Organic
Syntheses

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.

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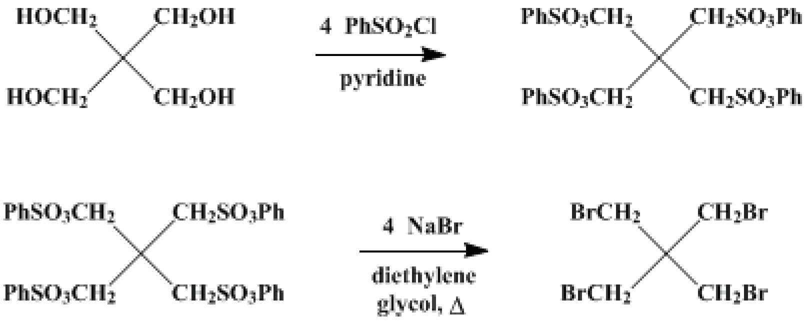
PENTAERYTHRITYL TETRABROMIDE

[Propane, 1,3-dibromo-2,2-bis(bromomethyl)-]



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1. Procedure

In a 5-l. three-necked round-bottomed flask equipped with a powerful mechanical stirrer (Note 1), a thermometer, and a 1-l. dropping funnel are placed 130 g. (0.96 mole) of technical grade pentaerythritol (Note 2) and 650 ml. of pyridine. The stirrer is started, and to the resulting suspension is added dropwise 750 g. (4.24 moles) of benzenesulfonyl chloride (Note 3) at such a rate that the temperature of the reaction does not rise above 30–35°. The addition requires about 2 hours. The resulting slurry is stirred at 40° for 1 hour after the addition is complete. The slurry is then added slowly (Note 4) to a vigorously stirred solution of 800 ml. of concentrated hydrochloric acid in 1 l. of water and 2 l. of methanol contained in a 9 by 15 in. battery jar. The resulting suspension of granular white pentaerythrityl benzenesulfonate is cooled by addition of 500 g. of ice, filtered with suction, and washed with 5 l. of water and then with 1 l. of cold methanol in two portions.

The crude, slightly wet pentaerythrityl benzenesulfonate is added to 1 l. of diethylene glycol (Note 5) in a 4-l. Erlenmeyer flask equipped with a Hershberg stirrer. Then 600 g. (5.8 moles) of sodium bromide is added, and the mixture is heated in an oil bath at 140–150° with slow stirring (60–120 r.p.m.) overnight. The resulting orange mixture is allowed to cool to about 90°, 2 l. of ice water is added rapidly with stirring, and finally the mixture is cooled to 10° by direct addition of ice. The precipitate is filtered with suction, washed with 2 l. of water, and pressed dry. The yield is 315–323 g. of a crude tan crystalline solid, m.p. 147–149°. The solid is dissolved in 2 l. of boiling acetone and filtered by gravity on a steam-heated funnel. On cooling, the solution deposits colorless glistening plates, which are filtered with suction and washed with 100 ml. of cold 95% ethanol, yielding 150–160 g. of pentaerythrityl tetrabromide, m.p. 159–160° (Note 6). By repeated concentration and cooling of the mother liquor, an additional 90–100 g. of pentaerythrityl tetrabromide, m.p. 156.5–158° (Note 6), is obtained. The combined yield is 228–260 g. (68–78%) (Note 7).

2. Notes

1. A powerful stirrer is necessary to mix the reactants, particularly in the later stages of the reaction when the mixture is quite viscous. The submitter and checkers used a "Lightnin" stirrer.
2. Heyden Chemical Corporation technical grade pentaerythritol (Pentek) was found to be satisfactory. It contains about 90% pentaerythritol, the remainder being principally dipentaerythritol.
3. Eastman Kodak Company practical grade benzenesulfonyl chloride was used.
4. Crystallization is extremely slow at first and becomes satisfactory only when the mixture is well seeded. It is well to remove a small portion first and work it up in the hydrochloric acid solution with a spatula to induce crystallization. The mixture should be added slowly at first but more rapidly toward the end.

5. Eastman Kodak Company practical grade diethylene glycol was used.
6. The checkers observed melting points about 2° lower.
7. The yield is based on the assumption that 90% of the starting material is pentaerythritol.

3. Discussion

The procedure given was developed by Buchman, Herzog, and Fujimoto.[2] Pentaerythrityl bromide has also been prepared from phosphorus tribromide and pentaerythritol,[3] and by the action of hydrobromic acid on pentaerythrityl tetraacetate in acetic acid.[4]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 153

References and Notes

1. California Institute of Technology, Pasadena, California.
2. Buchman, Herzog, and Fujimoto, unpublished results.
3. *Org. Syntheses Coll. Vol.* **2**, 476 (1943).
4. Perkin and Simonsen, *J. Chem. Soc.*, **87**, 860 (1905).

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

dipentaerythritol

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

methanol (67-56-1)

HYDROBROMIC ACID (10035-10-6)

sodium bromide (7647-15-6)

phosphorus tribromide (7789-60-8)

acetone (67-64-1)

Benzenesulfonyl chloride (98-09-9)

pyridine (110-86-1)

Pentaerythritol (115-77-5)

Pentaerythrityl bromide,
Pentaerythrityl tetrabromide,
Propane, 1,3-dibromo-2,2-bis(bromomethyl)- (3229-00-3)

pentaerythrityl tetraacetate (597-71-7)

diethylene glycol (111-46-6)

pentaerythrityl benzenesulfonate