



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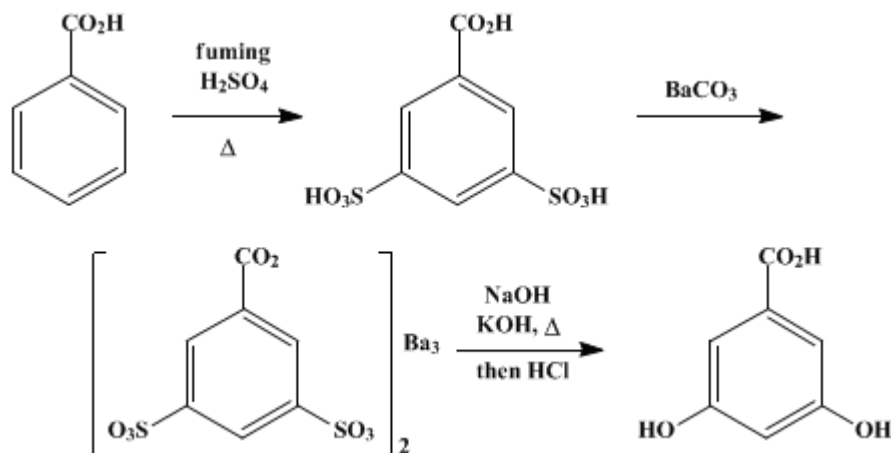
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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3,5-DIHYDROXYBENZOIC ACID

[α -Resorcylic acid]



Submitted by Arthur W. Weston and C. M. Suter.

Checked by C. F. H. Allen and John W. Gates, Jr..

1. Procedure

To 200 g. (1.64 moles) of [benzoic acid](#) in a 1-l. Kjeldahl flask, in the top of which is inserted a loosely fitting cold finger ([Note 1](#)), is added 500 ml. of fuming [sulfuric acid](#) ([Note 2](#)). The mixture is heated in an oil bath for 5 hours at 240–250° (bath temperature).

After standing overnight the syrupy liquid is poured slowly with stirring into 3 kg. of ice in a 3-gal. crock ([Note 3](#)). The solution is then neutralized by adding [barium carbonate](#) in 100-g. portions, stirring occasionally until the gas evolution slackens before each addition: 2.4–2.5 kg. is required. The pasty mass is filtered by suction on a 30-cm. Büchner funnel, and the [barium sulfate](#) is washed with five 300-ml. portions of water. The combined filtrates are evaporated nearly to dryness on a steam bath and finally dried in an oven at 125–140° ([Note 4](#)). The yield of crude barium salt is 640–800 g.

The operator should wear goggles and long-sleeved gloves during the next two operations. The dried, pulverized barium salt is introduced in 200-g. portions into a melt of 600 g. each of [sodium](#) and [potassium hydroxides](#) contained in a 14 by 20 cm. copper beaker. The mixture is stirred with a copper stirrer and the temperature determined with a thermometer in a copper well. ([Note 5](#)). Each portion is well stirred in before the next is added. The temperature is then slowly raised to 250–260°, at which point a vigorous reaction occurs with copious evolution of gas. After this has slackened (about 30 minutes) the temperature is raised to 280–310° and maintained there for 1 hour, then allowed to drop to 200°. The melt is ladled into 6 l. of water ([Note 6](#)) and ([Note 7](#)). The [barium sulfite](#) is filtered by suction, and the filtrate is acidified with concentrated [hydrochloric acid](#) (about 2.5 l. is required).

The resulting solution (about 9 l.) is divided into two portions and each is extracted three times, 600 ml. of [ether](#) being used each time ([Note 8](#)). The combined extracts are concentrated to about 1 l. and dried overnight over 150 g. of anhydrous [sodium sulfate](#). After filtration and evaporation of the [ether](#), there remains 137–160 g. (58–65%) of a slightly colored product, melting with decomposition at 227–229°. It is sufficiently pure for most purposes ([Note 9](#)) and ([Note 10](#)).

2. Notes

1. An ordinary glass funnel suspended in the neck serves less satisfactorily, whereas with a water condenser solidification of the [sulfur trioxide](#) causes difficulty.

2. This acid, approximately 30% sulfur trioxide, is made by mixing 500 g. each of fuming sulfuric acid containing 60% free sulfur trioxide and concentrated sulfuric acid (sp. gr. 1.84); 500 ml. of this mixture is used.
3. The reaction product may solidify at first, but it dissolves later.
4. The evaporation of the solution is most conveniently done overnight. The final drying is best done in flat metal trays; the length of time required depends upon the temperature. The checkers left trays on a steam coil over a week end.
5. An 18-cm. piece of 10- to 12-mm. copper tubing, pounded together at the lower end, is used. The stirrer can be made of the same tubing.
6. The addition of the hot melt causes some spattering.
7. Alternatively, the melt may be poured into shallow metal trays and allowed to cool and solidify. It is then pulverized and dissolved. Grinding is difficult and unpleasant. The melt should not be allowed to solidify in the reaction vessel.
8. A large automatic extraction apparatus may be used if available.
9. The color can be removed by recrystallization from hot acetic acid, using a decolorizing carbon. A solution of 16 g. of the crude acid in 85 ml. of hot acetic acid deposits 13.4 g. of white needles after filtration through a 2-mm. layer of Darco in a hot funnel and cooling. These are anhydrous after drying at 100° at 35 mm. for 2 hours; m.p. 234–235° with decomposition (cor.). The melting point varies with the rate of heating.
10. This material is partially hydrated.¹ The melting point is unchanged after recrystallization from water.

3. Discussion

3,5-Dihydroxybenzoic acid is most conveniently prepared by alkaline fusion of the disulfonic acid obtained by sulfonation of benzoic acid.^{1,2,3} It has also been prepared by alkaline fusion of the 3,5-dihalobenzoic acids^{4,5} or of 3-bromo-5-sulfobenzoic acid.⁶ Benzoic acid has been sulfonated using various strengths of sulfuric acid with or without catalysts.^{7,8}

References and Notes

1. Barth and Senhoefer, *Ann.*, **159**, 222 (1871); **164**, 109 (1872).
2. Graves and Adams, *J. Am. Chem. Soc.*, **45**, 2439 (1923).
3. Hohenemser, *Ber.*, **35**, 2305 (1902).
4. Ger. pat. 286,266 [*Frdl.*, **12**, 158 (1914–1916)].
5. U. S. pat. 1,321,271 [*C. A.*, **14**, 186 (1920)].
6. Böttinger, *Ber.*, **8**, 374 (1875); **9**, 180 (1876); Bülow and Riess, *Ber.*, **35**, 3901 (1902); Koller and Klein, *Monatsh.*, **64**, 85 (1935).
7. Herzig and Epstein, *Monatsh.*, **29**, 661 (1901); Brunner, *Monatsh.*, **50**, 216 (1928); Lock and Nottes, *Monatsh.*, **68**, 51 (1936); Suter and Weston, *J. Am. Chem. Soc.*, **61**, 232 (1939).
8. Birkenshaw and Bracken, *J. Chem. Soc.*, **1942**, 369.

Appendix

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

barium salt

potassium hydroxides

3,5-dihalobenzoic acids

sulfuric acid (7664-93-9)
hydrochloric acid (7647-01-0)
acetic acid (64-19-7)
ether (60-29-7)
sulfur trioxide (7446-11-9)
sodium sulfate (7757-82-6)
Benzoic acid (65-85-0)
barium sulfate (7727-43-7)
decolorizing carbon (7782-42-5)
sodium (13966-32-0)
barium carbonate (513-77-9)
3,5-Dihydroxybenzoic acid,
 α -Resorcylic acid (99-10-5)
barium sulfite
3-bromo-5-sulfobenzoic acid