

Objective:

In this experiment you will learn how to dehydrate an alcohol to form an alkene using a strong acid catalyst. The dehydration of cyclohexanol to cyclohexene will be performed. The product is recovered by fractional distillation from the reaction mixture. To verify the reaction went to completion, the product will be characterized using gas chromatography, infrared spectroscopy, refractive index and by doing chemical tests: the ammonium cerium (IV) nitrate test, the bromine test and the potassium permanganate (Baeyer) test.

* Gas Chromatography (GC) is extremely useful in determining the percent composition/purity of known liquids; however, the flame ionization detector does not detect if there is water present in the product. Infrared (IR) spectroscopy will be used in order to determine if the product has water contamination. When Infrared radiation is passed through a sample, some radiation is absorbed by the sample and some passes through (or is transmitted) resulting in a distinct spectrum with peaks that can be assigned to specific functional groups. The refractive index (R.I.) is also a useful physical property of a liquid. It can be used for identification purposes and as a measure of purity of the sample being examined. Prior to instrumental analysis, chemists used chemical tests to characterize compounds.

Reading Assignment:

MTOL: pp. 79-83 (distillation theory), 57-62 (gas chromatography) and: OCLT: pp. 254-262 (separation theory); 279-281 (fractional distillation); 139-153 (gas chromatography); 339-341 (FTIR); 342 & 348 (bromine test); and 343 & 354 (permanganate / Baeyer test).

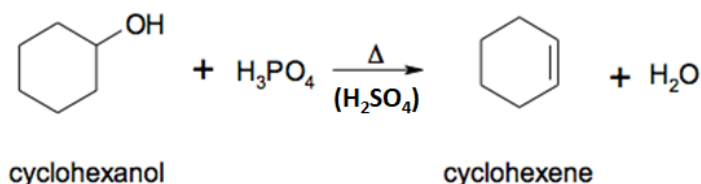
The ceric ammonium nitrate test is discussed after the procedure on page 3.

Concepts:

Boiling Point, Characterization Tests, Condensate, Condensation, Dehydration, Distillate, Distillation, Evaporation, Fourier Transform Infrared Spectroscopy (FTIR), Gas Chromatography (GC), Mobile Phase, Reflux, Refractive Index, Stationary Phase, Theoretical Plates, Vaporization

Chemicals:

Cyclohexanol, Cyclohexene, Phosphoric acid, Sulfuric acid, Sodium sulfate, Bromine, Ceric ammonium nitrate, Dichloromethane, 1,2-Dimethoxyethane (DME), Potassium Permanganate

Chemical Equation:**Safety Precautions:**

Wear chemical splash-proof goggles and appropriate attire at all times.

Cyclohexanol and cyclohexene are flammable liquids.

Hot glassware looks just like cold glassware.

Be careful when working with hot glassware! Do not to touch it!

Materials:

aluminum block, aluminum foil, beaker (100ml), Claisen head adapter, conical vial (5 ml), one disposable pipet & bulb, one disposable vial and cap, finger clamps (2), glass wool batting, Hickman still head, hot plate with magnetic stirrer, label (1-small), magnetic spin vane (large), ringstand, Teflon septum with hole in the center, and thermometer

Instruments:

FTIR spectrometer, Gas Chromatograph (maybe), Refractometer

Alcohol Dehydration Procedure

1. Preheat the hot plate and aluminum block at a heat setting of $\sim 130\text{-}145\text{ }^\circ\text{C}$ while you assemble your glassware.
2. Put together a fractional distillation set-up* as described in lecture.

***Note:** Verify that there is an o-ring (and only one o-ring) in each of the black caps before attaching the conical vial to the air condenser and the air condenser to the Hickman still head. If there is a sidearm on the Hickman still, verify the arm is capped. **Do not lower empty glassware into Al block; it will cause the glassware to crack.** Do not worry about adjusting thermometer height until glassware has been lowered into the Al block.

3. In a 5-ml conical vial, weigh out $\sim 1.925\text{ g}$ of cyclohexanol. Record the exact mass to the nearest mg (0.001g).* Record the physical properties of the reactant.

***Note:** The cyclohexanol should be weighed and the mass recorded to the nearest mg, since yield is based on its amount and small volumes cannot be measured accurately.

4. To the cyclohexanol in the 5-ml conical vial, add $\sim 1.5\text{ ml}$ H_3PO_4 (phosphoric acid) and 3 **drops** of H_2SO_4 (sulfuric acid). The acids are located in the hood.

***Note:** Be sure to add the phosphoric acid first. If the sulfuric acid is added first charring may occur.

5. Add the large magnetic spin vane (to regulate boiling and avoid bumping), attach the Claisen head adapter and Hickman still head and thermometer (as shown) and apply grease to the joints.

***Note:** Be sure to add a Teflon circle with a hole in it around the thermometer. The circle goes above the clamp to keep the thermometer from sliding into the vial and breaking. Do **not** clamp the thermometer tightly as it might break. Make sure the clamp is tight enough that the thermometer does not tilt and fall over. The bulb of the thermometer should be positioned so that the bulb is completely in the neck. The top of the bulb should be at the top of the neck of the Hickman still.

6. Cover the apparatus with glass wool, pinching it as close as possible to the glassware using the test tube clamps.

***Note:** It is important that no glass be exposed from the conical vial to the base of the Hickman still.

7. Adjust the temperature of the hotplate in order to regulate the boiling rate so that a smooth slow distillation is attained. Adjust the spinning of the vane such that there are no longer two layers visible.

***Note:** Do **not** allow the mixture to foam up into the Hickman. Do **not** set the temperature too high or else you will boil both the cyclohexanol (BP $\sim 160\text{ }^\circ\text{C}$) and the cyclohexene (BP $\sim 83\text{ }^\circ\text{C}$). - *Your objective is to separate them.* If the BP is extremely high, the sulfuric acid will decompose ($>290\text{ }^\circ\text{C}$).

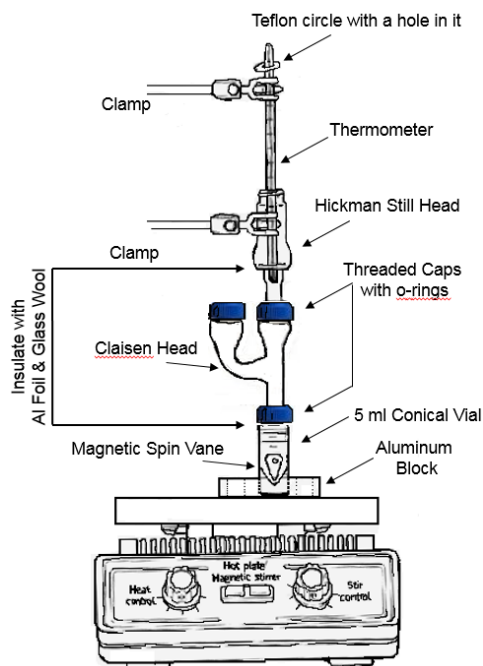


Figure 1: Alcohol Dehydration Set-up

8. Acquire from the supply cart, 1 disposable vial with a cap, a small label, a disposable pipet and pipet bulb. Label the vial cyclohexene. Place the vial in a 50 ml beaker so that it stands upright and does not tip over.
9. If condensation is slow in forming, cool the top of the Hickman still with compressed air. Record the temperature when the distillate condenses and first starts to drip down the inside of the Hickman still. (*This is the beginning of your boiling point range.*) Collect the cyclohexene in the BP range of 80-85 °C corresponding to the cyclohexene product, BP = 83 °C.*

***Note:** The expected boiling point range is 80-85 °C corresponding to the cyclohexene BP=83 °C. However, the actual ranges may differ from the expected ranges – especially if you are not using a mercury thermometer. The exact ranges may also differ from one experimenter to the next. Record the values that you actually observe for your distillate.

10. Allow the distillate to accumulate in the Hickman still until the well is at least half full. Record the highest temperature reached. (*This is the end of your boiling point range.*)
11. Then using a clean pipet, transfer this accumulated first fraction to the 1-mL disposable vial and cap it. (**Note:** All fractions will be collected in the same vial, but the vial needs to be capped in between collections to ensure that the collected distillate does not evaporate.)
12. As long as distillate is accumulating in the Hickman still, continue transferring the distillate to the disposable vial.
13. Continue the distillation until the temperature at the still head drops (by at least 15 °C) indicating that no more product is distilling over. Avoid excessive heating afterwards, which may cause decomposition. Turn off the heat on the hotplate. Allow the apparatus to cool slightly. Turn off the magnetic stirrer.
14. Look at the distillate in the disposable vial, check for two distinct layers. (Is there a definite meniscus?) If there are two layers, using a disposable pipet remove the lower water layer and transfer it to a waste beaker.
15. Dry the distillate with sodium sulfate, Na₂SO₄. Using your microspatula, add a small scoopful of Na₂SO₄ to the disposable vial. Place the cap on the disposable vial. Swirl the mixture. If the Na₂SO₄ is clumping, then add more Na₂SO₄ until the newly added salt is free-flowing. If the Na₂SO₄ is free-flowing, then decant (or transfer using a pipet) the distillate into a clean preweighed disposable vial. (Record the weight of the vial to the nearest mg.) Note that excessive addition of Na₂SO₄ may result in significant product loss.
16. Weigh the disposable vial with the distillate. Record the mass of the vial and the distillate to the nearest mg. Determine and record the mass of the distillate.
17. Disassemble the apparatus while still warm. Do not inhale any fumes. Pull your mini hood down to remove smelly toxic fumes. The brown still pot residue is primarily strong acids which are disposed of in the mineral acid waste container. (Mineral Acid Waste Container = A glass bottle in the waste hood.)
18. (Maybe, depends on GC availability.) Run GC of your product to determine the amount of cyclohexanol & cyclohexene present. Record the brand/model of the GC used. Record the parameters used. Record the Percent Composition in your results. Using scotch tape, tape the GC chromatogram to the back of the prelab yellow page.* Comment on the outcome in your conclusion.

***Note:** Be very careful not to cover any of the text on the chromatogram with tape. The tape will cause the text to disappear over the week.

19. Run FTIR of the product. (The TA will run the FTIR.) Label peaks corresponding to cyclohexene (and cyclohexanol or water if present) in your product. Attach FTIR to your lab report.

20. Using the white ceramic well plates, run chemical tests on the standards (cyclohexanol and cyclohexene) and your product: 2% Br₂ in CH₂Cl₂, 1% KMnO₄(aq) and Ce(NH₄)₂(NO₃)₆(aq).

Record any color changes for cyclohexanol, cyclohexene std. and your product. Be specific. Do not just record yes/no. Tabulate the results in your lab book. (Similar to the table below.) Comment on any similarities between your product and the standards in your conclusion. (**Note:** Some students in previous semesters have chosen to take a picture of their results and include the picture in their lab report. This is optional – not required.)

	Cyclohexanol standard	your product	Cyclohexene standard
2% Br ₂ in CH ₂ Cl ₂			
1% KMnO ₄ (aq) + DME			
Ce(NH ₄) ₂ (NO ₃) ₆ (aq) + DME			

21. If you have enough sample, determine the refractive index of the product using a digital refractometer and record your results. Be sure to cover the sample with a 1" watch glass to prevent selective evaporation during measurement. Record the brand and model of refractometer used. Record the temperature of the refractometer in order to correct the RI reading for temperature. (Consult your handouts for proper operation of the refractometers in lab.)

22. Dispose of chemicals appropriately. Clean and return all glassware and equipment.

Ceric Ammonium Nitrate Test

Ceric ammonium nitrate is a yellow solid that dissolves in dilute nitric acid. This yellow reagent forms red complexes with compounds that contain alcoholic hydroxyl groups. It does not react with carbonyl groups, so it is a good test to determine if aldehydes or ketones have been reduced to alcohols. The test works for primary, secondary and tertiary alcohols containing up to 10 carbons. A red complex also forms when the reagent is mixed with glycols, polyols, carbohydrates, hydroxy acids, hydroxy aldehydes and hydroxy ketones.

Note that changing the groups attached to certain inorganic ions such as Ce⁴⁺ results in a change to the electronic structure, which results in a color change. The red complex is the intermediate for the oxidation of alcohols by Ce⁴⁺ solutions. A second phase of the test involves the disappearance of the red color due to the oxidation of the coordinated alcohol and the reduction of the colored Ce(IV) complex to the colorless Ce(III) complex. Production of a reddish color therefore indicates the presence of an alcohol group, even if the color is not persistent.

Reference for Ceric Ammonium Nitrate Test

Shriner, Ralph L., Fuson, Reynold C., Curtin, David Y. and Morrill, Terence C. The Systematic Identification of Organic Compounds: A Laboratory Manual, 6th ed. John Wiley & Sons. New York: 1980. p. 147

Post Lab (Calculations and Conclusion):

1. Show calculations for RI corrections and the % error for the corrected RI.
2. Show the calculation for the %Error for the BP.
3. Show the calculation for the theoretical yield for the cyclohexene. (*Use your exact initial mass.*)

$$(\text{g cyclohexanol}) / (\text{molar mass cyclohexanol}) = \text{moles of cyclohexanol}$$

$$(\text{moles cyclohexanol}) \times (\text{mole ratio cyclohexene / cyclohexanol}) = \text{moles of cyclohexene}$$

$$(\text{moles of cyclohexene}) \times (\text{molar mass of cyclohexene}) = \text{g of cyclohexene} \quad (= \textit{theoretical yield})$$

4. Show the calculation for Percent Yield. (*Use your exact final mass as actual mass.*)

$$\% \text{ Yield} = (\text{Actual Yield (g)} / \text{Theoretical Yield (g)}) \times 100$$

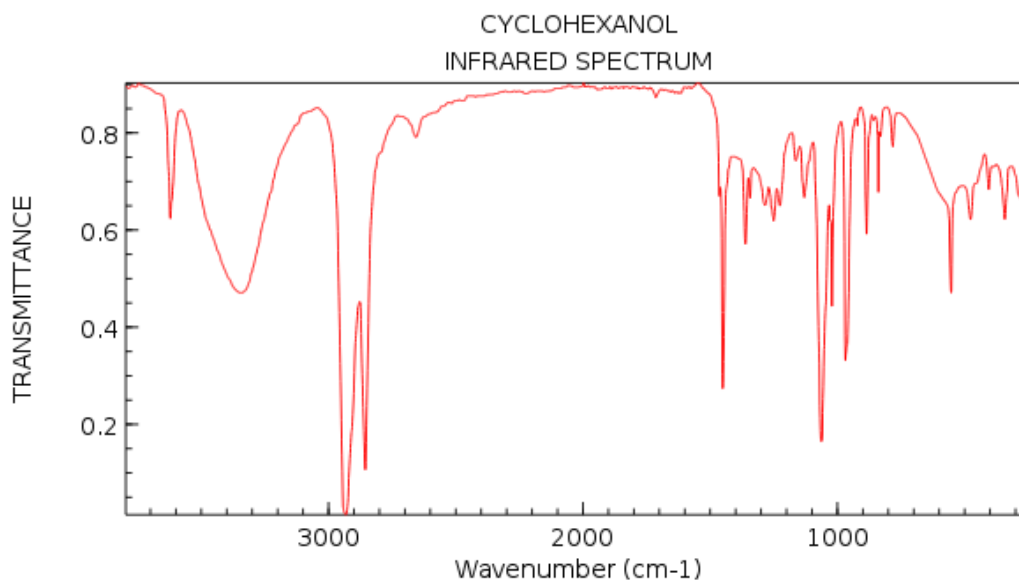
5. Tabulate the literature values, actual values and % errors.
6. In your conclusion, discuss the success of the reaction based on the results of the GC, FTIR, RI and chemical tests. If there were any problems, make suggestions for how they could be avoided if you were to redo the experiment.

Name: _____

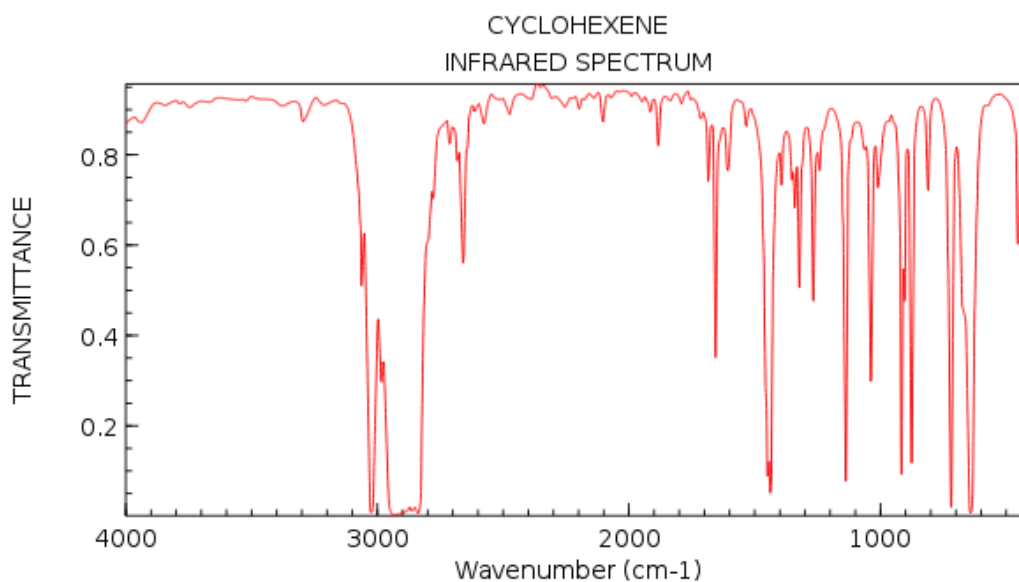
Section: _____

Directions: Label peaks on the FTIR below with the “bond types” indicated by the frequencies of the peaks listed. Tear off this page and submit with your lab report. (*Hint: Each Spectrum has 4 identifiable bond types.*)

bond type	vibration	type of compound	frequency (cm ⁻¹)
-C-H	(stretch)	alkanes	2800-3000
=C-H	(stretch)	alkenes, aromatics	3000-3100
-O-H	(stretch)	alcohols, phenols	3600-3650 (free) 3200-3500 (H-bonded) (broad)
-C=C-	(stretch)	alkenes	1600-1680
-C-H	(bending)	alkanes	1375 (methyl) 1460 (methyl and methylene)
-C-OH	(stretch)	secondary alcohols	1100



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