



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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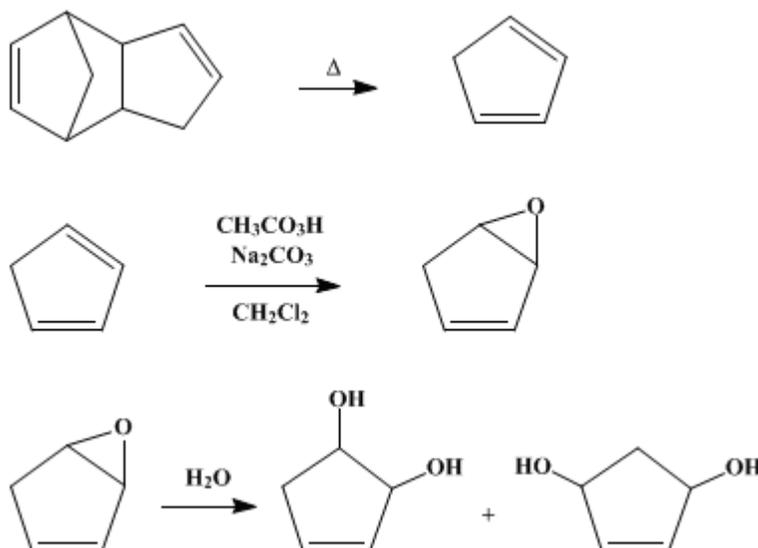
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.414 (1973); Vol. 42, p.50 (1962).

DIHYDROXYCYCLOPENTENE

[Cyclopentenediol]



Submitted by M. Korach, D. R. Nielsen, and W. H. Rideout¹.
Checked by William G. Dauben and Clifton Ashcraft.

1. Procedure

Caution! Reactions run with peracetic acid should be conducted with due regard to the properties of this reagent (Note 1).

In a 1-l. three-necked flask equipped with a dropping funnel, a thermometer, and an efficient fractionation column fitted with either a vapor- or liquid-splitting head (Note 2) is placed 400 ml. of mineral oil. The oil is heated to 240–270° and dicyclopentadiene (Note 3) is added at the rate of 5–10 ml. per minute. The reflux ratio and the rate of addition of dicyclopentadiene are adjusted to maintain the distillation head temperature at 40°. The cyclopentadiene is collected in a Dry Ice-acetone receiver (Note 4).

In a 1-l. three-necked flask fitted with a sealed stirrer, a thermometer, and a connecting tube with parallel side arm to which is attached an addition funnel and a reflux condenser are placed 56 g. (0.81 mole) of 96% cyclopentadiene, 106 g. (1.0 mole) of anhydrous sodium carbonate, and 500 ml. of methylene chloride. A solution of 2 g. of sodium acetate in 76 g. of 40% peracetic acid (0.40 mole) (Note 5) is added, with stirring, over a period of 30–45 minutes, and the temperature is maintained at 20° by intermittent external cooling. The resulting mixture is stirred for an additional hour at room temperature (Note 6). The solid in the reaction is removed by suction filtration, and the filter cake is washed three times with 75 ml. of methylene chloride. The combined filtrate and washings are added, with rapid stirring, over a period of 1 hour, to 250 ml. of cold distilled water (maintained at 5–10° by external cooling) contained in a 2-l. three-necked flask fitted with a condenser, a sealed stirrer, and an addition funnel (Note 7). The stirring is continued for 1 hour as the temperature is allowed to rise to room temperature, the layers are separated, and the lower methylene chloride layer is extracted twice with 25 ml. of distilled water. The aqueous extracts are combined with the aqueous phase obtained from the hydrolysis reaction, and the combined solution is distilled at approximately 30 mm. pressure to remove the water (Note 8). The residue is distilled at reduced pressure to give 26–28 g. of colorless oil, b.p. 82–105°/1 mm. (Note 9). The yield of mixed cyclopentenediols is 65–70% based on the quantity of

peracetic acid used.

The mixed cyclopentenediols can be separated by distillation through a 60-cm. spinning band column. The yield of pure 3-cyclopentene-1,2-diol, b.p. 65–68°/1 mm., n_D^{20} 1.4941–1.4951, is 4.5–5.5 g., and the yield of pure 2-cyclopentene-1,4-diol, b.p. 92–95°/1 mm., n_D^{20} 1.5000–1.5010, is 17–20 g. (Note 10).

2. Notes

1. When peracetic acid is used in organic synthesis the following precautions are recommended by the FMC Corporation, Inorganic Chemicals Division (Bulletins 4 and 69). All laboratory reactions and subsequent operations should be run behind a safety shield. The peracetic acid should be added to the organic material, never the reverse, and the rate of addition should be slow enough so that the peracid reacts as rapidly as it is added and no unreacted excess is allowed to build up. The reaction mixture should be stirred efficiently while the peracid is being added, and cooling facilities should be provided since most of the reactions of peracetic acid are exothermic. New or unfamiliar reactions, particularly those run at high temperatures, should be tried first on a very small scale. Reaction products should never be recovered from the final reaction mixture by distillation until all residual active oxygen compounds have been destroyed. This includes the hydrogen peroxide present in commercial 40% peracetic acid as well as the unreacted peracid. Decomposition may be readily accomplished by catalytic quantities of activated carbon or ferric sulfate added at 25–50°. The course of the decomposition may be followed by the titration described in (Note 5). (See also Note 1, p. 904).

A serious accident has occurred when the reaction described in this procedure was run on a scale ten times that described and some of the above precautions were not observed (G. Benoy, private communication).

2. The checkers used a 1 × 24 in. column packed with glass helices.

3. Commercially available dicyclopentadiene of 95% or 70% purity may be used. The higher-purity material yields a less colored product.

4. Any ice present in the product can be removed by filtration of the cyclopentadiene through glass wool. Cyclopentadiene can be stored at Dry Ice temperatures in a tightly capped bottle for several weeks without serious loss due to dimerization. Purification of a stored sample can be effected by distillation through a short Vigreux column at 10–30 mm. pressure and collection of the product in a receiver cooled by a Dry Ice-acetone bath until the temperature in the distilling flask rises to 10°. The distillate contains approximately the same concentration of cyclopentadiene as the freshly purified material (95–96%).

5. Peracetic acid (40%) is available commercially. Since the epoxycyclopentene reacts rapidly with water, it is desirable to keep the water content of the peracetic acid solution as low as possible. This is the reason for the use of the concentrated peracetic acid solution.

The peracetic acid content of the reagent may be determined by adding an aliquot to an equal volume of ice and water and titrating first with ceric sulfate solution until the orange color of the ceric ion remains (to eliminate hydrogen peroxide) and then adding potassium iodide and titrating with standard sodium thiosulfate solution.

6. The extent of peracetic acid consumption can be determined by titration of an aliquot as described in (Note 4).

7. Distilled epoxycyclopentene can be hydrolyzed under identical conditions. However, distillation of the crude epoxide has occasionally resulted in a rapid, highly exothermic reaction when the pot temperature rises above 60°. The safest method for isolating the epoxide from the crude product is to remove the methylene chloride by distillation at atmospheric pressure until the pot temperature reaches 50°, then strip off crude epoxycyclopentene at reduced pressure and at a temperature below 50°. The apparatus should be shielded and the temperature in the distillation flask should be monitored. The crude distillate of epoxide and methylene chloride can be safely redistilled at 75–100 mm. pressure.

8. A rotatory evaporator has been found to be quite suitable for the rapid removal of water.

9. In some cases the distillate is yellow. The color can be removed by redistillation in the presence of 0.1% anhydrous sodium carbonate.

10. The purity of the distillation fractions can be determined by gas-liquid chromatography, using a 5 ft. × ¼ in. column containing 20% Carbowax at a temperature of 200°.

3. Discussion

Cyclopentenediol isomers have previously been prepared by hydrolysis of acetates produced by reaction of dibromocyclopentene with potassium acetate in acetic acid;² by reaction of cyclopentene with selenium dioxide in acetic anhydride;³ or by reaction of cyclopentadiene with phenyl iodosoacetate,⁴ with lead tetraacetate,⁵ or with peracetic acid in the absence of base.⁶ Preparation of cyclopentenediol without intermediate formation of acetates has been accomplished by reaction of cyclopentadiene with hydrogen peroxide in the presence of osmium tetroxide in *tert*-butanol,⁷ and by reaction of cyclopentadiene with peracetic acid in a methylene chloride suspension of anhydrous sodium carbonate, followed by hydrolysis of the resulting epoxy-cyclopentene.⁸

4. Merits of Preparation

The present method of preparation utilizes inexpensive, readily available, non-toxic reagents, is less laborious than previous methods, produces an easily purified product, and results in improved yields (65–70% vs. 10–50% for the older methods). It is a useful starting material for a variety of compounds as illustrated by the preparations of 2-cyclopentenone (p. 326) and 2-cyclopentene-1, 4-dione (p. 324).

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 60
- Org. Syn. Coll. Vol. 5, 324
- Org. Syn. Coll. Vol. 5, 326
- Org. Syn. Coll. Vol. 5, 1088
- Org. Syn. Coll. Vol. 6, 145
- Org. Syn. Coll. Vol. 7, 339
- Org. Syn. Coll. Vol. 8, 13
- Org. Syn. Coll. Vol. 8, 298
- Org. Syn. Coll. Vol. 9, 132
- Org. Syn. Coll. Vol. 9, 136

References and Notes

1. Columbia-Southern Chemical Corp., subsidiary of Pittsburgh Plate Glass Co., P. O. Box 4026, Corpus Christi, Texas.
2. A. T. Blomquist and W. G. Mayes, *J. Org. Chem.*, **10**, 134 (1945).
3. E. Dane, J. Schmitt, and C. Rautenstrauch, *Ann.*, **532**, 29 (1937).
4. R. Criegee and H. Beucker, *Ann.*, **541**, 218 (1939).
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7. N. A. Milas and L. S. Maloney, *J. Am. Chem. Soc.*, **62**, 1841 (1940).
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Appendix

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

acetic acid (64-19-7)

acetic anhydride (108-24-7)

sodium acetate (127-09-3)
sodium carbonate (497-19-8)
potassium iodide (7681-11-0)
sodium thiosulfate (7772-98-7)
carbon (7782-42-5)
selenium dioxide (7446-08-4)
hydrogen peroxide (7722-84-1)
methylene chloride (75-09-2)
Cyclopentene (142-29-0)
potassium acetate (127-08-2)
peracetic acid (79-21-0)
osmium tetroxide (20816-12-0)
phenyl iodosoacetate
CYCLOPENTADIENE (542-92-7)
dicyclopentadiene (77-73-6)
3-cyclopentene-1,2-diol
ferric sulfate (10028-22-5)
epoxycyclopentene
ceric sulfate (13590-82-4)
dibromocyclopentene
tert-butanol (75-65-0)
2-cyclopentene-1, 4-dione (930-60-9)
Dihydroxycyclopentene,
Cyclopentenediol
2-cyclopentene-1,4-diol (4157-01-1)
2-Cyclopentenone (930-30-3)

lead tetraacetate (546-67-8)

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