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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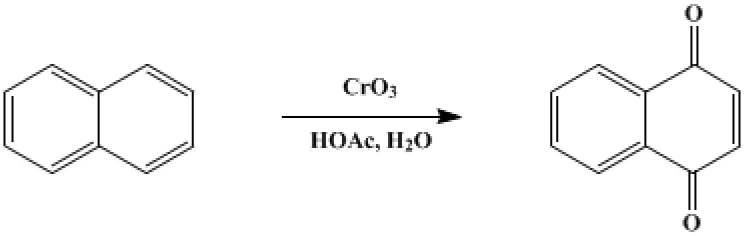
1,4-NAPHTHOQUINONE



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1. Procedure

In a 2-l. three-necked flask, fitted with a mechanical stirrer, a 1-l. dropping funnel, and a thermometer, is placed a solution of 120 g. (1.2 moles) of pure chromium trioxide (Note 1) in 150 ml. of 80% aqueous acetic acid. The flask is surrounded by a freezing mixture of ice and salt, and, when the temperature of the contents of the flask has fallen to 0°, a solution of 64 g. (0.5 mole) of naphthalene in 600 ml. of glacial acetic acid is gradually added, with constant stirring, over a period of 2–3 hours. The internal temperature is maintained at about 10–15°. Stirring is continued overnight, during which time the reaction mixture and cooling bath gradually attain room temperature (Note 2). The dark green solution is then set aside for 3 days and occasionally stirred.

The crude naphthoquinone is precipitated by pouring the reaction mixture into 6 l. of water. The yellow precipitate is filtered, washed with 200 ml. of water, and dried in a desiccator. The product can be crystallized from 500 ml. of petroleum ether (b.p. 80–100°) (Note 3) and separates in the form of long yellow needles, m.p. 124–125°. The yield is 14–17 g. (18–22%) (Note 4).

2. Notes

1. An equivalent quantity of technical grade chromium trioxide, ground to a fine powder, may be employed.
2. It is necessary to continue vigorous stirring at this stage in order to prevent local overheating and to keep the mixture from setting to a solid mass.
3. Crystallization from petroleum ether (b.p. 80–100°) is far more convenient than steam distillation as a method of purification, and a product of high purity is obtained after a single crystallization. The checkers used Skellysolve C (b.p. 88–115°) with consistent results. Crystallization from ether has also been employed.[2]
4. The yield is substantially unchanged on increasing the proportion of chromium trioxide used in the oxidation. The submitters report consistent yields of 25–28 g. (32–35%).

3. Discussion

The present method of preparation is adapted from Miller.[3] Although the yield is relatively low, the method is less costly and time-consuming than those starting from α-naphthol[2] or 1,4-benzoquinone.[4] Other methods that have been employed include the oxidation of naphthalene with hydrogen peroxide,[5] the oxidation of 1,4-naphthalenediamine[6] and naphthylaminesulfonic acid[7] and the oxidation of 4-amino-1-naphthol prepared by electrolytic reduction of 1-nitronaphthalene.[8]

References and Notes

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

petroleum ether

Skellysolve C

acetic acid (64-19-7)

ether (60-29-7)

α-naphthol (90-15-3)

Naphthalene (91-20-3)

hydrogen peroxide (7722-84-1)

1,4-benzoquinone (106-51-4)

1,4-Naphthoquinone,
naphthoquinone (130-15-4)

1,4-naphthalenediamine (2243-61-0)

1-nitronaphthalene (86-57-7)

chromium trioxide (1333-82-0)

naphthylaminesulfonic acid

4-amino-1-naphthol