



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

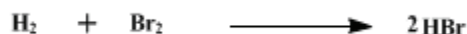
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 2, p.338 (1943); Vol. 15, p.35 (1935).*

## HYDROGEN BROMIDE (ANHYDROUS)

### [Hydrobromic acid]



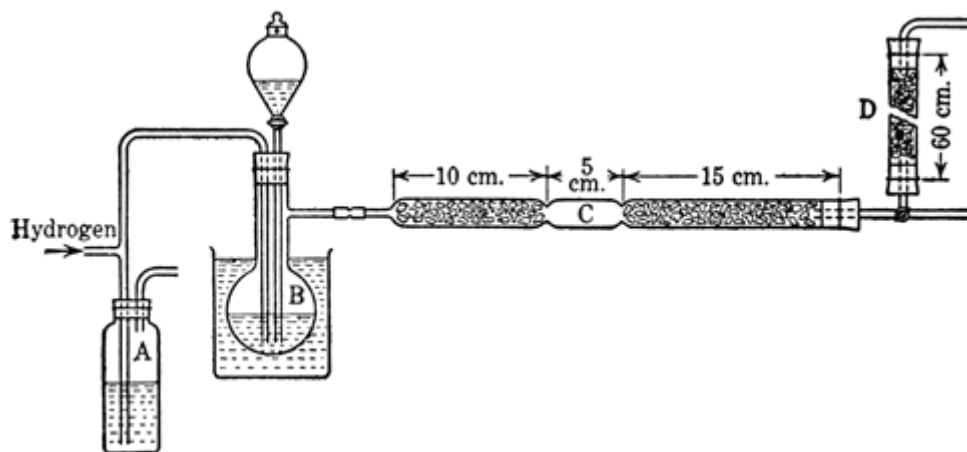
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Checked by W. H. Carothers and W. L. McEwen.

### 1. Procedure

(A) *Apparatus*.—A 125-cc. distilling flask (B, Fig. 9) (Note 1) is fitted with a two-holed rubber stopper bearing a 50-cc. dropping funnel (Note 2) and an inlet tube about 6 mm. in diameter, both of which reach to the bottom of the flask. The flask is supported in an 800-cc. beaker which serves as a water bath. The side arm of the flask is connected by means of a short piece of rubber tubing to the narrow end (Note 3) of the combustion tube C which is made of Pyrex glass and is 20 mm. in diameter (inside) and 30 cm. in length. It is packed with pieces of porous plate held in place by constrictions as shown in the figure, and it is supported at each end by a small clamp at a sufficient height to give a clearance of 3–4 cm. above a Bunsen burner. The open end of the tube is connected by means of stoppers and a three-way stopcock (Note 4) to the vertical tube D, of the same diameter as C and 60 cm. long. This tube is packed with copper turnings to remove any uncombined bromine which may escape from the combustion tube. A safety bottle A containing water or some other suitable liquid and having a tube leading to the vent of the hood is placed in the train to provide an outlet for the hydrogen in case an obstruction is formed in the apparatus. It also provides a convenient method for determining the hydrogen pressure (Note 5). Hydrogen is obtained from a cylinder fitted with a reducing valve.

Fig. 9

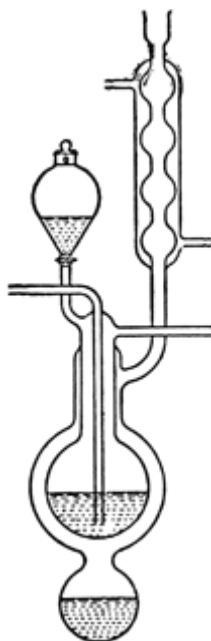


(B) *Operation*.—The tube D is disconnected from the combustion tube by turning the stopcock so that the gases pass directly to the hood. Bromine is placed in flask B; the water bath is heated to 38° and maintained at this temperature (Note 6). A slow stream of hydrogen is started through the apparatus, and, when the combustion tube is completely filled with bromine vapors, a low flame is placed under the empty section of the combustion tube. Soon a small yellow flame appears inside the heated portion of the tube, and, when all bromine vapor has been swept from the combustion tube, the latter is connected to the tube D (Note 7). The flame is adjusted to keep the lower part of the tube at a dull red heat; it may be necessary to raise or lower it, according to the rate of operation. The flow of hydrogen is regulated to give the desired output. The apparatus will conveniently produce 300 g. of hydrogen bromide per hour (Note 8).

### 2. Notes

1. It is convenient to bend the side arm of the distilling flask so that it is perpendicular to the neck.
  2. The stopcock of the dropping funnel should be held in place by means of a rubber band.
  3. The distilling flask may be connected to the combustion tube by means of a rubber stopper, but it is preferable to seal a piece of 6-mm. tubing to one end and to use a small piece of rubber tubing for the connection. Even with this arrangement the connection must be inspected from time to time to be sure that the tube is not obstructed. It is still more satisfactory to use a ground-glass joint.
  4. The three-way stopcock may be dispensed with, but it facilitates the starting operation and provides a quick method for venting the gas in case combination does not take place properly, thus preventing deterioration of the [copper turnings](#).
  5. When operating to produce about 300 g. of [hydrogen bromide](#) per hour the water level is depressed approximately 12 cm.
  6. The vapor pressure of [bromine](#) should be maintained at half an atmosphere. The vapor pressure of [bromine](#) is reported as 324 mm. at 35° and 392 mm. at 40°. If the bath becomes too warm, it should be cooled at once with ice; otherwise more [bromine](#) will be evaporated than will combine with the [hydrogen](#) present.
- A more convenient form of apparatus for the vaporization of [bromine](#) is shown in [Fig. 10](#). This is the same in principle as that described in the above procedure, but the [bromine](#) container instead of being heated by warm water is heated by the vapor of boiling [ethyl bromide](#) (38.4°). Thus no attention to a water bath is required.
7. The [copper turnings](#) remove any trace of [bromine](#) that may be present by converting it to black [cupric bromide](#). If the level of blackened [copper](#) rises, [bromine](#) is being carried over. The presence of a small quantity of moisture, however, will cause a slight darkening of all the [copper](#).

**Fig. 10**



Alternatively, [bromine](#) may be removed by passing the [hydrogen bromide](#) through a solution of [phenol](#) in [carbon tetrachloride](#) (*Org. Syn.* **20**, 65).

If very dry [hydrogen bromide](#) is desired, a small trap surrounded by solid [carbon dioxide](#) and placed in the train will condense the water and a small amount of [hydrogen bromide](#). Attention is necessary to prevent clogging of the trap.

8. According to the literature,<sup>1</sup> in the preparation of [hydrogen bromide](#) by combination of the elements the chief difficulties are avoiding explosive combination on the one hand and spontaneous extinction of the flame on the other hand. Neither of these difficulties has been encountered in repeated operations extending over many hours with the apparatus described above.

### 3. Discussion

The very extensive literature on the preparation of [hydrogen bromide](#) is completely and concisely reviewed in Gmelin's "Handbuch."<sup>1</sup> The methods most commonly used involve the hydrolysis of certain bromides, particularly the action of [bromine](#) on red phosphorus and water; the action of [bromine](#) on hydrocarbons, particularly on [tetralin](#); and the direct combination of the elements. The action of [bromine](#) on [tetralin](#) is a convenient one for small-scale laboratory operation.<sup>2</sup> The direct combination of the elements has certain advantages of simplicity and cleanliness especially when considerable amounts of [hydrogen bromide](#) are required. [Platinum](#) and charcoal have frequently been used as catalysts but they can be dispensed with at sufficiently high temperatures.<sup>3</sup>

Detailed directions for preparing [hydrogen bromide](#) by the bromination of and by the direct combination of [hydrogen](#) and [bromine](#) are given in Inorganic Syntheses.<sup>4</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 246](#)
- [Org. Syn. Coll. Vol. 3, 11](#)
- [Org. Syn. Coll. Vol. 3, 576](#)
- [Org. Syn. Coll. Vol. 5, 545](#)

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## References and Notes

1. Gmelin, "Handbuch der anorganischen Chemie," 8th ed., Part VII, p. 182, Verlag Chemie, Berlin, 1931.
  2. For details see Houben, "Die Methoden der organischen Chemie," 3rd ed., Vol. III, p. 1156, Verlag Georg Thieme, Leipzig, 1930.
  3. Ruhoff, Burnett, and Reid, J. Am. Chem. Soc. **56**, 2784 (1934).
  4. Inorganic Syntheses, **I**, 149, McGraw-Hill, New York, 1939.
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## Appendix

### Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

red phosphorus

[hydrogen](#) (1333-74-0)

[phenol](#) (108-95-2)

[HYDROBROMIC ACID](#),  
[hydrogen bromide](#) (10035-10-6)

[bromine](#) (7726-95-6)

[Ethyl bromide](#) (74-96-4)

[carbon tetrachloride](#) (56-23-5)

[carbon dioxide](#) (124-38-9)

[platinum](#) (7440-06-4)

copper,  
copper turnings (7440-50-8)

Tetralin (119-64-2)

cupric bromide (7789-45-9)