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.

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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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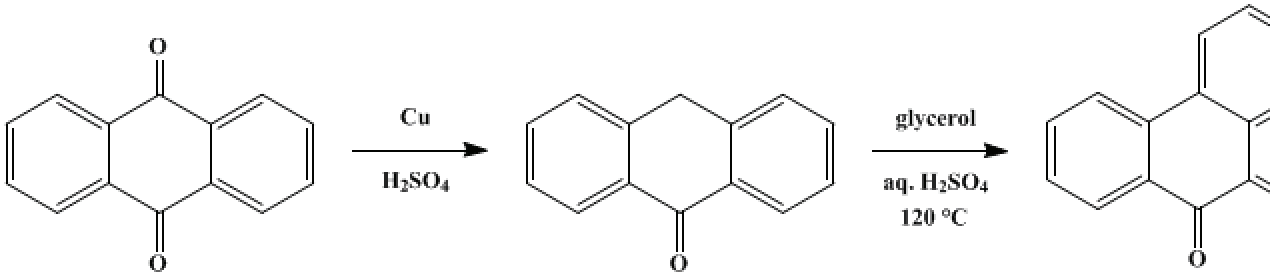
BENZANTHRONE

[7-Benz[*de*]anthracene-7-one]



Submitted by L. C. Macleod and C. F. H. Allen.
Checked by Louis F. Fieser and Max Tishler.

1. Procedure

In a 2-l. three-necked flask fitted with a mechanical stirrer and thermometer, 72 g. (0.35 mole) of anthraquinone (p. 554) is dissolved in 1060 g. of concentrated sulfuric acid by stirring at room temperature, and 42 cc. of water is then added to the red solution (Note 1). The flask is immersed up to the neck in an oil bath, and 48 g. (0.76 gram atom) of precipitated copper (Note 2) is added during one and one-half hours, the reaction mixture being kept at a temperature of 38–42°, if necessary by external heating, until all the copper has dissolved; this requires about three hours (Note 3).

A mixture of 96 g. (1.04 moles) of glycerol (Note 4) and 96 cc. of water is slowly introduced in the course of thirty minutes and the temperature is allowed to rise to 85–90°. The mixture is carefully heated to 120° during one and one-half hours, in such a way that the temperature rises uniformly at a rate of 1° every three minutes (Note 5). A temperature of 118–120° is maintained for an additional three-hour period; then the mixture is cooled to 70–80° and carefully poured with stirring into 4 l. of boiling water (Note 6). Spattering is avoided by pouring the acid mixture down the walls of the beaker while stirring. The suspension is boiled for a few minutes and preferably allowed to stand for several hours before being filtered.

The dark green benzanthrone is filtered on a large Büchner funnel, washed well with water, and boiled for thirty to forty minutes with 1.2 l. of 1 per cent sodium hydroxide solution. The product is filtered, washed free of the dark-colored liquor, and dried at 120°; weight, 67–71 g.; benzanthrone content, about 87 per cent. The crude material is boiled with 500 cc. of technical tetrachloroethane in which all but about 8 g. of a black char easily dissolves. The solution is boiled under reflux for fifteen minutes with 25 g. of decolorizing carbon, and then filtered while hot through a Büchner funnel directly into a 2-l. round-bottomed, long-necked flask, the residue being washed with hot tetrachloroethane (100–150 cc.) until the filtrate is colorless. After the addition of 400–500 cc. of hot water the solvent is removed by steam distillation, a process which requires but little time. The benzanthrone left as a residue is filtered and dried at 120°. The yield of yellow solid, which melts at 168–170° and is pure enough for many purposes, is 56–60 g. (70–75 per cent of the theoretical amount).

In order to secure a pure product the above material is dissolved in 175 cc. of tetrachloroethane by boiling and the solution is boiled under reflux for fifteen minutes with 12 g. of decolorizing carbon, and then filtered by suction into an Erlenmeyer flask, the charcoal being washed with about 50 cc. of hot solvent. The filtrate is kept hot, treated with 750 cc. of boiling alcohol, and set aside to crystallize. The benzanthrone separates as pure yellow needles melting at 170–171°; yield, 48–52 g. (60–65 per cent of the theoretical amount) (Note 7).

2. Notes

1. The solution of the anthraquinone is slower if the water is added at the outset.
2. The precipitated copper is prepared as on p. 446, using twice the quantities given.
3. The mixture becomes yellow-brown in color and some anthranol separates, but any unreacted copper can be seen on the bottom of the flask if the stirring is stopped for a few minutes.
4. The glycerol is a commercial, anhydrous product.
5. The heating must be done very carefully, and the temperature must never be allowed to rise above 120°. At higher temperatures much material is lost by charring.
6. A more granular and easily filterable product is obtained than when cold water is used.
7. On recovery of the tetrachloroethane by steam distillation of the mother liquor, a small additional quantity of material (5 g.) is obtained, but it is quite dark and of poor quality.

3. Discussion

Benzanthrone is commonly prepared by heating a reduction product of anthraquinone with sulfuric acid and glycerol,[1] [2] [3] [4] [5] or with a derivative of glycerol,[6] or with acrolein.[7] The anthraquinone is usually reduced in sulfuric acid solution, just prior to the reaction, by means of aniline sulfate,[2] iron,[3] or copper.[4] However, the simultaneous reduction and condensation has been reported to give better yields.[8] Benzanthrone has also been prepared by dehydrogenating phenyl α-naphthyl ketone with aluminum or ferric chloride,[9] by dehydration of 1-phenylnaphthalene-2-carboxylic acid,[10] and by heating cinnamalanthrone with sodium-aluminum chloride.[11]

References and Notes

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

aluminum or ferric chloride

7-Benz[de]anthracene-7-one

alcohol (64-17-5)

sulfuric acid (7664-93-9)

sodium hydroxide (1310-73-2)

Acrolein (107-02-8)

glycerol (56-81-5)

iron (7439-89-6)

Anthraquinone (84-65-1)

copper (7440-50-8)

decolorizing carbon (7782-42-5)

aniline sulfate

Benzanthrone (82-05-3)

tetrachloroethane (630-20-6)

anthranol (610-50-4)

phenyl α-naphthyl ketone

1-phenylnaphthalene-2-carboxylic acid

cinnamalanthrone

sodium-aluminum chloride