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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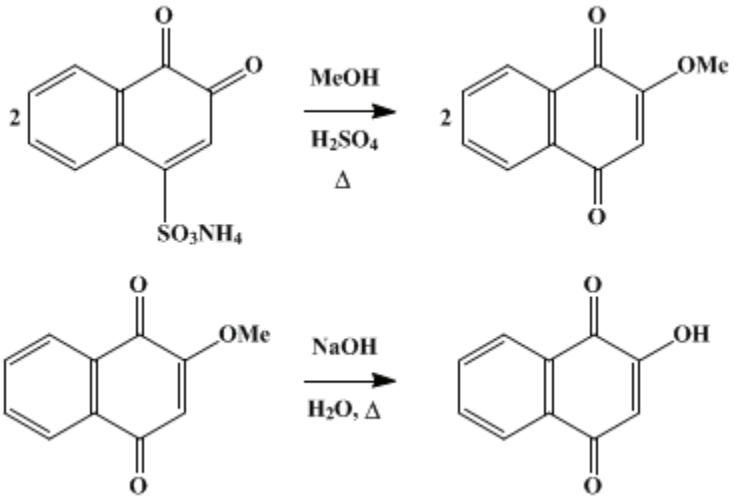
2-HYDROXY-1,4-NAPHTHOQUINONE

[1,4-Naphthoquinone, 2-hydroxy-]



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1. Procedure

One liter of absolute methanol is cooled in a 3-l. round-bottomed flask to 0° in an ice-salt bath, and 80 ml. of concentrated sulfuric acid is slowly added, with good shaking, the temperature being kept at 0°. The flask is removed from the freezing mixture, and 255 g. (1 mole) of ammonium 1,2-naphthoquinone-4-sulfonate (p. 633) is added and made into an even paste by thorough shaking. After standing for 30 minutes, during which time the temperature rises to 15–20°, the flask is heated gradually on the steam bath with continuous shaking and rotating so that the solution reaches its boiling point in about 15 minutes. The solution becomes red, sulfur dioxide is evolved, and methoxynaphthoquinone begins to separate. The mixture is kept boiling very gently, with continued shaking, for 15 minutes, when the paste of separated material becomes very stiff. Two hundred and fifty milliliters of methanol is added, and the heating and rotating continued for an additional 15–20 minutes. The reaction mixture is cooled to 20–25°, water and ice are added until the flask is nearly filled, and the methoxynaphthoquinone is collected on a 15-cm. Büchner funnel and washed with cold water until the filtrate is nearly colorless; about 2–2.5 l. of water is required (Note 1).

The moist material is washed into a solution of 30 g. of sodium hydroxide in 1.5 l. of water, and the mixture is heated rapidly nearly to the boiling point. In about 10 minutes all the ether is hydrolyzed and a deep red solution results (Note 2). The hot solution is filtered by suction from a trace of residue, transferred to a 2-l. beaker, and acidified while still hot by adding 130 ml. of 6 *N* hydrochloric acid slowly, and with good stirring. The yellow suspension of hydroxynaphthoquinone thus obtained is cooled to 0° and allowed to stand for 2 hours (Note 3). The hydroxynaphthoquinone is collected, washed with 2 l. of cold water, dried overnight at room temperature, and finally to constant weight at 60–80°. The yield is 101–112 g. (58–65% based on ammonium 1,2-naphthoquinone-4-sulfonate; 99%, based on methoxynaphthoquinone) (Note 4). The hydroxynaphthoquinone thus obtained is bright yellow, is granular, and melts, with decomposition, at about 188–189° (Note 5). It is of high quality and for ordinary uses requires no further purification (Note 6).

2. Notes

1. The methoxynaphthoquinone weighs 111–122 g. (59–65%). It melts at 181–182° and can be further

purified by crystallization from ethanol. The pure substance forms pale yellow needles, m.p. 183.5°.
2. Should the sodium salt separate during the heating or filtration, it is brought into solution by adding about 1 l. of water and heating.
3. By allowing the precipitate to stand for the indicated period, the final product is granular, and the filtration is rapid.
4. Numerous modifications have been tried without improving the yield. The loss is probably due to a partial reduction of the quinone sulfonate by the sulfur dioxide liberated, but this was not prevented by adding manganese dioxide to the reaction mixture and no pure product could be obtained from the mother liquor.
5. The temperature of decomposition varies with the rate of heating and with the nature of the glass capillary.
6. Crystallization from ethanol containing a trace of acetic acid gives glistening yellow needles, melting with decomposition at about 191–192°. The red samples of hydroxynaphthoquinone often mentioned in the literature are not completely pure. Such material, or crude material of any kind, is best purified through either the sodium salt or the methyl ether.

3. Discussion

Of the many reactions by which hydroxynaphthoquinone has been obtained,[1,2] two have been developed into practical preparative methods, and both utilize the inexpensive β-naphthol as the primary starting material. In the first method, this is converted into β-naphthoquinone [*Org. Syntheses* Coll. Vol. 2, 430 (1943)], which reacts with acetic anhydride-sulfuric acid to give 1,2,4-trihydroxynaphthalene triacetate, which is then hydrolyzed and oxidized to the desired product. The yield of the acetylation reaction is about 75%; that in the final step can be brought to 93% of the theoretical amount by hydrolyzing with ethanolic alkali in an atmosphere of nitrogen and with a trace of sodium hydrosulfite present, then diluting with water, acidifying, and adding ferric chloride. The overall yield from β-naphthol can thus be brought to 54%. The method is a good one, and it can be used to advantage for the preparation of many similar hydroxyquinones. With ordinary laboratory equipment, however, one is limited to 0.5 mole runs, and not more than about 50 g. of hydroxynaphthoquinone can be prepared at a time.

The second method is that described above: β-naphthol is converted through the nitroso derivative and 1-amino-2-naphthol-4-sulfonic acid into naphthoquinone sulfonate, and this is subjected to acid hydrolysis. The sulfonate can be converted directly into hydroxynaphthoquinone by the action of concentrated sulfuric acid,[3,4] but the process is not so easily controlled as when the quinone is etherified as it is formed and the ether subsequently hydrolyzed.[4] The overall yield from β-naphthol is 46% of the theoretical amount, but all the reagents are inexpensive, and with ordinary apparatus, 150 g. of hydroxynaphthoquinone can be made conveniently in one run (from 300 g. of β-naphthol).

The compound has also been prepared in good yield by air oxidation of 1,3-dihydroxynaphthalene,[5] which in turn was obtained from ethyl γ-phenylacetoacetate.[6]

References and Notes

1. Beilstein-Prager-Jacobson, VIII, 300 (1925).
2. Thiele and Winter, *Ann.*, **311**, 347 (1900).
3. Akt.-Ges. Anilinf., Ger. pat. 100,703 [*Chem. Zentr.*, **70**, 766 (1899)].
4. Fieser, *J. Am. Chem. Soc.*, **48**, 2929 (1926).
5. Soliman and Latif, *J. Chem. Soc.*, **1944**, 55.
6. Soliman and West, *J. Chem. Soc.*, **1944**, 53.

Appendix
Chemical Abstracts Nomenclature (Collective Index Number);

(Registry Number)

ethanol (64-17-5)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

methanol (67-56-1)

ether (60-29-7)

sodium hydroxide (1310-73-2)

sulfur dioxide (7446-09-5)

nitrogen (7727-37-9)

sodium hydrosulfite (7775-14-6)

β-naphthol (135-19-3)

methyl ether (115-10-6)

manganese dioxide (1313-13-9)

ferric chloride (7705-08-0)

1-AMINO-2-NAPHTHOL-4-SULFONIC ACID (116-63-2)

ethyl γ-phenylacetoacetate

β-naphthoquinone (524-42-5)

2-Hydroxy-1,4-naphthoquinone,
1,4-Naphthoquinone, 2-hydroxy-,
hydroxynaphthoquinone (83-72-7)

ammonium 1,2-naphthoquinone-4-sulfonate (53684-60-9)

methoxynaphthoquinone (2348-82-5)

acetic anhydride-sulfuric acid

1,2,4-trihydroxynaphthalene triacetate

naphthoquinone sulfonate

1,3-dihydroxynaphthalene (132-86-5)