



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). 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.

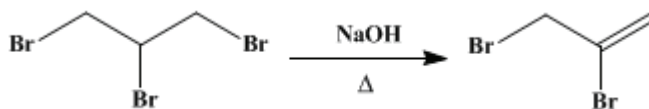
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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. 1, p.209 (1941); Vol. 5, p.49 (1925).

2,3-DIBROMOPROPENE

[Propene, 2,3-dibromo-]



Submitted by R. Lespieau and M. Bourguel.

Checked by C. S. Marvel, John R. Johnson, and W. L. McEwen.

1. Procedure

A 500-cc. round-bottomed flask is connected by a wide, bent glass tube to an efficient condenser, which is provided with an adapter leading into a 500-cc. receiving flask immersed in an ice bath. Two hundred grams (0.71 mole) of 1,2,3-tribromopropane (Note 1) and 10 cc. of water are placed in the reaction flask, and 50 g. (1.25 moles) of sodium hydroxide (Note 2) in small lumps (not pulverized) is added at once with shaking. The mixture warms up and the flask is immediately connected to the apparatus and heated directly by means of a Bunsen burner held in the hand. It is advisable to use a slightly luminous flame about 15 cm. high and to heat with a rotary motion, directing the flame against the sides of the flask.

The mixture is shaken occasionally, and the alkaline layer soon becomes partly emulsified. Heat is applied until vigorous ebullition occurs, whereupon a spontaneous distillation of the reaction product takes place (Note 3). When the reaction slackens, the flask is heated as before. The mass becomes solid as the volatile products are removed. This solid mass, which is brownish in color, is heated until no more liquid distils (Note 4). The entire operation up to this point requires twenty to thirty minutes.

The distillate in the receiving flask separates into two layers: an upper layer of water; and a heavy layer of colorless oil, consisting of a mixture of 2,3-dibromopropene and unchanged tribromopropane. The distillate is transferred to a 500-cc. separatory funnel and thoroughly agitated with an additional 150 cc. of water (Note 5). The lower layer is decanted and found to weigh 140–145 g. It is subjected to a preliminary distillation under reduced pressure to separate most of the unchanged tribromopropane. The material that passes over below 95° /75 mm. consists of 2,3-dibromopropene containing a small amount of water and tribromopropane, and weighs 120–130 g. The residue in the distilling flask consists of unchanged tribromopropane (15–25 g.) (Note 6).

The crude product is dried over calcium chloride and fractionally distilled under reduced pressure (Note 7). The yield of pure, colorless, 2,3-dibromopropene boiling at 73–76° /75 mm. is 105–120 g. (74–84 per cent of the theoretical amount). A small quantity of tribromopropane, usually about 5 per cent of the crude material, remains in the distilling flask (Note 6).

2. Notes

1. The crude tribromopropane, obtained as described on p. 521, may be used without lowering the yield.
2. Potassium hydroxide may be used in place of sodium hydroxide, but it was found that the reaction is much more violent and irregular and the yields are somewhat lower. If potassium hydroxide is used, it is advisable to provide the receiving flask with a reflux condenser to avoid loss when the initial violent reaction occurs. Since the reaction is so rapid, it would be very dangerous to use more than 200 g. of tribromopropane in a single run with potassium hydroxide.
3. In the initial vigorous ebullition, about one-half of the material distils during a few minutes and it is necessary to wait for this reaction to slacken before continuing to heat the flask. If sodium hydroxide is used, the reaction is vigorous but not violent, and it is possible to use 600 g. of tribromopropane in a 1-l. flask in a single run without danger if the reaction flask is connected with the condenser by means of a wide tube. The yields in larger runs are as good as when smaller runs are made.

4. A small additional quantity of distillate may be obtained by partially evacuating the apparatus, after replacing the adapter and receiving flask by a 250-cc. distilling flask. The amount of material obtained in this way amounts to only 1–2 g. if the reaction flask has been properly heated. It is well to note that flasks which have been repeatedly heated with very strong alkalis become fragile, and care should be used not to reduce the pressure too greatly.

5. The [dibromopropene](#) and the wash water have a strong lachrymatory effect and should be manipulated carefully.

6. When a sufficient quantity of these crude residues of [tribromopropane](#) has been collected, it may be used for preparing [2,3-dibromopropene](#). If allowance is made for this recovered material, the yield of [2,3-dibromopropene](#) is 82–87 per cent of the theoretical amount.

7. The separation of [2,3-dibromopropene](#) from [tribromopropane](#) is effected easily since their boiling points are quite different:

Pressure	2,3-Dibromopropene	Tribromopropane
18 mm.	42–43°	101–102°
75 mm.	75–76°	140–142°
760 mm.	140–143°	219–221°

These substances may be distilled under atmospheric pressure with only slight decomposition, but the products become highly colored on standing.

3. Discussion

[2,3-Dibromopropene](#) can be prepared by the action of [potassium](#)¹ or [sodium hydroxide](#)² on [tribromopropane](#), and by the action of [metallic sodium](#) on an ethereal solution of [tribromopropane](#).³

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 186](#)
- [Org. Syn. Coll. Vol. 5, 121](#)
- [Org. Syn. Coll. Vol. 5, 124](#)

References and Notes

1. Reboul, *Ann. chim. phys.* (3) **60**, 42 (1860); Lespieau, *ibid.* (7) **11**, 235 (1897); *Bull. soc. chim.* (4) **29**, 530 (1921); Henry, *Ann.* **154**, 371 (1870); *Ber.* **14**, 404 (1881).
2. Lespieau, *Ann. chim. phys.* (7) **11**, 235 (1897); *Bull. soc. chim.* (4) **29**, 530 (1921).
3. Tollens, *Ann.* **156**, 168 (1870).

Appendix

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

[calcium chloride](#) (10043-52-4)

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

[potassium hydroxide](#) (1310-58-3)

metallic sodium (13966-32-0)

potassium (7440-09-7)

2,3-Dibromopropene,
Propene, 2,3-dibromo- (513-31-5)

dibromopropene (13195-80-7)

1,2,3-Tribromopropane (96-11-7)

tribromopropane