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.

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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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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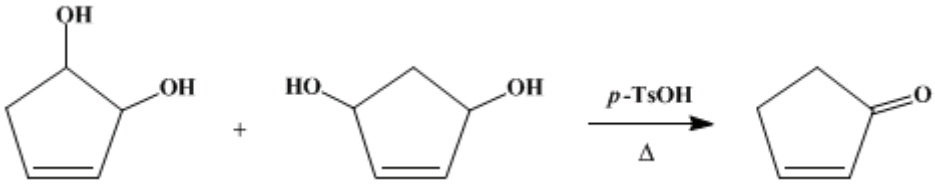
Organic Syntheses, Coll. Vol. 5, p.326 (1973); Vol. 42, p.38 (1962).

2-CYCLOPENTENONE

[2-Cyclopentene-1-one]



Submitted by Charles H. DePuy and K. L. Eilers[1].
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1. Procedure

In a 250-ml. round-bottomed flask fitted for vacuum distillation with a short path distilling head (Note 1), a condenser, and a 250-ml. receiving flask is placed 100 g. (1.0 mole) of a mixture of cyclopentenediols.[2] A few Carborundum boiling chips are added. The receiver is cooled in ice and the mixture heated to 50–55° (Note 2). At this time, the flask is opened momentarily and 1–2 g. of *p*-toluenesulfonic acid monohydrate is added. The flask is immediately closed and the pressure is reduced to 10–15 mm. Careful heating is continued, and a mixture of 2-cyclopentenone and water begins to distil with the temperature in the distilling head rising from 45° to 60° (Note 3). The temperature of the flask is gradually increased as necessary to maintain a reasonably rapid distillation rate.

The reaction is complete when approximately 10% of the original material remains in the distilling flask. The distillation normally requires 30–60 minutes.

The distillate, containing 2-cyclopentenone, water and varying amounts of cyclopentenediols, is dissolved in 150 ml. of methylene chloride and dried over anhydrous sodium sulfate. The solvent is carefully removed through a Vigreux column and the residue purified by distillation. After a forerun (b.p. 50–150°), there is collected 44–49 g. (53–60%) of pure 2-cyclopentenone, b.p. 151–154°. Cyclopentenediols may be recovered from the pot residue by distillation at 0.1 mm. The forerun contains appreciable amounts of cyclopentenone and should be added to a succeeding preparation before final distillation.

2. Notes

1. The distilling head should be short and unobstructed, for any attempt at fractionation at this stage leads to resinification of the 2-cyclopentenone by the acid. No capillary bleed is used, since the product is extremely sensitive to oxygen.
2. The submitters have found a 250-watt infrared heat lamp controlled by a Variac to be the most convenient source of heat. Occasionally, the reaction may become rapid and exothermic, and it is important to remove the heat source as quickly as possible. If an oil bath is used, the temperature is gradually increased until it approaches 150° at the end of the reaction.
3. If the temperature of the distillate rises much above 60° at this pressure, considerable amounts of diols co-distil and the yield of 2-cyclopentenone is diminished. If a reasonably rapid distillation does not occur with a head temperature below 60°, an additional gram of acid should be added after lowering the temperature of the distillation flask below 50°.

3. Discussion

Previous preparations of 2-cyclopentenone have involved the elimination of HCl from 2-chlorocyclopentanone[3] or its ketal.[4] The oxidation of 3-chloro-[5] or 3-hydroxycyclopentene[6] has been utilized as well as the direct oxidation of cyclopentene with H_2O_2.[7] Cyclopentenone has also been prepared from 1-dicyclopentadienol.[8]

4. Merits of Preparation

The α,β-unsaturated ketone system in 2-cyclopentenone makes possible a wide variety of reactions of the Michael and Diels-Alder type. Thus 2-cyclopentenone is a versatile starting material for preparing compounds containing a five-membered ring. The availability of the dihydroxycyclopentene mixture (p. 414) makes the present procedure the method of choice for its preparation.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 414
- Org. Syn. Coll. Vol. 7, 271

References and Notes

1. Department of Chemistry, Iowa State University, Ames, Iowa.
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3. E. J. Corey and K. Osugi, *Pharm. Bull. (Tokyo)*, **1**, 99 (1953).
4. H. Wanzlick, G. Gollmer, and M. Milz, *Ber.*, **88**, 69 (1955).
5. K. Alder and F. H. Flock, *Ber.*, **89**, 1732 (1956).
6. E. Dane and K. Eder, *Ann.*, **539**, 207 (1939).
7. W. Treibs, G. Franke, G. Leichsenring, and H. Roder, *Ber.*, **86**, 616 (1953).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

H_2O_2

1-dicyclopentadienol

HCl (7647-01-0)

sodium sulfate (7757-82-6)

oxygen (7782-44-7)

methylene chloride (75-09-2)

Cyclopentene (142-29-0)

2-Cyclopentenone,
2-Cyclopentene-1-one,
cyclopentenone (930-30-3)

2-chlorocyclopentanone (694-28-0)

p-toluenesulfonic acid monohydrate (6192-52-5)