



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.

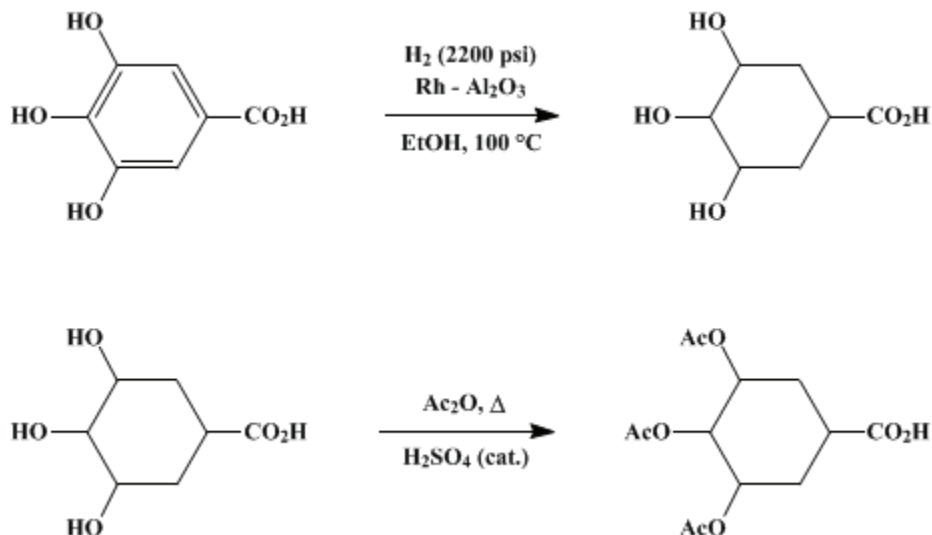
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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HEXAHYDROGALLIC ACID AND HEXAHYDROGALLIC ACID TRIACETATE

[Cyclohexanecarboxylic acid, 3,4,5-triol and triacetate]



Submitted by Albert W. Burgstahler and Zoe J. Bithos¹.
Checked by R. P. Lutz and John D. Roberts.

1. Procedure

A. *Hexahydrogallic acid*. A solution of 50 g. (0.266 mole) of recrystallized gallic acid monohydrate (Note 1) in 225 ml. of 95% ethanol (Note 2) is placed in a 1-l. high-pressure hydrogenation bomb (Note 3) with 8 g. of 5% rhodium-alumina catalyst (Note 4). The bomb is then closed, hydrogen admitted at full tank pressure (2200 lb., (Note 5)), and the temperature raised to 90–100° (Note 6) while agitation is commenced. When the hydrogen uptake is complete (8–12 hours), heating is discontinued and the bomb is allowed to cool. The residual hydrogen is bled off, and the contents of the bomb are rinsed out with two 40-ml. portions of warm distilled water and then heated to boiling on the steam bath for 5 minutes to dissolve any product which has crystallized on the catalyst. After removal of the catalyst by suction filtration (Note 7), the colorless filtrate (Note 8) is concentrated on the steam bath under reduced pressure (preferably using a rotary evaporator). The viscous residue which may have begun to deposit crystals is diluted with 75–100 ml. of ethyl acetate and the product allowed to crystallize at 0° for several hours or overnight. The product is collected on a 9-cm. Büchner funnel and washed with 75 ml. of cold 3:1 ethyl acetate-absolute ethanol and finally with 100 ml. of 30–40° petroleum ether. When dry, it weighs 21–24 g. (45–51%); an additional 2–4 g. can usually be obtained by concentration of the mother liquors and crystallization from ethyl acetate. Recrystallization is achieved by dissolution of the combined products in the minimum amount of boiling water (Note 9), suction filtration if necessary to remove suspended matter (Note 10), addition of hot ethanol to bring the volume of the solution to about 110 ml., and finally addition of about 35 ml. of acetone, sufficient to produce a faint cloudiness. The solution is allowed to cool slowly to room temperature and is then stored at 0° overnight. The fine, colorless crystals are collected on a 7-cm. Büchner funnel and washed with 80 ml. of cold 5:3 absolute ethanol-acetone, then with 100 ml. of 30–40° petroleum ether. The product when dry weighs 18–20 g. (38–43%). The yield may be increased somewhat by concentration of the combined mother liquor and washings, and treatment as before with ethanol and acetone. The melting point is not a useful criterion of purity, since the hexahydrogallic acid decomposes on heating (Note 11). The product is apparently substantially the all-*cis* isomer.²

B. *Hexahydrogallic acid triacetate*. A suspension of 10 g. (0.057 mole) of the dry, recrystallized

hexahydrogallic acid in 40 ml. of acetic anhydride is treated with 1 drop of concentrated sulfuric acid, which initiates the reaction (Note 12). Most of the solid then goes into solution with some evolution of heat. The reaction is completed on a steam bath for 30 minutes. The acetic acid and most of the excess anhydride are then removed on the steam bath under reduced pressure with the aid of an oil pump. Twenty-five milliliters of water is added, and the mixture is shaken and heated on the steam bath for 10 minutes in order to hydrolyze residual acetic anhydride and the mixed anhydride of the product and acetic acid. Most of the solvent is then removed under reduced pressure on the steam bath; the product usually crystallizes during this process. About 15 ml. of water is added, and the mixture is heated on the steam bath until the solids dissolve. The solution is first allowed to cool slowly to room temperature and then stored at 0° for several hours to complete crystallization. The colorless crystals are collected, washed rapidly with 10–15 ml. of cold water, and dried at 60° or