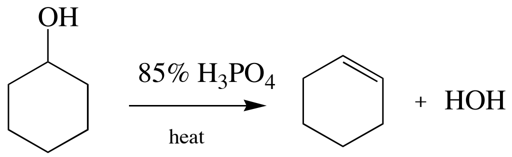
# Synthesis of Cyclohexene  The Dehydration of Cyclohexanol.

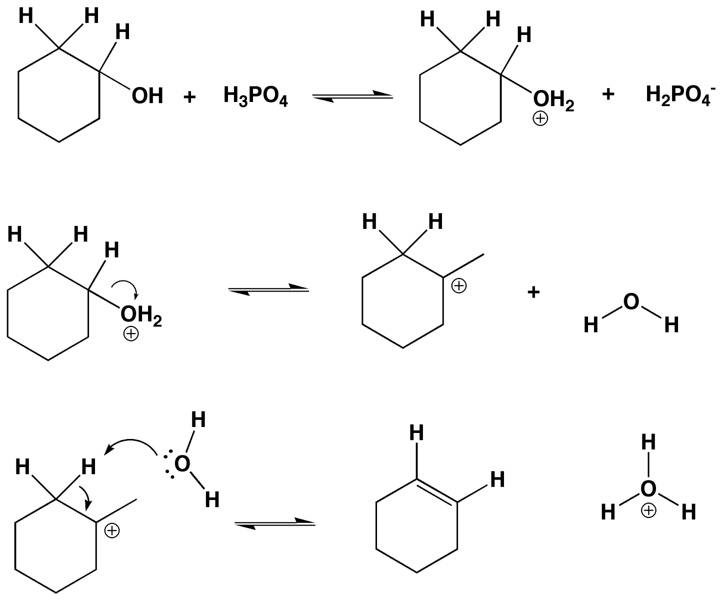
The general approach towards carrying out an organic reaction:

(1) Write out the balanced reaction, using structural formulas.
(2) Construct a table of relevant information for reactants and products – e.g., MPs, BPs, MWs, densities, hazardous properties.
(3) Calculate the correct molar ratios of reactants. Convert moles to grams and milliliters.
(4) Mix correct amounts of reactants, solvents, catalysts in correct order to give specific concentrations. Possibly heat or cool or irradiate with UV light, allow to react for necessary amount of time, possibly follow reaction progress using chromatography (e.g., TLC, GC) or spectroscopy (e.g., IR, NMR).
(5) After reaction is complete, the reaction mixture is usually a complex mixture of desired product(s), byproducts, unreacted starting materials, solvents, and catalyst. Product may be light, heat, or air ($O_2$) sensitive.
(6) Separation and purification steps (so-called reaction work-up). Some combination of extractions, distillations, recrystallizations, chromatography, etc are used for the work-up.
(7) Identify product(s) using spectroscopy (IR, NMR, etc), chromatography (GC, TLC, etc), physical properties (MP, BP, etc), and occasionally chemical tests.

**Cyclohexene**. In the presence of a strong acid, an alcohol can be dehydrated to form an alkene. The acid used in this experiment is 85% phosphoric acid and the alcohol is cyclohexanol. The phosphoric acid is a catalyst and as such increases the rate of reaction but does not affect the overall stoichiometry. It can be seen from the balanced reaction that 1 mole of alcohol produces 1 mole of alkene. The theoretical yield of alkene in moles is therefore equal to the number of moles of alcohol used.

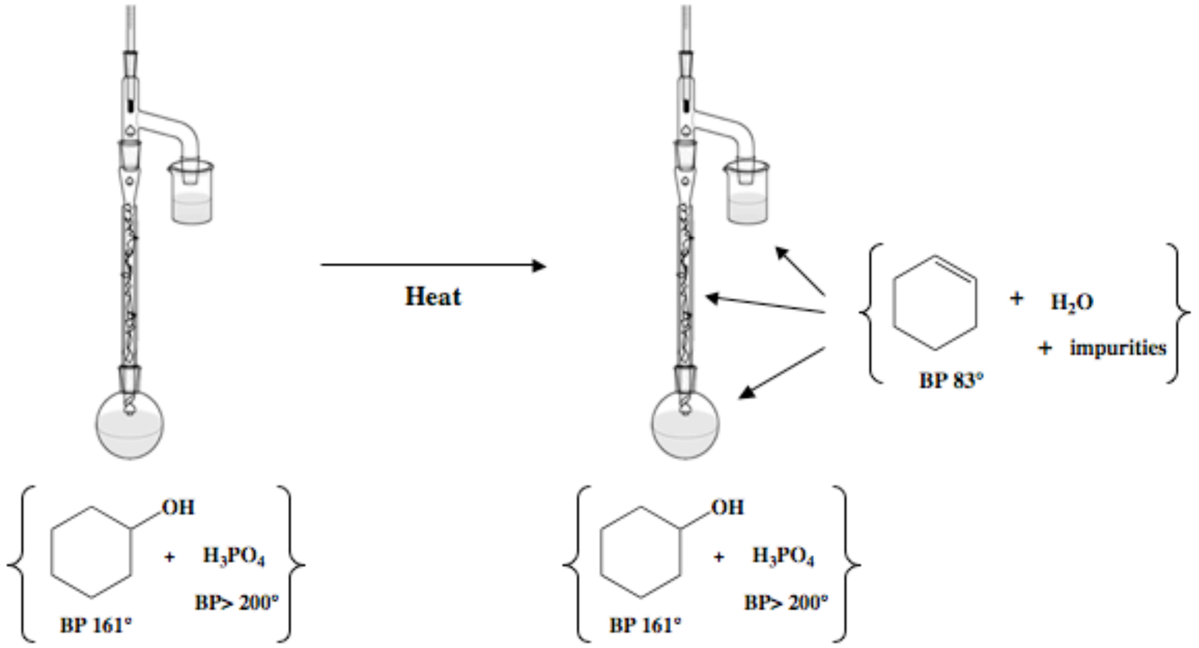


Mechanism.



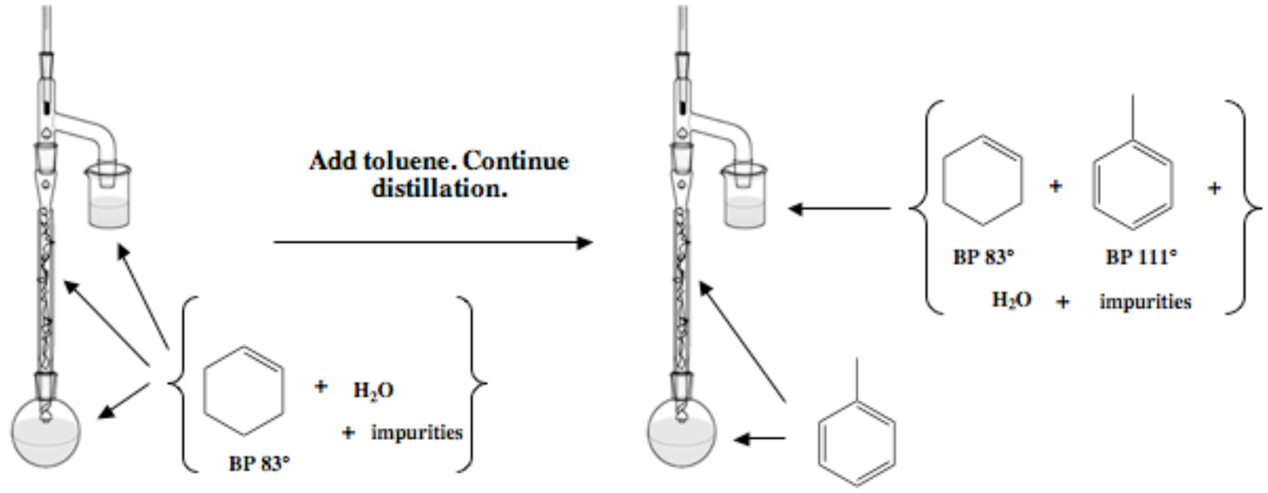
The first step in the mechanism is protonation of the alcohol group by the acid (slightly exothermic). The second step is the loss of water to form the carbocation (highly endothermic). The final step is removal of a *beta* hydrogen by base (water) to form the alkene (exothermic). The overall reaction is slightly endothermic.

General Approach. The reaction is carried out in a fractional distillation apparatus. As the alcohol and acid are heated, alkene and water are produced and co-distill into a collection vial. As in any distillation, unless precautions are taken, some of the product will be lost as hold-up in the apparatus. Hold-up would result in a reduced yield of product. To overcome this problem and to ensure that a maximum amount of product is distilled, a higher boiling "chaser" solvent is added to the distillation flask and the distillation is continued until the temperature rises well over the BP of cyclohexene. At this point it can be assumed that all product has distilled into the collection vial, along with some chaser.



**Cyclohexanol plus Phosphoric Acid are heated**

**As the reaction proceeds, cyclohexanol is being converted to cyclohexene and water (plus some impurities). The low-boiling cyclohexene and water boil at the high temperatures and distill up the column and into the collection vial. As with all distillations though some is left behind in the flask and in the column.**



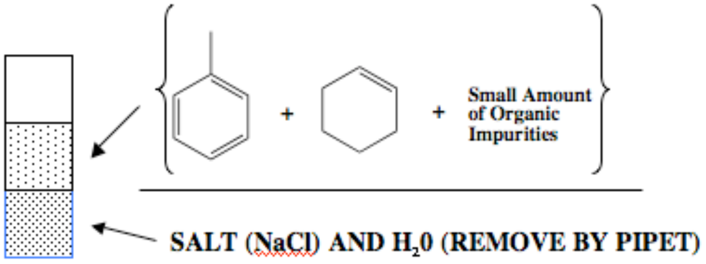
**If we stop the distillation here, a significant amount of product would be left behind and lost.**

**To maximize yield, stop the distillation, add chaser (toluene) and continue the distillation. The higher-boiling toluene pushes over (chases) the product into the collection vial.**

**Once the toluene distills up the column and reaches the thermometer, most of the cyclohexene and water has been pushed over into the collection vial along with some toluene. The distilling flask contains phosphoric acid, toluene, and higher-boiling impurities. The column contains mostly toluene.**

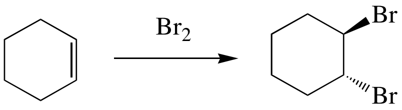
**What has been accomplished by adding chaser? Almost all of the desired product, cyclohexene, has been collected in the vial. The downside is that another impurity (toluene) has been added to the product.**

The collection vial now contains cyclohexene, water, toluene, and small amounts of other impurities. Because any water present will interfere with the distillation (water will co-distill and will not separate), prior to a final distillation, to obtain pure product, all water must be removed. This is done in two steps. First, the sample is mixed well with an aqueous saturated sodium chloride solution (sat'd salt) and the lower aqueous layer is removed and discarded. This is a pre-drying step that removes most of the water.

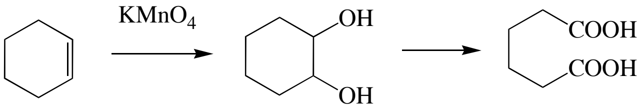


Next, anhydrous calcium chloride pellets are added. Anhydrous $CaCl_2$ is an inorganic drying agent that binds strongly with water and thus removes any traces of water from the solution. After about five minutes, the solution is separated from the pellets and transferred to the clean and dry fractional distillation apparatus. The dried solution is then fractionally distilled to produce purified cyclohexene. To achieve optimal separation, the distillation must be done at a slow steady rate. To ensure that the fraction collected as product is relatively pure cyclohexene, this fraction is collected over a narrow range at the boiling point of cyclohexene. The purity of the cyclohexene is determined by gas chromatographic (GC) analysis and a % yield calculated.

**Chemical Tests**. The presence of the alkene functional group can be indicated by carrying out simple reactions in which a color change can be observed. One such reaction is with bromine in dichloromethane. The bromine reagent is a reddish-orange color. When it is dripped slowly into a sample of alkene, the bromine reacts with the alkene to form a nearly colorless dibromide. Because the bromine is consumed, the mixture loses the reddish-orange color. If a sample decolorizes bromine under these conditions it can be inferred that an alkene functional group is likely present.

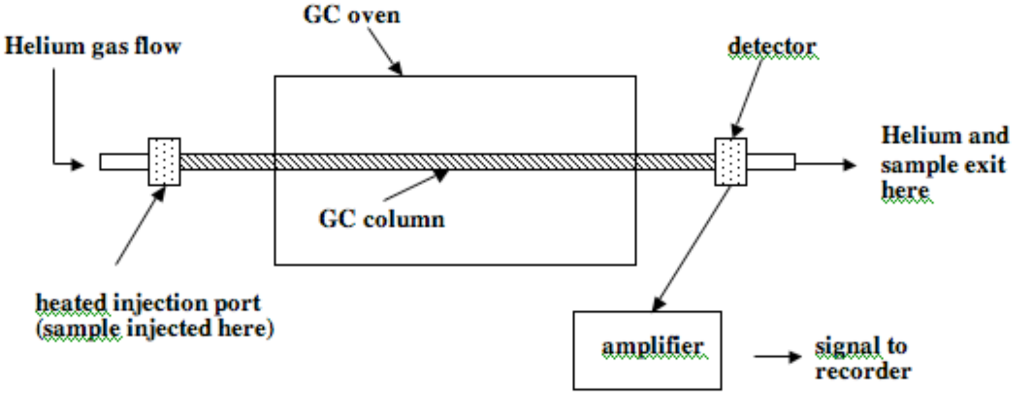


A second color test is the reaction with potassium permanganate. An alkene reacts with potassium permanganate to form a colorless diol. Under acid conditions the diol reacts further to form a mixture of colorless carboxylic acids or in the case of a cyclic alkene, a dicarboxylic acid. As the permanganate is consumed, the mixture loses its deep purple color. At the same time manganese dioxide, a brown precipitate, forms. If a sample decolorizes permanganate and forms a brown precipitate it can be inferred that an alkene functional group is present.



**Gas Chromatography (GC).**

**Schematic of a Gas Chromatograph**

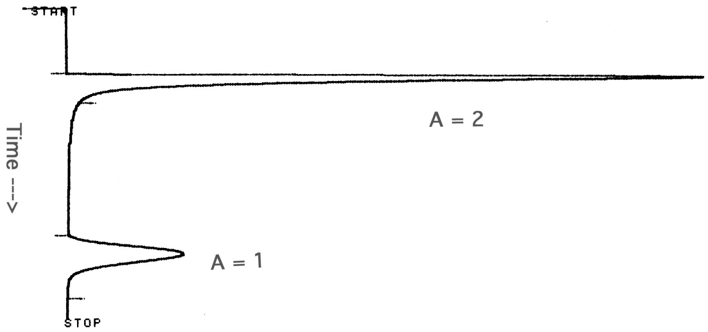


A very small sample ( ~ 0.1 µl = 0.0001 ml) is injected into the hot injector port.

The liquid vaporizes, helium pushes the plug of sample vapor through the thermostated column.

The lower-boiling liquid passes through more quickly than the higher-boiling liquid. As the vapor reaches the detector, a signal is sent to the amplifier and a recorder draws the chromatogram.

An example. The following GC trace is that of a mixture of a lower-boiling and higher-boiling liquid compound in a ratio of 2 : 1.



The injection point is at “start” at the top of the chromatogram. The peak labeled “A = 2” is due to the low-boiling liquid which reaches the detector first. The peak labeled “A = 1” is due to the high-boiling liquid which reaches the detector later.

The time between “start” and when the peak appears is known as the retention time.

The area of the peak, not the height, is proportional to the relative amounts of liquid 1 and liquid 2. (A on the chromatogram refers to area)

In our lab, the relative areas are reported by an electronic integrator.

This chromatogram would look similar to the chromatogram of a mixture of 2 parts cyclohexene to 1 part toluene.

Factors affecting separation in GC.

Column Material: chosen for compounds being separated.

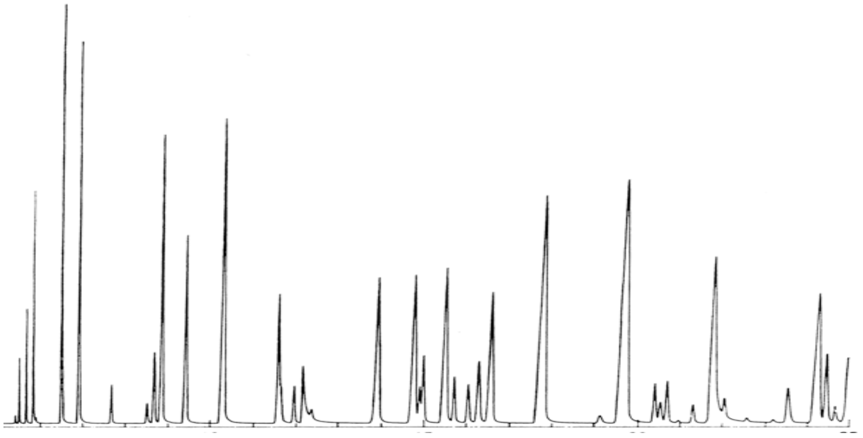
Column Length: the longer the column, the longer the compounds take to go through, resulting in a potentially better separation.

Column Temperature: higher temperature, shorter retention time. Lower temperature, longer retention time. A longer retention time may lead to a better separation.

Helium Flow Rate: higher flow rate, shorter retention time. Lower flow rate, longer retention time.

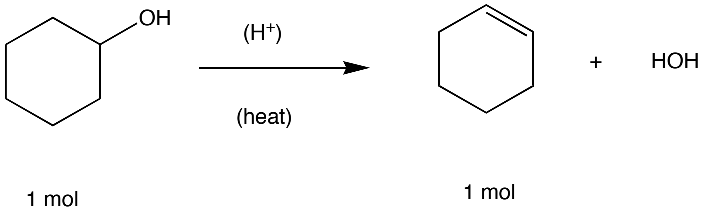
In practice, the column material and length is chosen to work with a particular mixture of compounds. Fine tuning of the separation is done by adjusting the temperature and flow rate. For example, if a poor separation is observed (overlapping peaks), the column temperature could be lowered, which would probably result in a better separation.

Another example of a GC analysis. The following is a GC of a fraction of crude oil (petroleum) approximately corresponding to a gasoline fraction, which contains the various isomers of the C4 – C7 hydrocarbons. Gasoline from different refineries and therefore different gas stations would have a slightly different amount of each compound. This would result in unique GCs which could be used for example as a “fingerprint” in arson investigations.



## Calculating the Percent Yield.

Theoretical yield. First write out the balanced equation. For this reaction, this is very simple. One reactant produces one product (water is also a product but we are only interested in the cyclohexene here) in a 1:1 ratio. Note that the phosphoric acid is a catalyst and is not involved in the yield calculation.



One molecule of cyclohexanol should produce one molecule of cyclohexene. One mole (mol) of cyclohexanol should produce one mole of cyclohexene.

If 2.05 g of cyclohexanol is used (use the actual amount used in your experiment) convert this to moles by dividing by the molecular weight of cyclohexanol (MW = 100.2 g/mol).

2.05 g cyclohexanol / 100.2 g/mol = 0.0205 mol (or 20.5 mmol)

Because 1 mol of cyclohexanol should produce 1 mol of cyclohexene, 0.0205 mol of cyclohexanol should produce 0.0205 mol of cyclohexene. Convert this number of moles of cyclohexene to grams of cyclohexene by multiplying by the MW of cyclohexene (82.1 g/mol).

0.0205 mol x 82.1 g/mol = 1.68 g cyclohexene

In other words, 2.05 g of cyclohexanol should produce 1.68 g of cyclohexene. This is the best-case yield also known as the theoretical yield.

**Percent Yield**. The theoretical yield is what would be obtained in an ideal world, if every molecule of cyclohexanol were converted to a molecule of cyclohexene. The percent yield is the percentage of the theoretical yield that you actually obtain after isolating product at the end of the procedure.

Let's say that after the final fractional distillation of the cyclohexene, 1.22 g was collected. The percent yield then would be

percent yield = (actual / theoretical) x 100 = (1.22 g / 1.68 g) x 100 = 73 %

This assumes that the 1.22 g that was obtained was 100% pure. Let's say that when the gas chromatographic analysis was done the sample was found to be 89% cyclohexene and 11% toluene. This means that the 1.22 g of liquid isolated in the distillation was not pure cyclohexene. The actual amount of cyclohexene collected then was 1.22 g x 0.89 = 1.09 g (<u>small print</u>: an assumption is being made: that the GC detector response is the same for cyclohexene and toluene. We will accept this assumption for our purposes. In fact it is a good assumption in this case).

The percent yield then would be (1.09 g actual / 1.68 g theoretical) x 100 = 65%.

**Postlab Questions**

1.) Draw the structure of the major product that would be obtained from the dehydration of 3,5-dimethylcyclohexanol.

2.) Mixing cyclohexanol with phosphoric acid is an exothermic process, whereas the overall reaction from cyclohexanol to cyclohexene is endothermic. Referring to the mechanism above, construct an energy diagram showing the course of the reaction. Label the diagram with the starting alcohol, the protonated alcohol, the carbocation, and the product.

3.) In GC, what effect would raising the column temperature have on the retention time?

4.) Looking at the fractional distillation curve above, draw a gas chromatogram for a one drop sample taken at the 60 drop mark. Label each peak clearly with the compound associated with that peak, and the relative amounts and relative retention times of each component.

5.) Draw the structure of the product from the reaction of cyclohexene plus bromine. Show stereochemistry clearly.