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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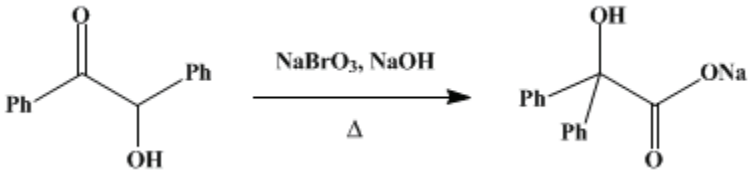
Organic Syntheses, Coll. Vol. 1, p.89 (1941); Vol. 1, p.29 (1921).

BENZILIC ACID



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1. Procedure

The reaction mixture of benzoin, prepared by the method described on p. 94, is permitted to stand until the next day, when it is filtered, washed with water but is not dried or purified. In a 30-cm. evaporating dish 500 g. (12.5 moles) of sodium hydroxide and 115 g. (0.76 mole) of sodium bromate (or 125 g. of potassium bromate) are dissolved in 880 cc. of water. The moist benzoin (450–460 g.) is added in portions to this solution and the mixture is stirred, preferably with a mechanical stirrer, while heated on the steam bath (Note 1). As heating continues the mixture thickens and more water is added from time to time. A total of 750–800 cc. is needed. The heating and stirring are continued for about five to six hours or until a test portion is completely or almost completely soluble in water.

The mixture is diluted with about 4 l. of water and is permitted to stand overnight. A small quantity of oily or solid impurity (benzohydrol) is removed by filtration, and dilute sulfuric acid (about 1300 cc. of a solution of 3 parts of water and 1 part of concentrated sulfuric acid, sp. gr. 1.84) is added to a point short of liberation of bromine. The product is filtered, washed with water and dried. Thus 450–484 g. (84–90 per cent of the theoretical amount based on the benzaldehyde) of benzilic acid melting at 149–150° is obtained (Note 2).

2. Notes

1. If the reaction mixture is heated to boiling, large quantities of benzohydrol are obtained. The temperature reached by heating on the steam bath is about 85–90°.
2. The high purity of the product obtained by this procedure really makes recrystallization unnecessary. Should further purification be desired it is best effected by crystallization from benzene. It may also be accomplished by crystallizing from hot water with the use of animal charcoal or by dissolving in alkali and reprecipitating by means of hydrochloric acid.

3. Discussion

Benzilic acid can be prepared by the action of potassium hydroxide on benzil, in concentrated aqueous solution,[1] in alcoholic solution[2] or in ether;[3] and by heating benzil in toluene with sodamide and then treating with water.[4] The procedure described has been published.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 224

References and Notes

1. Fischer and Bösler, Ber. **14**, 326 (footnote) (1881); Staudinger, Ann. **356**, 71 (1907).
2. Liebig, Ann. **25**, 27 (1838); Zinin, Ann. **31**, 329 (1839); Jena, Ann. **155**, 79 (1870); Liebig, Ber. **41**, 1644 (1908); Schönberg and Keller, Ber. **56**, 1638 (1923); Adams and Marvel, Org. Syn. **1**,

29 (1921).
3. Evans and Dehn, J. Am. Chem. Soc. **52**, 252 (1930).
4. Kasiwagi, Bull. Chem. Soc. Japan **1**, 66 (1926) [C. A. **20**, 2491 (1926)].
5. Evans and Dehn, J. Am. Chem. Soc. **52**, 3649 (1930).

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

Benzohydrol

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ether (60-29-7)

sodium hydroxide (1310-73-2)

bromine (7726-95-6)

benzaldehyde (100-52-7)

Benzil (134-81-6)

Benzoin (119-53-9)

Benzilic acid (76-93-7)

sodium bromate (7789-38-0)

potassium bromate (7758-01-2)

potassium hydroxide (1310-58-3)

toluene (108-88-3)

sodamide (7782-92-5)