



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.

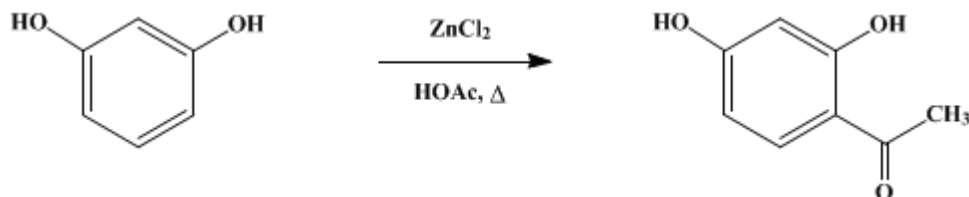
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.761 (1955); Vol. 21, p.103 (1941).

RESACETOPHENONE

[Acetophenone, 2,4-dihydroxy-]



Submitted by S. R. Cooper

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1. Procedure

One hundred and sixty-five grams (1.2 moles) of anhydrous zinc chloride (Note 1) is dissolved with the aid of heat in 165 g. (158 ml., 2.7 moles) of glacial acetic acid, which has been placed in a 1-l. beaker. To this hot mixture (about 140°), 110 g. (1 mole) of resorcinol is added with constant stirring. The solution is heated on a sand bath until it just begins to boil (about 152°). The flame is then removed and the reaction allowed to complete itself at a temperature not in excess of 159° (Note 2). After standing on the sand bath without further heating for 20 minutes, the solution is diluted with a mixture of 250 ml. of concentrated hydrochloric acid and 250 ml. of water. The dark red solution is placed in an ice bath and cooled at 5°. The resulting precipitate is collected on a filter and washed free from zinc salts with 1 l. of dilute (1:3) hydrochloric acid in 200-ml. portions. This orange-red product, after drying, weighs 104–110 g. and melts at 141–143°. It is distilled under reduced pressure (Note 3), and boils at 180–181° at 10 mm. (147–152° at 3–4 mm.). After most of the product has distilled, the temperature rises sharply, and the operation is discontinued when the temperature reaches 190°. The light-yellow distillate is removed from the receiver with hot ethanol and the ethanol is evaporated (Note 4). This product weighs 100–106 g. It is further purified as follows: the substance is dissolved in 1.8 l. of hot dilute (1:11) hydrochloric acid, filtered hot, and cooled to 5°. The crystals are removed by filtration, washed with two 200-ml. portions of ice water, and dried. The yield of tan-colored resacetophenone, melting at 142–144°, is 93–99 g. (61–65%).

2. Notes

1. Although finely ground zinc chloride dissolves more rapidly, lumps or sticks are satisfactory.
2. If the temperature rises much above the initial boiling point, the yield of red product increases at the expense of resacetophenone formation. The boiling point also may vary slightly.
3. Any convenient apparatus for distillation of a solid may be used.
4. It is convenient to remove most of the material by melting and pouring it out of the receiver. The remainder is removed with hot ethanol.

3. Discussion

Resacetophenone has been prepared by heating resorcinol with zinc chloride and acetic acid,^{1,2} with zinc chloride and acetic anhydride,² with zinc chloride and acetyl chloride,³ with boron trifluoride and acetic anhydride,⁴ and with aluminum chloride and acetyl chloride.⁵ It has been prepared by the action of zinc chloride on resorcinol diacetate,² by heating 4-methylumbelliferone with potassium hydroxide,⁶ by heating resacetophenone carbonic acid,⁷ and by the action of acetyl chloride on resorcinol.⁸

References and Notes

1. Robinson and Shah, *J. Chem. Soc.*, **1934**, 1491.
 2. Nencki and Sieber, *J. prakt. Chem.*, (2) **23**, 147 (1881).
 3. Eijkman, *Chem. Weekblad*, **1**, 453 (1904) [*Chem. Zentr.*, **75**, II, 1597 (1904)].
 4. Killelea and Lindwall, *J. Am. Chem. Soc.*, **70**, 428 (1948).
 5. Desai and Ekhlas, *Proc. Indian Acad. Sci.*, **8A**, 194 (1938).
 6. Pechmann and Duisberg, *Ber.*, **16**, 2119 (1883).
 7. Liebermann and Lindenbaum, *Ber.*, **40**, 3570 (1907).
 8. Cox, *Rec. trav. chim.*, **50**, 848 (1931).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

Resacetophenone

Acetophenone, 2,4-dihydroxy-

resacetophenone carbonic acid

[ethanol \(64-17-5\)](#)

[hydrochloric acid \(7647-01-0\)](#)

[acetic acid \(64-19-7\)](#)

[acetic anhydride \(108-24-7\)](#)

[acetyl chloride \(75-36-5\)](#)

[aluminum chloride \(3495-54-3\)](#)

[potassium hydroxide \(1310-58-3\)](#)

[zinc chloride \(7646-85-7\)](#)

[resorcinol \(108-46-3\)](#)

[boron trifluoride \(7637-07-2\)](#)

[4-methylumbelliferone \(90-33-5\)](#)

[resorcinol diacetate \(108-58-7\)](#)