



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.

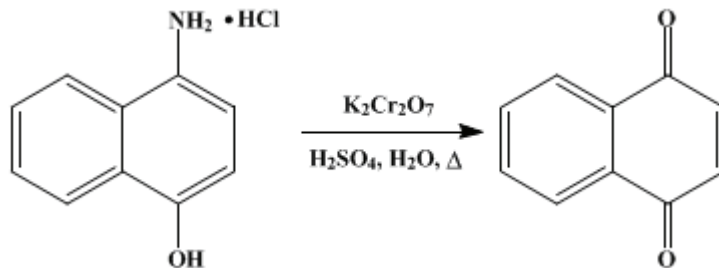
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.383 (1941); Vol. 5, p.79 (1925).

1,4-NAPHTHOQUINONE



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1. Procedure

A mixture of 70 g. (0.36 mole) of pure 1,4-aminonaphthol hydrochloride and 2100 cc. of water at 30° in a 5-l. flask is stirred for a few minutes in order to dissolve most of the material and then treated with 100 cc. of concentrated **sulfuric acid**. The mixture is heated to the boiling point until all the precipitated amine sulfate has been brought into solution. The solution is somewhat pink. The hot solution is poured rapidly through a large funnel (without a paper), which has been warmed on the steam bath, into a 5-l. round-bottomed flask containing a filtered solution at room temperature of 70 g. (2.4 moles) of **potassium dichromate** in 1 l. of water. The flask is shaken to mix the contents thoroughly. The quinone separates at once as a mass of fine, yellow needles. After cooling to 25° the material is collected, washed with water, and dried at 30–40°. The crude product is dull yellow; it melts at 124–125° to a dark liquid and weighs 53–55 g. (**Note 1**).

The crude **naphthoquinone** is warmed gently on the steam bath with 1.5 l. of **ether**, when it rapidly dissolves and leaves in suspension a slight amount of dark, fluffy material. The solution is shaken for ten minutes with 10 g. of **decolorizing carbon**; it is then filtered, and the **ether** is distilled from a steam bath until crystals begin to form. The solution is then allowed to cool undisturbed, and the clear canary-yellow prisms which separate are collected and washed with **ether**. The mother liquor is clarified by shaking as before with 7 g. of **decolorizing carbon**, filtered, and evaporated to a small volume until crystals begin to separate. The crystals are again washed with **ether**, and the mother liquor is clarified and evaporated once more. The final crop of material is dull in color but yields a pure product on recrystallization. All the material is of a high quality and melts at 124–125° to a clear yellow liquid; the yield is 44–46 g. (78–81 per cent of the theoretical amount) (**Note 2**).

2. Notes

1. The method of oxidation is essentially that of Russig.¹ The product obtained is slightly but definitely better than that produced at a lower temperature, or by adding the **sulfuric acid** to the dichromate solution, or by using **ferric chloride**. These latter procedures give the same yield, but the product is less pure and contains a black, ether-soluble impurity which must be washed out carefully after crystallization from **ether**.
2. This procedure² avoids the tedious purification by distillation with superheated steam in vacuum, which was described in the original method in *Org. Syn. Coll. Vol. I*, 375 (1932).

3. Discussion

1,4-Naphthoquinone can be prepared by the oxidation of **naphthalene**,³ 1,4-aminonaphthol,⁴ ⁵ 1,4-naphthylene diamine,⁴ and 1,4-naphthylamine sulfonic acid.⁶ Oxidation of 1,4-aminonaphthol is the most convenient method.⁷

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 310
- Org. Syn. Coll. Vol. 4, 698

References and Notes

1. Russig, J. prakt. Chem. (2) **62**, 31 (1900).
2. Fieser and Fieser, J. Am. Chem. Soc. **57**, 491 (1935).
3. Groves, Ann. **167**, 357 (1873); Plimpton, J. Chem. Soc. **37**, 634 (1880); Japp and Miller, *ibid.* **39**, 220 (1881); Miller, J. Russ. Phys. Chem. Soc. **16**, 414 (1884); Arnold and Larson, J. Org. Chem. **5**, 250 (1940).
4. Liebermann, Ann. **183**, 242 (1876).
5. Zincke and Wiegand, Ann. **286**, 70 (1895); Russig, J. prakt. Chem. (2) **62**, 31 (1900); Conant and Fieser, J. Am. Chem. Soc. **46**, 1862 (1924); Liebermann, Ber. **14**, 1796 (1881).
6. Monnet, Reverdin, and Nölting, Ber. **12**, 2306 (1879).
7. Conant and Fieser, J. Am. Chem. Soc. **46**, 1862 (1924).

Appendix

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

1,4-Aminonaphthol hydrochloride

1,4-Aminonaphthol

[sulfuric acid \(7664-93-9\)](#)

[ether \(60-29-7\)](#)

[decolorizing carbon \(7782-42-5\)](#)

[Naphthalene \(91-20-3\)](#)

[ferric chloride \(7705-08-0\)](#)

[potassium dichromate \(7778-50-9\)](#)

[1,4-Naphthoquinone,
naphthoquinone \(130-15-4\)](#)

[1,4-naphthylene diamine \(2243-61-0\)](#)

[1,4-naphthylamine sulfonic acid \(84-86-6\)](#)