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The Preparation of Higher Aliphatic Bromides

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The preparation of higher aliphatic bromides from the alcohol and aqueous hydrobromic acid, or hydrobromic-sulfuric acid mixtures, has not been found by us to be satisfactory; the yields are not high, and the purification of the product is difficult because of the presence of residual alcohol and some charred material—both of which give rise to troublesome emulsions after the usual washing of the crude bromide with concentrated sulfuric acid. However, by the use of anhydrous hydrobromic acid and a new method of washing, these difficulties are largely eliminated. The results are summarized in Table I.

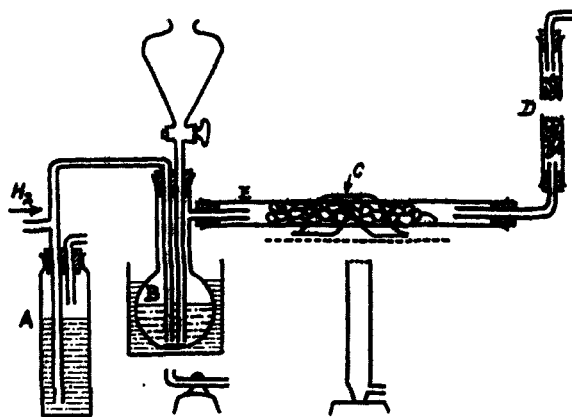


Fig. 1.—A, safety bottle; B, 125-cc. distilling flask, supported in a water-bath; C, one or two small pieces of asbestos paper;² D, tube 60 × 1.8 cm. filled with copper turnings to remove any uncombined bromine which may be carried over; E, reaction tube 30 × 1.8 cm., packed with pieces of porous plate about 8 mm. in diameter, and supported on a wire gauze, preferably with an asbestos center.

Gaseous hydrobromic acid is passed into the alcohol which is kept at about 100° until no more is absorbed. At least one and one-half hours is

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(2) The paper, which is to prevent the top of the tube from being cooled below the ignition temperature of an equimolar mixture of hydrogen and bromine, should not touch the tube, but should form a shield around it. If it is not placed in the proper position, the combination is incomplete, and free bromine is present in the hydrogen bromide.

TABLE I
THE PREPARATION OF HIGHER BROMIDES

Alcohol	Reaction temp., °C.	Concn. MeOH for washing, %	Soly. of bromide in wash MeOH, g. per 100 cc.	Yield of bromide, %
Cyclohexyl	80-100	65	<1.0	73
<i>n</i> -Heptyl	80-100	50	<0.5	88
Dodecyl	100-120	50	< .1	89
Tetradecyl	100-120	50	< .1	89
Octadecyl	100-120	90	< .1	90

allowed for saturation. Approximately 1.5 moles of acid per mole of alcohol is required to form the bromide and to saturate the water formed. The crude product, which has a very pale straw color, is washed first with concentrated sulfuric acid, which is run off; phenolphthalein is added, and the bromide is shaken with dilute methyl alcohol containing sufficient ammonia to neutralize any residual acid; it is finally washed with dilute methyl alcohol, dried with calcium chloride, filtered and distilled.

The sulfuric acid converts the residual alcohol present in the crude bromide to the alkyl acid sulfate, which is dissolved out by the dilute methyl alcohol and ammonia, but which is not appreciably soluble in sulfuric acid. The use of methyl alcohol instead of water in washing the crude bromide increases the sharpness and rapidity of the separation since the difference in density is greater and the tendency to form emulsions is less.

The anhydrous hydrobromic acid was obtained by the direct combination of hydrogen and bromine in an all-Pyrex apparatus shown in Fig. 1.³ The apparatus is thoroughly flushed out with hydrogen, bromine is immediately introduced into the flask B, and the Meker burner beneath C is lighted.⁴ After a minute or two a slow stream of hydrogen is turned on. A flickering yellow flame indicates that the reaction is occurring. The temperature of the water-bath is adjusted so that the vapor pressure of bromine is just less than half an atmosphere—about 40°. A length of at least 10 cm. of the combustion tube between the flask B and the flame should be maintained at about room temperature to prevent the flame from striking back. The apparatus will produce up to 300 g. of hydrobromic acid an hour, and may be operated as slowly as desired.

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(3) This is essentially a simplification of the method of Baxter and Coffin, *This Journal*, **31**, 297 (1909).

(4) A small electric furnace is preferable, but by no means necessary.