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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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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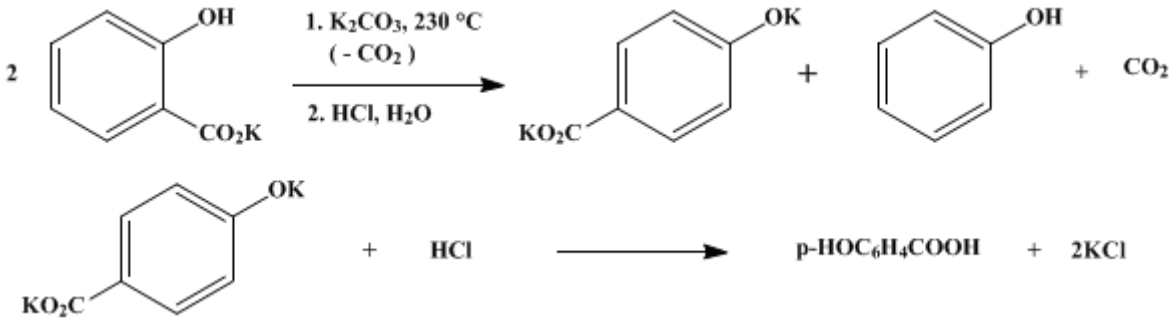
p-HYDROXYBENZOIC ACID

[Benzoic acid, *p*-hydroxy-]



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1. Procedure

Sixty grams (0.43 mole) of potassium carbonate (Note 1) is slowly stirred into a mixture of 100 g. (0.725 mole) of u.s.p. salicylic acid and 150 cc. of water contained in a 20-cm. porcelain dish. The solution is evaporated on a steam bath until a thick, pasty residue is obtained. This is broken up into small pieces and dried in an oven at 105–110° for two hours. The solid is then ground as finely as possible, dried for another two hours at 105–110°, and again ground to a fine powder.

The finely powdered mixture of potassium salicylate and carbonate is placed in a 500-cc. round-bottomed flask which is immersed in an oil bath so that only a small portion of the neck protrudes from the bath (Note 2). The bath is heated to 240° (Note 3) and maintained at this temperature for one and one-half hours. During this time the solid in the flask is stirred occasionally with a curved glass rod flattened at the end.

When the reaction is completed (Note 4), the product is transferred as completely as possible, while hot, to a 2-l. flask containing 1 l. of hot water. The reaction flask is rinsed with several portions of the hot solution. The alkaline solution is acidified with concentrated hydrochloric acid (about 75 cc. is required), heated nearly to boiling, treated with 5–6 g. of decolorizing charcoal, and filtered to remove a small quantity of brown resin. The filtrate is cooled under the tap, and the crude brown crystalline product is filtered with suction. The filtrate is concentrated to a volume of approximately 300 cc. and cooled as before. The second crop of crude acid is filtered with suction and combined with the main portion. The total weight of crude *p*-hydroxybenzoic acid, m.p. 208–211°, is 40–45 g.

The crude acid is dissolved in 300 cc. of hot water, boiled with 4–5 g. of decolorizing charcoal for a few minutes, and the solution filtered. After cooling thoroughly under the tap the purified product is filtered with suction and washed with 10–15 cc. of cold water. The purified acid weighs 35–40 g. (70–80 per cent of the theoretical amount) and melts at 211–212°.

2. Notes

1. An excess of potassium carbonate is used since it prevents the mass from caking during the subsequent heating. Although the original mixture is strongly alkaline a clear solution may not be obtained until the dish is heated.
2. In this way the phenol formed in the reaction is allowed to distil out of the mixture. This operation should be carried out in a hood.
3. The temperature reported is that of the oil bath; the internal temperature is approximately 230°. The temperature should be controlled carefully since pronounced decomposition sets in at higher

temperatures.
4. The completeness of the reaction may be determined roughly by treating a small test portion with 3–4 cc. of hot water and acidifying with concentrated hydrochloric acid. Since *p*-hydroxybenzoic acid is relatively soluble and salicylic acid only sparingly so, the absence of a precipitate in the warm solution indicates that the reaction is essentially complete.

3. Discussion

p-Hydroxybenzoic acid has been prepared by heating potassium phenoxide in a stream of carbon dioxide[1] or with carbon tetrachloride,[2] and by heating *p*-cresol with alkalies and various metallic oxides.[3] The procedure described above is similar to one which appears in the early literature.[4] When the dipotassium salt of salicylic acid is dehydrated by heating in vacuum and is then heated in a carbon dioxide atmosphere, essentially complete conversion to *p*-hydroxybenzoic acid is reported.[5]

References and Notes

1. Kolbe, J. prakt. Chem. (2) **10**, 100 (1874); Hartmann, ibid. (2) **16**, 39 (1877); Ost, ibid. (2) **20**, 208 (1879).
2. Reimer and Tiemann, Ber. **9**, 1285 (1876); Hasse, ibid. **10**, 2186 (1877).
3. Graebe and Kraft, Ber. **39**, 797 (1906); Friedländer and Löw-Beer, Ger. pat. 170,230 [Frdl. **8**, 158 (1905–07)].
4. Kolbe, J. prakt. Chem. (2) **11**, 24 (1875); Heyden, Ger. pat. 48,356 [Frdl. **2**, 132 (1887–90)].
5. Dow Chemical Company, U. S. pat. 1,937,477 [C. A. **28**, 1056 (1934)].

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

potassium carbonate (584-08-7)

hydrochloric acid (7647-01-0)

phenol (108-95-2)

carbonate (3812-32-6)

carbon tetrachloride (56-23-5)

salicylic acid

carbon dioxide (124-38-9)

potassium salicylate

potassium phenoxide

p-Hydroxybenzoic acid,
Benzoic acid, p-hydroxy- (99-96-7)

p-CRESOL (106-44-5)

dipotassium salt of salicylic acid