There are three distinct steps in most organic preparative reactions:

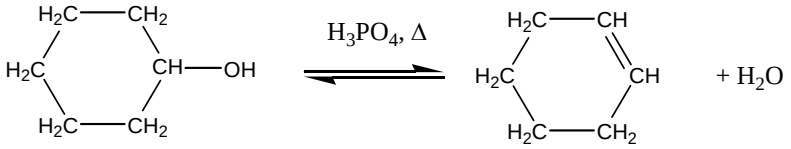
1) the reaction itself,

2) isolation of the crude product, and

3) final purification.

In some instances, as in the dehydration of an alcohol, it is necessary to combine the first two steps so that the product can be removed from the reaction mixture as it is formed. This serves to drive the equilibrium toward alkene formation and to minimize the possibility of oxidation or polymerization of the alkene.

General Dehydration Reaction:

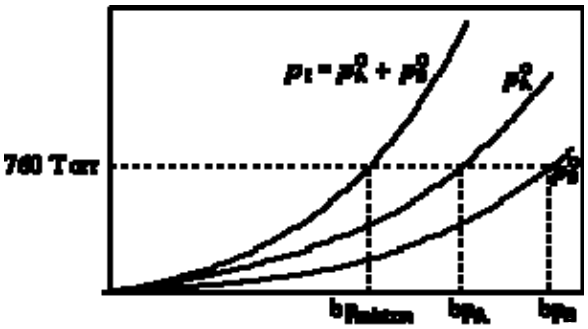


The phenomenon of *steam distillation* or *hydrodistillation* is observed in this experiment. Any water initially present in the mixture, and additional water formed us a result of the reaction, is immiscible with the alkene product. In the ethanol lab we learned that in a mixture of two miscible liquids the total vapor pressure is the sum of the partial pressures of each component.

There is a different situation in the distillation of a mixture of two compounds that are not mutually soluble. In this case each liquid exerts its own vapor pressure independently of the other.

$P_{Total} = P°_A + P°_B$ P^{o}_{A} is the vapor pressure of pure A at a particular temperature

As long as separate phases are present in the liquid, the mixture will have a constant boiling point that is lower than the boiling point of either of the components. In addition, the distillate will have a constant composition, which is determined by the ratio of the vapor pressures.

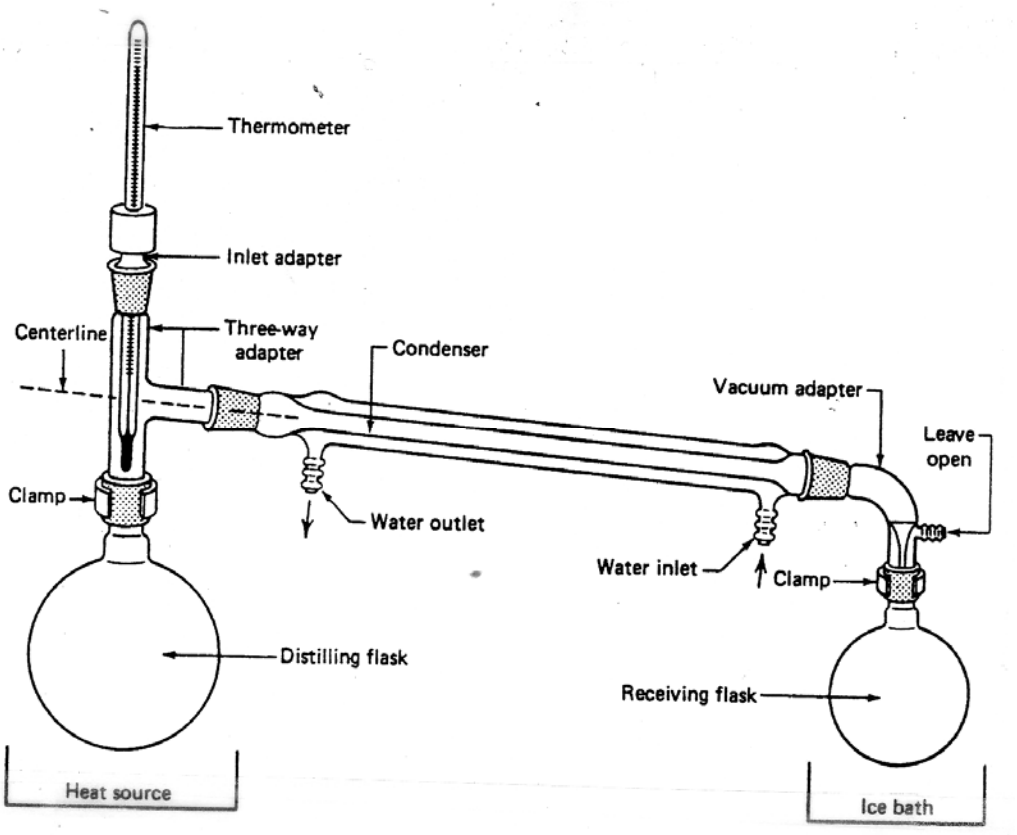


Vapor pressures of two immiscible compounds and their mixture as functions of the temperature. http://www.uwlax.edu/faculty/koster/Distillation305.htm

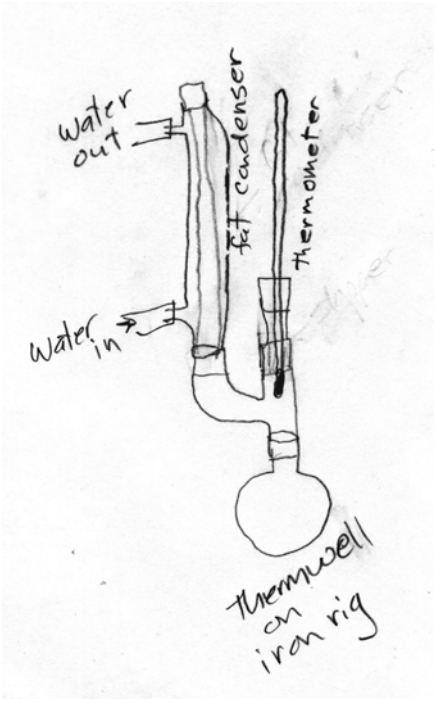
Based on Experiment 12 “The Dehydration of Methylcyclohexanols” in Palleros, D. R. (2000). Experimental organic chemistry. New York: Wiley.

Practical advice for distillations: (Zubrick chapter 20)

1. Always put several boiling chips in the distilling flask. Otherwise your liquid will boil over and shoot out of your condenser without bothering to vaporize first. Never drop a boiling stone into hot liquid, or you may be rewarded by having your body soaked in the hot liquid as it foams out at you.
2. Don't fill the distilling flask more than half full. The liquid needs room to boil. Again we are trying to avoid the dreaded boiling over phenomenon.
3. Make sure the joints are snug. Greasing them helps them to hang together but they must also be lined up properly.
4. Use clamps! A distillation setup should be held with at least two clamps and preferably three.
5. Be sure you can remove the heat source quickly if you need to. Prop up the thermwell on something that you can remove if the dreaded boiling over phenomenon begins to exert itself.
6. Be sure the thermometer bulb is below the side arm of the three-way adapter.
7. Always keep cold water running in the condenser. Remember the water should go in the bottom and out the top.
8. Do not make you apparatus airtight. If you do, it will quite simply explode.
9. Boiling point means "boiling range" just like with a melting point.
10. Ideally the receiving flask should be in an ice and water bath.



A. Apparatus

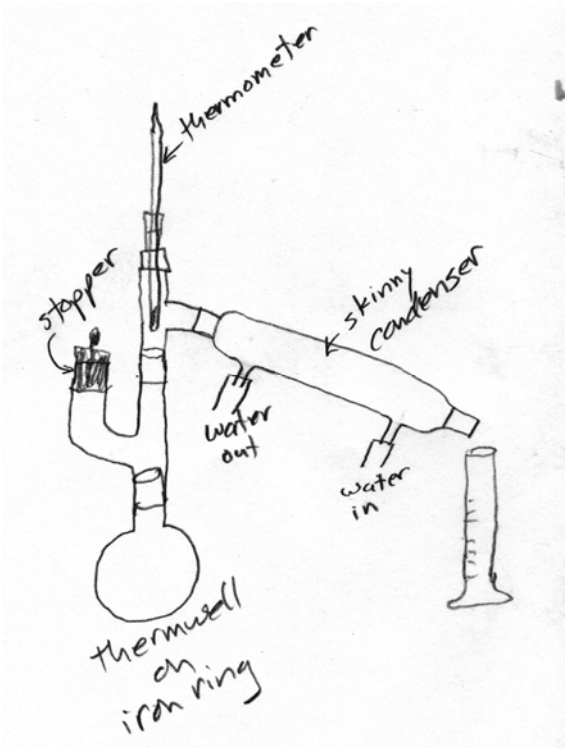


1. Construct the reflux apparatus using a 250-mL round-bottom flask. Use at least two clamps – one for the round bottom and another for the Claisen adapter.
2. Use a thermwell as a source of heat. Be sure to elevate the thermwell on a ring stand so that you can lower it away from the distillation flask in case of overheating.
3. Use your 200 or 250º C thermometer.

B1. Reflux

1. Add 23g of 4-methyl-1-cyclohexanol to the round-bottom flask. Weigh the alcohol directly into the distilling flask supported by a cork ring.
2. Carefully add 5 mL of 85% (14.7 M) phosphoric acid. Phosphoric acid is a strong acid!
3. Add two or three boiling chips to the flask and swirl to mix the layers.
4. Attach the flask to the Claisen adapter on the reflux apparatus.
5. Heat the mixture to boiling, and reflux for 10 minutes. Note the temperature of the vapor.

B2. Distillation



1. Remove the thermwell by lowering it away from the round bottom. Remove the thermometer adapter. Attach the "Y" adapter and distillation condenser. Support the distillation condenser with a ring stand and clamp.
2. Heat the mixture to boiling, and then adjust the heat input so that the temperature at the still head does not rise more than 10º above the boiling point of the expected alkene. (The vapor temperature will most likely remain somewhat below the boiling point of the pure alkene because of water codistilling with the hydrocarbon.)
3. Continue the distillation until there is about 5 mL of liquid left in the distilling flask. If a graduated cylinder is used as the receiver, the volume of distillate collected can be used to monitor the progress of the reaction.
4. Turn off the heat source and allow the distillation flask to cool for at least 15 minutes before you disassemble that part of the apparatus.

C. Purification

1. Transfer the distillate to your separatory funnel.
2. Draw off the lower aqueous layer and discard it.
3. Add about 15 mL of 5% sodium bicarbonate to the separatory funnel and product. Shake it well.

Caution - CO_2 is formed, frequent venting of the separatory funnel is necessary.

4. Drain out the lower (aqueous) layer and discard it.

5. Add about 15 mL of saturated NaCl to the separatory funnel and product. Shake it well. Venting of the separatory funnel is necessary.

6. Drain out the lower (aqueous) layer and discard it.

7. Transfer the crude organic product (top layer) to a clean dry 50-mL Erlenmeyer flask and add a teaspoon of anhydrous magnesium sulfate ($MgSO_4$) or sodium sulfate (Na_2SO_4) to cover the bottom of the flask. Seal the flask with a cork or Al foil and allow it to stand for <u>at least 10 minutes</u>. Swirl the contents occasionally.

8. Filter out the solid (gravity filtration) and record the mass of your liquid product.

D. Verification of Identity and Purity

Use refractive index, IR spectroscopy, and/or gas chromatography to determine the composition and purity of your product.

E. Qualitative test:

Put two drops of 5% Br_2 in dichloromethane in a test tube.
Note its color
Add your product to the test tubes dropwise with shaking.
What do you observe?

F. Clean up.

1. Hand in a properly labeled sample of your product:

your name date lab title product identity

2. Dispose of liquid waste in the liquid waste container

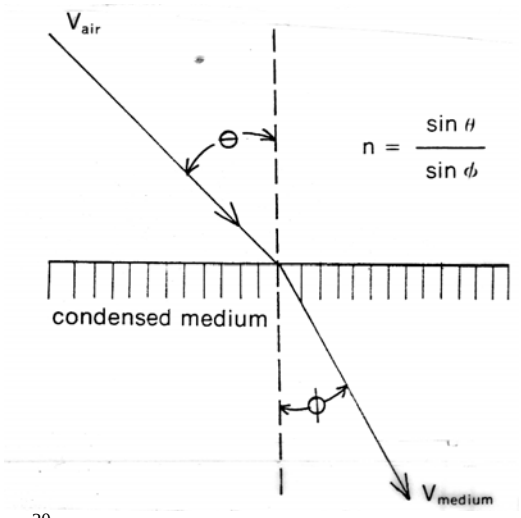
> How often have I said to you that when you have eliminated the impossible, whatever remains, however improbable, must be the truth.
>
> **Sir Arthur Conan Doyle**, The Sign of Four, Ch. 6

Background Information on Refractive Index

Refractive Index is an important physical constant characteristic of liquids and transparent solids.

The refractive index derives from the fact that light travels at a different velocity in condensed phases (liquids and solids) than it does in air. The refractive index "n" is defined as the ratio of the velocity of light in air to the velocity of light in the medium being measured.

The ratio of the velocities is not difficult to measure experimentally. It corresponds to $\sin\theta/\sin\phi$ where θ is the angle of incidence for a beam of light striking the surface of the medium, and ϕ is the angle of refraction of the beam of light within the medium.



The refractive index for a given medium is dependent of two variable factors. First, it is temperature dependent. The density of the medium changes with temperature and, hence, the speed of light in the medium also changes. Second, the refractive index is wavelength dependent. Beams of light with different wavelengths will be refracted to different extents in the same medium and will give different refractive indices for that medium. It is usual to report refractive indices measured at 20° C, using sodium discharge lamp as a source of illumination. The sodium lamp gives off yellow light of 589nm wavelength, the so-called "sodium D line." Under these conditions, the refractive index for water is reported in the following form: $n_D^{20} = 1.3330$ The superscript indicates the temperature, and the subscript indicates that the sodium D line was used for the measurement.

It should be noted that the refractive index for pure water has four decimal places. Therefore, refractive index is a very accurate physical constant for a given substance and can be used for identification. However, it is very sensitive to small amounts of impurity in the substance being measured.

In summary, the advantages of using refractive index as an analytical technique are:
1) Refractive index is very sensitive so it is a good way to tell one compound from another.
2) Refractive index is an easy, rapid and relatively inexpensive technique.
3) Refractive indices are characteristic of a given substance.
4) Refractive indices can be used to calculate the ratio of components in a mixture (such as alcohol in water).

The disadvantages of refractive index are:
1) Refractive index is very sensitive to the purity of the sample, the temperature and wavelength of the incident light.
2) Only transparent liquids and solids give reliable readings.
3) Refractive index doesn't give us any clues as to the chemical makeup of an unknown substance. Like melting points, it is a comparative technique.

(Zubrick Chapter 29 covers Refractometry)

Experimental Observations and Data:

Hand in a copy of your experimental observations and data before you leave lab.

Experimental Observations.

___ Appearance of reagents?

___ Record the mass (to the nearest 0.01 gram) of your alcohol.

___ What temperature changes did you observe during distillation?

___ How long did the distillation take?

___ What did your product look like?

___Compare your starting alcohol with the crude distilled product and the final product.

___ What is the appearance of the distilling flask at the end of the reaction?

___ Did you record interesting sights and smells?

Data:

___ Did you record the mass of your product?

___ What data did you collect from parts D. and E.?

Lab Report Checklist:

Results.

____ % yield of product → crude product mass x 100/theoretical yield

Discussion and Conclusion.

____ Was your percent yield acceptable? Explain why it was lower (or higher) than expected.

____ Did you obtain your predicted product? Explain using all relevant data.

____ Comment on the purity and composition of your product.
Explain using all relevant data.
Justify the presence of side reaction products.

____ What is going on in the qualitative test? Include at least one chemical structure.

____ **Green Question**: What common beverage contains phosphoric acid?