

of Wohlgemuth, do not give the "liquefaction" of starch by enzymes, but measure the reduction of the starch to substances giving no longer any reaction with iodine, which is arbitrary.

3. In the study of the action of enzymes upon the starches present or embodied in the textiles (process of desizing), the Lintner method and its various modifications are unsuitable, since we are interested not in the sugar production, but in the starch elimination.

4. A method is described for measuring the starch liquefying power (amylolytic action) of enzymes, which is practical and easily manipulated.

5. Comparing the starch liquefying powers of malt enzymes and enzymes obtained from *Aspergillus Oryzae* (water extract used known commercially as Polyzime) the first are found to give a higher Lintner value, while the second give a higher liquefying value. The ratio of the liquefying value to the Lintner value, in the case of the malt preparations, is 1 : 4 to 1 : 5, while in the case of *Aspergillus Oryzae* enzyme it is 1 : 1 to 1.5 : 1, so that the liquefying power of the latter, in comparison to its sugar producing (saccharogenic power), is 4 to 6 times as great as that of the malt preparations.

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ORGANIC CHEMICAL REAGENTS. V.¹ THE PREPARATION OF ALKYL AND ALKYLENE BROMIDES.

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Although alkyl bromides are among the most common of laboratory reagents and although they are prepared by the most elementary reactions met with in organic synthesis their preparation in the laboratory as well as on a relatively large scale requires further improvement. The preparation of ethyl bromide is described in practically all laboratory manuals and yet the methods are so unsatisfactory that two papers² have appeared recently recommending improvements in the process, mainly in an endeavor to avoid the formation of ethyl ether as a by-product. In many reactions in organic chemistry, yields of from 70 to 80% are considered highly satisfactory but not so with the preparation of such simple and extensively used compounds as the alkyl halides. The method described below was found more adaptable to the preparation of alkyl and alkylene bromides than those methods commonly employed; it has been applied to the prep-

¹ For other papers in this series see THIS JOURNAL, 40, 1285, 1950 (1918); 41, 276, 789 (1919).

² J. Chem. Soc., 107, 1489 (1915); 109, 1 (1916).

aration of *n*-butyl bromide, isoamyl bromide, trimethylene bromide, trimethylene chlorobromide, ethyl bromide, allyl bromide, *n*-octyl bromide, and lauryl bromide.

The preparation of alkyl halides from the corresponding alcohols by the use of halogen acids is a very old and well-known process. The use of aqueous solutions of halogen acids, for example the constant boiling mixtures of the halogen acids with water, as developed by Norris and his students,¹ offers distinct advantages over the older procedures. The method is very convenient as a laboratory preparation for student use and for this purpose is without doubt superior to the phosphorus-halide method. In view of the fact that the Norris method is appearing as recommended procedure in laboratory manuals,² this brief note dealing with an essential improvement of the method in its application to primary alcohols should be of value.

Norris has shown that primary, secondary, and tertiary alcohols differ greatly in the ease of reaction with aqueous halogen acids. When a primary alcohol is distilled with one, two, or three moles of aqueous hydrobromic acid (48%), a poor yield of alkyl bromide is usually obtained. Secondary alcohols react with greater ease, the result being that satisfactory yields are obtained, whereas tertiary alcohols react even without heating to give almost theoretical results. The shortcoming of the Norris method lies in its application to primary alcohols; although a large excess of hydrobromic acid is used the yields are so unsatisfactory that the method cannot be considered in its present form as of great practical value for the preparation of primary bromides.

In the present work it was observed that the addition of sulfuric acid increased greatly the yields of alkyl bromides obtained by the use of the Norris method. In the tables given below are shown the yields of *n*-butyl bromide obtained when one mole of *n*-butyl alcohol is distilled with various amounts of aqueous hydrobromic acid (sp. gr. 1.49) both with and without the addition of sulfuric acid. Other primary alcohols show a similar behavior but this individual example is chosen because the behavior of *n*-butyl alcohol with aqueous hydrobromic acid in the Norris method has not previously been recorded.

The results in Tables I and II were obtained by placing the materials in a one-liter round-bottom flask and distilling at such a rate that 30 minutes were required for the actual distillation of the alkyl halide. The yields in both series of experiments would be higher if the mixtures were refluxed for a short time preliminary to the distillation.³ In their present form, however, the results are comparable.

¹ *Am. Chem. J.*, **38**, 627 (1907); *THIS JOURNAL*, **38**, 1071 (1916).

² *Loc. cit.*, p. 1072.

³ This modification is adopted in the specific laboratory directions that follow.

TABLE I.

Aqueous HBr used for one mole of <i>n</i> -butyl alcohol. moles.	Crude product. G.	Product after washing with cold conc. H ₂ SO ₄ . G.	Yield. %.
1.....	90	46	34
2.....	105	79	58
3.....	115	89	65
4.....	121	109	80

TABLE II.

H ₂ SO ₄ added to 1.5 moles of aqueous HBr and one mole of <i>n</i> -butyl alcohol moles.	Crude product. G.	Product after washing with cold conc. H ₂ SO ₄ . G.	Yield. %.
0.5.....	116	93	68
1.0.....	125	115	84
1.5.....	130	122	89
2.0.....	132	130	94

It is thus seen that the addition of even one mole of sulfuric acid is more than sufficient to compensate for 2.5 moles of hydrobromic acid. This is, however, not the only advantage obtained by the addition of sulfuric acid. When a large excess of hydrobromic acid is used in the Norris method (1 alcohol : 4 HBr), a fair yield of product is obtained (80%), but this product requires washing with sulfuric acid in order to remove unchanged alcohol. When *n*-butyl alcohol is distilled with only 1.5 moles of hydrobromic in the presence of two moles of sulfuric acid, a product is obtained which for the most purposes is sufficiently free from alcohol. From 74 g. of *n*-butyl alcohol there were obtained thus 132 g. of product which after washing with sulfuric acid still weighed 130 g. All of the yields recorded in this paper with the exception of that of allyl bromide refer to material that has been washed with cold conc. sulfuric acid. Other details of manipulation are recorded in the experimental discussion below.

The effectiveness of sulfuric acid as is illustrated in Table II does not depend entirely upon the resulting removal of water from the reaction mixture but is also to be explained by the formation of an alkyl sulfuric acid which probably reacts more readily with hydrobromic acid. The effect of sulfuric acid in preventing the distillation of the alcohol from the reaction mixture is also an important factor. The *n*-butyl bromide prepared by the sulfuric acid method differed in no way from that prepared by the usual Norris method; neither product showed evidences of the presence of unsaturated compounds.¹

The effect of hydrobromic acid upon alcohols in the presence of very large quantities of sulfuric acid has been studied by Niemitowicz² who has suggested this method for the preparation of bromine substitution products of the alkyl bromides. It should be noted that with the con-

¹ Cf. *Ann.*, 379, 291 (1911); 393, 95 (1912).

² *Monatsh.*, 10, 813 (1889).

centration of sulfuric acid used in the experiments recorded in the present work, liberation of bromine by oxidation of hydrobromic acid does not take place.¹

Norris has shown that the reaction between the alcohols and hydrobromic acid becomes slower with increase in molecular weight of the alcohol. Thus 5 g. of normal octyl alcohol heated for one hour with 25.5 g. of hydrobromic acid yielded 3.5 g. of the bromide. When the experiment was repeated using the same quantity of alcohol but decreasing the amount of hydrobromic acid to 15 g. and adding 5 cc. of sulfuric acid, the yield of octyl bromide was 7 g., an improvement of 100%. Similarly, an alcohol with 12 carbon atoms (lauryl alcohol) was found to give a yield of over 90% of the corresponding bromide. The presence of sulfuric acid, therefore, obviates any difficulty found in converting an alcohol of high molecular weight into its bromide. One variation in experimental procedure should, however, be noted. Alkyl bromides of high molecular weight are but slowly volatile with water vapor. In such cases the mixture is heated under a reflux condenser until reaction is complete and the product isolated simply by separation of the layer of insoluble alkyl halide. In this manner there is avoided any decomposition of the product due to heating it with a gradually increasing concentration of sulfuric acid.

The use of sulfuric acid is recommended only for primary alcohol since secondary and tertiary alcohols react readily with aqueous hydrobromic acid alone. Moreover, sulfuric acid has a tendency to dehydrate many secondary and tertiary alcohols. According to the procedure described below, no ether is formed as a by-product in the preparation of alkyl halides. A sample of ethyl bromide prepared as above described suffers no appreciable loss in weight when it is washed with conc. sulfuric acid; this is in marked contrast to the results obtained with many of the older methods for the preparation of ethyl bromide.

The favorable results obtained in the preparation of alkyl bromides with aqueous hydrobromic acid to which sulfuric acid has been added will immediately suggest that practically the same result might be accomplished by the use of sodium bromide, water, and sulfuric acid in such ratios as to approximate the proportions used in the above experiments. This prediction is substantiated by experiment, although the yields obtained fall slightly below those obtained with mixtures of constant boiling hydrobromic and sulfuric acids.

For the preparation of alkyl bromides on a relatively large scale the use of hydrobromic acid offers no special disadvantages, since it may be prepared readily by the reduction of bromine by sulfur dioxide in the presence of sufficient water to give the strength of hydrobromic acid desired. The product obtained need not be distilled but may be used directly for

¹ *J. pharm. chim.*, [5] 24, 159 (1891).

the preparation of alkyl halides as has been shown by Bodroux.¹ The fact that $\frac{1}{2}$ mole of sulfuric acid is present for each mole of hydrogen bromide is not a disadvantage since the presence of sulfuric acid is desired and consequently a correspondingly smaller quantity need be added. If constant-boiling hydrobromic acid is desired it may be distilled directly from the sulfuric acid solution, practically no free bromine being liberated. In the preparation of an alkyl bromide it is advisable to use 25% excess of hydrobromic acid; this excess may, however, be recovered by distillation. In the preparation of trimethylene bromide it is found that most of the excess of hydrobromic acid is recovered during the first distillation of the reaction mixture.

In the notes below, two preparations (*n*-butyl bromide and trimethylene bromide) will serve as very satisfactory experiments for student use. Until a few years ago *n*-butyl alcohol and trimethylene glycol were not available as general laboratory reagents because of prohibitive cost but at the present time both of these alcohols are technical by-products and consequently have become suitable materials for laboratory use.

General Method for the Preparation of Alkyl and Alkylene Bromides.

In the experiments given below a general method is employed that will no doubt be applicable to the preparation in yields of 90% and over of many other halogen compounds in addition to the 8 individuals that have been selected. The method consists in treating the alcohol with 25% excess of aqueous hydrobromic acid together with sulfuric acid. The mixture is refluxed 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 direct distillation. 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 isoamyl bromide a somewhat smaller proportion of sulfuric acid is used in order to prevent charring; while halides of high molecular weight, because of their high boiling points, are separated from the reaction mixture mechanically instead of by distillation.

The Preparation of Hydrobromic Acid.

Hydrobromic acid may be prepared conveniently by the interaction of bromine and sulfur dioxide in the presence of water. Scott² has shown that an exceptionally pure product may be obtained in this manner. The constant boiling mixture of halogen acid prepared by this method

¹ *Compt. rend.*, 160, 206 (1915).

² *J. Chem. Soc.*, 77, 648 (1900).

although distilled from sulfuric acid solution, is free even from traces of bromine. Fortunately in the preparation of alkyl bromides a separation of the hydrobromic from the sulfuric acid is superfluous since the best yields of product are obtained in the presence of sulfuric acid. For certain purposes, however, the constant boiling acid may be required and accordingly the method for its preparation is here described.

In a 3-liter round-bottom flask are placed 1200 g. of bromine, 500 cc. of water, and 1500 g. of cracked ice. A fairly rapid stream of sulfur dioxide from a pressure tank is passed into the flask, the outlet of the gas-tube being placed below the surface of the bromine layer. 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 due to the large quantity of material reacting at one time. Although more than 100 reduction experiments were conducted with quantities of bromine varying from $1/2$ 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.

The flow of sulfur dioxide is adjusted at a rate such that the gas is completely absorbed. One or two hours will serve for the completion of the reaction, at which time the mixture will assume a yellow color which is not removed by further addition of sulfur dioxide. The intensity of color in the reduced solution appears to depend on the quality of bromine used, and with the technical product special care must be taken to observe the exact end-point of the reaction. An excess of sulfur dioxide is to be avoided for the reason given in the section dealing with the preparation of ethyl bromide.

To prevent loss of hydrogen bromide it is advisable to cool the mixture slightly during the progress of the reaction. 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 $125-126^{\circ}$ at 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 will rise to 130° and above, when water with only traces of acid distils 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 specific gravity determinations applied to the distillate. According to the above procedure, 20 kg. of 48% hydrobromic acid were prepared from 10.3 kg. of bromine. The actual time required by one man for the preparation of this quantity was 23 hours.

The Separation of Hydrochloric and Hydrobromic Acids.

In many laboratories alkyl bromides are used in connection with aluminum chloride in the Friedel and Crafts reaction. In such experiments halogen acid may be recovered by absorption in water but this by-product is usually considered valueless because it contains a considerable proportion of hydrochloric acid together with the more valuable hydrobromic acid. Although the boiling point of constant boiling hydrochloric acid (110°) lies close to that of the constant boiling hydrobromic acid (126°), the two products may be separated very readily by means of fractional distillation.

The Preparation of *n*-Butyl Bromide.

(a) **Hydrobromic Sulfuric Acid Method.**—In the preparation of hydrobromic acid for direct use in connection with the manufacture of alkyl bromides, a smaller proportion of water is used than would otherwise be the case. A mixture of 400 g. of bromine and 425 g. of ice is treated in a cooling mixture with sulfur dioxide until the bromine is reduced. 296 g. of *n*-butyl alcohol are then added, and following this there are added in several portions with shaking 200 g. of conc. sulfuric acid. The mixture is heated under a reflux condenser for a period of 2 hours, during which time the formation of butyl bromide is carried practically to completion. The product is accordingly removed from the reaction mixture by direct distillation. The crude material after washing with water weighs 534 g., and a purification with $\frac{1}{2}$ its volume of cold conc. sulfuric acid decreases this quantity by only 4 g. The product is washed with sodium carbonate solution, dried with a small quantity of calcium chloride, and distilled. The yield of product boiling at $101\text{--}104^{\circ}$ is 504 g., which corresponds to 92% of the theoretical amount. In a series of experiments in which 3 times the above quantities of materials were used, yields varying from 95% to 97% were obtained consistently. In experiments in which the mixture was distilled directly without refluxing, a yield of only 87% was obtained. The former product is of such purity that washing with conc. sulfuric acid is practically superfluous.

In organic preparations too large a quantity of drying agent is often employed with the resultant loss of a considerable amount of material due to absorption by the drying agent. In the present experiments it was found that after a careful separation of the butyl bromide from the water layer, 15 g. of calcium chloride were sufficient for the drying of 1500 g. of alkyl halide.

(b) **Sodium Bromide Method.**—In a 5-liter round-bottom flask are placed 1350 cc. of water and then with stirring 1545 g. (15 moles) of finely powdered sodium bromide are added. It is advisable to add the salt to water in this manner in place of the reverse procedure in order to avoid

caking of the sodium bromide. 888 g. (12 moles) of *n*-butyl alcohol are added and finally gradually 2000 g. of conc. (commercial) sulfuric acid. 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 agitated and finally refluxed during a period of 2 hours. The condenser is then reversed and the alkyl bromide removed by distillation.

The product is purified as in the preceding experiment. The yield is found to be somewhat lower (about 90%), due to the presence of some unchanged alcohol which is, of course, removed by the washing with sulfuric acid. The lower yield is probably due to the decreased solubility of the alcohol in the reaction mixture because of the presence of dissolved salts. On the other hand, when hydrobromic acid is used in place of sodium bromide, the alcohol dissolves completely, and the alkyl bromide separates from the mixture as it is formed. One would, therefore, predict that with alcohols of still higher molecular weights, still lower yields will be obtained with the sodium bromide method. This prediction was substantiated in experiments with isoamyl alcohol, where the sodium bromide method gave yields of only 70%, whereas the hydrobromic acid method gave yields of almost 90%.

Isoamyl Bromide.

(a) A mixture of 176 g. of isoamyl alcohol (b. p. 128–132°), 480 g. of 48% hydrobromic acid, and 110 cc. of conc. sulfuric acid is placed in an ordinary distilling flask and subjected to slow distillation. The weight of crude product is 277 g. and the weight after purification with conc. sulfuric acid is 240 g., which corresponds to 80% of the theoretical yield. The boiling point of the product is 118–120°. The yield in this preparation can be raised considerably by refluxing the reaction mixture preparatory to the distillation as is shown by the following experiment:

(b) A hydrobromic acid solution is prepared by passing sulfur dioxide into a mixture of 1000 g. of bromine (12.5 moles hydrogen bromide equivalent) and 1100 g. of ice. 880 g. of isoamyl alcohol (10 moles) and 800 g. of sulfuric acid are then added in the order mentioned. The clear homogeneous solution is refluxed gently. Even during the early stages of the heating period the separation of the isoamyl bromide is observed and the reaction appears to be complete after about one hour but it is advisable to continue the heating for one hour longer. The product is isolated as in the preparation of *n*-butyl bromide.

In a typical experiment carried out in accordance with the above directions, a yield of 1435 g. of crude product was obtained. After purification with conc. sulfuric acid this product weighed 1410 g., which corresponds to a yield of 93% before distillation. Upon fractionation it was found, however, that appreciable amounts of high-boiling products were

present and, therefore, the yield of fractionated material boiling over the range 116° to 120° was only 88% to 90%.

Trimethylene Bromide.

A hydrobromic acid solution is prepared from 1275 g. of ice and 1200 g. of bromine by reduction with sulfur dioxide as directed under the preparation of hydrobromic acid. 456 g. (6 moles) of trimethylene glycol and 1200 g. of conc. sulfuric acid are next added in the order given, the sulfuric acid being added slowly.¹ The mixture is refluxed during a period of one hour and then subjected to distillation until no water-insoluble product appears in the distillate. This distillation requires about one hour.

The trimethylene bromide is washed first with 200 g. of cold conc. sulfuric acid, next with a solution containing 50 g. of sodium carbonate, and after the separation from the latter it is dried with 30 g. of calcium chloride. The product is filtered from the drying agent and distilled. In a typical experiment a yield of 1088 g., boiling over the range 162 – 165° , was obtained, which corresponded to 90% of the amount theoretically possible. The lowest yield obtained was 88%, whereas the maximum obtained was 95%.

The yields of trimethylene bromide by the sodium bromide method were somewhat lower. Thus, from 1350 g. of water, 1545 g. of sodium bromide, 456 g. of trimethylene glycol, and 2500 g. of sulfuric acid, a yield of 1110 g. of crude product was obtained, from which, after purification and distillation, a yield of 1030 g. (85%) of bromide was obtained.

Trimethylene Chlorobromide.

A mixture of one mole of trimethylene chlorohydrin and two moles of constant boiling hydrobromic acid is treated gradually with two moles of sulfuric acid. The mixture is refluxed during a period of one hour and then subjected to distillation. The yield of purified product (b. p. 142 – 145°) is 140 g., whereas the theoretical yield is 157 g.

The preparation of ethylene chlorobromide from ethylene chlorohydrin and hydrobromic acid is found to be less satisfactory than the preparation of the trimethylene derivative. The reaction of ethylene with a solution of bromine monochloride in hydrochloric acid² is found to be a more satisfactory method for the preparation of ethylene chlorobromide.

Ethyl Bromide.

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. The evolution of gas during the distillation of the

¹ When dealing with more volatile bromides (ethyl, propyl, and allyl bromides), the sulfuric acid is best added while the flask is attached to a condenser.

² *J. prakt. Chem.*, [2] **26**, 380 (1882).

alkyl bromide will invariably result in a large loss of this volatile product (b. p. 38–39°).

To the solution resulting from the reduction of 1000 g. of bromine in the presence of 1075 g. of ice, there are added 500 g. of ordinary 92% alcohol. The flask is attached to a condenser ready for distillation and 1000 g. of conc. sulfuric acid added slowly through a separatory funnel. Because of the volatility of ethyl bromide the mixture is not heated under the reflux but is subjected instead to *slow* distillation. The product after separation from the ice water in which it should be collected is found to weigh 1055 g. A washing with 300 g. of sulfuric acid shows this treatment to be superfluous since a decrease in weight of only 10 g. is observed. This loss is due primarily to loss of ethyl bromide by evaporation.

The product is washed and purified as in the other alkyl bromide preparations. It distils over a range of 38–40° when distilled slowly from a water bath, provided chips of porous plate are added to prevent superheating. Final yields vary from 90% to 95% according to the precautions taken to prevent losses due to evaporation.

In the present experiment, a 25% excess of hydrobromic acid is used. With molecular quantities of materials, the yield will be somewhat lower, usually about 85%, and it is, therefore, questionable whether the method possesses much advantage over that proposed by Weston¹ for the preparation of ethyl bromide.

Allyl Bromide.

To the hydrobromic acid solution obtained by the sulfur dioxide reduction of 480 g. of bromine in the presence of 510 g. of water (added as ice) there are added 385 cc. of aqueous allyl alcohol, which according to bromine titration contain 232 g. of pure allyl alcohol. The flask is fitted to an efficient condenser set for downward distillation and 300 g. of conc. sulfuric acid are added gradually to the warm solution by means of a separatory funnel. The allyl bromide distils from the solution partly during the addition of the sulfuric acid and to facilitate the removal of the halide from the reaction mixture it is advisable to agitate the contents of the distilling flask. This is done best by means of a mechanical stirrer which is introduced through an oil or mercury seal. This distillation requires 1/2 to 1 hour. The crude allyl bromide is washed with dil. sodium carbonate solution, dried over calcium chloride and distilled. The yield of product boiling at 69–72° corresponds to 92–96% of that theoretically possible. A small high-boiling fraction is also obtained and examination has shown this to consist of propylene bromide.

Preparation of Alkyl Bromides of High Molecular Weights.

The method described above is well adapted to the preparation of alkyl bromides of high molecular weights. This was demonstrated by the prep-

¹ *J. Chem. Soc.*, 107, 1489 (1915).

paration of *n*-octyl bromide and lauryl bromide. Since the corresponding alcohols are quite expensive and only small quantities were available, the bromides were prepared only by using 48% hydrobromic acid and sulfuric acid. Because of the slow volatilities of these halides, considerable decomposition is liable to occur during the distillation of the alkyl bromides from the sulfuric acid reaction liquors. It is, therefore, advisable to separate the products from the acid layers by means of a separatory funnel instead of by distillation.

***n*-Octyl Bromide.**—In a 500 cc. round-bottom flask are placed 240 g. of hydrobromic acid (48%), 62 g. of conc. sulfuric acid, and 71 g. of *n*-octyl alcohol. The mixture is boiled under a reflux condenser for 2.5 hours. The solution is diluted with water and the bromide layer separated, washed once with a little cold conc. sulfuric acid, then with water, and finally with dil. sodium carbonate solution. The crude yield is 102 g.; this is dried over a little calcium chloride and distilled. The final yield is 96 g. (91% of the theoretical yield), and the boiling point ranges from 196° to 200°.

Lauryl Bromide.—In a 250 cc. round-bottom flask are placed 70 g. of hydrobromic acid (48%), 22 g. of conc. sulfuric acid, and 40 g. of lauryl alcohol. The mixture is boiled under a reflux condenser for 3 hours and the bromide then isolated as described in the preparation of octyl bromide. The product is distilled under reduced pressure. The yield is 49 g. or 91% of that theoretically possible. The product boils over a range of from 175° to 180° at 45 mm. pressure.

Summary.

1. Aqueous hydrobromic acid obtained by the reduction of bromine with sulfur dioxide in the presence of water is a convenient reagent for the preparation of primary alkyl bromides. The reduction mixture may be utilized directly without a preliminary distillation.

2. Mixtures of constant boiling hydrochloric and hydrobromic acids may readily be separated by means of fractional distillation.

3. A detailed study has been made of the preparation of *n*-butyl bromide from the corresponding alcohol by the hydrobromic acid method; addition of sulfuric acid to the reaction mixture was found to be of more value than an increase in the quantity of hydrobromic acid.

4. A general method is described for the preparation of primary alkyl bromides. The main variations from the Norris-Bodroux Method are (a) the addition of a considerable quantity of conc. sulfuric acid and (b) the recommendation of a refluxing period preliminary to the distillation of the reaction mixture.

5. Detailed directions have been given for the preparations of *n*-butyl bromide, isoamyl bromide, trimethylene bromide, trimethylene chlorobromide, ethyl bromide, allyl bromide, *n*-octyl bromide, and lauryl bromide.