[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Reactions of Phosphorus and Antimony Chlorides with Trimethylamine, Triethylamine and Trimethylphosphine[1]

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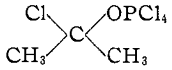
The reactions of phosphorus and antimony chlorides with trimethylamine, triethylamine and trimethylphosphine have resulted in the formation of a number of 1:1 and 2:1 complexes. The 1:1 complexes are considered to be of the donor acceptor variety with the chloride in each case acting as the acceptor molecule. The 2:1 complexes formed with the various chlorides and trimethylphosphine. The nature of these is less understood. In two cases, the reaction of trimethylamine and triethylamine on phosphorus pentachloride, reduction rather than complex formation occurred. The postulated products were phosphorus trichloride and $(Me_3N)_2Cl_2$ in the former case and phosphorus trichloride and Et_3NCl_2 in the latter.

The mechanism of organic reactions involving phosphorus and antimony halides is little understood. One of the chief reasons is the lack of available information concerning the nature of intermediates that might arise. However, in most of these reactions it is suspected that some type of preliminary complex forms; for example, in the chlorination of carbonyl compounds, complexes have been proposed[3] of the type



In order to gain a deeper understanding of the role of Group Vb chlorides in such reactions a long range program has been initiated dealing with varying approaches to the problem. In this paper complexing tendencies of both the tri- and pentachlorides are examined using trimethylamine, triethylamine and trimethylphosphine as reference bases. Treatment of the chlorides with trimethylarsine and trimethylstibine is the subject of the following paper.

The above series of bases was chosen initially as a result of the appearance of a paper by Trost[4] who reported the formation of 1:1 complexes between triethylamine and all of the known chlorides. He also reported the existence of complexes containing additional amine molecules with some of the chlorides. However, preliminary investigation by us failed to yield corroborative evidence for many of his compositions and a fuller investigation was deemed advisable. In addition, by using the series of bases, differences in complexing tendencies of the various chlorides may become apparent.

Experimental

Apparatus.—Due to the extreme reactivity in air of most of the compounds used in this investigation, essentially all of the reactions were carried out in an all-glass, high vacuum system similar to that described by Sanderson.[5] A special "reaction section" was constructed and is adequately described by Brown, Eddy and Wong.[6]

Materials.—Trimethylamine was prepared from its hydrochloride salt (Eastman Kodak Co.) by use of concentrated potassium hydroxide. The evolved gas was frozen in an ampoule and introduced into the vacuum system. It was dried by allowing it to remain in contact with phosphorus pentoxide *in vacuo* at 0° for 6 hr. Its vapor pressure was subsequently measured to be 681.2 mm. at 0°.

Triethylamine (Fisher, highest purity) was rectified in a 22 plate column packed with $^3/_8$ inch glass helices. Middle fractions boiling at 89.2° at atmospheric pressure were collected in glass ampoules, introduced into the vacuum line and dried over phosphorus pentoxide, which also acted to remove primary and secondary amines. The sample was fractionated in the line and tested for tensiometric homogeneity. The vapor pressure of all fractions was 18.3 mm. at 0°.

Trimethylphosphine was synthesized by a Grignard procedure similar to that outlined by Harris[7] using phosphorus trichloride and excess methylmagnesium chloride. The product was distilled from potassium hydroxide pellets, introduced into the line and dried over phosphorus pentoxide for 6 hr. The sample was tensiometrically homogeneous with a vapor pressure of 159.0 mm. at 0°. Yields were similar to that reported by Harris ($\sim$50%).

All the chlorides are commercially available. Phosphorus pentachloride (Mallinckrodt, reagent grade) and antimony trichloride (Baker and Adamson, reagent grade) were purified by vacuum sublimation. The sublimed material was collected in a tube which was opened in a dry box. The contents were transferred to a weighing bottle which was stored over phosphorus pentoxide in a desiccator, the latter being kept in the dry box to be dispensed as needed.

Antimony pentachloride (Baker and Adamson, reagent grade) and arsenic trichloride (Baker and Adamson, reagent grade) were purified by vacuum distillation.

Phosphorus trichloride (Baker and Adamson, reagent grade) was introduced into the vacuum line and fractionated by means of Dry Ice and liquid nitrogen cold traps. After fractionation it was found to be tensiometrically homogeneous and to have a vapor pressure of 35.7 mm. at 0°.

Procedure.—All purified compounds were introduced into the reaction section of the high vacuum system so as to avoid contamination. Gases and volatile liquids (phosphorus trichloride and the trialkyls) were introduced *via* an ampoule; after which the sample was fractionated and stored in the line.

In the case of less volatile liquids hypodermic syringe techniques similar to that described elsewhere[8] were used. After the requisite amount of material was placed in the reaction bulb, it was attached to the reaction section *via* a greaseless standard taper joint surrounded by a mercury cup.

In the case of a solid the desired amount was weighed into an appendage attached to the reaction bulb (using the dry box). After attachment of the reaction bulb to the line, the solid sample was sublimed slowly (using a heat lamp) from the appendage to the bulb. The appendage was then sealed off. In all cases the entire sample sublimed.

In carrying out a reaction, in general, a measured amount (a few mmoles) of the particular chloride of interest was introduced into the reaction bulb by one of the methods described above. The appropriate trialkyl compound was measured as a gas (usually a quantity several times in excess of the chloride) and condensed on the chloride in the

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[1] Presented in part before the Physical-Inorganic Division at the 132nd Meeting of the American Chemical Society, New York, N. Y., September, 1957. Based on a thesis submitted by Edgard F. Bertaut in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

[2] Research Corporation Fellow (1955–1957).

[3] F. Straus, *Ann.*, **393**, 235 (1912).

[4] W. R. Trost, *Can. J. Chem.*, **32**, 356 (1954).

[5] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[6] H. C. Brown, L. P. Eddy and R. Wong, THIS JOURNAL, **75**, 6275 (1953).

[7] R. H. Harris, Ph.D. Thesis, Purdue University, 1952

[8] H. C. Brown and R. R. Holmes, THIS JOURNAL, **77**, 1727 (1955)

reaction bulb. The mixture was allowed to warm up to the chosen reaction temperature and stirred by means of a stirrer enclosed in the system and operated externally by a periodically pulsed solenoid.

Since many of the reactions approached completeness slowly, the excess trialkyl was removed from time to time, the amount measured and re-introduced. No further reaction was evidenced when subsequent removal showed no further loss of trialkyl.

In certain cases it was found necessary to increase the temperature to 100° to obtain completeness of reaction in a reasonable time interval. Such reactions were conducted separate from the line in a one liter gas bulb fitted with a break tip and seal off. The components were introduced into the bulb which was sealed off from the line. The entire bulb was heated to 100° in a steam-bath. After reaction, the bulb was opened in the line *via* the break tip and its contents analyzed.

Trimethylamine Reactions. Me_3N-PCl_5.—Little or no reaction takes place between trimethylamine and phosphorus pentachloride at room temperature. Reaction does occur at elevated temperatures, however. Phosphorus pentachloride (0.73 mmole) was treated with excess trimethylamine (5.20 mmoles) in a liter gas bulb at 100° for 16 days. Small tinges of orange solid appeared but most of the product was a white solid. Fractionation and analysis of the volatile contents in the vacuum line resulted in recovery of 3.80 mmoles of trimethylamine; thus 1.40 mmoles of amine had reacted. In addition 0.50 mmole of phosphorus trichloride was present as indicated by vapor pressure measurements on the fractionated sample.

Me_3N-$SbCl_5$.—Antimony pentachloride (1.19 mmoles) and excess trimethylamine (3.09 mmoles) were stirred in the reaction section at 0° for approximately 20 hr.; after which, no further reaction took place. Recovery of 1.90 mmoles of trimethylamine indicated the composition of the resulting pale yellow solid to be $(Me_3N)_{1.00}SbCl_5$. This solid did not dissolve in or react with water.

Me_3N-$SbCl_3$.—The reaction of trimethylamine with antimony trichloride (1.40 mmoles) was initially very rapid at room temperature but began to taper off with successive additions of amine. The trichloride was then stirred with a total amount of amine of 7.20 mmoles for 19 hr. at −78°, the latter temperature being chosen to provide a liquid–solid rather than a gas–solid reaction which was the case at room temperature. The recovery of 5.66 mmoles of trimethylamine indicated the composition of the white solid products to be $(Me_3N)_{1.10}SbCl_3$. The product was soluble in acetone. On heating it began to turn brown at 150° and decomposed to a black solid in the range 200–210°.

Me_3N-$AsCl_3$.—Excess trimethylamine (6.26 mmoles) was condensed on 1.51 mmoles of arsenic trichloride in the reaction section and stirred for one day at −78°. The temperature was allowed to rise to 0° where the trimethylamine was refluxed over the chloride by means of a Dry Ice cone for 22 hr. A white solid formed whose composition was calculated to be $(Me_3N)_{0.82}AsCl_3$, based on the recovery of 5.03 mmoles of amine. Further treatment with amine resulted in no additional reaction as evidenced by the recovery of the same amount of amine. The solid formed slowly turned gray in air, indicating decomposition.

Triethylamine Reactions. Et_3N-PCl_5.—Liquid triethylamine (5.48 mmoles) was stirred with 0.81 mmole of phosphorus pentachloride for two days at room temperature in the line, resulting in the formation of an orange solid and volatile material (5.02 mmoles) as evidenced from vapor pressure readings on the excess amine removed from the system at various intervals. The volatile mixture was condensed over KOH pellets and allowed to stand in contact with them for one day at room temperature. After this treatment the material that was not absorbed (4.78 mmoles) had a vapor pressure of 18.3 mm. at 0° indicating it to be pure triethylamine. The reaction appeared therefore to be producing a volatile product that was absorbed by KOH, leaving excess unreacted triethylamine. Individual pure samples of phosphorus trichloride and triethylamine were condensed over KOH. Triethylamine remained unaffected while phosphorus trichloride was quantitatively absorbed within a one day period.

The recovered triethylamine was recondensed over the orange solid in the reaction section to test for further reaction. The mixture was stirred for two more days at room temperature. Slight additional reaction was found to occur, after analyzing the volatile products as above. The process was repeated once again for five days to ensure completeness of reaction. Negligible reaction took place. A total of 0.99 mmole of triethylamine had reacted and 0.40 mmole of postulated phosphorus trichloride was produced.

Et_3N-PCl_3.—No visible reaction took place between triethylamine and phosphorus trichloride at any temperature from −78° to 0°. Vapor pressure measurements made at 0° as a function of the mole fraction of reactants showed that as the amine content was increased, the total pressure slowly dropped from the vapor pressure of pure trichloride (34.7 mm. at 0°) toward that of pure amine (18.3 mm. at 0°). The data could not be used to calculate a pressure–composition curve since no information was available concerning the partial pressures. However, the data did indicate that there were no great deviations from ideal behavior; thus association of the components in solution is unlikely.

Et_3N-$SbCl_5$.—Reaction of triethylamine with 1.33 mmoles of solid antimony pentachloride was quite rapid at 0° until a mole ratio of about 0.9 had been reached. A slightly grayish solid was formed which was insoluble in excess amine. Reaction was complete when 1.34 mmoles of triethylamine had been taken up, corresponding to a product composition of $(Et_3N)_{1.01}SbCl_5$.

Et_3N-$SbCl_3$.—Triethylamine (8.01 mmoles) stirred for 43 hr. with antimony trichloride (1.28 mmoles) at 0° produced a slightly grayish solid whose composition was determined to be $(Et_3N)_{0.89}SbCl_3$. On warming to room temperature amine was evolved and the solid turned black.

An identical experiment carried out at room temperature instead of 0° gave the black solid of composition $(Et_3N)_{0.48}SbCl_3$. Thus it appears that a 1:1 compound forms at 0° but decomposes to black $(Et_3N)_{0.5}SbCl_3$ and triethylamine at higher temperatures. The black $^1/_2$:1 product may be a mixture rather than a true compound, suspicioned by the appearance of the black color (antimony perhaps).

Trimethylphosphine Reactions. Me_3P-PCl_5.—Excess trimethylphosphine did not react appreciably with solid phosphorus pentachloride at 0° or at room temperature. Attempts to cause reaction by heating the components in sealed bulbs at 100° for varying periods of time were tried. The results are shown in Table I.

TABLE I

REACTION OF PHOSPHORUS PENTACHLORIDE AND TRIMETHYLPHOSPHINE AT 100°

Reaction time	Product mole ratio
10 min.	0.57
2 hr.	0.70
5 days	1.22
24 days	1.59

The second column gives the mole ratios of phosphine to chloride. It is seen that reaction takes place but due to the slowness, completeness was never attained.

In view of this, bromobenzene solvent was used (about 20 mmoles) in which 0.68 mmole of phosphorus pentachloride was dissolved, the reaction being carried out in the high vacuum system at 0°. After each addition of trimethylphosphine the pressure over the system came to equilibrium at 0.8 mm. Since the vapor pressure of pure trimethylphosphine is 159.0 mm. at 0°, the lack of a permanent rise in reaction pressure precluded simple solution. The absorption continued with the formation of a non-volatile white solid until 1.34 mmoles of trimethylphosphine had been added. Further additions caused a rise in equilibrium pressure toward 13.0 mm. with a mole ratio of 2.92, showing simple solution of the excess trimethylphosphine in bromobenzene. The composition of the white solid formed hence was $(Me_3P)_{1.97}PCl_5$.

Me_3P-PCl_3.—Additions of trimethylphosphine to liquid phosphorus trichloride (0.78 mmole) at 0° resulted in the formation of a white powdery solid. The reaction section pressure remained at 35.7 mm., the vapor pressure of pure phosphorus trichloride, until 1.49 mmoles of trimethylphosphine had been admitted to the reaction section, corresponding to a phosphine–chloride mole ratio of 1.91. As more trimethylphosphine entered the reaction the pressure dropped toward zero. At this point 1.53 mmoles had reacted giving the powdery solid a composition of $(Me_3P)_{1.96}PCl_3$. Treatment with additional trimethylphosphine (0.66 mmole) gave no further reaction at 0°. The resulting liquid–solid mixture had a vapor pressure of 159.0 mm., the same value as the vapor pressure of pure trimethylphosphine. The 2:1 solid decomposed rapidly in air to a clear liquid.

Me_3P–$SbCl_5$.—An immediate and rapid reaction took place when trimethylphosphine (2.45 mmoles) was mixed with antimony pentachloride at 0° in the vacuum line. A white solid formed having the composition $(Me_3P)_{1.06}SbCl_5$ as attested by the recovery of unreacted trimethylphosphine. The solid was stable in dry air but reacted with water to give a yellow and then a white precipitate, characteristic of the hydrolysis of antimony pentachloride which forms yellow $SbOCl_3$ and then white SbOCl.

An experiment was designed to see whether further reaction would take place. In it 1.78 mmoles of antimony pentachloride was allowed to interact with 6.04 mmoles of trimethylphosphine in a sealed tube, first at room temperature and then for 29 days at 100°. At room temperature the two colorless liquids immediately formed the white solid which, however, turned gray when held at 100°. Analysis in the line of the volatile material from this reaction showed only the presence of excess trimethylphosphine (2.53 mmoles), giving a composition to the solid product of $(Me_3P)_{1.97}SbCl_5$. The latter solid was soluble in acetone and melted with decomposition in the range 55–65°.

Me_3P–$SbCl_3$.—The reaction of trimethylphosphine with antimony trichloride proceeded very slowly at 0°. For complete reaction of 1.12 mmoles of solid antimony trichloride with a 7:1 excess of trimethylphosphine, approximately 11 days were required. Indication of no further reaction was taken when, on successive removals of excess trimethylphosphine, no change in the amount recovered was found. The white solid that formed had a composition $(Me_3P)_{1.92}SbCl_3$.

Results and Discussion

The data concerning the reactions of phosphorus and antimony chlorides (and in one case arsenic chloride) with trimethylamine, triethylamine and trimethylphosphine are summarized in Table II.

TABLE II

SUMMARY OF DATA FOR THE REACTIONS OF PHOSPHORUS, ARSENIC AND ANTIMONY CHLORIDES WITH TRIMETHYLAMINE, TRIETHYLAMINE AND TRIMETHYLPHOSPHINE

System	Reaction temp., °C.	Product composition	Color
Me_3N–PCl_5	100	A mixture of $(Me_3N)_2Cl_2$ and PCl_3	White
Me_3N–$SbCl_5$	0	$(Me_3N)_{1.00}SbCl_5$	Pale yellow
Me_3N–$SbCl_3$	Room temp.	$(Me_3N)_{1.10}SbCl_3$	White
Me_3N–$AsCl_3$	0	$(Me_3N)_{0.82}AsCl_3$	White
Et_3N–PCl_5	Room temp.	Essentially a mixture of Et_3NCl_2 and PCl_3	Orange
Et_3N–PCl_3	−78 to 0	No reaction	..
Et_3N–$SbCl_5$	0	$(Et_3N)_{1.01}SbCl_5$	White
Et_3N–$SbCl_3$	0	$(Et_3N)_{0.89}SbCl_3$[a]	White
Et_3N–$SbCl_3$	Room temp.	$(Et_3N)_{0.48}SbCl_3$	Black
Me_3P–PCl_5	0 to 100	No reaction[b]	..
Me_3P–PCl_5	0	$(Me_3P)_{1.97}PCl_5$[c]	White
Me_3P–PCl_3	0	$(Me_3P)_{1.96}PCl_3$	White
Me_3P–$SnCl_5$	0	$(Me_3P)_{1.06}SbCl_5$	White
Me_3P–$SbCl_5$	100	$(Me_3P)_{1.97}SbCl_5$	Gray
Me_3P–$SbCl_3$	0	$(Me_3P)_{1.92}SbCl_3$	White

[a] Unstable with respect to forming $Et_3N \cdot 2SbCl_3$. [b] No reaction from 0° to room temperature, very slow reaction at 100°. [c] Formed in bromobenzene solvent rapidly. There is the possibility that the composition reported could involve bromobenzene as well.

In all the systems studied, other than the reaction of trimethyl- and triethylamine with phosphorus pentachloride, complex formation appeared to occur. With either trimethyl- or triethylamine the chlorides tended to form 1:1 complexes. With trimethylphosphine, however, the formation of product compositions having two moles of the phosphine predominated. Thus, of the four chlorides studied with trimethylphosphine, only antimony pentachloride was found to form a 1:1 complex. On studying this system at higher temperatures, though, an additional trimethylphosphine molecule reacted.

The structure of the 2:1 product compositions with either the trichlorides or the pentachlorides is not at all understood. They may in fact be mixtures. In any event further information should be accumulated before attempts at structural assignments are made.

All the 1:1 complexes are postulated to be of the acid–base type with the trichloride or the pentachloride, as the case may be, acting as the acidic component. For example, in $Me_3P \cdot SbCl_5$ there is postulated to be formed a P–Sb linkage where one element (phosphorus) of Group Vb is acting as a base and another element (antimony) of the same group is acting as an acid. In the case of a pentachloride a coördination number of six would be assumed in the complex, a known coördination number for phosphorus and antimony (PF_6^-, $SbCl_6^-$, etc.).[9] Electronically such a bonding process is favorable. However, in the case of the trichlorides acting as acids one must assume that an outer orbital is available for hybridization, either an s or a d type, if a coördination number of four is to be reached. Several possibilities would exist then for the resulting structure and again further information is necessary to distinguish among them.

Concerning the variation in acid strength of the trichlorides, phosphorus trichloride appears to be the weakest. No reaction was observed between it and triethylamine in this study. With trimethylamine[10] phosphorus trichloride does form a weak complex at low temperatures but on warming to 0°, it dissociates. In contrast to this behavior both arsenic trichloride and antimony trichloride form stable complexes with trimethylamine.

The results concerning the reaction of trimethylamine and triethylamine with the pentachlorides show a difference in behavior. Whereas, complex formation predominated with antimony pentachloride, reduction of phosphorus pentachloride to the trichloride took place with both amines. Chlorinated amine products, having the empirical compositions, $(Me_3N)_2Cl_2$ and Et_3NCl_2, were postulated to form, the latter being analogous to the known substances, Me_3NBr_2[11] and Et_3NBr_2.[12] The reactions were of an incomplete variety as judged from the less than quantitative amounts of phosphorus trichloride obtained.

Of the 1:1 triethylamine complexes with phosphorus and antimony chlorides reported by Trost,[4] $Et_3N \cdot SbCl_5$, $Et_3N \cdot PCl_5$, $Et_3N \cdot SbCl_3$, $Et_3N \cdot PCl_3$, we confirmed the existence of $Et_3N \cdot SbCl_5$ and $Et_3N \cdot SbCl_3$. The $Et_3N \cdot PCl_5$ composition reported by Trost was indicated to be a mixture of Et_3NCl_2 and PCl_3. In the Et_3N–PCl_3 system, we observed no reaction from temperatures ranging from −78 to 0° in direct contrast to Trost's work. However,

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(9) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. I, Oxford University Press, London, 1950, p. 800.

(10) An extensive analysis of vapor pressure data for the system PCl_3–NMe_3 is presently being undertaken and will be published soon

(11) A. Hantzsch and W. Graf, *Ber.*, **38**, 2154 (1905).

(12) Private communication

an immediate reaction was observed to take place with the formation of large amounts of solid in agreement with Trost's reports, if unpurified components are mixed out in the open. It is suspected that a catalyzed reaction of some type takes place as a result of the presence of impurities, thus accounting for the differences in behavior observed.

Lastly, neither of Trost's higher complexes, $3Et_3N \cdot PCl_3$ and $5Et_3N \cdot 2PCl_5$, were found in this study under the experimental conditions employed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Reduction of Phosphorus and Antimony Chlorides by Trimethylarsine and Trimethylstibine[1]

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Trimethylarsine formed 1:1 complexes with either phosphorus or antimony trichloride. With the corresponding pentachlorides, trimethylarsine acted to reduce them to the trichloride stage accompanied by the appearance of trimethylarsine dichloride. The reaction of trimethylstibine with both the tri- and pentachlorides led to complete reduction to the element and the formation of trimethylstibine dichloride in each case. The results suggested a four step mechanism for the over-all reduction process of the pentachlorides involving complex formation and the appearance of the trichloride as intermediate steps.

As shown in the previous paper,[3] when phosphorus or antimony chloride is treated with trimethylamine, triethylamine or trimethylphosphine, the primary result was complex formation. In only one instance did a reaction other than complex formation take place, namely, the reaction of phosphorus pentachloride with either trimethyl- or triethylamine. In the latter case reduction to the trichloride occurred. However, on going to heavier members of the series, trimethylarsine and trimethylstibine (concerning which prior literature is completely lacking), we found that reduction of the halide to the element became the predominant reaction. This action is particularly pronounced with trimethylstibine.

It was felt that an investigation of the path of the reduction might prove fruitful in allowing a general correlation to be made concerning the action of the various trimethyl derivatives of Group Vb on Group Vb chlorides.

Experimental

Apparatus and Procedures.—The apparatus and procedures for carrying out the reactions are the same as those reported in the previous paper,[3] the only significant modification being the construction of an additional reaction section so that two interactions could be studied simultaneously in the high vacuum system. This proved desirable because of the slowness with which the reduction reactions proceeded.

Materials.—The tri- and pentachlorides of phosphorus and antimony used in this study were purified in the same fashion as described in the previous paper.[3]

Trimethylarsine was prepared by variations of the methods outlined by Harris[4] and by Mann and Purdie.[5] This substance proved to be the most difficult of the trimethyl derivatives to prepare primarily because of the difficulty in isolating the trimethylarsine from the solvent used, diethyl ether. Harris used butyl ether as a solvent and separated trimethylarsine by a time consuming fractionation procedure. Mann and Purdie isolated the crude product using $(NH_4)_2PdCl_4$ to form $(Me_3As)_2PdCl_2$ and regenerated pure trimethylarsine by thermal decomposition of the latter complex *in vacuo*. We chose the latter course but discovered that the amount of trimethylarsine obtained depended considerably on the temperature at which the thermal decomposition was carried out. Mann and Purdie did not report any details concerning their preparation and we did not investigate this point fully. The yield we obtained was poor. To augment this, a sample prepared by Harris at Purdue University was used. The trimethylarsine was dried and purified in the line by a procedure similar to that described for trimethylphosphine in the previous paper.[3] Its vapor pressure at 0° was 101.0 mm.

Trimethylstibine was prepared by a procedure similar to that outlined by Harris[4] in which excess methylmagnesium chloride reacted with antimony trichloride in ethyl ether solution, the crude product being isolated by forming solid trimethylstibine dibromide, Me_3SbBr_2, with bromine. It melted with decomposition at 185.5–186.0°. Heating the dibromide with zinc metal in the presence of water freed the trimethylstibine. It was introduced into the line and dried in contact with phosphorus pentoxide and fractionated to a constant vapor pressure of 30.5 mm. at 0°.

Trimethylarsine Reactions. Me_3As–PCl_5.—Trimethylarsine (3.41 mmoles) reacted with phosphorus pentachloride (0.66 mmole) in the vacuum line at room temperature to form a white solid while giving off a volatile substance suspected to be phosphorus trichloride. After 15 days no further take up of trimethylarsine was observed. The volatile material recovered (3.20 mmoles; total vapor pressure, 88.5 mm. at 0°) from the reaction was condensed over KOH pellets to absorb the suspected phosphorus trichloride. Pure trimethylarsine remained (2.74 mmoles) as measured by its vapor pressure of 100.3 mm. at 0°. This corresponds to a mole ratio of 1.01 moles of trimethylarsine per mole of phosphorus pentachloride. The reaction occurring[6] would therefore be

$$Me_3As + PCl_5 \longrightarrow Me_3AsCl_2 + PCl_3$$

Me_3As–PCl_3.—The two liquid reactants, trimethylarsine (6.00 mmoles) and phosphorus trichloride (0.98 mmole), reacted rapidly at −29.5° to form a white solid, insoluble in excess trimethylarsine. On successive removal of small portions of the arsine, the vapor pressure remained constant at the vapor pressure of pure trimethylarsine (26.3 mm.) at this temperature until 5.03 mmoles had been removed. At this point the vapor pressure dropped to 8.8 mm. at −29.5° and remained constant with further arsine removal. The latter plateau corresponds to a reversible dissociation

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[1] Presented in part before the Physical Inorganic Division at the 132nd Meeting of the American Chemical Society, New York, N. Y., September, 1957. Based on a thesis submitted by Edgard F. Bertaut in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

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[3] R. R. Holmes and E. F. Bertaut, THIS JOURNAL, **80**, 2980 (1958).

[4] R. H. Harris, Ph.D. Thesis, Purdue University, 1952.

[5] F. G. Mann and D. Purdie, *J. Chem. Soc.*, 873 (1936).

[6] The analysis shows the formation of 0.46 mmole of phosphorus trichloride (0.66 mmole expected). It was noted that phosphorus trichloride slowly reacts with mercury in the vacuum system, possibly accounting for the reduced amount of phosphorus trichloride.