



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.

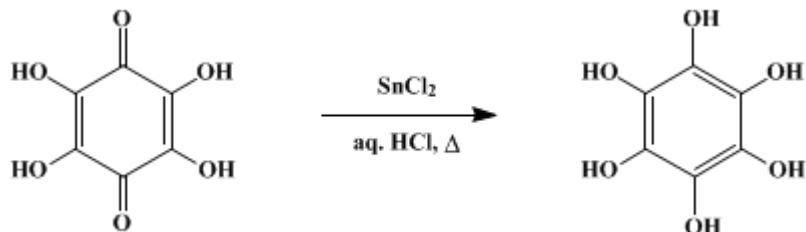
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.595 (1973); Vol. 42, p.66 (1962).

HEXAHYDROXYBENZENE

[Benzenehexol]



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Checked by B. C. McKusick and J. K. Williams.

1. Procedure

One hundred grams (0.44 mole) of stannous chloride dihydrate is added to a boiling solution of 10 g. (0.058 mole) of tetrahydroxyquinone² in 200 ml. of 2.4*N* hydrochloric acid contained in a 1.5-l. beaker. The initial deep-red color disappears, and grayish crystals of hexahydroxybenzene precipitate. Two hundred fifty milliliters of 12*N* hydrochloric acid is added, and the mixture is heated to boiling with constant stirring. The beaker is removed from the hot plate, an additional 600 ml. of 12*N* hydrochloric acid is added, and the solution is cooled in a refrigerator. The hexahydroxybenzene is collected on a Büchner funnel fitted with a sintered-glass disk (Note 1) and sucked dry.

The crude hexahydroxybenzene is dissolved in 450 ml. of hot 2.4*N* hydrochloric acid containing 3 g. of hydrated stannous chloride and 1 g. of decolorizing carbon. The solution is filtered while hot, and the carbon is rinsed with 75 ml. of boiling water that is combined with the filtrate. One liter of 12*N* hydrochloric acid is added, and the mixture is cooled in a refrigerator. The snow-white crystals of hexahydroxybenzene that separate are collected under carbon dioxide or nitrogen (Note 2) on a Büchner funnel fitted with a sintered-glass disk. The hexahydroxybenzene is washed with 100 ml. of a cold 1:1 mixture of ethanol and 12*N* hydrochloric acid and dried in a vacuum desiccator over sodium hydroxide pellets; yield 7.1–7.8 g. (70–77%). It fails to melt on a hot plate at 310° (Note 3).

2. Notes

1. Filter paper cannot be used because it is attacked by strong hydrochloric acid.
2. By rapid manipulation it is possible to obtain a product of fair quality. The moist product is susceptible to air oxidation, as is shown by a development of pink coloration on the crystals. The filtration is best carried out under a blanket of carbon dioxide or nitrogen obtained by inverting a funnel attached to a source of carbon dioxide or nitrogen over the Büchner funnel.
3. The decomposition point of hexahydroxybenzene is not a good criterion of purity. If the product is light in color, there can be no significant amount of oxidized material in it, for even traces of tetrahydroxyquinone cause intense coloration. Decomposition of a sample with nitric acid followed by evaporation and ignition of the residue should give a negligible amount of tin oxide. The product can be characterized as the hexaacetate, m.p. 202–203°, by treating it with acetic anhydride and sodium acetate.³

3. Discussion

The present procedure is a modification of the procedure of Anderson and Wallis.⁴ Hexahydroxybenzene can also be prepared by acidic hydrolysis of potassium carbonyl³ or by nitration and oxidation of diacetyl hydroquinone.⁵

4. Merits of the Procedure

This is the most convenient synthesis of hexahydroxybenzene, and the present procedure gives better yields than reported by Anderson and Wallis.⁴ Hexahydroxybenzene is of interest as the most highly hydroxylated member of the polyhydroxybenzene family.

It has been used as a source of the biologically important *myo*-inositol^{6,7} (1235/46 isomer) by hydrogenation over palladium and of *cis*-inositol (123456 isomer) by hydrogenation over palladium-on-carbon.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 1011

References and Notes

1. Department of Chemistry, The George Washington University, Washington, D C.
2. A. J. Fatiadi and W. F. Sager, *this volume*, p. 1011.
3. B. Nietzki and T. Benckiser, *Ber.*, **18**, 1834 (1885).
4. R. C. Anderson and E. S. Wallis, *J. Am. Chem. Soc.*, **70**, 2931 (1948).
5. B. Nietzki and T. Benckiser, *Ber.*, **18**, 500, 1842 (1885).
6. H. Wieland and R. S. Wishart, *Ber.*, **47**, 2082 (1914).
7. S. J. Angyal and D. J. McHugh, *Chem. & Ind. (London)*, 947 (1955).

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

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

acetic anhydride (108-24-7)

sodium acetate (127-09-3)

sodium hydroxide pellets (1310-73-2)

nitric acid (7697-37-2)

nitrogen (7727-37-9)

stannous chloride

carbon dioxide (124-38-9)

decolorizing carbon,
carbon (7782-42-5)

palladium (7440-05-3)

stannous chloride dihydrate (10025-69-1)

Hexahydroxybenzene,
Benzenehexol (608-80-0)

Tetrahydroxyquinone (319-89-1)

tin oxide

potassium carbonyl

diacetyl hydroquinone

myo-inositol (87-89-8)

cis-inositol

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