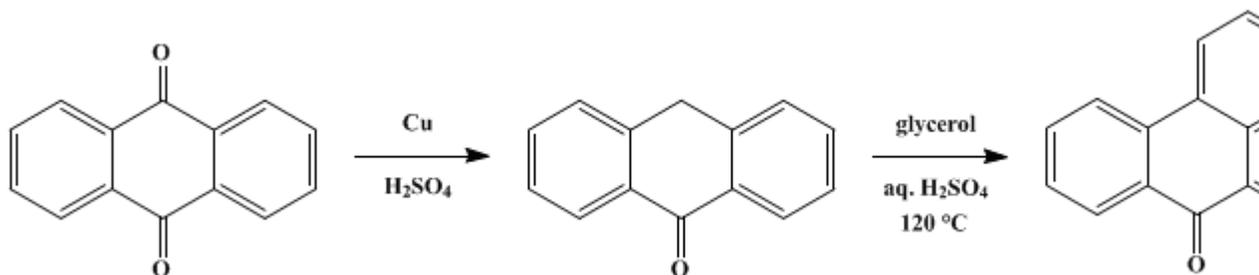


BENZANTHRONE

[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

[Benanthrone](#) 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 [Benanthrone](#) has also been prepared by dehydrogenating [phenyl \$\alpha\$ -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