

XXII. *Contributions to the History of the Phosphorus-Bases.**By* AUGUSTUS WILLIAM HOFMANN, *F.R.S.*

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## FIRST MEMOIR.

IN a paper\* published a few years ago by M. CAHOURS and myself, the remarkable phosphorus-compounds, whose existence was first pointed out by the experiments of M. PAUL THÉNARD, were subjected to a more complete examination than they had previously received.

The discovery of a better mode of preparation enabled us to gain a clearer view of the nature of this group of substances, and to throw additional light on their relations to the nitrogen-bases; but, owing to the overwhelming number of reactions which presented themselves, we were unable to submit the behaviour of the phosphorus-bases with other groups of bodies to a detailed examination.

In continuation of former experiments, I have lately been much engaged in the investigation of the polyatomic ammonias, the study of which was naturally suggested by the beautiful researches which have been published on the polyatomic alcohols. In the course of these experiments, I frequently had occasion to return to the phosphorus-bases, the employment of triethylphosphine in particular having in many instances led to results which would not easily have been obtained in any other way. The possibility of preparing this body in a state of perfect purity and in considerable quantity, by a series of processes, which, if not quite simple, are at least definite and certain, its position in the system of organic compounds, its conveniently situated boiling-point, the energy and precision of its reactions, and lastly, the simplicity which characterizes these reactions, in consequence of the absence of unreplaced hydrogen in triethylphosphine,—whereby the formation of a large number of compounds of subordinate theoretical interest is excluded,—all these conditions tend strongly to invite us to the study of a body, in whose chemical relations the leading questions of the day are not unfrequently mirrored with surprising distinctness.

It was originally my intention to put together—in one frame, as it were—the various facts which I have collected relating to the phosphorus-bases; but the material lies scattered in so many directions, that I deem it more advisable to publish these observations in a number of shorter memoirs, which, from the nature of the subject, must be more or less fragmentary.

\* Philosophical Transactions, vol. cxlvii. p. 575.

*Preparation of Triethylphosphine.*

The whole of the material used in my experiments was prepared by the process formerly described in detail by CAHOURS and myself. The only alteration, which has been found advisable, relates to the separation of the triethylphosphine from the chloride-of-zinc-compound, which is produced by the action of trichloride of phosphorus on zinc-ethyl. It was formerly our practice to throw solid hydrate of potassium into the viscid mass of this salt, and then to dissolve the potassa by gradually dropping water into the retort, the heat resulting from the reaction being sufficient to carry over the base nearly anhydrous. It is better, however, to mix the double salt at once with water, and then decompose it in a retort filled with hydrogen, by allowing strong potassa-solution slowly to flow into it. On subsequently distilling the mixture on a sand-bath in a continuous but very slow stream of hydrogen, the triethylphosphine passes over with the aqueous vapour and floats on the top of the condensed water in the receiver. By adopting this mode of proceeding, the reaction is more under the command of the operator, and as the phosphorus-base is not sensibly soluble in water, the quantity of the product is not thereby diminished.

By exact adherence to the prescribed conditions, it is by no means difficult to prepare considerable quantities of pure triethylphosphine; nevertheless the amount obtained is always less than it should be in proportion to the weight of the materials used. This loss is mainly due to the formation of secondary products, which cannot be wholly avoided even when the zinc-ethyl is carefully prepared, and to partial decomposition of the latter substance during distillation: for it is scarcely possible to imagine a more elegant reaction than that which takes place between trichloride of phosphorus and ready-formed zinc-ethyl. Under these circumstances, many attempts were naturally made to obtain the phosphorus-base in other ways; I have always, however, returned to our original process.

Totally unsuccessful was the attempt to obtain triethylphosphine, without previous preparation of zinc-ethyl, by exposing a mixture of 1 equiv. of trichloride of phosphorus and 3 equivs. of iodide of ethyl with excess of zinc in sealed tubes to a temperature of 150° C. The bodies react under these circumstances; but as only traces of triethylphosphine are produced, I have not thought it worth while to pursue this reaction further. A more favourable result was obtained by heating a mixture of zinc and phosphorus with anhydrous iodide of ethyl to between 150° and 160°. After several hours' digestion, the tubes were found to be coated with white crystals, and a considerable portion of the phosphorus had passed into the red modification. Powerful escape of gas always took place on opening the tubes, and in several instances they were shattered, even when their points were softened in the lamp-flame to diminish the violence of the concussion. Besides zinc-ethyl, the presence of which is indicated by the abundant evolution of hydride of ethyl which is observed on treating the contents of the tube with water, the chief products of this reaction are three phosphorus-compounds, which are formed in proportions varying according to the temperature and the duration of the action.

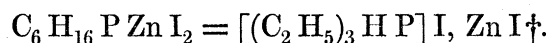
On extracting the brown residue in the tubes with warm water, and evaporating the clear solution, an oily substance separates which covers the bottom of the dish, and on cooling solidifies into a mass of hard crystals. By repeatedly crystallizing this substance from boiling water and from alcohol, large crystals are obtained, which give off triethylphosphine when treated with potassa even in the cold, and are found to consist of a compound of iodide of zinc with iodide of triethylphosphonium.

I. 0.3721 grm. of the compound dried at 100°, when burnt with a mixture of chromate of lead and oxide of copper\*, gave 0.2435 grm. of carbonic acid and 0.1320 grm. of water.

II. 0.3274 grm. of substance gave 0.3789 grm. of iodide of silver.

III. 0.3800 grm. of substance gave 0.4370 grm. of iodide of silver.

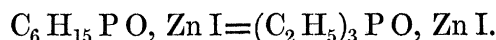
These experiments lead to the formula



Theory.			Experiment.		
	I.	II.	I.	II.	III.
C <sub>6</sub>	72	17.75	17.85	—	—
H <sub>16</sub>	16	3.95	3.94	—	—
P	31	7.65	—	—	—
Zn	32.5	8.01	—	—	—
I <sub>2</sub>	254	62.64	—	62.52	62.13
	<u>405.5</u>	<u>100.00</u>			

A solution of iodide of triethylphosphonium mixed with iodide of zinc immediately gives a crystalline compound of exactly similar characters.

The mother-liquor of the double salt yields, when further evaporated, another crystalline body which is more difficult to purify. After three or four crystallizations, however, well-developed crystals are obtained, which do not yield triethylphosphine when treated with potash, either in the cold or with aid of heat. The analysis, to be given further on, shows that this crystalline substance is a compound of iodide of zinc and oxide of triethylphosphine,



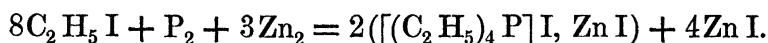
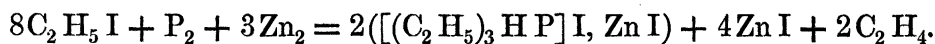
The third compound, which remains in the mother-liquor after the two former have crystallized out, and separates, on further evaporation, in beautiful needle-shaped crystals, may be recognized without difficulty as iodide of tetrethylphosphonium. The crystals are insoluble in cold potassa-solution, and give off triethylphosphine only when heated with solid hydrate of potassium.

\* The combustion of the phosphorus-compounds is not very easily effected. The experiment succeeds best with a mixture of chromate of lead and oxide of copper. All the carbon-determinations quoted in the following pages have been made with this mixture, unless another mode of proceeding is specially stated. All the substances analysed were dried at 100°, except in a few cases, when the mode of drying is also specially mentioned.

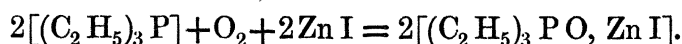
† H=1; O=16; S=32; C=12.

This iodide likewise unites with iodide of zinc; and as this latter salt is always present in the mother-liquor in considerable quantity, the double salt is generally obtained together with the simple iodide.

The mode of formation of these compounds is represented by the following equations:—



The compound containing oxide of triethylphosphine is evidently formed at the expense of the air in the tube:—



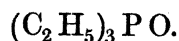
The above zinc-iodide-compounds of triethyl- and tetrethyl-phosphonium possess interest only in so far as they may serve for the preparation of the phosphorus-base. The mixture evaporated to dryness and distilled with hydrate of potassium in an atmosphere of hydrogen, does indeed yield appreciable quantities of triethylphosphine: the action of iodide of ethyl upon a mixture of zinc and phosphorus may therefore be recommended when it is desired to prepare a sample of this remarkable compound without specially arranged apparatus; but it is not adapted for the preparation of the phosphorus-base on the large scale.

I have endeavoured to prepare by this process *triethylphosphine* and *triallylphosphine*, but the results were not such as to encourage me to continue the experiments.

CAHOURS has recently made similar experiments, but with a difference in the mode of conducting them, which cannot fail to influence the result. Instead of subjecting iodide of ethyl to the action of a mechanical mixture of zinc and phosphorus, he has caused the compound  $\text{Zn}_3\text{P}$  to act upon iodide of ethyl at a high temperature. The reaction will doubtless proceed more regularly under these conditions; but the advantage which may perhaps be gained by avoiding the preparation of the zinc-ethyl is compromised, at least in part, by the time and trouble expended in the somewhat complicated preparation of trizincphosphide.

#### *Oxide of Triethylphosphine.*

The formation of the compound of this oxide with iodide of zinc to which I have alluded, induced me to subject to a careful examination the beautifully crystallized body produced from the phosphorus-base by exposure to the air. In our former experiments, CAHOURS and myself had often observed this substance, but we did not succeed in obtaining it in a state of purity fit for analysis. Nevertheless, founding our conclusion on the composition of the corresponding sulphur-compound, and having regard to the analogies presented by the bodies of the arsenic- and antimony-series, we regarded this body as the oxide of the phosphorus-base

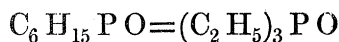


I have since confirmed this formula by analysis.

The difficulties which in our experiments opposed the preparation of this compound in the pure state, arose entirely from the comparatively small quantity of material with which we had to work. Nothing is easier than to obtain this oxide in a state of purity, provided the available quantity of material is sufficient for distillation. In the course of a number of preparations of triethylphosphine for the new experiments, a considerable quantity of the oxide had accumulated in the residues left after distilling the zinc-chloride-compound with potassa. On subjecting these residues to distillation in a copper retort, a large portion of the oxide passed over with the aqueous vapours, and a further quantity was obtained as a tolerably anhydrous but strongly coloured liquid, by dry distillation of the solid cake of salts which remained after all the water had passed over. The watery distillate, with or without addition of hydrochloric acid, was evaporated on the water-bath as far as practicable, and the concentrated solution was mixed with solid hydrate of potassium, which immediately separated the oxide in the form of an oily layer floating on the surface of the potash. The united products were then left in contact with solid potash for twenty-four hours, and again distilled. The first portion of the distillate still contained traces of water, a thin layer of triethylphosphine floating upon the surface. As soon as the distillate solidified, the receiver was changed, and the remaining portion (about nine-tenths) collected apart as the pure product. To prevent absorption of water, the quantity required for analysis was collected during the distillation.

0.2589 grm. of oxide of triethylphosphine gave 0.5098 grm. of carbonic acid and 0.2660 grm. of water.

The formula



requires the following values:—

	Theory.		Experiment.
C <sub>6</sub>	72	53.73	53.70
H <sub>15</sub>	15	11.20	11.41
P	31	23.13	—
O	16	11.94	—
	<hr/>	<hr/>	
	134	100.00	

With reference to the properties of oxide of triethylphosphine, I may add the following statements to the description formerly given\*. This substance crystallizes in beautiful delicate needles, which, if an appreciable quantity of the fused compound be allowed to cool slowly, frequently attain the length of several inches. I have been unable to obtain well-formed crystals; as yet I have not found a solvent from which this substance can be crystallized. It is soluble in all proportions, both in water and alcohol, and separates from these solvents on evaporation in the liquid condition, and solidifies only after every trace of water or alcohol is expelled. Addition of ether to the alcoholic solution precipitates this body likewise as a liquid. The melting point of oxide

\* Philosophical Transactions, 1857, p. 586.

of triethylphosphine is  $44^{\circ}$ ; the point of solidification at the same temperature. It boils at  $240^{\circ}$  C. (corrected).

As no determination of the vapour-density of any member of the group of compounds to which the oxide of triethylphosphine belongs has yet been made, it appeared to me of some interest to perform this experiment with the oxide in question. Since the determination by DUMAS' method could not have been performed without sacrificing a considerable amount of material, and GAY-LUSSAC'S was inapplicable on account of the high boiling-point of the compound, I adopted a modification of the latter, consisting essentially in generating the vapour in the closed arm of a U-shaped tube filled with mercury and immersed in a copper vessel containing heated paraffin, and calculating its volume from the weight of the mercury driven out of the other arm. As I intend to publish a full description of this method, which promises to be very useful in certain cases, I shall here content myself with stating the results obtained in one of the experiments.

Substance . . . . .	0.150 gm.
Volume of vapour . . . . .	49.1 cub. cent.
Thermometer (corrected) . . . . .	$266^{\circ}.6$ C.
Barometer at $0^{\circ}$ C. . . . .	0.7670 metre.
Additional mercury column at $0^{\circ}$ C. . . . .	0.1056 metre.

These numbers prove the vapour-density of oxide of triethylphosphine to be 66.30, referred to hydrogen as unity, or 4.60 referred to atmospheric air. Assuming that the molecule of oxide of triethylphosphine corresponds to 2 vols. of vapour\*, the calculated specific gravity of its vapour  $= \frac{134}{2} = 67$ , when referred to hydrogen, and 4.63 when referred to air. Hence we may conclude that in oxide of triethylphosphine, the elements are condensed in the same manner as in the majority of thoroughly investigated organic compounds.

From the facility with which triethylphosphine is converted into the oxide by exposure to the air, even at ordinary temperatures, and from the very high boiling-point of the resulting compound, in consequence of which its vapour can exert but a very slight tension at ordinary temperatures, I am induced to think that the phosphorus-base may be used in many cases for the volumetric estimation of oxygen. When a paper ball soaked in triethylphosphine is passed up into a portion of air confined over mercury, the mercury immediately begins to rise, and continues to do so for about two hours, after which the volume becomes constant, the diminution corresponding very nearly to the proportion of oxygen in the air. To obtain very exact results, however, it would probably be necessary in every case to remove the residual vapour of triethylphosphine by means of a ball saturated with sulphuric acid.

Oxide of triethylphosphine exhibits in general but small tendency to unite with other bodies; nevertheless it forms crystalline compounds with iodide and bromide of zinc. I have examined more particularly the zinc-iodide-compound already mentioned.

\*  $\text{H}_2\text{O} = 2$  vols. of vapour.

*Oxide of Triethylphosphine and Iodide of Zinc.*

On mixing the solutions of the two bodies, the compound separates, either as a crystalline precipitate or in oily drops, which soon solidify with crystalline structure. It is easily purified by recrystallization from alcohol.

I. 0.6535 gram. of the double salt gave 0.5884 gram. of carbonic acid and 0.3070 gram. of water.

II. 0.3685 gram. of the double salt gave 0.3299 gram. of carbonic acid and 0.1757 gram. of water.

III. 0.5985 gram. of the salt obtained in the same preparation gave 0.4782 gram. of iodide of silver.

IV. 1.1680 gram. of another preparation gave 0.9420 gram. of iodide of silver.

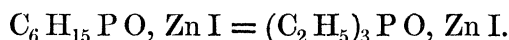
V. 0.3060 gram. of the double salt gave 0.2466 gram. of iodide of silver. The crystals used in this analysis had been obtained by the action of zinc and phosphorus on iodide of ethyl.

VI. 0.5456 gram. of substance gave 0.4333 gram. of iodide of silver.

VII. 1.1600 gram. of substance gave 0.9340 gram. of iodide of silver.

The salt employed in analyses VI. and VII. had been prepared by precipitating the hydrochloric solution of the oxide with iodide of zinc.

These analytical results establish the formula



Theory.			Experiment.						
			I.	II.	III.	IV.	V.	VI.	VII.
C <sub>6</sub>	72	24.53	24.55	24.39	—	—	—	—	—
H <sub>15</sub>	15	5.12	5.22	5.29	—	—	—	—	—
P	31	10.56	—	—	—	—	—	—	—
O	16	5.45	—	—	—	—	—	—	—
Zn	32.5	11.08	—	—	—	—	—	—	—
I	127	43.26	—	—	43.17	43.53	43.55	42.92	43.51
	293.5	100.00							

It is remarkable that this compound is formed in presence of a large excess of hydriodic and even of hydrochloric acid.

The crystals melt at 99°; they readily dissolve in warm water, and even more easily in alcohol. From the alcoholic solution well-formed crystals are frequently obtained.

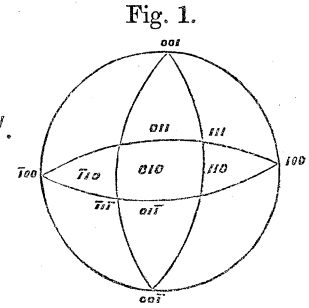
My friend QUINTINO SELLA has examined these crystals. This examination, as well as all the other crystallographical researches given in these papers, are parts of inquiries to which the celebrated crystallographer of Turin is devoting such leisure as is left to him by numerous professorial avocations and the onerous duties of an active parliamentary life. To his kindness I am indebted for the following description:—

“ System monoclinic:—

100, 101=34° 25'; 101, 001=48° 48'; 111, 010=50° 16'.

Forms observed:—

100, 010, 001, 110, 011, 111 (Fig. 1).



Angles.	Calculated.	Observed.	
		In hemitropic crystals.	In simple crystals.
100, 010 =	90°	—	—
100, 001 =	83 13	82 57	83 23
100, 110 =	47 39	47 48	47 42
100, 011 =	86 10	86 10	—
100, 111 =	50 37	50 21	—
010, 001 =	90	—	—
010, 110 =	42 21	—	42 19
010, 011 =	34 24	—	—
010, 111 =	50 16	—	—
001, 110 =	85 26	85 18	85 23
001, 011 =	55 36	55 44	—
001, 111 =	59 34	59 39	—
110, 110-bar =	84 42	84 29	84 38
110, 011 =	52 45	—	—
110, 011-bar =	61 55	—	—
110, 111 =	25 52	25 30	—
110, 111-bar =	87 49	—	—
011, 011-bar =	68 48	68 32	—
011, 111 =	35 33	35 44	—
011, 111-bar =	76 3	—	—
111, 111-bar =	100 32	100 37	—

According to NAUMANN:—

$$a : b : c = 1.3312 : 1 : 0.9052; \quad \gamma = 83^\circ 13'.$$

Forms observed:—

$$\infty P \infty, \infty P \infty, 0 P, \infty P, P \infty, -P.$$

According to WEISS:—

$$a : b : c = 1 : 0.9052 : 1.3312; \quad aoc = 96^\circ 47'.$$



Forms observed:—

$$a : \infty b : \infty c; \infty a : b : \infty c; \infty a : \infty b : c; a : b : \infty c; \infty a : b : c; a : b : c.$$

According to LEVY:—

$$MM=84^\circ 42'; MP=94^\circ 34'; b:h=1:0.9869.$$

Forms observed:—

$$h', g', P, M, e' d^{\frac{1}{2}}.$$

Combinations observed:—

110, 001 (Fig. 2).

110, 001; 100 (Figs. 3 & 4).

110, 001; 100, 010 (Fig. 5).

001, 100, 110, 111.

001, 100, 110, 111; 011.

001, 100, 110, 111; 011, 010 (Fig. 6).

Fig. 2.

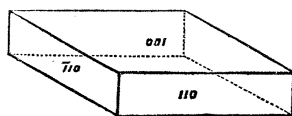


Fig. 3.

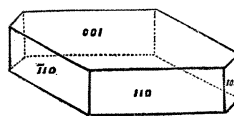


Fig. 4.

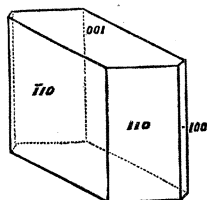


Fig. 5.

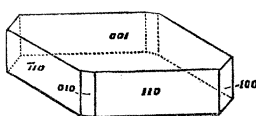
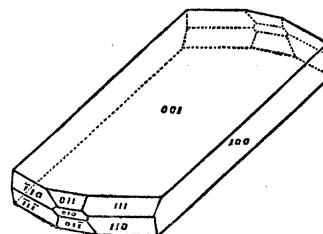


Fig. 6.



Hemitropic crystals with the axis of hemitropy  $[100]$ , with the face of hemitropy  $001=0P$  (NAUMANN) $=\infty a : \infty b : c$  (WEISS) $=P$  (LEVY).

Fig. 7.

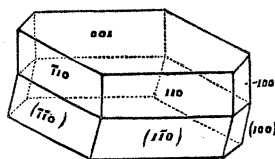


Fig. 8.

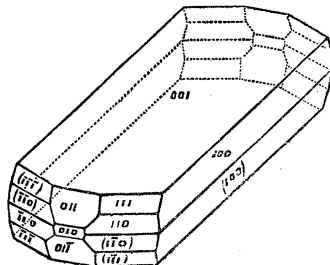
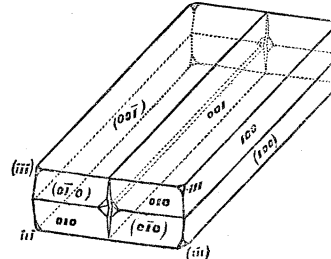


Fig. 9.



The hemitropic crystals are sometimes simple, as in Fig. 7; sometimes complicated, as in Fig. 8. It is then difficult to distinguish them from trimetric crystals; they become, however, intelligible by assuming that they result from four hemitropic crystals

grouped round  $[100]$ , as in Fig. 9. It is found sometimes that several crystals, like those of Fig. 8, are associated by  $001$ .

It deserves to be noticed that the crystals (Figs. 2, 3, 4, 5 and 7) were formed in the presence of hydrochloric acid, and that in the absence of this acid, only crystals of Fig. 8 are obtained, which, without the study of the cleavage and the optical characters, could not be distinguished from trimetric crystals.

Cleavages  $001$  and  $110$  distinct and easily obtained. The cleavage  $110$  of the hemitropic crystals (Fig. 8) exhibits re-entering angles.

Lustre vitreous on the fracture, fatty on the faces.

Hardness somewhat greater than that of gypsum.

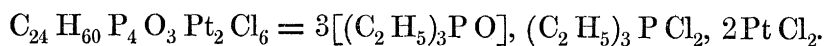
The crystals are optically positive; the line of symmetry  $[010]$  is their principal medium line. The coloured rings are visible through the faces of the cleavage  $110$ , and the plane of the optical axes appears to be perpendicular to the axis of the prism  $110$ . Through the cleavage  $110$  of the hemitropic crystals (Fig. 7), two systems of rings are seen.

The angle of the optical axes, seen through the faces  $110$  and  $\bar{1}10$ , is  $74^\circ$ . By rough measurement through  $001$  and  $01\bar{1}$ , the value of the smallest index of refraction  $\gamma=1.58$  was determined approximately; and since the apparent optical axes deviate only by a few degrees from lines normal to  $110$  and  $\bar{1}10$ , the conclusion is admissible that the internal angle of the optical axes differs but little from  $78^\circ$ .\*

#### *Oxide of Triethylphosphine and Dichloride of Platinum.*

No precipitate is formed on mixing the aqueous solutions of the two compounds, however concentrated; but on adding the anhydrous oxide to a concentrated solution of dichloride of platinum in absolute alcohol, a crystalline platinum-compound is deposited after a few moments. This compound is exceedingly soluble in water, easily soluble in alcohol, insoluble in ether. On adding ether to the alcoholic solution, the salt is precipitated, although with difficulty, in the crystalline state. The alcoholic solution, when evaporating spontaneously, yields beautiful hexagonal plates, frequently of rather large dimensions. On account of its extreme solubility, it is not quite easy to obtain this salt in considerable quantity.

Analysis has led to the somewhat complicated formula



I. 0.4187 gram. of the platinum-salt gave 0.4632 gram. of carbonic acid, and 0.2545 gram. of water.

II. 0.5185 gram. of the platinum-salt, precipitated with sulphuretted hydrogen, &c., gave 0.1092 gram. of platinum, and 0.4808 gram. of chloride of silver.

\* Some of SELLA's crystallographical researches were received whilst this paper was passing through the press. These researches will be published in detail in *Memorie della Reale Accademia delle Scienze di Torino*, Serie 2. tom. xx. under the title: *Sulle Forme Cristalline di alcuni Sali derivati dall' Ammoniaca per* QUINTINO SELLA, *Deputato al Parlamento Italiano.*

The above formula requires:—

	Theory.		Experiment.	
	I.	II.	I.	II.
C <sub>24</sub>	288	30.95	30.17	—
H <sub>60</sub>	60	6.45	6.75	—
P <sub>4</sub>	124	13.33	—	—
O <sub>3</sub>	48	5.16	—	—
Pt <sub>2</sub>	197.4	21.21	—	21.06
Cl <sub>6</sub>	213	22.90	—	22.93
	<u>930.4</u>	<u>100.00</u>		

The platinum-salt has likewise been examined by QUINTINO SELLA.

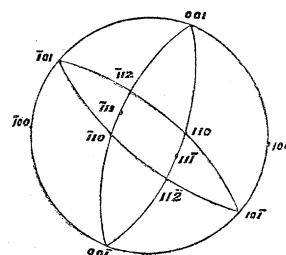
“System monoclinic:—

100, 101=27° 19'; 101, 001=46° 23'; 010, 111=41° 4'.

Forms observed:—

100, 001, 110,  $\bar{1}01$ ,  $\bar{1}11$ ,  $\bar{1}12$  (Fig. 10).

Fig. 10.



Angles.	Calculated.	Observed.
100, 001 =	73° 42'	73° 30'
100, 110 =	56 41	—
100, $\bar{1}01$ =	143 30	—
100, $\bar{1}11$ =	116 36	—
100, $\bar{1}12$ =	108 9	—
001, 110 =	81 8	81 8
001, $\bar{1}01$ =	69 48	69 48
001, $\bar{1}11$ =	78 55	78 51
001, $\bar{1}12$ =	61 10	61 14
110, $\bar{1}10$ =	66 38	66 38
110, $\bar{1}01$ =	116 12	116 23
110, $\bar{1}11$ =	63 22	—
110, $11\bar{1}$ =	19 57	—
110, $\bar{1}12$ =	63 19	—
110, $11\bar{2}$ =	37 42	—
$\bar{1}01$ , $\bar{1}11$ =	56 9	—
$\bar{1}01$ , $\bar{1}12$ =	52 53	52 32

Angles.	Calculated.
$\bar{1}11, 11\bar{1}$	$= 67^{\circ} 42'$
$\bar{1}11, \bar{1}12$	$= 17 44$
$\bar{1}11, 11\bar{2}$	$= 73 43$
$\bar{1}12, 11\bar{2}$	$= 84 11$

According to NAUMANN:—

$$a:b:c=1.5776:1:0.6308; \gamma=73^{\circ} 42'.$$

Forms observed:—

$$\infty P \infty, 0 P, \infty P, P \infty, P, \frac{1}{2}P.$$

According to WEISS:—

$$a:b:c=1:0.6308:1.5776; aoc=106^{\circ} 28'.$$

Forms observed:—

$$a:\infty b:\infty c; \infty a:\infty b:c; a:b:\infty c; -a:\infty b:c; -a:b:c; -a:b:\frac{1}{2}c.$$

According to LEVY:—

$$MM=66^{\circ} 38'; MP=98^{\circ} 52'; b:h=1:1.3343.$$

Forms observed:—

$$h', P, M, a', b^{\frac{1}{2}}, b'.$$

Combinations observed:—

$$001, 100, 110 \text{ (Fig. 11).}$$

$$001, 110, \bar{1}12, \bar{1}01.$$

$$001, 110, \bar{1}12, \bar{1}01, 100, \bar{1}11 \text{ (Fig. 12).}$$

Fig. 11.

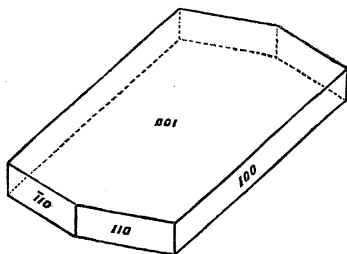
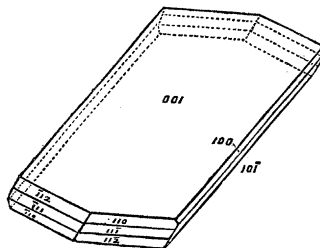


Fig. 12.



Cleavages  $\bar{1}01$  and  $110$  distinct and easily obtained.

Colour orange-red.

The optical axes are situated in  $010$ , *i. e.* in the plane of symmetry. They are seen through the faces  $001$  and the cleavages  $\bar{1}01$ , and they make an apparent angle of about  $64^{\circ}$ ."

On mixing a concentrated solution of the oxide of triethylphosphine with *trichloride*

of gold, a deep-yellow oil is separated, which crystallizes with difficulty after considerable standing. This compound is exceedingly soluble in water and in alcohol. When the aqueous solution is heated, the gold is reduced; the transformation which the oxide of triethylphosphine undergoes in this reaction has not been examined.

*Chloride of Tin* forms likewise an oily compound with the oxide: I have not succeeded in crystallizing this compound.

*Chloride of Mercury* is without any action on oxide of triethylphosphine.

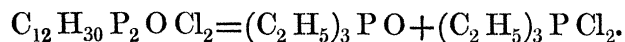
### *Oxychloride of Triethylphosphine.*

On passing a current of dry hydrochloric acid through a layer of oxide of triethylphosphine which is fused in a U-shaped tube surrounded by boiling water, brilliant crystals are soon formed. These crystals, however, rapidly disappear, the compound formed in the commencement of the reaction uniting with an excess of hydrochloric acid. The viscous liquid, which ultimately remains behind, loses, when heated, the excess of hydrochloric acid, leaving an exceedingly deliquescent crystalline mass, very soluble in alcohol, insoluble in ether.

For analysis, the new compound was washed with absolute ether, and dried over sulphuric acid *in vacuo*, either at the common temperature or at 40°. Three chlorine-determinations in specimens of different preparations yielded the following results:—

- I. 0.8845 grm. of substance gave 0.6920 grm. of chloride of silver.
- II. 0.3548 grm. of substance gave 0.2918 grm. of chloride of silver.
- III. 0.3557 grm. of substance gave 0.2979 grm. of chloride of silver.

The chlorine-percentages corresponding to these numbers exhibit far greater discrepancies than are generally observed in experiments of this description; this result is obviously due to the extremely deliquescent character of the crystals. It cannot, however, be doubted that the compound examined is an oxychloride of triethylphosphine represented by the formula



	Theory.		Experiment.		
			I.	II.	III.
2 equivs. Triethylphosphine .	236	73.07	—	—	—
1 equiv. Oxygen . . . . .	16	4.95	—	—	—
2 equivs. Chlorine . . . . .	71	21.98	19.35	20.35	20.72
1 equiv. Double Compound .	323	100.00			

The dichloride of triethylphosphine cannot be formed by the action of hydrochloric acid upon the oxide.

The oxychloride exhibits with other compounds the deportment of the oxide. It furnishes with dichloride of platinum the same platinum-salt which is obtained with

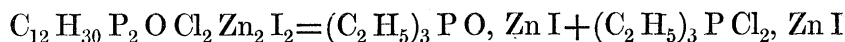
the oxide. In a similar manner, it gives with iodide of zinc the iodide-of-zinc-compound of the oxide previously described. Only once—under conditions not sharply enough observed at the time, and which I was afterwards unable to reproduce in repeated experiments—a compound of the oxychloride with iodide of zinc was formed. This substance, readily soluble in water and alcohol, crystallized from the latter solvent in beautiful colourless transparent octohedra, which, on analysis, gave the following result:—

0·2093 grm. of salt, precipitated by nitrate of silver, gave 0·2474 grm. of a mixture of iodide and chloride of silver.

With the probable assumption that the compound contains 1 equiv. of chlorine for 1 equiv. of iodine, this result corresponds to 50·74 per cent. of chlorine and iodine.

Accordingly the octohedra would be a double compound of the iodide-of-zinc-salts of the oxide and of the chloride of triethylphosphine.

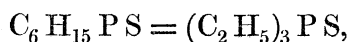
The formula



requires 50·62 per cent. of chlorine and iodine.

#### *Behaviour of Triethylphosphine with Sulphur-compounds.*

The remarkable tendency of the phosphorus-base to unite with sulphur has already been mentioned in the previous memoir; the combination of the two bodies is attended with evolution of heat, the result being a beautifully crystalline substance,



corresponding to the oxide of triethylphosphine.

This behaviour has induced me to study the action of several sulphur-compounds on the phosphorus-base. In the cases which I have examined, the ultimate product is almost invariably the sulphide of triethylphosphine, already mentioned as resulting from the direct combination of the phosphorus-base with sulphur; but the conditions under which this sulphide is produced vary considerably, and in the majority of cases it occurs only as a secondary product of the decomposition of other more direct compounds, some of which appeared to me sufficiently interesting to deserve more minute investigation.

In the course of the experiments which I am going to describe, I have prepared considerable quantities of the sulphide of triethylphosphine. This compound, although remarkable for the facility with which it crystallizes, is not easily procured in well-formed crystals. It was only once or twice that I obtained crystals with good faces. They were examined by QUINTINO SELLA, who communicates to me the following results:—

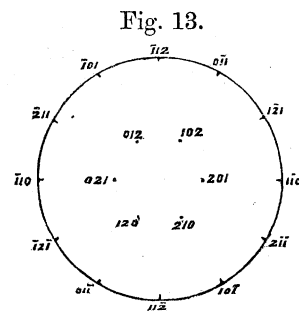
“System rhombohedric:—

$$100, 111 = 54^\circ 35'.$$

Forms observed:—

$$10\bar{1}, 2\bar{1}\bar{1}, 210 \text{ (Fig. 13).}$$

Angles.	Calculated.	Observed.
$10\bar{1}, 01\bar{1}$	$= 60^{\circ} 0'$	$60^{\circ} 1'$
$10\bar{1}, 2\bar{1}\bar{1}$	$= 30 0$	$29 59$
$10\bar{1}, 210$	$= 50 56$	$51 0$
$10\bar{1}, 120$	$= 71 38$	$71 34$
$2\bar{1}\bar{1}, 210$	$= 56 55$	—
$2\bar{1}\bar{1}, 120$	$= 90 0$	—
$210, 120$	$= 36 44$	$36 50$
$210, 021$	$= 66 10$	$66 20$
$210, 012$	$= 78 9$	—



According to NAUMANN:—

$$R=90^{\circ} 13'.$$

Forms observed:—

$$\infty P 2, \infty R, \frac{2}{3} P 2.$$

According to WEISS:—

$$a=0.8211.$$

Forms observed:—

$$a : \frac{1}{2} a : a : \infty c; \infty a : a : a : \infty c; a : \frac{1}{2} a : a : \frac{1}{3} c.$$

According to LEVY:—

$$P P=90^{\circ} 13'.$$

Forms observed:—

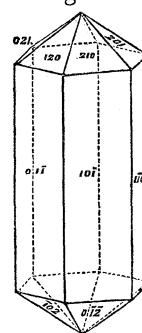
$$d', e^2, b^2.$$

Combinations observed:—

$$10\bar{1}, 210 \text{ (Fig. 14).}$$

$$10\bar{1}, 210; 2\bar{1}\bar{1}.$$

Fig. 14.



The summit of the hexagonal prisms is almost always badly terminated, since they are frequently hollow: bright faces  $210$  are but rarely met with. In one single case  $2\bar{1}\bar{1}$  could be distinctly traced. The general habitus of the crystals is that of thin, long, hexagonal needles. At summer heat, the crystals are very soft and flexible; they may be bent  $180^{\circ}$  without breaking. At lower temperatures, they are harder and much less flexible.

The crystals are optically positive. It is possible to measure the deviation through the faces of the hexagonal prism, whence it may be inferred that the index of refraction for the extraordinary ray  $\epsilon=1.65$ , and for the ordinary ray  $\omega=1.59$ ."

*Behaviour of Triethylphosphine with Sulphuretted Hydrogen.*

The phosphorus-base has no action on *sulphuretted hydrogen*. When it is brought in contact with hydrosulphuric acid over mercury, the gas does not exhibit any alteration. No sulphide of triethylphosphine is formed even in presence of air, as might indeed have been expected. The attraction of the phosphorus-base for oxygen prevents the oxida-

tion of the sulphuretted hydrogen; a solution of this gas in water, when mixed with a few drops of triethylphosphine, may be preserved in air-filled vessels much longer than without this addition.

*Behaviour of Triethylphosphine with Sulphide of Nitrogen.*

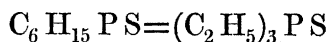
*Sulphide of Nitrogen*,  $N_2 S_2$  (?), prepared as recommended by FORDOS and GELIS, viz. by the action of ammonia on chloride of sulphur dissolved in disulphide of carbon, is decomposed by triethylphosphine, with evolution of light and heat. Gas is evolved, and at the same time a yellowish liquid is produced, which, on cooling, solidifies into a fibrous mass of crystals of the sulphide.

*Behaviour of Triethylphosphine with Mercaptan.*

When these two bodies are mixed together in an atmosphere of carbonic acid, no alteration takes place even if they are left in contact for some time, or if they are heated to  $100^\circ$  in sealed tubes for twenty-four hours. But if the mixture be poured into an air-filled flask, crystals of sulphide of triethylphosphine make their appearance in a few hours. The crystals increase if the air has free access to the mixture; but if the flask be corked, the crystallization is interrupted. On opening the flask, the entry of the air may be recognized by the light cloud which the phosphorus-base, diffused through the atmosphere of the vessel, forms with the oxygen. When a mixture containing excess of mercaptan was left for a few days in an open flask, every trace of phosphorus-base had disappeared, and the remaining colourless liquid was filled with crystals of the sulphide. On mixing this liquid with water, it separated into two layers, the upper of which quickly solidified, especially on exposure to the air, to an imperfectly crystalline mass, easily recognized as a mixture of sulphide of triethylphosphine with excess of mercaptan. The impure crystals were exposed for a while to the air and then recrystallized from boiling water.

0.3703 grm. of the crystals, dried over sulphuric acid *in vacuo*, gave 0.6485 grm. carbonic acid and 0.3304 water.

The formula



requires—

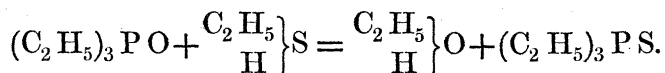
	Theory.		Experiment.
$C_6$	72	48.00	47.76
$H_{15}$	15	10.00	9.91
P	31	20.67	—
S	32	21.33	—
	<hr/>	<hr/>	
	150	100.00	

The lower stratum of liquid is aqueous alcohol containing small quantities of oxide of triethylphosphine and mercaptan. To remove the latter, the liquid was shaken up with recently precipitated mercuric oxide and distilled. The distillate, rectified several times



over lime, yielded a clear liquid, which burnt with a colourless flame and exhibited all the characters of alcohol.

The interpretation of this result appears at the first glance exceedingly simple; the sulphide of triethylphosphine cannot be formed directly from the phosphorus-base, but owes its origin to the oxide first produced by the action of air, this oxide being decomposed by the mercaptan and yielding sulphide of triethylphosphine and alcohol:



Experiment shows, however, that this equation illustrates only the final result of the reaction. Oxide of triethylphosphine and mercaptan, brought together under the most various conditions at ordinary temperatures and under pressure, do not yield a trace of sulphide of triethylphosphine; and we have to suppose, therefore, that the mercaptan interchanges its sulphur with the oxygen of the oxide of triethylphosphine, only at the instant of formation of the latter, or what comes to the same thing, that the oxygen of the air, in presence of a substance so greedy of sulphur as triethylphosphine, directly takes the place of the sulphur in the mercaptan.

In connexion with this subject, various attempts were made to replace the oxygen in oxide of triethylphosphine by sulphur. But neither by treatment with sulphide of ammonium, nor by continued boiling with the higher sulphides of potassium, could the oxide be converted into the corresponding sulphide, whereas the conversion of the sulphide into the oxide takes place without any difficulty. This, however, is not more than might have been expected from the behaviour of the oxide with hydrochloric acid, mentioned in one of the preceding paragraphs. The different degrees of stability which characterize the oxide and the sulphide of triethylphosphine may also be strikingly seen in the behaviour of these compounds with sodium, the sulphide being reduced, with the greatest facility, to free triethylphosphine, even below the melting-point of the sodium, whereas the oxide may be distilled from sodium without experiencing the slightest alteration\*. Ebullition with ordinary concentrated nitric acid likewise converts the sulphide into the oxide, the sulphur being at the same time transformed into sulphuric acid. The liquid filtered off from the precipitate obtained by barium-salts, when evaporated to dryness and fused with nitrate of potassium, yields no further trace of sulphur.

#### *Behaviour of Triethylphosphine with Disulphide of Carbon.*

These two bodies, when mixed in the anhydrous state, act upon one another with considerable force, amounting frequently to explosive violence, and unite into a red crystalline mass. The compound is best prepared by mixing the solutions of its constituents in alcohol or ether: the new body then instantly separates in beautiful red crystalline laminae.

\* In the previous memoir, it is stated that the phosphorus-base is reproduced from the oxide by the action of metallic sodium. Probably the oxide used in the former experiments contained a small quantity of free triethylphosphine, and thus led to an erroneous statement.

Several times recrystallized from alcohol and dried over sulphuric acid, the new body has furnished the following results on analysis:—

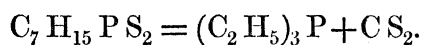
I. 0·3610 grm. of the disulphide-of-carbon-compound gave 0·5750 grm. of carbonic acid and 0·2490 grm. of water.

II. 0·3595 grm. of a new preparation gave 0·5790 grm. of carbonic acid and 0·2481 grm. of water.

III. 0·4180 grm. of a third preparation gave 0·6680 grm. of carbonic acid and 0·3027 grm. of water.

IV. 0·3505 grm. of substance, heated with a mixture of carbonate and chlorate of potassium, gave 0·8355 grm. of sulphate of barium.

These numbers lead to the formula



	Theory.		Experiment.			
			I.	II.	III.	IV.
C <sub>7</sub>	84	43·30	43·43	43·92	43·58	—
H <sub>15</sub>	15	7·73	7·66	7·67	8·04	—
P	31	15·98	—	—	—	—
S <sub>2</sub>	64	32·99	—	—	—	32·72
	<u>194</u>	<u>100·00</u>				

The red crystals are not the only product of the action of disulphide of carbon on triethylphosphine. A second beautifully crystallized compound is deposited after some time from the mother-liquor. This substance, probably a secondary product of the action of the air, is formed in extremely minute quantity; its nature is not yet established.

The compound of triethylphosphine with disulphide of carbon is insoluble in water, sparingly soluble in ether, moderately soluble in disulphide of carbon, and somewhat more soluble in alcohol, especially when heated. The solution has no action on vegetable colours. From the boiling alcoholic solution, it separates on cooling in red needles, somewhat resembling the crystals of chromic acid, which are formed by the action of strong sulphuric acid in a solution of chromate of potassium. The ethereal solution, left to evaporate in an open cylinder, deposits finely developed, deep-red crystals of considerable size. QUINTINO SELLA has examined these crystals with the following results.

“System monoclinic:—

$$100, 101 = 29^\circ 41\frac{1}{2}'; \quad 010, 111 = 74^\circ 4'; \quad 101, 001 = 27^\circ 7\frac{1}{2}'.$$

Forms observed:—

$$100, 010, 001, 110, \bar{1}01 \quad (\text{Fig. 15}).$$

Combinations observed:—

$$100, 110, 001, \bar{1}01 \quad (\text{Fig. 16}).$$

$$100, 110, 001, \bar{1}01, 010 \quad (\text{Fig. 17}).$$

Fig. 15.

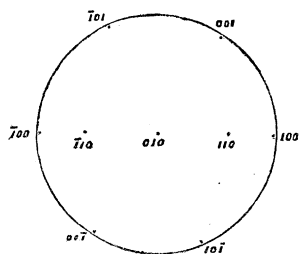


Fig. 16.

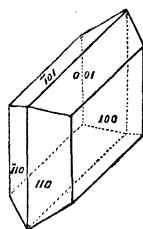
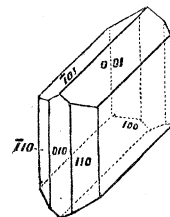


Fig. 17.



Angles.	Calculated.	Observed.
100, 010 =	90°	90° 5'
100, 001 =	56 49	56 49
100, 110 =	27 39	27 39
100, $\bar{1}01$ =	114 2	114 2
010, 001 =	90	90 6
010, 110 =	62 21	62 21
010, $\bar{1}01$ =	90	90
001, 110 =	61	60 55
001, $\bar{1}01$ =	57 13	57 13
110, $\bar{1}01$ =	111 9	110 55
110, $\bar{1}10$ =	124 41	124 42

According to NAUMANN:

$$a : b : c = 0.9205 : 1 : 1.5970; \quad aob = \gamma = 56^\circ 49'.$$

Forms observed:—

$$\infty P \infty, \infty R \infty, 0 P, \infty P, P \infty.$$

According to WEISS:—

$$a : b : c = 1 : 1.5970 : 0.9205; \quad aoc = 123^\circ 11'.$$

Forms observed:—

$$a : \infty b : \infty c; \quad \infty a : b : \infty c; \quad \infty a : \infty b : c; \quad a : b : \infty c; \quad -a : \infty b : c.$$

According to LEVY:—

$$MM = 124^\circ 41'; \quad MP = 119^\circ; \quad b : h = 1 : 0.4885.$$

Forms observed:—

$$h', g', P, M, a'.$$

The faces are all bright, with the exception of  $\bar{1}01$ , which is frequently dull, and which, on account of this difference of lustre, may be easily distinguished from  $001$ . The faces  $100$  and  $110$  exhibit delicate striæ parallel to the edge of intersection.

Cleavages:—

0 1 0 very distinct and easily obtained, although sometimes slightly curved.

1 0 0 easily obtained and fibrous.

The crystals are optically positive: the medium-line coincides with the axis of symmetry [0 1 0], and the angle of the optical axes is considerable; in a plate parallel to 0 1 0, the beginning of the rings may be seen, their centres being invisible. The centres may be seen, however, with the aid of a glass prism; and from this observation, together with the fact that the indices of refraction are not very far from 1.75, it may be inferred that the interior angle of the optical axes is not very different from 70°. The plane of the optical axes is nearly parallel to the face 0 0 1; it deviates only by a few degrees, exhibiting a tendency to approach the plane perpendicular to 1 0 0. The axis of symmetry, or of smallest elasticity, exhibits a violet-red colour, which even in very thin layers is very intense. The axis nearly parallel to [1 0 0], or the axis of greatest elasticity, exhibits a similar but much lighter red tint; the axis of mean elasticity shows in thin layers a straw-yellow, in thicker layers an orange-yellow. In polarized light one of the most beautiful examples of polychroism is observed by looking across the faces 0 1 0, the colour passing in the case of thin layers from a pure yellow to a deep red. But even in ordinary light the polychroism is perceptible; for the light passes with a violet-red through the faces 1 0 0, and with an orange-red colour of far less intensity through the faces 0 1 0.

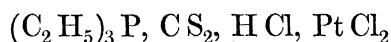
Hardness less than that of gypsum."

The red crystals appear to possess the character of a weak base. They dissolve in strong hydrochloric acid, forming a colourless liquid, from which potassa or ammonia throws down the compound in its original state, though somewhat lighter in colour, on account of its minute state of division. The acid solution forms with dichloride of platinum a light yellow amorphous salt, insoluble in alcohol and ether, which changes colour and somewhat decomposes on drying. It darkens in colour, even when dried at the common temperature *in vacuo*, hydrochloric acid fumes being evolved. The analysis of two different preparations gave the following results:—

0.7263 grm. platinum salt, treated with carbonate of sodium, &c., gave 0.1885 grm. = 25.95 per cent. of platinum, and 0.7450 grm. of chloride of silver = 25.37 per cent. of chlorine.

In a second determination, 0.1900 grm. of platinum-salt, analysed in the same manner, gave 0.200 grm. of chloride of silver = 26.04 per cent. of chlorine.

The formula



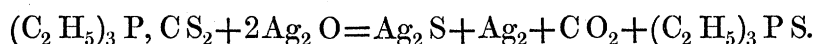
requires 24.66 per cent. of platinum and 26.61 per cent. of chlorine.

The gold-salt is obtained like the platinum-salt, and exhibits similar properties. This salt is not better adapted for analysis.

It is not very easy to form a clear notion of the constitution of the red crystals. According to the formula, the compound is the primary triethylphosphonium-salt of sulphocarbonic acid *minus* 1 equiv. of sulphuretted hydrogen, and corresponds therefore

to sulphocarbamic acid, the ammonium salt of which, as is well known, is produced by the action of ammonia on disulphide of carbon. There is, however, no analogy in the constitution of the two substances.

The new compound exhibits a remarkable tendency to pass into the sulphide of triethylphosphine. On mixing its alcoholic solution with oxide or nitrate of silver, carbonic acid is evolved, sulphide of silver and metallic silver are separated, and the filtered solution, when evaporated, deposits crystals of the sulphide:

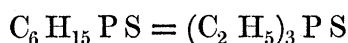


The disulphide-of-carbon-compound undergoes a similar change, even under the influence of moisture. Crystals, not dried with sufficient care, when kept in corked tubes, were changed after a few months into a yellowish white semifluid mass, of peculiar odour, which, by recrystallization from boiling water, furnished a considerable quantity of pure sulphide of triethylphosphine. To establish this transformation by numbers, the purified crystals were identified by analysis.

I. 0.5345 grm. of the sulphide gave 0.9440 grm. of carbonic acid and 0.4915 grm. of water.

II. 0.2460 grm. of the sulphide, oxidized with nitric acid, gave 0.3810 of sulphate of barium.

The formula



requires—

	Theory.		Experiment.	
			I.	II.
C <sub>6</sub>	72	48.00	48.16	—
H <sub>15</sub>	15	10.00	10.21	—
P	31	20.67	—	—
S	32	21.33	—	21.27
	<u>150</u>	<u>100.00</u>		

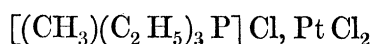
It is obvious that the transformation of the red crystals into the sulphide involves the co-operation of the elements of water. Perfectly dry crystals were preserved in sealed tubes for many months without the slightest alteration. The crystals fuse at 95° and volatilize at 100°; in the absence of moisture, they may be heated under pressure to 150° without undergoing any decomposition. The phenomena are very different in the presence of water. When exposed for some days in sealed tubes with water to a temperature of 100°, the red crystals are gradually transformed into white needles, which are easily recognized as sulphide of triethylphosphine. The transformation is independent of atmospheric air; for it takes place with equal facility in vessels filled with air, or carbonic acid, or *in vacuo*.

The products which accompany the sulphide formed in this reaction vary according to the time during which the red crystals are digested with water. If the tubes be allowed to cool after one or two days' digestion, the liquid generally becomes filled with

white needles, which are, however, still intermixed with red prisms, showing that the transformation is not yet complete. Scarcely any gas escapes when the tubes are opened, but when gently heated, the liquid yields abundance of disulphide of carbon. On the other hand, when the tubes are heated until the transformation of the red compound is accomplished,—which generally takes place after three or four days' digestion,—a large volume of gas escapes on opening, and the tubes are occasionally shattered. The gas which is thus evolved consists of sulphuretted hydrogen and carbonic acid, which are obviously secondary products of the reaction, arising from the protracted action of the water upon the disulphide of carbon which is separated in the first stage of the process. The liquid, from which the crystals of the sulphide have been deposited, has a distinctly alkaline reaction, belonging neither to the sulphide nor to the red crystals from which the sulphide arises, both these compounds being without action on vegetable colours. To seize the basic substance, the liquid was evaporated on the water-bath, till the sulphide had been as far as possible expelled, and then precipitated with iodide of zinc, which does not combine with the sulphide, traces of this body, which might have remained, being in this manner eliminated. The iodide-of-zinc-precipitate was semi-solid, and slowly became crystalline on treatment with alcohol; it did not, however, exhibit a sufficiently definite appearance to warrant its analysis. The bases were therefore at once liberated again by digesting the precipitate with oxide of silver; the powerfully alkaline liquid thus obtained gave, on addition of hydrochloric acid and dichloride of platinum, a difficultly soluble platinum-salt, crystallizing, after the necessary purification, from boiling water in splendid octohedra, which on analysis proved to be the methyl-triethylphosphonium-compound.

0·3799 grm. platinum-salt, treated with sulphuretted hydrogen, &c., gave 0·1110 grm. = 29·21 per cent. of platinum.

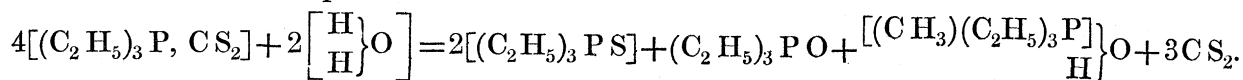
The formula



requires 29·18 per cent. of platinum.

The solution filtered off from the octohedral salt gave, on evaporation, the extremely soluble six-sided tables of the platinum-salt of oxide of triethylphosphine, which I have mentioned in the commencement of this paper.

The products of the action of water upon the red crystals, then, are sulphide of triethylphosphine—the principal product,—oxide of triethylphosphine, hydrate of methyl-triethylphosphonium, and disulphide of carbon, which may be partly or entirely converted into sulphuretted hydrogen and carbonic acid. Four molecules of the disulphide-of-carbon-compound and two molecules of water contain the elements of two molecules of the sulphide, one molecule of the oxide, one molecule of the hydrated phosphonium, and three molecules of disulphide of carbon.



Whilst engaged with the experiments involved in the elucidation of this subject, I

observed occasionally small, well-defined yellow crystals disseminated among the mixture of white and red needles, which are deposited when the digestion-tubes are allowed to cool, before the transformation is terminated. The yellow crystals appeared in greater quantity towards the close of the operation, and were found to be a secondary product formed by the action of the sulphuretted hydrogen, which is generated in the last stage of the process. I have since learnt to prepare the yellow crystals by a simpler and more definite method. This remarkable compound has become the starting-point of a new inquiry, the result of which I reserve for a later communication.

The formation of the red crystals by the union of triethylphosphine and disulphide of carbon takes place so rapidly, and with such facility, that ever since for the first time I observed this phenomenon, I have used the disulphide of carbon as a reagent for the detection of the phosphorus-bases; for trimethylphosphine exhibits a deportment perfectly similar to that of the ethyl-body. The minutest quantities of these bases may thus be readily and safely recognized. The reaction is best observed by pouring the liquid to be examined upon a watch-glass, and allowing the vapour of the disulphide of carbon to flow from an inclined bottle upon the liquid. Immediately the watch-glass is coated with a beautiful net-work of the red crystals. It requires scarcely to be mentioned that the crystals are not formed when the phosphorus-bases are combined with acids. They appear, however, readily on adding to a mixture of their salts and disulphide of carbon, a drop of potash, which liberates the bases.

On the other hand, triethylphosphine may be employed with the greatest advantage as a test for disulphide of carbon. There is, in fact, no test for this substance, which in delicacy could be compared with it. By its aid the presence of the disulphide in the most volatile fractions of coal-tar-benzol is readily proved; even the exceedingly small quantity of disulphide of carbon diffused in the most carefully purified coal-gas may, as I have shown already in another place\*, be recognized without any difficulty. When the gas is passed through a bulb-apparatus containing ether to which a few drops of triethylphosphine are added, the liquid soon assumes a reddish tint, which gradually increases in intensity, until, when the ether is evaporated, the interior of the apparatus appears coated with a delicate efflorescence of the red crystals. Scarcely more than half a cubic foot of the present London coal-gas is required for this experiment.

In order to satisfy myself that disulphide of carbon may be employed with safety as a test for the phosphorus-bases, it was necessary to examine the deportment of this compound with the *arsines* and *stibines*. Disulphide of carbon exhibits no reaction with *triethylarsine* and *triethylstibine*. I have left mixtures of these bases with the disulphide in contact for a considerable length of time, both at the common temperature and at 100°, without being able to observe the slightest alteration. I have also satisfied myself that disulphide of carbon, at all events at the common temperature, is without action upon *phosphoretted hydrogen*.

\* Quarterly Journal of the Chemical Society, vol. xiii. p. 87.

On examining somewhat minutely into the department of triethylphosphine with sulphur-compounds, the organic sulphocyanates could not be left unnoticed. My attention was in the first place fixed by the sulphocyanate of phenyl, which I had just discovered at the time I was engaged in the study of these reactions. I owe to the kindness of Dr. LEIBIUS a very considerable quantity of this somewhat difficultly obtainable sulphocyanate, the full description of which will be found in a paper on phenyl-derivatives shortly to be published. The department of this compound with triethylphosphine, however, is here given in connexion with the phosphorus-bases.

*Action of Sulphocyanate of Phenyl upon Triethylphosphine.*

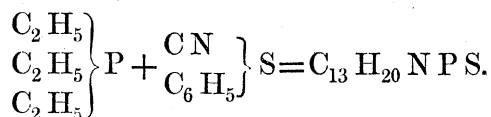
The reaction between the two substances in the anhydrous state is very violent, and frequently causes the inflammation of the phosphorus-base. The mixture assumes a deep-yellow colour, and on cooling deposits sometimes splendid uranium-yellow needles; often, however, it remains liquid for hours, and even for days, but suddenly solidifies, when touched with a glass rod, into a hard yellow crystalline mass. The new compound is most conveniently prepared by allowing the sulphocyanate to act upon the triethylphosphine in the presence of a considerable volume of ether. The product of the reaction, being difficultly soluble in cold ether, often separates in the crystalline state, more frequently as an oil, which solidifies after some time. In order to ensure perfect purity, it is only necessary to crystallize the compound once or twice from boiling ether.

I. 0.2160 grm. of the yellow crystals, dried *in vacuo* over sulphuric acid, gave 0.4923 grm. of carbonic acid and 0.1585 grm. of water.

II. 0.2242 grm. of crystals of a second preparation gave 0.5110 grm. of carbonic acid and 0.1675 grm. of water.

III. 0.3491 grm. of substance, burnt with carbonate of sodium and oxide of mercury, gave 0.3250 grm. of sulphate of barium\*.

These numbers characterize the new body as a combination of one molecule of triethylphosphine with one molecule of sulphocyanate of phenyl:



Theory.			Experiment.		
	I.	II.	I.	II.	III.
C <sub>13</sub>	156	61.66	62.16	62.16	—
H <sub>20</sub>	20	7.90	8.14	8.30	—
N	14	5.54	—	—	—
P	31	12.25	—	—	—
S	32	12.65	—	—	12.79
	253	100.00			

\* When attempting to determine the sulphur as sulphide of silver, I found that on ebullition of the



The above formula is fully corroborated by the analysis of several well-defined salts, which will be mentioned presently.

The yellow crystals are insoluble in water. Alcohol, both cold and hot, dissolves them in almost every proportion. The best crystals were obtained by the spontaneous evaporation of the ethereal solution in a high open cylinder. Some of these crystals were so well developed, that QUINTINO SELLA was enabled to submit them to a detailed crystallographic examination, which I here insert.

“System monoclinic:—

$$100, 001 = 61^\circ 2'; \quad 010, 110 = 44^\circ 27'.$$

Forms observed:—

$$100, 010, 001, 110 \quad (\text{Fig. 18}).$$

Combinations observed:—

$$110, 001 \quad (\text{Fig. 19}).$$

$$110, 100, 001 \quad (\text{Fig. 20}).$$

$$110, 001; \quad 100, 010 \quad (\text{Fig. 21}).$$

Fig. 18.

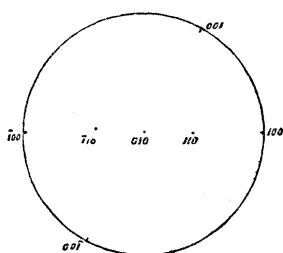


Fig. 19.

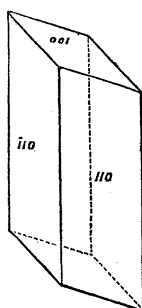


Fig. 20.

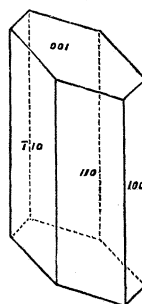
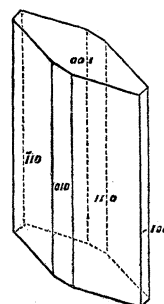


Fig. 21.



Angles.	Calculated.	Observed.
100, 010	= 90° 0'	90° 0'
100, 001	= 61° 2'	60° 53'
100, 110	= 45° 33'	45° 33'
010, 001	= 90° 0'	—
010, 110	= 44° 27'	44° 27'
001, 110	= 70° 10'	70° 24'
110, $\bar{1}10$	= 88° 54'	88° 54'

alcoholic solution with nitrate of silver not more than about one-half of the sulphur was separated as sulphide of silver. 0.3180 grm. of substance gave 0.1491 grm. of sulphide of silver=6.05 per cent. of sulphur. In the presence of ammonia the whole amount of sulphur is precipitated as sulphide of silver.

According to NAUMANN:—

$$b : c = 1 : 0.8583; \quad \gamma = 61^\circ 2'.$$

Forms observed:—

$$\infty P \infty, \infty R \infty, 0P, \infty P.$$

According to WEISS:—

$$a : b = 1 : 0.8583; \quad a o c = 118^\circ 58'.$$

Forms observed:—

$$a : \infty b : \infty c; \quad \infty a : b : \infty c; \quad \infty a : \infty b : c; \quad a : b : \infty c.$$

According to LEVY:—

$$M M = 88^\circ 54'; \quad M P = 109^\circ 50'.$$

Forms observed:—

$$h', g', P, M.$$

The faces 0 0 1 present less lustre than the others, which are very brilliant, when the crystals are taken from a tube which contains a number of the crystals. In contact with the air they become opaque, and the faces lose their lustre, but they become again transparent when returned to the tube containing the other crystals.

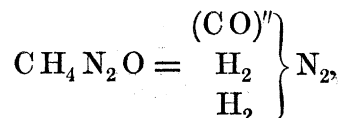
Cleavage 1 0 0 easily obtained; cleavage 1 1 0 fibrous.

Hardness nearly that of gypsum.

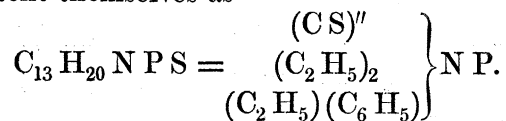
The plane of the optical axes is parallel to [0 1 0], or to the axis of symmetry.

Colour light yellow, with a tint of green."

If we endeavour to associate this compound with well-known bodies, in order to obtain some insight into the probable arrangement of its proximate constituents, both its formation and its deportment point to *urea*. Urea is generated by the combination of ammonia and cyanic acid: the yellow crystals are formed by the union of two compounds derived respectively from ammonia and cyanic acid; in urea the faculty possessed by ammonia of combining with acids has been preserved; the new compound likewise exhibits the sharply-defined characters of a monacid base. Whatever constitution be attributed to urea, must also be claimed for the new base. If urea be viewed as a monacid diamine,



the yellow crystals present themselves as



The new compound accordingly belongs to the type urea: it may be viewed as ordinary urea, the oxygen of which is replaced by sulphur, for the hydrogen of which ethyl and phenyl have been substituted, whilst phosphorus has taken the place of half the nitrogen. Regarded from this point of view, the formation of the new compound presents considerable interest; it offers the first example of the perfect substitution of the

hydrogen in urea, which had remained doubtful hitherto, and illustrates in a remarkable manner the persistence of the type urea under the influence of an almost overwhelming substitution. At the same time it deserves to be noticed that the corresponding oxygenated urea remains to be discovered.

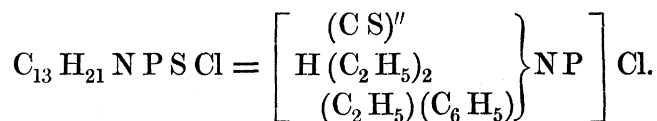
The new compound, as already mentioned, possesses the properties of a well-defined organic base. Insoluble in water, it dissolves with the greatest facility even in very diluted acids, giving rise in many cases to easily-crystallizable salts which are capable of double decomposition, and from which the base may be reprecipitated by the careful addition of potassa or ammonia.

*Chloride.*—The solution of the phenyl-compound in warm concentrated hydrochloric acid solidifies on cooling to a crystalline mass, which, when recrystallized from moderately warm water, furnishes splendid cadmium-yellow crystals, frequently an inch in length. Boiling water has to be avoided, since it decomposes the substance. Even the dry crystals are altered at 100°; they must therefore, like all the other salts of the base, be dried *in vacuo* over sulphuric acid.

I. 0.1953 grm. of substance gave 0.3850 grm. of carbonic acid and 0.1293 grm. of water.

II. 0.5635 grm. of substance gave 0.2850 grm. of chloride of silver.

These numbers correspond to the formula

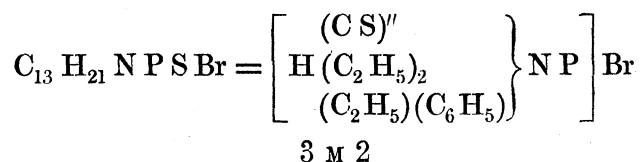


Theory.			Experiment.	
			I.	II.
C <sub>13</sub>	156	53.88	53.76	—
H <sub>21</sub>	21	7.25	7.36	—
N	14	4.84	—	—
P	31	10.71	—	—
S	32	11.06	—	—
Cl	35.5	12.26	—	12.51
	<u>289.5</u>	<u>100.00</u>		

*Bromide.*—Both in preparation and properties, precisely similar to the salt previously mentioned.

0.2835 grm. of bromide gave 0.1620 grm. of bromide of silver.

The formula



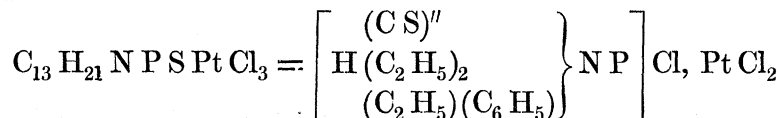
requires the following values:—

	Theory.		Experiment.
1 equiv. of Phenyl-compound . . . . .	253	75·76	—
1 equiv. of Hydrogen . . . . .	1	0·29	—
1 equiv. of Bromine . . . . .	80	23·95	24·31
1 equiv. of Bromide . . . . .	334	100·00	

*Platinum-salt.*—The solution of the chloride furnishes with dichloride of platinum a light-yellow crystalline precipitate. Dilute solutions slowly deposit this salt in somewhat better-formed crystals, which are frequently grouped in lily-shaped aggregations.

0·4690 grm. of platinum-salt, heated with carbonate of sodium, gave 0·0995 grm. of platinum and 0·4505 grm. of chloride of silver.

The formula



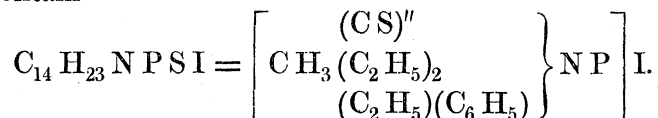
requires the following values:—

	Theory.		Experiment.
1 equiv. of Phenyl-compound . . . . .	253	55·11	—
1 equiv. of Hydrogen . . . . .	1	0·21	—
1 equiv. of Platinum . . . . .	98·7	21·49	21·22
3 equivs. of Chlorine . . . . .	106·5	23·19	23·75
1 equiv. of Platinum-salt . . . . .	459·2	100·00	

I did not succeed in preparing the sulphate or the nitrate of the base. The phenyl-compound is rapidly decomposed under the influence of these acids; it forms, however, beautifully crystallized salts with the iodides of methyl and ethyl. I have examined only the former of these compounds.

*Iodide-of-Methyl-compound.*—When iodide of methyl is poured into an ethereal solution of the urea, the new compound is at once separated as a heavy oil which rapidly solidifies into a crystalline mass. The crystals dissolve in boiling water which on cooling deposits the iodide in splendid needles of a golden-yellow colour.

These crystals contain

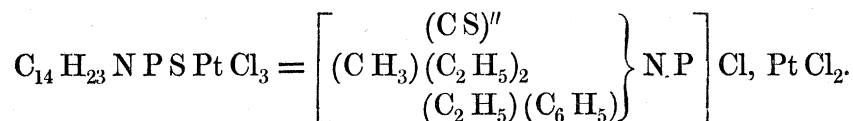


0·3885 grm. of iodide gave 0·2300 grm. of iodide of silver.

	Theory.		Experiment.
1 equiv. of Phenyl-compound . . . . .	253	64·06	—
1 equiv. of Methyl . . . . .	15	3·79	—
1 equiv. of Iodine . . . . .	127	32·15	31·97
1 equiv. of Iodide . . . . .	395	100·00	

*Platinum-salt of the Methyl-compound.*

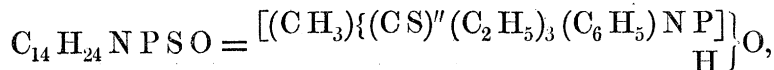
The chloride obtained by treating the iodide with chloride of silver, yields upon addition of dichloride of platinum, an acicular platinum-salt, which may be recrystallized without decomposition from boiling water. Its composition corresponds to that of the iodide:



0.3395 grm. of platinum-salt, treated with carbonate of sodium, gave 0.0700 grm. of platinum and 0.3095 grm. of chloride of silver.

	Theory.		Experiment.
1 equiv. of Phenyl-compound .	253	53.47	—
1 equiv. of Methyl . . . .	15	3.16	—
1 equiv. of Platinum . . . .	98.7	20.86	20.62
3 equivs. of Chlorine . . . .	106.5	22.51	22.55
1 equiv. of Platinum-salt . .	473.2	100.00	

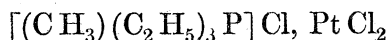
The iodide, when treated with oxide of silver, furnishes, together with iodide of silver, a very caustic liquid containing the corresponding hydrate. The presence in this liquid of the compound



is proved by the fact of the characteristic needle-shaped platinum-salt being immediately reproduced when it is saturated with hydrochloric acid and mixed with dichloride of platinum. The free base is, however, readily decomposed. On boiling, the odour of sulphocyanate of phenyl becomes at once perceptible; if ebullition be continued until the odour has disappeared, addition of hydrochloric acid and dichloride of platinum no longer furnishes the difficultly soluble needles. In their place, large well-developed orange-yellow octohedra are deposited on evaporation, which by analysis were found to be the platinum-salt of methyl-triethylphosphonium.

0.2210 grm. of platinum-salt, precipitated by sulphuretted hydrogen, &c., gave 0.0640 grm. = 28.96 per cent. of platinum.

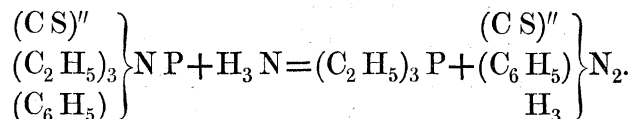
The formula



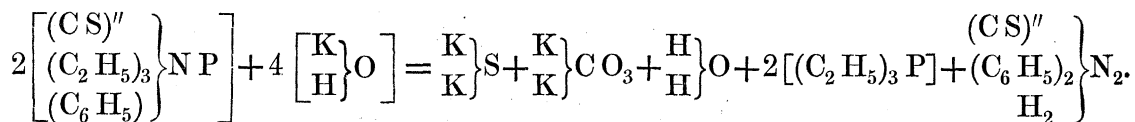
requires 29.18 per cent. of platinum.

The free methylated phenyl-base then simply splits by ebullition into sulphocyanate of phenyl and oxide of methyl-triethylphosphonium. When the solution is boiled by itself, the sulphocyanate is separated as such; when it is boiled in the presence of oxide of silver, the sulphocyanate is, partly at least, destroyed, the alkaline solution becoming acid and exhibiting the presence of considerable quantities of sulphuric acid. This transformation clearly shows how feebly the proximate constituents are held together

in the urea. The same instability is perceptible in the general department of the compound. Even extremely dilute nitric acid liberates the sulphocyanate of phenyl, whilst the phosphorus-base is converted into the oxide. The chloride is one of the more stable salts of the urea, but it is likewise readily altered; on addition of a large quantity of water, the solution of the salt becomes milky, the sulphocyanate of phenyl being separated in oily globules, and now contains the chloride of triethylphosphonium. On adding ammonia to the *concentrated* solution of the chloride, the urea, as has been already stated, is separated without change, and may be readily recovered by taking up with ether and crystallizing. If, on the other hand, the *dilute* solution be boiled with ammonia, the turbidity perceptible in the commencement disappears again, and after a few moments beautiful crystals of *phenyl-sulphocarbamide* are deposited, triethylphosphine being simultaneously liberated:



On treating the chloride with potassa, phenomena exactly analogous are observed; the crystals which are separated, are, however, *diphenyl-sulphocarbamide*:



If a few drops of disulphide of carbon be added to the solution of the urea, the liquid, when gently heated, assumes a deep red colour, and deposits on cooling the beautiful ruby-red crystals  $(\text{C}_2 \text{H}_5)_3 \text{P}$ ,  $\text{CS}_2$ , which I have mentioned in a previous paragraph of this paper. The mother-liquor of these crystals furnishes on evaporation oily droplets of sulphocyanate of phenyl. The urea, even when perfectly pure and dry, cannot be preserved without undergoing a gradual alteration. If the crystals be left under a bell-jar containing atmospheric air, they become dull, and at last moist and sticky, whilst a peculiar extremely disagreeable odour, distantly resembling that of hydrocyanic acid, becomes perceptible; at the same time, a delicate net-work of fine needles begins to appear on the glass, easily recognized as sulphide of triethylphosphine. The crystals of the urea fuse at  $57^\circ.5$ , forming a yellow liquid, which, in consequence of incipient decomposition, resolidifies but slowly and imperfectly. At  $100^\circ$  the phenomena just mentioned are much more distinctly observed, and especially the smelling body is unmistakably perceived. The peculiar-smelling body is likewise almost overwhelmingly produced on evaporating the ethereal mother-liquor of the compound. As yet I have not been able to lay hold of the possessor of this remarkable odour. The ethereal mother-liquor, when evaporated, leaves a brown syrup, which after some time deposits large crystals of sulphide of triethylphosphine. Submitted to distillation, this residue yields, together with other products, an additional quantity of the crystallized sulphur-compound.

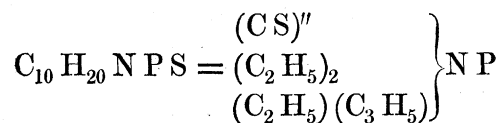
Transformations precisely similar are observed when the crystals of the urea, in sealed tubes, are exposed to a temperature of from 150° to 160°. The brown fused mass which is thus formed, solidifies on cooling with crystalline structure; the crystals, however, are no longer the original compound, but sulphide of triethylphosphine, which is surrounded by another substance. The examination of this reaction has not yet been completed. The nature of the final products of the metamorphosis may, however, be anticipated in some measure by the results obtained in studying the deportment of triethylphosphine with *sulphocyanate of ethyl* and *sulphocyanate of ethylene*, which will be briefly mentioned in some of the following paragraphs.

*Action of Sulphocyanate of Allyl upon Triethylphosphine.*

To generalize the relations established in the preceding paragraph, I was induced to examine the deportment of the phosphorus-base with oil of mustard. The two bodies act upon each other with extraordinary violence; the mixture turns brown, but does not solidify either by cooling or by agitation. After some days, however, the syrup yields brown crystals which are difficult to purify. The purification of the compound succeeds, however, without any difficulty when the reaction is allowed to take place in ether. In this manner a crystalline mass is easily obtained, which requires only to be washed with cold ether, and then once recrystallized from boiling ether.

0·3623 grm. of the substance, dried over sulphuric acid *in vacuo*, gave 0·7368 grm. of carbonic acid and 0·3040 grm. of water.

The formula



requires the following values:—

	Theory.		Experiment.
C <sub>10</sub>	120	55·30	55·46
H <sub>20</sub>	20	9·21	9·32
N	14	6·45	—
P	31	14·29	—
S	32	14·75	—
	<u>217</u>	<u>100·00</u>	

The allyl-compound behaves in all respects like the phenyl-compound. It is insoluble in water, but easily soluble in alcohol; the solution has a faintly alkaline reaction. It fuses at 68° and solidifies at 61°. At a higher temperature, it is decomposed exactly like the phenyl-compound. In this case also, a peculiar, and if possible, still more repulsive odour is evolved, while crystals of sulphide of triethylphosphine separate in large quantity.

The allyl-compound crystallizes with extraordinary facility. There is no difficulty in obtaining it in colourless transparent crystals half an inch in length, and perfectly deve-

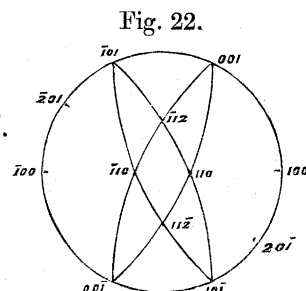
loped on all sides. I scarcely remember any other organic compound that crystallizes so readily. The crystals, as appears from the measurements of QUINTINO SELLA, are isomorphous with those of the corresponding phenyl-compound\*. SELLA has communicated to me the following details respecting his examination.

“System monoclinic:—

$100, 101=35^{\circ} 42'$ ;  $001, 101=29^{\circ} 3'$ ;  $010, 111=39^{\circ} 22'$ .

Forms observed:—

$100, 001, 110, \bar{1}01, \bar{2}01, \bar{1}12$  (Fig. 22).



Angles.	Calculated.	Observed.
$100, 001$	$= 64^{\circ} 45'$	$64^{\circ} 45'$
$100, 110$	$= 66 14$	$66 14$
$100, \bar{1}01$	$= 114 9$	$114 9$
$100, \bar{2}01$	$= 143 51$	$143 54$
$100, \bar{1}12$	$= 89 32$	$89 13$
$001, 110$	$= 80 15$	$80 10$
$001, \bar{1}01$	$= 49 24$	$49 25$
$001, \bar{2}01$	$= 79 6$	$79 7$
$001, \bar{1}12$	$= 51 8$	$51 17$
$110, \bar{1}10$	$= 47 33$	$47 31$
$110, \bar{1}01$	$= 99 30$	$99 30$
$110, \bar{2}01$	$= 109 0$	$108 54$
$110, \bar{1}12$	$= 48 23$	$48 41$
$110, 11\bar{2}$	$= 48 37$	$48 34$
$\bar{1}01, \bar{2}01$	$= 29 41$	$29 38$
$\bar{1}01, \bar{1}12$	$= 51 7$	$51 2$
$\bar{2}01, \bar{1}12$	$= 66 20$	$67 5$
$\bar{1}12, 11\bar{2}$	$= 87 31$	$87 55$

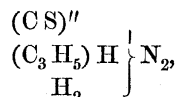
According to NAUMANN:—

$$a:b:c=0.8321:1:0.3984; \gamma=64^{\circ} 45'.$$

Forms observed:—

$$\infty P \infty; 0 P, \infty P, P \infty, 2P \infty, \frac{1}{2}P.$$

\* Both substances are isomorphous with thiosinamine or sulphallyl-urea,



the crystalline form of which has been determined by SCHABUS.



According to WEISS:—

$$a:b:c=1:0.3984:0.8321; aoc=115^{\circ} 15'.$$

Forms observed:—

$$a:\infty b:\infty c; \infty a:\infty b:c; a:b:\infty c; -a:\infty b:c; -\frac{1}{2}a:\infty b:c; -a:b:\frac{1}{2}c.$$

According to LEVY:—

$$MM=47^{\circ} 33'; MP=99^{\circ} 45'; b:h=1:0.7730.$$

Forms observed:—

$$h', P, M, a', a^{\frac{1}{2}}, b'.$$

Combinations observed:—

$$001, 100, 110 \text{ (Fig. 23).}$$

$$001, \bar{1}01, 110 \text{ (Fig. 24).}$$

$$100, 001, \bar{1}01, 110 \text{ (Fig. 25).}$$

$$100, 001, \bar{1}01, 110; \bar{1}12 \text{ (Fig. 26).}$$

$$100, 001, \bar{1}01, 110, \bar{2}01, \bar{1}12 \text{ (Fig. 27).}$$

Fig. 23.

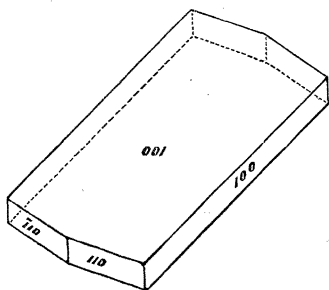


Fig. 24.

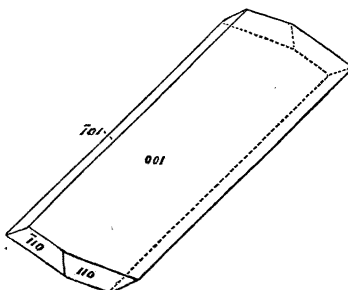
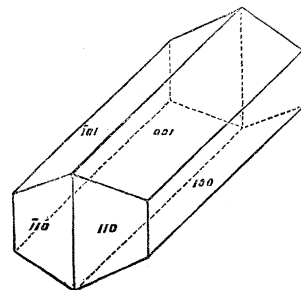


Fig. 25.



The crystals sometimes present the appearance of trimetric crystals (Fig. 25), sometimes they are flattened parallel with  $001$ , and considerably elongated in the direction  $[010]$  (Figs. 23, 24). The faces  $\bar{1}12$  are rounded off and cannot be well measured, although it is possible to verify the zones to which they belong: some of these faces are occasionally wanting, and many of the crystals present only two of these faces (Fig. 27).

Cleavages  $100$  and  $001$  distinct, and easily obtained.

Fig. 26.

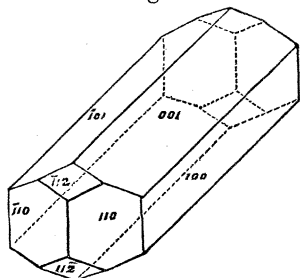
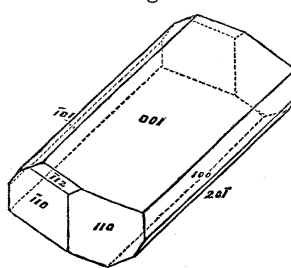


Fig. 27.



The optical axes are situated in the plane of symmetry, viz.  $010$ . The bisecting line is not very far from normal to  $\bar{1}01$ . A system of rings is observed both through the MDCCLX.

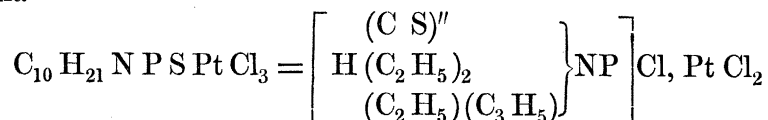
faces 1 0 0 and through the faces 2 0  $\bar{1}$ ; another system is seen through the faces 0 0 1. The apparent angle of the optical axes is about 38°, if the first system of rings be observed through 1 0 0, and about 68½° if this system be seen through 2 0  $\bar{1}$ . The mean index of refraction, *i. e.* of that which corresponds to a ray lying in a plane parallel to 0 1 0 and polarized in that plane, is  $\beta=1.657$ . Hence it follows that the internal angle of the optical axes is about 72½°.

Hardness less than that of gypsum."

*Platinum-salt.*—I have contented myself with verifying the formula of the allyl-urea by the analysis of the platinum-salt. The allyl-compound dissolves readily in hydrochloric acid, and the solution, when mixed with dichloride of platinum, yields a light-yellow scaly precipitate having a silky lustre, which fuses to a yellow oil in boiling water.

0.5605 grm. of the crystals, dried over sulphuric acid, precipitated by sulphuretted hydrogen, &c., gave 0.1282 grm. of platinum.

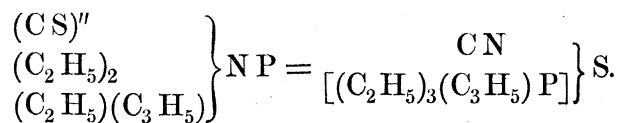
The formula



requires

	Theory.		Experiment.
1 equiv. of Allyl-compound . . .	217	51.28	—
1 equiv. of Hydrogen . . . . .	1	0.23	—
1 equiv. of Platinum . . . . .	98.7	23.32	22.87
3 equivs. of Chlorine . . . . .	106.5	25.17	—
1 equiv. of Platinum-salt . . . .	423.2	100.00	

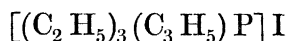
The allyl-base described in the preceding pages has the composition of sulphocyanate of triethyl-allylphosphonium:



I felt some interest in comparing the latter compound with the allyl-base. Iodide of allyl acts with the greatest energy upon triethylphosphine. The solid product of the reaction, recrystallized from alcohol, furnishes splendid needles of iodide of triethyl-allylphosphonium.

0.6740 grm. of iodide, dried *in vacuo*, gave 0.5535 grm. of iodide of silver = 44.38 per cent. of iodine.

The formula



requires 44.40 per cent. of iodine.

Treatment with chloride and oxide of silver yields the corresponding chloride and hydrate. They resemble in every respect the tetrethylphosphonium-compounds. The

chloride gives with dichloride of platinum an easily crystallizable octohedral platinum-salt.

The hydrate of triethyl-allylphosphonium forms with hydrosulphocyanic acid a difficultly crystallizable salt which is easily soluble in water, and differs, as might have been expected, entirely from the allyl-base, which has the same composition.

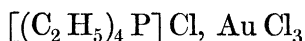
*Behaviour of Triethylphosphine with the Sulphocyanates of Ethyl and Ethylene.*

I have in vain endeavoured to produce, by the action of triethylphosphine on the sulphocyanates of methyl, ethyl, and amyl, compound ureas analogous to the allyl- and phenyl-bodies. It is true that these substances act upon triethylphosphine even at ordinary temperatures; in the case of sulphocyanate of methyl, indeed, the action is very brisk, but I did not succeed in obtaining definite compounds. Sulphocyanate of ethyl remained for months in contact with triethylphosphine without depositing any crystalline compound. The non-production of these ureas cannot, however, excite surprise, if we remember in how many respects, and especially in their relation to ammonia, the sulphocyanogen-compounds of ethyl and its homologues differ from those of allyl and phenyl.

When a mixture of triethylphosphine and one of the above-mentioned sulphocyanates is heated for some hours in a sealed tube to 100°, an abundant crop of crystals of sulphide of triethylphosphine is deposited from the liquid after cooling. These crystals are surrounded by a brown viscid substance, soluble to a certain extent in water, easily soluble with green colour in alcohol. In order to disentangle from this mixture the complementary product of the reaction, the semicrystalline mass, obtained by the action of sulphocyanate of ethyl, was shaken with ether to separate the sulphide, evaporated with an excess of hydrochloric acid, and the residue redissolved in water, when a quantity of the brown impurities remained insoluble. The filtered solution gave with trichloride of gold a dingy yellow precipitate, which by treatment with sulphuretted hydrogen, reprecipitation of the separated chloride by trichloride of gold, &c., ultimately assumed the characters of the pure gold-salt of *tetrethylphosphonium*.

0.2240 grm. of gold-salt, treated with sulphuretted hydrogen, &c., gave 0.0910 grm. = 40.62 per cent. of gold.

The formula

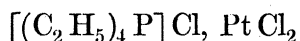


requires 40.53 per cent. of gold.

The chloride, prepared from the gold-salt, gave with dichloride of platinum beautiful octohedra of the platinum-salt of tetrethylphosphonium.

0.6300 grm. of platinum-salt, treated with sulphuretted hydrogen, &c., gave 0.1784 grm. = 28.31 per cent. of platinum.

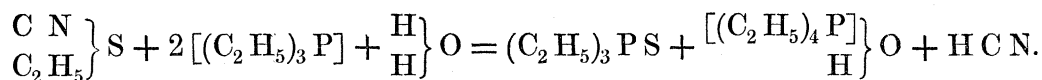
The formula



requires 28.02 per cent. of platinum.

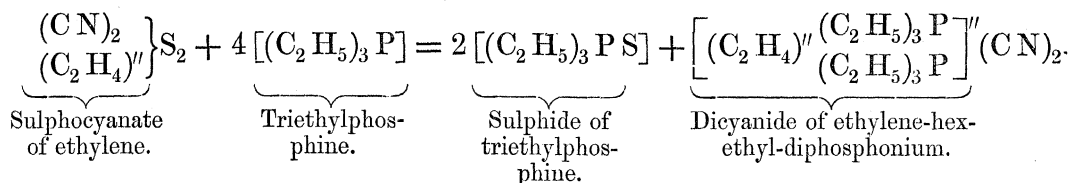
The action of sulphocyanate of ethyl upon triethylphosphine may be accordingly

represented by the equation



I have not been able to trace directly the hydrocyanic acid which figures in this equation, but this acid appears unmistakeably in its products of decomposition. The brown substance which accompanies the sulphide of triethylphosphine and the hydrate of tetrethylphosphonium is rich in nitrogen; boiled for some time with hydrochloric acid, it yields abundance of chloride of ammonium. In fact, it was on account of the presence of ammonia among the products of the reaction, that it became necessary to precipitate the tetrethylphosphonium in the first place in the form of the gold-compound.

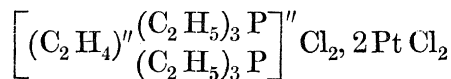
I have likewise examined the behaviour of disulphocyanate of ethylene with triethylphosphine. The reaction takes place with energy at ordinary temperatures. When triethylphosphine is poured into a concentrated alcoholic solution of sulphocyanate of ethylene, the liquid immediately solidifies to a dazzling white crystalline mass of sulphide of triethylphosphine. It deserves to be noticed that the same decomposition takes place also when the substances are allowed to react in the presence of anhydrous ether. The transformation which the sulphocyanate of ethylene undergoes under the influence of triethylphosphine is perfectly analogous to the change of the ethyl-compound when submitted to the same agent. Instead of a derivative of tetrethylphosphonium, the sulphocyanate of ethylene produces the cyanide of a diatomic metal, of *ethylene-hexethyl-diphosphonium*.



Owing to the low temperature at which the reaction is accomplished, the hydrocyanic acid is not changed in this case, and may be recognized without difficulty by the ordinary reagents. The diphosphonium, which is simultaneously formed, was traced as platinum-salt, exactly in the same manner as the tetrethylphosphonium in the process previously mentioned. The product of the reaction, freed as far as possible from the sulphide by repeated evaporation and ultimately by treatment with ether, was precipitated by dichloride of platinum. The dingy platinum-salt was purified by treatment with sulphuretted hydrogen and reprecipitation. Repeatedly treated in this manner, it assumed the character of a pure compound.

0.2745 grm. of this salt gave 0.0804 grm. = 29.29 per cent. of platinum.

The formula



requires 29.27 per cent. of platinum. Since I shall have to give a detailed account of

the diphosponium-compounds in one of the following sections of this inquiry, I need not for the present enter into further particulars regarding this reaction.

In concluding this paragraph, I may append a few remarks upon the deportment of sulphocyanate of triethylphosponium under the influence of heat. This salt is readily procured by dissolving triethylphosphine in hydrosulphocyanic acid. Submitted to the action of heat, it is partly volatilized without decomposition; the greater portion, however, is decomposed, the sulphide and the disulphide-of-carbon-compound of triethylphosphine, together with free disulphide of carbon, appearing among the volatile products of the reaction; while a brown ill-defined substance remains in the retort, yielding, when treated with an alkali, an appreciable quantity of ammonia. I have not examined this change in detail, but it is obvious that one of the direct products of the reaction is sulphocyanate of ammonium, the further decomposition of which explains the appearance of the disulphide of carbon, as well as the other products observed. The residue, of course, must contain the varied compounds generated by the action of heat on sulphocyanate of ammonium.

*Behaviour of the Arsines and Stibines with the Sulphocyanates of Phenyl and Allyl.*

The facility with which the compound ureas containing nitrogen and phosphorus are formed, induced me to attempt the production of analogous compounds with arsenic or antimony in place of phosphorus. I therefore treated sulphocyanate of phenyl and oil of mustard successively with triethylarsine and triethylstibine, first at ordinary and then at gradually increasing temperatures in sealed tubes. But not one of these experiments led to the expected result. The arsines and stibines differ, indeed, in their chemical characters much more from ammonia than the phosphines. Their incapability of forming saline compounds with acids is alone sufficient to render the formation of ureas containing arsenic and antimony somewhat improbable. When mixtures of triethylarsine with sulphocyanate of phenyl on the one hand, and sulphocyanate of allyl on the other, were left to stand for some time at ordinary temperatures, the liquid in both cases was found to be traversed by a small quantity of beautiful needle-shaped crystals. The crystals from both mixtures were found to be the same; they were readily identified with the white needles which are gradually formed in triethylarsine when left in contact with atmospheric air.

*Behaviour of Triethylphosphine with Cyanates.*

The formation of sulphuretted ureas containing phosphorus and nitrogen led me to try whether the corresponding oxygen-compounds could likewise be produced.

When *cyanate of phenyl* is mixed with the phosphorus-base, great heat is evolved, indicating a marked chemical reaction. The mixture on cooling solidifies into a mass of shining crystals which are insoluble in water, nearly insoluble in ether, and dissolve with difficulty even in boiling alcohol. By recrystallization from the last-mentioned solvent, the new body is easily obtained pure. The further examination of the resulting

crystals proved, however, that they by no means consisted of the compound urea of which I was in search. From the analysis, which I intend to give in connexion with other researches, it appeared that the crystals still possessed the composition of cyanate of phenyl, that, indeed, they were *cyanurate of phenyl*. The triethylphosphine in this case appears to induce nothing more than a new molecular disposition of the elements in cyanate of phenyl. The peculiar character of this metamorphosis may be perceived in the most beautiful manner by dipping a glass rod moistened with triethylphosphine into a considerable quantity of cyanate of phenyl. The liquid immediately becomes hot, and solidifies after a few seconds into a shining crystalline mass of the cyanurate.

Similar results were obtained by the action of the phosphorus-base on *cyanate of ethyl*. The two bodies may be mixed without evolution of heat, and the mixture does not solidify; but the transformation is soon indicated by the diminution of the penetrating odour of the cyanate. If, as soon as the odour has disappeared, the liquid be mixed with dilute hydrochloric acid which removes the free phosphorus-base, the oil which floats on the surface quickly solidifies into a solid crystalline mass exhibiting, when recrystallized from boiling water, all the properties of *cyanurate of ethyl*.—When a stream of *cyanic acid* gas is passed through triethylphosphine, the odour of the acid disappears, while the phosphorus-base becomes turbid, and yields a white deposit of *cyanuric acid*.

In connexion with these experiments, I have had occasion to convince myself that *cyanic acid* gas and *phosphoretted hydrogen* do not act upon one another, at least at ordinary temperatures.—I was naturally anxious to ascertain whether the peculiar action of the phosphorus-base on the cyanates extended likewise to the cyanides. I found, however, that *cyanide of methyl* (acetonitrile) or *cyanide of phenyl* (benzonitrile) may be left for days in contact with the phosphorus-base at temperatures varying from 100° to 150°, without experiencing the slightest alteration. Had these substances been changed under the above conditions, like the cyanates, their transformation into methyl- and phenyl-compounds corresponding to cyanethine might have been expected.

#### *Experiments in the Methyl-series.*

The information which I have collected with reference to the phosphorus-compounds, has been almost exclusively obtained by the study of triethylphosphine. In exceptional cases only have I worked in the methyl-series. Trimethylphosphine, on account of its volatility, is much less easily prepared than the ethyl-compound, and especially much more difficult to preserve. This body is oxidized with such rapidity, that it disappears from the hands of the operator during manipulation. Its odour, moreover, is insupportable for any length of time.

Nevertheless, I have made a few experiments with the methyl-compound, a slight sketch of which may form the conclusion of this paper.

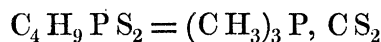
The phosphorus-derivatives of the methyl-series exhibit the most perfect analogy with the corresponding ethyl-compounds.

Oxide of trimethylphosphine produces with iodide of zinc, with dichloride of platinum, and with trichloride of gold, the homologues of the several compounds obtained from oxide of triethylphosphine.

When trimethylphosphine, either pure or dissolved in alcohol and ether, is submitted to the action of disulphide of carbon, all the phenomena are reproduced which I have mentioned at some length in describing the corresponding ethyl-base. The red crystals which are formed are somewhat paler, much more volatile, and much more readily altered. The disulphide-of-carbon-compounds of the methyl- and ethyl-series exhibit in their properties the same relation which obtains between the sulphides of the two series.

0.2586 grm. of the disulphide-of-carbon-compound gave 0.3030 grm. of carbonic acid and 0.1415 grm. of water.

The formula



requires the following values:—

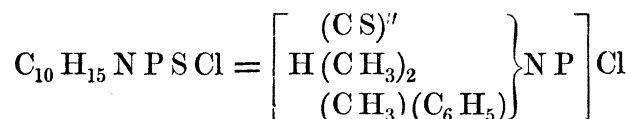
	Theory.		Experiment.
C <sub>4</sub>	48	31.58	31.95
H <sub>9</sub>	9	5.92	6.08
P	31	20.39	—
S <sub>2</sub>	64	42.11	—
	152	100.00	

The red crystals are changed with the utmost facility into sulphide of trimethylphosphine. In the hope of forming fine crystals, similar to those obtained with the ethyl-compound, a solution of the red crystals in warm ether was allowed to cool in a tall open cylinder. When the solution was examined next morning it had become colourless, leaving, upon spontaneous evaporation, the beautiful crystals of the sulphur-compound.

The sulphocyanates of phenyl and allyl readily combine with trimethylphosphine. The reaction is even more powerful than with the ethyl-base. The urea-body which trimethylphosphine produces with sulphocyanate of phenyl is a liquid which I have not been able to obtain in the solid state. Directly prepared from the constituents, or separated from one of its crystalline salts, it forms a slightly coloured oily liquid, soluble in water, difficultly soluble in ether, readily soluble in alcohol. On adding concentrated hydrochloric acid to the oil, it gradually solidifies to a crystalline mass of sulphur-yellow delicate, hair-like needles, which may be recrystallized both from water and from alcohol. I have fixed the composition of this phosphoretted urea by a chlorine-determination in the chloride.

0.2718 grm. gave 0.1540 grm. chloride of silver.

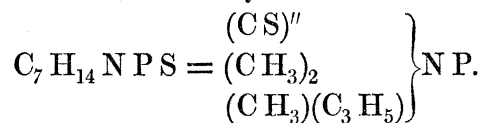
The formula



requires

	Theory.		Experiment.
1 equiv. of Urea-compound . . . .	211	85·25	—
1 equiv. of Hydrogen . . . . .	1	0·41	—
1 equiv. of Chlorine . . . . .	35·5	14·34	14·02
1 equiv. of Chloride . . . . .	247·5	100·00	

The brown liquid which is formed, with considerable evolution of heat, when trimethylphosphine is brought in contact with mustard oil, gradually deposits well-formed transparent colourless prisms, the habitus of which resembles that of the corresponding ethyl-compound. The crystals were not analysed, but there can be no doubt that they were the methylated phosphorus-urea of the allyl-series



Phosphoretted hydrogen is without action on the sulphocyanates of phenyl and allyl.

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In conclusion, I beg to thank Drs. A. LEIBIUS and M. HOLZMANN for their assistance in some of the experiments connected with this inquiry.