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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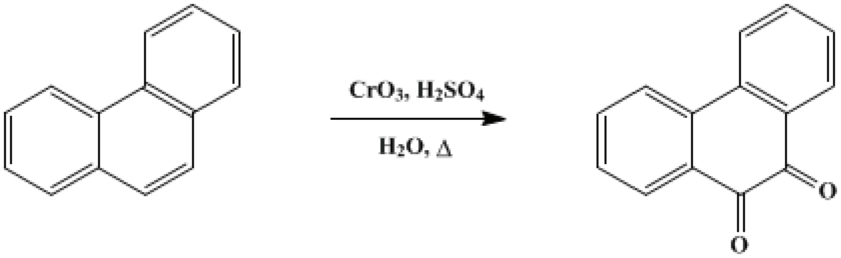
PHENANTHRENEQUINONE



Submitted by Ray Wendland and John LaLonde[1].
Checked by William S. Johnson and Sol Shulman.

1. Procedure

In a 3-l. three-necked flask equipped with a reflux condenser, a sealed mechanical stirrer, and a 1-l. dropping funnel, are placed 100 g. (0.56 mole) of phenanthrene (Note 1), 210 g. (2.1 moles) of chromic acid (Note 2), and 1 l. of water. The stirrer is started, and 450 ml. of concentrated sulfuric acid is added from the dropping funnel into the suspension at such a rate that gentle boiling is induced (Note 3). After addition of the sulfuric acid is complete, a mixture of 210 g. (2.1 moles) of chromic acid and 500 ml. of water is added carefully to the reaction mixture from the dropping funnel (Note 4). The resulting mixture is boiled under reflux for 20 minutes.

After being cooled to room temperature the reaction mixture is poured into an equal volume of water and chilled to 10° in an ice bath. The crude precipitate is separated by suction filtration and thoroughly washed with cold water until the washings no longer show any chrome green color. The precipitate is triturated with three 300-ml. portions of boiling water and filtered to remove the diphenic acid formed in the reaction. The precipitate is then triturated with several (4–6) 300-ml. portions of hot 40% sodium bisulfite solution and again filtered (Note 5). The insoluble material is a mixture of anthraquinone and some resinous products derived from anthracene and other contaminants present in the starting material (Note 6). The sodium bisulfite filtrates are combined and cooled to 5° in an ice bath. The precipitate which separates is collected by suction filtration; then it is transferred to a 1-l. beaker and finely dispersed in 300 ml. of water. To this suspension is added, with good stirring, 500 ml. of a saturated solution of sodium carbonate. The deep orange phenanthrenequinone which is liberated is separated by suction filtration (Note 7), washed well with cold water, and dried on a porcelain plate. The yield of product, melting at 205–208° cor., is 52–56 g. (44–48%). Further purification may be accomplished by crystallization from 95% ethanol (100 ml./ g.). The recovery of first-crop material is over 80%, m.p. 208.5–210° cor.

2. Notes

1. Reilly Tar and Chemical Company practical grade phenanthrene is crystallized from boiling toluene using Norit. One crystallization is sufficient to produce material melting at about 99.5°. The checkers employed Eastman Kodak Company technical grade (90%) phenanthrene.
2. Technical grade chromic acid (99.5% CrO_3) in flake form was used.
3. It is safe to add 100 ml. of acid all at once to start the oxidation, but as soon as the temperature rises to 70–75° the remainder must be added slowly in order to avoid violent boiling.
4. One-half (250 ml.) of the mixture is added carefully (the reaction may become vigorous at this stage), and 20–25 minutes is allowed for the oxidation to proceed spontaneously. The remaining mixture is then added slowly.
5. A heated Büchner funnel is preferably used to prevent clogging by crystallization.
6. The anthraquinone may be purified by extracting the insoluble material with a 150-ml. solution of potassium hydroxide and sodium hydrosulfite (approximately 10% by weight of each). The resulting red solution is quickly filtered by suction, and hydrogen peroxide is added to the filtrate until a yellow

precipitate appears. Dilute hydrochloric acid is added until the mixture is acidic to litmus, and the precipitate is collected by suction filtration, washed well with water, and air-dried. Five to seven grams of anthraquinone, m.p. 280–283°, may thus be obtained.
7. The filtrate should be treated with more sodium carbonate to test for completeness of precipitation.

3. Discussion

Phenanthrenequinone has been prepared by treatment of phenanthrene with chromic acid in acetic acid;[2] potassium dichromate in sulfuric acid;[3,4,5] hydrogen peroxide in acetic acid;[6,7] selenium dioxide above 250°;[8] iodic acid in acetic acid,[9] and chromyl chloride.[10] It also can be prepared from benzil with aluminum chloride at 120°[11] and from biphenyl-2,2'-dialdehyde with potassium cyanide.[12]

References and Notes

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

Diphenic acid

biphenyl-2,2'-dialdehyde

ethanol (64-17-5)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

sodium carbonate (497-19-8)

potassium cyanide (151-50-8)

sodium hydrosulfite (7775-14-6)

sodium bisulfite (7631-90-5)

Anthraquinone (84-65-1)

Norit (7782-42-5)

aluminum chloride (3495-54-3)

Benzil (134-81-6)

selenium dioxide (7446-08-4)

potassium hydroxide (1310-58-3)

toluene (108-88-3)

chromic acid (7738-94-5)

hydrogen peroxide (7722-84-1)

anthracene (120-12-7)

phenanthrenequinone (84-11-7)

iodic acid (7782-68-5)

potassium dichromate (7778-50-9)

chromyl chloride

phenanthrene (85-01-8)

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