



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.

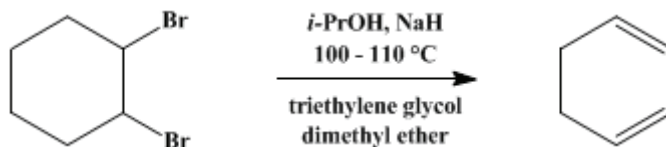
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.

Organic Syntheses, Coll. Vol. 5, p.285 (1973); Vol. 47, p.31 (1967).

1,3-CYCLOHEXADIENE



Submitted by John P. Schaefer and Leland Endres¹.

Checked by R. J. Crawford and Peter Yates.

1. Procedure

In a 3-l. three-necked, round-bottomed flask fitted with a mechanical stirrer and set up for a simple vacuum distillation are placed 500 ml. of [triethylene glycol dimethyl ether](#) ([Note 1](#)) and 300 ml. of [isopropyl alcohol](#). Mechanical stirring is started, and 53.5 g. (2.23 moles) of [sodium hydride](#) in a mineral oil suspension is added in small portions. After the addition is complete, the remaining neck of the flask is fitted with a Y-tube to which is connected a two-holed rubber stopper containing a thermometer which reaches into the flask below the liquid level and a piece of glass tubing which is connected to a nitrogen tank. A pressure-equalizing dropping funnel containing 242 g. (1.00 mole) of [1,2-dibromocyclohexane](#) ([Note 2](#)) is placed in the other arm of the Y-tube.

The temperature of the reaction flask is raised to 100–110°, and the receiving flask is cooled in a dry ice-isopropyl alcohol bath as a rapid stream of [nitrogen](#) is passed through the system. After most of the [isopropyl alcohol](#) has been removed by distillation ([Note 3](#)), the receiver is changed, and the system is evacuated by a water aspirator ([Note 4](#)). Dropwise addition of [1,2-dibromocyclohexane](#) is begun, and the rate of addition is adjusted so that the temperature of the reaction mixture is maintained at 100–110° without external heating. The addition requires about 30 minutes; the reaction is terminated when distillation becomes very slow.

The distillate is washed four times with 200-ml. portions of water, and the organic layer is dried with anhydrous [magnesium sulfate](#). The yield of [1,3-cyclohexadiene](#) is 56 g. (70%) ([Note 5](#)). The diene can be separated from higher-boiling contaminants by a simple distillation at atmospheric pressure under [nitrogen](#); b.p. 78–80°, yield 28–32 g. (35–40%) ([Note 6](#)).

2. Notes

- [1,2-Bis\(methoxyethoxy\)ethane](#) ([triethylene glycol dimethyl ether](#)) was obtained from Matheson, Coleman and Bell and used without further purification.
- The [1,2-dibromocyclohexane](#) was prepared by the method of Snyder and Brooks.² If the [cyclohexene](#) is cooled to *ca.* –30° with a dry ice-isopropyl alcohol bath and the [bromine](#) is not diluted, it is possible to run this preparation on a threefold scale in one-third of the recorded time. The product was always purified by the recommended procedure.
- If the flow of [nitrogen](#) is rapid, the distillation can be completed in about 1 hour; otherwise the distillation is very slow.
- A dry ice-isopropyl alcohol trap was inserted before the aspirator to catch any uncondensed product. The checkers also inserted a manometer between this trap and the aspirator, and maintained the pressure during the reaction at 130–170 mm. by careful adjustment of the regulator valve of the nitrogen cylinder.
- If the temperature rises too high or the vacuum is not sufficient to flash out the diene as it forms, the product will be contaminated with small amounts of [cyclohexene](#), [benzene](#), and [1,4-cyclohexadiene](#).
- The checkers found that distillation without the use of a [nitrogen](#) atmosphere gave 43–44 g. (54–55%) of product, b.p. 80–83°, of excellent purity as shown by n.m.r. spectroscopy.

3. Discussion

1,3-Cyclohexadiene has been prepared by dehydration of cyclohexen-3-ol,³ by pyrolysis at 540° of the diacetate of cyclohexane-1,2-diol,⁴ by dehydrobromination with quinoline of 3-bromocyclohexene,⁵ by treating the ethyl ether of cyclohexen-3-ol with potassium bisulfate,^{6,7} by heating cyclohexene oxide with phthalic anhydride,⁸ by treating cyclohexane-1,2-diol with concentrated sulfuric acid,⁹ by treatment of 1,2-dibromocyclohexane with tributylamine,¹⁰ with sodium hydroxide in ethylene glycol,¹⁰ and with quinoline,⁶ and by treatment of 3,6-dibromo-cyclohexene with sodium.⁶

4. Merits of the Preparation

Because of its convenience and simplicity this procedure is the method of choice for laboratory preparation of 1,3-cyclohexadiene. This olefin is an intermediate of some importance because it offers a route via the Diels-Alder reaction to a variety of bicyclic compounds.^{4,7,10}

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 8, 5](#)

References and Notes

1. Department of Chemistry, The University of Arizona, Tucson, Arizona.
2. [H. R. Snyder and L. A. Brooks, *Org. Syntheses*, Coll. Vol. 2, 171 \(1943\).](#)
3. G. Clement and J. Balaceanu, U. S. Patent 3,096,376 (1963) [*C.A.*, **59**, 13842 (1963)].
4. W. J. Bailey and W. B. Lawson, *J. Am. Chem. Soc.*, **79**, 1444 (1957).
5. N. A. Domnin and M. A. Larionova, *Zh. Obshch. Khim.*, **26**, 1398 (1956).
6. N. A. Domnin and A. S. Beletskaya, *Zh. Obshch. Khim.*, **24**, 1636 (1954).
7. R. Seka and O. Tramposch, *Ber.*, **75**, 1379 (1942).
8. P. Bedos and A. Ruyer, *Compt. Rend.*, **188**, 962 (1929).
9. J. B. Senderens, *Compt. Rend.*, **177**, 1183 (1923).
10. J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gardner, and M. Hine, *J. Am. Chem. Soc.*, **77**, 594 (1955).

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

diacetate of cyclohexane-1,2-diol

quinoline of 3-bromocyclohexene

[sulfuric acid \(7664-93-9\)](#)

[Benzene \(71-43-2\)](#)

[sodium hydroxide \(1310-73-2\)](#)

[Cyclohexene \(110-83-8\)](#)

[bromine \(7726-95-6\)](#)

[nitrogen \(7727-37-9\)](#)

phthalic anhydride (85-44-9)
potassium bisulfate (7646-93-7)
sodium (13966-32-0)
isopropyl alcohol (67-63-0)
ethylene glycol (107-21-1)
Cyclohexene oxide (286-20-4)
Quinoline (91-22-5)
magnesium sulfate (7487-88-9)
1,2-Dibromocyclohexane (5401-62-7)
cyclohexane-1,2-diol
sodium hydride (7646-69-7)
1,3-Cyclohexadiene (592-57-4)
triethylene glycol dimethyl ether,
1,2-Bis(methoxyethoxy)ethane (112-49-2)
1,4-cyclohexadiene
cyclohexen-3-ol
tributylamine (102-82-9)
3,6-dibromo-cyclohexene
ethyl ether of cyclohexen-3-ol