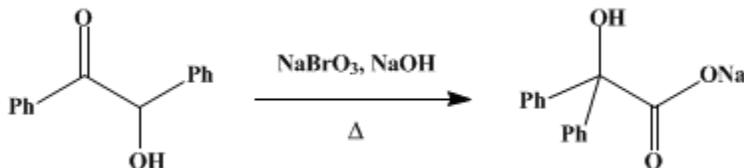


BENZILIC ACID



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Checked by C. S. Marvel and Tse-Tsing Chu.

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 solution² 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).
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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)