



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.

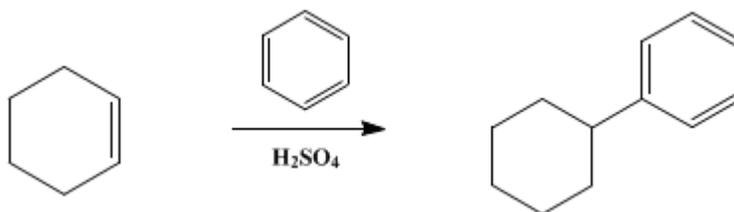
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.151 (1943); Vol. 19, p.36 (1939).

CYCLOHEXYLBENZENE

[Cyclohexane, phenyl-]



Submitted by B. B. Corson and V. N. Ipatieff.

Checked by John R. Johnson and E. A. Cleveland.

1. Procedure

In a 1-l. three-necked flask equipped with a mechanical stirrer, dropping funnel, and thermometer are placed 468 g. (530 cc., 6 moles) of [benzene](#) and 92 g. (50 cc.) of concentrated [sulfuric acid](#) (sp. gr. 1.84). The mixture is cooled in an ice bath, and 164 g. (203 cc., 2 moles) of [cyclohexene](#) ([Note 1](#)) is added with stirring over a period of one and one-half hours, while the temperature is maintained between 5° and 10°. Stirring is continued for an additional hour after all the [cyclohexene](#) has been added.

The hydrocarbon layer is separated, cooled in ice, and washed with four 50-cc. portions of cold concentrated [sulfuric acid](#) ([Note 2](#)). The material is then washed twice with warm water (50°), twice with 3 per cent [sodium hydroxide](#) solution, and twice with pure water ([Note 3](#)). The hydrocarbon mixture is dried over anhydrous [calcium chloride](#) ([Note 4](#)) and subjected twice to fractional distillation, using a 30-cm. Vigreux or similar column; the [cyclohexylbenzene](#) is collected at 238–243° ([Note 5](#)) and ([Note 6](#)). The yield is 210–220 g. (65–68 per cent of the theoretical amount).

2. Notes

1. For the preparation of moderate amounts of [cyclohexene](#) the dehydration of [cyclohexanol](#) with 85 per cent [phosphoric acid](#), according to the procedure of Dehn and Jackson, *J. Am. Chem. Soc.* **55**, 4285 (1933), is very convenient. Furthermore, very little carbonization occurs, in contrast with the [sulfuric acid](#) method described in *Org. Syn. Coll. Vol. I, 1941*, 183, where there is much carbonization and the product is contaminated with [sulfur dioxide](#).

In a 2-l. three-necked flask, carrying a separatory funnel and three-bulbed Wurtz column filled with broken glass tubing, is placed 200 g. of 85 per cent [phosphoric acid](#). The column is attached to an *efficient* condenser leading to a receiver cooled in an ice bath, and the flask is heated in an oil bath at 165–170°. Through the funnel 1 kg. (10 moles) of practical [cyclohexanol](#) is dropped in over a period of four to five hours. After the addition has been completed the temperature of the bath is raised gradually to 200° and maintained at 200° for one-half hour. During the whole operation the temperature at the top of the column does not rise above 90°. The upper layer of the distillate is separated (salt may be added to break up emulsions) and dried with anhydrous [magnesium sulfate](#); the lower aqueous layer is saved for reworking if desired; likewise the spent drying agent may be treated with water to recover admixed [cyclohexene](#). The crude [cyclohexene](#) is distilled in an efficient column, and the fraction boiling at 81–83° is collected. The yield is 660–690 g. (79–84 per cent of the theoretical amount). The residue consists largely of [cyclohexanol](#) and may be recycled as described below.

An additional 25–30 g. of [cyclohexene](#) may be obtained by combining the residue from the distillation of the crude [cyclohexene](#) with the water layer from the original distillate and distilling with 25 g. of 85 per cent [phosphoric acid](#). This distillate is added to the low-boiling fraction from the distillation of the crude [cyclohexene](#) and separated. The upper layer is dried with anhydrous [magnesium sulfate](#) and distilled as described above.

The [phosphoric acid](#) may be recovered by diluting with water and filtering, then evaporating with a little [nitric acid](#) to the proper concentration.

The same procedure when used with 86 g. (1 mole) of [cyclopentanol](#) and 15 cc. of 85 per cent [phosphoric acid](#) gave 55 g. (81 per cent of the theoretical amount) of [cyclopentene](#), b.p. 44–45°. No attempt was made to recover the [cyclopentanol](#). (Oliver Grummitt and John R. Johnson, private communication.)

2. The purpose of the [sulfuric acid](#) is to convert [dicyclohexyl sulfate](#) to [cyclohexyl hydrogen sulfate](#), which is removed by the subsequent washing operations.

3. To avoid emulsification as much as possible it is advantageous to use warm water rather than cold, and dilute alkali rather than concentrated. The milkiness of the aqueous wash liquid represents only a very small loss of material.

4. It is well to allow suspended water to settle by standing overnight and to separate again before adding the drying agent.

5. In a typical preparation the fractions collected during the second distillation were as follows: 78–85°, 296 g.; 85–235°, 2 g.; 235–238°, 2 g.; 238–243°, 215 g.; 243–265°, 2 g.; residue above 265°, 46 g.

6. The distillation residue becomes semi-solid on cooling owing to the separation of [1,4-dicyclohexylbenzene](#). The latter may be recovered by filtering with suction, washing with [methyl alcohol](#), and crystallizing from [acetone](#) (using 4 cc. of [acetone](#) per gram of the crude solid). The yield of purified [dicyclohexylbenzene](#), m.p. 100–101°, is 15–24 g.

3. Discussion

[Cyclohexylbenzene](#) has been prepared by the hydrogenation of [biphenyl](#)¹ and of [cyclohexenylbenzene](#);² by the reaction of [cyclohexyl chloride](#)³ or bromide⁴ with [benzene](#) in the presence of [aluminum chloride](#); and from [benzene](#) and [cyclohexene](#) or [cyclohexanol](#) in the presence of [aluminum chloride](#),⁵ [sulfuric acid](#),⁶ or boron halides.⁷

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 102](#)
- [Org. Syn. Coll. Vol. 2, 171](#)

References and Notes

1. Eijkman, *Chem. Weekblad* **1**, 7 (1903).
2. Sabatier and Murat, *Compt. rend.* **154**, 1390 (1912); Alder and Rickert, *Ber.* **71**, 379 (1938).
3. Kursanoff, *Ann.* **318**, 309 (1901).
4. Braun, *Ber.* **60**, 1180 (1927).
5. Bodroux, *Ann. chim. (10)* **11**, 511 (1929); Berry and Reid, *J. Am. Chem. Soc.* **49**, 3142 (1927); Corson and Ipatieff, *ibid.* **59**, 645 (1937); Nametkin and Pokrovskaya, *J. Gen. Chem. (U.S.S.R.)* **7**, 962 (1937) [*C. A.* **31**, 5332 (1937)]; Tsukervanik and Sidorova, *J. Gen. Chem. (U.S.S.R.)* **7**, 641 (1937) [*C. A.* **31**, 5780 (1937)].
6. Deschauer, *Ger. pat.* 515,177 (*Chem. Zentr.* **1931**, I, 1829); Truffault, *Compt. rend.* **202**, 1286 (1936); Corson and Ipatieff, *J. Am. Chem. Soc.* **59**, 645 (1937).
7. Hofmann and Wulff, *Brit. pat.* 307,802 (*Chem. Zentr.* **1929**, II, 2101); McKenna and Sowa, *J. Am. Chem. Soc.* **59**, 470 (1937).

Appendix

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

[calcium chloride](#) (10043-52-4)

sulfuric acid (7664-93-9)
Benzene (71-43-2)
methyl alcohol (67-56-1)
sodium hydroxide (1310-73-2)
nitric acid (7697-37-2)
Cyclohexanol (108-93-0)
Cyclohexene (110-83-8)
sulfur dioxide (7446-09-5)
acetone (67-64-1)
aluminum chloride (3495-54-3)
phosphoric acid (7664-38-2)
Biphenyl (92-52-4)
cyclohexyl chloride (542-18-7)
magnesium sulfate (7487-88-9)
Cyclohexylbenzene,
Cyclohexane, phenyl- (827-52-1)
cyclopentanol (96-41-3)
Cyclopentene (142-29-0)
dicyclohexyl sulfate
cyclohexyl hydrogen sulfate
1,4-dicyclohexylbenzene (1087-02-1)
cyclohexenylbenzene (771-98-2)
dicyclohexylbenzene