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(**Caution.** *It is very important to keep the phosphorus(III) chloride boiling vigorously at all times to prevent the formation of phosphorus(V) chloride, which will plug the inlet tube.*)

A 1-lb. weight is now placed on the platform of the scales. The chlorine is added as rapidly as possible until the lever arm returns to its zero point; at this point 453 g. (1 lb.) of chlorine will have been added.* After the addition of the chlorine, the flask is disconnected and the necks are closed with rubber stoppers. The phosphorus(III) chloride is then distilled by using a water bath and an ordinary condenser. It fumes in moist air and should be stored in a glass-stoppered or sealed bottle. The excess phosphorus may be recovered for future use. The yield, based on the amount of chlorine added, is about 94 per cent of the theoretical.

Properties

Phosphorus(III) chloride is a clear colorless liquid having a boiling point of 75.9° and a specific gravity of 1.574 (21°).

Reference

1. GRAEBE: *Ber.*, **34**, 645 (1901).

43. PHOSPHORUS(III) BROMIDE

$$P_4 + 6Br_2 \rightarrow 4PBr_3$$

SUBMITTED BY J. F. GAY† AND R. N. MAXSON†‡
CHECKED BY J. KLEINBERG§‖ AND R. E. HAAN§

The various published methods for the preparation of phosphorus(III) bromide are all variations of the simple but

* On large runs that may take considerable time, it would be quite possible to wire up the scales with an electric bell that would ring when the required amount of chlorine has been added. Thus unnecessary watching of the apparatus could be avoided.

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vigorous reaction of bromine with phosphorus. In order to reduce the violence and consequent danger of the reaction, it is best to use red phosphorus and to conduct the reaction in the presence of an inert solvent: carbon tetrachloride,[1] thiophene-free benzene,[2] or phosphorus(III) bromide itself.[3] By use of the last, the troublesome fractionation of two liquids at the end of the reaction is avoided.

Procedure

The apparatus shown in Fig. 17 is satisfactory for the rapid production of phosphorus(III) bromide. It consists of a Claisen flask of 1-l. capacity with a reflux condenser fitted into the neck to which the side arm is attached. The upper end of the condenser is fitted with a phosphorus(V) oxide drying tube. The side arm is closed with a short length of rubber tubing containing a rounded-end glass rod of slightly larger diameter than the side arm so that a good butt joint is formed. The tube for the introduction of bromine is inserted into the other neck. This tube is of pyrex glass and has an outside diameter slightly less than the inside diameter of the neck. This tube must be large to avoid plugging by the phosphorus(V) bromide that is sometimes formed. It extends from just above the bottom of the flask to just above the neck, where another smaller tube (large enough in diameter just to accommodate the end of the separatory funnel) is sealed onto it. Rubber tubing (about 2 in. long) is placed over the end of the small tubing and the separatory funnel placed in this rubber joint and pushed down far enough for the end of the separatory funnel to be seen through the smaller glass tubing. If ground-glass joints are not available, fittings for the reflux condenser and bromine introduction tube may be made of Neoprene or even cloth composition tape, *but not rubber tape.* Cloth tape is not greatly affected by phosphorus(III) bromide.

One hundred twenty-five grams of dry red phosphorus (dried in an oven for 3 hours at 105° and preserved for

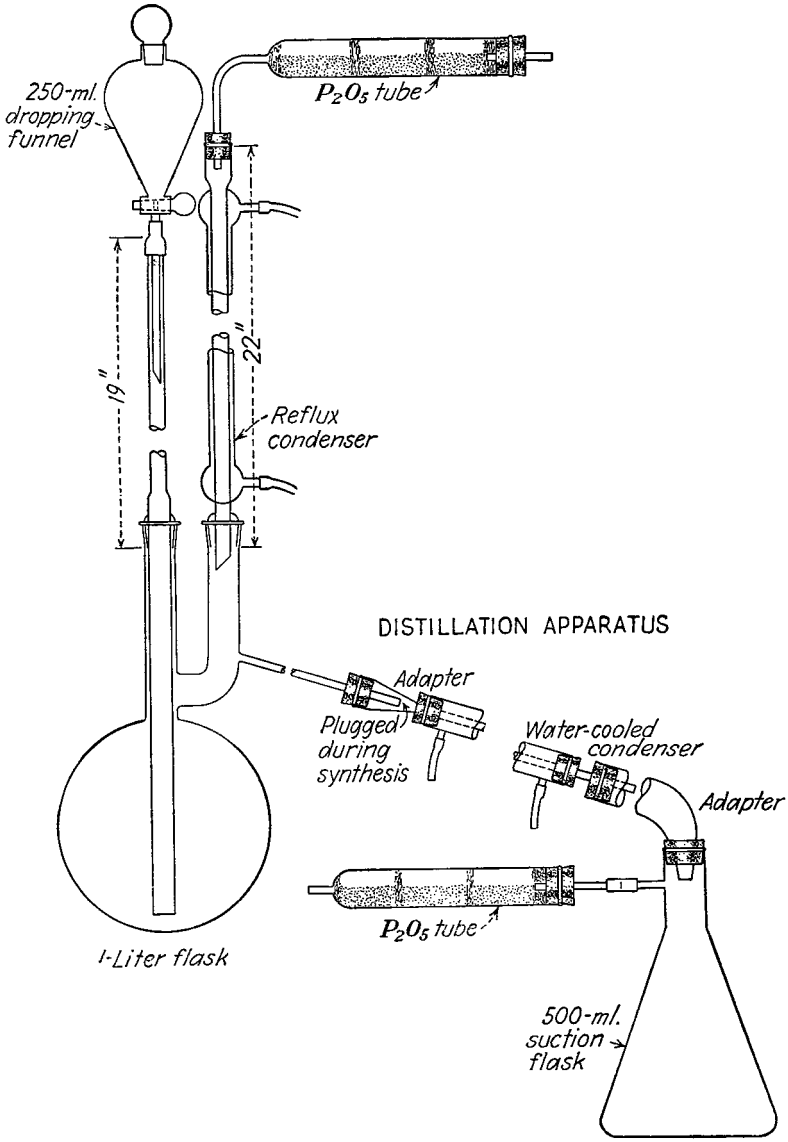

FIG. 17.—Apparatus for the preparation of phosphorus(III) bromide.

subsequent use in a desiccator containing sulfuric acid) is placed in the flask and covered with 500 g. of phosphorus(III) bromide. If no phosphorus(III) bromide is available, phosphorus(III) chloride will serve but only 295 g. need be added. [If phosphorus(III) chloride is used, it is necessary to fractionate the reaction mixture at the end of the run.]

Caution. *No less than the amount of phosphorus(III) bromide or phosphorus(III) chloride indicated for* 125 *g. of phosphorus should be used. If there is not enough liquid to make a mobile suspension of phosphorus, the phosphorus may hold back the vapors of the suspending medium long enough for them to build up sufficient vapor pressure to cause an explosion.*

An amount of bromine equivalent to 100 g. of phosphorus, 773.5 g., is weighed out and about half of it placed in the separatory funnel. An air bath is placed around the flask and the reaction mixture brought to boiling. The bromine is allowed to drop in slowly for a period of about 5 minutes until the inlet tube is filled with bromine vapor. The flame is now removed and the bromine added rapidly enough (about 20 ml./minute) to cause the reaction mixture to boil from the heat of reaction. After all the bromine has been added, the flame is replaced and boiling continued for 10 minutes.

Caution. *Excess phosphorus,* 25 *to* 35 *per cent, should be present at the end of the run to avoid the formation of phosphorus pentabromide.*

The side arm of the Claisen flask is connected to a short condenser that leads to a 500-ml. suction flask. The whole system is protected from the moisture of the air by means of a phosphorus(V) oxide drying tube connected to the side arm of the receiver. The first 15 to 20 ml. of distillate is colored with excess bromine and must be discarded or retained for additional runs.

The remainder of the distillate boils at 172.9° (corrected to 760 mm. pressure.) Yield 819 g. (94 per cent based on the bromine used.)

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Properties

Phosphorus(III) bromide is a clear, colorless, fuming liquid with a specific gravity of 2.852 and a normal boiling point of 172.9°. It is stable when dry but is readily hydrolyzed even at low temperatures to orthophosphorous acid and hydrobromic acid.

References

1. NOLLER and DINSMORE: "Organic Syntheses," Vol. 13, p. 21, John Wiley & Sons, Inc., New York, 1933.
2. CHRISTOMANOS: *Z. anorg. Chem.*, **41**, 276 (1904).
3. Editor's note: Independently of those submitting this synthesis, TSENG and HO, *Sci. Quart. Natl. Univ. Peking*, **5**, 324 (1935), have made a careful study of the phosphorus-bromine reaction and recommend the use of phosphorus(III) bromide as a diluent.

44. PHOSPHORUS(V) OXYBROMIDE

(Phosphoryl Tribromide)

$$PBr_3 + Br_2 \rightarrow PBr_5$$
$$P_4O_{10} + 6PBr_5 \rightarrow 10POBr_3$$

SUBMITTED BY HAROLD S. BOOTH* AND C. G. SEEGMILLER*
CHECKED BY PHILIP S. BAKER,† SOL WEXLER,† AND ROY D. JOHNSON†

Of the various possible methods[1–3] for the preparation of phosphorus(V) oxybromide that of digestion of phosphorus(V) oxide and bromide[1] presents the simplest procedure and yields the purest product.

Procedure

Phosphorus(V) bromide is first prepared by slowly adding 370 g. of liquid bromine to 630 g. of phosphorus(III) bromide (or by reaction between red phosphorus and bromine as described in synthesis 45) in a 1-liter pyrex distilling flask. The bromine is added through a separatory funnel inserted through one hole of a two-hole rubber stopper in the neck of the flask. To allow for expansion of gases and to prevent hydrolysis, a horizontal drying tube containing phosphorus(V) oxide is connected to a tubular

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