



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.

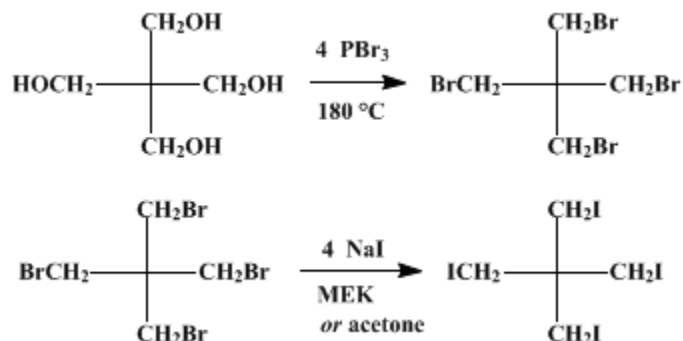
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.476 (1943); Vol. 17, p.73 (1937).

PENTAERYTHRITYL BROMIDE AND IODIDE

[[Methane, tetrakis(bromomethyl)- and (iodomethyl)-]]



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1. Procedure

(A) *Pentaerythrityl Bromide*.—One hundred twenty-five grams (0.92 mole) of dry *pentaerythritol* (*Org. Syn. Coll. Vol. I, 1941, 425*) is placed in a 500-cc. round-bottomed flask provided with an air-cooled reflux condenser bearing at the upper end a long-stemmed dropping funnel and a bent glass tube. The tube is connected to a suitable trap for absorbing the large quantity of *hydrogen bromide* which is evolved. The flask is heated on a steam bath, and 500 g. (175 cc., 1.85 moles) of freshly distilled *phosphorus tribromide* (p. 359) is added cautiously from the dropping funnel. When this addition has been completed the steam bath is replaced by an oil bath and the temperature is raised gradually to 170–180° (*Note 1*). After heating at this temperature for twenty hours, the orange-red reaction mixture is transferred to a beaker containing 1 l. of cold water and stirred thoroughly to reduce the lumps to a small size. The red, flocculent material is filtered with suction and washed several times with hot water; finally it is washed thoroughly with two 200-cc. portions of cold 95 per cent *ethyl alcohol* (*Note 2*). After drying, the material is transferred to a large Soxhlet extractor and extracted exhaustively with 95 per cent *alcohol* (*Note 3*). The *pentaerythrityl bromide* separates from the alcohol and after cooling is collected with suction. The yield of crude product melting at 158–160° is 245–270 g. (69–76 per cent of the theoretical amount); this material is sufficiently pure for conversion to the iodide (*Note 4*). For purification, the crude product may be recrystallized from 95 per cent *alcohol*, using 30 cc. of solvent per gram; the melting point is raised to 163°, and the recovery is about 85 per cent.

(B) *Pentaerythrityl Iodide*.—In a 500-cc. round-bottomed flask fitted with a reflux condenser, a mixture of 100 g. (0.67 mole) of *sodium iodide* (dried at 120°), 300 cc. (240 g.) of *ethyl methyl ketone* (*Note 5*), and 50 g. (0.13 mole) of crude *pentaerythrityl bromide* (m.p. 158–160°) is refluxed on a steam bath for forty-eight hours. The condenser is set for distillation, the solvent is distilled, and the residue is washed into a hot Büchner funnel with hot water. The product is washed thoroughly on the funnel with boiling water, pressed well, and transferred to a large Soxhlet extractor. To remove impurities the material is extracted with boiling 95 per cent *alcohol* until a sample removed from the extraction thimble melts at 233° (*Note 6*). The product is then removed from the thimble and dried; the yield is 66–73 g. (89–98 per cent of the theoretical amount). The crude product may be recrystallized from hot *benzene*, using about 18 cc. of solvent per gram. The recovery is about 80 per cent, and the melting point is not changed.

2. Notes

1. The temperature must be raised slowly to avoid formation of spontaneously inflammable hydrides of phosphorus which will ignite and destroy the preparation. A similar result occurs if the *phosphorus*

tribromide is added at 170°.

2. This washing eliminates intermediate bromohydrins.

3. Since the extraction is slow, it is advisable to divide the material into several portions and carry out a number of simultaneous extractions. The extractor used was a modified Soxhlet, arranged so that the extractor tube is heated by the vapor of the solvent (p. 524, Note 3).

4. The crude product has a disagreeable odor, probably due to the presence of a compound of phosphorus. The odor may be eliminated by heating at 120°, followed by several recrystallizations.

5. Acetone may be used as solvent in place of ethyl methyl ketone, but the reaction must then be carried out in a sealed vessel at 95–100° for thirty to thirty-six hours.

6. The extraction requires twelve to sixteen hours, depending upon the rate of refluxing of the alcohol.

3. Discussion

Pentaerythrityl bromide has been prepared by the action of phosphorus tribromide on pentaerythritol,^{1, 2} and of an acetic acid solution of hydrobromic acid on pentaerythrityl tetracetate.³ The iodide has been prepared by the action of red phosphorus and hydriodic acid on pentaerythritol⁴ and by treating the bromide with sodium iodide in acetone.²

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 753

References and Notes

1. Rave and Tollens, Ann. **276**, 61 (1893); Gustavson, J. prakt. Chem. (2) **54**, 98 (1896).
2. Backer and Schurink, Rec. trav. chim. **50**, 924 (1931).
3. Perkin and Simonsen, J. Chem. Soc. **87**, 860 (1905).
4. Tollens and Wigand, Ann. **265**, 331 (1891).

Appendix

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

red phosphorus

Methane, tetrakis(bromomethyl)- and (iodomethyl)-

ethyl alcohol,
alcohol (64-17-5)

acetic acid (64-19-7)

Benzene (71-43-2)

HYDROBROMIC ACID,
hydrogen bromide (10035-10-6)

phosphorus tribromide (7789-60-8)

acetone (67-64-1)

hydriodic acid (10034-85-2)

sodium iodide (7681-82-5)

Pentaerythritol (115-77-5)

iodide (20461-54-5)

ethyl methyl ketone (78-93-3)

Pentaerythrityl bromide (3229-00-3)

Pentaerythrityl iodide (1522-88-9)

pentaerythrityl tetracetate (597-71-7)