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.

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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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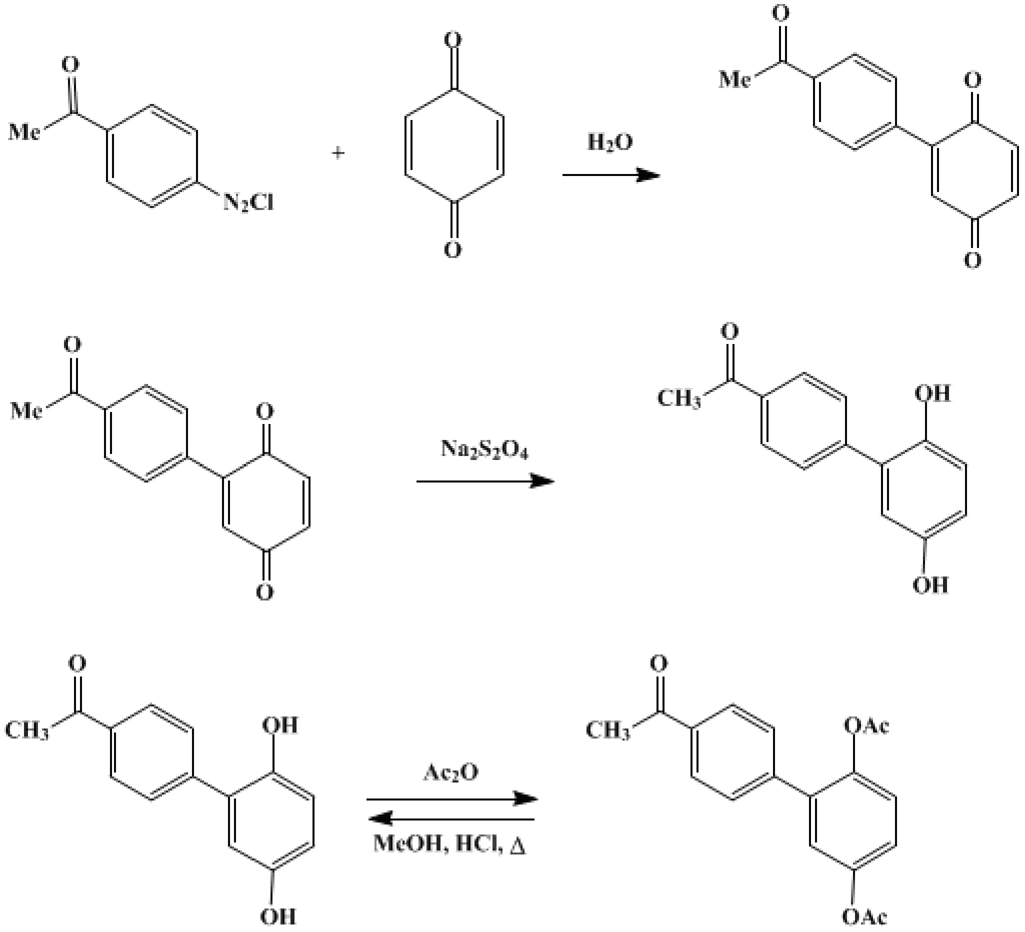
# 2-*p*-ACETYLPHENYLHYDROQUINONE

## [Acetophenone, 4'-(2,5-dihydroxyphenyl)-]



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## 1. Procedure

In a 500-ml. beaker equipped with a mechanical stirrer are placed 27 g. (0.2 mole) of *p*-aminoacetophenone (Note 1), 100 g. of chopped ice, and 53 ml. of concentrated hydrochloric acid (sp. gr. 1.19). To the stirred mixture is added, over a period of 5 minutes, a solution of 13.8 g. (0.2 mole) of sodium nitrite dissolved in 75 ml. of water. The stirring is continued for 15 minutes, during which all the insoluble amine hydrochloride reacts to form the soluble diazonium compound (Note 2).

In a 4-l. beaker, equipped with a high-speed stirrer (Note 3), are placed 20 g. (0.185 mole) of quinone (Note 4), 34 g. (0.4 mole) of sodium bicarbonate, 50 g. of chopped ice, and 500 ml. of water. About 10 ml. of the above diazonium salt solution is added (Note 5). After the frothing has subsided (Note 6), the diazonium salt solution is added in 10- to 20-ml. portions over a period of about an hour (Note 7). The temperature of the reaction mixture is kept below 15° during this period by the addition of ice. After the diazonium salt solution has been added, the mixture is allowed to warm to room temperature, and the stirring is continued for an additional hour. The precipitate of 2-*p*-acetylphenylquinone is collected on a Büchner funnel and washed thoroughly with approximately 1 l. of water. The yield of crude yellow-brown solid is 40–41 g. (96–98%). The melting point ranges from 125–135° to 134–136° (Note 8).

The crude quinone is dissolved in 250 ml. of chloroform (Note 9) and added to a solution of 40 g. of sodium hydrosulfite in 300 ml. of water. The mixture is shaken for 10 minutes, and the light-tan 2-*p*-acetylphenylhydroquinone which precipitates from solution is collected on a Büchner funnel and dried. The yield of crude hydroquinone is 32–37 g. (78–92%). The melting point ranges from 175–180° to 184–194° (Note 10).

A suspension of 35 g. (0.153 mole) of 2-*p*-acetylphenylhydroquinone in 77 ml. of acetic anhydride is treated with 0.5 ml. of concentrated sulfuric acid (sp. gr. 1.84). The hydroquinone goes into solution immediately with the evolution of much heat. The dark-colored solution is allowed to stand at room temperature overnight; then it is poured into 400 ml. of water. The acetylated material is collected by suction filtration and dried. The crude 2-*p*-acetylphenylhydroquinone diacetate is distilled at reduced pressure (b.p. 236–241°/1 mm. or 182–190°/0.1 mm.), and the hot distillate is poured into 20 ml. of *n*-butyl alcohol (Note 11). The product immediately separates as a colorless, crystalline mass, which is collected by suction filtration and dried. The yield is 32–35 g. (67–73%), m.p. 104–105°.

To a 300-ml. three-necked round-bottomed flask, equipped with a sealed stirrer, a condenser, and a gas inlet tube, is added a solution of 34 g. (0.11 mole) of 2-*p*-acetylphenylhydroquinone diacetate in 140 ml. of hot methanol. The solution is cooled to room temperature, causing some of the hydroquinone diacetate to crystallize. A slow stream of nitrogen is passed through the suspension, and 70 ml. of methanol containing 6.1 g. of anhydrous hydrogen chloride is added. The reaction mixture is stirred at room temperature for 2 hours under nitrogen, during which period the hydroquinone diacetate gradually dissolves. The pale yellow solution is poured onto 500 g. of chopped ice, and the colorless or faintly yellowish solid is collected by suction filtration and dried. The yield of *p*-acetylphenylhydroquinone melting at 193–194° is 24.8 g. (quantitative). The over-all yield of product based on quinone is 50–66%.

## 2. Notes

1. The purest grade of *p*-aminoacetophenone supplied by the Eastman Kodak Company was used without further purification.
2. This reaction has been successfully carried out on a 3-mole scale.
3. A "Lightnin" mixer (manufactured by the Mixing Equipment Company, Rochester, N. Y.) equipped with a propeller stirrer was used. If rapid stirring is not maintained, the reaction does not go to completion.
4. The checkers used a practical grade of quinone obtainable from the Eastman Kodak Company.
5. If nitrogen is not evolved immediately, the reaction may be initiated by the addition of a small amount of hydroquinone.
6. If the foaming becomes too violent, a few drops of octyl alcohol are added.
7. The checkers found it convenient to add the diazonium salt solution slowly from a dropping funnel. The time of addition was 25–45 minutes.
8. Recrystallization from butanol gives material melting at 139–140°. The pure substance is reported to melt at 152–153°.[2]
9. Ethanol can also be used as a solvent but has the disadvantage of more readily dissolving the hydroquinone, thus making it necessary to evaporate the solution nearly to dryness.
10. It is difficult to purify the crude hydroquinone by recrystallization; therefore the remainder of the procedure is recommended in order to obtain a highly purified product.
11. The checkers found it convenient to crystallize the viscous distillate from 125 ml. of methanol by chilling a hot solution in the refrigerator overnight. A small second crop amounting to about 2 g. may also be obtained by concentration of the mother liquors.

## 3. Discussion

This procedure is a modification of the method described for the preparation of 2-chlorophenylhydroquinone.[3] 2-*p*-Acetylphenylquinone has been prepared by carrying out the coupling in alcohol solution in the presence of sodium acetate instead of sodium bicarbonate.[2] Reduction by zinc, acetic acid, and a small amount of concentrated hydrochloric acid yielded 2-*p*-acetylphenylhydroquinone.[2]

## References and Notes

1. Eastman Kodak Company, Rochester, New York.
2. Kvalnes, *J. Am. Chem. Soc.*, **56**, 2478 (1934).
3. B.I.O.S., Report 1146 (1946). [Reports obtainable from British Intelligence Objectives Subcommittee, 32 Bryanston Sq., London, W. 1.]

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

ethanol (64-17-5)

sulfuric acid (7664-93-9)

hydrogen chloride,
hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

methanol (67-56-1)

acetic anhydride (108-24-7)

sodium acetate (127-09-3)

chloroform (67-66-3)

hydroquinone (123-31-9)

sodium bicarbonate (144-55-8)

nitrogen (7727-37-9)

sodium nitrite (7632-00-0)

sodium hydrosulfite (7775-14-6)

butanol,
n-butyl alcohol (71-36-3)

zinc (7440-66-6)

Quinone (106-51-4)

octyl alcohol (111-87-5)

Hydroquinone diacetate (1205-91-0)

2-chlorophenylhydroquinone (117-71-5)

2-p-Acetylphenylhydroquinone,
p-acetylphenylhydroquinone,
Acetophenone, 4'-(2,5-dihydroxyphenyl)- (3948-13-8)

p-aminoacetophenone (99-92-3)

2-p-acetylphenylquinone

2-p-acetylphenylhydroquinone diacetate