



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.

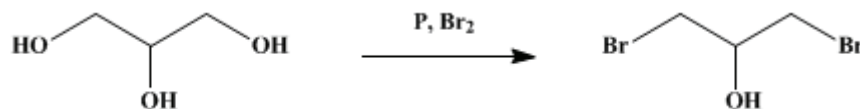
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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.308 (1943); Vol. 14, p.42 (1934).*

## GLYCEROL $\alpha,\gamma$ -DIBROMOHYDRIN

[2-Propanol, 1,3-dibromo-]



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### 1. Procedure

In a 3-l. three-necked, round-bottomed flask, fitted with a powerful glycerol-sealed stirrer, a dropping funnel, and an outlet tube for escaping gases, 1.6 kg. (17.4 moles) of [glycerol](#) is thoroughly mixed with 200 g. (6.5 gram atoms) of red phosphorus ([Note 1](#)). Nine hundred cubic centimeters (2808 g., 17.5 moles) of [bromine](#) ([Note 2](#)) is then gradually added, with effective stirring ([Note 3](#)), through the dropping funnel in the course of about eight hours. To minimize the escape of [bromine](#), the end of the dropping funnel should reach almost to the bottom of the flask. The by-product gases, consisting mainly of [hydrogen bromide](#) and some [bromine](#), are led over concentrated [sodium hydroxide](#) solution or to a gas trap. The reaction is exothermic, and the temperature quickly rises to 80–100°; then the addition of [bromine](#) is so regulated that this temperature is maintained. Toward the end of the period of addition of [bromine](#), the flask is placed in a water bath at 70–75°. After all the [bromine](#) has been added, the mixture is allowed to stand overnight and is then warmed on the water bath until all the [bromine](#) is consumed (one to two hours).

The reaction mixture is transferred to a 3-l. round-bottomed flask provided with a two-holed rubber stopper carrying a wide delivery tube and a capillary tube. The flask is heated in an oil bath, and distillation is begun under the reduced pressure of a water pump. The receiver is cooled with water. At first a mixture of [hydrobromic acid](#) and water passes over; later the dibromohydrin distils. The temperature of the bath is raised as fast as the boiling of the mass permits, and is eventually brought to 180°. The distillation is carefully watched at the end and immediately interrupted at the first sign of decomposition. This is clearly indicated by gas formation, in consequence of which the vacuum cannot be maintained at the previous level. To the straw-yellow distillate a slight excess of solid [sodium bicarbonate](#) is added with continuous shaking until effervescence ceases. The inorganic salts are removed by filtration, and the aqueous layer of the filtrate is separated from the crude dibromohydrin. The latter is purified by fractional distillation under reduced pressure from a 2-l. Claisen flask. The distillation is continued until no more water passes over and the inside temperature reaches 100°. Then the dibromohydrin is separated from the water in the distillate, dried with anhydrous [sodium sulfate](#), filtered, and poured back into the distilling flask. By this operation the water is largely removed ([Note 4](#)). Then the distillation is continued as before and, after a small fore-run, the dibromohydrin boils at 110–112° under 20 mm. pressure ([Note 5](#)). The yield is 2000–2050 g. (52–54 per cent of the theoretical amount) of a colorless product.

The dibromohydrin is a heavy, colorless liquid with a characteristic odor. On standing it gradually becomes yellow. Its specific gravity at 20° is about 2.14.

### 2. Notes

1. The red phosphorus should be thoroughly mixed with the [glycerol](#) before the addition of the [bromine](#). The [bromine](#) should not come into contact with the dry [phosphorus](#) or a violent reaction will occur.
2. Commercial 98 per cent [glycerol](#) and u.s.p. [bromine](#) may be used in the preparation.
3. A powerful stirrer is necessary because of the viscous nature of the reaction mixture.
4. The water derives from the chemical interaction of [phosphorous acid](#) with the [glycerol](#) or with the bromohydrins. Better yields are obtained when the theoretical amount of [bromine](#) is used, although on

account of this secondary reaction a smaller amount should suffice.

5. The crude dibromohydrin distils without any decomposition at 10–15 mm. pressure if the temperature of the oil bath is not raised over 190°. Above this temperature, formation of acrolein derivatives makes the dibromohydrin lachrymatory.

### 3. Discussion

Glycerol  $\alpha,\gamma$ -dibromohydrin has been prepared from [glycerol](#) and [phosphorus tribromide](#);<sup>1</sup> from [glycerol](#) and [bromine](#);<sup>2</sup> and from [glycerol](#), [phosphorus](#), and [bromine](#).<sup>3, 4, 5</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 256](#)

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### References and Notes

1. Berthelot and de Luca, *Ann. chim. phys.* (3) **48**, 306 (1856).
  2. Barth, *Ann.* **124**, 349 (1862).
  3. Aschan, *Ber.* **23**, 1826 (1890).
  4. Lespieau, *Ann. chim. phys.* (7) **11**, 236 (1897).
  5. Braun, *J. Am. Chem. Soc.* **52**, 3172 (1930).
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### Appendix

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

red phosphorus

Glycerol  $\alpha,\gamma$ -dibromohydrin

[sodium hydroxide](#) (1310-73-2)

[glycerol](#) (56-81-5)

[sodium bicarbonate](#) (144-55-8)

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

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

[PHOSPHORUS](#) (7723-14-0)

[sodium sulfate](#) (7757-82-6)

[phosphorus tribromide](#) (7789-60-8)

[2-Propanol, 1,3-dibromo-](#) (96-21-9)

[phosphorous acid](#) (13598-36-2)

