



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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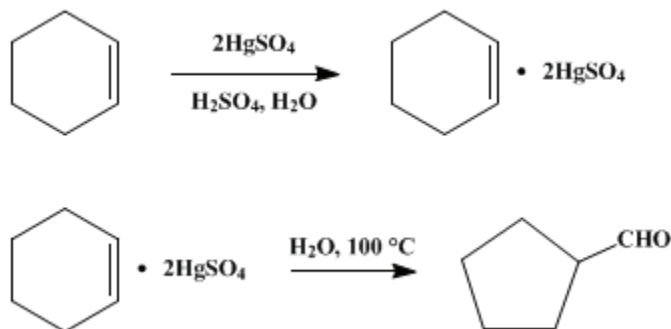
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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CYCLOPENTANECARBOXALDEHYDE



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1. Procedure

In a 5-l. three-necked flask fitted with reflux condenser, mechanical stirrer, thermometer, and nitrogen gas inlet is placed a solution of 80.0 g. (43.5 ml., 0.82 mole) of concentrated sulfuric acid in 3 l. of water. The solution is stirred under nitrogen, and 740.0 g. (2.49 moles) of reagent mercuric sulfate is added to form a suspension of deep-yellow, basic mercuric sulfate. The mixture is stirred and heated to 55° under nitrogen, and 82.0 g. (101 ml., 1.0 mole) of cyclohexene (Note 1) is added at once. A temperature of $55\text{--}65^\circ$ (Note 2) is maintained for 1 hour. During this time the color of the reaction mixture changes from a deep yellow to the cream color of the cyclohexene-mercuric sulfate complex.

At the end of 1 hour the condenser is set for distillation. The temperature of the reaction mixture is raised (Note 3), the mixture is stirred while a slow current of nitrogen is continued, and 300 ml. of a mixture of crude cyclopentanecarboxaldehyde and water is distilled over a period of approximately 2 hours. The crude product is removed in a separatory funnel from the aqueous layer, which is extracted with three 50-ml. portions of ether. The extracts are combined with the product and dried over anhydrous sodium sulfate. The solution is filtered into a 250-ml. Claisen flask set for vacuum distillation, the pressure is gradually reduced to 100 mm. to distil ether, and the cyclopentanecarboxaldehyde is distilled rapidly (Note 4) at $74\text{--}78^\circ$ (100 mm.). The yield of aldehyde (n_D^{20} 1.4420–1.4428) is 45–52 g. (46–53%).

Unless the aldehyde is to be used immediately, it is stored in a brown bottle at 0° after the addition of 0.1 g. of hydroquinone and a blanket of nitrogen (Note 5).

2. Notes

1. Cyclohexene from an unopened bottle or freshly distilled material (b.p. $82\text{--}84^\circ$) is used.
2. This is the optimal temperature range to form the cyclohexene-mercuric sulfate complex.^{2,3}
3. The complex undergoes oxidation-reduction at about 100° to give cyclopentanecarboxaldehyde, mercurous sulfate, and some mercury. If desired, the mercury products can be regenerated to mercuric sulfate. However, approximately 40–140 g. of mercuric sulfate will be lost in the various filtrates in the recovery operation. Best current practice dictates that these filtrates be collected and disposed of as toxic chemicals. Concentration of the filtrates is not advisable since acetone, nitric acid, and sulfuric acid are present along with the mercury compounds. If the mercuric sulfate is not regenerated, the water and sludge of mercurous sulfate and mercury, which remain after the distillation of cyclopentanecarboxaldehyde, should be disposed of with due regard to its toxic nature.

The regeneration procedure is as follows:

The water and sludge of mercurous sulfate and mercury, which remain after the distillation of cyclopentanecarboxaldehyde, are filtered with suction, washed with three 100-ml. portions of boiling water, three 100-ml. portions of acetone, and finally with three 100-ml. portions of boiling water. The

gray-black solid is sucked dry.

To the solid in a 3-l. Erlenmeyer flask is added 270 ml. of water, then 90 g. (65 ml., 1.0 mole) of concentrated **nitric acid** *slowly* (*Hood!*). The contents of the flask are swirled and allowed to stand until frothing and evolution of reddish brown oxides of nitrogen subsides. Dow-Corning Antifoam A helps to control frothing.

The mixture is heated *cautiously* on a hot plate to avoid excess frothing. When the frothing has almost subsided, additional concentrated **nitric acid** is added, 90 g. (65 ml., 1.0 mole) at a time, with swirling and intermittent heating to control the vigorous reaction. The solid changes from gray-black to a cream color after six 90-g. portions of concentrated **nitric acid** have been used.

Six hundred milliliters of concentrated **nitric acid** is then added with heating to form a clear, deep-orange solution of **mercuric nitrate**. This mixture is allowed to cool and is then filtered with suction through sintered glass to remove a small amount of solid.

Four hundred and sixty grams (250 ml., 4.7 moles) of concentrated **sulfuric acid** is added to the filtrate to precipitate **mercuric sulfate**. The mixture is boiled under the hood for 1 hour, cooled to 10–25°, and filtered with suction through sintered glass.

The solid **mercuric sulfate** is washed with three 100-ml. portions of approximately 40% aqueous **sulfuric acid** solution (110 ml. of concentrated **sulfuric acid** mixed with 300 ml. of water). The solid is sucked dry, transferred to an evaporating dish, broken up, and dried in the hood under a heat lamp.

The yield of recovered **mercuric sulfate** is 600–700 g. This material plus fresh **mercuric sulfate** to give 740 g. can be used in a subsequent preparation of **cyclopentanecarboxaldehyde** without affecting the yield.

4. **Cyclopentanecarboxaldehyde** may trimerize if heating is prolonged; hence a fast, simple distillation is done. When the distillation residue is cooled, a solid may appear. This solid can be distilled above 78° (100 mm.) as a clear liquid which solidifies when allowed to stand. Recrystallization of this material from 95% **ethanol** gives a white solid melting at 122–124°. This product was shown to be cyclopentanecarboxaldehyde trimer by a mixed melting-point determination with trimer prepared from **cyclopentanecarboxaldehyde** and 85% **phosphoric acid**.⁴

5. During storage there is a slow formation of cyclopentanecarboxaldehyde trimer.

3. Discussion

Cyclopentanecarboxaldehyde has been prepared by the procedure described above;^{2,3} by the reaction of aqueous **nitric acid** and **mercuric nitrate** with **cyclohexene**;⁵ by the action of **magnesium bromide etherate**⁶ or thoria⁷ on **cyclohexene oxide**; by the dehydration of *trans*-1,2-**cyclohexanediol** over alumina mixed with glass helices;⁸ by the dehydration of **divinyl glycol** over alumina followed by reduction;⁹ by the reaction of **cyclopentene** with a solution of $[\text{HFe}(\text{CO})_4]^-$ under a **carbon monoxide** atmosphere;¹⁰ and by the reaction of **cyclopentadiene** with dicobalt octacarbonyl under a **hydrogen** and **carbon monoxide** atmosphere.¹¹

4. Merits of the Preparation

This procedure uses readily available starting materials and in one operational step generally gives higher yields of **cyclopentanecarboxaldehyde** than other preparations described in the literature. Because **mercuric sulfate** is an expensive reactant, a method of regenerating the **mercury** products is given. **Cyclopentanecarboxaldehyde** is a useful intermediate for many cyclopentane derivatives.

References and Notes

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

oxides of nitrogen

alumina

thoria

Cyclohexene-mercuric sulfate complex

[HFe(CO)₄]⁻

ethanol (64-17-5)

sulfuric acid (7664-93-9)

ether (60-29-7)

hydrogen (1333-74-0)

carbon monoxide (630-08-0)

hydroquinone (123-31-9)

nitric acid (7697-37-2)

Cyclohexene (110-83-8)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

mercury (7439-97-6)

acetone (67-64-1)

phosphoric acid (7664-38-2)

Cyclohexene oxide (286-20-4)

mercuric sulfate (7783-35-9)

mercuric nitrate

Cyclopentene (142-29-0)

divinyl glycol (764-78-3)

CYCLOPENTADIENE (542-92-7)

Cyclopentanecarboxaldehyde,
cyclopentanecarboxyaldehyde (872-53-7)

mercurous sulfate (7783-36-0)

magnesium bromide etherate

trans-1,2-Cyclohexanediol (1460-57-7)