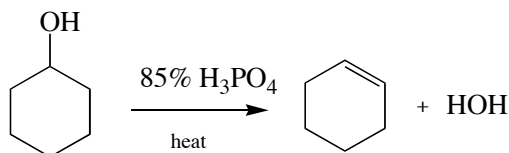


Synthesis of Cyclohexene The Dehydration of Cyclohexanol.

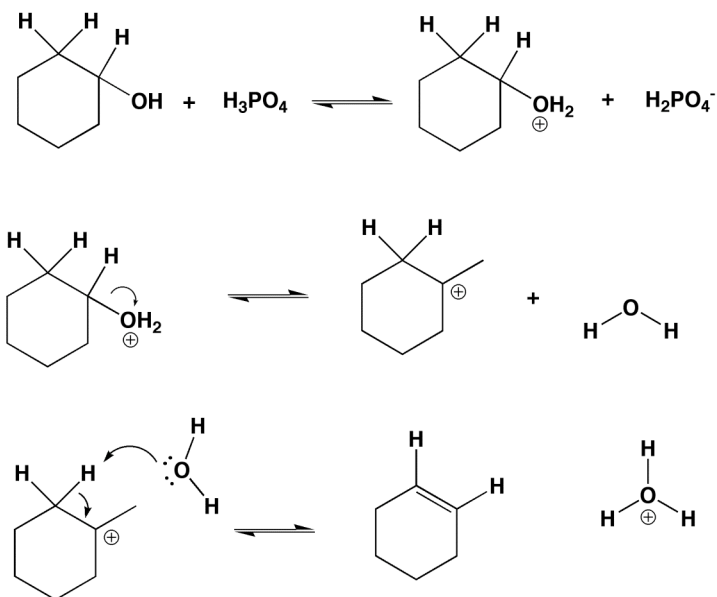
The general approach towards carrying out an organic reaction:

- (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), unreacted starting materials, solvents, catalyst. Product may be light, heat, or air (O₂) 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.

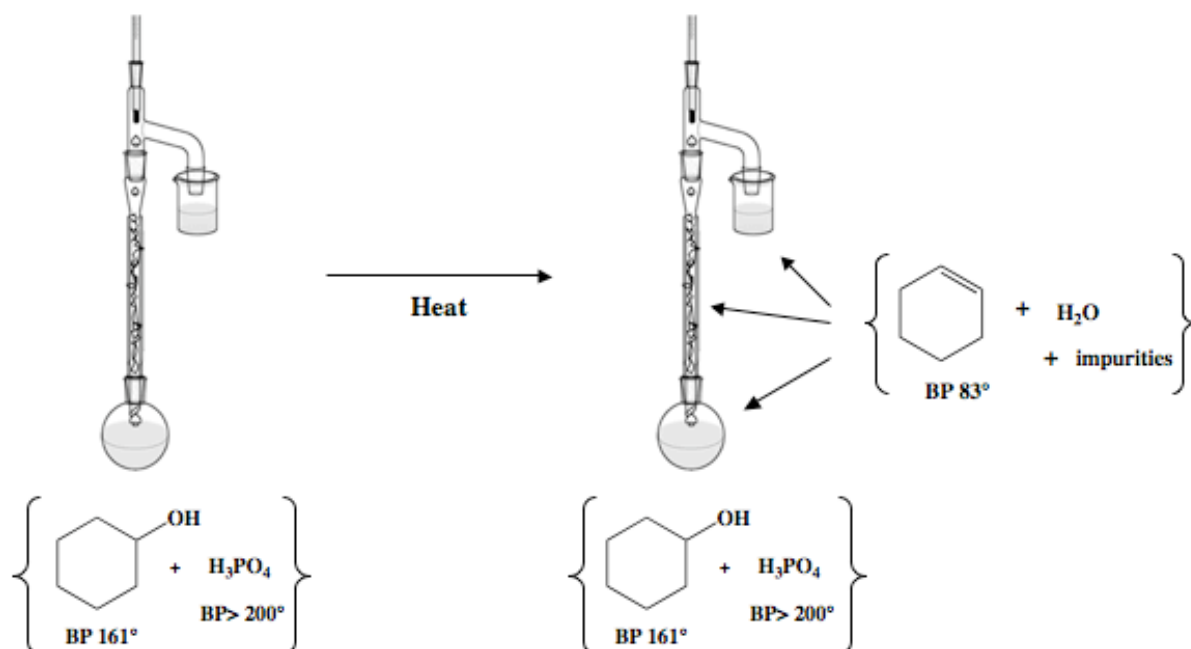


Mechanism.



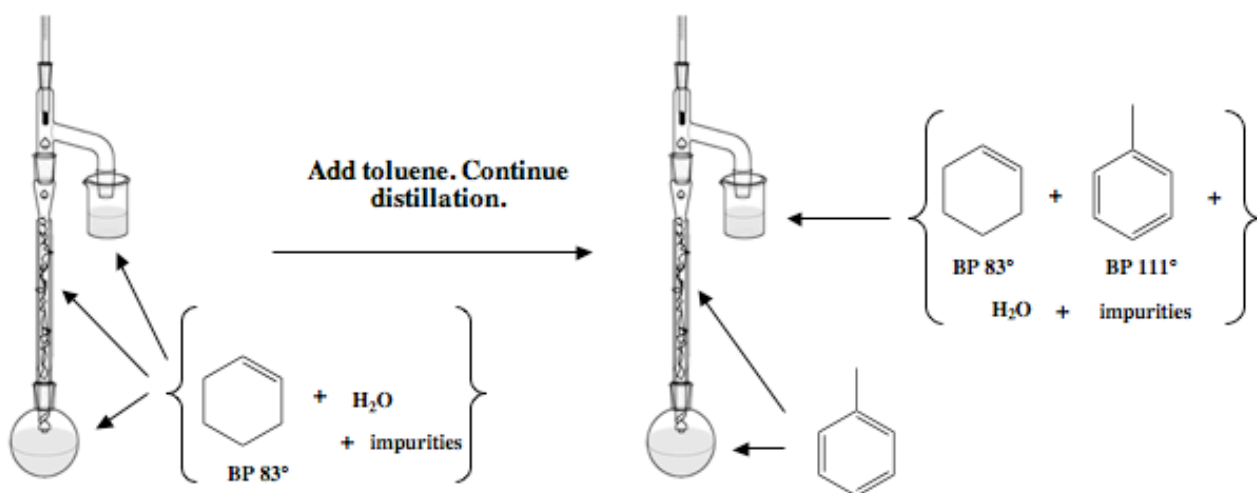
The first step in the mechanism is protonation of the alcohol group by the acid (slightly exothermic). The second step is the loss of water to form the carbocation (highly endothermic). The final step is removal of a *beta* hydrogen by base (water) to form the alkene (exothermic). The overall reaction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

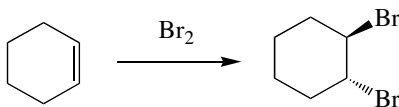
What has been accomplished by adding chaser? Almost all of the desired product, cyclohexene, has been collected in the vial. The downside is that another impurity (toluene) has been added to the product.

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.

