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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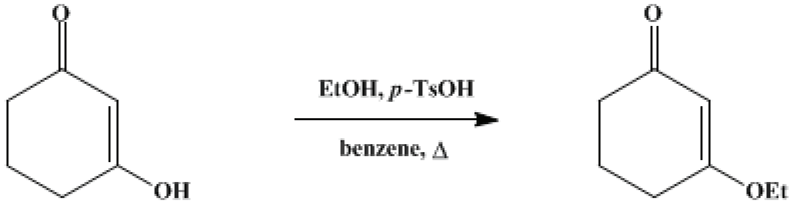
Organic Syntheses, Coll. Vol. 5, p.539 (1973); Vol. 40, p.41 (1960).

3-ETHOXY-2-CYCLOHEXENONE

[Dihydroresorcinol monoethyl ether]



Submitted by Walter F. Gannon and Herbert O. House[1].
Checked by William E. Parham, Wayland E. Noland, George Meisters, and Allan M. Huffman.

1. Procedure

In a 2-l. flask fitted with a total-reflux, variable-take-off distillation head is placed a solution of 53 g. (0.472 mole) of dihydroresorcinol (Note 1), 2.3 g. of *p*-toluenesulfonic acid monohydrate and 250 ml. of absolute ethanol in 900 ml. of benzene. The mixture is heated to boiling and the azeotrope composed of benzene, alcohol, and water is removed at the rate of 100 ml. per hour. When the temperature of the distilling vapor reaches 78° (Note 2), the distillation is stopped and the residual solution is washed with four 100-ml. portions of 10% aqueous sodium hydroxide which have been saturated with sodium chloride. The resulting organic solution is washed with successive 50-ml. portions of water until the aqueous washings are neutral and then concentrated under reduced pressure. The residual liquid is distilled under reduced pressure. The yield of 3-ethoxy-2-cyclohexenone (Note 3), b.p. 66–68.5°/0.4 mm. or 115–121°/11 mm., n_D^{29} 1.5015, is 46.6–49.9 g. (70–75%).

2. Notes

1. The preparation of dihydroresorcinol was described in an earlier volume of this series.[2]
2. This distillation requires 6–8 hours.
3. The product may be analyzed by gas chromatography on an 8 mm. × 215 cm. column heated to 220–240° and packed with Dow-Corning Silicone Fluid No. 550 suspended on 50–80 mesh ground firebrick. The chromatogram obtained with this column exhibits a single major peak. The ultraviolet spectrum of an ethanol solution of the product has a maxium at 250 mμ (ε = 17,200).

3. Discussion

3-Ethoxy-2-cyclohexenone has been prepared by reaction of the silver salt of dihydroresorcinol with ethyl iodide[3] and by the reaction of dihydroresorcinol with ethyl orthoformate, ethanol and sulfuric acid.[4] The acid-catalyzed reaction of dihydroresorcinol with ethanol in benzene solution utilized in this preparation is patterned after the procedure of Frank and Hall.[4,5]

This procedure can also be used to prepare other 2-alkoxy-2-cyclohexenones. For example, it has been reported that 2-isobutoxy-2-cyclohexenone can be prepared easily in high yield (91%) from dihydroresorcinol and isobutyl alcohol.[6] The use of isobutyl alcohol[7] often gives better yields of enol ethers.[8,9]

4. Use of 3-Ethoxy-2-cyclohexenone

The 3-alkoxy-2-cyclohexenones are useful intermediates in the synthesis of certain cyclohexenones. The reduction of 3-ethoxy-2-cyclohexenone with lithium aluminum hydride followed by hydrolysis and dehydration of the reduction product yields 2-cyclohexenone.[10] Similarly, the reaction of 3-alkoxy-2-cyclohexenones with organometallic reagents followed by hydrolysis and dehydration of the addition product affords a variety of 3-substituted 2-cyclohexenones.[3,5,6,8]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 294
- Org. Syn. Coll. Vol. 6, 679
- Org. Syn. Coll. Vol. 7, 208

References and Notes

1. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.
2. R. B. Thompson, *Org. Syntheses*, Coll. Vol. **3**, 278 (1955).
3. G. F. Woods and I. W. Tucker, *J. Am. Chem. Soc.*, **70**, 2174 (9148).
4. E. G. Meek, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, **811**, (1953).
5. R. L. Frank and H. K. Hall, Jr., *J. Am. Chem. Soc.*, **72**, 1645 (1950).
6. J. J. Panouse and C. Sannié, *Bull. Soc. Chim. France*, 1272 (1956).
7. B. H. Chase and J. Walker, *J. Chem. Soc.*, 3518 (1953).
8. A. Eschenmoser, J. Schreiber, and S. A. Julia, *Helv. Chim. Acta*, **36**, 482 (1953).
9. D. A. H. Taylor, private communication.
10. W. F. Gannon and H. O. House, this volume, p. 294.

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

ethanol (64-17-5)

sulfuric acid (7664-93-9)

Benzene (71-43-2)

sodium hydroxide (1310-73-2)

sodium chloride (7647-14-5)

Ethyl orthoformate

isobutyl alcohol (78-83-1)

Ethyl iodide (75-03-6)

lithium aluminum hydride (16853-85-3)

Dihydroresorcinol

2-Cyclohexenone (930-68-7)

3-Ethoxy-2-cyclohexenone,
Dihydroresorcinol monoethyl ether (5323-87-5)

2-isobutoxy-2-cyclohexenone

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

silver salt of dihydroresorcinol