



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.280 (1955); Vol. 28, p.42 (1948).

2,5-DIHYDROXYACETOPHENONE

[Acetophenone, 2,5-dihydroxy-; quinacetophenone]



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1. Procedure

A mixture of 50 g. (0.257 mole) of dry [hydroquinone diacetate](#) (p. 452) and 116 g. (0.87 mole) ([Note 1](#)) of anhydrous [aluminum chloride](#) is finely powdered in a mortar and introduced into a dry 500-ml. round-bottomed flask fitted with an air condenser protected by a [calcium chloride](#) tube and connected to a gas-absorption trap. The flask is placed in an oil bath ([Note 2](#)) which is heated slowly from room temperature so that at the end of about 30 minutes the temperature of the oil reaches 110–120°, at which point the evolution of [hydrogen chloride](#) begins. The temperature is then raised slowly to 160–165° and maintained at that point for about 3 hours ([Note 3](#)); at the end of about 2 hours the evolution of [hydrogen chloride](#) becomes very slow and the mass assumes a green color and becomes pasty in consistency ([Note 4](#)).

The flask is removed from the oil bath and allowed to cool to room temperature. The excess [aluminum chloride](#) is decomposed by treating the reaction mixture with 350 g. of crushed ice followed by 25 ml. of concentrated [hydrochloric acid](#). The solid obtained is collected on a Büchner funnel and washed with two 100-ml. portions of cold water. The crude product weighs about 35 g. (89–90%). Recrystallization from 4 l. of water yields 25–30 g. (64–77%) of green, silky needles melting at 202–203° ([Note 5](#)).

2. Notes

1. Ordinary commercial [aluminum chloride](#) can be used. If the amount of this reagent is less than 3 moles per mole of the ester the yield diminishes. To compensate for any inert ingredients in the commercial [aluminum chloride](#), the reagent is employed in an excess of about 10% over 3 moles.
2. The flask should not touch the bottom of the oil bath; if it does, the lower portion of the mixture may char.
3. If the evolution of the [hydrogen chloride](#) becomes vigorous, the [calcium chloride](#) tube may be removed temporarily and the top of the condenser connected directly to the gas-absorption trap. When the gas evolution slackens and there is no longer any danger that the [calcium chloride](#) tube will be blown off, the guard tube is reinserted.
4. The reaction requires about 2 hours, but the heating is continued another hour to ensure its completion.
5. The product may be recrystallized from 250 ml. of 95% [ethanol](#) rather than from the much larger quantity of water.

3. Discussion

2,5-Dihydroxyacetophenone has been prepared in 54% yield¹ by heating [hydroquinone diacetate](#), [hydroquinone](#), and anhydrous [aluminum chloride](#). It has also been prepared² by the reaction of [hydroquinone](#) with [acetic acid](#) in the presence of [zinc chloride](#).

The procedure given has also been applied in the Fries rearrangement of [hydroquinone dipropionate](#), with the production of 2,5-dihydroxypropiophenone in good yields.³

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 836](#)

References and Notes

1. Rosenmund and Lohfert, *Ber.*, **61**, 2606 (1928).
 2. Nencki and Schmid, *J. prakt. Chem.*, **23**, 546 (1881).
 3. Amin and Shah, *J. Indian Chem. Soc.*, **25**, 377 (1948).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

2,5-Dihydroxyacetophenone

2,5-dihydroxypropiophenone

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

[calcium chloride](#) (10043-52-4)

[hydrogen chloride](#),
[hydrochloric acid](#) (7647-01-0)

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

[hydroquinone](#) (123-31-9)

[Acetophenone](#) (98-86-2)

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

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

[Hydroquinone diacetate](#) (1205-91-0)

[hydroquinone dipropionate](#) (7402-28-0)