VIII.—*On the Action of Phosphide of Sodium on Haloid Ethers and on the Salts of Tetrabenzyl-Phosphonium.* By Professor LETTS and N. COLLIE, Esq.

The phosphines, or substances derived from phosphuretted hydrogen by the partial or complete replacement of its hydrogen by hydrocarbon radicals, have formed the subject of many valuable researches; but although their discovery was anterior to that of the compound ammonias, their study has made comparatively little progress. This is no doubt mainly due to the difficulty attending their preparation, a fact which is immediately forced upon the notice of any one who wishes to investigate them.

In spite of the undoubted analogies existing between phosphines and amines, the methods employed for obtaining the former are, with one exception, different from those by which the latter are usually prepared. The reason for this we may find in the great differences between the elements phosphorus and nitrogen—differences which are in many cases still apparent in their compounds. Thus, phosphorus forms no compound with carbon analogous to cyanogen; nor have any phosphorised bodies been obtained up to the present time analogous to the cyanides of hydrocarbon radicals. Neither has a phosphorised cyanic acid, (HCPO), nor its hydrocarbon salts been obtained.

And we have another link wanting in the chain of analogies existing between nitrogen and phosphorus, in the absence of compounds of the latter element analogous to the nitro-bodies. Now, the amines are usually prepared by one or other of the four following processes :—

1. Action of nascent hydrogen on the cyanide of a hydrocarbon radical.
2. Action of caustic potash on the cyanate of a hydrocarbon radical.
3. Action of nascent hydrogen on a nitro-body.
4. Action of ammonia on a compound of a hydrocarbon radical with a halogen.

For the reasons given above, the phosphines cannot be prepared by processes corresponding with the first three of these methods; but HOFMANN, in his masterly researches on these bodies, has shown that it is possible to directly replace hydrogen in phosphuretted hydrogen by hydrocarbon radicals, in a manner similar to that employed in the fourth of the above processes.

But this is not the only process we possess for obtaining the phosphines,

although it is the only one analogous to any of those employed for preparing amines; and we shall give a short sketch of the other methods by which, from time to time, the phosphines have been prepared.

PAUL THENARD was the discoverer of the first organic phosphorus compounds.* In the year 1843 he investigated the action of chloride of methyl on phosphide of calcium; and in 1847 he communicated to the Academy further results as to the nature of the bodies obtained in the reaction. The investigation was attended with great difficulties, owing to the labour involved in separating the different products, and in obtaining them in the pure state; also, on account of their explosive and inflammable nature, and their poisonous properties.

In spite, however, of these difficulties, THENARD appears to have isolated trimethyl-phosphine; a substance analogous to kakodyle, $P_2(CH_3)_4$; and a substance analogous to solid phosphide of hydrogen, $P_4(CH_3)_2$. The last he describes as an inert solid body; but the second, as a spontaneously inflammable liquid boiling at $250^\circ C.$ —very explosive, poisonous, and unstable.

THENARD recognised the relations existing between trimethyl-phosphine and ammonia, and predicted the existence of the then undiscovered organic compounds of nitrogen, arsenic, and antimony. In the meantime, WÜRTZ and HOFMANN had verified THENARD'S predictions, having discovered the compound ammonias; and LOEWIG and SCHWEITZER had obtained stib-ethyl.

HOFMANN and CAHOURS† turned their attention in 1855 to the study of the phosphines, and repeated THENARD'S experiments, with this difference, however, that they substituted phosphide of sodium for phosphide of calcium. They obtained trimethyl-phosphine, THENARD'S phosphorus kakodyle and iodide of tetramethyl-phosphonium—but only after great difficulty. Speaking of the action of phosphide of sodium on iodide of methyl, they say,—“The action is very energetic when the two are heated together (*à chaud*). Moreover, inflammable and detonating substances are formed, so that this method of preparation is not without danger, and exposes the fruit of one's labour to loss It is unreliable (*trop peu sûr*), and furnishes mixtures, of which the separation presents enormous difficulties.” For these reasons, they sought for a simpler and more certain process. This they found in the action of zinc ethers on terchloride of phosphorus, which gives a compound of chloride of zinc and the tertiary phosphine, from which potash separates the latter in a state of purity.

By means of this reaction, HOFMANN and CAHOURS prepared the tertiary phosphines of methyl, ethyl, and amyl. They determined some of their most

* Comptes Rendus, vols. xxi. and xxv.

† Comptes Rendus, xli.

important properties, and showed that in many respects they resemble the tertiary amines, especially in the readiness with which they combine with iodides of hydrocarbon radicals to give quaternary compounds. They found, however, that, unlike amines, tertiary phosphines are capable of directly combining with oxygen.

HOFMANN continued the study of the tertiary phosphines, and communicated the results of his experiments to the Royal Society* in 1860. He confined his experiments chiefly to triethyl-phosphine, and, in his lengthy memoir, describes accurately its properties and reactions. He prepared and analysed oxide of triethyl-phosphine and the characteristic red compound which bisulphide of carbon forms with the phosphine itself, and he investigated the action of the latter on a considerable number of organic compounds.

BERLÈ† attempted to obtain triethyl-phosphine by the action of phosphide of sodium on iodide of ethyl. The phosphide of sodium he prepared by the heating sodium and phosphorus together in rock oil. Iodide of ethyl only acted upon this at a high temperature, and he obtained only very small quantities of the tertiary phosphine. BERLÈ‡ next attempted to prepare the tertiary phosphine by heating sodium, phosphorus, and iodide of ethyl together in a sealed tube; but although the bodies reacted, he does not seem 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 (prepared by heating the metal in phosphorus vapour) at 180° C. The next experiments on the preparation of phosphines are very interesting and important.

Previous to these only tertiary and quaternary compounds had been obtained, but HOFMANN§ showed in an elegant manner that the primary and secondary bases may be formed by the action of phosphuretted hydrogen on the iodides of hydrocarbon radicals—a process exactly analogous to that employed by him for preparing the corresponding amines. Phosphuretted hydrogen, however, does not behave in exactly the same manner as ammonia in this reaction, for HOFMANN found that the replacement of hydrogen does not proceed further than the second atom; whereas with ammonia all the hydrogen is replaced step by step, and even quaternary compounds are formed.

Moreover, ammonia acts on the iodides of hydrocarbon radicals much more readily than phosphuretted hydrogen, and at lower temperatures.

* Transactions Royal Society, London, vol. cl. p. 409.

† Journ. für prac. Chem., lxvi. p. 73.

‡ Comptes Rendus, xlix.

§ Berichte der. deutsch. chem. Ges., iv. pp. 205, 372; v. p. 100.

HOFMANN's process for obtaining primary and secondary phosphines—which he employed successfully in the methyl, ethyl, and benzyl series—consists in heating a mixture of phosphonium iodide, zinc white, and the hydrocarbon iodide, in sealed tubes for some hours at a temperature of 160° – 180° . The tubes are then found to contain a white crystalline mass, consisting of compounds of the hydriodates of the primary and secondary bases with zinc iodide.

The reactions which occur are represented by the equations,

The separation of the primary from the secondary compound is accomplished with the greatest ease. It is only necessary to add water to the contents of the sealed tubes when the compound of the primary base is decomposed and the base itself set at liberty. When it has been distilled off, the addition of potash to the residue separates the secondary base.

HOFMANN also studied the action of phosphuretted hydrogen on the alcohols at a high temperature, and with a singularly interesting result.

Not only does phosphuretted hydrogen act on the alcohol, but the bodies produced consist entirely of tertiary and quaternary compounds, no primary or secondary compounds being formed at all. Thus the action of phosphuretted hydrogen on an iodide of a hydrocarbon radical is exactly complementary to its action on an alcohol.

In employing the action of phosphuretted hydrogen on ordinary alcohol for the preparation of the tertiary and quaternary phosphines, HOFMANN places iodide of phosphonium at the bottom of a sealed tube, and above it the alcohol in a smaller tube. The vapour of the phosphonium iodide thus comes in contact gradually with the alcohol. The reaction is complete after six to eight hours' digestion at 180° . The tubes are then found to be full of a white crystalline mass, from which caustic potash liberates the tertiary phosphine, whilst the iodide of the phosphonium remains in solution.

The reactions which occur are represented by the equations,

MICHAELIS* has comparatively recently added to our knowledge of the phosphines, and to the methods of preparing them.

By passing the mixed vapours of terchloride of phosphorus and benzol through a red hot tube he obtained *phosphenyl-chloride*,

* Liebig's Annalen, 181, p. 280.

a substance which he also prepared by the action of terchloride of phosphorus on mercury di-phenyl,

By the action of water on this body, *phosphenylous acid* is produced,

and this when destructively distilled yields phenyl-phosphine—the phosphorus analogue of aniline,

The same body results when hydriodate of phosphenyl-iodide (obtained by the action of hydriodic acid on phosphenyl-chloride) is decomposed with alcohol.

We were led in the first instance to the experiments to be presently described by the difficulty which one of us had experienced in preparing triethyl-phosphine on the large scale. HOFMANN's later method had been at first resorted to, but in spite of numerous experiments, it had led to no satisfactory results. The pressure produced when alcohol and iodide of phosphonium are heated together is enormous, especially at the high temperature (180°C.) at which they react, and in almost nine cases out of ten it was found that the sealed tubes burst.

Nor is the other process for preparing triethyl-phosphine, viz., by treating zinc-ethyl with terchloride of phosphorus, a simple operation. The preparation of zinc-ethyl is expensive and troublesome, and although it reacts readily with the terchloride, the reaction is not so simple as might be expected. Scarcely 50 per cent. of the theoretical quantity of crude phosphine can be obtained, and this crude product contains impurities in considerable quantities, which are very difficult to remove. The preparation of triethyl-phosphine is in fact an expensive, uncertain, and troublesome operation.

Such being the case, and one of us requiring large quantities of it, the question naturally presented itself—Is there no simpler and less expensive process for preparing a tertiary phosphine? It seemed to us that one of the processes—and in fact the earliest—for preparing these bodies ought to be an extremely good one, if the difficulties attending its general application could be removed. The process to which we allude depends upon the ease with which metallic phosphides can be formed, and the readiness with which haloid ethers act on them. As before stated, THENARD, BERLÈ, CAHOIRS, HOFMANN and others, have worked with this process, but it has not met with great favour, and was abandoned by HOFMANN (who employed phosphide of sodium) on

account of the uncertainty of the reaction, the frequent explosions, and the great difficulties in separating the resulting phosphines from each other,—“not to speak of the difficulty of obtaining the phosphide of sodium fit for the reaction.”

It seemed to us, however, that in phosphide of sodium an admirable reagent was at hand for the preparation of tertiary phosphines—provided only, to quote again HOFMANN'S words, that it can be obtained in a state “fit for the reaction.”

This conclusion has been borne out by our experiments. With proper precaution, phosphide of sodium may be obtained in any quantity, and in a perfectly safe condition. It reacts with haloid ethers in a perfectly smooth manner, nor have we ever had an explosion, nor remarked the production of explosive bodies.

Our first experiments were made with iodide of ethyl. The reaction occurs *at ordinary temperatures with ease*, the iodide of ethyl boils violently, and the chief product of the reaction appears to be the iodide of tetrethyl-phosphonium. We have not as yet, however, brought these experiments to a conclusion, because of the difficulties which he experienced in separating the phosphines and phosphonium salt from the iodide of sodium produced along with them in the reaction.

Our next experiments were made in the benzyl series, which we chose partly because neither tribenzyl-phosphine nor tetrabenzyl-phosphonium salts have hitherto been obtained, and partly because no deliquescent or volatile bodies were likely to be formed, thus rendering the investigation free from those difficulties which cause experiments in the methyl and ethyl series to be so troublesome and laborious. To these reasons for our choice of benzyl must be added its similarity to fatty radicals and the well-known ease with which its compounds react.

Before proceeding to describe our experiments on the preparation of phosphide of sodium, and on its action on chloride of benzyl, we consider it necessary to give a short account of HOFMANN'S researches on monobenzyl- and dibenzyl-phosphine, which we believe to be the only ones that have been made on benzyl-phosphines.

Benzyl Phosphines.

The following is an abstract of HOFMANN'S paper on “Aromatic Phosphines” *:—

He was induced to experiment on the aromatic series, in consequence of the readiness with which, by the use of iodide of phosphonium, he had obtained

* HOFFMAN, Ber. d. deutsch. chem. Ges., iv. p. 100.

methyl- and ethyl-phosphines. His first attempts were made with the view of obtaining a phenyl-phosphine analogous to aniline, a substance highly interesting from a theoretical point of view.

To obtain this body he heated, under varying conditions, phenyl-chloride and iodide of phosphonium; but the experiments did not lead to a successful result, the phenyl-chloride becoming reduced to benzol, which even at high temperatures was not further acted upon. That the reaction did not proceed in the desired manner was, as he says, not surprising, considering the inertness of chloride of phenyl and the fact that aniline cannot be obtained by acting on it with ammonia.

Equally unsuccessful were his efforts to obtain the tertiary phosphine and the quaternary compound by the action of phenol upon iodide of phosphonium, though phosphorised bodies resulted, the nature of which he did not ascertain.

Experiments to obtain a phosphorised toluidine led to no successful issue; but, on the other hand, the preparation of a phosphorus analogue of benzylamine presented no difficulty, as indeed he did not doubt, considering the readiness with which chloride of benzyl reacts with ammonia.

Benzyl Phosphine, $C_7H_7PH_2$.—This body is formed when chloride of benzyl (which may be employed in the crude condition) is heated for six hours at a temperature of 160° with a mixture of phosphonium iodide and zinc oxide. The substances are taken in the proportions of 2 molecules benzyl chloride, 2 of phosphonium iodide, and 1 of zinc oxide.

When complete reaction has occurred the sealed tubes in which the mixture has been heated contain a white crystalline mass. On opening them a large quantity of phosphuretted hydrogen is evolved. On distilling the product of the reaction with water a heavy, oily liquid passes over of highly characteristic odour. This is separated, dried with caustic potash, and distilled in hydrogen. The thermometer rises to 180° , and then remains stationary, whilst a considerable quantity of a colourless, highly refractive liquid distils. This is monobenzyl-phosphine, whilst the lower boiling fraction consists mainly of toluol, and the residue in the retort contains dibenzyl-phosphine and other products. A simple distillation of the crude benzyl-phosphine thus obtained gives the pure body boiling at 180° C. In its properties it resembles in the main other primary phosphines. It oxidises in contact with the air, its temperature rising to 100° C., thick white vapours being formed. It is insoluble in water, but easily soluble in alcohol and ether. It forms a colourless crystalline hydriodate, only slightly soluble in fuming hydriodic acid, and which, like other salts of primary phosphines, decomposes in contact with water into hydriodic acid and the free base. Monobenzyl-phosphine also combines with hydrochloric acid, and gives a yellow insoluble chloro-platinate.

Benzyl-phosphine is formed, according to the reaction,

This equation, however, only expresses one phase of the reaction, in which simultaneously with monobenzyl-phosphine other products are formed. Of these HOFMANN could only succeed in isolating—

Dibenzyl-Phosphine.—This compound is contained in the residues after the benzyl-phosphine has been distilled off. On long standing in contact with solid potash, these solidify to a soft crystalline mass, which is collected on a linen filter, well squeezed, dissolved in alcohol, and the solution decolorised with animal charcoal. It then deposits, on cooling, beautiful white crystals of the dibenzyl-phosphine, which only require to be recrystallised from alcohol to obtain them in a state of purity.

Dibenzyl-phosphine thus obtained forms glistening white needles of large size, which are tasteless and colourless. They are insoluble in water, sparingly soluble in cold alcohol, readily in hot alcohol. The crystals melt at 205° , and sublime at higher temperatures, but not without partial decomposition.

With the introduction of the second benzyl group the alkaline characters, which are perfectly apparent in monobenzyl-phosphine, disappear.

Dibenzyl-phosphine dissolves in no acid, nor could HOFMANN obtain its chloro-platinate. Its composition could, therefore, only be determined by an analysis of the purified substance. The formation of dibenzyl-phosphine may be expressed by the equation,

The mother liquors of the dibenzyl-phosphine contain another phosphorised body, which HOFMANN suspected to be tribenzyl-phosphine, but in spite of many efforts he was not able to prepare that body.

Phosphide of Sodium.

The success attending the use of this reagent for the preparation of phosphines depends entirely on the observance of certain conditions in its manufacture, which we have carefully determined by experiment.

The most essential of these are, the manner in which the sodium and phosphorus are allowed to combine, and the nature and quantity of the reagent employed to prevent the temperature from rising too high during their combination, and to protect the resulting phosphide from subsequent oxidation by the air.

If proper attention be paid to these precautions, phosphide of sodium may be prepared in a perfectly safe manner in large quantities and of uniform composition. Whatever this latter may be, the bulk of the phosphide behaves as Na_3P , as is evident from the nature of the products obtained from it.

We prepare the phosphide by melting sodium under xylol and adding ordinary phosphorus in small pieces,—shaking the vessel in which the mixture is made after each addition of the latter substance in order to bring it thoroughly into contact with the sodium. As regards the proportions of sodium and phosphorus, the theoretical quantities for the formation of the compound Na_3P , are, in round numbers, 7 of sodium and 3 of phosphorus; but our experiments show that with these proportions very bad results are obtained, as regards phosphine compounds. It appears to be necessary to employ a large excess of phosphorus—the proportions which we have found to be most suitable being 19 of that body to 20 of sodium—very nearly twice the theoretical quantity.

Considering that large quantities of phosphorus are converted into the amorphous modification, which does not apparently combine with sodium at those temperatures at which we operate, a simple explanation is afforded of the necessity for employing an excess of phosphorus; for, otherwise, unchanged sodium remains in the product, and, as we shall presently explain, this readily decomposes the chief phosphine compound produced when phosphide of sodium acts on chloride of benzyl. But, on the other hand, an excess of phosphorus over the proportions we have indicated also exercises a prejudicial influence on the quantity of phosphine compounds produced, and at present we can only explain this on the assumption that higher phosphides of sodium are formed, which are inactive.

The xylol necessary to prevent the reaction of the phosphorus and sodium from being too violent must be free from water and high boiling impurities. A single distillation of ordinary xylol is sufficient to purify it for this purpose. The proportion of xylol employed is also an important condition. This, however, we shall best consider when we describe our experiments on the action of the phosphide on chloride of benzyl.

The following is a description of the exact method we employ for preparing a batch of phosphide of sodium containing 78 grms. of sodium and phosphorus:—

40 grms. of freshly scraped sodium are placed in a flask of 500 cc. capacity,—fitted with a cork and wide glass tube placed vertically, and about 4 feet in height, to serve as a reversed condenser—and to it 200 grms. of xylol are added. The mixture is then warmed on a sand-bath until the sodium has melted. 38 grms. of phosphorus are cut into pieces the size of a pea, and these are placed in an evaporating basin containing xylol. They are then added gradually to the melted sodium. The first addition of the phosphorus causes a very violent reaction, so that care is necessary to prevent the xylol from boiling over. As soon as the xylol boils, the cork with its tube to serve as condenser is fitted into the flask, and the reaction allowed to proceed until the boiling ceases. More phosphorus is then added, and the flask well shaken after each addition. It is not necessary to heat the mixture, as the temperature remains sufficiently high to keep the reaction in progress to the end. The resulting product is a granular black powder, which is completely prevented from change by the xylol which surrounds it. We have kept a loosely corked flask containing it for upwards of six months without noticing that it had suffered change. But the slightest trace of moisture at once acts upon it, liberating spontaneously inflammable phosphuretted hydrogen.

Action of Chloride of Benzyl on Phosphide of Sodium.

Chloride of benzyl when boiled with the phosphide of sodium—prepared in the manner we have described—readily acts on it with the formation of common salt and compounds of benzyl and phosphorus. The main phosphine product is the chloride of tetrabenzyl-phosphonium, which may be obtained in large quantities by this method, and is easily isolated from the products of the reaction. Other phosphorised bodies are, however, formed in considerable quantity, the nature of which we shall discuss later.

As we have before stated, careful attention must be paid to the preparation of the phosphide of sodium, otherwise, as we have often observed, no chloride of the phosphonium results, although the whole of the phosphide of sodium may be acted on. On the other hand, the phosphide sometimes remains unacted on, or the reaction takes five or six times longer than is necessary in a properly conducted experiment. A very important condition of success is the right proportion of xylol employed in the preparation of the phosphide of sodium. We have found it advisable to take an excess of this substance in the first place, but to distil off this excess before adding the benzyl chloride.

With the quantities of sodium, phosphorus, and xylol mentioned already we distil off (in an oil bath) 170 grms., that is to say, a sufficient quantity to leave the phosphide of sodium almost dry, but in such a condition that the addition of a small quantity of benzyl-chloride may thoroughly wet the mass and permit of its being boiled without becoming superheated at the bottom. The chloride of benzyl is placed in a tap funnel, and allowed to

drop down the wide tube used as a reversed condenser in the preparation of the phosphide of sodium. The tap is turned so that the benzyl-chloride may drip fast on to the phosphide of sodium contained in the flask (in which it has been made), which is heated in an oil bath. Care must be taken, however, lest the benzyl-chloride run in too rapidly, as in that case the ebullition (caused by the reaction) may be so violent that liquid collects in the condensing tube and is blown out by the vapour.

That reaction is occurring in the proper manner may be known by the change of colour of the phosphide of sodium from black to orange. It is advisable after the reaction has proceeded for some time, to remove the flask from the oil bath and to shake it vigorously; but as the lower portions of the phosphide are apt to become superheated, the shaking must be done cautiously.

PREPARATION OF TETRABENZYL-PHOSPHONIUM CHLORIDE.

	1	2	3	4	5	6	7	8	9	10	11	12	
	Grms. 100	Grms. 160	Grms. 200	Grms. 115	Grms. 220	Grms. 220	Grms. 100	Grms. 100	Grms. 100	Grms. 200	Grms. 100	Grms. 100	
Benzyl-Chloride.....													
Xylol *.....	100	160	Toluol	Toluol	500	500	100-40	100-60	100-55	100-75	100-55	100-60	
Sodium	14	22.5	28	17	31	31	14	14	18	28	21	20	
Phosphorus.....	6	21	26	15	28	28	9	8	17	26	19	19	
Unacted on benzyl- chloride and xylol... }	...	...	...	...	...	...	...	...	...	...	...	...	
Yield of (C ₇ H ₇) ₄ PCl+....	12	23	7	7	12		Flask broke		4	23	38	17	38
Theoretical yield	88	141	176	101	193	193	88	88	88	176	88	88	

	13	14	15	16	17	18	19	20	21	22	23
	Grms. 100	Grms. 100	Grms. 100	Grms. 200	Grms. 100	Grms. 200	Grms. 200	Grms. 200	Grms. 200	Grms. 200	Grms. 200
Benzyl-Chloride.....											
Xylol *.....	100-25	100-25	100-25	245-200	120-100	200-170	200-180	230-205	220-175	220-178	220-176
Sodium	20	20	20	35	20	40	40	40	40	40	40
Phosphorus.....	19	19	19	33	19	38	38	38	38	38	38
Unacted on benzyl- chloride and xylol }	80	90	90	78	35	40	60	30	52	58	75
Yield of (C ₇ H ₇) ₄ PCl +..	18	7	5	20	43	70	70	40	65	137	137
Theoretical yield	88	88	88	176	88	176	176	176	176	176	176

* In 7 and subsequent experiments a quantity of the xylol was distilled off after the preparation of the phosphide of sodium, and before the chloride of benzyl was allowed to act on it. The numbers after the sign - show how much of the xylol was thus distilled off.

† The chloride was squeezed in a cloth filter until it was as dry as possible and then weighed.

When the reaction is at an end only a few black particles are visible—the solid portions of the product appearing of a dirty orange colour.

The preceding table shows the results of our experiments on the influence of the conditions which affect the yield of chloride of tetrabenzyl-phosphonium, which no doubt will be serviceable in experiments on the phosphines of other radicals.

Extraction of Chloride of Tetrabenzyl-Phosphonium from the Product.

The product of the reaction we have just described consists of a mixture of common salt, a small quantity of phosphide of sodium which remains unacted on, xylol, chloride of benzyl, and phosphorised bodies, of which the chief is the chloride of tetrabenzyl-phosphonium.

To extract the latter we have tried several different processes, the simplest and best of which is the following :—

The flask containing the product of the reaction is connected with a condenser, and heated in an oil bath at a temperature of 180° – 200° C.* as long as liquid distils. The mass remaining in the flask is then detached by a glass rod, and added by small portions at a time to cold water acidulated with hydrochloric acid; but as spontaneously inflammable phosphuretted hydrogen is evolved, the operation must be conducted cautiously. When this gas ceases to come off, the solution is filtered and the residue boiled with a considerable quantity of water (2 or 3 litres). The aqueous extract is then filtered (through a cloth filter), more water is added to the residue, and the two boiled together as before, the solution filtered, and this treatment repeated until a portion of the extract gives no crystalline precipitate when cooled and mixed with hydrochloric acid. The united aqueous extracts are then mixed with about 10 per cent. of their volume of strong hydrochloric acid and allowed to cool. Almost every trace of chloride of tetrabenzyl-phosphonium is then precipitated in the form of minute needles. The compound is collected on a linen filter, well squeezed to free it from mother liquor, and recrystallised from boiling water, from which it separates on cooling in beautiful needles often an inch and a half long, and almost perfectly white and pure. The residue which remains after extracting the phosphonium compound forms a reddish-brown insoluble solid mass. It contains phosphorised bodies, the nature of which we shall consider later.

Chloride of Tetrabenzyl-Phosphonium.—As this body forms the starting point from which the other salts of the phosphonium are obtained, we have examined its properties very carefully. It is sparingly soluble in cold water. (In a rough experiment 100 cc. of water at ordinary temperatures dissolved 0.35 grm.) It is much more soluble in boiling water, and crystallises from

* A higher temperature must be avoided, as we find that it materially diminishes the yield of phosphonium salt.

it on cooling in long needles, which are somewhat thick and are perfectly colourless. The addition of common salt, and especially of hydrochloric acid, to its aqueous solution reduces its solubility in a remarkable manner: in fact, it is practically insoluble in the dilute acid, and traces may be detected in solution by this means. Chloride of tetrabenzyl-phosphonium crystallises from an aqueous solution with two molecules of water of crystallisation. The dried salt is readily soluble in alcohol, and the solution on slow evaporation yields very beautiful, colourless, rhombic crystals of considerable size and perfect symmetry. These consist of the anhydrous compound. The dried salt is also easily dissolved by chloroform, and on evaporation, the solution yields large colourless crystals, which lose chloroform on exposure to the air, and appear to have effloresced. A determination of the loss which a specimen of the salt crystallised from chloroform suffered when heated to 100°C . showed that the chloride had crystallised with 1 molecule of chloroform. We are not aware that "chloroform of crystallisation" has been noticed before in any substance.

Chloride of tetrabenzyl-phosphonium fuses at 224°C ., and volatilises slowly at that temperature apparently unchanged. Heated more strongly it decomposes, yielding solid and liquid products, amongst the former being free phosphorus. Boiled with a solution of potash it suffers a change, which we shall refer to later (see p. 204).

The composition of the chloride was determined by estimations of carbon, hydrogen, chlorine, phosphorus, and water. The combustion was made with chromate of lead and oxide of copper. The chlorine was determined gravimetrically by precipitation as chloride of silver, and the phosphorus by titration with uranium solution after the salt had been fused with a mixture of caustic potash and nitrate of potassium.

Analysis of Chloride of Tetrabenzyl-Phosphonium.

Dried Salt.

* {	·294	gm.	gave	·837	carbonic anhydride	=	77·7	per cent.	carbon.
	·294	"	"	·188	water	=	7·1	"	hydrogen.
	·6943	"	"	·2298	chloride of silver	=	8·2	"	chlorine.
	·6625	"	"		by titration	=	6·6	"	phosphorus.

	Obtained.	Calculated for (C_7H_7) ₄ PCl.
Carbon,	77·7	78·0
Hydrogen,	7·1	6·5
Chlorine,	8·2	8·2
Phosphorus,	6·6	7·2
	<u>99·6</u>	<u>99·9</u>

* The hydrogen in this experiment is too high and the carbon too low, probably because the salt had not been completely dried.

Crystallised Salt.

(1)	26.055 grms. lost at 110°	2.03 grms. water	=	7.7 per cent.
2)*	3.2392 „ „	.258	=	8.0 „

	Obtained.		
	I.	II.	
Water,	7.7	8.0	Calculated for (C ₇ H ₇) ₄ PCl ₂ H ₂ O. 7.7

Crystallised from Chloroform.

4.2015 grms. lost at 110°	.8938 grm. chloroform	=	21.2 per cent.
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	Obtained.	
Chloroform,	21.2	Calculated for (C ₇ H ₇) ₄ PCl ₂ CHCl ₃ . 21.7

Chloroplatinate of Tetrabenzyl-Phosphonium.—This compound is easily formed on mixing aqueous or alcoholic solutions of chloride of platinum and chloride of tetrabenzyl-phosphonium. In the former case a light orange precipitate is produced, which appears to be amorphous to the naked eye. In the latter, if the two solutions are boiling and dilute, a distinctly crystalline precipitate is produced of a darker colour.

The chloroplatinate is very insoluble, almost absolutely so in water, and is only very slightly soluble in alcohol.

The composition of the salt was determined by a combustion with chromate of lead and oxide of copper—as in all chloroplatinates of phosphines and phosphoniums the determination of chlorine and platinum is very tedious and uncertain.

If attempts are made to determine platinum by the weight of the residue left on ignition, the results are often as much as 2 per cent. too high, owing to the formation of phosphide of platinum. Precipitation by sulphuretted hydrogen we have found to be always incomplete with chloroplatinates of benzyl-phosphines

HOFMANN'S method† gave us results which were too low. We could, in fact, discover no process for estimating the platinum in this salt, or the chlorine, and were in consequence obliged to fix its composition by an organic analysis. The results of this are as follows:—

.348 grm. gave .711 of carbonic anhydride	=	55.7 per cent. carbon.
.348 „ „ .1508 of water	=	4.8 per cent. hydrogen.
	Obtained.	Calculated for {(C ₇ H ₇) ₄ PCl} ₂ PtCl ₄ .
Carbon . . .	55.7	56.0
Hydrogen . . .	4.8	4.7

* In this experiment the salt was heated for a whole day, and probably some of it volatilised.

† Trans. Roy. Soc. Lond., vol. cxlvii. p. 575.

Sulphate of Tetrabenzyl-Phosphonium.—Nine grms. of the phosphonium chloride were dissolved in about a pint of hot water, the solution was then cooled somewhat, and sulphate of silver added until it ceased to be converted into chloride. The solution was then filtered and concentrated, and yielded a crop of very beautiful colourless rhombic plates of considerable size.* A determination of water of crystallisation and of sulphuric acid showed that these consisted of the normal sulphate crystallising with six molecules of water.

Salt dried at 120°.

Sulphuric Acid (1 and 2 volumetrically by the chromate method, 3 gravimetrically).

- (1) 0.5745 gm. required 2.6 cc. $\frac{1}{4}$ normal $\text{BaCl}_2 = 0.0520 \text{ SO}_3 = 9.0$ per cent.
 (2) 0.4203 " " 3.8 " $\frac{1}{8}$ " " = 0.038 " = 9.0 "
 (3) 0.5053 " gave 0.131 gm. $\text{BaSO}_4 = 0.045$ " = 8.9 "

Air-dried Salt.

Sulphuric Acid.

0.6865 gm. required 5.6 cc. $\frac{1}{8}$ normal $\text{BaCl}_2 = 0.056 \text{ SO}_3 = 8.2$ per cent.

Water (by heating to 125° C.).

0.5704 lost 0.0574 $\text{H}_2\text{O} = 10.0$ per cent.

	Obtained.			
	Dry Salt.		Undried.	
	I.	II.	III.	Salt.
Sulphuric anhydride, .	9.0	9.0	8.9	8.2
Water,	—	—	—	10.0

	Calculated.	
	$\{(\text{C}_7\text{H}_7)_4\text{P}\}_2\text{SO}_4$.	$\{(\text{C}_7\text{H}_7)_4\text{P}\}_2\text{SO}_4, 6\text{H}_2\text{O}$.
Sulphuric anhydride, .	9.0	8.1
Water,	—	10.8

The normal sulphate is one of the most soluble salts of the phosphonium. It has no definite melting point. It grows pasty at 195°, but is not completely fused until 220°.

Action of Sulphuric Acid on Chloride of Tetrabenzyl-Phosphonium.—When

* In our notice of these experiments in the "Proceedings," we stated that the action of sulphate of silver on the phosphonium chloride yields the *acid* sulphate, and not the *normal* sulphate of the phosphonium. There can be but little doubt that we did obtain and analyse the acid salt, but its formation was probably due to the fact that we acted on a *boiling* solution of the chloride with sulphate of silver, and the filtered solution therefore contained a considerable quantity of the latter salt which we decomposed by sulphuretted hydrogen, thus setting free sulphuric acid which combined with the normal sulphate; and as the acid sulphate thus formed is much less soluble than the normal sulphate, it is probable, as we analysed the first crop of crystals, that they consisted entirely of the acid sulphate. We have verified the correctness of this explanation by an experiment conducted in a similar manner.

oil of vitriol is poured on to the chloride, an immediate effervescence occurs and clouds of hydrochloric acid are produced. Heated on the water bath, the mixture grows dark and eventually becomes completely liquid, provided that an excess of sulphuric acid has been taken. As soon as the whole of the hydrochloric acid has been driven off, the mixture is poured into a small quantity of cold water. A solid substance of a grey colour is precipitated, which by washing with a little cold water becomes free from sulphuric acid. It is then boiled with a tolerably large quantity of water, when it almost completely dissolves, leaving, however, a slight residue containing most of the black colouring matter. On cooling, almost colourless crystals are deposited, which are apparently rhombohedral plates united into spear-shaped forms.

A single recrystallisation gives the new compound in a state of purity.

Its analysis shows it to be the—

Acid Sulphate of Tetrabenzyl-Phosponium.—The chloride has therefore been acted on by sulphuric acid in the same manner as common salt. Its analysis gave the following numbers:—

·397	gram.	gave ·9907 CO ₂	=	68·1	per cent.	carbon.
·397	"	" ·2176 H ₂ O	=	6·1	"	hydrogen.
·5252	"	" ·2445 BaSO ₄	=	16·0	"	sulphuric anhydride.

	Obtained.	Calculated for (C ₇ H ₇) ₄ PHSO ₄ .
Carbon,	68·1	68·3
Hydrogen,	6·1	5·9
Sulphuric anhydride, .	16·0	16·2

Acid sulphate of tetrabenzyl-phosponium is rather more soluble in water than the chloride, and very much less so than the normal sulphate; it readily crystallises from hot water. The addition of hydrochloric acid to its solution causes the precipitation of the chloride. It has a sour taste, and its solution reddens litmus paper.

It does not suffer any loss when heated to 100° C., and therefore contains no water of crystallisation.

It fuses at 217° C., suddenly effervesces at higher temperatures, and suffers decomposition (see p. 214).

Action of Hydrate of Barium on the Acid Sulphate.—The action which occurs when solutions of these two bodies are mixed varies in a remarkable manner with the conditions of the experiment.

We naturally supposed that the hydrate of tetrabenzyl-phosphonium would be produced. Thus—

In our first attempts to prepare the base by this method 3 grms. of the acid sulphate were dissolved in about half a litre of water, and a solution of caustic baryta (in boiling water) was added until no more sulphate of barium was precipitated. The solution was then filtered and a stream of carbonic acid passed through it until all excess of baryta was converted into carbonate. It was then boiled and filtered, and the filtered solution concentrated until it amounted to about 50 cc. in volume. Tufts of needles separated out, though in small quantity; but on allowing the solution to stand for a couple of days, large rhombohedral plates appeared, which were colourless and of striking refractive power—resembling, in fact, iodide of phosphonium. They were washed with a little water and their mother liquor evaporated down, when a second crop of tabular crystals separated. The two crops were mixed and recrystallised from water. The resulting crystals were analysed.

Heated in a drying oven to 110° C. they became opaque, and lost in weight, thus showing that they contained water of crystallisation. As, however, during drying they developed a smell, recalling that of bitter almonds, we cannot place much reliance on the water determination, as the compound no doubt volatilised slightly. It was, however, necessary to dry it for organic analysis, and we therefore heated it quickly in a small beaker placed in an oil bath until it had partially fused. As this only occurred at a temperature above 200° C., there can be no doubt that we obtained a dry product.

Its combustion thus dried gave numbers agreeing with those required for the base.

0.2065 grm. gave 0.620 CO_2 = 81.8 per cent. carbon.
 0.2065 „ „ 0.1256 H_2O = 6.8 „ hydrogen.

	Obtained.	Calculated for $(\text{C}_7\text{H}_7)_4\text{P}(\text{OH})$.
Carbon, . . .	81.8	81.5
Hydrogen, . . .	6.8	7.0

Wishing to prepare another quantity of the base, we proceeded in a similar manner, using however more concentrated solutions; but on filtering and evaporating (after getting rid of excess of baryta), no base could be obtained. This curious result induced us to examine the precipitated sulphate of barium, which we found to contain a substance readily soluble in alcohol, though quite insoluble in water. It separated from its alcoholic solution in white needles. These were recrystallised until of constant melting point, viz., 210–212° C.

They were then dried at 120° , but did not lose weight, so they were at once submitted to an elementary analysis.

0.4234 gave 1.230 $\text{CO}_2 = 79.2$ per cent. carbon.
 0.4234 „ 0.2589 $\text{H}_2\text{O} = 6.8$ „ hydrogen.

These results, so different from those required by the hydrate, we could not explain, and therefore again repeated the experiment with the acid sulphate and caustic baryta as far as possible under the same conditions as before—with larger quantities, however—but with exactly the same result. No body soluble in water was produced, but an insoluble body was precipitated with the sulphate of barium, soluble, however, as we had before noticed, in alcohol, and having on recrystallisation the same melting point (210 – 212° C.). Its analysis gave numbers agreeing with those we had previously obtained.

0.5958 gave 1.7221 $\text{CO}_2 = 78.8$ per cent. carbon.
 0.5958 „ 0.3636 $\text{H}_2\text{O} = 6.8$ „ hydrogen.

Obviously then two distinct substances are formed by the action of caustic baryta on the acid sulphate, under conditions which vary only slightly from each other.

On consideration, but one explanation appeared probable, viz., that the base suffered decomposition; and the only change which appeared at all likely for it to undergo was a loss of hydrogen and benzyl, and, consequently, the formation of oxide of tribenzyl-phosphine. This change would be analogous to the decomposition which HOFMANN observed on heating the hydrate of tetrethyl-phosphonium, which he found to decompose with formation of ethane and oxide of triethyl-phosphine,

Similarly, hydrate of tetrabenzyl-phosphonium might split up into toluol and the phosphine oxide,

On comparing the percentages of hydrogen and carbon required for the oxide of tribenzyl-phosphine, with the results of our analyses of the body soluble in alcohol, we found that they corresponded.

	Obtained.				Calculated for	
	I.		II.		$(\text{C}_7\text{H}_7)_3\text{PO}.$	
Carbon, . . .	79.2	.	78.8	.	78.75	
Hydrogen, . . .	6.8	.	6.8	.	6.56	

It only remained to ascertain whether toluol was produced in the reaction. 7 grms. of the acid sulphate were placed in a distilling flask, and about the same

proportion of water as we employed in our two previous experiments. The two were then boiled until the sulphate had dissolved, and a boiling and concentrated solution of caustic baryta was added in excess. The distilling flask was then connected with a condenser, and its contents heated. An oily liquid passed over with the water, which had the odour of toluol, and a boiling point of 112° —exactly that of toluol. Moreover, its weight amounted to 1.0 gm., whereas the quantity we ought to have obtained was 1.2 gm.

There can be no doubt then that the base very easily decomposes into toluol and tribenzyl-phosphine oxide.

That this decomposition is effected by the temperature we must doubt, as we concentrated the solution of the base by boiling, and it suffered no change. But, on the other hand, there can be no doubt that if *weak* solutions of the acid sulphate and baryta are employed, the base is almost—if not altogether the sole product—whilst with *strong* solutions only the oxide is formed.

Action of Carbonate of Barium on the Acid Sulphate.—Carbonate of barium, when added to a solution of the acid sulphate, at once effervesces, and sulphate of barium is formed, whilst the base remains in solution, from which it is easily obtained by evaporation and subsequent cooling.

The reaction occurs according to the equation,

We have not observed the production of any oxide of tribenzyl-phosphine in this reaction, even when a very concentrated solution of the acid sulphate is employed, and we therefore recommend it as the simplest and most certain method for obtaining the base, for the acid sulphate is very easily formed from the chloride.

This reaction also shows that no carbonate of tetrabenzyl-phosphonium can exist; nor ought we to be surprised at this, considering that the alkaline power of aromatic phosphines, like that of corresponding amines, is very markedly less than it is in the case of ethyl or methyl phosphines or amines.

Hydrate of Tetrabenzyl-Phosphonium.—This body is one of the most beautiful of all the compounds of tetrabenzyl-phosphonium. It is very soluble even in cold water, and crystallises in very beautiful rhombohedral plates, which we have on one occasion obtained nearly $\frac{1}{2}$ an inch long and $\frac{1}{4}$ inch broad. The crystals have a very striking refractive power, so that they resemble in appearance the large crystals of phosphonium iodide, which may be formed by slow sublimation.

The hydrate is readily soluble in alcohol ; and the crystals obtained from the solution contain alcohol.

0.8746 heated to 110° lost 0.1076 grm. alcohol = 12.3 per cent.

	Obtained.	Calculated for (C ₇ H ₇) ₄ P(OH) ₂ C ₂ H ₅ OH.
Alcohol, .	12.3	12.8

Solutions of the base have an alkaline reaction, and they neutralise acids—salts of the phosphonium resulting.

When the anhydrous base is heated, it begins to fuse at 190°, but a portion remains unfused to 211°. It is probable, therefore, that the base cannot be melted without decomposition. Heated to higher temperatures it decomposes, and gives solid and liquid products, the nature of which we shall discuss later.

Bromide of Tetrabenzyl-Phosphonium.—This compound was obtained by mixing aqueous solutions of bromide of barium and the acid sulphate. The precipitated sulphate of barium contains the greater quantity of the bromide, which is sparingly soluble. It was extracted with alcohol, and the filtered solution mixed with water. On cooling, long silky needles were deposited. Their composition was verified by a bromine determination.

0.303 grm. required 6.3 cc. decinormal AgNO₃ soln. = 0.0504 Br = 16.6 per cent.

	Obtained.	Calculated for (C ₇ H ₇) ₄ PBr.
Bromine, .	16.6	16.8

The bromide is less soluble in water than the chloride. It melts at 216° to 217°C.

Iodide of Tetrabenzyl-Phosphonium was prepared by a similar process. It is almost insoluble in water, but is soluble in a mixture of water and alcohol, and crystallises from the solution in needles resembling the chloride.

For its analysis, a quantity was fused, weighed, dissolved, and titrated with decinormal silver solution.

0.2103 grm. required 4 cc. AgNO₃ soln. = 0.0508 I = 24.2 per cent.

	Obtained.	Theory for (C ₇ H ₇) ₄ PI.
Iodine, .	24.2	24.3

Nitrate of Tetrabenzyl-Phosphonium.—A solution of the base was saturated with a dilute solution of nitric acid ; long silky needles separated. They were not analysed.

Chromate of Tetrabenzyl-Phosphonium.—This salt was obtained by acting on a solution of the chloride with chromate of silver. On extracting the precipitate

with boiling alcohol, and adding water to the filtered solution, small lemon-yellow plates separated as the solution cooled. They were not analysed.

Oxalate of Tetrabenzyl-Phosphonium.—On adding excess of oxalic acid to a dilute and hot solution of the base, and then allowing the mixture to cool, long needles separated. The salt was analysed by drying at 100° C., and determining oxalic acid in the dried compound by precipitation with chloride of calcium, the oxalate of calcium being eventually ignited and converted into quicklime.

0.741	gave	0.088 CaO=0.1383 C ₂ O ₄ =17.9 per cent.
0.770	lost	0.029 H ₂ O= 3.7 „

	Obtained.	Calculated for (C ₇ H ₇) ₄ PHC ₂ O ₄ .
C ₂ O ₄ . . .	17.9 . . .	18.1
		{(C ₇ H ₇) ₄ PHC ₂ O ₄ }, H ₂ O.
H ₂ O . . .	3.7 . . .	3.6

Acetate of Tetrabenzyl-Phosphonium.—This salt is the most soluble of any of the compounds of tetrabenzyl-phosphonium which we have examined. It is obtained by the action of the chloride on acetate of silver, and crystallises from alcohol with difficulty. It was not analysed.

Chlorate of Tetrabenzyl-Phosphonium.—This salt was prepared by the action of chlorate of barium on the acid sulphate. It crystallises in long needles from a moderately concentrated solution. Heated above its melting point, it puffs.

Examination of the Residues from the Preparation of Chloride of Tetrabenzyl-Phosphonium.

After extracting the chloride of the phosphonium from the product of action of chloride of benzyl on phosphide of sodium (by boiling the latter repeatedly with water) a solid orange-coloured mass remains, which contains large quantities of amorphous phosphorus, and also organic phosphorus compounds.

We thought it possible, if not indeed probable, that these would contain tribenzyl-phosphine, for it is only natural to suppose that that body is first formed in the reaction, and is only converted into the phosphonium compound by the continued action of the chloride of benzyl. If this were the case some of the phosphine might, we considered, remain unacted upon, and would be found in the residues.

Moreover, we thought that phosphides of sodium of a different composition from the tri-sodium phosphide might be formed along with that body by the

action of phosphorus on sodium; for instance, a phosphide analogous in composition to the liquid phosphide of hydrogen, viz., Na_4P_2 , or even to the solid phosphide, viz., Na_2P_4 . If these bodies were indeed formed, they might give by their action on chloride of benzyl analogous benzyl compounds, and of these the phosphorised cacodyl of benzyl, *i.e.* $(\text{C}_7\text{H}_7)_4\text{P}_2$, would possess a great interest.

We therefore determined to submit the residues to a very careful examination, the result of which we have now to communicate.

On boiling them with chloroform, the whole of the organic ingredients appeared to be dissolved, and the residue consisted apparently of amorphous phosphorus only. The chloroform extract was distilled to dryness, and there remained a solid gummy, slightly crystalline mass. This was boiled with alcohol, when the greater part dissolved, leaving about one-third undissolved in the form of a brown amorphous solid. The brown alcoholic extract was filtered and mixed with about one and a half times its volume of boiling water; the mixture was then boiled and filtered from a brown resinous substance which had been precipitated. The filtered solution deposited on cooling a considerable quantity of a crystalline substance, though in a very impure condition.

We thus split up the residues into three portions—

1. *Soluble in chloroform only.*
2. *Soluble in chloroform and alcohol.*
3. *Soluble in chloroform, alcohol, and a mixture of alcohol and water.*

We may here observe that as the portion of the residues No. 1 was not very inviting, in later experiments the residues were at once extracted with alcohol, so as to obtain only portions 2 and 3.

Examination of Residue soluble in Chloroform, Alcohol, and Alcohol and Water.—This portion of the residue was distinctly crystalline, but highly charged with a brown resinous substance, which threatened at first to render its purification difficult.

At first we attempted to recrystallise it from alcohol, but although well-defined crystals were easily obtained, the colouring matter adhered persistently; animal charcoal was then boiled with the alcoholic solution of some of the crystals which were only slightly coloured, and eventually by this process a colourless, crystalline, and highly refractive substance was obtained.

But we soon found that the crude and strongly coloured residue could be purified in a far easier and simpler manner. On treating it with ether or bisulphide of carbon, the colouring matter was at once dissolved, but the crystalline substance was quite insoluble, so that by simple washing with either of these liquids, an almost colourless residue was obtained, which only required to be recrystallised once or twice from hot alcohol. The crystals thus obtained

consisted of brilliant needles of considerable length and thickness, and were apparently quadratic prisms. They fused at 212° C., and appeared to volatilise at higher temperatures almost unchanged. They were analysed by combustion with chromate of lead and oxide of copper.

0.468 gave $1.360 \text{ CO}_2 = 79.2$ per cent. carbon.
 0.468 „ $0.2895 \text{ H}_2\text{O} = 6.8$ „ hydrogen.

Carbon,	79.2
Hydrogen,	6.8

That they contained phosphorus was at once shown by the livid green colour which they imparted to the flame of a Bunsen's burner when heated on a platinum wire.

The numbers required for tribenzyl-phosphine do not agree with those obtained with this substance; but, on the other hand, those calculated for a phosphorised cacodyl are almost identical with them.

Thus—

	Obtained.	Calculated for (C_7H_7) $_4\text{P}_2$.	Calculated for (C_7H_7) $_3\text{P}$.
Carbon,	79.2 . . .	78.9 . . .	82.9
Hydrogen,	6.8 . . .	6.6 . . .	6.9

As for the reasons we have given above, we almost expected to find the cacodyl in the residues, we assumed that we really had obtained such a body. But the experiments which we tried to confirm this supposition did not lead to the results which we anticipated.

A phosphorised cacodyl, even of an aromatic radical, ought to possess a strong tendency to absorb oxygen, and therefore would, even if it did not take up oxygen from the air, at least act as a powerful reducing agent. But the body in question showed no reducing tendencies whatever. A solution of nitrate of silver was not altered when boiled with its solution. Chloride of platinum at once produced a crystalline precipitate, which was not changed by boiling. This want of reducing power we considered a strong argument against the supposition that the substance was a phosphorised cacodyl. Moreover, we noticed that it showed an indifference towards those reagents which react energetically with cacodyl. It is true that we obtained a compound with bromine, and also one with sulphur; but the result of their analyses could not be reconciled with the supposition that they were derivatives of a phosphorised cacodyl.

On looking over our notes, we were struck with the fact that, so far as carbon and hydrogen are concerned, both oxide of tribenzyl-phosphine and a

phosphorised benzyl-cacodyl have an almost identical composition; and we also noticed that dibenzyl-phosphine would require similar numbers.

Thus—

		Calculated for		
		$(C_7H_7)_4P_2$.	$(C_7H_7)_3PO$.	$(C_7H_7)_2HP$.
Carbon,	.	78.9	79.7	78.9
Hydrogen,	.	6.6	6.6	6.6

We did not think it likely that dibenzyl-phosphine had been formed in the reaction, as we could not account for the hydrogen atom which it requires; but bearing in mind the results of our experiments on the action of baryta on the acid sulphate of tetrabenzyl-phosphonium, it did not appear impossible that oxide of tribenzyl-phosphine had been formed; for, by the action of phosphide of sodium on water, caustic soda is produced: this might react on chloride of tetrabenzyl-phosphonium, and give rise to oxide of tribenzyl-phosphine and toluol.

At first sight, such a supposition may not appear probable, as haloid salts of methyl- and ethyl-phosphonium are not changed by caustic alkalies; but we have shown that corresponding salts of benzyl-phosphonium possess very different properties from these bodies. On treating the product of the action of phosphide of sodium on chloride of benzyl with water, abundance of phosphuretted-hydrogen was evolved, showing that a considerable quantity of phosphide of sodium had remained unacted on. The solution was boiled; and thus, if alkalies really act on chloride of tetrabenzyl-phosphonium in the manner we have indicated, we have the necessary conditions for the production of oxide of tribenzyl phosphine.*

As a further argument for supposing that the oxide had really been obtained, and not the cacodyl, it will be noticed that, although the percentage of carbon calculated for the two bodies varies by only 0.8 per cent., the results of our analyses are more favourable to the supposition that the body is the oxide, and not the cacodyl. For we obtained 0.3 per cent. too much carbon for the cacodyl, and therefore 0.5 per cent. too little for the oxide; and in carefully conducted organic analyses the carbon is often too low, but seldom too high.

We had noticed that oxide of tribenzyl-phosphine (obtained as described at p. 198) combines with iodide of zinc to form a compound (analogous to HOFMANN'S zinc iodide compound of triethyl-phosphine oxide) of characteristic crystalline form. If, then, the substance were the phosphine oxide, the

* We have since proved that alkalies act very readily on chloride of tetrabenzyl-phosphonium. On boiling a solution of the chloride in alcohol with potash or soda for a few minutes, decomposition occurs, chloride of the alkaline metal is precipitated and the solution contains oxide of tribenzyl-phosphine, which is easily identified by its insolubility in water and other characteristic properties.

production of this salt would be an almost crucial test. We therefore proceeded with the supposed cacodyl as we had done with the oxide of tribenzyl-phosphine, and operating under exactly the same conditions, obtained a double salt with zinc iodide, which could not be distinguished from that of the oxide, either in crystalline form or in composition.

We have further verified the identity of the supposed cacodyl with oxide of tribenzyl-phosphine, by processes which we may consider along with the properties of that substance.

Since writing the above, we have noticed that oxide of tribenzyl-phosphine has been obtained by F. FLEISSNER,* by the action of benzal chloride on iodide of phosphonium. The results of FLEISSNER's investigations on the properties of the oxide, so far as they go, are in accordance with our own.

Oxide of Tribenzyl-Phosphine.—Subjoined are the results of the analysis of the oxide prepared by three different methods :—

I. *Obtained as just described from the residues.*

II. and III. *Obtained by the action of caustic baryta on chloride of tetra-benzyl-phosphonium.*

IV. *Obtained during experiments on the action of sodium on chloride of tetrabenzyl-phosphonium (see p. 211).*

	Obtained.				Calculated for $P(C_7H_7)_3O$
	I.	II.	III.	IV.	
Carbon,	79.2	79.2	78.8	78.3	78.75
Hydrogen,	6.8	6.8	6.8	6.7	6.56
Phosphorus,	8.5 8.8	—	—	8.4	9.68
Oxygen,	—	—	—	—	5.01
					<hr/> 100.00 <hr/>

The three specimens were quite different in appearance.

I. Crystallised in thick needles of great refractive power, and quite transparent.

II. and III. In opaque plates of indefinite form.

IV. In very bulky, silky needles.

We could not at first reconcile ourselves to the belief that they were one and the same body.

The following carefully conducted experiments, however, appear to prove beyond doubt that they were so :—

Melting Point.—This was determined in the ordinary manner, by heating the carefully dried and pulverised substance in a capillary tube tied to a thermo-

* Ber. d. deutsch. chem. Ges., xiii., 1665.

meter, both thermometer* and capillary tube being placed in a beaker containing sulphuric acid.

I.	II. and III.	IV.
(a) 212° C.	212°	212°
(b) 212°	212°	210-212°

The temperature is uncorrected.

Double Salt with Zinc Iodide.—This compound was formed easily with any of the three specimens, by adding to its alcoholic solution an alcoholic solution of zinc iodide, and evaporating to small bulk. The double compound separates in thin transparent plates of characteristic form.

Examined under the microscope *no difference could be detected in the crystalline form of the double salt prepared with any of the three specimens of the oxide.*

The salt was analysed by volumetric determination† of iodine in specimens of Nos. I. and of II. and III.—

I.	0.606	gram.	required	12.4	cc.	decinormal	AgNO ₃	=0.15748	=26.0	per cent.	iodine.
II. and III.	0.232	"	"	4.7	"	"	"	=0.05969	=25.9	"	"
Calculated for {P(C ₇ H ₇) ₃ O} ₂ ZnI ₂ .									26.4	"	"

Chloroplatinate.—This salt is characteristic, and is formed with ease on mixing dilute alcoholic solutions of the oxide and chloride of platinum. It separates almost immediately as a light orange-coloured granular powder—which, under the microscope, is seen to consist of groups of needles, thick, four-sided, and with blunt ends. Very commonly two needles form a cross, at other times several radiate from a common centre. *No difference could be detected in the crystalline form of the chloroplatinate prepared with any of the specimens.*

The salt was analysed by determination of carbon, hydrogen, and in one specimen of chlorine also :—

I.

Chlorine.

0.4356	gram.	required	15.3	cc.	decinormal	AgNO ₃	=0.054315	Cl=12.4	per cent.‡
0.4605	"	"	16.4	cc.	"	"	=0.05822	"=12.6	per cent.§

IV.

Carbon and Hydrogen.

(A)	0.3932	gram.	gave	0.8497	CO ₂	=	0.25491	C	=	58.9	per cent.
	0.3932	"	"		0.1874	H ₂ O	=	0.02082	H	=	5.3
(B)	0.2738	"	"		0.5975	CO ₂	=	0.16295	C	=	59.4
	0.2738	"	"		0.1350	H ₂ O	=	0.015	H	=	5.4

* One of CASELLA'S.

† VOLHARDT'S method.

‡ HOFMANN'S method.

§ By precipitating the platinum with sulphuretted hydrogen and titrating the filtered solution.

	I.	IV.
Carbon,		58.9 59.4
Hydrogen,		5.3 5.4
Chlorine,	12.4 12.6 . . .	— —
Platinum,	— —	— —

The formula which HOFMANN* gives for the chloroplatinate of the oxide of triethyl-phosphine is $3(\text{Et}_3\text{PO}), \text{Et}_3\text{PCl}_2, \text{PtCl}_4$; but this formula does not appear to be a very probable one. It seems to us to be more likely that the chloroplatinate is a compound of the phosphine oxide with hydrochloric acid and chloride of platinum, and we find that the numbers calculated for such a formula, viz., $4(\text{Et}_3\text{PO}), 2\text{HCl}, \text{PtCl}_4$, agree as closely with those obtained by HOFMANN in the analysis of the chloroplatinate, as do those calculated from his formula, thus—

	Obtained.	Calculated for
		$3(\text{Et}_3\text{PO}), (\text{Et}_3\text{PCl}_2), \text{PtCl}_4$ $4(\text{Et}_3\text{PO}), 2\text{HCl}, \text{PtCl}_4$.
Carbon,	30.17	 30.9 30.4
Hydrogen,	6.75	 6.4 6.3
Platinum,	21.06	 21.2 20.8
Chlorine,	22.93	 22.9 22.5

It will be seen that the only difference between these two formulæ is that the one on the right hand contains an atom more oxygen and two atoms more hydrogen than the one on the left; that is to say, a difference of 18 as regards molecular weight. As the latter amounts to 930 in HOFMANN'S formula, the difference in the calculated percentage of each element is very slight, and this is still more the case with the chloroplatinate of the benzyl compound—the molecular weight of which with HOFMANN'S formula is 1674, and with our formula 1692.

But, on the other hand, the proportion of carbon is so large that the percentage of that element is perceptibly different with the two formulæ, and it will be seen that this difference is decidedly in favour of the formula which we propose.

We may add that it appears to us to be highly improbable that O should be replaced by Cl_2 , by simply mixing at ordinary temperatures chloride of platinum and the phosphine oxide.†

The results of our analysis, compared with the numbers calculated for the two formulæ are—

	Obtained.	Calculated for			Calculated for		
		$3\{(\text{C}_7\text{H}_7)_3\text{PO}\}, \{(\text{C}_7\text{H}_7)_3\text{PCl}_2\}, \text{PtCl}_4.$			$4\{(\text{C}_7\text{H}_7)_3\text{PO}\} 2\text{HCl}, \text{PtCl}_4.$		
Carbon,	59.2	.	.	60.2	.	.	59.5
Hydrogen,	5.3	.	.	5.0	.	.	5.0
Platinum,	—	.	.	11.7	.	.	11.7
Chlorine,	12.5	.	.	12.7	.	.	12.5

* Trans. Roy. Soc. Lond., 1860, p. 418.

† The experiments of CRAFTS and SILVA (*loc. cit.*) show that this replacement does not occur.

Brominated Compound.—This is a very characteristic substance, and its production, with all of the specimens of the supposed oxide, we considered to be a strong proof of their identity.

It is formed by dissolving the phosphine oxide in glacial acetic acid (boiling), and adding bromine in excess. No visible reaction occurs, except that the bromine is at first decolorised. On cooling, the compound is precipitated as a granular crystalline powder of bright yellow colour. Sometimes needles are observed; but these are found, when examined under the microscope, to consist of cubical or rhombohedral crystals united; the crystalline powder consisting of the same forms isolated.

For analysis, the compound was simply dried *in vacuo* for some time, and was not recrystallised.

Carbon and Hydrogen.*

0.4746 grm. gave 0.9915 CO₂ = 0.2704C = 56.9 per cent.

0.4746 „ „ 0.2117 H₂O = 0.0235H = 4.9 „

Phosphorus.†

0.6777 required 16.1 cc. uranium solution = 0.0368 P = 5.2 per cent.

Bromine.‡

0.1685 required 6.0 cc. silver solution = 0.048 Br = 28.4 per cent.

0.2128 „ 7.55 cc. „ „ = 0.060 Br = 28.3 „

0.3498 „ 12.37 cc. „ „ = 0.099 Br = 28.3 „

These numbers agree closely with the rather curious formula,

but with no other that appeared probable.

	Obtained.				Calculated.
	I.	II.	III.		
Carbon, . . .	56.9	—	—	. . .	56.3
Hydrogen, . . .	4.9	—	—	. . .	4.7
Phosphorus, . . .	5.2	—	—	. . .	6.9
Bromine, . . .	28.4	28.3	28.3	. . .	28.5

The bromine compound when treated with acetic acid loses bromine. It cannot, therefore, be readily recrystallised. Heated by itself it fuses, but at no definite temperature, to a deep yellow liquid. Hydrobromic acid is then given off, and later bromide of benzyl (?) distills. Heated with alcohol it dissolves, and the solution (at first yellow) gradually becomes colourless, and the odour of bromide of benzyl is apparent; but a considerable quantity of bromine may be precipitated by nitrate of silver from the alcoholic solution. When boiled with water it decomposes, and bromine is evolved.

* By combustion with oxide of copper and chromate of lead.

† Fused in a silver dish with caustic potash and nitrate of potash, and subsequently titrated with uranium solution.

‡ Fused in a silver dish with caustic potash, and subsequently titrated by VOLHARDT'S method.

Sulphuretted Compound.—When the phosphine 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 ($\text{P}(\text{C}_7\text{H}_7)_3\text{O} : \text{S}_2$) and the temperature is kept at the melting point of the oxide or rather higher (240°), the sulphur dissolves, no gas is evolved, and the product dissolves completely in a large quantity of boiling alcohol. The solution on cooling deposits beautiful silky needles of a light buff colour, which do not readily change in appearance (nor alter in their melting point) by recrystallisation. That the new substance contains sulphur is shown by burning it on platinum foil, when a strong odour of sulphurous anhydride is at once observed.

The substance fuses at 211° – 212° (uncorrected). It is insoluble in water, and sparingly soluble in alcohol. The only determinations made were of the carbon and hydrogen which it contains.

0.2103 gave 0.597 $\text{CO}_2 = 0.16254 \text{ C} = 77.3$ per cent.

0.2103 „ 0.132 $\text{H}_2\text{O} = 0.01466 \text{ H} = 6.9$ „

These numbers do not agree with any simple addition product. The only probable formula which agrees with the numbers obtained is,

Thus—

	Obtained.	Calculated.
Carbon,	77.3	77.3
Hydrogen,	6.9	6.4

Examination of Residue, soluble in Chloroform and Alcohol only.

This portion of the residue was contained in the dark brown mother liquors of the crystalline substance, which the preceding experiments have shown was oxide of tribenzyl-phosphine.

On evaporating off the alcohol a dark brown syrupy mass remained, which solidified on cooling to a resin. This contained some crystalline matter, which we could not succeed in separating. We have subjected the resin to many experiments with the view of obtaining definite products, only, however, with partial success.

In one of our earlier experiments we subjected it to the action of heat. 55 grms. were heated in a distilling flask. The thermometer rose rapidly to 380° , and a small quantity of a solid substance distilled. The temperature then fell suddenly, and a liquid distillate was obtained. After some time the temperature again rose above the boiling point of mercury, and the residue began to char. The products of this distillation were collected together and

redistilled. They began to boil a little above 100° C. The distillate was divided into two fractions, viz., from 100°–200° C., and from 200°–320° C.

The first of these was liquid, and on redistillation passed almost entirely between 110°–114° C. (chiefly at 112° C.), and had all the properties of toluol. The second was solid, and contained a *large quantity of free phosphorus*. As its fractional distillation did not give satisfactory results it was dissolved in boiling alcohol. Free phosphorus in some quantity remained undissolved, and on filtering and cooling the solution, colourless crystals separated. They were collected and recrystallised until their melting point was constant, viz., 118° C.

This is the melting point given by LAURENT for stilbene, and the crystalline habit which is so characteristic was exactly the same as that of the substance under examination. On combustion we obtained numbers agreeing fairly well with those calculated for that hydrocarbon.

0.3135 gave 1.0815 carbonic anhydride = 0.29495 carbon = 94.1 per cent.
 0.3135 „ 0.1965 water = 0.02183 hydrogen = 6.9 „

	Obtained.	Calculated.
Carbon,	94.1	93.3
Hydrogen,	6.9	6.6

The mother liquors from which it had been separated were concentrated, and yielded a batch of colourless crystals, which were not examined. The mother liquors from them were considerably concentrated, and yielded another crop of colourless crystals, which, after repeated recrystallisation, ceased to alter in melting point. This was 51° C, which is that of dibenzyl. We have not analysed the substance, as we considered its identity with dibenzyl proved by its melting point and characteristic odour.

We had thus proved that the resin split up on heating into free phosphorus, stilbene, dibenzyl, and toluol—a result which might occur supposing it to have consisted of tribenzyl-phosphine. The equation,

shows this.

This supposition is strengthened by the fact that sulphide of benzyl yields stilbene when heated; and one of us has shown that organic compounds of phosphorus and sulphur often behave in a similar manner.

Moreover, subsequent experiments showed that chloride of tetrabenzyl-phosphonium is decomposed by heat into hydrochloric acid, and the same products as we obtained on heating the resin. We also heated the resin with chloride of benzyl in a sealed tube for some time at 180°–190° C. Nothing par-

ticular appeared to have occurred, the contents of the tube consisting of a brown viscous mass. But on boiling this with water, and cooling the solution, chloride of tetrabenzyl-phosphonium crystallised out, and was proved to be pure by a determination of chlorine.

0.656 required 13.5 cc. decinormal $\text{AgNO}_3 = 7.3$ per cent. Cl.
 $(\text{C}_7\text{H}_7)_4\text{PCl} \cdot 2\text{H}_2\text{O}$ requires . . . 7.6 „ „

This experiment would have definitely proved the resin to consist of tribenzyl-phosphine, had the phosphonium chloride been produced in large quantity; but such was not the case, for about 20 grms. of resin only gave about 2 grms. of the chloride; still it shows that the resin contained the phosphine.

As HOFMANN (*loc. cit.*) has found that dibenzyl-phosphine does not combine with acids, we could scarcely expect to obtain salts of the tertiary-phosphine. We, however, heated the resin with fuming hydrochloric acid, but, as we expected, obtained no salt. We have also tried to obtain the well characterised oxide of tribenzyl-phosphine, by treating the resin with various oxidising agents, but without success. Nor could we obtain any definite compounds on treating the resin with bromine, chloride of platinum, or iodide of zinc. We therefore abandoned its further investigation.

Attempts to prepare Tribenzyl-Phosphine.

So far as we are aware, no method has been discovered for converting the oxide of a tertiary-phosphine or a salt of a compound phosphonium into a tertiary-phosphine itself.

Considering the remarkable stability of the former class of bodies, and the tenacity with which the oxygen adheres to the phosphorus, we scarcely expected to effect the reduction of the oxide of tribenzyl-phosphine. We, however, subjected it to the action of potassium, of sodium, and of zinc dust, but, as we expected, it either remained unchanged, or suffered complete decomposition.

We hoped, however, to meet with better success in attempting to obtain tribenzyl-phosphine from chloride of tetrabenzyl-phosphonium. Two methods suggested themselves to us, the first being to act on the chloride with sodium, which we anticipated would give chloride of sodium, dibenzyl, and the phosphine,

A preliminary experiment showed that when chloride of tetrabenzyl-phosphonium is boiled for some hours with xylol and sodium, chloride of sodium is produced.

We therefore made a carefully conducted experiment as follows:—

24 grms. of the pure chloride were carefully dried and introduced into a

flask connected with a reversed condenser. 100 grms. of redistilled xylol (boiling point 135° – 137° C.) were then added together with 1.3 gm. of sodium. A current of hydrogen was then passed through the apparatus, and the mixture kept gently boiling. When most of the sodium had been acted on (which required some days' digestion), the xylol was poured off and filtered. On cooling, it deposited an abundance of crystalline matter. This was collected on a cloth filter, well squeezed to free it from adhering xylol, and dissolved in boiling alcohol. On cooling, crystals separated having the appearance of oxide of tribenzyl-phosphine, and which were proved to consist of that body. The xylol from which this oxide had separated was distilled to dryness, and the residue taken up with boiling alcohol. The solution on cooling deposited beautiful silky needles, which were recrystallised twice from alcohol. In spite of their very different appearance from other specimens of oxide of tribenzyl-phosphine, a most careful examination showed that they consisted of that body (see p. 205). We are completely unable to account for the difference in appearance of the two quantities of the oxide obtained in this experiment. No one would imagine that they were the same body. We could not obtain any other definite products from this experiment.

Now the production of the oxide may be accounted for in two ways—(1) the chloride of tetrabenzyl phosphonium was not perfectly dry, and caustic soda was formed, which then acted upon it (as we have already shown), to give toluol, common salt, and the oxide; (2) tribenzyl-phosphine was formed, and absorbed oxygen from the air during the subsequent processes to which the product of the reaction was submitted. We have repeated the experiment several times, using every precaution to prevent water or oxygen from coming in contact with the mixture of sodium, xylol, and the phosphonium chloride, but always with the same result—viz., production of large quantities of the oxide. At present we do not know which of the two explanations we have given of its production is the correct one.

We may mention that finely divided silver acts on the chloride of tetrabenzyl-phosphonium when the two are heated together; the action, however, only occurs to a slight extent, and we were not successful in obtaining any definite product.

The other method that occurred to us for obtaining tribenzyl-phosphine from the chloride of tetrabenzyl-phosphonium was to treat the latter with phosphide of sodium, which we hoped would react so as to give tribenzyl-phosphine and chloride of sodium,

The following experiment was made :—3 grms. of phosphide of sodium and a little xylol were heated in a sealed tube, with 13 grms. of chloride of tetrabenzyl-

phosphonium. After three days' heating at a temperature of 180° – 190° most of the phosphide was acted on. The tube was then opened and repeatedly extracted with dry chloroform. The extract was distilled to dryness, and the residue treated with ether, which dissolved most of it, but left a small quantity of the oxide of tribenzyl-phosphine. The ethereal extract was evaporated to dryness, and left a light-coloured soft resin, which partly crystallised. A phosphorus determination showed that this contained the quantity of that element calculated for tribenzyl phosphine,

$$\begin{array}{lcl} 0.651 \text{ required* } 29.1 \text{ cc. uranium solution} & = & 9.9 \text{ per cent. P} \\ (\text{C}_7\text{H}_7)_3\text{P requires} & & 10.2 \text{ „} \end{array}$$

The quantity, however, of the resin at our disposal was so small that we could not make a thorough investigation of it. But we are inclined to the belief that both it and the resin obtained as a bye product in the preparation of the chloride of tetrabenzyl-phosphonium consisted mainly of tribenzyl-phosphine (see p. 209).

Action of Heat on the Salts of Tetrabenzyl-Phosphonium.

During the experiments we have described, we obtained on heating several of the salts of tetrabenzyl-phosphonium, results which invited a closer investigation. Partly on this account, and partly from the interesting results which Drs CRUM BROWN and BLAICKIE† have obtained by the action of heat on the salts of trimethyl-sulphine, we determined to study the behaviour of one or two of the compounds of tetrabenzyl-phosphonium when heated.

Action of Heat on Chloride of Tetrabenzyl-Phosphonium.—We hoped that the salt would dissociate when submitted to the action of heat into chloride of benzyl and tribenzyl-phosphine.

A considerable quantity of the chloride previously dried and fused was placed in a small distilling flask and heated in an air bath. Nothing particular occurred until the temperature had risen to about 300° C., when the fused salt began to grow brown, and a colourless liquid distilled. When a considerable quantity of this had passed over, hydrochloric acid was evolved, and later the distillate was yellow, and contained an abundance of free phosphorus. The heating was continued until nothing further distilled. There remained a considerable residue, consisting chiefly of charcoal.

The whole of the distillate was fractionated. Hydrochloric acid was evolved in abundance; the thermometer then rose to 109° , and by far the larger quantity of the product passed over between that temperature and 115° . This fraction on redistillation boiled constantly at 110° – 113° , and had the odour of toluol. It was not further examined, and was considered to be that substance.

* After fusion with a mixture of nitrate of potash and caustic potash.

† Proceedings Roy. Soc., Edin.

The higher boiling residue passed between 280° – 300° , and solidified in the condenser. It was dissolved in alcohol, and recrystallised several times. The recrystallised substance had the characteristic form and melting point (118° C.) of stilbene.

In the mother liquors there remained a solid of lower melting point, and having the odour of dibenzyl; but its quantity was too small to enable us to identify it absolutely. We think that there can be but little doubt that it consisted of that body.

No chloride of benzyl could be found, although the liquid product certainly smelt of it. Its quantity was therefore insignificant.

This experiment shows that the phosphonium chloride is not dissociated by heat, but splits up in a somewhat complicated manner. Very possibly the first action of heat is to give stilbene, hydrochloric acid, and tribenzyl-phosphine.

The phosphine splitting up later into toluol, stilbene, and dibenzyl.

It is however quite possible, considering the large quantity of toluol which is formed in proportion to the stilbene, and also considering the considerable amount of charred matter which remains, that the tribenzyl-phosphine splits up into toluol, and the residue $\boxed{\text{C}_6\text{H}_5-\text{C}}$, only, the latter becoming carbonised.

Action of Heat on the Acid Sulphate.—8 grms. of the acid sulphate were carefully dried, and heated in a small retort connected with a wide condensing tube. The salt fused, then effervesced violently, and a colourless liquid distilled which solidified in the condenser. Sulphurous anhydride was given off at the end of the operation, and a slight residue of syrupy consistency and of a dark brown colour remained in the retort. The crystalline product was washed with alcohol until quite colourless, and then recrystallised several times from the same liquid, in which it was not very soluble. It crystallised in very thin needles of considerable length. These melted at 205° – 206° C. It did not precipitate chloride of barium, but contained sulphur, as it gave the sulphuric acid reaction after it had been oxidised with a mixture of

nitric acid and chlorate of potash; and molybdate of ammonia showed that phosphoric acid was also present in the substance thus oxidised. No chloroplatinate could be obtained, but on mixing alcoholic solutions of the substance and of chloride of platinum a black precipitate was produced, consisting either of reduced platinum or of its sulphide.

The substance was burnt with chromate of lead and oxide of copper, and gave numbers agreeing with those required for the sulphide of tribenzylphosphine.

0.3567 gave 1.0097 CO_2 = 0.27587 C = 74.4 per cent.
 0.3567 „ 0.2114 H_2O = 0.02348 H = 6.6 „

	Obtained.	Calculated for (C_7H_7) ₃ PS.
Carbon, . . .	74.4 . . .	75.0
Hydrogen, . . .	6.6 . . .	6.2

The compound was not further examined.

Action of Heat on the Hydrate.—From the experiments described at p. 196 on the action of caustic baryta on the acid sulphate, we were led to think that the latter would easily split up into toluol and oxide of tribenzylphosphine, and we therefore determined to ascertain if this supposition were correct.

A quantity of the hydrate crystallised from alcohol was placed in a distilling flask and heated in an oil bath. The alcohol of crystallisation first passed off, and at 250° C. the compound melted, and immediately a colourless liquid began to distil, which ceased to pass over at 260° C. The liquid was redistilled and boiled constantly at 111°–112° C. It consisted therefore of toluol.

The residue in the distilling flask crystallised on cooling, was insoluble in water (whereas the hydrate readily dissolves), but was soluble in alcohol, and crystallised in the characteristic form of the oxide. Its melting point was found to be 212° C., and it gave the characteristic brominated compound and chloroplatinate of the oxide.

The decomposition which the hydrate suffers when heated may therefore be expressed by the equation—

Action of Heat on Oxide of Tribenzyl-Phosphine.—The oxide partly volatilises unchanged when it is heated, and partly decomposes into toluol, free phosphorus, charred matters, and other substances obtained in too small quantity to be investigated.