 „

Analysis of Barium Salt from B.

0·5691 gave 0·3878 $BaSO_4$ = 0·228019 Ba = 40·06 per cent.
0·5691 lost at 110° C. 0·0289 H_2O = 5·07 „

	Obtained.		Calculated for $(C_7H_7)PO_2SBa,H_2O$
	A.	B.	
Barium, . .	39·75	40·06	40·17
Water, . .	5·37	5·07	5·27

On attempting to obtain the acid by decomposing the barium salt with sulphuric acid, sulphuretted hydrogen was evolved—no doubt, with formation of benzyl phosphinic acid—

$$C_7H_7PO_2SH_2 + H_2O = C_7H_7PO_3H_2 + H_2S.$$

The results of this experiment indicate that when the phosphine is warmed with sulphur, pyro-benzyl-thio-phosphinic acid is formed,

$$2C_7H_7PH_2 + 5S = (C_7H_7)_2P_2S_5H_2 + H_2S,$$

and this with water is decomposed into mono-thio-phosphinic acid, with evolution of sulphuretted hydrogen,

$$(C_7H_7)_2P_2S_5H_2 + 6H_2O = 2C_7H_7PS(OH)_2 + 5H_2S.$$

In a second experiment we attempted to obtain derivatives of the pyro acid. A quantity of the phosphine was heated as before with excess of sulphur until sulphuretted hydrogen ceased to be evolved. The product deposited a minute quantity of colourless plates, which were not obtained in sufficient quantity for analysis.

A quantity of the product was boiled with a solution prepared by saturating barium hydrate with sulphuretted hydrogen, and then adding an equal quantity of the hydrate. Sulphuretted hydrogen was evolved, and when the solution had become very concentrated, it deposited colourless crystals on cooling, which were collected and analysed.

Analysis.

$$0{\cdot}1516\begin{cases}\text{lost at 110° C. } 0{\cdot}0096 = 6{\cdot}33 \text{ per cent. water.}\\ \text{gave } 0{\cdot}0647\ BaSO_4 = 0{\cdot}038042\ Ba = 25{\cdot}09 \text{ per cent. barium.}\end{cases}$$

	Obtained.	Calculated for $(C_7H_7)_2P_2S_3O_2Ba,2H_2O$
Barium, . . .	25·09	25·13
Water, . . .	6·33	6·60

The production of the pyro acid is thus to a certain extent confirmed, its barium salt, which is no doubt formed in the first instance, being subsequently decomposed by water, thus—

$$(1)\quad (C_7H_7)_2P_2S_5H_2 + BaS = (C_7H_7)_2P_2S_5Ba + H_2S$$
$$(2)\quad (C_7H_7)_2P_2S_5Ba + 2H_2O = (C_7H_7)_2P_2S_3O_2Ba + 2H_2S.$$

We may also mention, that on dissolving the product of the action of sulphur on the phosphine in alcohol and adding mercuric chloride, a white amorphous precipitate was produced in abundance. We did not analyse it, as it darkened slowly on drying.

We have already mentioned that MICHAELIS studied the action of sulphur on phenyl phosphine and obtained two products—a liquid $(C_6H_5)PH_2S$, and a solid $(C_6H_5P)_3S$. The experiments we have just described show that benzyl phosphine behaves in a totally different manner, and they also prove that sulphur and oxygen do not react in an analogous manner upon a primary phosphine.

Action of Halogens on Monobenzyl Phosphine.—If bromine is mixed with the phosphine an explosive action occurs, and torrents of hydrobromic acid are disengaged. But when the vapour of bromine comes in contact with the base, the action proceeds quietly, and a white solid is produced. If both the bromine and phosphine are dissolved in glacial acetic acid, the reaction is completely under control. If the vessel in which the mixture is made is kept cool and the bromine gradually added, a colourless crystalline salt is produced, and its amount increases as the bromine is added, up to a certain point, but it then diminishes.

A quantity of this solid was filtered off, washed with glacial acetic acid, and then boiled with acetic acid until it dissolved. In dissolving it effervesced from the escape of hydrobromic acid. As the solution cooled colourless plate-shaped crystals separated. These were dried *in vacuo*, and analysed.

Analysis.

0·3639 gave 0·3300 AgBr = 0·1404 Br = 38·58 per cent.

$$0{\cdot}4480 \begin{cases} \text{gave } 0{\cdot}2033\ H_2O = 0{\cdot}02258\ H = 5{\cdot}04 \text{ per cent.} \\ \text{,,}\quad 0{\cdot}6799\ CO_2 = 0{\cdot}18542\ C = 41{\cdot}38 \quad \text{,,} \end{cases}$$

	Obtained.	Calculated for $(C_7H_7)PH_2.HBr$
Bromine, . . .	38·58	39·02
Carbon, . . .	41·38	40·97
Hydrogen, . . .	5·04	4·88

The crystalline solid was thus shown to be the hydrobromate of the phosphine, and all its properties pointed to the same conclusion. One or both of the following reactions must have occurred:—

$$(C_7H_7)PH_2 + Br_2 = HBr + (C_7H_7)PHBr$$

$$(C_7H_7)PH_2 + 2Br_2 = 2HBr + (C_7H_7)PBr_2.$$

The hydrobromic acid set free combining with the phosphine remaining in excess, and thus the quantity of hydrobromate produced would increase until the bromine began to be in excess, when, no doubt, it (the hydrobromate) was also attacked in the same way as the phosphine itself.

The mother-liquors from which the hydrobromate had separated ought to have contained one or other of the two brominated derivatives whose formulæ we have written above, but we had not sufficient of the product to be able to isolate either of them.

On evaporation they left a solid crystalline mass, which dissolved in water (leaving a few oily drops), and when the solution was neutralised with baryta and boiled, a crystalline salt was precipitated, having the appearance of benzyl phosphinate, but we did not obtain it in sufficient quantity for analysis.

Action of Bisulphide of Carbon on Monobenzyl Phosphine.—The following experiments were made:—

(1) 2 grms. of the pure phosphine were heated in a sealed tube with 2 grms. of bisulphide of carbon at 120° C. for two days. The contents of the tube then consisted of a viscous colourless substance and a number of colourless needle-shaped crystals. On opening the tube a considerable quantity of sulphuretted hydrogen escaped.

(2) About 4·5 grms. of the phosphine and about 9 grms. of the bisulphide of carbon were heated for two days at 130°–160°, when exactly the same phenomena were observed. The contents of each of the two tubes were separately treated with bisulphide of carbon, which dissolved the viscous substance, but left the crystals. The latter were repeatedly washed with bisulphide of carbon, then dried and analysed.

Analysis of Crystalline Product from Experiment 1.

$$\text{Carbon and hydrogen, } 0{\cdot}2175 \text{ gave} \left\{ \begin{array}{l} 0{\cdot}107 \ H_2O = 0{\cdot}0118 \ H = \ 5{\cdot}42 \text{ per cent.} \\ 0{\cdot}4335 \ CO_2 = 0{\cdot}11823 \ C = 54{\cdot}30 \quad \text{„} \end{array} \right.$$

Analysis of Crystalline Product from Experiment 2.

$$\text{Carbon and hydrogen, } 0{\cdot}2850 \text{ gave} \left\{ \begin{array}{l} 0{\cdot}1336 \ H_2O = 0{\cdot}014844 \ H = \ 5{\cdot}20 \text{ per cent.} \\ 0{\cdot}5652 \ CO_2 = 0{\cdot}154145 \ C = 54{\cdot}08 \quad \text{„} \end{array} \right.$$

	Obtained.		Calculated for		
	I.	II.	$(C_7H_7)PH_2S$	$(C_7H_7)PHS$	C_7H_7PS
Carbon, . . .	54·30	54·08	53·85	54·19	54·54
Hydrogen, . . .	5·42	5·20	5·76	5·16	4·54

The bisulphide of carbon washings from the crystals were warmed to get rid of the bisulphide, and left a pale yellow gummy mass, which was insoluble in water and ether, and very sparingly soluble in alcohol. No definite products could be obtained from this gummy mass by the action of various reagents. It was, however, found that it was soluble to a certain extent in boiling glacial acetic acid, so the whole of the product from the first experiment was boiled with a large quantity of the acid. The filtered solution deposited oily droplets on cooling, which eventually formed a viscous mass exactly like the original substance (specimen A). The acetic solution filtered from this was evaporated to dryness in a water-bath, and heated until the whole of the acetic acid had volatilised. A gummy mass remained also like the original product (specimen B).

The whole of the product from the second experiment was repeatedly boiled with alcohol, then washed with cold alcohol and dried (specimen C).

The three products were then analysed.

Analysis.

A.

$$0{\cdot}4355 \text{ gave} \left\{ \begin{array}{l} 0{\cdot}1982 \ H_2O = 0{\cdot}02202 \ H = \ 5{\cdot}05 \text{ per cent.} \\ 0{\cdot}8280 \ CO_2 = 0{\cdot}22582 \ C = 51{\cdot}80 \quad \text{„} \end{array} \right.$$

B.

$$0{\cdot}3463 \text{ gave} \left\{ \begin{array}{l} 0{\cdot}1595 \ H_2O = 0{\cdot}01772 \ H = \ 5{\cdot}10 \text{ per cent.} \\ 0{\cdot}6540 \ CO_2 = 0{\cdot}17836 \ C = 51{\cdot}5 \quad \text{„} \end{array} \right.$$

C.

$$0{\cdot}2645 \text{ gave} \left\{ \begin{array}{l} 0{\cdot}1287 \ H_2O = 0{\cdot}0143 \ H = \ 5{\cdot}40 \text{ per cent.} \\ 0{\cdot}4889 \ CO_2 = 0{\cdot}13333 \ C = 50{\cdot}40 \quad \text{„} \end{array} \right.$$

	Obtained.			Calculated for
	A.	B.	C.	$(C_7H_7PHCS)_2S$
Carbon, . .	51·80	51·50	50·41	52·45
Hydrogen, . .	5·05	5·10	5·40	4·37

To the best of our belief, the action of bisulphide of carbon on a primary phosphine has been studied in only one other case, viz., in that of phenyl phosphine.

MICHAELIS and DITTLER found that the two substances react under pressure at 150° with evolution of sulphuretted hydrogen, and formation of a resin having the composition $(C_6H_5PHCS)_2S$, the reaction occurring according to the equation,

$$2C_6H_5PH_2 + 2CS_2 = (C_6H_5PHCS)_2S + H_2S.$$

The compound which they name *phenyl-diphospho-sulpho-carbamic acid* dissolves in alkalies, and is reprecipitated unchanged on the addition of an acid. Its discoverers do not mention any other substance as being formed at the same time analogous to the crystalline body which we obtained.

We cannot be at all certain of the composition of either of the two substances obtained by us. As regards the crystalline product, the analytical results agree fairly well with the formula $(C_7H_7)_2P_2H_2S_2$, but we did not obtain it in our experiments on the direct action of sulphur on the phosphine, as we should have done in all probability if the above formula were correct. It was produced in too small a quantity for further investigation. With respect to the viscous product, we cannot believe that it is analogous to the phenylated body, for it has no acid properties, and the analytical results are not sufficiently in accordance with the formula. For the present we remain in doubt as to the nature of the substances.

Action of Sulphuric Acid on Monobenzyl Phosphine.—If sulphuric acid (concentrated) is added to the phosphine cautiously, and the mixture kept cold, it solidifies to a crystalline mass; but if it is not cooled a violent action soon occurs, and sulphurous anhydride is evolved in abundance. It may be inferred that the phosphine forms a crystalline sulphate which is very unstable, and probably decomposes into benzyl phosphinic acid and sulphurous anhydride.

Attempts to obtain the sulphate for analysis were unsuccessful.

Action of Chloracetic Acid on Monobenzyl Phosphine.—Three separate experiments were tried, with similar results in each case. When equivalent quantities of the phosphine and chloracetic acid are mixed no action occurs, but some of the acid dissolves. On gently warming the mixture the whole of the acid dissolves, but separates out again on cooling. If the two substances are heated in a sealed tube at 120° for some hours, a dark brown viscous mass results, and on opening the tube pressure is noticed, due to carbonic anhydride. The product undoubtedly contains chloride of acetyl, for it has its very characteristic odour, and fumes in moist air. On removing it from the product by shaking the latter with ether, and then treating the residue with water, a strongly acid solution results, while a little tarry matter remains undissolved. On neutralising the acid solution with baryta and then warming, a crystalline salt is precipitated. This we submitted to analysis (after recrystallisation), and found it to consist of benzyl phosphinate of barium.

Analysis.

$$0{\cdot}4794\left\{\begin{array}{l}\text{lost at } 110^\circ\text{ C.} \qquad 0{\cdot}047 \quad H_2O = \ 9{\cdot}80 \text{ per cent.}\\ \text{gave } 0{\cdot}3189\ BaSO_4 = 0{\cdot}1875077\ Ba = 39{\cdot}11 \quad ,,\end{array}\right.$$

	Obtained.	Calculated for $(C_7H_7)PO_3Ba,2H_2O$
Barium, ...	39·11	39·94
Water, ...	9·80	10·49

We think that the main course of the reaction must proceed as follows:—

$$C_7H_7PH_2 + 3CH_2Cl.CO_2H = C_7H_7PH_2O_2 + 3CH.COCl.$$

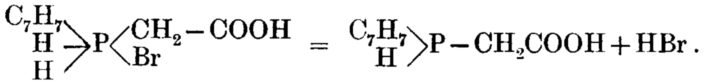
It is remarkable that the phosphine should thus seize upon the oxygen of the carboxyl group, and not upon the halogen.

It is probable that another reaction occurs to a slight extent, viz.:—

$$C_7H_7PH_2 + CH_2Cl - COOH = (C_7H_7)(CH_3)PH,HCl + CO_2 .$$

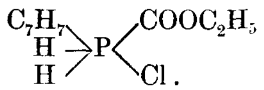
This equation, at all events, accounts for the liberation of carbonic anhydride, and is supported to a certain extent by the experiments which one of us has made on the action of chloracetic acid on triethyl-phosphine, or rather upon that of heat upon the product.*

Action of Bromacetic Acid upon Monobenzyl Phosphine.—We have not fully investigated the nature of this action, but we found that when the two substances were mixed, the bromacetic acid dissolved, and in a short time a crystalline product resulted. In about half an hour's time, however, an explosive decomposition of this substance occurred spontaneously, torrents of hydrobromic acid coming off, and a viscous liquid resulting, which was insoluble in water. We did not investigate the product, as nearly all of it was shot out of the vessel in which the experiment was made when the explosive action occurred. It is probable, we think, that a product of addition is first formed, which may then decompose in the following way:—



$$\left.\begin{matrix}C_7H_7\\ H\\ H\end{matrix}\right> P \left< \begin{matrix}CH_2 - COOH\\ Br\end{matrix}\right. = \left.\begin{matrix}C_7H_7\\ H\end{matrix}\right> P - CH_2COOH + HBr .$$

Action of Chlorocarbonic Ether on Monobenzyl Phosphine.—When the two substances are sealed up together a reaction gradually occurs, and thin quadratic plates of fair size are slowly deposited. On opening the tube pressure is observed. We could not obtain the crystals in a sufficiently pure state for analysis. They were so deliquescent that on attempting to dry them on filter-paper, they almost instantly deliquesced. They dissolved in alcohol, ether, and benzol. Alcoholic chloride of platinum gave a yellow slimy precipitate; alcoholic corrosive sublimate, a white amorphous precipitate, which soon turned grey. On warming them with baryta solution, carbonate of barium was precipitated. We think that these properties indicate that the substance is a product of addition—



$$\left.\begin{matrix}C_7H_7\\ H\\ H\end{matrix}\right> P \left< \begin{matrix}COOC_2H_5\\ Cl .\end{matrix}\right.$$

HOFMANN'S "DIBENZYL" PHOSPHINE.

In his well-known researches on the phosphines, HOFMANN has apparently shown that when an alkyl haloid is heated with phosphonium iodide and oxide of zinc, primary and secondary phosphines alone result; whereas when an alcohol is heated with iodide of phosphonium alone, tertiary and quaternary phosphines are formed exclusively. Thus the two reactions are complementary to each other. Among the

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* LETTS, these *Transactions*, xxx. part 1, p. 285.

series to which he extended his investigations was that of benzyl, and in the paper published in the *Berichte*, to which we have already referred, he describes the preparation and properties of dibenzyl phosphine. He isolated it from the product of the sealed tube reaction (occurring between benzyl chloride, phosphonium iodide, and oxide of zinc), but it is not quite clear from the original memoir whether he obtained it from the residue left on distilling the primary phosphine in a current of steam from the product of the reaction, or the residue left on distilling the crude primary phosphine itself. He states that a crystalline substance remains after distilling off the primary phosphine, which solidifies, especially (*zumal*) in contact with solid potash, and that after pressing it between linen, dissolving in alcohol, and decolorising the solution with charcoal, crystals are obtained, which after a single recrystallisation from alcohol are perfectly pure.

The crystals melted at 205°, and their analysis gave the following numbers :—

	Obtained.			Calculated for $(C_7H_7)_2PH$
	I.	II.	III.	
Carbon, . . .	78·75	78·37	...	78·50
Hydrogen, . .	6·99	6·77	...	7·01
Phosphorus, . .	...	...	13·6	14·49

He says :—" With the entrance of the second group the basic properties, which in benzyl phosphine appear in a perfectly definite manner, have entirely disappeared. Dibenzyl phosphine dissolves in no acid, neither have I succeeded in obtaining its platinum salt. The aromatic secondary phosphine thus distinguishes itself very materially from the secondary phosphines of the ethyl and methyl series."

In a paper read before this Society, one of us, in conjunction with W. Wheeler, described further investigations on this body, and we showed that it forms a series of compounds of a somewhat remarkable nature for a secondary phosphine. We isolated it as follows :—After submitting the contents of the sealed tubes to the action of steam and water (to drive off the primary phosphine), the residue, consisting of a brownish viscous mass, was boiled with aqueous potash for some time, and the viscous insoluble mass which remained was then extracted with hot alcohol. The solution on cooling deposited colourless needle-shaped crystals strongly impregnated with oily matter, and these by repeated recrystallisation from spirit were obtained pure.

The remarkable nature of this substance, on the assumption that it is in reality a secondary phosphine, coupled with some other facts which attracted our attention, gradually led us to suspect that it was not dibenzyl phosphine at all, but the *oxide of tribenzyl phosphine*. Accordingly, the investigation was reopened with Mr R. F. Blake, and its course has been as follows :—

1. On carefully recrystallising the substance from alcohol, its corrected melting-point was found to be 215°–215°·5 C., while that of two specimens of oxide of tribenzyl phosphine (prepared by two different methods) was found to be the same.

2. Very little difference exists in the percentage amount of carbon and hydrogen in dibenzyl phosphine and oxide of tribenzyl phosphine, as the following numbers show:—

	$(C_7H_7)_2HP$	$(C_7H_7)_3PO$
Carbon, . . .	78·50	78·75
Hydrogen, . . .	7·01	6·56

Consequently it would not be possible to decide with absolute precision between the two substances by a mere combustion. On the other hand, there is a considerable difference between the two bodies in their percentage of phosphorus—

	$(C_7H_7)_2HP$	$(C_7H_7)_3PO$
Phosphorus, . . .	14·48	9·69

Unfortunately, however, as we have again and again found, the processes for phosphorus determinations in ordinary organic substances are absolutely untrustworthy when applied to phosphines. A new method was therefore necessary, and after many trials we believe we have found one which is perfectly accurate, trustworthy, and capable of general application. It is extremely simple, though somewhat tedious in carrying out. It consists in making an ordinary combustion of the substance with *pure* oxide of copper, and afterwards dissolving the contents of the combustion tube in nitric acid, and determining the phosphorus with molybdate of ammonia, &c. Applying this method to the analysis of the supposed dibenzyl phosphine, we obtained the following results (IV. and V.).

We give at the same time the determinations of phosphorus made both by HOFMANN (I.) (by a method not described) and by one of us and W. WHEELER (II. and III.), by burning the substance with lime in a stream of oxygen, dissolving and titrating with standard uranium solution,

	Obtained.				
	I.	II.	III.	IV.	V.
Phosphorus, . . .	13·6	14·35	15·00	9·86	9·98

As we have before stated, many of the compounds of the supposed dibenzyl phosphine were prepared and analysed, and although their composition appeared remarkable for the compounds of a secondary phosphine, the analytical results agreed fairly well in most cases with formulæ of derivatives of dibenzyl phosphine. We even concluded, from the existence of these compounds, that the exceptional properties of the phosphine were due to its consisting of a double molecule, viz.:—

$$(C_7H_7)_2H{\equiv}P=P{\equiv}(C_7H_7)_2H\,.$$

It is a remarkable coincidence that the analytical results agree equally well for compounds of the oxide of tribenzyl phosphine. This fact has added considerably to the difficulties and uncertainty of the research, but at the same time it has caused us to exercise great caution in the inferences to be drawn from the analyses.

Subjoined is a brief account of the chief compounds we have examined of HOFMANN's dibenzyl phosphine, and we give at the same time the results obtained (in some cases) with compounds of what was known to be oxide of tribenzyl phosphine. We may add that many of the compounds are unstable, and their composition frequently varies with the method employed in their preparation. In many cases indeed it appears to be almost impossible to obtain them pure.

Bromide.—This compound, which is highly characteristic, was obtained by adding bromine to a solution of the body in glacial acetic acid. It usually crystallises in yellow needles, which under the microscope appear to consist of aggregations of minute rhombohedra. It is unstable, and gives off bromine when boiled with water or glacial acetic acid, and its composition varies considerably (see p. 625).

	Prepared from	
	Hofmann's Dibenzyl Phosphine.	Oxide of Tribenzyl Phosphine.
	Obtained.	Obtained.
Bromine, ...	26·7[*]	28·4[†]
Carbon, ...	56·5[‡]	56·9
Hydrogen, ...	5·3[‡]	4·9

	Calculated for		
	$\{(C_7H_7)_2HP\}_2,Br_2$	$7(C_7H_7)_3PO,5Br_2$	$5(C_7H_7)_3PO,4Br_2$
Bromine, ...	27·2	26·31	28·5
Carbon, ...	57·1	58·00	56·3
Hydrogen, ...	5·1	4·83	4·7

Iodide.—Prepared like the bromide. It crystallises in minute red crystals of the same colour as ferricyanide of potassium.

	Obtained.	Calculated for		
		$\{(C_7H_7)_2HP\}_2,I_2$	$7(C_7H_7)_3PO,5I_2$	$5(C_7H_7)_3PO,4I_2$
Iodine, . .	36·86	37·24	36·18	38·84

Chloride.—Obtained by passing chlorine into a solution of the body dissolved to saturation in warm acetic acid. It crystallises when the solution cools in pale yellow crystals, much like pentachloride of phosphorus in appearance. The compound is most unstable, and loses chlorine rapidly *in vacuo*, and probably also when air-dried.

	Obtained.	Calculated for	
		$\{(C_7H_7)_2HP\}_2,Cl_2$	$7(C_7H_7)_3PO,5Cl_2$
Chlorine, . .	12·00	14·23	14·68

Hydriodate.—Obtained by saturating a solution of the body in glacial acetic acid with hydriodic acid gas, and separated as the solution cooled in colourless crystals.

	Obtained.	Calculated for	
		$2(C_7H_7)_2PH,HI$	$3(C_7H_7)_3PO,2HI$
Iodine, . .	21·0 21·5	22·8	21·05

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[*] Mean of ten determinations of different preparations of the compound. The extremes were 25·9 to 27·2.

[†] An old analysis by one of us and N. COLLIE, these *Transactions*, xxx. part 1.

[‡] Mean of three determinations.

Hydrobromate.—Obtained in the same way as the hydriodate :—

	Obtained.		Calculated for	
			$2(C_7H_7)_2HP,HBr$	$3(C_7H_7)_3PO,2HBr$
Bromine,	(1)	19·5	15·9	14·44
	(2)	20·5		
	(3)	16·3		

Platinum Salt.—Prepared by mixing alcoholic solutions of chloride of platinum and of the substance. The compound crystallises out in minute leaflets. Its composition varies with the conditions under which it is prepared.

	Obtained from				
	Hofmann's Dibenzyl Phosphine.			Oxide of Tribenzyl Phosphine.	
	I.	II.	III.	IV.	V.
Carbon,	59·5	56·5	58·5	58·9	59·4
Hydrogen,	5·8	5·3	5·9	5·3	5·4
Chlorine,	...	...	...	12·4 12·6	...
Platinum,	12·8	13·1	13·1	...	...

(I., II., III., IV., and V. were all different preparations.)

	Calculated for	
	$5(C_7H_7)_2PH,PtCl_4$	$4(C_7H_7)_3PO,2HCl,PtCl_4$
Carbon,	59·5	59·5
Hydrogen,	5·3	5·0
Chlorine,	...	11·7
Platinum,	14·0	12·5

Nitro-Compound.—Obtained by dissolving the body in cold fuming nitric acid, and then precipitating with water. Amorphous.

	Obtained. (With Hofmann's Dibenzyl Phosphine.)	Calculated for	
		$(C_7H_6NO_2)_2HP$	$(C_7H_6NO_2)_3PO$
Carbon,	55·23	55·26	55·38
Hydrogen,	4·30	4·27	3·95

Double Salt with Iodide of Zinc.—This compound separates out when fairly strong alcoholic solutions of the body and iodide of zinc are mixed, in tufts of characteristic needles.

	Obtained from		
	Hofmann's Dibenzyl Phosphine.	Oxide of Tribenzyl Phosphine.	
		I.	II.
Iodine,	26·57	26·0	25·9

	Calculated for	
	$3(C_7H_7)_2HP,ZnI_2$	$2(C_7H_7)_3PO,ZnI_2$
Iodine,	26·43	26·48

Action of fused Potash on Hofmann's "Dibenzyl Phosphine."—In the paper by one of us and W. **Wheeler**, already referred to, the statement is made that when **Hofmann**'s dibenzyl phosphine is heated with caustic, potash, or soda, "it fuses and floats on the surface of the melted alkali. No violent action occurs, but on cooling the mixture and treating it with water the greater portion dissolves, and acids then precipitate a flocky crystalline substance, which is dibenzyl phosphinic acid." In corroboration of this statement, the melting point of the acid and analyses of its lead and barium salts were given, all in accordance with the required numbers. After we had satisfied ourselves that HOFMANN'S dibenzyl phosphine was oxide of tribenzyl phosphine, and nothing else, this reaction recurred to our minds as a further and very striking excuse for the mistake which we (and HOFMANN) had fallen into, and we thought it of importance to verify the previous observation. This we have accordingly done, both with HOFMANN'S dibenzyl phosphine and with a specimen of oxide of tribenzyl phosphine prepared by a different process.

The phenomena observed were exactly the same as those previously described, and the melting point of the acid obtained after two recrystallisations from alcohol was found to be 192° C. (corr.), which is the melting point of pure dibenzyl phosphinic acid. Our previous observations are thus fully confirmed.

The reaction in all probability occurs as follows :—

$$(C_7H_7)_3PO + KHO = C_7H_8 + (C_7H_7)_2KPO_2 .$$

INVESTIGATION OF THE PRODUCT OF THE SEALED TUBE REACTION FOR THE SECONDARY AND TERTIARY PHOSPHINE.

The occurrence of oxide of tribenzyl phosphine among the products of the sealed tube reaction led us to suspect that the tertiary phosphine had been formed in the first instance, but was subsequently oxidised by the air, as in isolating the oxide all the operations had been performed in open vessels. Quite accidentally, our suspicions received strong confirmation.

In one of our later experiments, after the primary phosphine had been distilled from the crude product of the reaction in a current of steam, the viscous mass remaining was treated with an alcoholic solution of potash, instead of an aqueous solution as we had used in our earlier experiments.

After boiling for about four hours with alcoholic potash, in a flask fitted with an upright condenser, the solution was filtered from oxide of zinc, &c., and on cooling deposited feathery crystals like sal-ammoniac, and not at all like the needle-shaped crystals of oxide of tribenzyl phosphine. The liquid was decanted from these crystals, and to remove adhering potash they were washed with cold water, and were then pressed between filter-paper to dry them. *On unfolding the paper, the crystalline mass grew very hot, and after repeated recrystallisation from alcohol (in an open vessel), the resulting crystals were needle-shaped, and had a melting point of* 215°·5 (corr.).

The conclusions we drew from this result were that the tertiary phosphine *is* formed in the reaction, and that it is a solid crystalline body which rapidly absorbs oxygen from the air with disengagement of heat, and is eventually converted into its oxide.

Another experiment was made in a similar manner, when the same phenomena recurred, the crystalline cake growing so hot that we thought it would ignite.

The problem we had now to solve was to isolate the tertiary phosphine from the numerous bye products, and this we foresaw would be no easy task, as all the operations would have to be performed in closed vessels and in an inactive gas. We scarcely hoped to be able to purify the phosphine by distillation, as it would almost certainly have a boiling point higher than that of triphenyl phosphine, which distils above 360°. The only available plan for its purification appeared to be crystallisation from alcohol. Accordingly, we constructed an apparatus for liberating the phosphine, and crystallising it from alcohol in hydrogen. (Fig. 2 of the Plate.)

Experiment 1.—Twelve sealed tubes, each charged with 16 grms. phosphonium iodide, 12 grms. benzyl chloride, and 4 grms. zinc oxide, were heated for six hours at 120°. Their contents were then transferred, as we have described on p. 541, to a flask, and the primary phosphine liberated by water and steam and distilled off. The residual brown resinous mass was steamed three times with water, and was then transferred to the flask A, and drained from water as far as possible. 50 grms. of potash were dissolved in 400–500 c.c. of alcohol; the flask A connected with the condenser, filled with hydrogen, and the potash solution added through C. D was then closed (with an india-rubber tube and a glass rod), and C left open for the escape of hydrogen. The mixture in A was then boiled for about three hours, during which a gentle stream of hydrogen was allowed to flow through the apparatus. C was now closed. D connected with E, and pushed down so that its end was at the bottom of A. The hydrogen thus forced the liquid into F (previously filled with the gas), when it was filtered into H. As it cooled crystals separated, but in addition an oily liquid also. After the lapse of some time H was closed by the pinchcock G, F disconnected, the ends of K and I closed, and H inverted. The alcoholic mother-liquors were separated from the crystals and oily liquid by attaching K to the hydrogen generator, and opening G, when they were forced out. The crystals and oily liquid were washed twice with water added through G. Next, after draining off the water, alcohol was run in and the crystals boiled with it, while a stream of hydrogen passed. On cooling both the crystals and oily liquid separated out again. The mother-liquors were drained off as before, and the crystals and oil dried in a stream of hydrogen (H being placed in boiling water).

An attempt was then made to separate the phosphine by distillation *in vacuo*, but without success. A little liquid passed over at first, but free phosphorus soon separated, and the temperature suddenly rose above 360°, with complete decomposition.

There had remained in the funnel F, in this experiment, a considerable quantity of a dirty oily liquid mixed with some crystals. It was washed two or three times with water, and was then examined.

(1) A portion mixed with iodide of methyl soon reacted, the mixture grew very hot and entered into ebullition, and after a short time an oily liquid resulted.

(2) Another quantity was mixed with crystallised iodide of benzyl, when a good deal

of heat was also developed, sufficient indeed to cause the water mechanically mixed with the product to boil. On cooling the product partly solidified. By recrystallising it from alcohol several times, colourless rhombohedral crystals were obtained, identical in form with tetrabenzyl phosphonium iodide, and having a melting point of 189°·5 (corr.) (that of the pure iodide being 189°).

These results pointed to the conclusion that after all tribenzyl phosphine is not a solid, but an oily liquid, which is sparingly soluble in alcohol, and that the spontaneous oxidation and heating of the crystalline cake which we have mentioned was due to the oxidation of liquid tribenzyl phosphine adhering to the solid oxide. In our next experiment we proceeded somewhat differently.

Experiment 2.—The contents of twelve sealed tubes were steamed, &c., and 30 grms. of crude primary phosphine obtained. The viscous residue was twice steamed with fresh quantities of water to remove the hydracids and zinc salts. It was then boiled in the flask A with 50 grms. of caustic potash and about 300 c.c. of alcohol for an hour. The tube D was now pushed down below the alcholic solution, while L was connected with a condenser and the condenser B removed, and a cork substituted for it. Steam was next blown through D until all the alcohol was distilled off and a good deal of water had condensed in A. At the bottom of this was a layer of oxide of zinc, while above it an oily layer floated. The whole was allowed to cool in a current of hydrogen, when the oily layer solidified. A was now inverted, and a current of cold water run in through D, and allowed to run out through L. By this means the solidified oily matter was thoroughly washed without coming in contact with air, and freed from potash and oxide of zinc. Experiments tried with it showed that it reacted energetically with iodide of benzyl, giving tetrabenzyl-phosphonium iodide, also that it dissolved for the greater part in a hot solution of hydriodic acid of constant boiling point, and the solution after filtration through asbestos deposited a bulky crystalline precipitate. It was also found that ether dissolved the greater portion of the solidified oil, but left an insoluble crystalline solid.

We therefore treated the whole of the solidified oil with ether, and filtered the solution from the solid crystalline mass remaining. The latter, when extracted with spirit and the solution crystallised, gave oxide of tribenzyl phosphine, which was identified by its melting point, 215°–215°·5, and other properties.

Now as all the operations had been conducted out of contact with air, this substance could not have been formed by the oxidation of tribenzyl phosphine. We shall consider its probable origin later on.

We decided to precipitate the ethereal solution with gaseous hydriodic acid, and to examine the crystalline hydriodate which we anticipated would be that of the tertiary phosphine. In a preliminary experiment, we easily obtained a bulky crystalline precipitate. This, after washing with ether, was dissolved in hot solution of hydriodic acid, the solution filtered through asbestos, and allowed to cool, when a colourless bulky crystalline precipitate formed. This was thrown into a funnel plugged with glass wool, then drained on a plate of unglazed porcelain, and placed in a desiccator to dry, but it became so brown from separated iodine that it was not deemed advisable to analyse it. It was decomposed with a hot solution of caustic potash, when an oily liquid resulted, which was washed with water. Some of this, when exposed to the air and warmed, gradually became crystalline, and the crystals when recrystallised from alcohol had the appearance of oxide of tribenzyl phosphine. Another portion, when mixed with crystallised iodide of benzyl, evolved heat, and the product when recrystallised from alcohol separated in the characteristic form of tetrabenzyl phosphonium iodide, and had the melting point 189° C. After these preliminary experiments, it was decided to precipitate the remainder of the ethereal solution with hydriodic acid gas; but as the ethereal solution contained a little water, fractional precipitation was resorted to, as we considered it probable that the first portions of the precipitated hydriodate would carry down the whole of the water. This surmise was fully borne out by experiment, for on passing hydriodic acid through the solution a quantity of a slimy white precipitate separated, and on filtering from this and passing hydriodic acid through the filtrate, a pure white flocculent precipitate was obtained, which was (after the solution had been saturated) thoroughly washed with dry ether, and then dried *in vacuo*. On analysis, the following numbers were obtained :—

Analysis.

(1) 1·0223 required 26 c.c $\frac{n}{10}$ $AgNO_3$ = 0·3302 I = 32·29 per cent.

(2) 0·5028 „ 12·3 c.c $\frac{n}{10}$ „ = 0·15621 I = 31·06 „

		Found.	Calculated for $(C_7H_7)_2HP.HI$	Calculated for $(C_7H_7)_3P.HI$
Iodine, . .	(1)	31·06	37·13	29·39
„ . .	(2)	32·29	...	...

The above analyses indicated, in our opinion, that the compound was a mixture of the hydriodates of dibenzyl phosphine and tribenzyl phosphine, a view of its composition which was rendered the more probable from the experiments described on p. 568 on the action of iodide of benzyl on the primary phosphine, which were made almost at the same time. We therefore decided to obtain a fresh and larger quantity of the hydriodates.

Experiment 3.—The contents of twelve sealed tubes were treated exactly as in experiment 2, and an ethereal solution obtained of the "solidified oil."

The bulk of this was treated with gaseous hydriodic acid, when a large quantity of a white precipitate was formed. An attempt was made to saturate the solution with hydriodic acid, but unfortunately the ether itself was rapidly attacked, yielding water and iodide of ethyl, with the result that the hydriodates of the phosphines were partly dissolved and a slimy mass obtained, which we could not dry nor do anything with.

Some of the ethereal solution of the cake of crude phosphines was mixed with a filtered solution of sulphur in bisulphide of carbon, when much heat was evolved, and a dense white precipitate formed. This was thrown into a filter, and then washed about six times with ether. Then, to remove any sulphur, it was boiled with chloroform (in which very little dissolved), thrown into a filter, and washed with chloroform. It was then dried and analysed.

Analysis.

$$0{\cdot}4248 \text{ gave } \begin{cases} 1{\cdot}1443\ \mathrm{CO_2} = 0{\cdot}312082\ \mathrm{C} = 73{\cdot}46 \text{ per cent.} \\ 0{\cdot}2514\ \mathrm{H_2O} = 0{\cdot}027904\ \mathrm{H} = 6{\cdot}57 \quad ,, \end{cases}$$

	Obtained.	Calculated for $(C_7H_7)_3PS$
Carbon, . . .	73·46	75·00
Hydrogen, . . .	6·57	6·25

The compound was evidently not pure, but as it was insoluble in alcohol, and only sparingly soluble in chloroform, no method of purification suggested itself immediately. Eventually it was found that it would be recrystallised from boiling glacial acetic acid, in which it is slightly soluble, crystallising as the solution cools in tufts of needles. Some of the product was thus recrystallised several times and analysed.

Analysis.

$$0{\cdot}1792 \text{ gave } \begin{cases} 0{\cdot}1089\ \mathrm{H_2O} = 0{\cdot}0121 \quad \mathrm{H} = 6{\cdot}75 \text{ per cent.} \\ 0{\cdot}4883\ \mathrm{CO_2} = 0{\cdot}1331727\ \mathrm{C} = 74{\cdot}31 \quad ,, \end{cases}$$

	Obtained.	Calculated for $(C_7H_7)_3PS$
Carbon, . .	74·31	75·00
Hydrogen, . .	6·75	6·25

Sulphide of tribenzyl phosphine fuses at 276° (corr.), and darkens on exposure to light. It is evidently difficult to purify.

Experiment 4.—The contents of eleven sealed tubes were treated as before, and an ethereal solution obtained of the "solidified oil." This was filtered and distilled to dryness in a current of carbonic anhydride. The residue consisted of about 50 c.c. of a yellow fluorescent liquid which was very viscous. It was mixed with about 500 c.c. of pure dry benzol, in which it easily dissolved on agitation. On leaving this mixture undisturbed (the flask being filled with carbonic anhydride to prevent oxidation) a bulky crystalline precipitate formed after some hours. This we at first took to be oxide of tribenzyl phosphine, but subsequent investigations proved it to be a totally different substance. We shall refer to it later as the "Insoluble crystalline body."

The benzol solution filtered from it was saturated with dry hydriodic acid, when an abundant white crystalline precipitate of the phosphine hydriodates was formed. This was collected on a cloth filter, and washed two or three times with dry ether. The mass drained as far as possible from adhering ether by pressure between filter paper weighed 88 grms.

It was next boiled in a stream of hydrogen with solution of caustic potash as long as either benzol or ether passed over; the mixture allowed to cool, and the oily layer (after syphoning off the potash solution) mixed with ether. This latter did not, however, dissolve the whole product, but left a considerable quantity of a white slimy substance. The ethereal solution was filtered off, and distilled to dryness in a current of hydrogen. The residue thus obtained weighed from 20–30 grms.

It was submitted to distillation under diminished pressure, the distilling flask containing it being immersed in a bath of fusible metal. Average pressure during distillation 90 mm.; temperature of fusible metal, 260°–300° C.; temperature of liquid distilling over, 100°–180°. The distillation was stopped after about one-fifth of the total product had passed over, as signs of decomposition began to appear in the residue.

The distillate was a colourless liquid. The residue when cold, a fluorescent, viscous (almost solid) mass. The distillate had the following properties:—

(1) Exposed to the air it oxidised violently, and gave white fumes; it grew so hot that a vessel containing it could not be touched. A syrup resulted. This had an acid reaction, and dissolved for the greater part in potash solution, leaving a slight residue, which was viscous. On adding hydrochloric acid to the potash solution, no precipitate of dibenzyl phosphinic acid was produced. On adding sulphate of copper to the neutralised potash solutions, no precipitate was produced in the cold, but on warming, the characteristic precipitate of monobenzyl phosphinite of copper was thrown down.

(2) Treated with crystallised benzyl iodide, the mixture grew slightly warm, and from the product only a very small quantity of iodide of tetrabenzyl phosphonium could be obtained.

These results show that monobenzyl phosphine was contained in the distillate, and probably only minute quantities of di- or tribenzyl phosphine.

Our experiments so far, have undoubtedly shown that the semisolid mass which is left on digesting the sealed tube product with potash, &c., contains both the secondary and tertiary phosphines, but whence comes the primary phosphine? Provisionally, we must assume that it is derived from the destructive distillation of the secondary phosphine.

$$2(C_7H_7)_2P = (C_7H_7)PH_2 + (C_7H_7)_3P ,$$

and that the tertiary phosphine also is scarcely volatile without decomposition.

It was at all events proved that we need not attempt to isolate the secondary and tertiary phosphine by distillation, and that some other method must be devised.

Experiment 5.—The contents of twelve sealed tubes were treated as before with steam, and afterwards with potash, &c. The remaining semisolid cake of phosphines weighed about 97 grms.

The cake was treated with a considerable quantity of ether, and the residue (A) reserved for examination. The filtered ethereal solution, together with the ethereal washings from the insoluble matter, were left undisturbed for about sixteen hours, when a good deal of crystalline matter (B) was precipitated. On filtering from this, and adding an additional quantity of ether to the solution, more insoluble crystalline matter was precipitated. The addition of ether was continued until no further precipitation occurred.

The filtered ethereal solution was then boiled to dryness in a current of carbonic anhydride, when a yellowish liquid remained, which on cooling became semicrystalline. When perfectly dry it weighed 64·5 grms. It was examined as follows:—

(1) On adding ether, a good deal remained undissolved (probably "insoluble crystalline body").

(2) Six grms. of the crude product were mixed with 6 grms. of crystallised iodide of benzyl. On agitation the mixture grew excessively hot. When cold the mass was extracted with ether (to remove the excess of iodide of benzyl and any other impurities), then boiled with alcohol, and the solution allowed to crystallise. The resulting crystalline mass of crude iodide of tetrabenzyl phosphonium weighed when dry 5·5 grms., which with the quantity of substance operated upon correspond with 53 per cent. of tribenzyl phosphine.

The crude iodide was purified by recrystallising it four times from alcohol.

Analysis.

0·3956 gave 0·1758 AgI = 0·095006 I = 24·01 per cent.

	Obtained.	Calculated for $(C_7H_7)_4PI$
Iodine, . .	24·01	24·32

To identify the iodide with absolute precision some of it was converted into acid sulphate (by boiling with diluted sulphuric acid), and an analysis made of the purified product.

Analysis.

0·5726 grms. gave 0·2679 $BaSO_4$ = 0·1103793 SO_4 = 19·27 per cent.

	Found.	Calculated for $(C_7H_7)_4P.HSO_4$
SO_4	19·27	19·51

(3) 5·6755 grms. were exposed to the air in a platinum dish, but no heat was developed. Weak baryta solution was then added, and the mixture evaporated to dryness: redissolved several times with fresh quantities of water and evaporated to dryness, in order to ensure complete oxidation. The residue was then boiled with water, the solution filtered and mixed with hydrochloric acid, but no definite precipitate of dibenzyl phosphinic acid could be obtained.

However, on boiling the residue with caustic potash, then extracting with water and acidulating the solution with hydrochloric acid, a very bulky precipitate of dibenzyl phosphinic acid was obtained, which weighed when washed and dried 1·1300 grms.* The insoluble residue from the potash treatment was oily. It was extracted with ether several times, and the ethereal solution evaporated to dryness: the residue weighed 0·9401 grms. The residue from the ether treatment was boiled with alcohol, the solution filtered and evaporated to dryness, when 2·4420 grms. of crude oxide of tribenzyl phosphine were obtained.

There remained after the treatment with alcohol 1·1233 grms. of insoluble matter, which was proved to contain the substance we have called above "Insoluble crystalline body."

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* At first we thought it possible that the dibenzyl phosphinic acid might have owed its origin to the action of the potash solution on oxide of tribenzyl phosphine (see p. 558). But that this reaction does not occur when oxide of tribenzyl phosphine is boiled with caustic potash solution, we proved by an actual experiment.

Tabulating the above results, we obtained by oxidising 5·6755 grms. of the crude product,

Crude dibenzyl phosphinic acid, ...	1·1300 grms.
Substances soluble in ether, ...	·9401 „
Crude oxide of tribenzyl phosphine, ...	2·4420 „
Substances insoluble in alcohol (containing " insoluble crystalline body "),	1·1223 „
	5·6344

The weight of dibenzyl phosphinic acid corresponds roughly with 20 per cent. of dibenzyl phosphine, and that of the oxide of tribenzyl phosphine with about 50 per cent. of tribenzyl phosphine. The experiment confirms former results, and shows that the product is a complex mixture, but is composed mainly of the two phosphines.

Having thus definitely proved that the two phosphines are produced in HOFMANN'S reaction, we had next to devise a method for separating them from each other and for isolating them in the pure state. We had already tried fractional distillation, and had failed in accomplishing the desired object; we had also tried, though without any large measure of success, to isolate the tertiary phosphine by crystallising it from alcohol. The experiment had indeed left us somewhat in doubt as to whether it is a solid or a viscous liquid. At the time, however, we had only a very crude and impure product at our disposal, containing a large quantity of oxide of tribenzyl phosphine; whereas now we had a product, comparatively speaking, pure and free from that substance. As no other method could be devised for isolating the tertiary phosphine, we decided once more to see whether it was a solid substance capable of being crystallised from alcohol. Accordingly the remainder of the product, some 50 grms., was first treated with a somewhat large quantity of ether, when a considerable quantity of " insoluble crystalline body " was obtained. It was perfectly colourless, and weighed when dry 2 grms. The ethereal extract was filtered from this, and again diluted with ether, to see whether any more insoluble crystalline matter would be precipitated, but the solution remained clear. The ethereal solution was then distilled to dryness in a current of carbonic anhydride, and alcohol added to the hot solution in such quantity that the mixture when boiled gave a clear solution, with only a few oily drops. This mixture (contained in a flask full of carbonic anhydride) deposited on cooling a good deal of a viscous liquid, and then after about twenty-four hours' rest a considerable quantity of minute colourless crystals separated, which when examined with a lens appeared to be thick quadratic plates.

The following experiments were made with portions of the crystals :—

(1) Warmed with crystallised iodide of benzyl, reaction occurred, and iodide of tetrabenzyl phosphonium was obtained.

(2) The crystals seemed to be volatile without decomposition.

(3) They were soluble in ether, but on exposure to air the solution grew turbid rapidly, and needle-shaped crystals separated out, which had the characteristic form of oxide of tribenzyl phosphine, and which gave its characteristic compound when treated with a solution of bromine in acetic acid.

(4) A quantity of the crystals were removed, quickly dried from adhering oily matter by pressure between filter-paper, then dissolved in bisulphide of carbon and mixed after filtration with a solution of sulphur in bisulphide of carbon. An immediate precipitate of fine needles occurred. These were filtered off, dried by pressure, then recrystallised from boiling glacial acetic acid, in which they are only sparingly soluble. On cooling nearly the whole of the compound separated in tufts of colourless fine needles. After a single recrystallisation from acetic acid, the corrected melting point of the substance was found to be 276° C. An organic analysis gave the following results:—

Analysis.

$$(1)\quad 0{\cdot}2921 \text{ gave} \begin{cases} 0{\cdot}7935\ CO_2 = 0{\cdot}216409\ C = 74{\cdot}08 \text{ per cent.} \\ 0{\cdot}1704\ H_2O = 0{\cdot}018933\ H = \ 6{\cdot}48 \quad ,, \end{cases}$$

$$(2)\quad 0{\cdot}2654 \text{ gave} \begin{cases} 0{\cdot}7180\ CO_2 = 0{\cdot}195818\ C = 73{\cdot}78 \text{ per cent.} \\ 0{\cdot}1558\ H_2O = 0{\cdot}017311\ H = \ 6{\cdot}52 \quad ,, \end{cases}$$

	Obtained.		Calculated for $(C_7H_7)_3PS$
	(1)	(2)	
Carbon, . . .	74·08	73·78	75·00
Hydrogen, . . .	6·48	6·52	6·25

We have already mentioned that sulphide of tribenzyl phosphine is very difficult to purify. Its melting point we had previously found to be 276.

(5) Another quantity of the crystals, removed from the upper portions of the crystalline cake, and which looked pure and free from the oily matter, was very carefully removed and rapidly thrown into a filter placed in a funnel in a deep beaker full of carbonic anhydride. They were then several times washed with alcohol and the filter containing them rapidly transferred to a wide glass tube full of carbonic anhydride, which was then plugged with a perforated cork, and a stream of dry carbonic anhydride passed through it, while the tube was gently warmed. By these means the crystals were washed and dried with a minimum chance of oxidation. The dry crystals were then rapidly transferred to a small tube full of carbonic anhydride, and a combined organic analysis and phosphorus determination made by the method already alluded to.

Analysis.

$$0{\cdot}3634 \text{ gave} \begin{cases} 1{\cdot}0823\ CO \quad = 0{\cdot}295172\ C = \ 81{\cdot}22 \text{ per cent.} \\ 0{\cdot}2455\ H_2O \quad = 0{\cdot}027277 H = \ 7{\cdot}5 \quad ,, \\ 0{\cdot}1352\ Mg_2P_2O_7 = 0{\cdot}037758\ P = 10{\cdot}39 \quad ,, \end{cases}$$

	Obtained.	Calculated for $(C_7H_7)_3P$
Carbon, . . .	81·22	82·89
Hydrogen, . . .	7·50 *	6·90
Phosphorus, . . .	10·39	10·19

The numbers obtained in the above analysis are sufficiently close to those calculated for tribenzyl phosphine, to prove that we had at last succeeded in isolating that substance, if not in an absolutely pure condition.

In another experiment we still further identified the tertiary phosphine by obtaining

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* The hydrogen is no doubt too high, as the combustion tube was not warmed, and cold oxide of copper was used—both no doubt containing hygroscopic moisture.

its selenium compound. To produce this substance some of the ethereal solution, obtained as we have described above, was mixed with bisulphide of carbon and freshly precipitated selenium. The selenium rapidly disappeared, and a white precipitate was formed. This was boiled with alcohol, in which it was insoluble, then dissolved in a large quantity of boiling glacial acetic acid, the solution filtered from excess of selenium, and allowed to cool, when beautiful silky needles separated, which were colourless. They melted at 256°·5, and on analysis gave the following numbers :—

Analysis.

$$0{\cdot}2786 \text{ gave } \begin{cases} 0{\cdot}1487\ H_2O = 0{\cdot}016522\ H = \ 5{\cdot}93 \text{ per cent.} \\ 0{\cdot}6800\ CO_2 = 0{\cdot}185454\ C = 66{\cdot}56 \quad ,, \end{cases}$$

	Obtained.	Calculated for $(C_7H_7)_3PSe$
Carbon, ...	66·56	65·96
Hydrogen, . . .	5·93	5·49

The selenium compound decomposes slowly on exposure to light.

Action of the Haloid Compounds of Benzyl on the Primary Phosphine.

Action of Benzyl Iodide on Monobenzyl Phosphine.—We investigated this action chiefly with the view of obtaining dibenzyl phosphine, but also with the object of obtaining from it tribenzyl phosphine, by the further action of benzyl iodide.

We naturally anticipated that if the reaction between the two substances occurred at all it would be of the usual kind, and would at once give rise to a simple product. Experiment has, however, shown that such is not the case, as the following results show.

Experiment 1.—6 grms. of crystallised benzyl iodide * were placed in a tube, which was then filled with carbonic anhydride, and 5 grms.† of the primary phosphine were added. The tube was sealed and the mixture agitated, when the benzyl iodide liquefied, and a turbid fluid resulted (probably from a trace of water in the benzyl iodide). After about ten minutes the mixture solidified to a snow-white crystalline mass, but no sensible rise of temperature occurred. The tube was opened after two days, and the hard solid mass which it contained broken up, and treated with washed and distilled ether. The ether was, however, not sufficiently dry, and as a consequence the mass became pasty from absorption of water. It was then thrown into a filter, which was placed in a desiccator *in vacuo*. It soon became hard and brown at the edges.

It was found that boiling chloroform dissolved the product, and that crystals—presumably of hydriodate of dibenzyl phosphine—separated on cooling. Accordingly, the whole was dissolved in boiling chloroform, but on cooling only a very small quantity of crystalline matter was obtained.

Moreover, on evaporating off the chloroform, no solid product remained, but only a viscous liquid, from which we did not succeed in obtaining any definite substances.

Experiment 2.—12 grms. of the primary phosphine of boiling point 170°–190° C.

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* Prepared by a very simple method discovered by us, namely, by saturating benzyl alcohol with dry hydriodic acid and washing the product with water when it solidifies. The yield appears to be quantitative.

† A large excess of the primary phosphine was therefore employed, as the molecular weight of C_7H_7I is 218, while that of $C_7H_7PH_2$ is 124 ; so that, roughly speaking, 2 parts of the former is required for 1 of the latter.

were mixed with 70 c.c. of absolutely dry ether.* 22 grms. of pure iodide of benzyl were dissolved in 150 c.c. of dry ether, and the two solutions mixed. A colourless liquid resulted, which, with the exception of growing slightly turbid, did not suffer any noticeable change after twenty-four hours.

The ether was therefore distilled off. When most of it had passed over, the viscous residue began to crystallise rapidly, and a brisk action appeared to occur, *a considerable quantity of hydriodic acid coming off.* The flask was removed from the water-bath in which it had been heated, and when cold a quantity of dry ether was added to its contents, which consisted partly of crystalline matter, but chiefly of a brown viscous mass. The latter, in contact with the ether, gradually became white and crystalline, eventually completely so. This crystalline product was pounded up, and carefully washed with dry ether.

Some of the product thus purified was boiled with water, and yielded an oily liquid, which on cooling partly solidified. This was treated with ether, when a white crystalline solid remained, and on crystallising it from alcohol it had the characteristic form of iodide of tetrabenzyl phosphonium. The whole of the product was treated with water and steam in a current of hydrogen to decompose the hydriodates and to liberate the phosphines. No primary phosphine passed over. The water when cold was poured off, and the semisolid mass again steamed with fresh water, and this poured off when cold. Next the mass was shaken with ether and the solution filtered from undissolved crystalline matter. The latter, on recrystallisation, had the characteristic form of oxide of tribenzyl phosphine.

The ethereal solution on keeping deposited a good deal of crystalline matter. After a day or two it was decanted from this, and boiled to dryness in a stream of hydrogen. A colourless liquid remained, which gradually deposited crystals. The whole was distilled *in vacuo*, the distilling flask being immersed in a fusible metal bath. Pressure about 190 mm.; temperature of metal bath, 260°–270°. A fair quantity of liquid distilled, its vapour having a temperature during distillation of 120°–125°. The residue decomposed somewhat. (We discuss the properties of this distillate on p. 570.)

Experiment 3.—22 grms. of crystallised iodide of benzyl were placed in a flask full of carbonic anhydride, and 12 grms. of the primary phosphine (boiling point 170°–190°) added. The iodide of benzyl dissolved on agitation, then action gradually set in, and after some hours the mixture became solid. After about twenty-four hours, some of the solid product was removed, pounded up in a mortar, and washed six times by decantation with dry ether, until a drop of the washings left no appreciable residue on evaporation. It was then placed *in vacuo*, and formed when dry a colourless powder.

Analysis.

0·4428 gave 0·3032 AgI = 0·163857 I = 37·00 per cent.

	Obtained.	Calculated for $(C_7H_7)_3PH.HI$
Iodine, . . .	37·0	37·13

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* Distilled from phosphoric anhydride.

The rest of the product was washed with dry ether, and then decomposed by potash in a flask through which a stream of hydrogen flowed. A current of steam was then passed to complete the decomposition, and to drive off any volatile matters. The aqueous solution was then decanted, and the oily liquid reserved for examination.

(1) On mixing some of this liquid with iodide of benzyl in excess, much heat was disengaged, and on cooling a viscous mass resulted. This boiled with caustic potash gave a solid substance, and on crystallising the latter from alcohol two sets of crystals were obtained, one having the characteristic form of iodide of tetrabenzyl phosphonium, the other that of tribenzyl phosphine oxide.

(2) The rest of the oily liquid was left for some time and became semisolid. On treating this with ether, a white crystalline solid remained undissolved, which was apparently oxide of tribenzyl phosphine. The ethereal solution filtered from this was distilled off in a stream of hydrogen, and left about 10 grms. of a colourless liquid, which was distilled *in vacuo*.

It behaved in exactly the same manner as described with the corresponding liquid obtained in Experiment 2; that is to say a little liquid distilled over—say about one-third of the original quantity operated on—and the residue then showed unequivocable signs of decomposition with separation of red phosphorus. The distillate was mixed with the corresponding distillate described under Experiment 2, and the mixture submitted to an oxidation experiment conducted quantitatively.

1·3995 grms. were weighed out in a sealed tube and transferred to a beaker. Dense white fumes were produced at first, and a syrupy liquid resulted. After twelve hours, baryta solution was added, and the mixture evaporated to dryness several times, with addition of water. The aqueous solution was then filtered and mixed with hydrochloric acid, when a crystalline precipitate of dibenzyl phosphinic acid was produced, which weighed when dry 0·0912 grms. The residue insoluble in water was treated with a little hydrochloric acid to remove carbonate of barium, then washed and dried. Its weight amounted to 0·1098 grms. It consisted mainly at all events of oxide of tribenzyl phosphine.*

The filtrate from the dibenzyl phosphinic acid and the hydrochloric acid washings from the oxide of tribenzyl phosphine were evaporated on a water-bath to drive off excess of hydrochloric acid, the residue neutralised with baryta, and again evaporated to dryness, and extracted with alcohol. The alcoholic extract when dry weighed 0·3786 grms. This residue gave all the characteristic reactions of benzyl phosphinite of barium, and was considered to be that substance. The residue from the alcoholic extraction was dissolved in water, and the solution boiled, when the characteristic crystals of benzyl phosphinate of barium were precipitated.

These results prove that the distilled liquid was chiefly monobenzyl phosphine mixed with smaller quantities of dibenzyl and tribenzyl phosphine.

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* The dibenzyl phosphinic acid was identified by its melting point (191°·5–192°) after recrystallisation. The oxide of tribenzyl phosphine by its characteristic crystalline form and by the production of its crystalline compound with bromine in acetic acid.

The percentage weights of the oxidised products referred to the weights of the original liquid are as follows :—

From—

$(C_7H_7)PH_2$	$\left\{\begin{array}{l}(C_7H_7)PH_2O_2\\(C_7H_7)PH_2O_3\end{array}\right.$	18·8 ?
$(C_7H_7)_2PH$	$(C_7H_7)_2PHO_2$	6·53
$(C_7H_7)_3P$	$(C_7H_7)_3PO$	7·84

Experiment 4.—22 grms. of benzyl iodide were placed in a flask, and the latter filled with carbonic anhydride, and 12 grms. of the phosphine (several times rectified and boiling from 175°–185° C.) were then added. The mixture was very slightly warmed, so as to melt the iodide of benzyl, and then agitated to ensure thorough mixing.

Although the crystallised benzyl iodide had been dried as far as possible by pressure between filter-paper, it must have been wet, as small drops of water were distinctly visible in the mixture.

The flask containing it was loosely corked, and set aside. In about ten minutes solidification commenced and proceeded gradually, but suddenly, after the lapse of about twenty minutes more, the partially solidified mass grew hot, and emitted a cloud of hydriodic acid. It was left at rest for some hours, and had by that time become brown at the edges. It was now removed from the flask, pounded up, and repeatedly washed with ether until nothing further was extracted. The product consisted of a snow-white powder. It was dried by pressure between filter-paper and finally *in vacuo*.

The following experiments were made with it :—

(1) 4·693 grms. were mixed with caustic potash solution, and the mixture evaporated to dryness on a water bath; redissolved in water, again evaporated, and so on two or three times to ensure complete oxidation. The residue was then treated with water, and the solution filtered from the colourless insoluble matter which remained.

The solution and washings were then precipitated with hydrochloric acid, when an abundant precipitate of dibenzyl phosphinic acid separated which, when washed and dried, weighed 1·304 grms. It was identified by its melting point, which after one crystallisation from alcohol, was found to be 193°.

The insoluble matter was dried, and weighed 0·816 grms. After one crystallisation from alcohol, it had melting point of 211°, that of oxide of tribenzyl phosphine being 215°·5.

Calculating from these numbers the quantities of dibenzyl phosphine hydriodate and tribenzyl phosphine hydriodate in the original product, the first would amount to about 38 per cent., the second to about 23 per cent.

(2) We wished to ascertain with certainty whether the product contained, in addition to the secondary and tertiary compound, the quarternary iodide also. As the latter gives the oxide when boiled with potash solution, we decided to decompose the product with water. Accordingly, the remainder of it was placed in a small separating funnel, and

steamed for about an hour, while a current of carbonic anhydride passed at the same time to prevent oxidation.

The oily liquid which resulted was washed two or three times with water, afterwards with a dilute and cold potash solution, and then shaken up with ether. A white powder remained undissolved, which was dissolved in a little hot alcohol. The solution deposited on cooling crystals having the characteristic form of tetrabenzyl phosphonium iodide. But we did not obtain sufficient for investigation.

The results of the above experiments are curious and interesting. We think that only one conclusion can be drawn from them, namely, that the primary phosphine acts upon iodide of benzyl in the same manner that ammonia does upon an alkyl iodide, the three following reactions occurring:—

$$(1)\quad (C_7H_7)PH_2 + C_7H_7I = (C_7H_7)_2HPHI$$

$$(2)\quad (C_7H_7)PH_2 + 2C_7H_7I = (C_7H_7)_3P.HI + HI$$

$$(3)\quad (C_7H_7)PH_2 + 3C_7H_7I = (C_7H_7)_4PI + 2HI\,.$$

Thus confirming the results of our investigation of HOFMANN'S sealed tube reaction (see p. 566).

The only other explanation, viz., that the primary phosphine used contained both the secondary and tertiary bases as impurities, is, we venture to think, untenable, for it had been repeatedly rectified, and the boiling points of di- and tri-benzyl phosphine, as we have shown, are at very high temperatures—so high indeed that they decompose almost completely when distilled. Moreover, in our experiments on the oxidation of the primary phosphine, no dibenzyl phosphinic acid nor tribenzyl phosphine oxide were obtained, and we should certainly have noticed them had they been produced. These views have been materially strengthened by our experiments on the action of chloride of benzyl on the primary phosphine.

Action of Chloride of Benzyl on Monobenzyl Phosphine—Experiment 1.—Five grms. of the primary phosphine (boiling point 175°–185°) were placed in a tube previously filled with carbonic anhydride, and 5 grms. of chloride of benzyl were added. The tube was then sealed and left for a night, but no signs of any reaction having occurred were apparent. The tube was then heated for about six hours at 130° C. Its contents then consisted of a somewhat viscous liquid, and on opening pressure was observed.

A quantitative oxidation experiment was made with the product. 4·3255 grms. were evaporated with water in a dish. It fumed, and the mass quickly grew crystalline. The product was crystallised once from alcohol, and then had a melting point of 213°, and all the appearance of oxide of tribenzyl phosphine. It weighed 0·8373 grms. The alcoholic mother-liquors solidified when warmed with baryta solution, and the solid mass thus obtained appeared to consist of crude tribenzyl phosphine oxide also. It weighed when dry 0·8623 grms. The aqueous extracts and the baryta solution filtered from the crude oxide *gave scarcely a trace of dibenzyl phosphinic acid,* but they gave the reactions of benzyl phosphinous acid.

These results show that the product of the reaction yielded nearly 40 per cent. of its weight of tribenzyl phosphine oxide, and contained some benzyl phosphinous acid.*

Experiment 2.—This experiment was made chiefly with the view to ascertaining whether the reaction gives rise to a phosphonium salt in addition to the tertiary phosphine. 2 grms. of the phosphine and 2 grms. of chloride of benzyl were heated to 160° C. for five or six hours. The tube then contained a syrupy liquid and some amorphous phosphorus. On opening it there was very decided pressure from phosphuretted hydrogen (proved by its action on nitrate of silver). The viscous liquid fumed powerfully from escape of hydrochloric acid, and on adding water all the phenomena described in Experiment 1 were reproduced. After thorough oxidation the solid mass was boiled with water, and the solution on cooling gave the characteristic long needles of chloride of tetrabenzyl phosphonium. These, after repeated recrystallisation from water, had a melting point of 228°·5 C.—exactly that of the pure chloride—and we estimated that over 1 grm. had been formed.

The residue insoluble in water was extracted with potash, the solution filtered, and treated with hydrochloric acid, when *no trace of dibenzyl phosphinic acid was precipitated.* But on boiling the insoluble residue with alcohol plenty of tribenzyl phosphine oxide was obtained.

The above experiments fully confirm the results of those which we made with benzyl iodide. They show that the action of the haloid derivatives of benzyl on the primary phosphine varies not only with the particular halogen present, but also with the conditions under which the action occurs. Thus, when benzyl iodide is employed at ordinary temperatures, the secondary phosphine is the chief product, while a considerable quantity of the tertiary phosphine is also formed, and only a small quantity of the phosphonium salt, but we suspect that at higher temperatures the proportions of these three products would not be the same.

With benzyl chloride no action occurs at ordinary temperatures, but under the influence of heat a reaction takes place, the tertiary phosphine and the phosphonium chloride being formed, while if the temperature is high the phosphonium salt is the chief product, and no secondary phosphine is produced at all.

Properties of Dibenzyl and Tribenzyl Phosphine.—Although we have not isolated the first of these in the pure state, and have only obtained the second in small quantities, we have so often examined a mixture of the two that we are enabled to state with probable correctness what their chief properties are.

Dibenzyl Phosphine.—A liquid which cannot be distilled even *in vacuo* without considerable decomposition. This decomposition gives rise to the primary and tertiary bases,

$$2(C_7H_7)_2HP=(C_7H_7)PH_2+(C_7H_7)_3P\,.$$

Dibenzyl phosphine combines with hydriodic acid, and probably with other hydracids,

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* The rest of the product was evaporated down with aqueous potash, and also yielded oxide of tribenzyl phosphine in abundance, some benzyl phosphinous acid, but scarcely a trace of dibenzyl phosphinic acid.

forming solid crystalline compounds which are decomposed by water. It forms an amorphous (?) orange-coloured chloroplatinate.

It probably oxidises in the air, and there is some reason for believing that it then gives rise to an oxide $C_{14}H_{15}PO$ (see p. 585). It certainly oxidises in contact with warm caustic potash solution and air, the product of its oxidation being then dibenzyl phosphinic acid, $C_{14}H_{15}PO_2$.

It is readily soluble in ether and benzol, but is sparingly soluble in alcohol.

Tribenzyl Phosphine.—A solid crystalline substance of high boiling point. Possibly volatile *in vacuo* without decomposition or with only partial decomposition. It combines with hydracids, forming solid compounds which are decomposed by water. Its chloroplatinate is amorphous and buff-coloured.

It oxidises in the air and fumes when warmed, spontaneous oxidation occurring very readily, the product being the oxide $(C_7H_7)_3PO$. It also combines energetically with sulphur and selenium to give colourless crystalline compounds, which are insoluble or very sparingly soluble in water, alcohol, ether, bisulphide of carbon, and chloroform, but are soluble in boiling glacial acetic acid, from which they may be crystallised. Both compounds decompose on exposure to light, and have the formulæ $(C_7H_7)_3S$ and $(C_7H_7)_3Se$, respectively. Tribenzyl phosphine combines energetically with benzyl iodide to give tetrabenzyl phosphonium iodide.

We may mention that attempts have been made to obtain tribenzyl phosphine by several other methods, but without success. Among them were—

(1) The action of chloride of benzyl on phosphide of sodium.*

(2) The action of benzyl alcohol on phosphonium iodide in a sealed tube. This action has also been studied by LEDERMANN.† Apparently only the phosphonium iodide is produced.

(3) The action of sodium on a mixture of chloride of phosphorus and benzyl bromide. It was by a corresponding method that MICHAELIS‡ obtained triphenyl phosphine. We found that no action occurred.

(4) The action of sodium on tetrabenzyl phosphonium chloride.§

(5) The action of heat on chloride of tetrabenzyl phosphonium.||

COMPOUNDS OF TETRABENZYL PHOSPHONIUM.

Salts of tetrabenzyl phosphonium have been obtained by the following methods:—

The chloride, (1) by the action of chloride of benzyl on phosphide of sodium (LETTS and COLLIE).¶ The method is an excellent one, being easily carried out, and giving a good yield of the compound.

(2) It is also formed by the action of chloride of benzyl on the primary phosphine (p. 573).

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* LETTS and COLLIE, these *Transactions*, xxx. part 1.

† LEDERMANN, *Berichte*, xxi. (1888) 405A.

‡ MICHAELIS, *Berichte*, xv. (1882) 801A.

§ LETTS and COLLIE, *loc. cit.*

|| LETTS and COLLIE, *loc. cit.*

¶ LETTS and COLLIE, *loc. cit.*, p. 181.

The iodide (1), by the action of phosphonium iodide on benzyl alcohol (LEDERMANN),[*]

(2) By the union of tribenzyl phosphine with iodide of benzyl (p. 566).

(3) In small quantities by the action of iodide of benzyl on the primary phosphine.

The salts of the phosphonium are beautifully crystalline, and are readily obtained in a state of purity. All are soluble in alcohol and many in water; they are insoluble in ether. When heated they decompose as a rule, and in many cases give rise to perfectly definite products.

Chloride $(C_7H_7)_4PCl,2H_2O$.—Colourless salt crystallising from boiling water in long needles. It is sparingly soluble in cold water (100 c.c. of cold water dissolve about 0·35 grms.) and almost insoluble in dilute hydrochloric acid or common salt solution (traces may be detected in an aqueous solution by adding these reagents). The dried salt dissolves readily in alcohol, and the solution on slow evaporation yields beautiful colourless rhombic crystals of considerable size, which are anhydrous. The dried salt also dissolves readily in chloroform, and on spontaneous evaporation large crystals are also obtained, which grow opaque in the air from loss of chloroform. The crystals thus obtained contain one molecule of "chloroform of crystallisation." The anhydrous salt fuses at 228°·5 (corr.).

The chloride combines with chloride of platinum and some other metallic chlorides, giving insoluble or separately soluble compounds.

Chloroplatinate, $2(C_7H_7)_4PCl,PtCl_4$ (LETTS and COLLIE).—Obtained in minute orange-coloured crystals by mixing alcoholic solutions of the two chlorides. Almost insoluble.

Double Salt with Mercuric Chloride (LEDERMANN)—$(C_7H_7)_4PCl,HgCl_2,H_2O$.—Insoluble precipitate obtained like the chloroplatinate.

Double Salt with Stannic Chloride, $2(C_7H_7)_4PCl,SnCl_4$ (LEDERMANN).—Sparingly soluble crystalline compound obtained like the preceding salts.

Bromide, $(C_7H_7)_4PBr$, resembles the chloride, but is less soluble in water. It dissolves readily in alcohol, and crystallises from a mixture of alcohol and water in long silky needles. Melting point, 216°–217° C. (uncorrected).

Iodide, $(C_7H_7)_4PI$, is almost insoluble in water, and only sparingly soluble in alcohol. From a hot alcoholic solution it crystallises in small rhombic crystals.[†]

All the haloid salts appear to be decomposed completely when boiled with alkalies into the tertiary phosphine oxide and toluol,

$$(C_7H_7)_4PX + MOH = MX + (C_7H_7)_3PO + C_7H_8.$$

Acid Sulphate, $(C_7H_7)_4PHSO_4$, is most readily obtained by warming the chloride with oil of vitriol on a water-bath until hydrochloric acid ceases to come off, and then crystallising the product once or twice from boiling water. It is rather more soluble than the chloride, and crystallises in small rhombic or triclinic crystals. When boiled

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[*] LEDERMANN, *Berichte*, xxi. (1888) 405A.

[†] We are of opinion that when this compound is crystallised from alcohol, the crystals have the formula $2(C_7H_7)_4PI,C_2H_6O$.

with caustic baryta it is partly converted into the hydrate and partly into the tertiary phosphine oxide, and toluol,

$$(1)\quad (C_7H_7)_4PHSO_4+Ba(OH)_2=(C_7H_7)_4POH+BaSO_4+H_2O$$

$$(2)\quad (C_7H_7)_4PHSO_4+Ba(OH)_2=(C_7H_7)_3PO\ +BaSO_4+2H_2O+C_7H_8.$$

Treated with carbonate of barium, the hydrate *only* is obtained—

$$(C_7H_7)_4PHSO_4+BaCO_3=(C_7H_7)_4POH+BaSO_4+CO_2.$$

Normal Sulphate, $\{(C_7H_7)_4P\}_2SO_4$, $6H_2O$.—Obtained by decomposing a solution of the chloride with sulphate of silver. It crystallises from a hot concentrated solution in large rhombic plates.

Nitrate, $(C_7H_7)_4PNO_3$.—Long silky needles, soluble in water.

Chromate, $\{(C_7H_7)_4P\}_2CrO_4$?—Obtained by double decomposition from the chloride and chromate of silver. Small lemon yellow plates.

Acetate, $(C_7H_7)_4P(C_2H_3O_2)$.—Very soluble in water.

Chlorate, $(C_7H_7)_4P(ClO_3)$.—Crystallises in long needles from a moderately concentrated solution. When heated it puffs.

Picrate, $(C_7H_7)_4P\{C_6H_2(NO_2)_3O\}$ (LEDERMANN).—Obtained by mixing alcoholic solutions of the iodide and picric acid; the compound separating as the solution cooled in beautiful yellow crystals.

Hydrate, $(C_7H_7)_4P(OH)$.—Obtained best by the action of carbonate of barium on a solution of the acid sulphate. Very soluble even in cold water, and crystallises by slow evaporation in beautiful rhombohedral plates sometimes half an inch long. The crystals are transparent and highly refractive. The hydrate dissolves readily in alcohol, and the crystals obtained from the solution contain alcohol of crystallisation, their formula being $(C_7H_7)_4P(OH),C_2H_6O$. Solutions of the base have an alkaline reaction. They neutralise acids with formation of salts of the phosphonium. When heated the hydrate decomposes into the tertiary oxide and toluol,

$$(C_7H_7)_4POH=(C_7H_7)_3PO+C_7H_8.$$

THE BYE PRODUCTS FORMED IN HOFMANN'S SEALED TUBE REACTION.

In separating the benzyl phosphines from the products of HOFMANN'S sealed tube reaction we obtained a considerable number of bye products, among which were the following:—

(*A*). A crystalline substance precipitated on addition of hydrochloric acid to the potash solution which had been employed to extract the viscous mass containing tribenzyl phosphine, &c.

(*B*). A crystalline substance which separated spontaneously from the aqueous solution obtained by treating the contents of the sealed tubes with water.

(*C*). A crystalline zinc salt, also contained in the same aqueous solution.

(*D*). A crystalline solid of low melting point remaining in the alcoholic mother-liquors from which oxide of tribenzyl phosphine had crystallised out. (This substance we call "Crystalline Oil".)

We obtained all of these bye products in our earlier experiments, in which after steaming the contents of the sealed tubes with water to liberate the primary phosphine, the residual viscous insoluble mass was boiled with *aqueous* potash.

In our later investigations other bye products were obtained, but we shall first discuss the composition of the first three we have just enumerated.

A. *Crystalline Substance precipitated by Hydrochloric Acid from the Potash Solution used for extracting the viscous mass containing Tribenzyl Phosphine, &c.*—This body was precipitated in crystalline flocks. It was very sparingly soluble in cold water, rather more so in hot water, and crystallised from a boiling aqueous solution in indistinct leaflets. That the substance had acid properties was proved by the readiness with which it dissolved in potash and baryta solutions. A slight residue was, however, left in both cases, and indeed an impurity appeared to be present which was extremely difficult to eliminate, as the following analyses show.

Analysis.

	Obtained.			Calculated for
	I.	II.	III.	$(C_7H_7)_2PO_2H$
Carbon, . .	59·69	66·30	67·06	68·29
Hydrogen, . .	5·80	6·30	6·50	6·09

(1) Crude product washed with water.

(2) Precipitated from a solution of the crude product in baryta, and carefully washed.

(3) Several times dissolved in baryta and reprecipitated by hydrochloric acid, then recrystallised from alcohol and water.

The identity of the substance was, however, fully established by analyses of some of its salts.

Barium Salt.—Obtained by dissolving the crude product in baryta water, and subsequent precipitation of the excess of baryta by a stream of carbonic anhydride. The salt crystallised from the highly concentrated solution in tufts of thin plates.

Analysis.

	Obtained.		Calculated for
	I.	II.	$\{(C_7H_7)_2PO_2\}_2Ba$
Barium (in salt dried at 110),	22·2	21·8	21·8

Zinc Salt.—Obtained as a white amorphous precipitate on adding acetate of zinc to a solution of the barium salt.

Analysis.

	Obtained.	Calculated for $\{(C_7H_7)_2PO_2\}_2Zn$
Zinc, ...	12·1	11·7

Silver Salt.—Obtained by adding a strong solution of nitrate of silver to a solution of the acid in alcohol, when the salt separated in thin colourless needles.

Analysis.

	Obtained.	Calculated for $(C_7H_7)_2PO_2Ag$
Silver, ...	30·1	30·6

Subsequently we obtained dibenzyl phosphinic acid by other methods, and satisfied ourselves that it was identical with the substance in question.

B. *Solid Substance which separated spontaneously from the Aqueous Solution obtained by treating the contents of the Sealed Tubes with Water.*—This body separated from the solution as a white powder stained brown by free iodine. On boiling with dilute spirit it dissolved, and the solution on cooling deposited thin colourless plates, which when dried had the lustre of mother-of-pearl. An analysis was not made, as the melting point (192° corr.) and other properties proved sufficiently that the substance was dibenzyl phosphinic acid. It may be mentioned that this body is also produced when chloride of benzyl and phosphonium iodide are heated alone in a sealed tube, the product of action being afterwards treated with water.

C. *Crystalline Zinc Salt contained in the Aqueous Solution obtained by treating the contents of the Sealed Tubes with Water.*—This salt was obtained as follows:—The aqueous solution filtered from B (dibenzyl phosphinic acid) was mixed with excess of acetate of lead (in order to precipitate hydriodic acid), then after filtering from iodide of lead saturated with sulphuretted hydrogen, again filtered and evaporated to small volume. When most of the acetic acid had volatilised a zinc salt crystallised out in small nodules. Determinations of zinc and water indicated that this salt was benzyl phosphinate of zinc, but it was not obtained in sufficient quantity for further examination.

Analysis.

	Obtained.	Calculated for $(C_7H_7)PO_3Zn,H_2O$
Zinc, ...	25·7	25·7
Water, ...	6·9	7·1

In a later series of experiments a different method of treatment was employed, with the object of obtaining all the bye products of the reaction.

The contents of the sealed tubes were steamed with water as already described, and the aqueous solution decanted. The brown viscous mass remaining was then steamed a second time with water, and the solution decanted and mixed with the first. The viscous mass, now fairly free from soluble zinc salts and hydracids, was repeatedly extracted with alcohol, when a considerable quantity was dissolved, leaving, however, a resinous mass coloured with red phosphorus. This latter was repeatedly boiled with baryta, and then extracted with chloroform, which dissolved a resin having a strong green fluorescence, and containing phosphorus. We have not succeeded in ascertaining its nature. The alcoholic extracts were thrown into a large volume of caustic baryta solution and boiled for a considerable time, and this treatment repeated with what remained undissolved. The resinous matter at first precipitated became crystalline during the ebullition, and eventually the crystals were found to consist of oxide of tribenzyl phosphine. The baryta extracts filtered off were mixed with those which had been employed in extracting the resin which was insoluble in alcohol, and the mixture deposited on cooling a small quantity of oxide of tribenzyl phosphine. This was filtered off, and excess of baryta removed from the solution by a current of carbonic anhydride. The filtered solution gave on concentration a considerable quantity of "crystalline oil," which was filtered off. To the filtrate from this, hydrochloric acid was added, when an oily liquid was precipitated which rapidly solidified to a crystalline mass. The latter was recrystallised from alcohol, and was identified by its melting point (190° corr.), appearance, and by an analysis of its barium salt as dibenzyl phosphinic acid.

Analysis of Barium Salt.

	Obtained.	Calculated for $\{(C_7H_7)_2PO_2\}_2Ba,8H_2O$
Barium, . . .	16·99	17·77
Water, . . .	18·58	18·67

The mother-liquors from which the acid had been separated by hydrochloric acid were mixed with sulphuric acid, filtered from the precipitated sulphate of barium, and evaporated on a water-bath until all hydrochloric and hydriodic acid had volatilised. The residue was diluted, neutralised with chalk, filtered and evaporated to small bulk, when a sparingly soluble calcium salt separated in crystalline crusts. These, after being washed first with water and then with spirit, were dried at 110° and a determination of calcium made.

Analysis.

	Obtained.	Calculated for $\{(C_7H_7)HPO_2\}_2Ca$
Calcium, ...	11·08	11·42

The properties of the acid from which the calcium salt was prepared, such as the production of the primary phosphine on heating, and the characteristic reaction with a copper salt, further identified it as benzyl phosphinous acid.

D. *A Crystalline Substance of low Melting Point* (*"Crystalline Oil"*).—This substance was contained in the viscous mass which remained after treating the product of the sealed tube reaction with aqueous caustic potash, or, if alcoholic potash is employed, it passes into solution.

It dissolved sparingly in water, and separated out from a hot solution in oily drops, which eventually solidified.

It was produced in only small quantity—the largest amount which we have ever obtained being about 9 grms. from the contents of twenty-four tubes, representing 288 grms. of chloride of benzyl.

The investigation of this substance has given us a great deal of trouble, and we are still uncertain as to its composition. The following analyses were made by one of us and W. WHEELER :*—

(I.) Crude substance washed with ether.

$$0{\cdot}2741 \text{ gave } \begin{cases} 0{\cdot}6922 \ CO_2 = 0{\cdot}18879 \ C = 68{\cdot}88 \text{ per cent.} \\ 0{\cdot}1650 \ H_2O = 0{\cdot}01833 \ H = 6{\cdot}68 \quad ,, \end{cases}$$

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* *Proceedings*, 1887, p. 82.

(II.) The crude substance was dissolved in boiling dilute baryta solution, the baryta was then precipitated by carbonic anhydride, and the substance obtained from the concentrated solution.

$$0{\cdot}3355 \text{ gave } \begin{cases} 0{\cdot}8790\ CO_2 = 0{\cdot}2397 & C = 71{\cdot}45 \text{ per cent.} \\ 0{\cdot}2072\ H_2O = 0{\cdot}02302 & H = \ \ 6{\cdot}86 \quad ,, \end{cases}$$

(III.) The crude substance was recrystallised twice from water.

$$0{\cdot}2474 \text{ gave } \begin{cases} 0{\cdot}647\ \ CO_2 = 0{\cdot}1764 & C = 71{\cdot}30 \text{ per cent.} \\ 0{\cdot}1553\ H_2O = 0{\cdot}01725 & H = \ \ 6{\cdot}97 \quad ,, \end{cases}$$

(IV.) Another specimen also recrystallised twice from water.

$$0{\cdot}4412 \text{ gave } \begin{cases} 1{\cdot}1606\ CO_2 = 0{\cdot}3165 & C = 71{\cdot}73 \text{ per cent.} \\ 0{\cdot}2677\ H_2O = 0{\cdot}02974 & H = \ \ 6{\cdot}74 \quad ,, \end{cases}$$

The next set of analyses were made by us after the investigation had been re-opened, and we were in possession of a fresh quantity of the substance.

Its corrected melting point we now found to be 111°·0.

(V.) The specimen was twice recrystallised, and melted at 111°·0–111°·1.

$$0{\cdot}3146 \text{ gave } \begin{cases} 0{\cdot}8360\ CO_2 = 0{\cdot}2280 & C = 72{\cdot}47 \text{ per cent.} \\ 0{\cdot}1923\ H_2O = 0{\cdot}021366 & H = \ \ 6{\cdot}79 \quad ,, \end{cases}$$

(VI.) The specimen was obtained from the mercuric chloride compound (*vide infra*), by decomposing it with sulphuretted hydrogen. In the combustion, oxide of copper unmixed with chromate of lead was used.

$$0{\cdot}2490 \text{ gave } \begin{cases} 0{\cdot}6727\ CO_2 = 0{\cdot}183463 & C = 73{\cdot}67 \text{ per cent.} \\ 0{\cdot}1607\ H_2O = 0{\cdot}017855 & H = \ \ 7{\cdot}17 \quad ,, \end{cases}$$

(VII.) The same specimen as was employed for No. V. analysis. The combustion was made with pure oxide of copper, and a phosphorus determination subsequently made (see p. 556).

$$0{\cdot}2917 \text{ gave } \begin{cases} 0{\cdot}7826\ CO_2 & = 0{\cdot}213436 & C = 73{\cdot}16 \text{ per cent.} \\ 0{\cdot}1912\ H_2O & = 0{\cdot}021244 & H = \ \ 7{\cdot}28 \quad ,, \\ 0{\cdot}1481\ Mg_2P_2O_7 & = 0{\cdot}041361 & P = 14{\cdot}18 \quad ,, \end{cases}$$

(VIII.) A different specimen recrystallised four times, and of constant melting point 111°·0. The analysis was performed in the same way as VII.

$$0{\cdot}3247 \text{ gave } \begin{cases} 0{\cdot}8662\ CO_2 & = 0{\cdot}236236 & C = 72{\cdot}75 \text{ per cent.} \\ 0{\cdot}2143\ H_2O & = 0{\cdot}023811 & H = \ \ 7{\cdot}33 \quad ,, \\ 0{\cdot}1623\ Mg_2P_2O_7 & = 0{\cdot}045327 & P = 13{\cdot}95 \quad ,, \end{cases}$$

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Carbon, . . .	68·88	71·45	71·30	71·73	72·47	73·67	73·16	72·75
Hydrogen, . .	6·68	6·86	6·97	6·74	6·79	7·17	7·28	7·33
Phosphorus, . .	...	...	...	...	...	...	14·18	13·95
Oxygen (by difference),	...	...	...	...	...	...	5·38	5·97
							100·00	100·00

The substance had the following properties :—

(1) When heated most of it appeared to volatilise unchanged, but at the same time a slight odour of the primary phosphine was noticed.

(2) Chloride of platinum gave no sparingly soluble nor crystalline compound.

(3) Bromine vapour liquefied it, while the addition of liquid bromine caused the disengagement of heat and escape of hydrobromic acid.

(4) Its aqueous solution when mixed with corrosive sublimate remained clear, but on warming the mixture a colourless amorphous precipitate was suddenly produced.

(5) When iodide of cadmium was added to its hot aqueous solution oily drops separated out, and these gradually solidified, the resulting crystals being minute cubes or quadratic forms, very refractive to light. This compound was very sparingly soluble.

(6) Iodide of zinc gave an oily precipitate, which refused to crystallise.

(7) Stannic chloride and stannous chloride both gave white precipitates—probably consisting of minute oily drops.

The iodide of cadmium compound was prepared several times, and analysed with the following results :—

Analysis of Cadmium Iodide Compound.

(I.)

$$0{\cdot}6448 \text{ gave} \left\{ \begin{array}{l} 0{\cdot}3764 \ \text{AgI} = 0{\cdot}2034 \ \text{I} \ = 31{\cdot}5 \text{ per cent.} \\ 0{\cdot}0796 \ \text{CdO} = 0{\cdot}0796 \ \text{Cd} = 12{\cdot}3 \quad ,, \end{array} \right.$$

(II.) A different specimen.

$$1{\cdot}8267 \text{ gave} \left\{ \begin{array}{l} 0{\cdot}9687 \ \text{AgI} = 0{\cdot}5235 \quad \text{I} \ = 28{\cdot}65 \text{ per cent.} \\ 0{\cdot}2676 \ \text{CdO} = 0{\cdot}2341 \ \ \text{Cd} = 12{\cdot}81 \quad ,, \end{array} \right.$$

$$0{\cdot}5729 \quad ,, \quad \left\{ \begin{array}{l} 0{\cdot}8559 \ \text{CO}_2 = 0{\cdot}2334 \ \text{CO}_2 = 40{\cdot}74 \quad ,, \\ 0{\cdot}1979 \ \text{H}_2\text{O} = 0{\cdot}021989 \ \text{H} = \ 3{\cdot}84 \quad ,, \end{array} \right.$$

(III.) A different specimen recrystallised from water.

$$1{\cdot}2994 \left\{ \begin{array}{l} \text{required } 29{\cdot}8 \text{ c.c}\tfrac{n}{10}\text{AgNO}_3 = 0{\cdot}37846 \ \text{I} \quad = 29{\cdot}12 \text{ per cent.} \\ \text{gave} \qquad 0{\cdot}1783 \ \text{CdO} \quad = 0{\cdot}156012 \ \text{Cd} = 12{\cdot}00 \quad ,, \end{array} \right.$$

(IV.) A different specimen. The substance was burnt with pure oxide of copper, and the phosphorus determined by molybdate, &c.

$$0{\cdot}497 \text{ gave } 0{\cdot}1471 \ \text{Mg}_2\text{P}_2\text{O}_7 = 0{\cdot}041081 \ \text{P} = 8{\cdot}26 \text{ per cent.}$$

(V.) The same specimen as IV., the analysis being performed in the same way.

$$0{\cdot}3109 \text{ gave } 0{\cdot}0919 \ \text{Mg}_2\text{P}_2\text{O}_7 = 0{\cdot}025665 \ \text{P} = 8{\cdot}25 \text{ per cent.}$$

(VI.) The specimen was prepared from pure crystalline oil.

$$0{\cdot}6010 \quad \text{gave} \quad \left\{ \begin{array}{l} 0{\cdot}8980 \ \text{CO}_2 = 0{\cdot}244909 \ \ \text{C} = 40{\cdot}75 \text{ per cent.} \\ 0{\cdot}2070 \ \text{H}_2\text{O} = 0{\cdot}230 \qquad \text{H} = \ 3{\cdot}82 \quad ,, \end{array} \right.$$

$$1{\cdot}1950 \quad \text{gave} \quad \left\{ \begin{array}{l} 0{\cdot}6845 \ \text{AgI} = 0{\cdot}369921 \ \ \text{I} = 30{\cdot}95 \quad ,, \\ 0{\cdot}1550 \ \text{CdO} = 0{\cdot}135625 \, \text{Cd} = 11{\cdot}34 \quad ,, \end{array} \right.$$

0·7947 gave 0·1209 CdO = 0·1057875 Cd = 13·31 per cent.
·7340 „ 0·1020 CdO = 0·08925 Cd = 12·15 „
1·0631 „ 0·6234 AgI = 0·336901 I = 31·69 „

	I.	II.	III.	IV.	V.	VI.		
Cadmium,	12·3	12·81	12·00	...	...	11·34	13·31	12·15
Iodine,	31·5	28·65	29·12	...	...	30·95	31·69	...
Carbon,	...	40·74	...	...	...	40·75	...	...
Hydrogen,	...	3·84	...	...	...	3·82	...	...
Phosphorus,	...	...	...	8·26	8·25	...	...	...
Oxygen (by difference),	...	...	...	...	...	...	...	...

We had hoped that the analysis of the cadmium iodide compound would definitely settle the question of the composition of the crystalline oil, but such was unfortunately not the case, as we shall show presently in discussing the analytical results. As the quantity of crystalline oil at our disposal was very small, we were unable to study its properties exhaustively, and the difficulty of the investigation was thus increased.

Eventually we decided to turn our attention to the corrosive sublimate compound which is very characteristic. It was easily obtained by mixing dilute aqueous solutions of the crystalline oil and corrosive sublimate and warming the mixture, when a bulky amorphous precipitate was produced, which had a faint blue tinge. This, when washed and dried, formed a light powder, which was extraordinarily electric. The compound was twice prepared and analysed, with the following results:—

Analysis.

(1) 0·8605 gave { 0·4397 Hg = 51·09 per cent.
0·3215 AgCl = 0·07953 Cl = 9·24 „

(2) 0·5359 gave { 0·2387 Hg = 44·54 per cent.
0·03763 Cl (volumetrically) = 7·02 „

The ratio of mercury to chlorine is in both cases Hg : Cl, for—

(1) 200 : 35·5 :: 51·09 : 9·07
(2) 200 : 35·5 :: 44·54 : 7·90

The mercury and chlorine were thus shown to be present as calomel, proving that part at least of the compound had been decomposed and probably oxidised.

As the mercury compound employed in the two analyses were different preparations, it is evident that its composition is not constant, and in all probability it consists of calomel containing varying quantities of the original substance; for, on decomposing some of it with sulphuretted hydrogen and concentrating the filtered solution, oily drops separated like the original body, and these gradually crystallised in its characteristic manner, and on analysis were found to contain the same proportions of carbon and hydrogen as the crystalline oil (No. VI. determination). The product of oxidation was easily found and identified in the mother-liquors of the calomel compound; for, on concentration and cooling, they deposited crystalline scales having the appearance of dibenzyl phosphinic acid. To obtain them as pure as possible, they were dissolved up by warming, and a current of sulphuretted hydrogen passed through the solution until the whole of the mercury was precipitated. On filtering the hot solution and allowing it to cool the scaly crystalline compound again came down, and a little more of it was obtained on evaporating its mother-liquors. The whole was then recrystallised from water, in which it was very sparingly soluble.

It was identified as dibenzyl phosphinic acid by its melting point 193° (that of the pure acid being 192° C.), by its solubility relations, by its crystalline form, and also, though not very satisfactorily, owing to the small quantity at our disposal, by a combustion.

Analysis.

$$0{\cdot}2647 \text{ gave} \begin{cases} 0{\cdot}1477 \ H_2O = 0{\cdot}016411 \ H = \ 6{\cdot}19 \text{ per cent.} \\ 0{\cdot}6507 \ CO_2 = 0{\cdot}177463 \ C = 67{\cdot}04 \quad " \end{cases}$$

	Obtained.	Calculated for $(C_7H_7)_2HPO_2$
Carbon, . . .	67·04	68·29
Hydrogen, . . .	6·19	6·09

We have been unable to go any further with our investigations, as the whole stock of crystalline oil at our disposal became exhausted, and, as we have before stated, we are still in doubt as to its composition.

That it is an oxidised derivative is shown by the deficiency which remains when the percentages of the constituents both of it and of its cadmium iodide compound (which were actually determined) are added together.

There can also be no doubt that it gives rise to dibenzyl phosphinic acid when oxidised, and therefore in all probability it contains the element of dibenzyl phosphine.

It will be noticed that of the eight analyses made of the crystalline oil itself, Nos. II., III., and IV. agree fairly well with each other, but differ from Nos. V., VI., VII., and VIII., which also agree (though not so closely) with each other. Thus—

	Mean of II., III., and IV.	Mean of V., VI., VII., and VIII.
Carbon, ...	71·50	73·01
Hydrogen, . . .	6·87	7·14

The first set of analyses agree with the formula $C_{13}H_{15}PO$, so far as the percentage amounts of carbon and hydrogen are concerned, while the second set agree in a similar manner with $C_{15}H_{17}PO$. The percentage amount of phosphorus, however, from Nos. VII. and VIII. agrees with the first formula. Thus—

	Obtained.		Calculated for	
	I.	II.	$C_{13}H_{15}PO$	$C_{15}H_{17}PO$
Carbon, . . .	71·50	73·42	71·56	73·30
Hydrogen, . . .	6·87	7·23	6·88	6·97
Phosphorus, . .	...	14·06	14·42	12·70

The mean results of the whole of the analyses are as follows :—

Carbon,	73·36
Hydrogen,	7·02
Phosphorus,	14·06
Oxygen (by difference),	6·56

And the atomic ratios, taking the percentage of phosphorus as representing one atom of that element—

$$C_{13\cdot3}H_{15\cdot5}P_1O_{0\cdot9}.$$

Next as regards the analysis of the cadmium iodide compound. It will be seen that the percentages of cadmium and iodine vary to a considerable extent in the different determinations. This must be attributed to the analytical difficulties we experienced in separating the two substances from such a complex body. On the other hand, the two phosphorus determinations and the two combustions agree with each other exceedingly well. The mean results are as follows :—

Cadmium,	12·32
Iodine,	30·38
Carbon,	40·74
Hydrogen,	3·83
Phosphorus,	8·25
Oxygen (by difference),	4·48
	100·00

and the atomic ratios, taking the percentage of phosphorus as representing 1 atom of that element,

$$C_{13\cdot8}H_{14\cdot3}P_1O_1.$$

Thus the calculated atomic ratios of the crystalline oil and of the cadmium iodide compound are not very different, and so far the comparison is satisfactory. But, on the other hand, if we compare the percentage numbers obtained with those required for a cadmium iodide compound of either $C_{13}H_{15}PO$ or $C_{15}H_{17}PO$, a total discordance is seen. Thus—

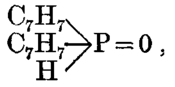
	Calculated for	
	$(C_{13}H_{15}PO)_2CdI_2$	$(C_{15}H_{17}PO)_2CdI_2$
Cadmium,	13·96	13·1
Iodine,	31·67	29·7
Carbon,	38·90	42·1
Hydrogen,	3·70	3·9
Phosphorus,	7·73	7·26

In fact, no formula can be devised which will agree exactly with the analytical results obtained with both the crystalline oil and its cadmium iodide compound. The numbers, however, calculated for the formula $C_{14}H_{15}PO$ approximate pretty closely to those obtained.

Thus—

	Calculated for	
	$C_{14}H_{15}PO$	$(C_{14}H_{15}PO)_2CdI_2$
Cadmium, ...	...	13·56
Iodine, ...	...	30·85
Carbon, ...	73·04	40·68
Hydrogen, . . .	6·52	3·63
Phosphorus, . . .	13·48	7·50

This would be the formula of an oxide of dibenzyl phosphine,



$$\left.\begin{array}{l}C_7H_7\\C_7H_7\\H\end{array}\right\rangle P=0\,,$$

a substance which would probably not have acid properties, and which would easily be oxidised to dibenzyl phosphinic acid.

We may mention that quite accidentally we discovered that when the high boiling residues obtained in fractionating the primary phosphine are allowed to oxidise spontaneously, the crystalline oil is produced; and as we have shown that the secondary phosphine is formed in the sealed tube reaction, we think it quite possible that the crystalline oil is its oxide.

No such body has been obtained hitherto, but then the products of the spontaneous oxidation of secondary phosphines have scarcely if at all been investigated. The point is one of some interest, and we intend to submit it to enquiry.

E. "*Insoluble Crystalline Body.*"—We obtained this substance in some of our later experiments. It remained undissolved when the oily mass containing the secondary and tertiary phosphine was treated with ether, accompanied by oxide of tribenzyl phosphine. It was separated from this latter body by boiling with alcohol, in which it was insoluble.

We also found it in the ethereal solution of the phosphines, from which it was slowly deposited spontaneously.

It was insoluble in water, alcohol, and ether, but sparingly soluble in boiling glacial acetic acid, from which it was deposited on cooling in colourless needles of characteristic crooked form. Twice recrystallised from acetic acid, its corrected melting point was found to be 276°–277°. Two analyses were made, one a combustion with oxide of copper and chromate of lead, the other a combustion with pure oxide of copper, in order to determine the phosphorus as well as carbon and hydrogen.

Analysis.

(1) Combustion with oxide of copper and chromate of lead.

$$0\cdot2288 \text{ gave} \left\{\begin{array}{l}0\cdot6355\ CO_2=0\cdot173318\ C=75\cdot75 \text{ per cent.}\\0\cdot1360\ H_2O=0\cdot015111\ H=\ 6\cdot60 \quad ,,\end{array}\right.$$

(2) Combustion with pure oxide of copper.

$$0{\cdot}3779 \text{ gave} \begin{cases} 1{\cdot}0432\ CO_2 = 0{\cdot}284509 & C = 75{\cdot}28 \text{ per cent.} \\ 0{\cdot}2258\ H_2O = 0{\cdot}025088 & H = 6{\cdot}63 \quad ,, \\ 0{\cdot}1277\ Mg_2P_2O_7 = 0{\cdot}0356639 & P = 9{\cdot}43 \quad ,, \end{cases}$$

	Obtained.		Calculated for $(C_7H_7)_3PO_2$
	I.	II.	
Carbon, . .	75·28	75·75	75·00
Hydrogen, . .	6 63	6·60	6·25
Phosphorus, . .	9·43	...	9·22

It is very singular that this substance has the same melting point as sulphide of tribenzyl phosphine, and precisely the same solubility relations. The percentage amounts of carbon, hydrogen, and phosphorus are also identical. Its crystalline habit is, however, different, and we were unable to detect any sulphur in it, whereas by the test we employed (ignition with caustic potash and chlorate of potash) we readily found the sulphur in a specimen of the sulphide.

We had not sufficient of the substance to study its properties exhaustively, but we ascertained that it readily yielded oxide of tribenzyl phosphine. This we accomplished by dissolving it in hot acetic acid, and adding bromine, in excess, when the characteristic compound of the oxide separated, which was identified by analysis.

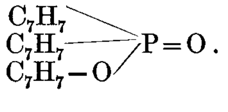
Analysis.

$$0{\cdot}6789 \text{ required } 22{\cdot}3 \text{ c.c} \tfrac{n}{10}\ AgNO_3 = 0{\cdot}1784\ Br = 26{\cdot}27 \text{ per cent.}$$

	Obtained.	Mean of ten Determinations of the Bromine Compound of Tribenzyl Phosphine Oxide.
Bromine, ...	26·27	26·70

A quantity of the brominated body was boiled with caustic soda solution, and the product, after washing, recrystallised. Its melting point was now found to be 215°–215°·5 —exactly that of the oxide, and it had its crystalline form.

It is very improbable that a tertiary phosphine peroxide could be formed under the conditions in which the substance in question was produced, and as yet no such body has been described. But it seems equally improbable, from the properties of the substance, that it is the isomer, viz., dibenzyl phosphinate of benzyl,



We therefore remain in doubt as to its nature.

We have thus separated from the products of HOFMANN's sealed tube reaction the following ten bodies (or have proved them to be present):—

(1) Monobenzyl phosphine, ... $(C_7H_7)H_2P$
(2) Benzyl phosphinous acid, ... $(C_7H_7)H_2PO_2$
(3) Benzyl phosphinic acid, ... $(C_7H_7)H_2PO_3$
(4) Dibenzyl phosphine, ... $(C_7H_7)_2HP$
(5) Dibenzyl phosphine oxide (?), (" crystalline oil "), . . $(C_7H_7)_2HPO(?)$
(6) Dibenzyl phosphinic acid, ... $(C_7H_7)_2HPO_2$
(7) Tribenzyl phosphine, ... $(C_7H_7)_3P$
(8) Tribenzyl phosphine oxide, ... $(C_7H_7)_3PO$
(9) ("Insoluble crystalline body"), ... $(C_7H_7)_3PO_2(?)$
(10) A resin containing phosphorus, insoluble in alcohol and ether, but soluble in chloroform.

It is not possible for us to say how many of these different substances exist as such in the original product of the sealed tube reaction, and how many are formed in the subsequent treatment to which it is subjected.

The three phosphines no doubt exist in the original product as hydriodates or hydrochlorates combined with chloride or iodide of zinc, and we think that their production is of great interest, for hitherto only primary and secondary phosphines have been obtained when an alkyl iodide, oxide of zinc, and phosphonium iodide are heated together under pressure; whereas we prove that, when chloride of benzyl is substituted for an alkyl iodide, the tertiary phosphine is formed also.

It is well-nigh impossible for us to say definitely whether the quaternary compound is formed as well, for it would certainly combine with chloride or iodide of zinc, and would be very troublesome to separate from these substances. But the occurrence of oxide of tribenzyl phosphine, after the product of the sealed tube reaction had been steamed and treated with potash in a hydrogen atmosphere, is, in our opinion, almost conclusive proof that tetrabenzyl phosphonium was orignally present, and had been decomposed by the alkali,

$$(C_7H_7)_4PI + KHO = (C_7H_7)_3PO + C_7H_8 + KI,$$

a reaction which occurs with the greatest ease when the two substances are boiled together in aqueous or alcoholic solution. How otherwise could the oxide be produced in quantities so large as those we observed?

If we assume that all four phosphorised derivatives are produced, the reaction becomes analogous to that which occurs when a haloid compound of a hydrocarbon radical is treated with ammonia, the only difference being that hydracid (hydrochloric) is liberated in the case of phosphuretted hydrogen, and is found in the gases contained in the sealed tubes.

Whether the substitution of an alkyl chloride for an iodide is the cause of the production of a tertiary and (probably) quaternary compound in addition to the primary and secondary phosphines, or whether benzyl behaves differently in HOFMANN'S reaction from other alkyl radicals, we have not as yet decided. There can, however, be very little doubt that HOFMANN's experiments in the ethyl and methyl series prove conclusively, that a tertiary phosphine is not formed when their iodides are employed.

As regards the other substances isolated from the sealed tube reaction, which consist chiefly of the products of the oxidation of the benzyl phosphines, we think it probable that benzyl phosphinous acid and benzyl phosphinic acid were produced by the oxidation of the primary phosphine by the air, for it was impossible to prevent the introduction of some air while steaming out the contents of the sealed tubes. The same remark might apply to the "crystalline oil" and to the dibenzyl phosphinic acid, formed in a similar manner from dibenzyl phosphine. But, of course, it is also perfectly possible that all three acids and the crystalline oil were produced by some complicated interaction with oxide of zinc—and this is very likely to be the case with (some at least of) the dibenzyl phosphinic acid, as it was found in the aqueous solution of the product, before it had been boiled with potash to liberate the secondary and tertiary phosphine.

In conclusion, we have only to add that this research has extended over a very long period, and has envolved an expenditure of time, energy, and material probably quite out of proportion to its value.

PART II.—THE ACTION OF ALCOHOLS ON A MIXTURE OF PHOSPHORUS AND ITS IODIDE.

The methods which have as yet been discovered for the preparation of the phosphines and their derivatives are, as a rule, very tedious, troublesome, and unsatisfactory in point of yield,—a fact which no doubt has considerably retarded the investigation of this interesting group of organic compounds, and which soon becomes unpleasantly apparent to any one who makes them a study.

To the best of our belief the following are the only methods of any importance:—

(1) *Action of the Haloid Derivatives of Hydrocarbon Radicals on Metallic Phosphides.*—It was by this reaction that PAUL THENARD * discovered the first members of the phosphine group in 1843–1847. He experimented with chloride of methyl and phosphide of calcium, the investigation being attended with considerable difficulties, owing to the labour involved in separating the different products and in obtaining them in a pure state; also on account of their poisonous properties and their explosive and inflammable nature.

In spite, however, of these difficulties, THENARD apparently isolated trimethyl phosphine, a substance analogous to kakodyle, $(CH_3)_4P_2$, and methylated solid phosphide of hydrogen $(CH_3)_2P_4$. The latter he described as an inert solid body, the second as a spontaneously inflammable liquid, boiling at 250° C.—very explosive, poisonous, and unstable.

THENARD recognised the relationship of trimethyl phosphine to ammonia, and predicted the existence of the then undiscovered organic compounds of nitrogen and antimony.

WURTZ in 1848, and HOFMANN in 1850, verified THENARD'S prediction by discovering the compound ammonias; and LŒWIG and SCHWEITZER a little later obtained stibethyl.

In 1855 HOFMANN and CAHOURS † investigated the action of iodide of methyl on phosphide of sodium, and obtained, in addition to trimethyl phosphine and the phosphorised kakodyle of THENARD, iodide of tetramethyl phosphonium. They found that the reaction was very energetic when iodide of methyl and phosphide of sodium were heated together, and that inflammable and explosive substances were formed, rendering the method dangerous, and exposing, as they said, the fruits of their labour to loss. Moreover, it was unreliable, and furnished mixtures the separation of which presented enormous difficulties.

BERLÈ ‡ about the same time obtained triethyl phosphine by the action of phosphide of sodium on iodide of ethyl, the former substance being prepared by heating sodium and phosphorus together in rock oil. Iodide of ethyl only acted upon this at a high temperature, and only very small quantities of the phosphine were produced.

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* *Comptes Rendus*, xxi. p. 144, and xxv. p. 892.

† HOFMANN and CAHOURS, *Phil. Trans.*, 1857; and *Ann. de Chim. et de Phys.* (3), lxi. p. 5.

‡ BERLÈ, *Jour. f. Prac. Chem.*, lxvi. p. 73.

BERLÈ next attempted [*] to prepare the tertiary phosphine by heating sodium, phosphorus, and iodide of ethyl together in a sealed tube, but although a reaction occurred, he does not appear to have obtained any very satisfactory results.

CAHOURS [†] in 1859 prepared iodide of tetrethyl phosphonium by the action of iodide of ethyl on crystallised phosphide of zinc (obtained by heating the metal in phosphorus vapour at 180° C.).

In 1882 one of us and N. COLLIE [‡] investigated the action of benzyl chloride on phosphide of sodium. The latter substance was obtained with perfect ease and safety by acting upon sodium with phosphorus under the surface of dry xylol. The two bodies (chloride of benzyl and the metallic phosphide) react readily when they are heated together, and chloride of tetrabenzyl phosphonium is produced in abundance. Experiments were also commenced with the haloid derivatives of some other hydrocarbons, but were not completed. The results obtained were on the whole satisfactory, and no doubt this method for producing tertiary and quaternary phosphorus derivatives will find a more extended application in the future.

(2) *Action of Organo-Metallic Bodies on Trichloride of Phosphorus.*—The action of zinc alkyls on trichloride of phosphorus was first investigated by HOFMANN and CAHOURS,[§] and was further studied by HOFMANN alone.[||] It is in a sense the reverse of the action of a metallic phosphide on a haloid ether, but resembles it in that the action in both cases is determined by the attraction of halogen for metal. By this method tertiary phosphines are exclusively formed—

$$3R_2Zn+2PCl_3=2R_3P+3ZnCl_2.$$

It is necessary to treat the product of the reaction with caustic potash, in order to decompose the compound of phosphine and chloride of zinc and to liberate the former. By its means HOFMANN and CAHOURS obtained trimethyl and triethyl phosphine, and submitted them to an exhaustive examination. They showed that tertiary phosphines resemble the corresponding amines in many respects, especially in the readiness with which they combine with the iodides of hydrocarbon radicals to give quaternary compounds. On the other hand, they proved that, unlike the amines, tertiary phosphines readily combine with oxygen to give very stable compounds of the general formula R_3PO.

(3) *Action of Alcohols on Phosphonium Iodide; and* (4) *Action of Alkyl Iodides on Phosphonium Iodide and Oxide of Zinc* (HOFMANN'S methods).—In the year 1871, seventeen years after his experiments with CAHOURS, HOFMANN again took up the study of the phosphines, and succeeded in discovering a simple method not only for obtaining the tertiary and quaternary compounds, but also the primary and secondary bases,—substances which had not been previously obtained, and whose investigation

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[*] BERLÈ, *Comp. Rend.*, xlix.

[†] CAHOURS, *Comp. Rend.*, xlix. p. 87; and *Jahresbericht*, 1859, p. 430.

[‡] LETTS and COLLIE, these *Transactions*, xxx. part 1, p. 181.

[§] HOFMANN and CAHOURS, *Ann. de Chim. et de Phys.* (3), li.

[||] HOFMANN, *Ibid.*, lxii., lxiii., lxiv.

led to very interesting and important results. In searching for some general method for obtaining the phosphines, HOFMANN was influenced by his well-known and beautiful researches on the preparation of the compound ammonias. "The question arose," he says,* "should not the series of phosphines be capable of production by a general reaction similar to that which had yielded me the compound ammonias twenty years ago? For that purpose it was necessary to allow phosphuretted hydrogen to react upon alcohol iodides under suitable conditions."

In his first experiments in this direction, HOFMANN heated iodide of phosphonium in a sealed tube, in which was also placed a narrower tube containing iodide of ethyl and a little water. The sealed tube thus charged was heated in a horizontal position for several hours to a temperature ranging from 160°–180° C., when a reaction occurred in the desired manner, triethyl phosphine and tetrethyl phosphonium iodide resulting. The yield, however, was very small, owing to the large quantity of hydriodic acid set free. To avoid this, HOFMANN took advantage of the fact that phosphonium iodide when heated with alcohol yields phosphuretted hydrogen, iodide of ethyl, and water. Accordingly, he next charged the sealed tubes simply with alcohol and phosphonium iodide. When this mixture was heated for eight hours at 180° C., the reaction was complete. The cooled tubes were found to be full of a snow-white crystalline mass, and on opening them scarcely a trace of gas escaped. On adding water, the solid dissolved to a homogeneous liquid, showing that no iodide of ethyl remained, neither was any alcohol left undecomposed. The crystals showed themselves to consist of a mixture in nearly equal parts, of triethyl phosphine hydriodate, and tetrethyl phosphonium iodide. Their separation presented no difficulty, for on addition of caustic soda, triethyl phosphine separated as a clear liquid, while the solution gave on evaporation beautiful crystals of tetrethyl phosphonium iodide.

As regards the most favourable proportions of iodide of phosphonium and alcohol (which are of great importance), HOFMANN found that one molecular weight of the former should be taken for three molecular weights of the latter. "In this case," he says, "the quantities heated in the tubes can be increased in an extraordinary manner without fear of explosions. In one experiment there was placed in a single tube 25 grms. of phosphonium iodide and 22 grms. of alcohol."

HOFMANN next investigated the course of the reaction, to decide whether iodide of ethyl was first formed and was then acted upon by the phosphuretted hydrogen, or whether the alcohol and phosphonium iodide acted upon each other directly—

$$(1)\quad PH_4I+3C_2H_6O=(C_2H_5)_3PHI+3H_2O$$
$$(2)\quad PH_4I+4C_2H_6O=(C_2H_5)_4PI\ +4H_2O.$$

To decide this question the tubes were heated for four hours only. On cooling, two layers of liquid were visible. The tubes when opened showed great pressure, and on distilling their contents iodide of ethyl passed over in abundance. It may be taken for granted then that the reaction occurs in two phases, in the first of which iodide of ethyl

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* HOFMANN, *Berichte*, iv. (1871) 205.

is liberated, which then acts upon phosphuretted hydrogen in the same way as it acts upon ammonia. HOFMANN had thus discovered a simple and elegant general reaction for the preparation of tertiary and quaternary compounds, which he employed successfully in the methyl,* ethyl,† propyl,‡ butyl,§ and amyl‖ series.

But the primary and secondary bases were still wanting, though the possibility of their existence could scarcely be doubted in view of the well-established analogies existing between the derivatives of ammonia and phosphuretted hydrogen. HOFMANN therefore again took up the matter, and began a new series of investigations which led to brilliant results.

The direction of these new experiments was, as he says, clearly indicated, for as both the tertiary and quaternary derivatives are obtained by direct substitution from phosphuretted hydrogen, so also ought the primary and secondary bases to be produced. For if three and four molecules respectively of the alcohol can be made to react upon one molecule of phosphonium iodide, one and two molecules ought also to react in a similar manner under suitable conditions—

$$(1)\quad PH_4I + C_2H_6O = (C_2H_5)PH_2.HI + H_2O.$$
$$(2)\quad PH_4I + 2C_2H_6O = (C_2H_5)_2PH.HI + 2H_2O.$$

HOFMANN ¶ therefore sought to achieve the desired object by altering the proportions of phosphonium iodide and alcohol, but without success, the tertiary base being alone produced, or a mixture of the tertiary and quaternary compounds; while, with the proportions required for the second of the above equations, the tubes invariably exploded.

In the meantime DRECHSEL and FINKENSTEIN ** believed that they had succeeded in obtaining the primary bases of the ethyl and methyl series by saturating the iodides of those radicals with phosphuretted hydrogen, and allowing the solutions to remain for some time at ordinary temperatures or by heating them to 100° C. Under these conditions a crystalline body was obtained, which was not phosphonium iodide, as it dissolved in water without evolution of gas, and which they therefore concluded to be the hydriodate of the primary base.

Also, by heating an ethereal solution of iodide of zinc saturated with phosphuretted hydrogen, with iodide of methyl, they believed that they had obtained the same substance.

HOFMANN †† repeated these experiments, and showed that the primary bases were not formed at all, whereas the tertiary and quaternary derivatives were.

The idea then occurred to him of heating the alkyl iodide with iodide of phosphonium in presence of a metallic oxide, with the happiest results; for on heating a mixture of phosphonium iodide, ethyl iodide, and oxide of zinc, in the proportions of two molecules of each of the former to one molecule of the latter in sealed tubes at 150° C. for from six to

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* HOFMANN, *Berichte*, iv. (1871) p. 209.

† HOFMANN, *Berichte*, iv. (1871) p. 205.

‡ *Ibid.*, *Berichte*, vi. (1873) p. 292.

§ *Ibid.*, *Berichte*, vi. (1873) p. 296.

‖ *Ibid.*, *Berichte*, vi. (1873) p. 297.

¶ *Ibid.*, *Berichte*, iv. (1871) p. 372.

** DRECHSEL and FINKENSTEIN, *Berichte*, iv. (1871) p. 352.

†† HOFMANN *Berichte*, iv. (1871) p. 372.

eight hours, a complete reaction occurred, the tubes when cold containing a crystalline mass consisting exclusively of the hydriodates of the primary and secondary bases, the former being the chief product, while the latter was only formed in small quantities. The separation of the two was accomplished in the simplest manner possible, the addition of water to the product of reaction liberating the primary phosphine alone, which was distilled off in a hydrogen atmosphere, while the secondary phosphine was subsequently set at liberty by the action of an alkali.

Thus HOFMANN discovered for the first time a general method for preparing primary and secondary phosphines, the reaction being exactly complementary to that by which he had obtained the tertiary and quaternary compounds; like it the method was distinguished by its simplicity and the readiness with which it may be carried out.

By its means he prepared methyl,[*] ethyl,[†] propyl,[‡] butyl,[§] amyl,[||] and benzyl[¶] phosphines.

(5) *Michaelis' Methods.*—HOFMANN'S methods, although of excellent service for obtaining the phosphines of those radicals which form alcohols, could not be employed in the preparation of phosphines containing purely aromatic radicals. He in vain endeavoured to obtain phenyl phosphines,[**] but neither by the action of chlorobenzol on phosphonium iodide, nor by heating a mixture of phenol and phosphonium iodide, was a trace of those substances produced, and he was equally unsuccessful in his attempts to prepare tolyl phosphines.

MICHAELIS, on the other hand, by approaching the question from an entirely different direction, not only succeeded in obtaining all the phenyl phosphines, but also in discovering a fairly general method for the production of primary phosphines. The substance forming the starting-point for the preparation of phosphines by these methods is trichloride of phosphorus. One atom of chlorine is first replaced in that body by one or other of the following processes:—

(1) The mixed vapours of a hydrocarbon and the trichloride are repeatedly passed through a red hot tube. Thus, when benzol is employed, "phosphenyl" chloride is obtained—

$$PCl_3 + C_6H_6 = (C_6H_5)PCl_2 + HCl.$$

(2) A mercury ether is heated with the trichloride under pressure. Thus, when mercury ethyl is employed, ethyl-phosphorus chloride is obtained together with ethyl chloride of mercury—

$$PCl_3 + (C_2H_5)_2Hg = (C_2H_5)PCl_2 + Hg(C_2H_5)Cl.$$

(3) By digesting a hydrocarbon with the trichloride and aluminum chloride, the reaction being the same as 1. Other substances besides hydrocarbons yield substituted phosphorus chlorides when submitted to this reaction. Thus a mixture of acetone,

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[*] HOFMANN, *Berichte*, iv. (1871) p. 430.

[†] HOFMANN, *Ibid.*, iv. (1871) p. 605.

[‡] *Ibid.*, vi. (1873) p. 292.

[§] *Ibid.*, vi. (1873) p. 296.

[||] *Ibid.*, vi. (1873) p. 297.

[¶] *Ibid.*, v. (1872) p. 100.

[**] *Ibid.*, *Berichte*, v. (1872) p. 100.

phosphorus trichloride, and aluminum chloride react spontaneously, the reaction proceeding according to the equation—

$$2(CH_3)_2CO + PCl_3 = 2HCl + (CH_3 - CO - CH_2)_2PCl\,.$$

By means of these different reactions **Michaelis** and his pupils have obtained a considerable number of substituted phosphorus-chlorides, among which are—

Phenyl[*]	phosphorus-chloride	by methods	1, 2, and 3.
Tolyl[†]	„	„	3
Xylyl[‡]	„	„	3
Ethyl[§]	„	„	2
Propyl[§]	„	„	2
Naphthyl[‖]	„	„	2
Acetonyl[¶]	„	„	3

The substituted chlorides resemble trichloride of phosphorus itself, not only in composition, but also in properties. As a rule they are fuming liquids, combining readily with chlorine to give solid compounds analogous to pentachloride of phosphorus; treated with water they yield *phosphinous* acids. Thus phenyl phosphorus chloride gives phenyl phosphinous acid—

$$(C_6H_5)PCl_2 + 2H_2O = (C_6H_5)PH_2O_2 + 2HCl\,.$$

While the products of addition which they form with chlorine react with water to give *phosphinic* acids—

$$(C_6H_5)PCl_4 + 3H_2O = (C_6H_5)PH_2O_3 + 4HCl\,.$$

Having obtained the substituted chlorides, **Michaelis** sought for some method for converting them into the corresponding primary phosphines, but the reduction proved to be more difficult than he anticipated. In his first experiments (with phenyl phosphorus chloride) he endeavoured to accomplish it by means of nascent hydrogen (evolved by the action of hydrochloric acid on zinc dust, and also by that of glacial acetic acid on zinc or on sodium amalgam). In these experiments only a trifling reduction occurred, mere traces of the primary phosphine being formed.

He next studied the action of hydriodic acid on the chloride, and found that when the gaseous hydracid was passed into the chloride, chlorine was gradually replaced by iodine and the resulting iodide combined with hydriodic acid, thus—

$$C_6H_5PCl_2 + 3HI = C_6H_5PI_2HI + 2HCl\,.$$

From this iodide **Michaelis** obtained phenyl phosphine by a similar reaction to that which gives rise to phosphuretted hydrogen from iodide of phosphorus, only instead of employing water for its decomposition alcohol was used. He gives the following equation as representing the reaction which occurs—

$$3C_6H_5PI_2,HI + 9C_2H_6O = C_6H_5PH_2 + 2C_6H_5PO_3H_2 + 3H_2O + 9C_2H_5I\,.$$

In later experiments he abandoned this method and employed a much simpler one,

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[*] *Berichte*, vi. (1873) 601; viii. (1875) 922; xii. (1879) 1009.

[†] *Berichte*, xiii. (1880) 653.

[‡] *Annalen*, 212, pp. 203 and 209.

[§] *Ibid.*, xiii. (1880) 2174.

[‖] *Berichte*, ix. (1876) 1051.

[¶] *Ibid.*, xvii. (1884) 1273.

namely, the destructive distillation of the phosphinous acid (which, as already stated, is produced by the action of water or alcohol on the substituted chloride[*]). The phosphinous acid decomposes in an analogous manner to phosphorous acid when heated, the products of the reaction being the corresponding phosphinic acid and the primary phosphine—

$$3C_6H_5PO_2H_2 = C_6H_5PH_2 + 2C_6H_5PO_3H_2.$$

The following details illustrate the application of this method to the preparation of phenyl phosphine:—

100 grms. of the crude phenyl phosphorus chloride are gradually mixed with excess of alcohol and the mixture filtered. The excess of alcohol, &c., is then distilled off in a current of carbonic anhydride and the syrupy residue placed in a distilling flask (through which a current of carbonic anhydride is passed), and heated over the naked flame. At first a little alcohol distils, then at 250° phenyl phosphine passes over. The flame may be removed when once the reaction has commenced, as it continues by itself. 14 grms. of the pure phosphine, or 60 per cent. of the theoretical yield, may be thus obtained.

From phenyl phosphorus chloride MICHAELIS obtained diphenyl phosphine by the following reactions:—

(1) The chloride is digested with mercury diphenyl at 200°, when diphenyl phosphorus chloride results[†]—

$$(C_6H_5)PCl_2 + Hg(C_6H_5)_2 = (C_6H_5)_2PCl + HgCl(C_6H_5);$$

or it is heated for some time at a temperature of 280° C., when the following reaction occurs—

$$2(C_6H_5)PCl_2 = (C_6H_5)_2PCl + PCl_3.$$

(2) Diphenyl phosphorus chloride, when heated with water or dilute soda solution, decomposes in the following manner:[‡]—

$$2(C_6H_5)_2PCl + 2H_2O = (C_6H_5)_2PH + (C_6H_5)_2HPO_2 + 2HCl.$$

He also obtained the tertiary base: at first by acting upon a mixture of phenyl phosphorus chloride and bromide of phenyl with sodium[§]—

$$(C_6H_5)PCl_2 + 2(C_6H_5)Br + 3Na = 2NaCl + NaBr + (C_6H_5)_3P;$$

but later this method was modified in a remarkable manner by substituting for phenyl phosphorus chloride, phosphorus chloride alone, the reaction occurring quite easily and very energetically at ordinary temperatures, according to the equation—

$$PCl_3 + 3(C_6H_5)Br + 6Na = 3NaCl + 3NaBr + (C_6H_5)_3P.$$

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[*] By modifying the conditions of the experiment a totally different reaction may be made to occur. The phosphinous acid is obtained by adding the chloride to excess of water; whereas by employing an insufficient quantity, there are produced in addition phenyl phosphinic acid, diphenyl phosphinic acid, and a solid compound of phenyl, hydrogen, and phosphorus, $(C_6H_5)HP_4$ (phenylated solid phosphide of hydrogen). MICHAELIS gives the following equations:—

(1) $(C_6H_5)PCl_2 + 2H_2O = (C_6H_5)PH_2O_2 + 2HCl.$

(2) $(C_6H_5)PCl_2 + (C_6H_5)PH_2O_2 = 2(C_6H_5)PO + 2HCl.$

(3) $5(C_6H_5)PO = (C_6H_4)_4P_2O_3 + P_2 + C_6H_5PO_2.$

(4) $5(C_6H_5)PO + H_2O + 3P_2 = 2(C_6H_5)P_4H + 3C_6H_5PO_2 = 2(C_6H_5)_2P_5O_2H + C_6H_5PO_2.$

[†] *Berichte*, viii. 1304.

[‡] MICHAELIS and GLEICHMANN, *Berichte*, xv. (1882) p. 801.

[§] MICHAELIS and GLEICHMANN, *Ibid.*, p. 820.

A perusal of the preceding sketch of the different methods hitherto discovered for the preparation of the phosphines will be sufficient to convince any one that to obtain these bodies in quantity is no easy task, for in nearly every case operations are involved which demand considerable expenditure of time and material, and frequently the yield of product is small.

One of us had for a long time sought for some easier and more direct method than any of those mentioned, and had made many attempts with that object in view in different directions, but without success.

At last the idea presented itself that the germ of a new process for obtaining phosphines ought to exist in the well-known and ordinary method for preparing phosphonium iodide.

In this reaction, as every one knows, water is allowed to act upon a mixture of phosphorus and its iodide, when iodide of phosphonium is obtained on the one hand, while phosphoric and phosphorous acids are produced on the other.

Now, it seemed not unreasonable to suppose that analogous reactions would occur, if instead of water an alcohol were used, and if this were the case a new and simple process for obtaining phosphines would be at hand.

Our first experiments to test the truth of this surmise have been made with benzyl alcohol, and the results have been unexpectedly gratifying, for not only does the reaction occur with the greatest ease, but the number of phosphorised derivatives of benzyl produced is remarkably large. Moreover, we have without the slightest difficulty obtained most of them in considerable quantity, so that we have been able to make a fairly exhaustive examination of their properties.

In short, the method has placed at our disposal a number of highly interesting substances, which could not have been obtained in sufficient quantity by any other means as yet known, and we have thus been enabled to fill up many *lacunæ* in the history of the benzyl phosphines and their derivatives. We may, however, state at the outset that the reaction which occurs between benzyl alcohol, iodide of phosphorus, and phosphorus, does not take place in exactly the manner we anticipated.

The Action of Benzyl Alcohol on a Mixture of Phosphorus and its Iodide.

We may remark at the outset that we employed in all our experiments the same mixture of phosphorus and phosphorus iodide as is used for the preparation of phosphonium iodide. It was prepared as follows:—40 parts by weight of vitreous phosphorus (carefully dried) were dissolved in an equal weight of dry and freshly-redistilled bisulphide of carbon, and to the solution 68 parts of iodine were gradually added. The retort in which the mixture was made was then heated in a water-bath and a current of dry carbonic anhydride passed through it until every trace of bisulphide had distilled off. We shall call the product, for the sake of brevity, "the phosphorus mixture."

We may also mention that in most of our experiments the quantity of benzyl alcohol taken was about the equivalent of the quantity of water used in the preparation of phosphonium iodide. Thus, for the above quantities of phosphorus and iodine 24 parts of water are required, and the equivalent quantity of benzyl alcohol ($H_2O : C_7H_8O$) is 144 parts.

Experiment 1.—30 grms. of the phosphorus mixture were placed in a flask fitted with an upright condenser, and 33 grms. of benzyl alcohol were added.

The mixture became warm on shaking, but no very energetic reaction occurred until the flask containing it was heated in a paraffin-bath; then, however, an action began and increased so rapidly as to become explosive,—the mixture being shot out of the condenser, while dense white vapours were evolved, evidently of iodide of benzyl, from their intolerably irritating effect on the eyes.

A second experiment, conducted in the same way and with the same quantities, led to precisely similar results.

What was left of the product from these two experiments consisted of a brownish resinous mass. It was first extracted with ether, which, however, did not dissolve very much, then the residue was boiled with alcohol and a solution obtained which deposited abundance of crystals (A) on cooling. These were filtered off and the mother-liquors concentrated, when a second crystalline product (B) was obtained.

(A) was recrystallised from spirit. It contained iodine, and when dried became very brown. A determination of iodine gave the following result:—

0·4863 gave 0·0488 AgI = 0·0263 I = 5·4 per cent.

It was evidently an impure product, so it was again dissolved in hot spirit. As the solution cooled, two distinct sets of crystals separated. One had the colour of bichromate of potash, while the other was colourless.

Eventually it was found that the red crystals were much less soluble in spirit than the colourless ones, and by repeated recrystallisation the latter were separated and obtained of the constant melting point 192° C. (corr.), while (B), when purified, had the same melting point.

The appearance and melting point led us to believe that the colourless crystals from (A) and (B) were both dibenzyl phosphinic acid, and this belief was strengthened by the fact that they dissolved readily in a solution of caustic baryta. The solution thus obtained was treated with carbonic anhydride (to remove excess of baryta), filtered and evaporated to small bulk. As the solution cooled, colourless plates separated out, which on analysis gave numbers showing that they were by no means pure.

Analysis.

0·4156 gave 0·106 $BaSO_4$ = ·06256 Ba = 15·05 per cent.
0·3930 lost at 110° C. 0·0893 H_2O = 22·70 „

	Obtained.	Calculated for $\{(C_7H_7)_2PO_2\}_2Ba,8H_2O$
Barium, ...	15·05	17·75
Water, ...	22·70	18·67

All the impure solid products were united and boiled with solution of caustic baryta to remove dibenzyl phosphinic acid. The residue was washed with water and dilute hydrochloric acid, and then boiled with alcohol. The filtered solution gave on cooling a crop of colourless needles, mixed with a few of the red crystals, but by recrystallisation they were obtained pure. They had a melting point of 212° C. (uncorr.), agreeing with that of tribenzyl phosphine oxide, and they also gave the compound with iodide of zinc, microscopically identical with a specimen prepared with a known sample of the oxide. The red crystals we did not obtain in sufficient quantity to examine.

Experiment 2.—In order to avoid the very violent action which had occurred in our first experiments, we now allowed the benzyl alcohol to drip down the inverted condenser slowly on to the phosphorus mixture from a tap funnel. The first drops occasioned a very violent action, even in the cold, the flask becoming full of white fumes and iodine vapour; but as more of the benzyl alcohol was added the action moderated, though it continued to be pretty brisk, and sufficiently so to keep the mixture in ebullition. When all the alcohol had been thus cautiously added, and the reaction appeared to be over, a little more of the phosphorus mixture was added, and further action occurred, but it was not very violent. Finally, the flask containing the product of the reaction was heated for some time in an oil-bath and then allowed to cool.

This product consisted of a dark brown viscid mass. To it a quantity of water was added, when heat was developed. The flask in which it was contained was next connected with a Liebig's condenser, and a current of steam blown through it, when a somewhat brisk action occurred, and an oily liquid distilled over. This was in fairly large quantity, and was readily identified by its boiling point (111° C.) and odour as toluol. The residue in the flask after steaming, consisting of a dark brown oily substance swimming on the surface of the water, rapidly solidified. The aqueous solution was decanted, and the residue (which had by this time completely solidified) was extracted two or three times with boiling water. The aqueous solutions were mixed, and gave on cooling an abundant colourless crystalline precipitate (A).

The residue after thorough extraction with water was pounded up in a dish and extracted several times with baryta solution, then washed with water, and finally boiled several times with alcohol, until nothing remained apparently but amorphous phosphorus. The alcoholic solutions were evaporated down, and gave on cooling an abundant crop of colourless needles (B).

The mother-liquors from (A) were pressed out through linen and evaporated until fumes of hydriodic acid came off. They were then allowed to cool, when the solution solidified to a radiating crystalline mass (C). The mother-liquors were squeezed out through linen and heated on a steam-bath for a considerable time, during which they not only fumed, owing to evolution of hydriodic acid, but also effervesced, and the effervescence increased on stirring. On heating some of the liquid in a tube it frothed considerably, and iodide of phosphonium sublimed, while later the odour of monobenzyl phosphine became very distinct and its hydriodate volatilised.

Examination of Product A.—This was freed as far as possible from adhering mother-liquors and warmed with baryta solution, when most of it dissolved. The solution was mixed with the baryta extracts of the insoluble product (from which B was eventually obtained), and after removing the excess of baryta by a current of carbonic anhydride, the filtered solution was evaporated down, once more filtered from a white insoluble substance which had separated, and then allowed to cool, when a crop of crystals was deposited, consisting of thin plates. These were rapidly washed and dried, first in air and then at 110° C.

Analysis.

(1) 2·1655 gave 0·7852 $BaSO_4 = 0·46168$ Ba = 21·31 per cent.
(2) 1·6808 „ 0·6116 „ = 0·35961 „ = 21·39 „

As the salt dissolved in hot alcohol and readily separated as the solution cooled, a quantity was thus recrystallised, the crystals dried as before, and a barium determination made—

(3) 1·6086 gave 0·5918 $BaSO_4 = 0·34796$ Ba = 21·63 per cent.

The numbers obtained show that the salt was dibenzyl phosphinate of barium.

	Obtained.			Calculated for $\{(C_7H_7)_2PO_2\}_2Ba$
	I.	II.	III.	
Barium, . .	21·31	21·39	21·63	21·84

On adding hydrochloric acid to its solution dibenzyl phosphinic acid was precipitated in the characteristic form.

Examination of Product B.—This product consisted of colourless needles. They were thoroughly drained in a filter, washed well with spirit, and a melting-point determination made, which agreed fairly well with that of tribenzyl phosphine oxide. Unfortunately the pure product was accidentally lost, so that no combustion of it was made. For that purpose a product obtained from the mother-liquors was used, which was once recrystallised.

Analysis.

$$0·3526 \text{ grms. gave} \begin{cases} 1·0329\ CO_2 = 0·2817\ C = 79·9 \text{ per cent.} \\ 0·2262\ H_2O = 0·025133\ H = 7·12 \text{ „} \end{cases}$$

	Obtained.	Calculated for $(C_7H_7)_3PO$
Carbon, ...	79·90	78·75
Hydrogen, ...	7·12	6·56

Although both the carbon and hydrogen were too high, there could be no question regarding the identity of the substance, for it gave all the reactions of tribenzyl phosphine oxide, especially the very characteristic yellow crystalline compound with bromine. Moreover, in other experiments a number of these compounds was obtained and analysed.

Examination of Product C.—The crystals were colourless, and consisted of tufts of radiating needles. They were readily soluble in water and in alcohol. Their aqueous solution reacted as follows:—With,

(1) Acetate of lead, an immediate white precipitate.

(2) Sulphate of zinc, no precipitate.
(3) Sulphate of magnesium, no precipitate.
(4) Caustic baryta, no precipitate; but on warming the neutral solution a crystalline salt at once separated.

This behaviour with baryta seemed to afford a method for separating the product from phosphoric and hydriodic acids, and for obtaining it in a state of purity.

Accordingly, the whole of it (after removal of adhering mother-liquor by pressure between filter-paper) was dissolved in warm water, and bartya added until the solution was nearly neutralised. A slight white precipitate was filtered off, and the filtrate heated gradually in a water-bath, when a considerable quantity of a salt separated in very thin iridescent plates, which were collected on a filter, washed and dried at 110° C.

Analysis.

1·6607 gave 1·2748 $BaSO_4$ = 0·74956 Ba = 45·13 per cent.

	Obtained.	Calculated for $C_7H_7PO_3Ba$
Barium, ...	45·13	44·62

The mother-liquors from which this salt had separated, when evaporated to small volume, gave a very soluble crystalline salt, which was also analysed.

Analysis.

1·4198 lost at 110° C. 0·1457 H_2O = 10·26 per cent.
1·4198 gave 0·6232 $BaSO_4$ = 0·36643 Ba = 25·79 „

	Obtained.	Calculated for $(C_7H_7HPO_3)_2Ba,3H_2O$
Water, ...	10·26	10·13
Barium, ...	25·79	25·61

There could then be very little doubt as to the composition of the original product. It was benzyl phosphinic acid and its two barium compounds which were analysed, the normal and acid salts respectively. To be quite certain on this point, a quantity of the normal barium salt was decomposed with the exact quantity of sulphuric acid, and the filtered solution evaporated down. The acid then separated in colourless crystalline crusts. These were dried by pressure and recrystallised from water, then dried, first on filter-paper and subsequently at 110° C.

Analysis.

$$0{\cdot}3631 \text{ gave} \begin{cases} 0{\cdot}6485\ CO_2 = 0{\cdot}176863\ C = 48{\cdot}70 \text{ per cent.} \\ 0{\cdot}1842\ H_2O = 0{\cdot}0204666\ H = 5{\cdot}63 \quad „ \end{cases}$$

	Obtained.	Calculated for $(C_7H_7)PO_3H_2$
Carbon, ...	48·70	48·83
Hydrogen, ...	5·63	5·23

Monobenzyl phosphinic acid had not been obtained previously. We describe its properties and salts on p. 612.

In the experiment, the results of which we have just described, we thus obtained and analysed three different phosphorised benzyl derivatives, which may be considered as the products of the oxidation of the primary, secondary, and tertiary phosphines respectively; while, on concentrating the mother-liquors from the monobenzyl phosphinic acid, we obtained a fourth, viz., monobenzyl phosphine, which we suspected to originate from a fifth, namely, benzyl phosphinous acid, $C_7H_7.PO_2H_2$.

Fresh experiments were therefore necessary, not only to decide whether this latter compound is really produced, but also to ascertain the quantities of the different substances formed, the nature of the reactions which yield them, and the conditions under which they are originated.

Experiment 3.—Three quantities, each consisting of 50 grms. benzyl alcohol and 50 grms. of the phosphorus mixture (very carefully prepared with pure materials and thoroughly free from bisulphide of carbon), were worked up as follows:—

The weighed quantity of phosphorus mixture was placed in a flask of about 500 c.c. capacity. The flask was then filled with carbonic anhydride, attached to an upright condenser, and the benzyl alcohol allowed to drop from a tap funnel down the condenser. Action occurred spontaneously as soon as some of the phosphorus mixture became moistened with the alcohol, and at first violet vapours of free iodine appeared. It seemed better to run in the alcohol in tolerably large quantities, so as to keep up a brisk action, sufficient to cause rapid ebullition, but care had to be exercised, or the reaction became unmanageable. When most of the alcohol had been added the reaction grew sluggish, but was started afresh by shaking the flask, so as to thoroughly mix its contents.

In the case of two of the quantities the flasks were heated after all action was over, but we think this was not advisable, as a sudden puff of hydriodic acid occurred. Always towards the close of the reaction a little phosphonium iodide sublimed in the condenser.

The product in each case consisted of a dark brown resinous mass. About 300 c.c. of cold water were next added to the contents of each flask and thoroughly incorporated with them by shaking, when the mixture grew slightly warm. A current of steam was next passed as long as oily liquid distilled over. By this means, from the three quantities operated upon, 45 grms. of toluol were obtained boiling at 110°-120° C. A small quantity of a less volatile liquid remained above this temperature, but its amount was trifling. Each of the products was steamed with three separate quantities of water, so as to extract all soluble substances as thoroughly as possible. The residue was well squeezed in a linen bag, and repeatedly digested with baryta solution as long as anything was dissolved. For this purpose the mass was pounded in a mortar with hot baryta solution, the extract decanted through a linen filter, and the operation repeated. Finally, the residue was well squeezed in a linen filter, and next again and again boiled with alcohol so long as anything was dissolved out. What remained undissolved consisted apparently of amorphous phosphorus, and weighed 35 grms.

The product of the reaction was thus split up into—

(1) Aqueous extracts, containing hydriodic acid, monobenzyl phosphinic acid, some

dibenzyl phosphinic acid (which rapidly separated from the solution almost completely), and other soluble substances.

(2) Baryta extracts, containing chiefly dibenzyl phosphinate of barium.

(3) Alcoholic extracts, containing tribenzyl phosphine oxide.

(4) Insoluble matter, chiefly amorphous phosphorus.

The treatment of the different extracts was as follows :—

Aqueous Extracts.—These were filtered from the dibenzyl phosphinic acid which had separated out,* then evaporated to small bulk, and allowed to crystallise, when a solid mass of benzyl phosphinic acid resulted. This, after squeezing as far as possible in a linen bag, weighed 28 grms. The mother-liquors were evaporated in a water-bath until dense fumes of hydriodic acid came off, and they were then allowed to cool, when another quantity of the phosphinic acid was obtained, which weighed, after drying by pressure, 32 grms. The mother-liquors, on further concentration, gave no more phosphinic acid. Thus, in all nearly 60 grms. of crude acid were obtained.

A quantity of the mother-liquors when heated in a distilling flask gave at first a distillate of hydriodic acid of constant boiling point, then phosphuretted hydrogen (some of which exploded in the condenser), a little iodide of phosphonium, and later hydriodate of monobenzyl phosphine. Another portion of the mother-liquors was heated in a distilling flask immersed in an oil-bath, and lost about half its volume of hydriodic acid of constant boiling point. The viscous residue was diluted with water, and neutralised with baryta, when a large quantity of a white amorphous precipitate was formed. It was filtered off, washed and analysed, and was found to consist of barium phosphate.

Analysis.

1·1814 lost when ignited 0·0460 = 3·89 per cent.
2·2540 (dried at 110° C.) gave 2·2634 $BaSO_4$ = 1·33084 Ba = 59·04 per cent.

	Obtained.	Calculated for $BaHPO_4$
Barium, ...	59·04	58·80
Water, ...	3·89	3·86

30 grms. of barium phosphate were obtained from the portion of the mother-liquors experimented upon, and it was estimated that 50 grms. would have been obtained if the whole of the mother-liquors had been employed.

Baryta Extracts.—These contained dibenzyl phosphinic acid almost exclusively. They were evaporated to dryness, and the residue heated for a day at 110° C. It weighed 68 grms., which correspond with 53·3 grms. of the acid. It was redissolved in water, and the acid obtained by precipitation with sulphuric acid and extraction of the precipitate with alcohol.

Alcoholic Extracts.—These contained principally tribenzyl phosphine oxide. They were evaporated to small bulk and allowed to cool, when the crude oxide separated. It

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* This was well washed, dissolved in baryta, and the solution added to the baryta extracts.

weighed, when dried as far as possible by pressure, 30 grms. The residual mother-liquors left on evaporation 3 to 4 grms. of a viscous mass, which was not further examined.

Experiment 4.—We had as yet not proved the production of benzyl phosphinous acid, though we had reason for suspecting its presence, as well as that of either phosphorous or hypophosphorous acids. For, on heating the mother-liquors from the crude phosphinic acid, we had noticed the production of the primary phosphine (or rather its hydriodate) and phosphonium iodide, and their formation seemed to be most readily explained on the hypothesis that the acids we have named were present originally, but were decomposed by heat.

To decide this question we performed a new experiment.*

Three quantities of benzyl alcohol, amounting in all to 145 grms., and three quantities of the phosphorus mixture, amounting to 200 grms., were worked up as described in Experiment 3, with this difference, that the benzyl alcohol was run in rather more slowly, so that the action was not quite so violent. The treatment of the crude product was at first substantially the same as in the previous experiment.

The tribenzyl phosphine oxide, however, at once showed itself to be impure, for when dried it became brown. It would not dissolve completely in cold acetic acid, whereas the pure oxide dissolves with the greatest ease. On boiling with acetic acid it entirely dissolved, but as the solution cooled, a substance separated in feathery crystals like sal-ammoniac, quite unlike the oxide of tribenzyl phosphine, which crystallises in needles. From the appearance of these crystals we were led to suspect that they were iodide of tetrabenzyl phosphonium,—a suspicion which was verified both by their analysis (after recrystallisation from alcohol) and by their properties.

Analysis.

0·7732 gave 0·3390 AgI = 0·183204 I = 23·69 per cent.

	Obtained.	Calculated for $(C_7H_7)_4PI$
Iodine, ...	23·69	24·32

When boiled with alcoholic soda solution they were decomposed, and on washing with water and recrystallising from alcohol, needles were obtained, melting at 216° C. (corr.). (The pure oxide melting at 215°·5.)† Some of the crystals were dissolved in alcohol, decomposed with oxide of silver, the product boiled with hydrochloric acid, and extracted with boiling water. The solution gave on cooling the characteristic needles of chloride of tetrabenzyl phosphonium, a further proof that the original substance was the iodide.

The main object of this experiment was, as we have said, to ascertain whether benzyl phosphinous acid was formed in the reaction. As it is a very soluble substance, we expected to find it, if it was produced at all, in the mother-liquors from the phosphinic

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* In the meantime we had obtained benzyl phosphinous acid from other sources, and had become acquainted with some of its properties. Among them, we had ascertained that it yields the primary phosphine when heated.

† One of us and N. COLLIE have shown that the haloid salts of tetrabenzyl phosphonium are decomposed when treated with an alkali, and yield the tertiary phosphine oxide (see p. 575).

acid, and we had already had some evidence of its presence there. We searched for it by the following method :—

The mother-liquors remaining, after the phosphinic acid had been separated as far as possible by concentration and crystallisation, were diluted and mixed with excess of acetate of lead. The insoluble lead salts produced (chiefly iodide and phosphate) were filtered off and the excess of lead removed by a current of sulphuretted hydrogen. The solution was filtered and evaporated until all acetic acid was driven off, and nothing but a syrupy liquid remained, which gave off benzyl phosphine on heating. The investigation of this syrup, which evidently contained the phosphinous acid, proved troublesome. A portion was neutralised with chalk and evaporated to small bulk, when a salt separated in crystalline crusts.

Analysis.

0·3965 (dried at 110° C.) gave 0·0768 $CaO = 0·0548$ $Ca = 13·82$ per cent.

	Obtained.	Calculated for $\{(C_7H_7)HPO_2\}_2Ca$
Calcium, ...	13·82	11·42

This showed that the calcium salt was not pure.

The rest of the syrup was neutralised with baryta and evaporated to small bulk, when the solution crystallised on cooling, and apparently two sets of crystals were formed. They were dried as far as possible by pressure, dissolved in a very little water, and then alcohol was added to the solution, when a crystalline salt was precipitated. This was washed and analysed.

Analysis.

0·6294 (dried at 110° C.) gave 0·5456 $BaSO_4 = 0·3208$ $Ba = 50·96$ per cent.

	Obtained.	Calculated for $(PH_2O_2)_2Ba$
Barium, ...	50·96	51·31

The salt gave all the reactions of a hypophosphite. Heated, it evolved phosphuretted hydrogen; boiled with sulphate of copper, the copper was reduced, &c.

The mother-liquors from which it had separated gave on evaporation in the desiccator a cake of crystals. Some of these were drained on filter-paper, then dried at 110° C. until they were of constant weight.

Analysis.

0·5564 gave 0·3251 $BaSO_4 = 0·1911$ $Ba = 34·34$ per cent.

	Obtained.	Calculated for $\{(C_7H_7)PO_2H\}_2Ba$
Barium, ...	34·34	30·64

A solution of this salt behaved with acetate of copper in the manner so characteristic of benzyl phosphinite, giving a greenish precipitate in a strong solution, no precipitate in a weak solution, but an immediate green precipitate on boiling. Moreover, the mother-liquors from the copper salt obtained from a strong solution deposited the green salt immediately on boiling.

As the percentages both of calcium and barium in the respective salts analysed indicated that they did not consist of the pure phosphinites, but contained some hypophosphite, it was determined to obtain the zinc salt, which is deposited in a very characteristic way on boiling a weak solution of the phosphinous acid with acetate of zinc. Accordingly, the remainder of the barium salt was exactly decomposed with sulphuric acid, the solution filtered from the precipitated sulphate of barium and diluted. Acetate of zinc was then added (to the boiling solution), when it became turbid, and deposited a small quantity of a resinous salt. This was filtered off and excess of acetate of zinc added, when a salt was precipitated (when the solution had been boiled for some time) in the characteristic form of the phosphinite, viz., minute droplets, with crystalline points projecting in all directions. A determination of zinc proved it to be the pure substance.

Analysis.

0·3044 gave 0·0670 ZnO = 0·0537 Zn = 17·64 per cent.

	Obtained.	Calculated for $\{(C_7H_7)PO_2H\}_2Zn$
Zinc, ...	17·64	17·33

The results of these experiments show that in the reaction occurring between benzyl alcohol and the phosphorus mixture *all* the possible products of the oxidation of the three benzyl phosphines are produced, while in addition, in the experiment last described, iodide of tetrabenzyl phosphonium was also formed. In this experiment the conditions were slightly different from those of the preceding, for an excess of the phosphorus mixture was employed, but whether this influenced the course of the reaction or not we have not had the opportunity to decide.

When we come to inquire into the mechanism (so to speak) of the reaction by which these different substances are formed, our attention is first arrested by the fact that two series of phosphorised derivatives are produced by the action of benzyl alcohol on the mixture of phosphorus and its iodide. One of these (excluding toluol) is represented by a solitary substance, viz., iodide of tetrabenzyl phosphonium, which contains less oxygen than the alcohol. The other includes all the possible products of the oxidation of benzyl phosphines, and, with the exception of oxide of tribenzyl phosphine, contains more oxygen than benzyl alcohol. To a certain extent, therefore, the reaction is analogous to that which occurs between water and the phosphorus mixture, in which phosphonium iodide is a product of reduction, while phosphorous and phosphoric acids are products of oxidation. To account for this double set of actions in the case of benzyl alcohol (*i.e.*, reduction and oxidation) is not difficult. The primary reducing agents are phosphorus and its iodide, while in the later stages of the reaction there is hydriodic acid also. As to the oxidising agent, iodine is visibly liberated in the first phases of the reaction, and probably water also, so that we think it probable that it is by their interaction that some of the oxidised products are formed. It is, however, very difficult, if not indeed impossible, to gain a complete insight into the changes which occur. But, on the other hand, it is easy to write a set of equations to account for the formation of the different products. Thus, the following may be written:—

(1) $PI_2+C_7H_7OH+H_2O=(C_7H_7)H_2PO_2+HI+I$.
(2) $PI_2+C_7H_7OH+2H_2O+I=(C_7H_7)H_2PO_3+3HI$.
(3) $PI_2+2C_7H_7OH=(C_7H_7)_2HPO_2+HI+I$.
(4) $PI_2+3C_7H_7OH+HI=(C_7H_7)_3PO+2H_2O+3I$.
(5) $PI_2+4C_7H_7OH+4HI=(C_7H_7)_4PI+4H_2O+5I$.
(6) $PI_2+2H_2O=H_3PO_2+HI+I$.
(7) $PI_2+4H_2O+3I=H_3PO_4+5HI$.
(8) $2HI+C_7H_7OH=C_7H_8+H_2O+I_2$.
(9) $P+I_2=PI_2$.

Let us next compare the quantities of the different substances actually obtained with those required for the above reactions, remembering that the "balance sheet" will be extremely rough. In Experiment 3 the following were the quantities employed and produced:—

Employed in the Reaction.		Produced by the Reaction.	
Phosphorus,	55·5	Crude monobenzyl phosphinic acid,	60·0
		„ dibenzyl „ „	53·5
		„ tribenzyl phosphine oxide,	30·0
		„ toluol,	45·0
Iodine,	94·5	Hydriodic acid (calculated),	95·2
		Phosphoric acid (calculated from 50 grms. $BaHPO_4$),	21·0
Benzyl alcohol,	159·0	Amorphous phosphorus,	35·0
	309		339·7

The quantities of phosphorus, water, and benzyl alcohol, taking part in the reaction, may be accounted for as follows :—

Phosphorus—

Taken,	55·5 grms.
Remaining,	35·0 „
Used up in the reactions,	20·5 „

The phosphorus used up in the reactions is accounted for thus—

60	grms.	$(C_7H_7)H_2PO_3$	contains	10·8 phosphorus.
53·5	„	$(C_7H_7)_2HPO_2$	„	6·7 „
30·0	„	$(C_7H_7)_3PO$	„	2·9 „
50·0	„	$BaHPO_4$	„	6·6 „
				27·0 „

Water—	
Set free in reaction, 4	3·4 ? grms.
„ „ 5	? „
„ „ 8	8·8 „
	12·2 „
Required for reaction, 1	? (traces)
„ „ 2	12·5
„ „ 6	? (traces)
„ „ 7	15·4
	27·9
Benzyl alcohol—	
Taken,	159·0
Accounted for thus—	
Required for reaction, 1	? (traces)
„ „ 2	37·6
„ „ 3	47·0
„ „ 4	30·3
„ „ 5	? (traces)
„ „ 8	52·8
	167·7

In glancing over the foregoing table, the following points become apparent:—

(1) The quantity of products is of greater weight than the sum of the quantities of benzyl alcohol, phosphorus, and iodine employed.

(2) The quantity of phosphorus used up in the reactions is less than that required for the weights of the different substances obtained. This is probably due to the following causes:—

(A) The "unacted upon" phosphorus is not pure phosphorus, but contains organic compounds; therefore the real quantity used up was probably rather more than 20·5 grms. (B) All the products were weighed in a slightly moist condition, hence their real weights are no doubt slightly less than those actually obtained, and this is also shown by the fact that the benzyl alcohol required for the reactions is about 5 per cent. higher than the amount used. (C) The whole of the phosphate of barium was not weighed, but its amount calculated, on the assumption that $\frac{3}{5}$ of the total quantity were actually weighed.

(3) The quantity of water set free (or supposed to be set free) is less than one-half of that which is required for those reactions in which it is supposed to take part. This is important, as, we think, it clearly points to the fact that at least some of the above equations do not represent the actual changes occurring, *but that in all probability iodized derivatives are produced in the first instance, which are subsequently decomposed by the water which is added.* Thus, the difference in the water supposed to be set free and required in the equations (14·1 grms.), almost agrees with the amount required for the

production of the phosphoric acid (15·4 grms.). And that this supposition is a true one is also clearly shown by the rise in temperature which takes place when the product of the reaction is treated by water, and by the complete change which occurs in its appearance, as well as by the fact that the weight of products is greater than the collective weights of phosphorus, benzyl, alcohol, and iodine originally taken.

It is also quite possible that the whole of the tribenzyl phosphine oxide is formed by the action of caustic baryta on iodide of tetrabenzyl phosphonium produced in the first instance: but we have not decided this point.

(4) The quantity of benzyl alcohol employed is less than the quantity calculated as being equivalent to the weights of the different substances obtained. The difference, however, is not great (about 5 per cent.), and is accounted for, no doubt, as we have explained.

The reaction with benzyl alcohol is a very interesting one, and we believe that it is capable of extension to other alcohols. Some preliminary experiments which we have made justify us in this belief, and we intend to pursue the inquiry.

PART III.—THE PRODUCTS OF THE OXIDATION OF BENZYL PHOSPHINES.

The substances which we describe in this part of our paper are four in number, viz., benzyl phosphinous acid and benzyl phosphinic acid, derived from the primary phosphine; dibenzyl phosphinic acid, from the secondary phosphine; and oxide of tribenzyl phosphine, from the tertiary base.* Benzyl phosphinous acid we obtained for the first time by the oxidation of the primary phosphine, while we discovered benzyl phosphinic acid during our investigations on the action of benzyl alcohol on a mixture of phosphorus and its iodide. One of us and W. Wheeler were the first to obtain dibenzyl phosphinic acid, which we isolated from the products of Hofmann's sealed tube reaction. In this part of our communication we describe the properties and compounds of the three acids, as well as those of the tertiary phosphine oxide, which we have so frequently, and at times unexpectedly, encountered in the course of our investigations.

(1) *Benzyl Phosphinous Acid*, $(C_7H_7)H_2PO_2$.

We have obtained this acid in three different ways—(1) By the oxidation of monobenzyl phosphine; (2) Among the products of Hofmann's sealed tube reaction; (3) Among the products of the action of benzyl alcohol on a mixture of phosphorus and its iodide. We have already described the steps which we employed for isolating it in each of these three cases, but it may not be unadvisable to describe the best method of obtaining it.

The primary phosphine is allowed to oxidise in the air, care being taken to prevent the temperature from rising too high. The final product is a thick syrupy liquid, which contains phosphoric acid and benzyl phosphinic acid, in addition to the phosphinous acid. Either of the two following methods may be employed for isolating the latter:—

(1) The viscous mass is dissolved in water and the solution just neutralised with baryta. It is then filtered from the precipitated phosphate of barium and evaporated to a small volume, when practically the whole of the phosphinate of barium separates out. The phosphinous acid is then obtained by decomposing the filtered solution with the proper quantity of sulphuric acid.

(2) The aqueous solution of the product of oxidation is dissolved in water and precipitated with acetate of lead, filtered from the phosphate and phosphinate of lead, which separates, precipitated with sulphuretted hydrogen, and the filtered solution evaporated until the whole of the acetic acid has passed off.

Properties.—Benzyl phosphinous acid is a syrupy liquid which refuses to crystallise. It is fairly soluble in water, but separates from a strong solution in oily drops. It dis-

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* As we have mentioned on p. 585, it is possible that other oxidised derivatives exist, but the above are the most important.

solves easily in alcohol, and it is also soluble in ether. It is a monobasic acid, and most of its salts are very soluble. They are consequently troublesome to obtain pure, but the following were prepared and analysed.

Barium Benzyl Phosphinite.—Obtained by neutralising the crude acid formed by the oxidation of the primary phosphine, filtering off the barium phosphate, boiling to precipitate the barium phosphinate, again filtering and concentrating to a syrup. The latter placed *in vacuo* solidified to a granular crystalline mass. This was squeezed as dry as possible in a cloth filter, and for analysis a sample was pounded up and exposed to the air until it ceased to lose weight.

Analysis.

1·1383 lost at 110° C. 0·1443 $H_2O = 12·67$ per cent.
1·1383 gave 0·5119 $BaSO_4 = 0·301$ Ba = 26·44 „

	Obtained.	Calculated for $(C_7H_7HPO_2)_2Ba,4H_2O$
Water, . . .	12·67	13·87
Barium, . . .	26·44	26·39

The salt in all probability suffers a slight decomposition at 110° C., and also becomes partially oxidised. For after it had been heated and was dissolved in water, a distinct odour of the primary phosphine was observed. No doubt these facts account for the discrepancy between the observed loss at 110° C., and the calculated amount of water of crystallisation.

Calcium benzyl phosphinite was obtained by neutralising a solution of the acid with chalk and evaporating the filtered solution. The salt separated out in crystalline crusts during the evaporation in a very characteristic manner. It appears to be less soluble in hot than in cold water.

Analysis.

·6943 lost at 110° C. 0·0113 = 1·62 per cent.
·6943 gave 0·1070 CaO = 0·76428 Ca = 11·00 „

	Obtained.	Calculated for $3\{(C_7H_7HPO_2)_2Ca\},H_2O$
Water, ...	1·62	1·68
Calcium, . . .	11·00	11·23

Magnesium Benzyl Phosphinite.—This salt was prepared by boiling a solution of the acid with excess of carbonate of magnesium, filtering and concentrating the solution first in a water-bath, and afterwards *in vacuo* over sulphuric acid. When the solution grew syrupy, crystalline crusts were slowly deposited.

Analysis.

0·7354 lost (after 8 days' heating) at 110° C. 0·1538 $H_2O = 20·91$ per cent.
0·7354 gave 0·1938 $Mg_2P_2O_7 = 0·0419$ Mg = 5·69 „

	Obtained.	Calculated for $(C_7H_7HPO_2)_2Mg,5H_2O$
Magnesium, . .	5·69	5·66
Water, . . .	20·91	21·22

Zinc Benzyl Phosphinite.—Obtained by adding acetate of zinc in excess to a rather dilute solution of the acid and boiling for some time, when the compound was deposited as a granular crystalline powder. The salt is anhydrous.

Analysis.

(I.) 0·3044 gave 0·067 ZnO = 0·0537 Zn = 17·64 per cent.
(II.) 0·5145 „ 0·1133 „ = 0·09091 „ = 17·66 „
(III.) 0·8757 „ 0·1946 „ = 0·15616 „ = 17·83 „

	Obtained.			Calculated for $\{(C_7H_7)HPO_2\}_2Zn$
	I.	II.	III.	
Zinc, . .	17·64	17·66	17·83	17·33

Cadmium Benzyl Phosphinite.—This salt was prepared by decomposing a solution of the barium salt with the equivalent quantity of cadmium sulphate, filtering from the sulphate of barium and evaporating the filtrate. When the solution grew concentrated a white flocculent salt separated, which was filtered off and analysed. The mother-liquors, when further concentrated, gave a slimy deposit, and on cooling a crystalline salt.

Analysis.

0·4953 gave 0·1569 CdO = 0·137287 Cd = 27·71 per cent.

	Obtained.	Calculated for $\{(C_7H_7)HPO_2\}_2Cd$
Cadmium, ...	27·71	26·54

Lead Benzyl Phosphinite.—A rather concentrated solution of the pure phosphinous acid (obtained by decomposing the barium salt with sulphuric acid) was mixed with the calculated quantity of acetate of lead. The solution was filtered from a slight white precipitate which had been thrown down, slightly acidulated with acetic acid and warmed, when a colourless crystalline salt was precipitated. It was rapidly washed, dried, and analysed.

Analysis.

0·4269 (air-dried salt) lost at 110° C. 0·0061 H_2O = 1·42 per cent.
0·4269 gave 0·2446 $PbSO_4$ = 0·1671 Pb = 39·14 „

	Obtained.	Calculated for $2(C_7H_7HPO_2)_2Pb,H_2O$
Water, ...	1·42	1·14
Lead, ...	39·14	39·35

The salt fused when dried at 110° C., and smelt slightly of the primary phosphine. It dissolves readily in water. When its solution is concentrated by boiling it separates out in oily drops.

Attempts to prepare Benzyl Phosphinite of Copper.—The behaviour of benzyl phosphinite of barium (or any other phosphinite) with acetate of copper is very characteristic. On mixing the two solutions a pale green precipitate is produced in a strong solution, but no precipitate in a weak solution. A specimen of the green precipitate was prepared and analysed.

Analysis. (The salt lost 7·43 per cent. on drying it at 110° C.)

0·10273 gave 0·0304 CuO = 0·0242 Cu = 25·26 per cent.

		Calculated for	
	Obtained.	$C_7H_7PO_3Cu$	$(C_7H_7HPO_2)_2Cu$
Copper, ...	25·26	27·03	17·00

The salt was probably impure benzyl phosphinate of copper, and not phosphinite at all. The mother-liquors which had been filtered from it rapidly decomposed and a yellow to red precipitate separated, having the appearance of cuprous oxide. On warming the wash waters, especially if they contain excess of acetate of copper, the light green salt is precipitated, but redissolves as the solution cools. It appears, therefore, that benzyl phosphinite of copper, if it exists at all, is a very unstable substance, and rapidly oxidises to phosphinate. The behaviour of a phosphinite with a copper salt affords an excellent test for the acid.

Action of Heat on Benzyl Phosphinous Acid.—A quantity of the acid was heated in a small retort. It rapidly decomposed, and a liquid distilled, having the characteristic odour of the primary phosphine, smoking on coming in contact with the air, and giving a crystalline compound with hydriodic acid, which volatilised in that gas in the characteristic manner of the phosphine hydriodate. The reaction probably proceeds according to the equation—

$$3(C_7H_7)H_2PO_2 = 2(C_7H_7)H_2PO_3 + (C_7H_7)H_2P\,,$$

giving the primary phosphine and benzyl phosphinic acid, and is analogous to the decomposition which phenyl phosphinous acid suffers when heated.*

(2) *Benzyl Phosphinic Acid*, $(C_7H_7)H_2PO_3$.

This acid is produced along with the benzyl phosphinous acid in the three reactions we have mentioned above, but it is only formed in very small quantity during the oxidation of the primary phosphine, benzyl phosphinous acid being, as we have mentioned, by far the chief product. A similar remark applies to the reaction occurring between oxide of zinc, benzyl chloride, and phosphonium iodide, only very small quantities of the benzyl phosphinic acid being found among the products. The only satisfactory method for obtaining it is by the third process we have mentioned, *i.e.*, the action of benzyl alcohol on a mixture of phosphorus and phosphorus iodide, when it is produced in large quantities, and is easily separated from the other products of the reaction.

The following are the details of the process:—55·5 grms. of phosphorus are dissolved in an equal weight of bisulphide of carbon in a flask about 1 litre in capacity, and 94·5 grms. of iodine are gradually added. The bisulphide is then distilled off and the last traces removed by a current of dry carbonic anhydride. An upright condenser is now fitted to the flask (which must be filled with dry carbonic anhydride) and 159 grms. of benzyl alcohol cautiously added through the condenser from a tap funnel. As soon as

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* MICHAELIS and ANANOFF, *Ber.*, vii. 1688; and KOHLER and MICHAELIS, *Ber.*, x. 807.

the mixture of phosphorus and its iodide is moistened with the benzyl alcohol a violent reaction occurs—violet vapours of iodine appearing and a dense white smoke. It is advisable, as soon as the reaction has commenced, to run in the benzyl alcohol in fairly large portions, waiting, however, each time until it moderates. By this means constant ebullition is kept up until the end of the reaction. Towards the close of the operation (that is to say when all or most of the alcohol has been added) the flask is well shaken from time to time, so as to mix its contents thoroughly. This generally starts the reaction afresh, and ebullition becomes energetic.

When all action is over, the product is allowed to cool, water is added until the flask is half full, and the mixture thoroughly shaken, when it becomes warm. Then a current of steam is blown through it and the vapours condensed, as they contain toluol, &c., the steaming being continued so long as volatile matters pass over. The aqueous solution is next decanted through a linen filter from the brown resinous mass which remains, and the latter is again mixed with water and steamed as before, the operation being repeated a third time. All the aqueous extracts are united and allowed to cool, when a considerable quantity of dibenzyl phosphinic acid separates out. This is filtered off through a linen filter and well squeezed, so as to avoid loss of liquid. The solution is next evaporated until fumes of hydriodic acid appear, and then allowed to stand for some hours, when the crude benzyl phosphinic acid separates out. It is thoroughly squeezed in a linen filter, and the mother-liquors again concentrated, &c., when a fresh quantity of the acid usually separates.

The yield of crude acid from the quantities mentioned should be about 60 grms. The acid thus obtained is very impure, and contains considerable quantities of hydriodic and phosphoric acids. It may be recrystallised from water, but cannot be readily purified by that means, as the impurities cling most tenaciously to it. By far the best method of purification consists in converting it into its barium salt, and decomposing the latter with sulphuric acid. The barium salt is easily obtained pure by neutralising a *dilute* solution of the acid with caustic baryta, filtering from the precipitate of phosphate of barium and boiling the solution, when it separates in the crystalline state.

Properties.—Monobenzyl phosphinic acid is a colourless body which crystallises from a hot and concentrated aqueous solution. It is readily soluble in water and alcohol. Its melting point was found to be 169°–169°·5 (corr.). It is a dibasic acid, and forms a number of salts, most of which crystallise easily from water.

For analysis a quantity of the acid was prepared from the barium salt, and was dried first in a desiccator then for a short time at 110° C.

Analysis.

$$0{\cdot}3631 \text{ gave} \left\{ \begin{array}{l} 0{\cdot}1842 \ H_2O = {\cdot}020466 \ H = \ 5{\cdot}63 \text{ per cent.} \\ 0{\cdot}6485 \ CO_2 = {\cdot}176863 \ C = 48{\cdot}70 \quad ,, \end{array} \right.$$

$$* \ 0{\cdot}2559 \text{ gave } 0{\cdot}1608 \ Mg_2P_2O_7 \qquad = {\cdot}044908 \ P. = 17{\cdot}54 \quad ,,$$

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* By the oxide of copper method.

	Obtained.	Calculated for $(C_7H_7)H_2PO_3$
Carbon, ...	48·70	48·83
Hydrogen, . . .	5·63	5·23
Phosphorus, . . .	17·54	18·02

Salts.—

Barium Benzyl Phosphinate (*normal*) $(C_7H_7)BaPO_3,2H_2O$.—This is an extremely characteristic compound, and is readily obtained by neutralising a fairly strong solution of the acid with a warm solution of caustic baryta, when it crystallises out in thin plates. As it is much less soluble in hot than in cold water, it is precipitated on warming a weak solution, and if the heat is applied gradually (for instance by immersing the vessel containing the solution in a water-bath full of cold water and then heating the latter) it separates in large scales with the lustre of mother-of-pearl. This property furnishes an easy method for identifying the acid and separating it from other substances.

Analysis.

1·4246 (dried at 110° C.) gave 1·0809 $BaSO_4$ = 0·63555 Ba = 44·61 per cent.

	Obtained.	Calculated for $C_7H_7PO_3Ba$
Barium, ...	44·61	44·62

1·3643 lost at 110° C. 0·1389 = 10·18 per cent.

	Obtained.	Calculated for $C_7H_7BaPO_3,2H_2O$
Water, ...	10·18	10·49

Solubility.—An excess of the salt was allowed to stand for some days with water, well shaken repeatedly at intervals and the mixture filtered. Temperature of solution before filtering, 9°·7 C. 100 c.c. of this solution weighed (at 9°·7 C.) 101·446 grms., and left on evaporation 1·6115 grms. of the anhydrous salt = 1·8005 grms. hydrated salt. Therefore, at 9°·7 C.,

100 c.c. of saturated solution contain 1·8005 grms. hydrated salt.
100 grms. of water dissolve 1·807 „ „

Another quantity of the cold saturated solution was boiled for some time, then filtered through a hot-water funnel and cooled to 9°·7 C.

100 c.c. of this solution weighed (at 9°·7 C.) 100·475 grms., and left on evaporation 0·3855 grm. of salt (dried at 110° C.). Therefore, at 100° C. (or rather at the boiling point of the solution)

100 c.c. of solution contain (about) 0·4307 grm. hydrated salt.
100 grms. of water dissolve 0·4305 „ „

Acid Barium Benzyl Phosphinate, $(C_7H_7 . HPO_3)_2Ba,3H_2O$.—This salt was obtained by adding to a solution of the normal salt the calculated quantity of benzyl phosphinic acid and evaporating the mixture to a very small bulk, when, on cooling, the compound separated as a crystalline mass. It is very soluble in water.

Analysis.

2·7733 grms. lost at 110° C. 0·2884 grm. = 10·39 per cent.
2·7733 „ gave 1·2159 $BaSO_4$ = 0·7149 Ba = 25·77 „

	Obtained.	Calculated for $(C_7H_7HPO_3)_2Ba,3H_2O$
Water, ...	10·39	10·13
Barium, ...	25·77	25·70

Calcium Benzyl Phosphinate (*normal*), $(C_7H_7)CaPO_3,H_2O$.—This salt was obtained by mixing a solution of the acid with a neutral solution of acetate of calcium and warming the mixture. The calcium salt was then precipitated in glittering scales, very similar in appearance to the barium salt. Prepared by this method it is thrown down on warming, even in weak solutions. The molecule of water which it contains is water of *halhydration*, as it is not lost at 110° C., and not completely at 200° C.

Analysis.

0·6177 lost at 200° C. 0·0428 H_2O = 6·92 per cent.

I. 0·6459 (dried at 110° C.) gave 0·1563 CaO = 0·11164 Ca = 17·28 per cent.
II. 0·6177 „ „ „ 0·1542 CaO = 0·11014 Ca = 17·83 „

	Obtained.		Calculated for
	I.	II.	$(C_7H_7)CaPO_3,H_2O$
Water, . .	...	6·92	7·89
Calcium, . .	17·28	17·83	17·54

Magnesium Benzyl-Phosphinate (*normal*), $(C_7H_7)MgPO_3,H_2O$.—Was prepared in exactly the same way as the calcium salt, that is to say, by adding a solution of acetate of magnesium to the acid and warming the mixture. It is then precipitated, even in a fairly dilute solution, as a granular white powder. The water which it contains must be considered as water of *halhydration*, as it is only driven off at 200° C.

Analysis.

0·7858 (dried at 110° C.) lost at 200° C. 0·0683 H_2O = 8·69 per cent.
1·0681 „ „ gave 0·5617 $Mg_2P_2O_7$ = 0·12144 Mg = 11·36 „

	Obtained.	Calculated for $(C_7H_7)MgPO_3,H_2O$
Water, ...	8·69	8·49
Magnesium, ...	11·36	11·32

Zinc Benzyl Phosphinate, $(C_7H_7)ZnPO_3,H_2O$.—Was prepared by adding acetate of zinc to a boiling solution of the acid, when it was thrown down as a white amorphous and bulky precipitate. On concentrating the mother-liquors a granular white powder separated, which was not examined. The molecule of water which the salt contains is driven off at 110° C.

Analysis.

0·7902 lost at 110° C. 0·0551 = 6·97 per cent.
0·7902 gave 0·2544 ZnO = 0·20414 Zn = 25·83 „

	Obtained.	Calculated for $(C_7H_7)ZnPO_3,H_2O$
Water, ...	6·97	7·11
Zinc, ...	25·83	25·69

Cadmium Benzyl Phosphinate, $(C_7H_7)CdPO_3,H_2O$.—A solution of the pure acid was largely diluted and mixed with a freshly prepared solution of acetate of cadmium. No precipitate was produced until the cadmium salt was added in considerable excess; then however a salt was precipitated in minute spherical crystalline masses. On concentrating the mother-liquors only a trifling quantity of salt was obtained.

Analysis.

1·0181 lost (after 3 days' heating) at 200° C. 0·0571 H_2O = 5·60 per cent.
1·0181 gave 0·4312 CdO = 0·3773 Cd = 37·05 „

	Obtained.	Calculated for $(C_7H_7)PO_3Cd,H_2O$
Water, ...	5·60	6·00
Cadmium, . . .	37·05	37·33

Lead Benzyl Phosphinate, $(C_7H_7)PbPO_3,H_2O$.—Was obtained as an amorphous white precipitate on boiling a solution of the acid with acetate of lead. The molecule of water which the salt contains is only lost at a temperature of 200° C.

Analysis.

1·4939 lost at 200° C. 0·0341 H_2O = 2·28 per cent.
1·4939 gave 1·1748 $PbSO_4$ = 0·8025 Pb = 53·71 „

	Obtained.	Calculated for $(C_7H_7PbPO_3)_2,H_2O$
Water, ...	2·28	2·33
Lead, ...	53·71	53·62

Copper Benzyl Phosphinate, $(C_7H_7)CuPO_3,H_2O$.—On mixing a solution of the acid with acetate of copper a light blue precipitate of the copper salt is thrown down.

Analysis.

0·939 lost (after 4 days' heating) at 200° C. 0·0571 = 6·08 per cent.
(On the 4th day the salt began to decompose.)
0·939 gave 0·2973 CuO = 0·23708 Cu = 25·24 per cent.

	Obtained.	Calculated for $(C_7H_7)CuPO_3,H_2O$
Water, ...	6·08	7·17
Copper, ...	25·24	25·09

Silver Benzyl Phosphinate.—This salt is thrown down as a bulky white precipitate on mixing a neutral solution of the potassium salt with nitrate of silver. It darkens when warmed, and is unstable. It was not analysed owing to this fact.

Potassium Benzyl Phosphinate was prepared by neutralising the acid with caustic potash solution and evaporating to small bulk, when eventually a crystalline mass remained. The salt is very soluble both in water and alcohol.

Analysis.

$$0·4047 \begin{cases} \text{lost at 110° C., 0·0278 } H_2O = 6·86 \text{ per cent.} \\ \text{gave 0·7392 } K_2PtCl_6 = 0·11815\ K = 29·19\ „ \end{cases}$$

	Obtained.	Calculated for $(C_7H_7)K_2PO_3,H_2O$
Potassium, . . .	29·19	29·32
Water, ...	6·86	6·76

Sodium Benzyl Phosphinate and *Ammonium Benzyl Phosphinate* resemble the potassium compound, and were prepared in a similar manner. They were not analysed.

Action of a Moderate Heat on Benzyl Phosphinic Acid.—When moderately heated the acid loses water, the amount finally lost varying apparently with the conditions of the experiment. In one experiment about five grms. of the acid* were placed in a distilling flask, through which a slow current of hydrogen passed, and the flask was heated in an oil-bath for some hours at a temperature ranging from 180°–195° C., then to 220°–230° C. for nearly a week. During this time a trace of the acid or some product of its decomposition appeared to volatilise. At the end of this time the loss amounted to 4·19 per cent. The equation—

$$2C_7H_7H_2PO_3 = H_2O + (C_7H_7)_2H_2P_2O_5$$

requiring 5·23 per cent. The product was light brown in colour, and very crystalline. On boiling with water it appeared to be quite insoluble. A little of it, mixed with a solution of caustic baryta, gave at once a crystalline deposit, which seemed to be very insoluble. The whole of the product was pounded in a mortar and boiled with water, in which some, but not all dissolved. The solution, which was fairly dilute, was then mixed with a slight excess of caustic baryta and gradually heated. Long slender needles separated, which were well washed and air dried.

Analysis.

1·2391 lost at 240° C. 0·1173 = 9·46 per cent.
1·2391 gave 0·5733 $BaSO_4$ = 0·337 Ba = 27·19 „
0·6822 „ 0·8146 CO_2 = 0·222163 C = 32·56 „
0·6822 „ 0·2363 H_2O = 0·026255 H = 3·84 „

	Obtained.	Calculated for $(C_7H_7)_2P_2O_5Ba,3H_2O$
Water, ...	9·46	10·48
Barium, ...	27·19	26·60
Carbon, ...	32·56	32·62
Hydrogen, ...	3·84	3·88

In another experiment about 5 grms. of the acid† were heated at once to 230° C., and kept at that temperature for a considerable time. The final loss amounted to 14·44 per cent. The equation—

$$2(C_7H_7)H_2PO_3,H_2O = 3H_2O + (C_7H_7)_2H_2P_2O_5$$

requires a loss of 14·21 per cent.

It would appear from this result that the two specimens of acid experimented with were different, the latter containing water of crystallisation, the former none. The product from this second experiment was broken up, pounded fine, and boiled with water, in which it ultimately dissolved. The solution was divided into three parts, A, B, and C.

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* Not absolutely pure, but recrystallised two or three times from the crude product.

† A very pure specimen of the acid, which had been obtained from the barium salt, and was snow-white.

A was *slightly* evaporated, and on cooling gave a crop of colourless crystals, unlike the original acid, and probably the pyro acid.

B was evaporated to a small bulk, and was completely converted into the original acid, as was proved by the production of the characteristic barium salt.

C was neutralised with caustic baryta, and gave the long needles of the pyrophosphinate exactly similar to those obtained in the first experiment.

We may conclude, then, that at a temperature of 200°–230° C., benzyl phosphinic acid is converted into the pyro acid, $(C_7H_7)_2H_2P_2O_5$ (which gives a characteristic barium salt, and is less soluble than the original acid). The pyro acid, on boiling for a long time with water, is rehydrated, and gives the original benzyl phosphinic acid.*

Action of a Rapid Heat on Benzyl Phosphinic Acid.—5 grms. of the acid were cautiously heated in a small retort over the naked flame of a Bunsen burner. At first a few drops of water passed over, then a yellowish oil distilled, and presently a sudden decomposition occurred, the mass charring. The lamp was instantly removed, but the decomposition went on spontaneously.

The receiver contained 1 to 2 c.c. of a yellowish oil, smelling very slightly of the primary phosphine, and partly solidifying on cooling. The black tarry matter in the retort contained a little free phosphorus. It was boiled with water and the solution filtered. The filtrate was neutralised with caustic baryta, and gave a white amorphous precipitate, which, when filtered off and dissolved in nitric acid, gave a strong phosphoric acid reaction with molybdate of ammonium.

The filtrate from the amorphous precipitate, when boiled, gave characteristic crystals of barium benzyl phosphinate, showing that some of the acid had escaped decomposition. According to MICHAELIS and MATTHIAS (*loc. cit.*), phenyl phosphinic acid decomposes at 250° C. into benzol and meta-phosphoric acid, with charring—

$$C_6H_5H_2PO_3 = C_6H_6 + HPO_3.$$

They do not mention how the benzol was identified.

We had not sufficient of the oily distillate to determine its boiling point or to identify it as toluol, but as the production of phosphoric acid was proved, it is probable that benzyl-phosphinic acid decomposes like the phenylated acid thus—

$$C_7H_7H_2PO_3 = C_7H_8 + HPO_3.$$

Action of Phosphorous Acid on Benzyl Phosphinic Acid.—Having obtained the benzyl phosphinic acid in large quantities, and with ease, we were anxious to discover some method by which it could be reduced to the phosphine, and as we had proved that the action of heat alone did not lead to the desired result, we decided to try the effect of

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* MICHAELIS and MATTHIAS (*Ber.*, vii. 1070) and MICHAELIS (*Annalen*, 181, p. 323) found that the corresponding phenyl phosphinic acid, when heated to 200° C., loses sufficient water to give the pyro acid analogous to the one we obtained, viz., $(C_6H_5)_2H_2P_2O_5$; while at 210° C. three molecules of the acid lose two molecules of water, giving, they suppose, $(C_6H_5)_3H_2P_3O_7$. They did not succeed in isolating either of the pyro acids or in obtaining their salts, as they re-hydrate when treated with water.

heating the acid with crystalline phosphorous acid, in the hope that a reaction would occur according to the following equation :—

$$3H_3PO_3+C_7H_7H_2PO_3=3H_3PO_4+C_7H_7H_2P,$$

which would be analogous to the reaction which phosphorous acid suffers when heated alone—

$$4H_3PO_3=3H_3PO_4+PH_3.$$

Accordingly, 5 grms. of benzyl phosphinic acid were mixed with a large excess (20 grms., the calculated quantity being only 7·1 grms.) of crystallised phosphorous acid, and the mixture heated in a distilling flask. It soon fused to a clear liquid, and then a little water came off. Presently the mass began to disengage phosphuretted hydrogen, and to froth considerably. After some time an oily liquid distilled, which was colourless, and finally decomposition and charring occurred. The whole of the liquid distillate was redistilled, and gave 1·3 c.c. of an oil having the smell and properties of the primary phosphine. The reaction seems then to proceed in the desired manner, and if the whole of the liquid obtained consisted of the phosphine, the yield was nearly 50 per cent. of the theoretical quantity. In all probability other phosphinic acids would be reduced by phosphorous acid, and, if so, the action is of some importance, as we believe that no other method for their reduction has yet been discovered.

Action of Pentachloride of Phosphorus on Benzyl Phosphinic Acid.—We were anxious to obtain the two chlorides, $(C_7H_7)ClHPO_2$ and $(C_7H_7)Cl_2PO$.

10 grms. of the benzyl phosphinic acid and 14 grms. of pentachloride of phosphorus were mixed in a distilling flask, when a pretty brisk action occurred spontaneously, the mixture growing very hot and torrents of hydrochloric acid coming off. As soon as the action had moderated, the mixture was heated, and 8 grms. of liquid were obtained distilling below 110° C. The residue in the flask was allowed to cool, and hardened into a brown viscous mass. It was then heated, when the thermometer rose slowly to 300° C., during which a colourless liquid distilled. There remained in the flask a black liquid, which solidified to a hard resin, and which contained free phosphorus. The distillate boiling from 110°–300° C. was in too small a quantity to redistil, but it probably contains one of the two chlorides, for when left for some time in contact with the air, it was converted into a crystalline mass, presumably benzyl phosphinic acid. The reaction was not sufficiently definite to invite further investigation.

(3) *Dibenzyl Phosphinic Acid*, $(C_7H_7)_2HPO_2$.

We have obtained this acid by the second and third reaction described at the beginning of this part of our paper, and also by fusing the tertiary phosphine oxide with caustic potash. To isolate it from the products of the reaction occurring between phosphonium iodide, zinc oxide, and benzyl chloride, the contents of the sealed tubes, after having been steamed with water to drive off the primary phosphine, are boiled for a long time with caustic potash or caustic baryta solution. This is then decanted off and acidulated with hydrochloric acid, when dibenzyl phosphinic acid is precipitated, but in a very impure condition, and only a small quantity is obtained. The reaction occurring between benzyl alcohol and a mixture of phosphorus and its iodide yields it in large quantities, and with ease. We have on p. 612 described this reaction, and have explained how the crude dibenzyl phosphinic acid is separated.

In order to purify it, the crude product is thoroughly washed with water and recrystallised from boiling alcohol.

Properties.—Dibenzyl-phosphinic acid is a colourless substance, almost insoluble in water, but fairly soluble in hot alcohol. It crystallises from the latter solvent in very thin iridescent plates, which, when dry, have a mother-of-pearl lustre. Its melting point, determined with an Anschütz thermometer, was found to be 192° C. Heated above its melting point, it decomposes, but also partly volatilises unchanged. Heated with pentachloride of phosphorus, it appears to decompose, and to give among other products chloride of benzyl. It forms a number of very characteristic salts, many of which are beautifully crystalline.

*Analysis.**

$$\cdot5639 \text{ gave} \begin{cases} 1\cdot4058 \ CO_2 = 0\cdot3834 \ C = 67\cdot99 \text{ per cent.} \\ 0\cdot3315 \ H_2O = 0\cdot036833 \ H = 6\cdot53 \quad , \\ 0\cdot2639 \ Mg_2P_2O_7 = 0\cdot073701 \ P = 13\cdot06 \quad „ \end{cases}$$

	Obtained.	Calculated for $(C_7H_7)_2HPO_2$
Carbon, ...	67·99	68·29
Hydrogen, ...	6·53	6·09
Phosphorus, ...	13·06	12·60

Salts.—

Barium Dibenzyl Phosphinate, $\{(C_7H_7)_2PO_2\}_2Ba,8H_2O$.—This salt was obtained by neutralising a hot and concentrated solution of caustic baryta with the acid, filtering from a few insoluble flakes,† and allowing the solution to cool, when very thin plates separated with the lustre of mother-of-pearl. The mother-liquors, on spontaneous evaporation, gave large and very beautiful thin plates, radiating from a common centre.

Analysis.

(1) 0·4637 grms. lost at 110° C., 0·0855 = 18·43 per cent.
(2) 1·1392 „ „ „ 0·2112 = 18·53 „
11392 grms. gave 0·3439 $BaSO_4$ = 0·2022 Ba. = 17·74 „

	Obtained.		Calculated for
	I.	II.	$\{(C_7H_7)_2PO_2\}_2Ba,8H_2O$
Water, . . .	18·53	18·43	18·67
Barium, . . .	17·74	...	17·76

The salt effloresces in dry air. It is soluble in alcohol.

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* The combustion was made with pure oxide of copper, and the phosphorus determined as described at p. 556.

† We do not know to what these are due.

Calcium Dibenzyl Phosphinate, $\{(C_7H_7)_2PO_2\}_2Ca,8H_2O$.—This compound was prepared by warming the acid with a little water and slaked lime, until the solution was neutral. The filtered solution gave on cooling thin plates very much like the barium salt. On boiling the crystals with their mother-liquors they grew opaque and insoluble, no doubt from loss of water.

Analysis.

1·0637 lost at 110° C., 0·2227 = 20·93 per cent.
1·0637 gave 0·0902 CaO = 0·0644 Ca = 6·05 „

	Obtained.	Calculated for $\{(C_7H_7)_2PO_2\}_2Ca,8H_2O$
Water, . .	20·93	21·36
Calcium, . .	6·05	5·93

Magnesium Dibenzyl Phosphinate, $\{(C_7H_7)_2PO_2\}_2Mg,3H_2O$. — This salt is very characteristic. It was prepared by slowly warming a dilute solution of the potassium salt with acetate of magnesium, when it was slowly deposited in colourless needles of considerable length.

Analysis.

0·6422 lost at 110° C., 0·0563 = 8·76 per cent.
0·6422 gave 0·1301 $Mg_2P_2O_7$ = 0·0281 Mg = 4·37 „

	Obtained.	Calculated for $\{(C_7H_7)_2PO_2\}_2Mg,3H_2O$
Water, . .	8·76	9·50
Magnesium, .	4·37	4·22

Cadmium Dibenzyl Phosphinate, $\{(C_7H_7)_2PO_2\}_2Cd$.—Was obtained by adding sulphate of cadmium to a solution of the potassium salt, when an amorphous white precipitate was thrown down, which rapidly became crystalline.

Analysis.

0·8052 gave 0·1757 CdO = 0·1537 Cd = 19·08 per cent.

	Obtained.	Calculated for $(C_7H_7)_2PO_2\}_2Cd$
Cadmium, . . .	19·08	18·60

The mother-liquors, on evaporation, gave a considerable quantity of a crystalline salt.

Copper Dibenzyl Phosphinate, $\{(C_7H_7)_2PO_2\}_2Cu$.—This body was prepared by adding sulphate of copper to a solution of the potassium salt, when a blue amorphous precipitate came down. This was washed, air-dried, and analysed.

Analysis.

1·0037 gave 0·1482 CuO = 0·1183 Cu = 11·78 per cent.

	Obtained.	Calculated for $\{(C_7H_7)_2PO_2\}_2Cu$
Copper, . . .	11·78	11·47

The mother-liquors when boiled gave a green precipitate, and the blue salt, on simply standing with water, also seemed to become green. The green compound was not investigated.

Silver Dibenzyl Phosphinate, $(C_7H_7)_2PO_2Ag$.—Was prepared by dissolving some of the acid in alcohol and adding strong aqueous nitrate of silver solution, when the silver salt was precipitated in very fine colourless needles. These blackened slightly when dried.

Analysis.

0·3122 grm. gave 0·125 AgCl = 0·094087 Ag = 30·13 per cent.

	Obtained.	Calculated for $(C_7H_7)_2PO_2Ag$
Silver, . . .	30·13	30·59

Sodium Dibenzyl Phosphinate, $2\{(C_7H_7)_2PO_2Na\},7H_2O$.—Prepared by neutralising caustic soda solution with the solid acid and evaporating to a small volume, when the salt crystallised out in plates, and was easily recrystallised from boiling water. It is readily soluble.

Analysis.

(1) 1·3114 lost at 110° C., 0·2492 = 19·00 per cent.
(2) 1·3999 „ „ 0·2660 = 19·00 „

	Obtained.		Calculated for $2\{(C_7H_7)_2PO_2Na\},7H_2O$
	I.	II.	
Water, . .	19·00	19·00	19·03

Potassium Dibenzyl Phosphinate, $2\{(C_7H_7)_2PO_2K\},7H_2O$. — Prepared in the same manner as the sodium salt, and has similar properties.

Analysis.

1·2054 lost at 110° C., 0·2213 = 18·35 per cent.
1·2054 gave 0·860 K_2PtCl_6 = 0·1374 K = 11·39 „

	Obtained.	Calculated for $\{(C_7H_7)_2PO_2K\}_2,7H_2O$
Water, ...	18·35	18·15
Potassium, . . .	11·39	11·23

Ammonium Dibenzyl Phosphinate, $(C_7H_7)_2PO_2NH_4,7H_2O$.—This salt was prepared by neutralising the acid with ammonia. The solution, when highly concentrated, solidified to a crystalline mass.

*Analysis.**

0·9105 gave 0·2339 Pt = 0·0427 NH_4 = 4·68 per cent.

	Obtained.	Calculated for $(C_7H_7)_2PO_2NH_4,7H_2O$
Ammonium, . . .	4·68	4·62

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* The salt was distilled with caustic potash and the ammonia which was evolved absorbed by hydrochloric acid and precipitated as chloroplatinate, the latter being subsequently ignited, and the ammonia calculated from the weight of platinum left.

Action of Heat on Dibenzyl Phosphinic Acid.—Preliminary experiments with the pure acid in a test-tube seemed to show that it distilled unchanged. A quantity was heated in a distilling flask. It boiled above the boiling point of mercury, and the distillate on cooling formed a semi-solid crystalline mass, smelling very slightly of the primary phosphine. As the distillation proceeded, the residue in the flask darkened. The whole of the distillate was warmed with caustic potash, in which most of it seemed to dissolve, but a crystalline residue remained saturated with some oily matter. The solution was filtered from this residue, precipitated with excess of hydrochloric acid, and the washed precipitate recrystallised from alcohol. It separated in characteristic thin plates of dibenzyl phosphinic acid, and was identified by its melting point and other properties as that body. The crystalline matter insoluble in potash was well washed with water and then crystallised from hot alcohol, when it separated in needles, having the melting point of tribenzyl phosphine oxide, and it was further identified as that body by the production of the characteristic bromine compound.

The residue in the distilling flask was black and tarry, and was dissolved when boiled with caustic soda. The solution thus obtained, when acidulated with hydrochloric acid, gave a crystalline precipitate (probably crude dibenzyl phosphinic acid), and when filtered from this, was found to contain abundance of phosphoric acid.

We may conclude from the above results that when dibenzyl phosphinic acid is heated it volatilises in a great measure unchanged, but that a portion decomposes, giving phosphoric acid, tribenzyl phosphine oxide, and toluol—

$$2(C_7H_7)_2HPO_2 = (C_7H_7)_3PO + HPO_3 + C_7H_8.$$

Action of Pentachloride of Phosphorus on Dibenzyl Phosphinic Acid.—10 grms. of the acid and 10 grms. of pentachloride of phosphorus* were placed in a distilling flask, and the latter gradually treated in a paraffin-bath. A reaction soon occurred, and torrents of hydrochloric acid gas came off. As soon as the action had moderated the product was distilled. 7 grms. of liquid came off before 110° C., then the thermometer rose slowly to 300° C., without remaining constant at any temperature, during which about 7 grms. of an oily liquid came off. By this time the residue in the distilling flask was very syrupy and of a brown colour, and on admitting air it smoked, and seemed to be giving off free phosphorus.

The two distillates, when redistilled, passed over in a great measure below 110° C. They were shaken with water, and after decomposition an oily liquid floated on the surface (in all about 2 grms.), which was unmistakably benzyl chloride. We could not isolate any acid chloride, $(C_7H_7)_2POCl$, and a profound decomposition seems to occur, possibly according to the equation—

$$(C_7H_7)_2HPO_2 + 3PCl_5 = 2PCl_3O + HCl + 2PCl_3 + 2C_7H_7Cl.$$

---

* The quantities required for the equation $(C_7H_7)_2HPO_2 + PCl_5 = (C_7H_7)_2POCl + HCl + POCl_3$ are 10 grms. of the acid and 8·5 grms. of pentachloride of phosphorus.

(4) *Tribenzyl Phosphine Oxide*, $(C_7H_7)_3PO$.

This body has been obtained by a number of different methods, among which are the following:—

(1) Action of benzyl chloride on phosphonium iodide (FLEISSNER).*
(2) From the products of the action of benzyl chloride on phosphide of sodium (LETTS and COLLIE).†
(3) From the products of HOFMANN'S sealed tube reaction (between benzyl chloride, zinc oxide, and phosphonium iodide) (LETTS and BLAKE).‡
(4) From the products of the action of benzyl alcohol on a mixture of phosphorus and phosphorus iodide (LETTS and BLAKE).§
(5) From the products of the action of benzyl alcohol on phosphonium iodide (LEDERMANN).||
(6) By the action of alkalies on salts of tetrabenzyl phosphonium (LETTS and COLLIE).¶
(7) By the action of heat on hydrate of tetrabenzyl phosphonium (LETTS and COLLIE).**
(8) By the oxidation of the tertiary phosphine (LETTS and BLAKE).††
(9) By the action of fused potash on dibenzyl phosphinic acid (LETTS and BLAKE).††

Properties.—Crystallises in colourless highly refractive needles. These are sometimes thick, at others quite fine and silky. The body is soluble in alcohol, bisulphide of carbon, glacial acetic acid, and chloroform; almost insoluble in water and ether. When heated it melts at 216°–216°·5 C. (corr.), and sublimes at a higher temperature with considerable decomposition.

It combines with hydracids, halogens, and chloride of platinum to form unstable and possibly indefinite compounds, but its compound with iodide of zinc is stable and definite, and so is its nitro body, its sulphonic acid, and some other derivatives.

Bromide, either $7(C_7H_7)_3PO,5Br_2$ or $5(C_7H_7)_3PO,4Br_2$.—This compound is highly characteristic, and its production affords a ready means of identifying the oxide. It is readily obtained by adding bromine to a solution of the oxide in glacial acetic acid, and it crystallises in orange needles, which, when seen under the microscope, are found to consist of aggregations of minute rhombic plates. It may be recrystallised from a warm solution in glacial acetic acid (to which a little bromine is added). It is unstable, and loses bromine when boiled with water or glacial acetic acid. It is instantly decomposed

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* FSLEISNER, *Berichte*, xiii. (1880) 1665.

† LETTS and COLLIE, these *Transactions*, xxx. part 1, p. 202.

‡ LETTS and BLAKE, this communication, p. 554.

§ LETTS and BLAKE, this communication, p. 599.

|| LEDERMANN, *Berichte*, xxi. (1888) 405*a*.

¶ LETTS and COLLIE, *loc. cit.*, p. 196.

** LETTS and COLLIE, *loc. cit.*, p. 215.

†† LETTS and BLAKE, this communication, p. 574.

by caustic potash, and the oxide re-formed. The bromine is, in fact, very loosely combined—as loosely as water of crystallisation is in ordinary salts.

The compound has been repeatedly analysed, and we think it advisable to give the full results:—

*Analysis.**

		Obtained.	
Bromine,	(1)	26·0	Prepared with a hot solution of the oxide.
„	(2)	26·4	„ „ „ „
„	(3)	27·2	„ cold „ „
„	(4)	26·7	„ „ „ „
„	(5)	26·6	„ „ „ „
„	(6)	26·64	Prepared with a cold solution of the oxide.
„	(7)	26·85	Recrystallised from acetic acid.
„	(8)	26·58	„ „
„	(9)	28·4	Prepared with a boiling solution of the oxide in glacial acetic acid, and dried *in vacuo.*
„	(10)	28·3	
„	(11)	28·3	

	(2)	(4)	(12)	(9)
Carbon,	56·5	56·4	56·5	56·9
Hydrogen,	5·3	5·6	5·0	4·9

	Calculated for	
	$7(C_7H_7)_3PO,5Br_2$	$5(C_7H_7)_3PO,4Br_2$
Bromine, . . .	26·31	28·5
Carbon, ...	58·00	56·3
Hydrogen, . . .	4·83	4·7

Chloride.—Obtained by passing chlorine gas into a solution of the oxide in warm acetic acid to saturation, and crystallised as the solution cooled in pale yellow crystals, having the appearance of pentachloride of phosphorus. The compound is very unstable, and loses chlorine *in vacuo.*

Analysis.

	Obtained.	Calculated for $7(C_7H_7)_3PO,5Cl_2$
Chlorine, . . .	12·0	13·68

(It is probable that on drying the compound for analysis some chlorine was lost.)

Iodide.—Prepared by mixing hot solutions of iodine and the oxide in glacial acetic acid. Crystallises in minute red crystals of the colour of ferricyanide of potassium.

Analysis.

	Obtained.	Calculated for $7(C_7H_7)_3PO,5I_2$
Iodine, . . .	36·86	36·18

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* Analyses 1–5 were made by LETTS and W. WHEELER, and from 6–8 by LETTS and BLAKE, and the preparations obtained in both cases from HOFMANN'S "dibenzyl phosphine" (*see* p. 554). Analyses 9–11 were made by LETTS and COLLIE, the preparation being made from the oxide obtained from the products of the action of sodium phosphide on benzyl chloride.

*Hydrochlorate.**—When warmed with an aqueous solution of hydrochloric acid, the oxide remains unchanged, but if a current of the dry gas be passed over the finely powdered oxide, it is readily absorbed, and a compound is obtained which is unchanged in the air, but decomposes when heated or boiled with water into its constituents.

Its formula appears to be $4(C_7H_7)_3PO,3HCl$.

Hydrobromate.—According to Collie (*loc. cit.*), a similar compound is formed with hydrobromic acid. One of us and W. Wheeler obtained a compound by saturating a hot solution of the oxide in glacial acetic acid with hydrobromic acid gas, when it separated as the solution cooled in colourless crystals. Its composition varied widely in two separate preparations.

Analysis.

	Obtained.		Calculated for		
	I.	II.	$4(C_7H_7)_3PO,3HBr$	$3(C_7H_7)_3PO,2HBr$	$(C_7H_7)_3PO,HBr$
Bromine,	19·5 to 20·5	16·3	15·75	14·26	19·95

Hydriodate.—Obtained by one of us and W. Wheeler by the same method as the hydrobromate.

Analysis.

	Obtained.		Calculated for		
	I.	II.	$4(C_7H_7)_3PO,3HI$	$3(C_7H_7)_3PO,2HI$	$(C_7H_7)_3PO,HI$
Iodine,	21·0	21·5	22·9	20·88	28·34

Platinum Salt.—Prepared by mixing alcoholic solutions of the oxide and chloride of platinum, and crystallised in minute orange leaflets. It is somewhat unstable, and its composition varies with the conditions under which it is obtained. Its probable formula is—

$4(C_7H_7)_3PO,2HCl,PtCl_4$,† but possibly $3(C_7H_7)_3PO,PtCl_4$.‡

Palladium Salt.—Fleissner obtained this body by precipitating a solution of the oxide with palladous chloride. It is a brown-red crystalline mass of the formula $3(C_7H_7)_3PO,PdCl_2$.

Ferric Chloride Compound.—Sulphur yellow prisms of considerable size. Formula: $3(C_7H_7)_3PO,Fe_2Cl_6$ (Fleissner).

Mercuric Chloride Compound.—Beautiful colourless prisms or pyramids. Formula: $3(C_7H_7)_3PO,HgCl_2$ (Fleissner).

Cobaltous Chloride Compound.—Blue needles. Formula: $3(C_7H_7)_3PO,CoCl_2$ (Fleissner).

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* Collie, *Chem. Soc. Jour.*, 1889, p. 227.

† Letts and Collie, *loc. cit.*

‡ Fleissner, *loc. cit.*

Zinc Iodide Compound.—Obtained by mixing alcoholic solutions of the two bodies, and separated from the fairly concentrated solution in tufts of colourless plates of characteristic form. Formula: $2(C_7H_7)_3PO,ZnI_2$ (LETTS and COLLIE).

Acetyl Chloride Compound (COLLIE).—Obtained by slowly evaporating a solution of the oxide in glacial acetic acid and chloride of acetyl, as a crystalline compound. Formula: $(C_7H_7)_3PO.(CH_3.COCl)$. It is unstable, and is decomposed into its constituents by heat: when treated with boiling water and when mixed with an alkali.

Sulphur Compound (LETTS and COLLIE).—When the oxide is fused with sulphur a reaction occurs, which apparently varies with the temperature, and with the quantity of sulphur employed. If much sulphur is taken and the mixture heated to a high temperature, sulphuretted hydrogen is evolved, the mass becomes dark coloured and resinous products are formed. But if the proportion of sulphur is low (one molecule of the oxide to two atoms of sulphur), and the temperature kept at 240° C., the sulphur dissolves, no gas is evolved, and the product dissolves completely in a large quantity of boiling alcohol. The solution deposits on cooling long silky needles of a light buff colour of the composition, $5(C_7H_7)_3PO,S$. The melting point was found to be 211°–212° C. (uncorrected).

Nitro Compound.—Obtained by COLLIE by dissolving the oxide in cold sulphuric acid, adding excess of nitric acid, and pouring the mixture into water. Prepared by us by dissolving the oxide in cold fuming nitric acid and pouring the solution into water.* White amorphous mass soluble in glacial acetic acid, melting at 100° C., and deflagrating at a higher temperature. Formula: $\{C_7H_6(NO_2)\}_3PO$. It is unchanged when boiled with chromic acid, but is oxidised to para-nitro benzoic acid (and presumably phosphoric acid) when warmed with an akaline solution of permanganate of potash (COLLIE). Attempts by Dr COLLIE and ourselves to obtain the corresponding amido body were unsuccessful.

Sulphonic Acid (COLLIE).—The oxide, when dissolved in strong sulphuric acid, does not react unless the temperature is raised above 100° C.; between 150° C. and 170° C., the whole of the oxide is readily converted into a sulphonic acid, $(C_7H_6SO_3H)_3PO$. This acid is soluble in water, and can be obtained pure from its barium salt. It is semicrystalline, and dries to a syrup over sulphuric acid. *Monoacid Barium Salt*, $\{(C_7H_6SO_3)_2Ba\ (C_7H_6)SO_3H\}PO$.—Obtained by neutralising the acid with caustic baryta. Is uncrystallisable. *Silver Salt.*—White flocculent precipitate. *Copper Salt.*—Green, and soluble in water. *Lead Salt.*—Soluble.

The acid behaves with oxidising agents like the nitro body.

Action of Fused Caustic Potash on the Oxide.—When the oxide is heated with caustic

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* The discovery of the nitro compound was made independently by Dr COLLIE and ourselves.

potash or soda, it fuses and floats on the surface of the melted alkali. No violent action occurs, but on cooling the mixture and treating it with water, the greater portion dissolves, and acids then precipitate dibenzyl phosphinic acid. The following reaction therefore occurs :—

$$(C_7H_7)_3PO + KHO = (C_7H_7)_2PO_2K + C_7H_8 .$$

Singularly enough, when dibenzyl-phosphinic acid is heated by itself, the oxide is formed—

$$2(C_7H_7)_2PO_2H = (C_7H_7)_3PO + HPO_3 + C_7H_8 .$$

PROFESSOR LETTS AND MR R. F. BLAKE ON BENZYL PHOSPHINES.

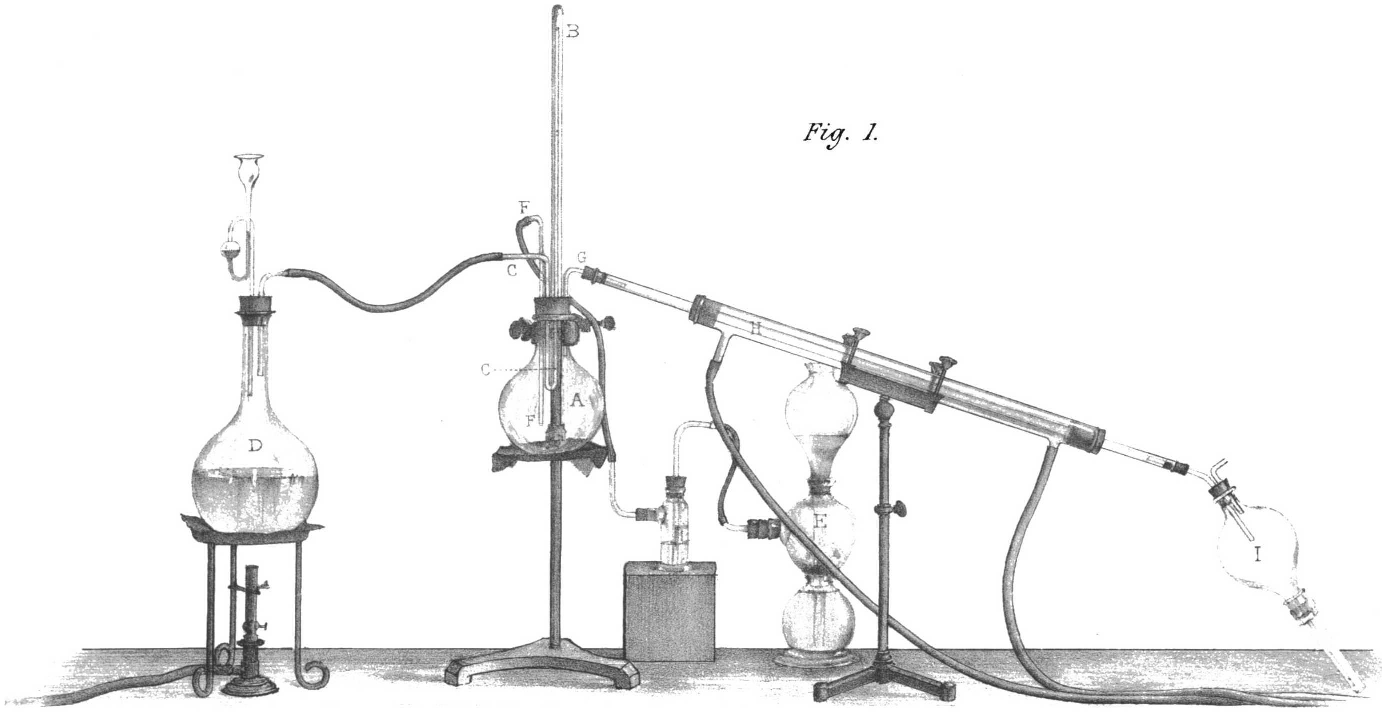

Fig. 1.

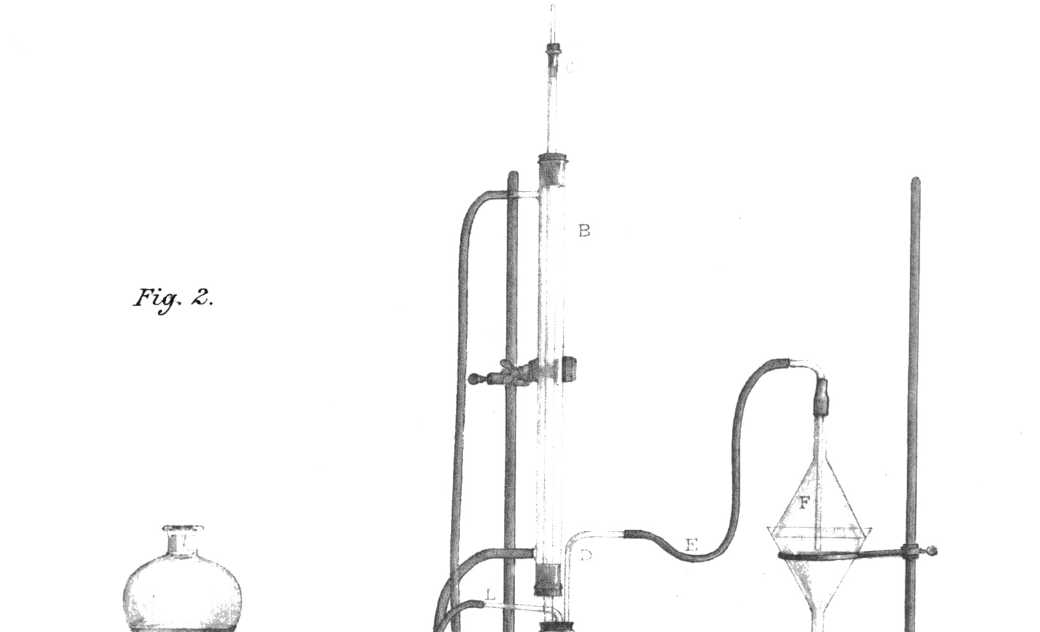

Fig. 2.

F. Huth Lithr Edinr