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.

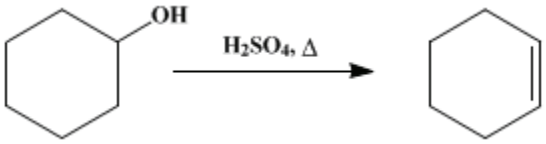
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

DOI:10.15227/orgsyn.005.0033

Organic Syntheses, Coll. Vol. 1, p.183 (1941); Vol. 5, p.33 (1925).

CYCLOHEXENE



Submitted by G. H. Coleman and H. F. Johnstone.
Checked by C. S. Marvel and A. B. Adams.

1. Procedure

In a 500-cc. modified Claisen flask (p. 130) are placed 400 g. (4 moles) of cyclohexanol (Note 1) and 12 cc. of concentrated sulfuric acid, and the flask is connected to a condenser and receiver surrounded by an ice bath. It is then placed in an oil bath which is heated to a temperature of 130–140°. The distillation is continued until only a small residue remains and the odor of sulfur dioxide is apparent. Toward the end of the distillation the temperature of the bath may be raised to 150°. The receiver is kept cold (Note 2) during the entire distillation, which requires from five to six hours (Note 3).

The distillate is saturated with salt, and the cyclohexene is separated from the water layer. It is dried with calcium chloride and fractionated through an efficient column (Note 4). The fraction boiling at 80–82° (uncorr.) is collected separately. It may be necessary to refractionate the low- and high-boiling portions once or twice (Note 5). The high-boiling fraction is finally added to the next run. The yield of cyclohexene is 260–285 g. (79–87 per cent of the theoretical amount) (Note 6).

2. Notes

1. The ordinary commercial grade of cyclohexanol was used in these experiments. It contained no more than a trace of phenol, and 90–95 per cent of it distilled at 158–163°.
2. In transferring cyclohexene, it is best to keep it well cooled to avoid small losses by evaporation.
3. The time required for this distillation can be reduced to about two hours by boiling the mixture in a round-bottomed flask provided with a reflux condenser with water maintained at about 75°. A tube at the top of the reflux condenser leads to a downward cold-water condenser.[1]
4. The partial condenser illustrated in Org. Syn. **20**, 27, which is a modification of an apparatus described by Hahn,[2] is very efficient in the purification of cyclohexene (A. W. Hutchison, private communication).
5. It has been suggested that the crude fraction be refluxed with sodium to remove cyclohexanol prior to a final fractionation.[3]
6. For the preparation of cyclohexene in large quantity, distillation of cyclohexanol over silica gel[4] or, better, activated alumina is more rapid and efficient. Using a 25-mm. tube packed with 8- to 14- mesh activated alumina (Aluminum Company of America) and heated to 380–450° over a 30-cm. length, 1683 g. of cyclohexanol was dehydrated in about four hours. After separating the water, drying with sodium sulfate, and fractionating with a simple column, 1222 g. (89 per cent yield) of cyclohexene, b.p. 82–84°, was obtained. (E. B. Hershberg and John R. Ruhoff, private communication, and Org. Syn. **17**, 27.)

3. Discussion

Cyclohexene can be prepared from cyclohexanol by dehydration with potassium bisulfate,[5] oxalic acid,[6] sulfuric acid,[7] *p*-toluenesulfonic acid,[8] phosphoric acid,[9] iodine,[10] and at elevated temperatures over various catalysts.[4], [11] Cyclohexene has also been prepared from cyclohexyl chloride by passage with steam over activated carbon at 260–300°,[12] and from benzene by treatment with the substance $Ca(NH_3)_6$.[13] The procedure described is a slight modification of that described by Senderens[7] and later modified by Osterberg and Kendall.[7]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 158
- Org. Syn. Coll. Vol. 2, 102
- Org. Syn. Coll. Vol. 2, 151
- Org. Syn. Coll. Vol. 2, 171
- Org. Syn. Coll. Vol. 3, 217
- Org. Syn. Coll. Vol. 3, 231

References and Notes

1. Kistiakowsky, Ruhoff, Smith, and Vaughan, J. Am. Chem. Soc. **58**, 140 (1936).
2. Hahn, Ber. **43**, 419 (1910).
3. Waterman and van Westen, Rec. trav. chim. **48**, 637 (1929).
4. Bartlett and Berry, J. Am. Chem. Soc. **56**, 2684 (1934).
5. Brunel, Bull. soc. chim. (3) **33**, 270 (1905); Willstätter and Hatt, Ber. **45**, 1466 (1912).
6. Zelinsky and Zelikov, Ber. **34**, 3252 (1901); Willstätter and Hatt, Ber. **45**, 1466 (1912); Zelinsky, J. Russ. Phys. Chem. Soc. **43**, 1222 (1911) [Chem. Zentr. I, 139 (1912)]; Juery, Bull. soc. chim. (4) **17**, 174 (1915).
7. Senderens, Compt. rend. **154**, 1169 (1912); **177**, 1183 (1923); Osterberg and Kendall, J. Am. Chem. Soc. **42**, 2620 (1920).
8. Evans and Witzemann, Bull. soc. chim. Belg. **26**, 304 (1912) [Chem. Zentr. II, 1006 (1912)].
9. Dehn and Jackson, J. Am. Chem. Soc. **55**, 4285 (1933).
10. Hibbert, J. Am. Chem. Soc. **37**, 1754 (1915).
11. Ipatiev, Ber. **43**, 3385 (1910); Friedr. Bayer and Co., Ger. pat. 241,895 [Frdl. **10**, 1032 (1910–12)]; Senderens, Ann. chim. phys. (8) **25**, 461, 500 (1912).
12. Zal'kind and Markov, Narodnyi Komissariat Tyazheloi Prom. S. S. S. R. Nauch.-Issledovatel. Inst. Plasticheskikh Mass., Plasticheskie Massy. Sbornik, **2**, 331 (1937) [C. A. **31**, 3875 (1937)].
13. Kazanskii and Glushnev, J. Gen. Chem. (U.S.S.R.) **8**, 642 (1938) [C. A. **33**, 1279 (1939)].

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

alumina

silica gel

$Ca(NH_3)_6$

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

Benzene (71-43-2)

Cyclohexanol (108-93-0)

phenol (108-95-2)

Cyclohexene (110-83-8)

sulfur dioxide (7446-09-5)

sodium sulfate (7757-82-6)

Oxalic acid (144-62-7)

potassium bisulfate (7646-93-7)

iodine (7553-56-2)

activated carbon (7782-42-5)

sodium (13966-32-0)

phosphoric acid (7664-38-2)

cyclohexyl chloride (542-18-7)

p-toluenesulfonic acid (104-15-4)