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.

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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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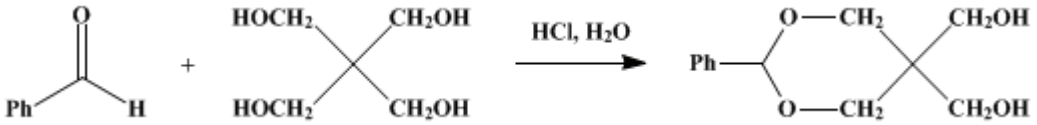
MONOBENZALPENTAERYTHRITOL

[*m*-Dioxane-5,5-dimethanol, 2-phenyl-]



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1. Procedure

In an open 3-l. three-necked flask are placed 180 g. (1.32 moles) of pentaerythritol (Note 1) and 1.3 l. of water. The flask is fitted with an efficient mechanical stirrer and a graduated dropping funnel containing 147 g. (1.38 moles) of benzaldehyde (Note 2). The mixture in the flask is heated until all the solid dissolves and is then allowed to cool undisturbed (Note 3).

When the solution has cooled to room temperature, stirring is started and 6.6 ml. of concentrated hydrochloric acid is added through the open neck of the flask, followed by 30 ml. of benzaldehyde from the dropping funnel. When the precipitate of monobenzalpentaerythritol starts forming, dropwise addition of benzaldehyde is begun (Note 4). After the addition of benzaldehyde is completed, the mixture is stirred for an additional 3 hours (Note 5). The precipitate is collected (Note 6) on a Büchner funnel and washed with ice-cold water which has been made slightly alkaline by addition of sodium carbonate. The solid is transferred to a 3-l. round-bottomed flask, 1 l. of water (slightly alkaline with sodium carbonate) is added, and the mixture is heated to 100° (Note 7). After about 10 minutes at this temperature the hot mixture is filtered quickly through a fluted filter paper (Note 8). The solid remaining on the filter paper is washed with 50 ml. of hot water (made slightly alkaline with sodium carbonate) (Note 9). The combined aqueous filtrates are cooled in an ice bath for several hours, and the crystals are collected on a Büchner funnel and dried. The dry product is heated under reflux for 15 minutes in an Erlenmeyer flask with 200 ml. of toluene, and the hot mixture is allowed to cool to room temperature, with continuous agitation (stirring rod) to prevent formation of hard lumps. Finally, the mixture is cooled in an ice bath for 5 hours, and the solid product is collected on a Büchner funnel and dried (Note 10). The yield of monobenzalpentaerythritol melting at 134–135° is 215–227 g. (73–77%).

2. Notes

1. Eastman Kodak Company white label grade pentaerythritol was used. The checkers used a commercial sample obtained from the Heyden Chemical Corporation.
2. The third neck may be left open and used later for addition of hydrochloric acid and for introduction of the thermometer.
3. The temperature of the solution should not be allowed to go below 25°; otherwise pentaerythritol will precipitate.
4. The addition should take about 2.5 hours. The temperature of the mixture should be kept at 25–29°.
5. If stirring is continued for a substantially longer period, the yield of monobenzalpentaerythritol is somewhat decreased.
6. The product should be collected immediately, as losses result if there is delay at this point.
7. The mixture should be stirred continuously during the heating. The use of a mechanical stirrer is recommended.
8. Use of a steam-heated funnel is recommended.
9. The solid remaining finally on the filter paper may be recrystallized from 1-butanol to give 1–2 g. of dibenzalpentaerythritol melting at 159–160°.
10. The product and the toluene in the Erlenmeyer flask form a solid mass which is difficult to remove. The operation is made easier by adding 70 ml. of ice-cold toluene to the flask and stirring, before

transferring the product to the Büchner funnel. One or two additional 20-ml. portions of cold toluene may be used to remove the product completely.

3. Discussion

The procedure described is based on the method of E. Bograchov.[2]

References and Notes

1. American University of Beirut, Beirut, Lebanon.
2. E. Bograchov, *J. Am. Chem. Soc.*, **72**, 2268 (1950).

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

hydrochloric acid (7647-01-0)

sodium carbonate (497-19-8)

benzaldehyde (100-52-7)

1-butanol (71-36-3)

toluene (108-88-3)

Pentaerythritol (115-77-5)

Monobenzalpentaerythritol

dibenzalpentaerythritol

m-Dioxane-5,5-dimethanol, 2-phenyl- (2425-41-4)