



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.

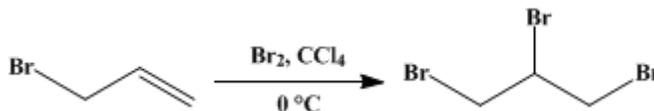
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 1, p.521 (1941); Vol. 5, p.99 (1925).*

## 1,2,3-TRIBROMOPROPANE



Submitted by John R. Johnson and W. L. McEwen.  
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### 1. Procedure

A 1-l. round-bottomed flask is provided with a mechanical stirrer, a dropping funnel, a calcium chloride exit tube, and a thermometer which reaches nearly to the bottom of the flask. In the flask are placed 181.5 g. (1.5 moles) of [allyl bromide](#) ([Note 1](#)) and 250 cc. of dry [carbon tetrachloride](#) ([Note 2](#)). In the dropping funnel is placed 255 g. (80 cc., 1.56 moles) of [bromine](#) which has been washed once with an equal volume of concentrated [sulfuric acid](#). The mechanical agitation is started and the flask is cooled in a mixture of ice and salt. When the temperature has fallen to  $-5^{\circ}$ , the [bromine](#) is allowed to drop in slowly at such a rate that the temperature remains at about  $-5^{\circ}$  and never rises above  $0^{\circ}$  ([Note 3](#)). The addition of the [bromine](#) requires about one and one-half hours. The solution is usually orange-red in color at the end of the reaction, owing to the slight excess of [bromine](#). It is allowed to warm up to room temperature with continuous stirring (about one-half hour) and is then transferred to a large separatory funnel. The flask is washed once with a 10–15 cc. portion of [carbon tetrachloride](#).

A 500-cc. Claisen flask is arranged for distilling the solvent and the solution is dropped in from the funnel at such a rate that the flask is never more than two-thirds full. The Claisen flask is heated in an oil bath, and the [carbon tetrachloride](#) distils when the oil bath reaches about  $120^{\circ}$ . As much as possible of the solvent is removed at atmospheric pressure by allowing the temperature of the oil bath to rise to  $150^{\circ}$ . The remainder of the [carbon tetrachloride](#) is removed under a pressure of about 20 mm. by collecting a fraction until the thermometer registers a sudden rise (temperature of the oil bath about  $120^{\circ}$ ).

The residue in the distilling flask is practically pure [1,2,3-tribromopropane](#) ([Note 4](#)) and boils at  $100\text{--}103^{\circ}/18$  mm. On cooling in an ice-salt mixture and scratching vigorously, the [tribromopropane](#) solidifies to a mass of white needles, which melt below room temperature. The yield is 406–413 g. (96–98 per cent of the theoretical amount). If an absolutely colorless product is desired, it is advisable to collect the first few drops of distillate separately, since they may be slightly yellow. The product on long standing becomes yellow, but when the colored product is used in reactions it gives yields that indicate a high degree of purity.

### 2. Notes

- [Allyl bromide](#) ([p. 27](#)) was dried with [calcium chloride](#) and distilled through a fractionating column. The portion boiling at  $69.5\text{--}71.5^{\circ}$  was collected.
- [Carbon tetrachloride](#) was purified by distilling the commercial product and rejecting the first 10 per cent of the distillate, thus eliminating the water.
- A yield of 93 per cent of the theoretical amount is obtained when the reaction is run at a temperature of  $25\text{--}30^{\circ}$ . At the higher temperature, there is a small amount of high-boiling product left in the flask after the final distillation.
- The crude [1,2,3-tribromopropane](#) which remains after complete removal of the [carbon tetrachloride](#) weighs 418–420 g. It is almost pure and can be used for a number of reactions without further purification.

### 3. Discussion

[1,2,3-Tribromopropane](#) can be prepared by the action of [phosphorus pentabromide](#) on either

epibromohydrin<sup>1</sup> or symmetrical dibromohydrin;<sup>1,2</sup> by the action of bromine, in the presence of iron, on propylene bromide;<sup>3</sup> by the addition of bromine to allyl bromide;<sup>4</sup> by the addition of hydrogen bromide to 1,3-dibromopropene;<sup>5</sup> and by the action of bromine and phosphorus on glycerol.<sup>6</sup> The procedure described is essentially that of Perkin and Simonsen.<sup>4</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 209](#)

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## References and Notes

1. Berthelot and Luca, *Ann.* **101**, 76 (1857).
  2. Henry, *Ann.* **154**, 369 (1870).
  3. Kronstein, *Ber.* **24**, 4245 (1891); Tapley and Giesy, *J. Am. Pharm. Assoc.* **15**, 173 (1926).
  4. Tollens and Henninger, *Ann.* **156**, 168 (1870); Perkin and Simonsen, *J. Chem. Soc.* **87**, 859 (1905).
  5. Kirmann and Renn, *Compt. rend.* **202**, 1934 (1936).
  6. Goshorn and Degering, *Proc. Indiana Acad. Sci.* **45**, 139 (1935) [*C. A.* **31**, 1004 (1937)].
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## Appendix

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

symmetrical dibromohydrin

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

[sulfuric acid](#) (7664-93-9)

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

[iron](#) (7439-89-6)

[hydrogen bromide](#) (10035-10-6)

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

[Allyl bromide](#) (106-95-6)

[propylene bromide](#) (78-75-1)

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

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

[1,2,3-Tribromopropane](#) (96-11-7)

[tribromopropane](#)

phosphorus pentabromide (7789-69-7)

Epibromohydrin (3132-64-7)

1,3-dibromopropene

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