



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.

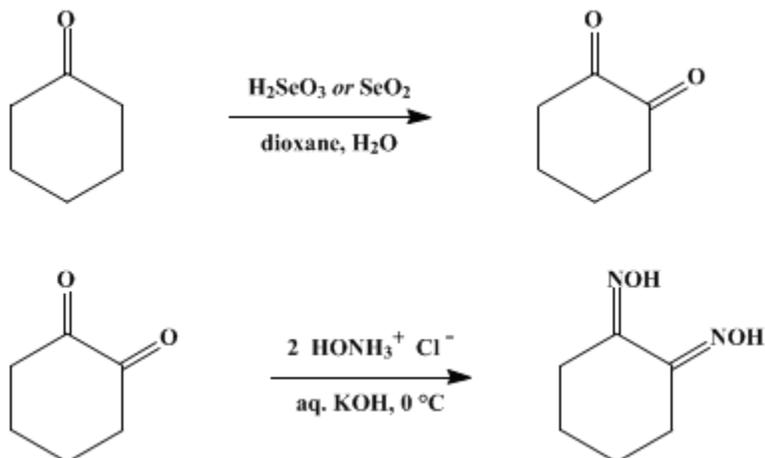
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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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1,2-CYCLOHEXANEDIONE DIOXIME



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1. Procedure

A. *1,2-Cyclohexanedione*. A 3-l. round-bottomed flask, fitted with stirrer and dropping funnel, is placed in a water bath containing a copper coil through which cooling water may be circulated. In the 3-l. flask is placed 1708 g. (17.4 moles, 1.8 l.) of cyclohexanone (Note 1). Tap water is circulated through the cooling coil (Note 2), and a solution containing 387 g. (3 moles) of selenious acid (H_2SeO_3) (Note 3), 500 ml. of dioxane, and 100 ml. of water is added dropwise and with stirring to the cyclohexanone over a period of 3 hours. The reaction mixture immediately turns yellow, and red amorphous selenium gradually appears. Stirring is continued for 5 additional hours at water-bath temperatures and then for 6 more hours at room temperature. Removal of the bulky, amorphous selenium is accomplished with the aid of a 6-in. Büchner funnel. The selenium is returned to the reaction flask and extracted with 300 ml. of boiling 95% ethanol for 1 hour (Note 4). The solution, obtained by decantation from the compact gray selenium, is combined with the above filtrate in a 4-l. distilling flask. Distillation under reduced pressure gives two fractions. The lower-boiling fraction ($25\text{--}60^\circ/16$ mm.) consists mainly of ethanol, water, dioxane, and cyclohexanone; the higher-boiling one ($60\text{--}90^\circ/16$ mm.) contains cyclohexanone and 1,2-cyclohexanedione with traces of water and dioxane. The yield of crude product is approximately 322 g.

The higher-boiling fraction is redistilled (Note 5), and again two fractions, boiling at $25\text{--}75^\circ/16$ mm. and $75\text{--}79^\circ/16$ mm., are collected. The latter fraction is essentially pure 1,2-cyclohexanedione and crystallizes at 34° to ice-like crystals which become light yellow-green when exposed to the air; yield 202.5 g. (60% based on selenous acid). A considerable amount of light-brown, clear, resinous residue remains in the distilling flask.

B. *1,2-Cyclohexanedione dioxime*. In a 1-l. Erlenmeyer flask is placed 200 ml. of water and 100 g. of cracked ice. To this ice-water mixture is added 86.9 g. (1.25 moles) of hydroxylammonium chloride. An ice-cold basic solution is prepared by dissolving 82.4 g. (1.25 moles) of 85% potassium hydroxide in 50 ml. of water and then adding 150 g. of cracked ice. The ice-cold potassium hydroxide solution is added to the hydroxylammonium chloride solution, and the mixture is thoroughly shaken. To the mixture is added about 0.5 g. of nioxime (1,2-cyclohexanedione dioxime) with stirring (Note 6). The solution turns red owing to the reaction of the nioxime with quantities of iron and other impurities in the reagents. Four grams of Norit is added; the mixture is thoroughly shaken and then filtered with the aid of a 5-in. Büchner funnel. After this operation the filtrate should be water white.

The cold solution is transferred to a 1-l. Erlenmeyer flask and is placed in an ice bath. To the stirred

solution is added slowly 56 g. (0.5 mole) of melted 1,2-cyclohexanedione. Precipitation of the 1,2-cyclohexanedione dioxime should take place almost immediately. If not, the solution may be seeded to initiate rapid precipitation. The mixture is stirred for 30 minutes after the addition of the 1,2-cyclohexanedione, and the precipitate is then collected on a 5-in. Büchner funnel. The precipitate is thoroughly washed with water to remove inorganic salts. The 1,2-cyclohexanedione dioxime is partially dried by suction and finally dried in a vacuum desiccator to give snow-white crystals; yield 52.5 g. (74%); m.p. 185–188° (darkening at 170°) (Note 7). The crude 1,2-cyclohexanedione dioxime is recrystallized from 550 ml. of water using 2.5 g. of iron-free Norit; yield 39.3 g. (55%); m.p. 186–188°.

2. Notes

1. The cyclohexanone need not be freshly distilled. Commercial cyclohexanone, obtained from the Barrett Division, Allied Chemical & Dye Corporation, New York, New York, gave practically the same yield as carefully fractionated cyclohexanone.
2. If too much selenous acid is added at once, or the cooling discontinued, the solution will heat up and the reaction will become extremely vigorous with subsequent decrease in yield.
3. Selenous acid or selenium dioxide can apparently be used interchangeably.
4. The selenium filtered from the reaction mixture is refluxed with 3 l. of 95% ethanol for 1 hour; this converts the red amorphous form to the gray hexagonal form and frees it of organic matter. This metallic selenium is removed by filtration, washed with water, and converted to the dioxide by the method of Baker and Maxson.²
5. A distilling head such as J-1104 obtained from Scientific Glass Apparatus Company, Bloomfield, New Jersey, was used.
6. This treatment must obviously be omitted on the first preparation; the product will be light pink rather than snow white, as obtained when the reagents are purified in this manner.
7. This material is 96.5% pure as determined by precipitation of the nickel compound and is satisfactory as an analytical reagent.

3. Discussion

1,2-Cyclohexanedione has been prepared by brominating cyclohexanone and treating the resulting 2,6-dibromocyclohexanone with aqueous potassium hydroxide to obtain the dihydroxy compound which loses water to yield the dione;³ by heating divinyl glycol with copper;⁴ and by oxidizing cyclohexanone with selenium dioxide in an ethanolic solution.^{5,6}

1,2-Cyclohexanedione dioxime has been prepared by oximating 1,2-cyclohexanedione with hydroxylammonium chloride in aqueous potassium hydroxide solution;^{3,6} by oximating 2-isonitrosocyclohexanone with hydroxylammonium chloride;^{7,8} by oximating sodium 2-isonitrosocyclohexanone with hydroxylammonium chloride in methanolic solution;⁶ and by the reaction of hydroxylamine with 2-chloro-⁹ or 2-bromocyclohexanone,¹⁰ and with perhydro-4a,9a-epoxydibenzo-*p*-dioxin-5a,10a-diol.¹¹

References and Notes

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

ethanol (64-17-5)

iron (7439-89-6)

Cyclohexanone (108-94-1)

copper (7440-50-8)

nickel (7440-02-0)

Norit (7782-42-5)

selenium dioxide (7446-08-4)

potassium hydroxide (1310-58-3)

hydroxylamine (7803-49-8)

dioxane (123-91-1)

selenium

selenious acid,
selenous acid (7783-00-8)

1,2-Cyclohexanedione (765-87-7)

1,2-Cyclohexanedione dioxime,
nioxime (492-99-9)

hydroxylammonium chloride

2,6-dibromocyclohexanone

divinyl glycol (764-78-3)

2-isonitrosocyclohexanone

sodium 2-isonitrosocyclohexanone

2-bromocyclohexanone

perhydro-4a,9a-epoxydibenzo-p-dioxin-5a,10a-diol