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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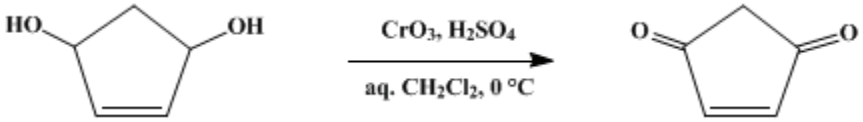
2-CYCLOPENTENE-1,4-DIONE



Submitted by Gary H. Rasmusson[1], Herbert O. House[1], Edward F. Zaweski[2], and Charles H. DePuy[2].
Checked by William G. Dauben, Philip E. Eaton, and Richard Schneider.

1. Procedure

In a 2-l. three-necked flask equipped with a thermometer, a mechanical stirrer, and a dropping funnel (Note 1) is placed a mixture of 45.1 g. (0.45 mole) of a dihydroxycyclopentene mixture (Note 2), 200 ml. of water, and 300 ml. of methylene chloride. After this mixture has been cooled to −5° to 0° by means of an external cooling bath (Note 3), the addition of a solution of 100 g. (1.0 mole) of chromium trioxide and 160 ml. of concentrated sulfuric acid in 450 ml. of water is begun. The solution of the oxidant is added dropwise, and with stirring, at such a rate that the temperature of the reaction mixture remains between −5° and 0°. After the addition is complete (Note 4), the mixture is stirred at −5° to 0° for 1 hour and then 200 ml. of chloroform is added. The resulting mixture is stirred for 10 minutes, the organic layer is separated, and then the aqueous layer is extracted with two 200-ml. portions of a mixture (1:1 by volume) of chloroform and methylene chloride. The combined organic extracts are washed with 100 ml. of water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure at room temperature. The yield of 2-cyclopentene-1,4-dione (Note 5), which crystallizes as yellow plates melting at 30.0–32°, is 17–22 g. (39–50% based on the dihydroxycyclopentene mixture) (Note 6).

2. Notes

1. All glassware must be washed with acid before use.
2. The dihydroxycyclopentene mixture was prepared from cyclopentene and peracetic acid.[3] The mixture contains approximately 70% of 2-cyclopentene-1,4-diol.
3. The submitters found a cooling bath composed of a Dry Ice and methanol-water mixture (1:3 by volume) to be convenient.
4. At this point in the preparation, an excess of the oxidant should be present. The presence of excess oxidant may be established by diluting 2 drops of the aqueous phase from the reaction mixture with 2 ml. of water and then adding 1 drop of a 0.4% solution of sodium diphenylaminesulfonate in water. A deepening in color is observed if excess oxidant is present.
5. This product is sufficiently pure for most applications. Further purification may be achieved either by sublimation of the product at 30–40°/0.1 mm. or by recrystallization of the dione from diethyl ether at Dry Ice temperatures. The dione decomposes rapidly at temperatures above 40°. An ethanol solution of pure dione, m.p. 35–36°, exhibits a maximum in the ultraviolet at 222 mμ (log ε 4.16).
6. Starting with pure 2-cyclopentene-1,4-diol, the submitters obtained the dione in 67–79% yield.

3. Discussion

2-Cyclopentene-1,4-dione has been prepared by oxidation of 2-cyclopentene-1,4-diol with chromium trioxide in aqueous acetic acid[4,5] or in aqueous acetone,[4] and with silver chromate.[6] The present method eliminates the tedious removal of large amounts of acetic acid and gives a higher yield.

4. Merits of Preparation

2-Cyclopentene-1,4-dione is a very reactive dienophile in the Diels-Alder reaction and thus provides access to a variety of compounds containing the reactive β-dicarbonyl grouping in a five-

membered ring.[4] Also, its multiple functionality makes it a versatile starting material for other types of reactions as well.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 414

References and Notes

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

ethanol (64-17-5)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

diethyl ether (60-29-7)

chloroform (67-66-3)

acetone (67-64-1)

methylene chloride (75-09-2)

magnesium sulfate (7487-88-9)

chromium trioxide (1333-82-0)

Cyclopentene (142-29-0)

peracetic acid (79-21-0)

2-Cyclopentene-1,4-dione (930-60-9)

Dihydroxycyclopentene

2-cyclopentene-1,4-diol (4157-01-1)

sodium diphenylaminesulfonate

silver chromate (7784-01-2)