

Experiment 8: Preparation of Cyclohexene from Cyclohexanol

Objectives

The purpose of this experiment is to

1. prepare a pure sample of cyclohexene from cyclohexanol using an acid catalyzed dehydration reaction, and
2. acquire more experience with the techniques of simple distillation and liquid-liquid separations, and the use of drying agents.

Background Information

In this experiment you will use several techniques from previous experiments to carry out your first synthetic reaction in the lab (e.g., using a separatory funnel, drying of organic solvents, distillation, IR spectroscopy). In addition, you will learn how to pre-dry an organic solvent using sodium chloride (a.k.a. 'salting-out').

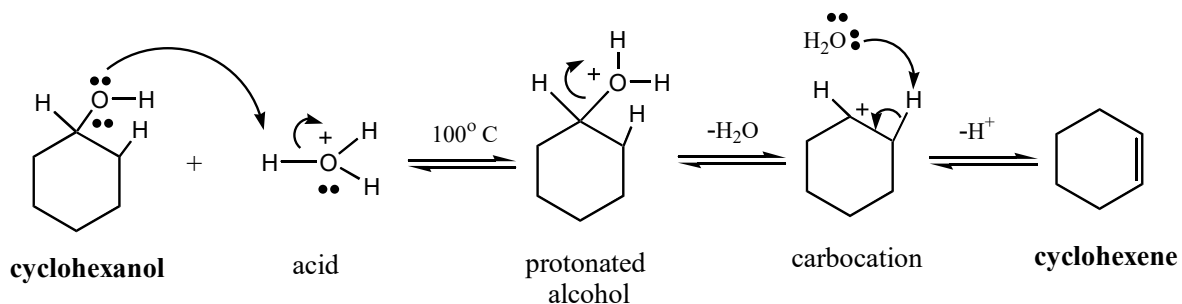
One of the most widely used methods of preparing alkenes is the **acid-catalyzed dehydration** of an alcohol. In this experiment, you will use the sample of cyclohexanol you purified in Experiment 3A. This reaction is a reversible E1 elimination type reaction (E1 = elimination, unimolecular) and usually follows Zaitzev's rule. Once the product (cyclohexene) is formed, steps must be taken immediately to safeguard the product from reverting back to the starting reagent. First it is removed from the reaction mixture by distillation. Additional steps are taken in the reaction workup to minimize the formation of side products.

E1 Reaction Mechanism

The reaction used in this experiment (cyclohexanol in the presence of 85% phosphoric acid and heat (100°C) occurs via a three-step mechanism:

- 1) protonation of the alcohol oxygen,
- 2) loss of water to generate a carbocation intermediate, and

3) loss of a proton from the neighbouring carbon atom and formation of a double bond.



In our experiment, the overall equilibrium is shifted to the right by the removal of cyclohexene and water from the reaction mixture as they are formed. This is achieved by the process of distillation. Once the crude product is obtained, the cyclohexene must be purified by removing the water and any traces of acid which may still be present. Thus, the product is washed with aqueous sodium chloride (i.e., sodium chloride crystals are added to aqueous layer) followed by aqueous sodium carbonate and then dried over anhydrous calcium chloride. Finally, the cyclohexene is distilled, and the fraction boiling in the range $80\text{-}85^\circ\text{C}$ is collected.

Tertiary alcohols will react faster than secondary, which will react faster than primary alcohols ($3^\circ > 2^\circ > 1^\circ$). This is because the tertiary alcohol carbocation is more stable than the secondary or primary carbocations. Please note that fairly harsh conditions were required to form the cyclohexanol carbocation in this experiment. A more sensitive alcohol molecule would not survive such treatment.

In practice, only tertiary alcohols are commonly dehydrated with acid. Phosphorus oxychloride (POCl_3) in pyridine at 0°C is routinely used for dehydrating secondary alcohols however this reaction proceeds via an E2 mechanism.

Byproducts of acid-catalyzed dehydrations

