



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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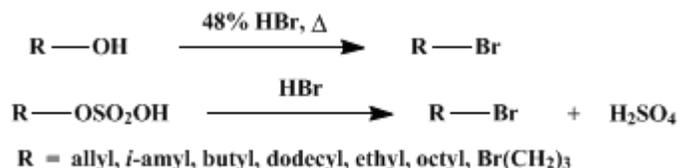
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.25 (1941); Vol. 1, p.3 (1921).

ALKYL AND ALKYLENE BROMIDES

[I. HYDROBROMIC ACID METHOD]



Submitted by Oliver Kamm and C. S. Marvel.

Checked by H. T. Clarke and Anne W. Davis.

1. Procedure

A given primary alcohol is treated with 25 per cent excess of aqueous (48 per cent) [hydrobromic acid](#) ([Note 1](#)) together with [sulfuric acid](#) ([Note 2](#)). The mixture is refluxed ([Note 3](#)) in order to convert the alcohol as completely as possible into the corresponding bromide, and the latter is then removed from the reaction mixture by distillation. The water-insoluble layer is separated; washed successively with water, cold concentrated [sulfuric acid](#) ([Note 4](#)), and a [sodium carbonate](#) solution; separated; dried with [calcium chloride](#) ([Note 5](#)); and distilled. Slight variations from this procedure depend upon the physical and chemical properties of the alcohol used, or of the bromide formed in the reaction. For example, in the preparations of [ethyl](#) and [allyl bromides](#), the reaction mixture is not refluxed because of the volatility of the former compound, and because of the chemical reactivity of the latter; in the preparation of [iso-amyl bromide](#), too large a proportion of [sulfuric acid](#) may produce appreciable decomposition, whereas halides of high molecular weight, because of their low volatility, are separated from the reaction mixture mechanically, instead of by distillation.

The use of a modified sodium bromide-sulfuric acid method ([Note 6](#)) for the preparation of alkyl bromides is described in connection with the preparation of [n-butyl bromide](#). This method has been used also for the preparations of [iso-amyl](#) and [trimethylene bromides](#), but, in general, the yields were found to be somewhat lower than those obtained with the hydrobromic-sulfuric acid method.

Preparation of Hydrobromic Acid.—[Hydrobromic acid](#) may be prepared conveniently by the interaction of [bromine](#) and [sulfur dioxide](#) in the presence of water¹ ([Note 7](#)).

In a 3-l. round-bottomed flask are placed 1200 g. (377 cc., 7.5 moles) of [bromine](#), 500 cc. of water, and 1500 g. of crushed ice. A fairly rapid stream of [sulfur dioxide](#) is allowed to pass from a pressure tank into the flask, the outlet of the gas-tube being placed below the surface of the bromine layer. The flow of [sulfur dioxide](#) is adjusted at such a rate that the gas is completely absorbed. It is advisable to agitate the mixture occasionally during the first stage of the reduction ([Note 8](#)). About two hours will serve for the completion of the reduction, at which time the mixture will assume a yellow color ([Note 9](#)) which is not removed by further addition of [sulfur dioxide](#), an excess of which is to be avoided ([Note 10](#)). To prevent loss by gaseous [hydrogen bromide](#), it is advisable to cool the mixture during the progress of the reduction.

When the reduction is completed, the flask is connected with a condenser and the mixture subjected to distillation. The boiling point of constant boiling [hydrobromic acid](#) is 125–126° /760 mm., but it must be remembered that, in distilling the product from the [sulfuric acid](#) mixture, the thermometer reading should not be relied upon as an index to the composition of the distillate. Towards the end of the distillation the thermometer may rise to 130° and above, when water with only traces of acid distills from the [sulfuric acid](#) residue. Upon redistillation of the product the thermometer reading may be relied upon. For many uses a product free from traces of [sulfuric acid](#) is not required and one distillation is sufficient. In such cases the progress of the distillation is followed by determinations of the specific gravity of the distillate.

According to the above procedure, 20 kg. of 48 per cent **hydrobromic acid** (92 per cent of the theoretical amount) may be prepared from 10.3 kg. of **bromine**. The actual time required by one person for the preparation of this quantity is twenty-three hours.

For the preparation of alkyl bromides on a relatively large scale the **hydrobromic acid** need not be distilled but may be used directly for the subsequent preparation. The fact that 0.5 mole of **sulfuric acid** is present for each mole of **hydrobromic acid** is not a disadvantage, since the presence of **sulfuric acid** is desired, and consequently a correspondingly smaller quantity need be added.

(A) **ALLYL BROMIDE, CH₂=CHCH₂Br**

[Propene, 3-bromo-]

In a 3-l. round-bottomed flask, a **hydrobromic acid** solution is prepared (p. 26) by the **sulfur dioxide** reduction of 480 g. (150.5 cc., 3 moles) of **bromine** in the presence of 510 g. of ice water or a mixture is made of 1 kg. (5.9 moles) of aqueous 48 per cent **hydrobromic acid** and 300 g. (162 cc.) of concentrated **sulfuric acid**. To this is added 385 cc. of aqueous **allyl alcohol** (p. 42), which, according to **bromine** titration, contains 233 g. (4 moles) of pure **allyl alcohol**. The 3-l. round-bottomed flask is fitted with a mechanical stirrer (Note 11), separatory funnel, and an efficient condenser set for downward distillation. Stirring is started, and 300 g. (162 cc.) of concentrated **sulfuric acid** is added gradually through the separatory funnel to the warm solution. The **allyl bromide** distils over completely in about one-half to one hour. The crude **allyl bromide** is washed with dilute **sodium carbonate** solution, dried over **calcium chloride**, and then distilled. The yield of product boiling at 69–72° from a number of experiments varies from 445–465 g. (92–96 per cent of the theoretical amount). A small high-boiling fraction is also obtained and examination has shown this to consist of **propylene bromide**.

(B) **iso-AMYL BROMIDE, (CH₃)₂CHCH₂CH₂Br**

[Butane, 1-bromo-3-methyl-]

In a 5-l. round-bottomed flask, a **hydrobromic acid** solution is prepared (p. 26) by passing **sulfur dioxide** into a mixture of 1100 g. of crushed ice and 1 kg. (314 cc., 6.25 moles) of **bromine**. This is equivalent to a mixture of 2.1 kg. (12.5 moles) of 48 per cent **hydrobromic acid** and 600 g. of concentrated **sulfuric acid**. There are then added, in the order mentioned, 880 g. (1086 cc., 10 moles) of **iso-amyl alcohol** (b.p. 130–132°) and 100 g. (54.5 cc.) of concentrated **sulfuric acid**. The clear homogeneous solution is refluxed gently during a period of five to six hours. Even during the early stages of the heating, the separation of **iso-amyl bromide** is observed, and the reaction appears to be complete after about one hour. The product is isolated as in the preparation of **n-butyl bromide** below.

A yield of 1435 g. of crude product is obtained. After purification with concentrated **sulfuric acid** the product weighs 1410 g. (93 per cent of the theoretical amount). Upon fractionation, however, it is found that appreciable amounts of a high-boiling product are present, and therefore the yield of fractionated material boiling over the range 116–120° varies in different experiments from 1330 to 1360 g. (88–90 per cent of the theoretical amount).

(C) **n-BUTYL BROMIDE, CH₃(CH₂)₃Br**

[Butane, 1-bromo-]

Hydrobromic-Sulfuric Acid Method.—In a 5-l. round-bottomed flask are placed 1300 g. of crushed ice and 1200 g. (376 cc., 7.5 moles) of **bromine**. The flask is cooled in an ice-water bath and **sulfur dioxide** is passed into the mixture until the red color due to free **bromine** has just disappeared (p. 26). This mixture is equivalent to 2500 g. (14.8 moles) of 48 per cent **hydrobromic acid** to which 750 g. of concentrated **sulfuric acid** has been added.

To the **sulfuric-hydrobromic acid** mixture is added 888 g. (1096 cc., 12 moles) of **n-butyl alcohol**. Following this, 600 g. (324 cc.) of concentrated **sulfuric acid** is added in several portions, with shaking. The flask is then attached to a reflux condenser and the mixture is refluxed during a period of five to six hours, during which time the formation of **butyl bromide** is carried practically to completion. The flask is now fitted with a condenser set downward and the product removed from the reaction mixture by

direct distillation (about one hour). The water-insoluble layer is separated, washed first with water, then with 200 g. (109 cc.) of cold concentrated **sulfuric acid**, and finally with a **sodium carbonate** solution (50 g. of **sodium carbonate** in 500 cc. of water). The product is separated as completely as possible from the aqueous layer, dried during several hours with a small quantity (15–25 g.) of **calcium chloride**, and distilled. The yield of product boiling between 101–104° is 1560 g. (95 per cent of the theoretical amount).

Sodium Bromide Method.—In a 5-l. round-bottomed flask is placed 1350 cc. of water, and then with stirring 1545 g. (15 moles) of finely powdered **sodium bromide** is added. It is advisable to add the salt to the water in this manner in place of the reverse procedure, in order to avoid caking of the **sodium bromide**. First, 888 g. (12 moles) of *n*-butyl alcohol and then gradually 2 kg. (1087 cc.) of concentrated **sulfuric acid** are added. The last half of the acid is added through a dropping funnel after the flask has been connected with a reflux condenser. The mixture is shaken occasionally during the addition of the **sulfuric acid** because of a tendency to separate into layers, and is finally refluxed during a period of two hours. The condenser is then set downward and the **butyl bromide** removed by distillation. The product is purified as in the preceding experiment for the preparation of *n*-butyl bromide by the hydrobromic-sulfuric acid method. The yield of *n*-butyl bromide boiling between 101–104° is 1480 g. (90 per cent of the theoretical amount).

(D) *n*-DODECYL BROMIDE, $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{Br}$

[Lauryl Bromide]

In a 250-cc. round-bottomed flask are placed 70 g. (0.42 mole) of **hydrobromic acid** (48 per cent) (p. 26) and 22 g. (12 cc.) of concentrated **sulfuric acid**. To this mixture is added 40 g. (0.22 mole) of **lauryl alcohol** (b.p. 188–192° /110 mm.) (Org. Syn. **10**, 62), and the mixture is then refluxed for five to six hours. The bromide is isolated as described in the preparation of *n*-octyl bromide (p. 30). The product is distilled under reduced pressure and is collected from 175–180° /45 mm. The yield is 49 g. (91 per cent of the theoretical amount) (Note 12).

(E) ETHYL BROMIDE, $\text{CH}_3\text{CH}_2\text{Br}$

[Ethane, bromo-]

In the preparation of **hydrobromic acid** for the manufacture of **ethyl bromide**, particular care must be taken to avoid the presence of any excess of **sulfur dioxide** gas. The evolution of gas during the distillation of the **ethyl bromide** will invariably result in a large loss of this volatile product (b.p. 38–39°).

A **hydrobromic acid** solution is prepared (p. 26) in a 5-l. round-bottomed flask by the reduction of 1 kg. (314 cc., 6.25 moles) of **bromine** in the presence of 1.1 kg. of cracked ice. A mixture of 2075 g. (12.3 moles) of 48 per cent **hydrobromic acid** and 600 g. (324 cc.) of concentrated **sulfuric acid** may be used in place of the above reduction mixture. After the addition of 500 g. (622 cc., 10 moles) of 95 per cent **ethyl alcohol**, the flask is attached to a long condenser set ready for distillation, and 1 kg. (544 cc.) of concentrated **sulfuric acid** is slowly added through a separatory funnel. Because of the volatility of **ethyl bromide**, the mixture is not heated under a reflux condenser, but is subjected instead to slow distillation. The end of the condenser is provided with an adapter tube, and the distillate is collected in a flask containing ice water. The crude **ethyl bromide**, weighing 1055 g., is purified as directed under the *n*-butyl bromide experiment (p. 28). The washing with concentrated **sulfuric acid** is almost superfluous unless a product of special purity is desired; for instance, in the present experiment a washing with 300 g. of concentrated acid results in a decrease in weight of only 10 g.

The **ethyl bromide** is distilled from a water bath and boils at 38.5–39.5° provided that chips of porous plate are added to prevent superheating. Final yields vary from 980 to 1035 g. (90–95 per cent of the theoretical amount) according to the precautions taken to prevent losses due to evaporation.

(F) *n*-OCTYL BROMIDE, $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{Br}$

[Octane, 1-bromo-]

In a 500-cc. round-bottomed flask are placed 240 g. (1.4 moles) of [hydrobromic acid](#) (48 per cent) (p. 26), 62 g. (34 cc.) of concentrated [sulfuric acid](#), and 71 g. (0.55 mole) of *n*-octyl alcohol (b.p. 135–140° /100 mm.). The mixture is boiled under reflux for five to six hours. The solution is diluted with water and the bromide layer is separated, washed once with a little cold concentrated [sulfuric acid](#), then with water and finally with dilute [sodium carbonate](#) solution, after the procedure described for *n*-butyl bromide. The crude yield is 102 g.; this is dried over a little [calcium chloride](#) and distilled. The product is collected at 196–200° (91–93° /22 mm.) and amounts to 96 g. (91 per cent of the theoretical amount).

(G) TRIMETHYLENE BROMIDE, $\text{Br}(\text{CH}_2)_3\text{Br}$

[Propane, 1,3-dibromo-]

Hydrobromic-Sulfuric Acid Method.—In a 5-l. round-bottomed flask are placed 1200 g. (377 cc., 7.5 moles) of bromine and 1300 g. of crushed ice, and the bromine is reduced with [sulfur dioxide](#) to [hydrobromic acid](#) (p. 26). In place of the above reduction mixture, there may be used a mixture of 2.5 kg. (14.8 moles) of aqueous 48 per cent [hydrobromic acid](#) and 750 g. (408 cc.) of concentrated [sulfuric acid](#).

First, 456 g. (433 cc., 6 moles) of [trimethylene glycol](#) (b.p. 210–215°) is added, and then 1200 g. (652 cc.) of concentrated [sulfuric acid](#), the [sulfuric acid](#) being added slowly. The mixture is refluxed (Note 13) during a period of five to six hours and is then subjected to distillation until no water-insoluble product appears in the distillate (about one hour).

The [trimethylene bromide](#) is purified (Note 14) in accordance with the method used for *n*-butyl bromide (p. 28). A yield of 1065–1142 g. boiling at 162–165° (88–95 per cent of the theoretical amount) is obtained.

Sodium Bromide Method.—The yields of [trimethylene bromide](#) by the [sodium bromide](#) method as described for *n*-butyl bromide (p. 29) are slightly lower than those given above. Thus, from 1350 g. of water, 1545 g. (15 moles) of [sodium bromide](#), 456 g. (6 moles) of [trimethylene glycol](#), and 2500 g. of [sulfuric acid](#), a yield of 1110 g. of crude product is obtained, from which, after purification (Note 14) and distillation, a yield of 1030 g. of bromide (85 per cent of the theoretical amount) is obtained.

2. Notes

1. When an alcohol is heated with aqueous 48 per cent [hydrobromic acid](#), a partial conversion takes place into the corresponding bromide. The reaction is more rapid and more complete, however, in the presence of [sulfuric acid](#). Although the constant boiling [hydrobromic acid](#) obtainable on the market may be used in all the preparations described, its formation by the [sulfur dioxide](#) reduction of bromine will be considerably less expensive and equally convenient, provided that a cylinder of [sulfur dioxide](#) is available. For use in the preparation of alkyl bromides, distillation of the [bromine-sulfur dioxide](#) reduction mixture is superfluous.

2. The procedure described is quite general for the preparation of primary bromides. The presence of [sulfuric acid](#) would usually be objectionable in the preparation of secondary and tertiary bromides because of the ease of dehydration of the corresponding alcohols and the formation of isomers. This is also true of *iso*-butyl bromide and to some extent of *iso*-amyl bromide. These bromides may be obtained in good yields by the phosphorus tribromide method described in Org. Syn. 13, 20.

In the preparations described, a more dilute [hydrobromic acid](#) solution may be used, provided that the proportion of [sulfuric acid](#) is increased. Aqueous solutions of alcohols may also be used if the proportion of [sulfuric acid](#) is suitably adjusted. In the [allyl alcohol](#) experiment, material was used as obtained from the [glycerol-formic acid](#) preparation (p. 42) after one salting out with [potassium carbonate](#).

3. The reaction mixture is heated under the reflux condenser for several hours preliminary to the first distillation of the alkyl bromide. This is done in order to convert the alcohol as completely as possible into the corresponding bromide and thus to prevent its volatilization with the bromide. Direct distillation of the reaction mixture without refluxing will usually result in a decrease in yield of 5–15 per cent. Alkyl bromides of low molecular weight may, however, be distilled directly from the reaction mixture without the necessity of refluxing, providing the process of distillation is conducted very slowly. Alkyl

halides of high molecular weight are separated from the reaction liquors mechanically instead of by distillation. This is done in order to avoid the decomposition due to heating the slightly volatile material with a gradually increasing concentration of **sulfuric acid**.

4. The main impurities usually found in alkyl halides are the corresponding alcohols and ethers. Cold concentrated **sulfuric acid** is an efficient reagent for the removal of these impurities in all cases where the alkyl halide itself is not attacked by this reagent. Whenever a product contains a considerable quantity of unchanged alcohol, several washings with the cold concentrated acid may be required.

5. In many organic preparations too large a quantity of drying agent is usually employed, with the resulting loss of a considerable amount of material due to absorption by the drying agent. In the present experiments it is found that after a careful separation of the alkyl halide from the water layer as small a quantity as 15 g. of **calcium chloride** is sufficient for the drying of 1500 g. of alkyl halide.

6. The favorable results obtained in the preparation of alkyl bromides with aqueous **hydrobromic acid** to which **sulfuric acid** has been added suggest that practically the same result might be accomplished by the use of **sodium bromide**, water, and **sulfuric acid** in such ratios as approximate the proportions used in the first instance. In actual practice this modified **sodium bromide** method was found fairly satisfactory for the preparation of *n*-butyl bromide and of trimethylene bromide. Slightly lower yields are due to the decreased solubilities of the alcohols in the reaction mixtures because of the presence of dissolved salts. One would therefore predict that, with alcohols of still higher molecular weights, even lower yields would be obtained with the **sodium bromide** method. This prediction is substantiated in experiments with *iso*-amyl alcohol, where the **sodium bromide** method gives yields of only 70 per cent of the theoretical amount, whereas the **hydrobromic acid** method gives yields of almost 90 per cent. The **sodium bromide** method is therefore not recommended for the preparation of alkyl bromides of high molecular weight.

7. In the **sulfur dioxide** reduction of **bromine**, it should be noted that the proportion of water used depends upon whether the reduction mixture is to be distilled for the preparation of 48 per cent **hydrobromic acid**, or whether it is to be used directly for the manufacture of alkyl bromides.

8. During the first stage of the reduction, the flask should be shaken from time to time in order to avoid the accumulation of **sulfur dioxide**, or possibly of **sulfuryl bromide**, which would result in a violent reaction owing to a large quantity of the material reacting at one time. In more than a hundred reduction experiments conducted with quantities of **bromine** varying from 0.5 to 2 kg., this sudden reaction was noted in only one or two instances, in spite of the fact that there was usually no agitation other than that furnished by the entering gas stream.

Mechanical stirring is frequently important in obtaining successful yields. In Fig. 2, A and B represent two convenient types of stirring devices² where refluxing and stirring are desired at the same time. When the stopper of the flask is so small that it will hold only the mechanical stirrer, a Y-tube such as is shown in Fig. 3 B fitted with either form of stirrer is suitable. It often happens that a separatory funnel or thermometer must also be inserted in the flask in addition to the reflux condenser. A three-necked flask such as is shown in Fig. 3 A is especially convenient, the middle opening being used for the stirrer, the two smaller ones for thermometer and reflux condenser.

Fig. 2.

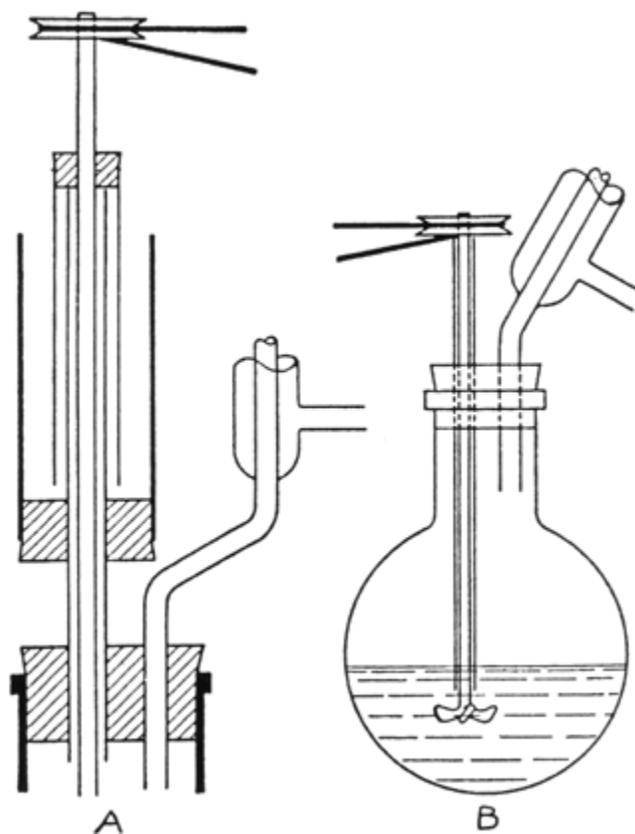
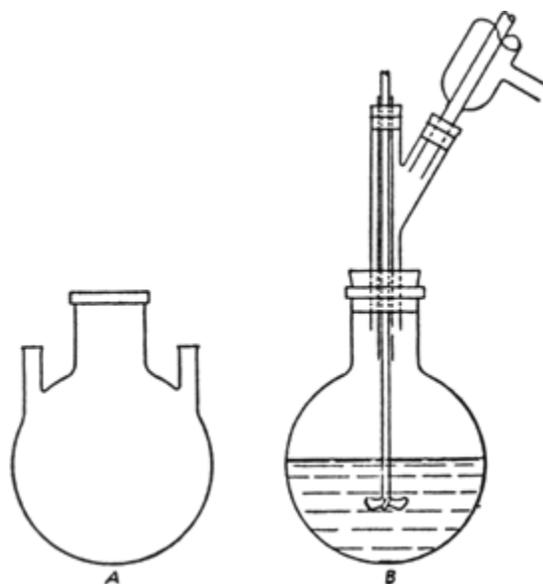


Fig. 3.



9. The intensity of the color in the reduced bromine solution depends somewhat on the quality of bromine used, and with the technical product special care is needed in noting the end point of the reduction, i.e., the transition from the bromine color to a yellowish-brown color.

10. An excess of sulfur dioxide is to be avoided for the reason that evolution of gas during the distillation of the product will result in a considerable loss of alkyl bromide through volatilization. This loss is especially marked in the preparations of ethyl and allyl bromides if this precaution is not observed.

11. In the preparation of allyl bromide, appreciable loss may occur, not only because of carbonization

but primarily because of the reaction of the **allyl bromide** with **hydrobromic acid** to form **propylene bromide**. Stirring during the formation of the alkyl bromide prevents the formation of two layers in the reaction mixture and thus assures a rapid and smooth distillation. An efficient condenser is of course essential.

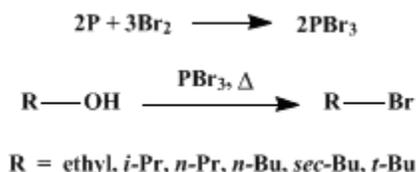
12. The troublesome emulsions often encountered when **lauryl bromide** is shaken with **sulfuric acid** may be avoided by the following alternative method of purification. The reaction mixture, after the heating is completed, is diluted with water and the layer of **lauryl bromide** is separated. The bromide is washed with water and then with **potassium carbonate** solution. The washing with water should be sufficiently thorough so that there is no appreciable foaming on shaking with the carbonate. The bromide is then dried with **calcium chloride** and distilled.

Lauryl bromide and the bromides of other primary alcohols of high molecular weight can also be prepared by saturating the alcohol at 100–120° with **hydrogen bromide** as described in Org. Syn. **15**, 24. This **hydrogen bromide** procedure has been reported to be superior for preparing **lauryl bromide** to the **hydrobromic acid-sulfuric acid** method described above.

13. **Trimethylene bromide**, prepared by direct distillation of the reaction mixture without the preliminary refluxing period, contains appreciable amounts of **trimethylene bromohydrin**.

14. In the purification of **trimethylene bromide** with **sulfuric acid** the high specific gravity of the former (1.987) must be borne in mind. Vigorous shaking with **sulfuric acid** may result in the formation of emulsions.

[II. PHOSPHORUS AND BROMINE METHOD]



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Checked by R. L. Shriner and F. J. Wolf.

1. Procedure

(A) **ETHYL BROMIDE**, $\text{CH}_3\text{CH}_2\text{Br}$

[Ethane, bromo-]

A 1-l. three-necked, round-bottomed flask is fitted with an Allihn condenser and a dropping funnel, the stem of which reaches to the bottom of the flask. By means of a bent glass tube the top of the Allihn condenser is connected to a Liebig condenser the end of which dips just beneath the surface of a mixture of ice and water (about 800 g.) contained in a 2-l. beaker (Note 1).

In the reaction flask are placed 363 g. of 95 per cent **ethyl alcohol** (7.5 moles), 25 g. of red phosphorus, and 15 g. of yellow phosphorus (1.29 gram atoms) (Note 2). The mixture is heated by means of the oil bath until gentle refluxing takes place (bath temperature at 100–110°), and 377 g. of **bromine** (121 cc., 2.36 moles) is slowly added through the dropping funnel over a period of three hours (Note 3), (Note 4). The water is drained from the Allihn condenser, and distillation is continued at a rate of forty to fifty drops per minute up to a temperature of about 94° (a thermometer may be placed in the flask in place of the dropping funnel) (bath at about 155°). When the distillation is complete the two condensers are disconnected first and the burner removed (Note 5).

The distillate is washed with 20 cc. of ice-cold 5 per cent **sodium hydroxide** solution, then with 50 cc. of ice-water. The product is dried over anhydrous **calcium chloride** and distilled through a short column, the distillate being collected in a dry receiver packed in an ice-salt mixture. The yield of colorless **ethyl bromide** distilling between 37° and 40° is 420–465 g. (82–90 per cent of the theoretical amount based on the **bromine**) (Note 6).

(B) *iso*-PROPYL BROMIDE, (CH₃)₂CHBr

[Propane, 2-bromo-]

The procedure for the preparation of *iso*-propyl bromide is similar to that for ethyl bromide except for the quantities of the reactants and the temperature of the bath. A mixture of 180 g. (228 cc., 3.0 moles) of *iso*-propyl alcohol, 6 g. of red phosphorus, and 4 g. of yellow phosphorus (0.3 gram atom) is placed in the reaction flask. Then, 135 g. (43.2 cc., 0.84 mole) of bromine is added over a period of three hours, the temperature of the oil bath being maintained between 85° and 95° (preferably at 90°). The distillate is collected up to a temperature of 145° (bath temperature 155–185°). In the second distillation after washing and drying the crude product, the fraction boiling between 59° and 62° is collected. The yield of product is 143–152 g. or 69–73 per cent of the theoretical amount (Note 7).

(C) *n*-PROPYL BROMIDE, CH₃CH₂CH₂Br

[Propane, 1-bromo-]

The procedure for the preparation of *n*-propyl bromide is similar to that for ethyl bromide except for the quantities of the reactants and the temperature of the bath. A mixture of 180 g. (224 cc., 3.0 moles) of *n*-propyl alcohol, 6 g. of red phosphorus, and 4 g. of yellow phosphorus (0.3 gram atom) is placed in the reaction flask. Then 135 g. (43.2 cc., 0.84 mole) of bromine is added slowly over a period of three hours, the temperature of the oil bath being maintained between 125° and 140°. The distillate is collected up to a temperature of 140° (bath temperature 190–210°). In the second distillation, after washing and drying the crude product, the fraction boiling between 70–73° (Note 8) is collected. The yield of *n*-propyl bromide is 170–186 g. (82–90 per cent of the theoretical amount).

(D) *n*-BUTYL BROMIDE, CH₃(CH₂)₃Br

[Butane, 1-bromo-]

The same apparatus as described in the preparation of ethyl bromide may be used with the omission of the Liebig condenser.

In the reaction flask are placed 138 g. (170 cc., 1.86 moles) of *n*-butyl alcohol, 6 g. of red phosphorus, and 4 g. of yellow phosphorus (0.3 gram atom). The oil bath is heated to 175°, and 94 g. (30.1 cc., 0.58 mole) of bromine is added slowly through the dropping funnel at such a rate that the dense white vapors which form remain near the top of the Allihn condenser. The optimum period for the addition of bromine is about one hour, during which time the bath temperature slowly decreases to 165°. The mixture is distilled directly from the reaction flask which is attached to a condenser set for downward distillation. When the distillation becomes slow about 25 cc. of water is added through the dropping funnel to assist in carrying over the butyl bromide. The final bath temperature is about 210°. The distillate is washed with 20 cc. of 5 per cent sodium hydroxide solution and then with 50 cc. of water. The product is dried with calcium chloride and distilled through a Vigreux column. The fraction boiling from 97° to 99.5° is collected and amounts to 145–150 g. (90–93 per cent of the theoretical amount).

(E) *sec.*-BUTYL BROMIDE, CH₃CH₂CHBrCH₃

[Butane, 2-bromo-]

The procedure for secondary butyl bromide is similar to that used in the preparation of *n*-butyl bromide, except that bromine is added at a bath temperature of 140–150°, and the distillate (bath temperature up to 190°) from the reaction mixture is washed with water and dried over anhydrous sodium sulfate before redistilling. The yield (b.p. 86–87°) is about 135–137 g. (84–85 per cent of the theoretical amount).

(F) *tert.*-BUTYL BROMIDE, (CH₃)₃CBr

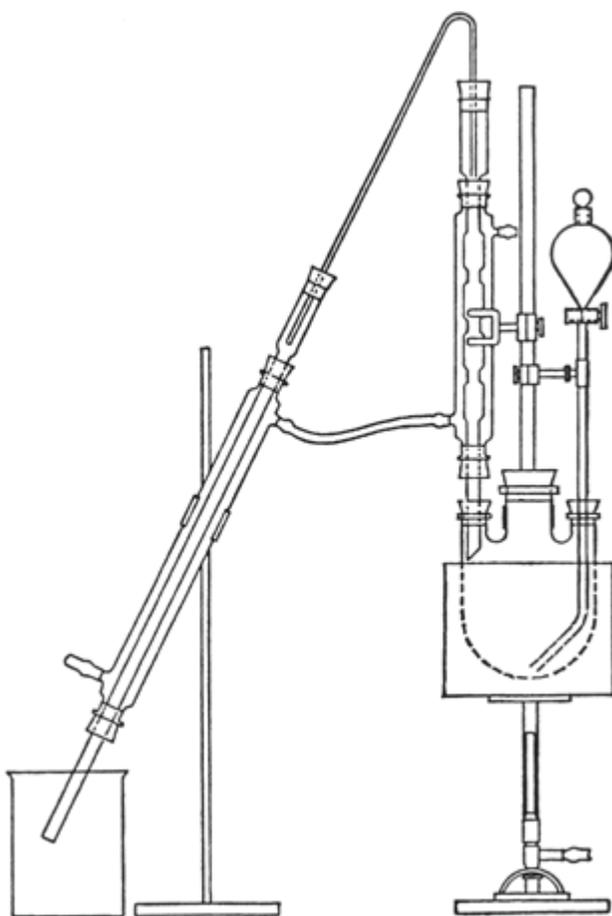
[Propane, 2-bromo-2-methyl-]

In a 500-cc. three-necked, round-bottomed flask fitted with a dropping funnel and a mechanical stirrer is placed 5 g. (0.16 gram atom) of red phosphorus. The flask is cooled on a bath of cold water, and 47 g. (15 cc., 0.29 mole) of bromine is added *very slowly* at first (Note 9). After the initial reaction has moderated the remainder of the bromine is added over a period of one and a half to two hours. The stirrer is started, and 69 g. (0.93 mole) of *tert*-butyl alcohol is placed in the separatory funnel and added slowly to the phosphorus bromide. The stirrer and separatory funnel are removed; the flask is connected to a condenser and arranged for vacuum distillation. By means of a water pump the pressure is gradually reduced to 20–30 mm. and the bromide distilled by raising the bath temperature slowly to 70–80°. The distillate is washed quickly with 50 cc. of ice-water, dried with anhydrous calcium chloride, and redistilled. The fraction boiling from 69° to 71° is collected. The yield is 32 to 34 g. (39–42 per cent of the theoretical amount).

2. Notes

1. A diagram of the apparatus used is shown in Fig. 4.

Fig. 4.



2. Nearly as good yields are obtained if yellow phosphorus is used alone. However, a much smoother and more readily controllable reaction is obtained if some red phosphorus is used along with the yellow phosphorus. Care must be exercised in handling yellow phosphorus since it ignites spontaneously in the air. It should be kept under water and transferred quickly to the flask which already contains the alcohol.
3. A vigorous reaction, with some bumping and the formation of white vapors, accompanies the first addition. As the density of the vapors decreases, the rate of addition of bromine may be increased to the extent that some of the white vapors are carried over into the Liebig condenser.
4. There is a tendency for water to be sucked from the ice bath into the apparatus because of sudden changes in pressure within the system. This difficulty may be avoided by adding the bromine at a constant rate, by maintaining a constant reflux rate, and by maintaining the temperature of the oil bath

nearly constant, allowing any changes in temperature, especially lowering, to take place slowly. If water is sucked into the reaction flask, the addition of bromine may as well be discontinued because the alcohol has become diluted and the yield will be low.

5. Care must be exercised in the disposal of the residue in the flask since it sometimes contains unreacted phosphorus which ignites spontaneously when dry and exposed to the air. After the residue has cooled, it should be drowned in a large volume of water and the mixture washed down the drain with a good stream of water.

6. Ethyl bromide is quite volatile, and hence care must be taken to keep it cold during the washing operations and to use efficient condensing systems.

7. In washing the product a lachrymator is noticed, and in the final distillation a residue of 30–36 g. possessing highly lachrymatory properties is observed.

8. The residue has lachrymatory properties and a pungent odor.

9. Care should be taken to add the bromine very slowly at first since sometimes the heat of the reaction is sufficient to ignite the phosphorus and it burns until all the oxygen is removed from the flask.

3. Discussion

Alkyl bromides are prepared most conveniently from the corresponding alcohols. The reagents commonly employed are: phosphorus bromide,³ a metallic bromide and sulfuric acid,⁴ very concentrated or fuming hydrobromic acid, often under pressure,⁵ and aqueous hydrobromic acid in accordance with the method suggested by Norris.⁶ Allyl, propyl, and isobutyl bromides have been prepared⁷ by a modification of this last method: bromine was reduced by means of sulfur dioxide, the alcohol was added, and the mixture distilled. The procedure described has two essential modifications: the addition of concentrated sulfuric acid and a refluxing period preliminary to the distillation. The sodium bromide method has been improved by similar modifications. Purer alkyl bromides have been reported by a slight variation in the method of purification.⁸ Since trimethylene glycol is now a by-product from the purification of glycerol, it is a convenient compound for the preparation of trimethylene bromide. A method involving the use of gaseous hydrobromic acid has been described,⁹ but the aqueous hydrobromic-sulfuric acid method¹⁰ has been found to be a considerable improvement.

Comparative studies of the preparation of a number of alkyl bromides show that phosphorus tribromide gives better results than red phosphorus and bromine,¹¹ while a comparison of different methods of preparing *n*-butyl bromide shows that the best yields are obtained with hydrogen bromide and sulfuric acid.¹²

Other procedures which have been described for the preparation of alkyl bromides include: the addition of hydrogen bromide to ethylenic hydrocarbons in the presence of an absorbent hydrous metal oxide gel;¹³ heating an alcohol or its sulfuric acid ester with hydrobromic acid in aqueous solution at 110–180°, under pressure to avoid formation of a vapor phase;¹⁴ treatment of a dialkyl sulfate with hydrogen bromide in the vapor phase;¹⁵ heating an alcohol saturated with hydrogen bromide in the hydrogen bromide salt of a nitrogenous heterocyclic compound such as pyridine hydrobromide;¹⁶ and cleaving aliphatic ethers with hydrogen bromide and steam in the presence of a dehydrating catalyst.¹⁷ Alkyl bromides have been prepared from alcohols of high molecular weight by saturating the alcohol with hydrogen bromide at 100°C.¹⁸

This preparation is referenced from:

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- Org. Syn. Coll. Vol. 1, 117
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

red phosphorus

yellow phosphorus

ethyl alcohol (64-17-5)

calcium chloride (10043-52-4)

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

sodium hydroxide (1310-73-2)

glycerol (56-81-5)

HYDROBROMIC ACID,
hydrogen bromide (10035-10-6)

sodium carbonate (497-19-8)

bromine (7726-95-6)

sulfur dioxide (7446-09-5)

Allyl bromide,
Propene, 3-bromo- (106-95-6)

Allyl alcohol (107-18-6)

propylene bromide (78-75-1)

Butane, 1-bromo-3-methyl-,
iso-amyl bromide (107-82-4)

Butane, 1-bromo-,
Butyl bromide,
n-butyl bromide (109-65-9)

sodium bromide (7647-15-6)

Lauryl Bromide,
n-DODECYL BROMIDE (143-15-7)

Lauryl alcohol (112-53-8)

Ethyl bromide,
Ethane, bromo- (74-96-4)

Octane, 1-bromo-,
n-octyl bromide (111-83-1)

Trimethylene bromide,
Propane, 1,3-dibromo- (109-64-8)

trimethylene glycol (504-63-2)

sulfuryl bromide

trimethylene bromohydrin (627-18-9)

PHOSPHORUS (7723-14-0)

Propane, 2-bromo-,
iso-PROPYL BROMIDE (75-26-3)

Propane, 1-bromo-,
Propyl bromide,
n-PROPYL BROMIDE (106-94-5)

Butane, 2-bromo-,
2-Bromobutane,
sec.-BUTYL BROMIDE (78-76-2)

sodium sulfate (7757-82-6)

Propane, 2-bromo-2-methyl-,
tert.-BUTYL BROMIDE (507-19-7)

oxygen (7782-44-7)

phosphorus tribromide (7789-60-8)

pyridine hydrobromide (18820-82-1)

formic acid (64-18-6)

n-butyl alcohol (71-36-3)

iso-propyl alcohol (67-63-0)

n-propyl alcohol (71-23-8)

iso-amyl alcohol (123-51-3)

n-octyl alcohol (111-87-5)

Isobutyl bromide,
iso-butyl bromide (78-77-3)

tert-butyl alcohol (75-65-0)