LABORATORY MANUAL
ORGANIC CHEMISTRY 240

FIFTH EDITION

Dr. Steven Fawl
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Dr. Steven Fawl

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Napa, California
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PREFACE

Chemistry is an experimental science. Thus, it is important that students of chemistry do experiments in the laboratory to more fully understand applications of the theories they study in lecture and how to critically evaluate experimental data. The laboratory can also aid the student in the study of the science by clearly illustrating the principles and concepts involved. Finally, laboratory experimentation allows students the opportunity to develop techniques and other manipulative skills that students of science must master.

The faculty of the Napa Valley College clearly understands the importance of laboratory work in the study of chemistry. The Department is committed to this component of your education and hopes that you will take full advantage of this opportunity to explore the science of chemistry.

A unique aspect of this laboratory program is that a concerted effort has been made to use environmentally less toxic or non-toxic materials in these experiments. This was not only done to protect students but also to lessen the impact of this program upon the environment. This commitment to the environment has presented an enormous challenge, as many traditional experiments could not be used due to the negative impact of the chemicals involved. Some experiments are completely environmentally safe and in these the products can be disposed of by placing solids in the wastebasket and solutions down the drain. Others contain a very limited amount of hazardous waste and in these cases the waste must be collected in the proper container for treatment and disposal. The Department is committed to the further development of environmentally safe experiments which still clearly illustrate the important principles and techniques.

The sequence of experiments in this Laboratory Manual is designed to follow the lecture curriculum. However, instructors will sometimes vary the order of material covered in lecture and thus certain experiments may come before the concepts illustrated are covered in lecture or after the material has been covered. Some instructors strongly feel that the lecture should lead the laboratory while other instructors just as strongly believe that the laboratory experiments should lead the lecture, and still a third group feel that they should be done concurrently. While there is no "best" way, it is important that you carefully prepare for each experiment by reading the related text material before coming to the laboratory. In this way you can maximize the laboratory experience.

In conclusion, we view this manual as one of continual modification and improvement. Over the past few years many improvements have come from student comments and criticisms. We encourage you to discuss ideas for improvements or suggestions for new experiments with your instructor. Finally, we hope you find this laboratory manual helpful in your study of chemistry.
LABORATORY SAFETY RULES

Your participation in this laboratory requires that you follow safe laboratory practices. You are required to adhere to the safety guidelines listed below, as well as any other safety procedures given by your instructor(s) in charge of the course. You will be asked to sign this form certifying that you were informed of the safety guidelines and emergency procedures for this laboratory. Violations of these rules are grounds for expulsion from the laboratory.

Note: You have the right to ask questions regarding your safety in this laboratory, either directly or anonymously, without fear of reprisal.

- **Goggles must be worn at all times while in lab.** You must purchase a pair of goggle for yourself and you may store them in your locker. You will be advised of the appropriate goggles to be purchased.
- Locate the emergency evacuation plan posted by the door. Know your exit routes!
- Locate emergency shower, eyewash station, fire extinguisher, fire alarm, and fire blanket.
- Dispose of all broken glassware in the proper receptacle. Never put broken glass in the trashcan.
- Notify you instructor immediately if you are injured in the laboratory; no matter how slight.
- Never pipette fluids by mouth. Check odors cautiously (i.e. wafting). Never taste a chemical.
- Shoes must be worn in the laboratory. These shoes must fully enclose your foot.
- Long hair must be tied up in a bun during lab work. Loose long sleeves should be avoided in the lab.
- Children and pets are not allowed in the laboratory.
- Eating or drinking in the lab is prohibited. Do not drink from the laboratory taps.
- Wash your hands before and after working in the lab.
- Turn off the Bunsen burner when you are not using it.
- If any reagents are spilled, notify your instructor at once.
- Follow the instructor’s directions for disposal of chemicals.
- Only perform the assigned experiment. No unauthorized experiments are allowed.
- Every chemical in a laboratory must be properly labeled. If a label is unclear, notify your instructor.
- Use the proper instrument (eye-dropper, scoopula, etc.) to remove reagents from bottles. Never return unused chemicals to the original container. Do not cross contaminate reagents by using the same instrument for 2 different reagents. (e.g. don’t use the mustard knife in the mayonnaise jar)
- Material Safety Data Sheets (MSDS) are available for your reference. These contain all known health hazards of the chemicals used in this course. In addition, there is information concerning protocols for accidental exposure to the chemical. You are advised to inspect this binder.
LAB CHECK-IN

SECTION I - Introduction to Chemical Structure

10pts Covalent Bonding and Molecular Models (1 week)

SECTION II - Specific Laboratory Techniques

10pts Isolation of Caffeine from Vivarin (2 weeks)
20pts Simple and Fractional Distillations - Calculation of a Theoretical Plate, HETP, Column Efficiency (2 weeks)

SECTION III - Synthetic Techniques and Principles

20pts Kinetics Lab: Solvolysis Effects on SN1 Reactions (1 week)
10pts Synthesis of Cyclohexene from Cyclohexanol (2 weeks)
10pts Synthesis of t-Butyl Bromide from t-Butyl Alcohol (2 weeks)
10pts Williamson Ether Synthesis of Butyl Methyl Ether (2 weeks)
EXPERIMENT ONE

COVALENT BONDING AND MOLECULAR MODELS

Today you will use ball-and-stick molecular model kits to better understand covalent bonding. You will figure out the structures of several different covalent molecules and then use the models to make those molecules.

In order to draw proper Lewis structures chemists use two rules,

**Rule #1:** \# of valence electrons + \# of bonds = 8

**Rule #2:** All atoms, except hydrogen, want eight electrons (also known as the octet rule).

Valence electrons are determined by the column on the periodic table in which the atom is found. Carbon is found in column four of the periodic table and therefore has four valence electrons. To find the column an atom is in, simply count from left to right across the periodic table, ignoring the transition metals. Most periodic tables have the column number marked at the top of each column (in Roman numerals).

If we know the number of valence electrons an atom has then it is a simple matter to determine how many bonds the atom must have. The table below gives the valence and the number of bonds for several common atoms as predicted by Rule #1.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Valence</th>
<th>Bonds</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>4</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>N</td>
<td>5</td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>O</td>
<td>6</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Cl</td>
<td>7</td>
<td>1</td>
<td>8</td>
</tr>
</tbody>
</table>

Each bond has two electrons and as can be seen by the table carbon has four bonds which means that these bonds account for eight electrons around the carbon. This is the number of electrons required by Rule #2. Nitrogen on the other hand has three bonds which account for six electrons. In order to fulfill the requirements of Rule #2 we must add two more electrons to nitrogen that are not used in bonding. These electrons are called lone pair electrons. Nitrogen needs one set of lone pair electrons (1 pair = 2 electrons). The following table tells you how many bonds and how many lone pair electrons are to be found on some common atoms.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Bonds</th>
<th>Lone Pair e-</th>
<th>Total e-</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>4</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>N</td>
<td>3</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>O</td>
<td>2</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Cl</td>
<td>1</td>
<td>3</td>
<td>8</td>
</tr>
</tbody>
</table>
In this lab you will draw these molecules and then make them using the molecular model kits provided in the lab. In each kit each ball represents a different kind of atom:

- **yellow** balls, with 1 hole each, represent **hydrogen**;
- **orange, green, and purple** balls, with 1 hole each, represent the **halogens**—F, Cl, Br, I;
- **red** balls, with 2 holes each, represent **oxygen or sulfur**;
- **black** balls, with 4 holes each, represent **carbon or silicon**.

In addition there are wooden pegs and metal springs and/or plastic tubing which represent bonds. [Ignore the fact that some of the wood sticks are longer than others.] Use **two** pieces of plastic tubing or two springs for a double bond and three pieces for a triple bond. When removing springs from the holes in the balls, please be **gentle with the springs** so their shapes are not distorted.

**EXPERIMENT:** First, draw the structure of each molecule given below. Don't forget to count bonds and to look for symmetry and draw in the lone pair electrons. Then using the balls, springs, and sticks make a model of the molecule. Compare the completed model with your drawing. The model kits do not allow for lone pair electrons so do not expect to include them in your model. Your drawing and model should agree as to what atoms are bonded to what other atoms and what kinds (single, double or triple) of bonds are formed. Do **not** worry about bond angles. Then do the same for the next molecule on the list. If you have time, draw the Lewis electron-dot structure of at least one compound in each group (paragraph). If you need help—**ASK**!
MOLeCULAR MODELS WORKSHEET

Draw and name each of the following compounds. Make sure you actually MAKE the compound and draw what you make. It is easy to tell if you are drawing these compounds and not actually making them.

1) Draw, then make: CH₄, CCl₄, HCCl₃, and CCl₂F₂.

2) Draw, then make: C₂H₆, C₃H₈, and C₄H₁₀. Do you see a pattern here? (The next member of this series is C₅H₁₂) Write down the mathematical relationship between carbons and hydrogens in these molecules (one rule for all of them). There are two ways of drawing C₄H₁₀, draw both of them.

3) Draw, then make: C₂H₄, C₃H₆, and C₄H₈. Do you see a pattern here? Write down the mathematical relationship between carbons and hydrogens in this molecule (one rule for all of them). There are six different ways of drawing C₄H₈, please draw them all.
4) Draw, then make: \( \text{C}_2\text{H}_2 \), \( \text{C}_2\text{Cl}_2 \), and \( \text{C}_3\text{H}_4 \). There are three ways of drawing \( \text{C}_3\text{H}_4 \), please draw all of them (one of them cannot be made with the model kits without breaking the models).

5) There are two ways of making \( \text{C}_2\text{H}_6\text{O} \). One of these isomers is \( \text{CH}_3\text{OCH}_3 \) (dimethyl ether) and the other is written, \( \text{C}_2\text{H}_5\text{OH} \) (ethyl alcohol). Draw each isomer and use the balls and sticks to make these two isomers.

6) There are 11 ways of drawing \( \text{C}_3\text{H}_6\text{O} \), please draw all of them. One of them is particularly difficult to see, ask for help.
7) Draw and make three isomers of C$_2$H$_2$Cl$_2$. Hint: the isomers are very similar. Remember, the breaking of bonds is required to change one isomer into another.

8) The molecule C$_4$H$_{10}$O can be drawn in a number of ways. Two of the molecules are mirror images of one another. Make the molecule below and its mirror image. Are these two molecules the same or different?

```
H   H   OH H
|   |   |   |
H—C—C—C—C—H
|   |   |   |
H   H   H   H
```
Caffeine is an alkaloid found in tea, coffee, cola nuts, and several other plants. It is a mild stimulant and may be used medically for this purpose (for example, in Vivarin tablets). Structurally, caffeine belongs to a class of nitrogen bases called purines. It is a colorless, crystalline solid that melts at 235-236°C, but it can readily be sublimed under reduced pressure at temperatures below its melting point. It is moderately soluble in water (2.2g/100mL) but is more soluble in common organic solvents.

One technique that you will use during this lab is called multiple extraction. When we separate the caffeine from the alkaline water we will use three 20 mL portions of methylene chloride instead of a single 60 mL portion. If the caffeine is twice as soluble in the methylene chloride as it is in the water then three 20 mL portions will extract about 20% more caffeine from the water than a single 60 mL portion of methylene chloride.

**CHEMICALS**

3 Vivarin  
60 mL methylene chloride  
5 mL benzene  
1 mL Petroleum ether

**EQUIPMENT**

400 mL beaker  
250 mL Erlenmeyer flask  
250 mL separatory funnel

**TIME**: 2 hours

**EXPERIMENT**

Add three crushed Vivarin tablets to 100 mL of water in a 250-mL Erlenmeyer flask. Then boil the mixture for 10 min to ensure solution of the caffeine. The binder in the tablets will remain in suspension. Filter off the binder by suction filtration. Save the liquid. Cool the extract to room temperature, transfer it to a 250 mL separatory funnel, and extract the aqueous solution three times with 20-ml portions of methylene chloride. Do not shake the layers vigorously; use a swirling motion so as not to form an emulsion.
Combine the methylene chloride extracts and evaporate the extract to dryness on the steam bath (HOOD). Do not heat the residue any longer than necessary to evaporate the solvent. The residue that remains after evaporation of the solvent is crude caffeine; some mint smell will be evident. The caffeine may be purified by recrystallization as described below.

**PURIFICATION PROCEDURE**

Transfer the crude caffeine to a clean 50-ml beaker, add 5 ml benzene, and heat on a hot water bath to dissolve the caffeine. Remove the beaker from the heat source, add 10 ml petroleum ether (boiling range 60-90°C), and allow the caffeine to crystallize. Collect the product by suction filtration, wash it with 1 mL petroleum ether, allow it to air-dry, and determine its melting point.

**LAB REPORT**

Vivarin contain 200 mg (0.200 g) caffeine per tablet. Your theoretical yield is 600 mg (0.600 g) of caffeine. Calculate the percent yield before and after recrystallization and the melting point of your recrystallized caffeine. Compare your melting point to the actual melting point.
Extraction of Caffeine from Vivarin Worksheet

<table>
<thead>
<tr>
<th>Grams of Caffeine in Tablets</th>
<th>Grams of Caffeine Extracted</th>
<th>Percent Yield</th>
<th>Melting Point</th>
<th>CRC =</th>
<th>Exptl =</th>
</tr>
</thead>
</table>

**Questions**

1) Why do you swirl the separatory funnel instead of shake it?

2) Why do you use three 20 mL portions of methylene chloride in the extraction instead of one 60 mL portion?

3) Petroleum ether was added to the benzene solution of caffeine to cause the caffeine to recrystallize. Petroleum ether is not an ether it is a mixture of low boiling alkanes (C5-C7). What did this "ether" do to the methylene chloride that made the caffeine crystallize? Consider the polarity of methylene chloride, caffeine and hexane (pet.ether) in answering your question.

4) Caffeine is soluble in benzene, water, and methylene chloride. In which of these solvents should caffeine be most soluble? Rank them according to solubility.
Discussion

This experiment is a simple distillation of a mixture of cyclohexane and toluene. We will first describe the general steps used in any simple distillation, then mention some specific features of this experiment.

Figure 3: The apparatus for a simple distillation.
**Steps in a Simple Distillation**

The apparatus for a simple distillation is shown in the figure above. Study this figure carefully, noting the placement and clamping of the distillation flask, the distillation head, and the condenser. Note that water flows into the bottom of the condenser's cooling jacket and out the top. If the water inlet were at the top, the condenser would not fill. Also, note the placement of the thermometer bulb, just below the level of the side arm of the distillation head. If the bulb were placed higher than this position, it would not be in the vapor path and consequently would show an erroneously low reading for the boiling point.

>>>SAFETY NOTE: Distillation of noxious or toxic substances should always be carried out in a fume hood. Special precautions should also be taken with distillations of highly flammable substances, such as most solvents. Never use a burner in these cases, and avoid allowing an excess of uncondensed vapors to flow into the room.

1) **The distillation flask.** Use only a round-bottom flask, never an Erlenmeyer flask, for distillation. The flask should be large enough that the material to be distilled fills 1/3 of its volume. If the flask is overly large, a substantial amount of distillate will be lost as vapor filling the flask at the end of the distillation. If the flask is too small, boiling material may foam, splash, or boil up into the distillation head, thus ruining the separation.

Grease the ground-glass joint of the flask lightly, then securely clamp the flask to a ring stand or rack. Before adding liquid, support the bottom of the flask with an iron ring and a heating mantle. The heating mantle should fit snugly around the flask. Introduce the liquid into the distillation flask, using a funnel with a stem to prevent the liquid from contaminating the ground-glass joint. Finally, add three or four boiling chips. (CAUTION: Never add boiling chips to a hot liquid!)

2) **The distillation head.** Grease the ground-glass joints of the distillation head lightly and place the head on the flask. It is generally not necessary to clamp the head. (Do not attach the thermometer at this time).

3) **The condenser.** Grease the ground-glass joints of the condenser lightly and attach rubber tubing firmly to the jacket inlet and outlet (which should not be greased). A strong clamp (oversized, if available) is needed to hold the condenser in place. Because of the weight and angle of the condenser it will tend to pull away from the distillation head. For this reason, check the tightness of this joint frequently before and during a distillation.

Attach the rubber tubing from the lower end of the condenser to an adapter on the water faucet. Place the end of the upper outlet tubing from the condenser in the sink or drainage trough. Turn on the water cautiously; after it fills the condenser and flows out, adjust the flow to a "heavy trickle." Water should flow, not drip, from the outlet tubing; however, a forceful flow of water is likely to cause the tubing to pop off the condenser. If you leave a distillation unattended for even a short while, twist short pieces of wire around the tubing; on the condenser inlet and outlet to
secure them. Because of variations in water pressure and because many faucets tend to tighten gradually, check the flow of water frequently during the distillation.

4) **The Adaptor.** The adapter directs the flow of distillate plus uncondensed vapors into the receiving flask. If desired, a piece of rubber tubing attached to the vacuum adapter can be used to carry fumes to the floor. (Rubber tubing is no substitute for a fume hood, however.) Whichever type of adapter is used, grease its joint lightly before attaching it to the condenser. A rubber band may be used to secure the adapter.

5) **The receiving flask.** Almost any container can be used as a receiver, as long as it is large enough to receive the expected quantity of distillate. An Erlenmeyer flask is recommended. A beaker is not recommended because its wide top allows vapors and splashes to escape and allows dirt to get into the distillate. Either set the receiving flask on the bench top or clamp it in place. (It is not good practice to prop up a receiving flask on a stack of books.) If you are collecting several fractions, prepare a series of clean, dry, tared (weighed empty) flasks. If the volume, rather than the weight, of distillate is to be determined, you may use a clean, dry graduated cylinder as the receiver. A round-bottom flask with a ground-glass joint is also a good receiver.

>>>>SAFETY NOTE When distilling at atmospheric pressure, always leave the apparatus open to the air at the adapter-receiver end. If you attempt a distillation with a closed system, the pressure build-up inside the apparatus may cause it to explode.

6) **The thermometer.** Attach the thermometer last (and remove it first) because thermometers are expensive and easily broken. The easiest type of thermometer to insert is one with a ground-glass joint that fits a joint at the top of the distillation head. Neoprene adapters are available for attaching ordinary thermometers. Alternatively, a short piece of rubber tubing used as a sleeve can be used to hold the thermometer in place. A one-hole rubber stopper is not recommended because the hot vapors and condensate of the distilling liquid may dissolve the rubber, which can discolor the distillate. When attaching the thermometer, be sure to place the bulb just below the level of the side arm, as shown in the figure.

7) **The actual distillation.** Before proceeding, check the water flow through the condenser and make sure that all ground-glass joints are snug. Plug the heating mantle into a rheostat, then plug the rheostat into the wall socket. If you use a burner, check the vicinity for flammable solvents. (Do not use a burner when distilling a flammable compound!)

Slowly heat the mixture in the distilling flask to a gentle boil. You will then see the reflux level (the ring of condensate, or upper level of vapor condensing and running back into the flask) rise up the walls of the flask to the thermometer and side arm. At this time, the temperature reading on the thermometer will rise rapidly until it registers the initial boiling point, which should be recorded. The vapors and condensate will pass through the side arm and into the condenser, where most of the vapor will condense to liquid, and will finally drip from the adapter into the receiving flask.
The proper rate of distillation is one drop of distillate every 1-2 seconds. This rate is achieved by controlling the amount of heat supplied to the distillation flask. A too slow rate means that not enough vapor is passing the thermometer to give an accurate boiling point. A too rapid rate leads to a lack of separation of components and also to uncondensed vapor being carried through the condenser and into the room. It is generally necessary to increase the amount of heat applied to the distillation flask (by increasing the rheostat setting) during the course of a distillation.

8) Collecting the fractions. Volatile impurities are the first compounds to distil. This first fraction, called the fore-run, is generally collected separately. When the temperature has risen to the desired level and has been recorded, place a fresh receiver under the adapter to collect the main fraction. In some cases, the main fraction can be collected in a single receiver. In other cases, it should be collected as a series of smaller fractions. Each time you change a receiver, note the temperature reading and record the boiling range of the fraction. After checking the purity of a group of fractions, you may want to combine some of these fractions later.

Impurities that are higher boiling than the desired material are generally not distilled, but are left in the distillation flask as the residue. If higher-boiling impurities are present in large quantities, the temperature may rise from the desired level as the impurities begin to distil. However, the temperature frequently drops after the main fractions have distilled. This happens because not enough vapor and condensate are present in the head to keep the thermometer bulb hot. If the temperature drops at the end of a distillation, the last temperature to record is the highest temperature, before the drop occurred. At the conclusion of a distillation, remove the heat source. Turn off a heating mantle and lower it from the flask immediately. Allow the entire apparatus to cool before dismantling it.

>>>SAFETY NOTE: Never carry out a distillation to dryness, but always leave a small amount of residue in the distillation flask. The presence of boiling residue will prevent the flask from overheating and breaking and will also prevent the formation of pyrolytic tars (difficult to wash out).

In the simple distillation of the mixture of ethyl acetate and n-propyl acetate, you will collect the distillate in eleven fractions and measure the refractive index of each. Using this information, you will construct two graphs: (1) boiling point versus total volume of distillate; and (2) refractive index versus total volume of distillate (see sample graphs below). When you do the fractional distillation, you will be able to compare the graphs of each experiment to see how the two types of distillation differ in their ability to separate mixtures.
Figure 4: Sample graphs for the simple distillation of a mixture of cyclohexane and toluene.

EQUIPMENT:
condenser
condenser adapter
distillation head with thermometer adapter
droppers or disposable pipets
10-mL and 50-mL graduated cylinders heating mantle for 100-mL flask, with rheostat long-stemmed funnel
refractometer
100-mL round-bottom flask
eleven test tubes with corks
test-tube holder
thermometer

CHEMICALS
Cyclohexane 25 mL
Toluene 25 mL

TIME REQUIRED - 2 1/2 hours

PROCEDURE
Add 25 mL of cyclohexane, 25 mL of toluene, and 3-4 boiling chips to a 100 mL round bottom flask, clamped to a ring stand and supported by a 100 mL heating mantle. Assemble the distillation apparatus as shown, following the instructions found in the discussion of this handout (see above).

Assemble eleven clean, dry test tubes of the same size: add 5.0 mL of water to one and set it in a test tube rack. The volume of liquid in this test tube is used to estimate (by comparison) the volumes of the distillation fractions.

Plug the heating mantle into a rheostat, then plug the rheostat into the wall socket. A setting of 4 should bring this particular mixture to a boil. Increase or decrease the voltage setting to achieve a steady boil that maintains a drip rate of distillate of about 1 drop every 2 seconds.

Collect about 1 mL of the initial distillate and then continue by collecting 5-mL fractions in the test tubes. Record the temperature at the start and at the end of each fraction. Cork each test tube after the fraction has been collected to prevent evaporation. The very first 1 mL portion is very important! Collect it carefully and run it's refractive index immediately.

The distillation is complete when the distillation flask is almost empty and the temperature starts to drop or fluctuate. (Because of hold-up, your last fraction will not be 5 mL.) When the apparatus is cool, transfer the residue to a small graduated cylinder and record the volume.

Measure the refractive index of each fraction, along with the refractive indexes of the starting cyclohexane and toluene. Record these data in your notebook. Construct two graphs: one of boiling point versus mL distilled and the other of refractive index versus mL distilled. Use the upper value of the boiling range for each fraction as the boiling point in your graph. The graphs that you obtain should look similar to those given in the handout.
PROBLEMS

1) As a liquid begins to distil, a student notes that the boiling chips are missing. The student removes the thermometer and drops a few chips into the flask. What will probably happen? What is the correct procedure?

2) n-Propyl acetate (bp 102°C) evaporates rapidly when exposed to air, but water (bp 100°C) does not. Explain.

3) During a distillation, you observe that the thermometer bulb is dry. List at least three possible causes, and state what you should do in each case.

4) When a solvent is used to extract a small amount of a high-boiling product from a reaction mixture, it is common practice to first distil the solvent by simple distillation, transfer the residue to a smaller flask, and isolate the product in a second distillation. Why not just continue the first distillation to isolate the product?
Part Two - Fractional Distillations

Discussion

Like the previous experiment, this experiment is the distillation of a mixture of cyclohexane and toluene. Unlike the previous experiment, you will use a fractionation column so that you can compare the efficiency of fractional distillation to that of simple distillation in separating mixtures.

Steps in Fractional Distillation

The following general procedure applies to fractional distillations in general, not only the distillation in this experiment.

1) Packing the fractionation column. The technique for packing a fractionation column depends on the packing material. Metal turnings or sponges are best pulled up into the column with a hook on the end of a wire. If the packing is glass beads, glass helices, or small metal turnings, first place a piece of metal sponge or metal wool in the bottom of the column to support the packing. Then pour or drop the pieces of packing in. Regardless of the type of packing used, it should be loosely, but uniformly, packed. "Holes" in the packing will decrease efficiency,
while spots of very tight packing may plug the column. Use a combination of beads and broken tubing.

2) Setting up the apparatus. Assemble the apparatus as shown with the fractionation column clamped in a vertical position. When high-boiling compounds are distilled, the column should be insulated around the outside with glass cloth, dry rags, or a double layer of loosely wrapped aluminum foil. Whenever practical, however, it is preferable to leave the column uncovered so that the behavior of the liquid-vapor mixture in the column can be observed. Leave the column uncovered in this experiment. Clamp the distillation flask (1/3 full, containing boiling chips, and with its joint lightly greased) to the fractionation column. Clamp the receiving flask in position, then insert the thermometer into the distillation head.

>>>>> SAFETY NOTE Before heating, check that all joints are snug, that fresh boiling chips have been added, and that the system is open to the atmosphere at the receiver.

3) The fractional distillation. Heat the distillation flask slowly. When the solution boils, you will observe the ring of condensate rising up the fractionation column. If heating is too rapid and the condensate is pushed up too rapidly, equilibration between liquid and vapor will not occur and separation of the components will not be satisfactory.

If you heat the distillation flask too strongly before the column has been warmed by hot vapors and condensate, the column may flood, or show an excessive amount of liquid in one or more portions of the packing. Flooding is due to lack of equilibration between condensate and vapor and is more likely to occur if the packing has not been inserted uniformly. Ideally, the packing should appear wet throughout, but no portion of it should be clogged with liquid.

Flooding can be stopped by lowering the heat source. As the boiling of the liquid diminishes, the excess liquid in the column flows back into the distillation flask. At this time, resume heating, but more slowly than before. If flooding recurs, insulate the column as described in Step (2) so that the vapors will have less tendency to condense. If the flooding is due to an incorrectly packed column, cool the apparatus, repack the column, and begin again.

4) Collecting the fractions. In a fractional distillation, read the boiling points and collect the fractions just as in a simple distillation. It is always better to collect a large number of small fractions than a few large ones. Small fractions of the same composition can always be combined, but a fraction that contains too many components must be redistilled.
EQUIPMENT

same as in the previous experiment, plus:
additional condenser or fractionation column
 copper turnings or other column packing

CHEMICALS

same as in previous experiment

TIME REQUIRED

fractional distillation: 2 hours
refractive indexes: 1/2 hour

STOPPING POINT: after the distillation

>>>>SAFETY NOTE: Cyclohexane and toluene are volatile and flammable. There must be no flames in the laboratory.

PROCEDURE

Assemble the fractional distillation apparatus as described in the discussion, using a 100-mL distillation flask containing 25 mL of cyclohexane, 25 mL of toluene, and 3-4 boiling chips (see Experimental Note).

Distill the mixture and collect the fractions as described in the previous experiment. Because of the hold-up on the fractionation column, you will collect only nine fractions. Superimpose the data onto the graphs made in the previous experiment. Compare the curves from the simple and fractional graphs and record your conclusions.
Problems

1) Which of the following circumstances might contribute to column flooding and why?

a) "holes" in the packing
b) packing too tight
c) heating too rapidly
d) column too cold

2) Explain why flooding in the fractionation can lead to a poor separation of distilling components.

3) A chemist has a small amount of a compound (B.P. 65°C) that must be fractionally distilled. Yet, the chemist does not want to lose any of the compound to hold-up on the column. What can the chemist do, that is, how would the chemist push this liquid through the column?
SAMPLE CALCULATION WORKSHEET
FOR THE SIMPLE AND FRACTIONAL DISTILLATIONS

In this lab you will calculate the enrichment factor \( \alpha \), the number of theoretical plates added by the fractionating column, the Height Equivalence to a Theoretical Plate (HETP) and the number of theoretical plates needed to obtain a 95\% enrichment of the mixture. We will begin by explaining some of the terms and processes you will need to know about distillations.

Some General Considerations

When a mixture of any two liquids begins to boil, the vapor produced will always be enriched with the more volatile component. The more volatile component is always the liquid with the lowest boiling point. Thus in a mixture of toluene (BP = 110.6°C) and cyclohexane (BP = 80.7°C) the vapor will contain more cyclohexane than toluene. When this vapor condenses the liquid produced will be enriched in cyclohexane compared to the original boiling mixture.

Within the boiling flask there is a region above the liquid that is available to the vapor for evaporation. During a distillation it is this region that allows the vapor to become enriched in the more volatile component. By definition this region allows for one level of enrichment and is known as one theoretical plate. A theoretical plate is not a thing of substance it is the area above the boiling liquid in the flask. If you were to take the vapor and condense it and place it into a second flask and boiled the liquid then you would have used two theoretical plates in your separation, that is, the original liquid would have been enriched twice.

The enrichment factor \( \alpha \) can be calculated using the data from your simple distillation and using the following equation.

\[
\alpha^{n+1} = \frac{X_{1,\text{vap}}/X_{2,\text{vap}}}{X_{1,\text{liq}}/X_{2,\text{liq}}}
\]

Where \( n+1 \) is the number of theoretical plates, \( X_{1,\text{vap}} \) is the mole fraction of the vapor due to liquid #1, \( X_{2,\text{vap}} \) is the mole fraction of the vapor due to liquid #2, \( X_{1,\text{liq}} \) is mole fraction of liquid #1, and \( X_{2,\text{liq}} \) is the mole fraction of liquid #2. For a simple distillation \( n = 0 \) since there can be at most only one theoretical plate in a simple distillation. A value for \( n \) will be obtained later when a fractionating column adds more theoretical plates to the simple boiling flask. Since \( \alpha^{n+1} = \alpha^1 = \alpha \) we can calculate the enrichment factor \( \alpha \) if we have values for all of the mole fractions.
Calculating the Mole Fractions

The Liquids

The simplest method for calculating the mole fractions for the liquids is to calculate the number of moles based on the amount taken. Since 25 mL are taken in each case one then only needs to know the density of the liquids to calculate their mass and subsequently the total number of moles. You can find the density of your liquids in the CRC Handbook. I will use approximate values to illustrate the principles but you must look up the densities for yourself.

Assume that the density of Cyclohexane is 0.7785 g/mL and is 0.8623 g/mL for toluene. For 25 mL of solution the moles of each would be;

\[
\frac{(25 \text{ mL} \times 0.7785 \text{ g/mL})}{84.12 \text{ g/mol}} = 0.2314 \text{ mole cyclohexane}
\]

\[
\frac{(25 \text{ mL} \times 0.8623 \text{ g/mL})}{92.14 \text{ g/mol}} = 0.2340 \text{ mole toluene}
\]

The mole fraction of cyclohexane would therefore be;

\[
0.2314/(0.2314 + 0.2340) = 0.4972 \text{ mole fract. cyclohexane} = X_{1,\text{liq}}
\]

The mole fraction of toluene would be;

\[
1 - 0.4972 = 0.5028 \text{ mole fract. toluene} = X_{2,\text{liq}}
\]

The Vapors

To calculate the mole fraction of each of the vapors we will make use of a very convenient fact: When two liquids are mixed and form an ideal mixture the refractive index of the mixture is directly related to the mole fraction of each component. Fortunately our liquids form ideal solutions and we are able to use the refractive index to calculate the mole fractions. If a mixture of liquids is not ideal then significant deviations in this law can occur.

Mathematically the relationship between the refractive index (nD) and mole fraction can be written as;

\[
nD_{\text{obs}} = nD_1X_1 + nD_2X_2
\]

Using the relation that \(X_1 + X_2 = 1\) we can simplify the above expression;

\[
nD_{\text{obs}} = nD_1X_1 + nD_2(1-X_1) = nD_2 + X_1(nD_1-nD_2)
\]

Figure 1: This is an example of what would be seen in a refractometer. The refractive index of this liquid would be 1.5148.
Solving for $X_1$

$$X_1 = \frac{(nD_{\text{obs}}-nD_2)}{(nD_1-nD_2)}$$

We now have a relationship that expresses the mole fraction of component one strictly in terms of measurable values of the refractive index. According to the CRC Handbook the refractive index for cyclohexane is about 1.37 and the refractive index of toluene is about 1.38. If the first milliliter of liquid from the simple distillation has an observed refractive index of 1.3734 then the mole fraction of cyclohexane would be;

$$X_{1,\text{vap}} = \frac{(1.3734 - 1.38)}{(1.37 - 1.38)} = 0.66 \text{ mole fraction cyclohexane}$$

and the mole fraction of toluene would be;

$$X_{2,\text{vap}} = 1 - 0.66 = 0.34 \text{ mole fraction toluene}$$

**Calculating the Enrichment Factor $\alpha$**

Once all of the mole fractions have been obtained it is easy to calculate the enrichment factor. Applying eq.(1) where $n = 0$ we have,

$$\alpha = \frac{0.66/0.34}{0.4972/0.5028} = 1.963$$

Therefore we can say that a simple distillation, representing one theoretical plate, can cause the more volatile component of our mixture to become 1.963 time more concentrated in the vapor phase.

**Calculating the Number of Theoretical Plates Added by a Fractionating Column**

Thus far we have only been concerned with the results derived from the simple distillation data. The addition of a fractionating column increases the number of theoretical plates and therefore allows for a greater amount of separation in a single step. These additional theoretical plates give a value to "n" in eq.(1). To calculate a numerical value for $n$ for a fractional distillation we follow the exact same procedure for obtaining the mole fractions found in eq.(1). Where we differ is that we leave $n$ in our final expression and solve for it instead of $\alpha$ (it was determined earlier for the simple distillation).

Suppose that for the first milliliter of distillate from our fractional distillation that we calculated the mole fraction of cyclohexane was 0.75 and the mole fraction of toluene was 0.25. We could then calculate a value for $n$ by using the following mathematical procedure;

$$\alpha^{n+1} = \frac{0.75/0.25}{0.4972/0.5028} = 3.0338$$
Since $\alpha = 1.963$ we have,

$$\alpha^{n+1} = 1.963^{n+1} = 3.0338$$

To solve for $n$ we must take the $\log_{10}$ of each side,

$$(n+1)\log_{10}(1.963) = \log_{10}(3.0338)$$

Therefore,

$$n+1 = \frac{\log_{10}(3.0338)}{\log_{10}(1.963)}$$

and

$$n = \left[ \frac{\log_{10}(3.0338)}{\log_{10}(1.963)} \right] - 1 = 0.6455$$

theoretical plates

Thus we can say that the fractionating column has added 0.6455 more theoretical plates to our simple distillation apparatus.

**Calculating the HETP**

How tall must the fractionating column be to add 1 more theoretical plate to a simple distillation? This is answered by the HETP (Height Equivalence to a Theoretical Plate). Based on our calculations the column used here came a bit short of giving us one additional theoretical plate. If the length of our column was 25 cm then our HETP would be,

$$\text{HETP} = \frac{\text{Length}}{n} = \frac{25 \text{ cm}}{0.6455} = 38.73 \text{ cm/theoretical plate}$$

Therefore to have a distillation apparatus capable of giving us two levels of enrichment in a single step we would use our distillation flask (one theoretical plate) and add a 38.73 cm fractionating column to it (another theoretical plate).
Name ___________________________  Date ___________________________

Distillation Worksheet

<table>
<thead>
<tr>
<th>Molecular Properties</th>
<th>Cyclohexane</th>
<th>Toluene</th>
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</thead>
<tbody>
<tr>
<td>Property</td>
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<tr>
<td>Formula Weight</td>
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<td>Ref. Index Expt.</td>
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<td>B.P. Expt.</td>
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<tr>
<td>Density (CRC)</td>
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<tr>
<td>Length of Column</td>
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<table>
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<th>Simple Distillation Data Sheet</th>
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NOT NEEDED
<table>
<thead>
<tr>
<th># mL</th>
<th>Temperature</th>
<th>Refractive Index</th>
<th>Xcyclohexane</th>
<th>Xtoluene</th>
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</tbody>
</table>

**CALCULATIONS**

Simple Distillation

Mole Fraction of Liquid Components

Mole Fraction of Vapor Components
Calculation of $\alpha$

Fractional Distillation

Mole Fraction of Liquid Components

Mole Fraction of Vapor Components (see above)

Calculation of $n$

Calculation of HETP
EXPERIMENT FOUR

Solvent Effects in an S$_N$1 Solvolysis Reaction
A Kinetics Study

DISCUSSION

In this experiment, you will not conduct a detailed quantitative kinetics study. Instead, you will determine the relative rates of the solvolysis of t-butyl chloride in three different solvent systems (methanol-water, ethanol-water, and acetone-water) and express the results in graphic form.

In the first two solvent systems, mixtures of organic products are formed because the alcohols contain hydroxyl (-OH) groups. With the acetone-water mixture, only the water participates in the solvolysis reaction. Regardless of the solvent system, the inorganic product is HCl. Note that for each molecule of t-butyl chloride that undergoes reaction, one molecule of HCl is generated. Because of this 1:1 correspondence, the course of the reaction can be conveniently followed by measuring the acidity of the reaction mixture.

In this experiment, you will be comparing the time it takes for each of several solvolysis reactions to reach the same percent of completion. Because this is a study of relative rates, the exact percent of completion does not matter as long as all the reactions are carried to the same point. (Your solvolysis reactions will be carried to only about 5% completion). Detecting the percent completion point is accomplished by adding a measured amount of NaOH to each reaction mixture. Under these conditions, each mixture remains alkaline until the NaOH has been neutralized by the HCl being generated. Then, the solvolysis mixture will turn acidic as additional HCl is generated. We can detect the change from an alkaline solution to one that is acidic by including phenolphthalein in the solvolysis mixture. When the mixture becomes acidic, the solution changes from pink to colorless. From a plot of the percent water in each solvent system versus the time required to reach the phenolphthalein end-point, we can compare the effects of various solvent systems upon the rate of the SN1 reaction. The experiment as described is semi-quantitative, and the results cannot be used to calculate the rate constant.

---

1 Under the conditions of this experiment, a tertiary alkyl halide can also undergo elimination by an E1 or E2 path. In this experiment, these side reactions are ignored. If you carry out titrations of aliquots of the reaction mixture (instead of adding NaOH directly to the reaction mixture), side reactions are minimized.
EQUIPMENT:

two burets
clock with a second hand
dropper or disposable pipet
3-5 styrofoam cups
15 test tubes, 13 x 100 mm, with corks
thermometer

CHEMICALS:

acetone, 6-10 mL
t-butyl chloride, less than 5 mL
95% ethanol, 6-10 mL
methanol, 6-10 mL
phenolphthalein indicator
a few drops 0.5 M sodium hydroxide, less than 5 mL

TIME REQUIRED: 2-3 hours

STOPPING POINTS: Although the experiment could be stopped after any batch has been run, it is preferable to run all the solvolysis reactions in the same laboratory period. This will ensure that the same droppers and the same NaOH solution are used.

PROCEDURE:

The solvent systems to be tested are listed in the table below. Because 15 separate mixtures will be tested, plan to run 3-5 reactions simultaneously. Each reaction requires 5-30 minutes; therefore, your various runs should be planned to overlap.

<table>
<thead>
<tr>
<th>COMPOSITION PERCENT BY VOLUME SOLVENT: WATER</th>
<th>VOLUMES FOR 2.0 mL OF MIXTURE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SOLVENT</td>
</tr>
<tr>
<td>50:50</td>
<td>1.0 mL</td>
</tr>
<tr>
<td>55:45</td>
<td>1.1 mL</td>
</tr>
<tr>
<td>60:40</td>
<td>1.2 mL</td>
</tr>
<tr>
<td>65:35</td>
<td>1.3 mL</td>
</tr>
<tr>
<td>70:30</td>
<td>1.4 mL</td>
</tr>
</tbody>
</table>
Place 2.0 mL of the appropriate solvent mixture in a clean, labeled test tube. Use a buret to add the proper volume of solvent and a second buret to add the distilled water (see Experimental Note 1). Cork the test tubes and place them in a constant-temperature bath for about 5 minutes to come to thermal equilibrium. A styrofoam coffee cup is a convenient insulating container for a constant-temperature bath. Place water at 30°C +/- 1° in the cup, along with a thermometer. During the course of the experiment, add a few milliliters of warm water to the bath to maintain the temperature at 30°C.

To each test tube, add 3 drops of 0.5N sodium hydroxide solution and 1-2 drops of phenolphthalein indicator (see Experimental Note 2).

To one tube at a time, add 3 drops of t-butyl chloride. Mix or shake the contents of the tube immediately and record the time of the addition to the nearest second. Continue shaking. When the pink color disappears, again record the time. Repeat this procedure for each of the solvent systems.

Calculate the elapsed time for reaction in each solvent system to the nearest 0.1 minute. Plot percent water in each solvent system versus elapsed time. (Place all three plots on the same graph). Compare the three plots and record your observations and conclusions.

**EXPERIMENTAL NOTES:**

1) Your instructor will set up communal burets containing the solvents and water for the experiment.

2) The actual size of a drop of liquid varies, depending upon the dropper. For consistent results, use one dropper for all NaOH additions and another dropper for all t-butyl chloride additions.
Name __________________________ Date ___________________

SOLVOLYSIS WORKSHEET

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>Acetone</th>
</tr>
</thead>
<tbody>
<tr>
<td>50:50</td>
<td></td>
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<tr>
<td>55:45</td>
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<td>65:35</td>
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<tr>
<td>70:30</td>
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</tbody>
</table>

Include a graph of Time vs. Composition showing the relationship between all three solvents.

Questions

1) What is the reaction that is occurring, and is this reaction first or second order?

2) Why is it necessary to control the temperature, and what would have happened had the temperature been lower than 30°C?

3) Explain why one solvent slows the reaction while another seems to speed it up.

4) Look up the structure of each of the following solvents and determine whether they will speed up or slow down the reaction as compared to ethanol (they all dissolve in water).
   
   Tetrahydrofuran, Dimethyl sulfoxide, Isopropanol, Glycerol
EXPERIMENT FIVE

Preparation of Cyclohexene from Cyclohexanol: an Elimination Reaction

DISCUSSION

A secondary alcohol, such as cyclohexanol, undergoes dehydration by an E1 mechanism. The key intermediate in the mechanism is a cyclohexyl cation, which can undergo substitution as well as elimination. To prepare an alkene in good yield, it is necessary to suppress the substitution reaction. In this experiment, the substitution reaction is suppressed by: (1) the use of strong acids with anions that are relatively poor nucleophiles; (2) a high reaction temperature, which favors elimination; and (3) distillation of cyclohexene from the reaction mixture as it is formed.

Any strong acid can be used as the dehydrating agent. Sulfuric, phosphoric, and oxalic acids, and even potassium hydrogen sulfate, have all been employed successfully. The anions of these acids (sulfate, hydrogen phosphate, and oxalate ions) are all poor nucleophiles, and thus substitution reactions are not favored. Other strong acids, such as HBr, have nucleophilic anions, and thus yield more substitution than elimination products. Concentrated sulfuric acid alone causes both oxidation and polymerization of the product alkene. Fewer side reactions occur when concentrated phosphoric acid is used as the dehydrating agent, but the rate of the alkene formation is slow. Consequently, a mixture of sulfuric and phosphoric acids is used as the dehydrating agent in this experiment.

Removal of the alkene by distillation as it is being formed in the reaction mixture is an excellent technique for preventing side reactions. Unfortunately, this technique is applicable only for dehydration reactions that produce low-boiling alkenes, such as cyclohexene. Removal of the alkene reduces tar (polymer) formation by minimizing the contact time between the acid and the alkene. Water is also removed from the acidic reaction mixture in this distillation, which prevents the reverse reaction (reconversion of the cyclohexene to cyclohexanol) from occurring.

The distillate is an azeotrope of cyclohexene and water (90% cyclohexene-10% water, bp 71°C). Although cyclohexanol is high-boiling (bp 161°C), it also forms an azeotrope (bp 98°C) with water. Even with careful distillation, the cyclohexene-water distillate will be contaminated with some cyclohexanol, which must be removed in the subsequent work-up.

The crude distillate is transferred to a separatory funnel and the aqueous layer is drawn off. Since cyclohexanol is slightly water-soluble, it is removed from the crude cyclohexene by a water extraction. Next, the cyclohexene is extracted with saturated NaCl solution as a preliminary drying step. Because cyclohexene forms an azeotrope with water, it must be scrupulously dried at this point or the final product will be wet. Anhydrous CaCl₂ is the drying agent of choice because it forms molecular complexes with alcohols, as well as with water, and thus removes the last traces of cyclohexanol. After drying, the cyclohexene is purified by distillation.
EQUIPMENT:

distillation assembly
125-mL Erlenmeyer flask
50-mL flask with ground-glass stopper
10-mL graduated cylinder
ice bath
50-mL and 100-mL round-bottom flasks
125-mL separatory funnel

CHEMICALS:

anhydrous calcium chloride, about 2 g
cyclohexanol, 20 g
85% phosphoric acid, 5 mL
saturated NaCl solution, 10 mL
conc. sulfuric acid, 2 mL

TIME REQUIRED: about 2 1/2 Hours

STOPPING POINT: while the cyclohexene is being dried with CaCl₂

>>>>> SAFETY NOTE 1: Both sulfuric and phosphoric acids are strong, corrosive acids. If any acid is splashed on your skin or clothing, wash immediately with copious amounts of water.

>>>>> SAFETY NOTE 2: Cyclohexene is very volatile and very flammable. It should be stored in a glass-stoppered bottle with a lightly greased stopper. Its distillations should be carried out slowly, with an efficient condenser, and into a flask that is well chilled in an ice bath. There should be no open flames in the vicinity. Because cyclohexene vapors are heavier than air, they will accumulate in the sink and drain. As an added precaution against fire, water washes containing traces of cyclohexene should be disposed of in the fume-hood sink.

PROCEDURE

Place 20.0 g of cyclohexanol in a 100-mL round-bottom flask. Add 5 mL of 85% phosphoric acid and 2 mL of concentrated sulfuric acid (CAUTION: strong acids!). Mix the acidic solution by swirling, add 2-3 carborundum boiling chips, and equip the flask for simple distillation with a receiver adapter on the condenser. Slowly distil the contents of the distillation flask into a 125-mL Erlenmeyer flask chilled in an ice bath. (CAUTION: flammable. See Safety Note 2.) Adjust the rate of the distillation so that it takes about 45 minutes. Stop the distillation when about 8 mL of residue remains in the distillation flask (see Experimental Note). Approximately 17 g of water and crude cyclohexene will be collected in the receiver. The residue (CAUTION: strong acid!) should be poured onto ice, diluted with water, and flushed down the drain with a generous amount of additional water.
Transfer the distillate to a 125-mL separatory funnel. Drain the lower aqueous layer, then wash the cyclohexene remaining in the separatory funnel with 10 mL of water followed by 10 mL of saturated NaCl solution. Discard the aqueous layers in the hood sink when the extraction is completed. Because of the volatility of cyclohexene, conduct these washings as quickly as possible.

Drain the cyclohexene from the separatory funnel into a 50-mL, standard-taper, round-bottom flask. Add 2 g of anhydrous calcium chloride, and stopper the flask snugly with a lightly greased, ground-glass stopper. Allow the material to dry for at least 20 minutes, with occasional swirling to hasten the drying. Overnight drying is better.

After drying, remove the grease from the joint of the flask with a tissue, then carefully, but quickly, decant the bulk of the cyclohexene into a dry 50-mL round-bottom flask. (Because of the volatility of cyclohexene, filtration of the CaCl₂ is not advised.) Add 2-3 boiling chips to the cyclohexene, and distil it into a tared, 125-mL flask chilled in an ice bath (CAUTION: flammable).

There should be no distillation forerun. The bulk of the cyclohexene distills at 78-83°C. A typical yield is 12.0 g (73%), nD = 1.4468. The product should be stored in a bottle with a lightly greased, ground-glass stopper.

**EXPERIMENTAL NOTE**

Toward the end of the first distillation, the residue turns yellow to dark brown, and the temperature of the distillate may approach 83°C.
Cyclohexene Worksheet

<table>
<thead>
<tr>
<th>Compound</th>
<th>Boiling Point</th>
<th>Ref.Index</th>
<th>Yield (grams)</th>
<th>Percent Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexene (exptl)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CRC values</td>
<td></td>
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</tr>
</tbody>
</table>

1) Please give the complete mechanism of this reaction.

2) List the techniques used in this experiment to maximize the yield of cyclohexene and minimize the yield of by-products.

3) A chemist desires to dehydrate 1-octanol by the procedure used in this experiment.
   (a) What is the expected product?
   (b) Would a higher or lower temperature be needed in the first distillation? Explain.

4) The procedure states that you should leave about 8 mL of residue when distilling the crude cyclohexene. What are the reasons for this (what is in the residue)?
5) Write equations that show the mechanism of the dehydration of 3-pentanol. Two possible products can form, show both and indicate which one is the major product.

6) In this experiment a student's reaction mixture becomes black and tarry. Using equations, describe what has occurred. (hint: look up cationic polymer formation in your text)
EXPERIMENT SIX

Synthesis of 1-Bromobutane from 1-Butanol

DISCUSSION

The treatment of a primary alcohol with a hydrogen halide yields a primary alkyl halide. The reaction proceeds by an $S_{N}2$ mechanism, and competing dehydration is minimal. The reaction requires a strong acid to protonate the hydroxyl group. Aqueous HBr, gaseous HBr, and "constant boiling" HI (57% aqueous solution) can all be employed, without additional catalyst, to prepare the alkyl halide. In this experiment, HBr is generated in the reaction mixture by treatment of NaBr with H$_2$SO$_4$.

$$\text{NaBr} + \text{H}_2\text{SO}_4 \rightarrow \text{HBr} + \text{NaHSO}_4$$

When the mixture of alcohol, H$_2$SO$_4$, and NaBr is heated, gaseous HBr is given off; therefore, if the reaction is not carried out in a fume hood, a trap for the HBr must be arranged (See Figure). In the trap, the HBr emitted from the reflux condenser is passed over aqueous sodium hydroxide and thus converted by an acid-base reaction to sodium bromide and water.
An excess of sulfuric acid is used in the experiment to provide a strongly acidic medium for the protonation of the alcohol. Sulfuric acid, which is a dehydrating agent, also combines with the water that is formed as a product of the substitution reaction.

A number of side reactions occur in this reaction. 1-Butanol can react with $\text{HSO}_4^-$ ions present in solution to yield a hydrogen sulfate ester ($\text{ROSO}_3\text{H}$). This inorganic ester, in turn, can undergo elimination to yield 1-butene (a gas that is lost during the reflux and work-up) or substitution with 1-butanol to yield di-n-butyl ether (which must be removed during work-up).

Another side reaction that occurs is oxidation of the 1-butanol by either $\text{H}_2\text{SO}_4$ or $\text{Br}^+$ (formed by oxidation of $\text{Br}^-$ by $\text{H}_2\text{SO}_4$).

At the end of the reaction, the mixture consists of two phases. The upper layer contains the desired 1-bromobutane plus organic by-products, and the lower layer contains the inorganic components. The work-up techniques in this experiment consist of four steps: (1) an initial steam distillation; (2) extraction; (3) drying; and (4) a final distillation to purify the product. In the steam distillation, the water and 1-bromobutane co-distil, leaving the inorganic compounds behind in the distillation residue. Unfortunately, di-n-butyl ether, butanoic acid, and unreacted 1-butanol also co-distil with water and must be removed from the distillate by extraction.

The first extraction, a water wash, removes some of the 1-butanol, which is slightly soluble in water. The second extraction is with cold, concentrated sulfuric acid. (If the acid is not cold, extensive charring of the organic material will occur.) Each of the two major impurities (1-butanol as di-n-butyl ether) and the minor impurity (butanoic acid) contains an oxygen atom. In strong acid, each of these compounds is protonated to yield a sulfuric acid-soluble salt. 1-Bromobutane does not form a salt with sulfuric acid; consequently, it remains in the separatory funnel as a separate layer. This extraction is thus an example of a chemically active extraction.

A subsequent extraction with aqueous sodium hydroxide solution removes any sulfuric acid clinging to the sides of the separatory funnel. The wet alkyl halide is then dried with anhydrous calcium chloride. Calcium chloride is the drying agent of choice in this reaction because it forms complexes with any residual alcohol, as well as with water. After drying, the 1-bromobutane is purified by distillation.

**EQUIPMENT**

- condenser for reflux
- distillation assembly
- dropper or disposable pipet
- three 50-mL and one 125-mL Erlenmeyer flasks
- funnel, glass tubing, and rubber tubing (or fume hood)
- 100-mL graduated cylinder
- heating mantle and rheostat
- ice bath
- 250-mL round-bottom flask
- 50-mL round-bottom flask with glass stopper
- 125-mL separatory funnel
- thermometer
CHEMICALS

anhydrous calcium chloride
about 2 g 10% aqueous sodium hydroxide
25 mL 1-butanol, 18.5 g
conc. sulfuric acid, 50 mL
sodium bromide, 30 g

TIME REQUIRED: approximately 4 hours

STOPPING POINTS: after the reflux period; while the 1–bromobutane is being dried with CaCl$_2$

>>>SAFETY NOTE 1: During the reflux period, this reaction releases gaseous HBr, which is both corrosive and toxic (10-20 times more toxic than carbon monoxide and about as toxic as chlorine). The reaction must be carried out in a fume hood, or else the reflux condenser must be fitted with an HBr trap (see Experimental Note 1). If you use a trap, be sure the funnel is not submerged; otherwise, the trap liquid may be pulled into the reaction flask!

>>>SAFETY NOTE 2: Take extreme care in shaking a separatory funnel containing concentrated H$_2$SO$_4$. Vent frequently. Any accident, even a leaky stopcock, might result in acid being sprayed on yourself, your neighbors, or your work area. Any splashes on your skin or clothing should be flushed immediately with copious amounts of water.

PROCEDURE

Place 30 g of sodium bromide and 30 mL of water in a 250-mL round-bottom flask. Swirl the flask until most of the salt has dissolved. Add 18.5 g of 1-butanol, and cool the flask to 5-10°C in an ice bath. Slowly add 25 mL of concentrated sulfuric acid. (CAUTION: strong acid!). Fit the flask with a reflux condenser in the fume hood. If a hood is not available, fit the condenser with a gas trap. Add a few acid-resistant carborundum boiling chips, and heat the mixture at reflux for 30 minutes, using a heating mantle. During the reflux period, the reaction mixture will form two layers.

Allow the reaction flask to cool (or use an ice bath) to a temperature at which it can be handled. Add 2-3 fresh carborundum boiling chips and equip the flask for simple distillation. Distil until the temperature of the distilling mixture reaches 110-115°C. The distillate consists of two phases (1- bromobutane and water), which are most apparent at the start of the distillation. At the end of the distillation, the 1 -bromobutane should no longer be visible in the drops of distillate (see Experimental Note 2). The residue of the distillation (strong acid !) should be discarded by pouring it onto ice, diluting it with water, then flushing it down the drain with generous amounts of additional water.
Transfer the distillate to a 125-mL separatory funnel, and add about 25 mL of water. Shake the funnel and allow the phases to separate. Drain the lower layer of 1-bromobutane into an Erlenmeyer flask (see Experimental Note 3). Discard the upper layer.

Add 25 mL of ice-cold, concentrated sulfuric acid to the 1-bromobutane. (CAUTION: See Safety Note 2!) Swirl the flask to mix the contents. If the mixture becomes warm, chill the flask in an ice bath. Then transfer the mixture to the separatory funnel. Concentrated sulfuric acid (d = 1.84) is more dense than 1-bromobutane (d = 1.28). Therefore, 1-bromobutane now forms the upper layer. Shake the funnel gently or swirl it to avoid an emulsion, then allow it to stand for 5-10 minutes (see Experimental Note 4). Drain off the lower layer (CAUTION: strong acid!) and discard by pouring it onto ice, diluting the ice mixture, and flushing the solution down the drain.

Extract the bromobutane remaining in the separatory funnel with 25 mL of water to remove the bulk of the residual sulfuric acid. 1-Bromobutane is more dense than this aqueous solution; therefore, the bromobutane now forms the lower layer. Shake the funnel, then drain this lower layer into a clean, dry flask (or a second separatory funnel). Discard the aqueous layer remaining in the separatory funnel, then return the bromobutane to the funnel. Extract the bromobutane with 25 mL of 10% NaOH solution. In this extraction, as in the previous one, the bromobutane forms the lower layer in the separatory funnel. Drain the bromobutane into another clean flask, add 2 g of anhydrous calcium chloride, stopper the flask tightly, and allow the mixture to stand until the liquid is clear. (Overnight is best.) Because 1-bromobutane is quite volatile, a glass-stoppered flask is the preferred drying vessel.

Decant the clear bromobutane into a dry, 50-mL, round-bottom flask using a disposable pipet or dropper to transfer the residual liquid. Take care not to transfer any solid calcium chloride. Add 2-3 boiling chips, distil the dried 1-bromobutane with a dry distillation apparatus, and collect the fraction boiling at 98-103°C. (If the distillate is cloudy it is wet - it should be redried and redistilled). A typical yield is 17g (50%), nD = 1.4392 - 1.4400.
EXPERIMENTAL NOTES

1) The arrangement of an HBr trap is shown in the figure. The liquid in the beaker is approximately 5% aqueous NaOH. (CAUTION caustic!)

2) To verify that no oil is co-distilling with the water toward the end of the distillation, collect a few milliliters of the distillate in a test tube. Shake or flick the test tube with your finger. If any oil droplets are present, they will become visible when you hold the test tube up to the light.

3) Pay careful attention to the identification of the layers in the separatory funnel during this experiment. During one extraction, the product is in the lower layer; during another, it is in the upper layer. It is prudent to save all layers in labeled flasks until the completion of the experiment to avoid inadvertently throwing away the wrong layer.

4) Emulsions are common in the extraction, and standing time will be necessary to allow the phases to separate. Even so, the interface between the layers may be indistinct, and judgment may be necessary when the layers are separated.
1) Please give the mechanism of this reaction.

2a) Why was sulfuric acid used in the reaction of 1-butanol with sodium bromide instead of HNO₃ or HCl?

2b) Could concentrated HI be substituted for sulfuric acid in this experiment? Explain.

3) Which of the following types of boiling chips would be suitable for the reflux of reactants in this experiment? Explain.
   (a) marble (CaCO₃)
   (b) alumina (Al₂O₃)
   (C) silicon carbide (SiC)

4) To prevent gaseous HBr from contaminating the laboratory, one student corks the top of his reflux condenser. Why is this a bad idea?
5) Suggest a reason why the product 1-bromobutane does not react with water in the reaction mixture and revert to 1-butanol.

6) Suppose that you have only 15 g of 1-butanol to use in this experiment. What is your theoretical yield of 1-bromobutane?

7) If this experiment were carried out using the following alcohols in place of 1-butanol, what organic products and by-products would you expect in each case?

(a) 2-hexanol
(b) benzyl alcohol (C₆H₅CH₂OH)
(C) methanol
EXPERIMENT SEVEN
Williamson Ether Synthesis
of Butyl Methyl Ether

DISCUSSION

A Williamson ether synthesis consists of two separate reactions: the preparation of an alkoxide, and the reaction of this reagent with the alkyl halide.

Sodium methoxide is prepared by the addition of sodium metal to methanol. In the reaction, sodium metal is oxidized to sodium cations and the hydrogen atoms of the -OH groups are reduced to hydrogen gas. A large excess of methanol is used to act as a solvent for the sodium methoxide.

The exothermic nature of the reaction causes the methanol to boil. To prevent the methanol from boiling away, an upright condenser, called a reflux condenser, is attached to the reaction flask. Methanol vapors condense in the condenser and the liquid runs back into the flask.

Because of the vigor of the reaction, the sodium must be added slowly; otherwise, the methanol will boil violently, overwhelm the capacity of the reflux condenser, and spew out the top of the condenser. An uncontrolled reaction of this type, called a runaway reaction, may erupt like a volcano, throwing flammable solvent and corrosive chemicals over laboratory workers and the work area.

There are a number of techniques by which a solid can be added to a reaction mixture. In this experiment, small pieces of sodium are added to the flask through the reflux condenser tube. Most solids (generally powders) should not be added to reaction vessels in this manner because they tend to stick to the sides of the condenser. Should the sodium stick to the side of the condenser, a long glass rod or tubing can be used to push it down into the methanol. (It is prudent to bend an L at one end of the glass rod so that it cannot drop completely through the condenser and puncture the flask.)

After all the sodium has reacted, excess methanol is removed by distillation. Decreasing the volume of solvent increases the rate of reaction of sodium methoxide with 1-bromobutane and permits the entire reaction sequence to be carried out in a single laboratory period.
It is possible to stop the synthesis at this point until the next laboratory period. However, it is not desirable to do this because sodium methoxide is strongly basic. It absorbs moisture from the air and is converted to methanol and NaOH.

\[ \text{CH}_3\text{O}^- + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{OH}^- \]

If it is necessary to store the sodium methoxide, the flask must be sealed with a well-greased glass stopper.

After the excess methanol has been distilled, the flask containing the sodium methoxide is refitted with the reflux condenser, and 1-bromobutane is added in small portions through the condenser. The vigorous spontaneous reaction should be allowed to subside before each addition. As the reaction proceeds, sodium bromide precipitates. After all the 1-bromobutane has been added, the reaction mixture is heated at reflux (heated to boiling with a reflux condenser attached to the flask) to complete the reaction.

After a reaction has been carried out, the product must be isolated from the reaction mixture and purified. The general procedure is termed a work-up. A specific work-up procedure is dictated by the physical and chemical properties of the products and by-products in the mixture. In this experiment, the first step in the work-up is the addition of water to dissolve the sodium bromide. Two phases result: an aqueous-methanol phase and an organic phase. These two phases could be separated in a separatory funnel; however, the separation would be poor because the product n-butyl methyl ether is partly soluble in the methanol-water phase. Because n-butyl methyl ether and methanol form an azeotrope that boils at 56°C, they are easily separated from the mixture by a distillation. The distillate contains n-butyl methyl ether and methanol, while the residue contains water, sodium bromide, and the bulk of the methanol.

The next step in the work-up procedure is to remove the methanol from the product ether. Methanol is water-soluble, but the ether is not. An aqueous extraction of the methanol can be used at this point because most of the solvent methanol was left behind in the distillation step. An aqueous solution of calcium chloride instead of pure water is used to extract the methanol from the ether. The presence of the salt in the aqueous layer "salts out" the ether so that it is not carried into the water solution by the methanol. After extraction, the ether is dried with calcium chloride. Calcium chloride forms solid molecular complexes with both methanol and water; therefore, any residual methanol and water are removed from the product.

Finally, the product is purified by distillation. If the earlier distillation and drying steps were carried out carefully, only the clear product (bp 65-68°C) will distill. If the distillate is cloudy, it contains water and must be redried and redistilled. If part of the material boils at 56°C, the boiling point of the ether-methanol azeotrope, then all the methanol was not removed. In this case, the product must be rewashed with aqueous calcium chloride, redried, and redistilled.
EQUIPMENT

condenser
distillation assembly droppers
two 50-mL Erlenmeyer flasks
glass rod or tubing with an L at one end
100-mL graduated cylinder
heating mantle and rheostat
ice bath
50-mL, 100-mL, and 250-mL round-bottom flasks
125-mL separatory funnel
ground-glass stopper (optional)

CHEMICALS:

1-bromobutane
27.5 g anhydrous calcium chloride
3 g 25% aqueous calcium chloride
45 mL methanol
7 g diced sodium metal

TIME REQUIRED: 4-5 hours

STOPPING POINTS: after preparation of sodium methoxide (if necessary); after the reaction with 1-bromobutane; while the ether is being dried with CaCl₂.

>>>>> SAFETY NOTE: Methanol is toxic and flammable. Ingestion or excessive inhalation of the vapors can cause blindness or death. Use an efficient condenser when distilling it. (If possible, use the fume hood.) Wash any splashes on your skin with water.

>>>>> SAFETY NOTE 2: The sodium metal must not come into contact with water! Do not throw sodium scraps down the sink or wash the work area with a wet towel or sponge. The reason is twofold:

(a) The reaction of sodium with water is very exothermic and the hydrogen gas formed usually ignites and explodes.

(b) The other product of the reaction is concentrated NaOH, which is corrosive to both clothing and skin. Follow the procedure outlined in Experimental Note 2 for handling sodium.

>>>>> SAFETY NOTE 3: Hydrogen gas is given off in this experiment. Flames cannot be used in the laboratory, and adequate ventilation must be provided. In some laboratories, it may be advisable to carry out the preparation of sodium methoxide in the fume hood.
SAFETY NOTE 4 Sodium methoxide is a strong base and very caustic. Wash any spills with copious amounts of water.

PROCEDURE

Step 1: Preparation of Sodium Methoxide.

Place 200 mL of methanol in a 250-mL round-bottom flask and fit the flask with a reflux condenser (see Experimental Note 1). Add 7.0 g of diced sodium metal through the condenser, 3 or 4 pieces at a time, allowing the reaction to subside before adding the next piece (see Safety Note 2 and Experimental Note 2). If the sodium sticks to the inside of the condenser tube, push it into the reaction flask with a long glass tube or rod.

After the sodium has completely reacted, fit the flask for a simple distillation, add 3-4 boiling chips, and distil 125 mL of methanol (bp 64°C) into a graduated cylinder. (CAUTION: See Safety Notes 1 and 4.) If it is necessary to stop the experiment at this point, store the sodium methoxide in the round bottom flask with a heavily greased glass stopper.

Step 2: Reaction of Sodium Methoxide and 1-Bromobutane.

Fit the 250-mL round-bottom flask containing the sodium methoxide with a reflux condenser. Cool the flask to room temperature with an ice bath, if necessary. Weigh 27.5 g of 1-bromobutane into a 50-mL Erlenmeyer flask. Using a dropper, add the bromobutane to the reaction vessel through the top of the condenser in 1-2-mL aliquots over about a 10-minute period. Although warming may be required to start the reaction, the reaction is quite exothermic. Do not add all the bromobutane in one portion. Cool the reaction flask with an ice bath, if necessary, during the addition. Cork the Erlenmeyer flask between additions so that the 1-bromobutane does not evaporate.

After the addition has been completed, let the reaction vessel stand at room temperature until the exothermic reaction has subsided and the methanol ceases to reflux. Then heat the mixture at a gentle reflux, or “simmer,” for one-half hour with a heating mantle. The mixture will bump because of the precipitated solid; therefore, do not attempt a vigorous reflux.

After the reflux, cool the reaction vessel with a water or ice bath and add 20-30 mL of water to the reaction mixture through the reflux condenser. If all the sodium bromide does not dissolve, add a few additional milliliters of water. Dissolving the sodium bromide prevents bumping in the next step, a distillation.

Equip the flask for simple distillation and add 2-3 boiling chips. Distil the two-layered mixture, collecting the material that boils up to 64°C. The volume of distillate should be about 40 mL. Transfer the distillate to a 125-mL separatory funnel and extract it with three 15-mL portions of 25% aqueous calcium chloride. (The calcium chloride solution is the lower layer in this extraction, and the interface is difficult to see.) Pour the product from the separatory funnel into a 100-mL round-bottom flask, add about 3 g of anhydrous calcium chloride, stopper the flask, and let it stand overnight.
Decant the dried product into a 50-mL round-bottom flask. Use a dropper to transfer the final portion, being careful not to transfer any solid. Add 2-3 boiling chips to the flask; fit it for simple distillation; and distil the product, collecting the material boiling at 65-68°C. You should obtain about 10 g (57%) of n-butyl methyl ether.

Measure the refractive index of the product, and calculate your per cent yield. Transfer the product to a correctly labeled vial and hand it in to your instructor.

**EXPERIMENTAL NOTES**

1) A reflux condenser is an ordinary condenser arranged in an upright position, as shown in the figure, so that vapors from a boiling liquid are condensed and returned to the flask. A reflux condenser can be used during spontaneous exothermic reactions or when a liquid is being boiled by a heat source. The purposes of reflux are twofold: the reaction temperature can be maintained and the solvent is not lost to the atmosphere.

2) Sodium is stored under mineral oil to protect it from air and moisture. If the sodium has been diced by the storeroom personnel, remove the pieces with tweezers, blot off excess mineral oil with a laboratory tissue, and weigh the sodium on a tared watch glass. Do not allow it to sit in the air for any length of time.

If the sodium has not been diced, use the following procedure. Remove a lump from the jar and blot off the oil. Dip your fingers in fresh mineral oil (not the sodium jar!) to provide a protective coating. (Using latex gloves is unwise. If a fire should occur, the latex can catch fire and cause severe burns.) Cut the crust from the sodium with a razor blade or knife to expose the shiny metal. Cut a wedge of the fresh metal and transfer it to a watch glass for dicing into pieces about the size of small peas, smaller than the inside diameter of the condenser.

After the sodium has been cut, return all small slivers of the metal back to the main jar. *Clean all utensils, desk, and watch glasses with a tissue dampened with isopropyl alcohol or methanol.* Soak the tissues used for cleaning in a beaker with methanol in the hood for one hour before disposing of them (or before allowing them to come into contact with water). Clean your hands with a tissue soaked in isopropyl alcohol, then wash them thoroughly with soap and water.
Williamson Ether Synthesis

<table>
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<th>Grams</th>
<th>% Yield</th>
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<tr>
<td>CRC/Theoretical</td>
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<td></td>
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</tbody>
</table>

1a) Why is sodium metal stored under mineral oil?

1b) What is the crust that forms on sodium metal?

2) A chemist desires to wash the mineral oil off some sodium with a solvent. Which solvent or solvents would be appropriate?

   a) water       b) ethanol       c) pentane       d) petroleum ether
3) What would be the expected results of each of the following actions by a student while carrying out this experiment? [Use equations in your answers to (d) and (e).]

(a) Removing the reflux condenser to add Na to the methanol.

(b) Adding the Na rapidly through the condenser.

(c) Distilling 175 mL of methanol from the sodium methoxide instead of the 125 mL called for. (Give the immediate results and the results in subsequent reaction with 1-bromobutane.)

(d) Using 95% ethanol instead of methanol in the experiment.

(e) Leaving the sodium methoxide solution exposed to the air until the next laboratory period before adding the 1-bromobutane.

(f) Pouring the 1-bromobutane through the condenser in one portion.
4) Explain why the bulk of the methanol is removed before the sodium methoxide is treated with 1-bromobutane.

5) By error, a student used 1-bromopropane instead of 1-bromobutane in this experiment.
   a) What will the product be?

b) What is the theoretical yield of this product?
Chem 240 Practice Problems
Exam 1

Nomenclature
  Isomers
Rotational Energy Diagrams
Free Radical Halogenation
  Hybridization
  Sigma and Pi bonds
Boat Chair Configurations
  Intermolecular Forces
  Polarity and Dipoles
  Resonance Structures
Analysis of Dimethylcyclohexane Using Chem3D Pro
All Values in kJoules

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<tr>
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Cis 1, 2

Trans 1, 2

Cis 1, 3

Trans 1, 3

Cis 1, 4

Trans 1, 4
Mechanism of Free Radical Halogenation using Bromine

**Chain Initiation**

\[ \text{Br}_2 \xrightarrow{\text{light}} 2 \text{Br}^* \]

**Chain Propagation**

\[ \text{Br}^* + \text{H}_2\text{C} = \text{C} = \text{C} = \text{CH} \xrightarrow{\text{Br}_2} \text{HBr} + \text{H}_2\text{C} = \text{C} = \text{C} = \text{C} = \text{CH}^* \]

\[ \text{H}_2\text{C} = \text{C} = \text{C} = \text{CH} \xrightarrow{\text{Br}_2} \text{H}_2\text{C} = \text{C} = \text{C} = \text{C} = \text{CH} + \text{Br}^* \]

**Chain Termination**

\[ \text{Br}^* + \text{Br}^* \xrightarrow{\text{Br}_2} \]

\[ \text{Br}^* \xrightarrow{\text{Br}_2} \text{H}_2\text{C} = \text{C} = \text{C} = \text{CH} \]

\[ \text{H}_2\text{C} = \text{C} = \text{C} = \text{C} = \text{CH} \xrightarrow{\text{Br}_2} \]

<table>
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<tr>
<td>Bromination</td>
<td>1</td>
<td>97</td>
<td>∞</td>
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</table>
1) Please draw the rotational energy diagram for the rotation of 2,3-dimethyl butane around the C2-C3 bond.

Draw the molecule below, convert it to a Newman projection and then rotate it about the C2-C3 bond. Based on your rotations, draw the energy diagram above.

2) Please draw the rotational energy diagram for the rotation of 3-methyl pentane around the C2-C3 bond.

Draw the molecule below, convert it to a Newman projection and then rotate it about the C2-C3 bond. Based on your rotations, draw the energy diagram above.
3) Please draw all of the isomers of \( \text{C}_4\text{H}_7\text{Cl} \). There are more than a dozen.

4) Please draw all of the isomers of \( \text{C}_3\text{H}_5\text{Cl} \).

5) Please draw all of the isomers of \( \text{C}_3\text{H}_4\text{Cl}_2 \).

6) Please draw all of the isomers of \( \text{C}_3\text{H}_8\text{O} \).

7) Please answer the following questions concerning the molecule given below.
   a) How many pi and sigma bonds are in this compound?
   b) What is the hybridization on the following atoms;

   1 5 7 8 9

8) Please answer the following questions concerning the molecule given below.
   a) How many pi and sigma bonds are in this compound?
   b) What is the hybridization on the following atoms;

   2 3 4 5 7 8

9) Please answer the following questions concerning the molecule given below.
   a) How many pi and sigma bonds are in this compound?
   b) What is the hybridization on the following atoms;

   1 2 5 7
10) Please draw the most stable form of trans 1,2 dimethyl cyclohexane.

11) Please draw the most stable form of cis 1,3 dihydroxy cyclohexane.

12) Please draw the most stable form of cis 1,3 dimethyl cyclohexane.

13) Please draw the most stable form of cis 1,3 cyclopentadiol.

14) Please describe what happens to the melting point of a large alkene (C20 or larger) if the double bond changes from cis to trans. Also explain why it does this.

15) Please explain what happens to the melting point of an alkane as it becomes more branched.

16) What kinds of compounds can hydrogen bond? What is hydrogen bonding?

17) What is the major intermolecular bonding type for each of the following compounds?
   \[ \text{CH}_3\text{CH}_2\text{NH}_2 \quad \text{CH}_2\text{Cl} \quad \text{CH}_3\text{COOH} \]

18) Which compound in each pair has the highest boiling point?
   \[ \text{CH}_3\text{OCH}_2\text{CH}_3 \quad \text{or} \quad \text{CH}_3\text{CH(OH)}\text{CH}_3 \]
   \[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \quad \text{or} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \]
   \[ (\text{CH}_3)_2\text{CHCH}_3 \quad \text{or} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \]

19) Please predict the primary type of bonding that will occur in each of the following liquids.
   \[ \text{CCl}_4 \quad \text{H-bond} \quad \text{Dipole-Dipole} \quad \text{Dispersion} \]
   \[ \text{C}_{16}\text{H}_{34} \quad \text{H-bond} \quad \text{Dipole-Dipole} \quad \text{Dispersion} \]
   \[ \text{Propanone} \quad \text{H-bond} \quad \text{Dipole-Dipole} \quad \text{Dispersion} \]
1) Please draw the rotational energy diagram for the rotation of 2,3-dimethyl butane around the C2-C3 bond.

Draw the molecule below, convert it to a Newman projection and then rotate it about the C2-C3 bond. Based on your rotations, draw the energy diagram above.
2) Please draw the rotational energy diagram for the rotation of 3-methyl pentane around the C2-C3 bond.

Draw the molecule below, convert it to a Newman projection and then rotate it about the C2-C3 bond. Based on your rotations, draw the energy diagram above.
3) Please draw all of the isomers of C₄H₇Cl. There are more than a dozen.

4) Please draw all of the isomers of C₃H₅Cl.

5) Please draw all of the isomers of C₃H₄Cl₂.

6) Please draw all of the isomers of C₃H₈O
7) Please answer the following questions concerning the molecule given below.

a) How many pi and sigma bonds are in this compound?  5 pi and 16 sigma

b) What is the hybridization on the following atoms;

1 sp2  5 sp  7 sp2  8 sp2  9 sp3

8) Please answer the following questions concerning the molecule given below.

a) How many pi and sigma bonds are in this compound?

4 pi and 16 sigma

b) What is the hybridization on the following atoms;

2 sp2  3 sp3  4 sp2  5 sp  7 sp3  8 sp3

9) Please answer the following questions concerning the molecule given below.

a) How many pi and sigma bonds are in this compound?

3 pi and 21 sigma

b) What is the hybridization on the following atoms;

1 sp2  2 sp2  5 sp3  7 sp2  8 sp3

10) Please draw the most stable form of trans 1,2 dimethyl cyclohexane.

11) Please draw the most stable form of cis 1,3 dihydroxy cyclohexane.
12) Please draw the most stable form of cis 1,3 dimethyl cyclohexane.

\[ \text{H}_3\text{C} - \text{H}_3\text{C} \]

13) Please draw the most stable form of cis 1,3 cyclopentadiol.

\[ \text{OH} - \text{OH} \]

14) Please describe what happens to the melting point of a large alkene (C20 or larger) if the double bond changes from cis to trans. Also explain why it does this.

*The melting point increases. A cis bond puts a kink in the chain that makes it hard to stack. By changing the cis to a trans the chain straightens out and makes it easier to stack. This allows for more dispersion forces and increases the melting point.*

15) Please explain what happens to the melting point of an alkane as it becomes more branched.

The more branched an alkane becomes the lower the melting point. Branching makes it more difficult to stack the molecules and this reduces the molecules ability to use dispersion forces for bonding.

16) What kinds of compounds can hydrogen bond? What is hydrogen bonding?

Hydrogen bonds are formed between molecules that have OH or NH bonds (also HF but HF is not an organic compound).

A hydrogen bond is a sharing of protons between the oxygen or nitrogen molecules. The hydrogen atoms freely move between the oxygens or nitrogens by sharing grabbing onto the lone pair electrons found on these atoms. Each atom of oxygen or nitrogen can have up to 4 atoms of hydrogen surrounding them, each of them sharing their electrons.

17) What is the major intermolecular bonding type for each of the following compounds?

\[ \text{CH}_3\text{CH}_2\text{NH}_2 = \text{H bond} \quad \text{CH}_2\text{Cl}_2 = \text{Dipole-dipole} \quad \text{CH}_3\text{COOH} = \text{H bond} \]
18) Which compound in each pair has the highest boiling point?

CH₃OCH₂CH₃  or  CH₃CH(OH)CH₃ (*because of H bonds*)

CH₃CH₂CH₂CH₂CH₃ (*because it is bigger*)  or  CH₃CH₂CH₂CH₃

(CH₃)₂CHCH₃  or  CH₃CH₂CH₂CH₃ (*because it is less branched*)

19) Please predict the primary type of bonding that will occur in each of the following liquids.

<table>
<thead>
<tr>
<th>Compound</th>
<th>H-bond</th>
<th>Dipole-Dipole</th>
<th>Dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td></td>
<td></td>
<td><strong>Dispersion</strong></td>
</tr>
<tr>
<td>C₁₆H₃₄</td>
<td></td>
<td></td>
<td><strong>Dispersion</strong></td>
</tr>
<tr>
<td>Propanone</td>
<td>H-bond</td>
<td><strong>Dipole-Dipole</strong></td>
<td>Dispersion</td>
</tr>
</tbody>
</table>
1) Please name or draw the structure of the following compounds.

![Chemical structure 1]

![Chemical structure 2]

![Chemical structure 3]

![Chemical structure 4]

![Chemical structure 5]

![Chemical structure 6]

![Chemical structure 7]
2) Please draw the rotational energy diagram for the rotation of 2,3-dichlorobutane around the C2-C3 bond.

Draw the molecule below, convert it to a Newman projection and then rotate it about the C2-C3 bond. Based on your rotations, draw the energy diagram above.

3) Please draw all of the isomers of C₃H₃Cl

4) Please answer the following questions concerning the molecule given below.
a) How many pi and sigma bonds are in this compound?

b) What is the hybridization on the following atoms;

1 2 3 4

5) Please draw the LEAST stable form of trans 1,2 dichlorocyclohexane. You have the freedom to draw the molecule in whatever form you believe is the LEAST stable.

6a) Please write down all the steps in the mechanism of the free radical chlorination of 2-methylbutane.
6b) What is the ratio of products formed in the free radical chlorination of bicyclo [3,2,0] heptane?

7a) What are the advantages of using bromine instead of chlorine in a free radical halogenation?
   a) 
   b) 

7b) What happens to the boiling point of an alkane when it becomes branched?

7c) How do the intermolecular bonding forces change when acids become larger?

7d) What is the primary intermolecular bonding force in each of the following compounds?

<table>
<thead>
<tr>
<th>Compound</th>
<th>H-Bond</th>
<th>Dipole-Dipole</th>
<th>Dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropyl Alcohol</td>
<td>H-Bond</td>
<td>Dipole-Dipole</td>
<td>Dispersion</td>
</tr>
<tr>
<td>1,3-dichloropropane</td>
<td>H-Bond</td>
<td>Dipole-Dipole</td>
<td>Dispersion</td>
</tr>
<tr>
<td>C_{12}H_{25}NH_{2}</td>
<td>H-Bond</td>
<td>Dipole-Dipole</td>
<td>Dispersion</td>
</tr>
<tr>
<td>methylcyclohexane</td>
<td>H-Bond</td>
<td>Dipole-Dipole</td>
<td>Dispersion</td>
</tr>
</tbody>
</table>
1) Please name or draw the structure of the following compounds.

Bicyclo [4, 2, 1] nonane

S-3-chloro-2-methylbutane

cis-1,4-dimethylcyclohexane

2,2,4-trimethylpentane

Z-bromo-1,2-dichlorocyclobutane

2-bromo-2-methylpropane
2) Please draw the rotational energy diagram for the rotation of 2,3-dichlorobutane around the C2-C3 bond.

![Energy Diagram](image)

Draw the molecule below, convert it to a Newman projection and then rotate it about the C2-C3 bond. Based on your rotations, draw the energy diagram above.

![Molecule Diagram](image)

3) Please draw all of the isomers of C₃H₃Cl

![Isomers Diagram](image)
4) Please answer the following questions concerning the molecule given below.

![Molecule Diagram]

a) How many pi and sigma bonds are in this compound?
   20 sigma and 6 pi

b) What is the hybridization on the following atoms:
   1: sp  2: sp3  3: sp3  4: sp3

5) Please draw the LEAST stable form of trans 1,2 dichlorocyclohexane. You have the freedom to draw the molecule in whatever form you believe is the LEAST stable.

![Molecule Diagram]

6a) Please write down all the steps in the mechanism of the free radical chlorination of 2-methylbutane.

**Chain Initiation**

\[ \text{Cl}_2 \xrightarrow{\text{light}} 2 \text{Cl}^* \]

**Chain Propagation**

\[ \text{Cl}^* + \text{H}_3\text{C} - \text{C} = \text{C}_2\text{H}_3 \rightarrow \text{HCl} + \text{H}_3\text{C} - \text{C} = \text{C}_2\text{H}_3^* \]

\[ \text{H}_3\text{C} - \text{C} = \text{C}_2\text{H}_3^* + \text{Cl}_2 \]

**Chain Termination**

\[ \text{Cl}^* + \text{Cl}^* \rightarrow \text{Cl}_2 \]

\[ \text{Cl}^* + \text{H}_3\text{C} - \text{C} = \text{C}_2\text{H}_3 \rightarrow \text{H}_3\text{C} - \text{C} = \text{C}_2\text{H}_3 \]

\[ \text{H}_3\text{C} - \text{C} = \text{C}_2\text{H}_3 \rightarrow \text{H}_3\text{C} - \text{C} = \text{C}_2\text{H}_3 \]
6b) What is the ratio of products formed in the free radical chlorination of bicyclo [3,2,0]
heptane?

\[
\frac{X}{100-X} = \frac{10 \times 3.5}{5}
\]

\[X = 77.78\% \text{ secondary}
\]
\[22.22\% \text{ tertiary}
\]

7a) What are the advantages of using bromine instead of chlorine in a free radical
halogenation?

a) fewer by-products

b) higher yield

7b) What happens to the boiling point of an alkane when it becomes branched?

The boiling point goes down

7c) How do the intermolecular bonding forces change when acids become larger?

As acids get larger they get less soluble in water so the intermolecular bonding
force changes from being mostly H-bond to mostly dispersion forces

7d) What is the primary intermolecular bonding force in each of the following
compounds?

<table>
<thead>
<tr>
<th>Compound</th>
<th>H-Bond</th>
<th>Dipole-Dipole</th>
<th>Dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropyl Alcohol</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-dichloropropane</td>
<td>H-Bond</td>
<td>Dipole-Dipole</td>
<td>Dispersion</td>
</tr>
<tr>
<td>C_{12}H_{25}NH_{2}</td>
<td>H-Bond</td>
<td></td>
<td>Dispersion</td>
</tr>
<tr>
<td>methylcyclohexane</td>
<td>H-Bond</td>
<td>Dipole-Dipole</td>
<td>Dispersion</td>
</tr>
</tbody>
</table>
1) Please name or draw the structure of the following compounds.

\[
\begin{align*}
&\text{Cl} & \text{Cl} \\
&\text{H}_3\text{C} & \text{Cl}
\end{align*}
\]

\[
\begin{align*}
&\text{C} & \text{C} & \text{CH}_3 \\
&\text{H}_3\text{C} & \text{CH} & \text{C} & \text{C} & \text{CH}_3 \\
&\text{C} & \text{C} & \text{C} & \text{CH}_3 \\
&\text{H}_3\text{C} & \text{Cl} & \text{Cl} & \text{H} & \text{H} & \text{C}_2\text{H}_5
\end{align*}
\]
2) Please draw the rotational energy diagram for the rotation of 2,2 dichloropentane around the C2-C3 bond.

Draw the molecule below, convert it to a Newman projection and then rotate it about the C2-C3 bond. Based on your rotations, draw the energy diagram above.

3) Please draw all of the isomers of $\text{C}_3\text{H}_4\text{Cl}_2$
4) Please answer the following questions concerning the molecule given below.

a) How many pi and sigma bonds are in this compound?

b) What is the hybridization on the following atoms:

5) Please draw the LEAST stable form of trans 1,2 dichlorocyclohexane.

6) Please predict the percentage of products made by the free radical chlorination of bicycle [4,2,0] octane.

7a) Hexane and cyclohexane both have six carbons but one has a higher boiling point than the other. Which one has the higher boiling point and why?

7b) Rank the following compounds from highest to lowest boiling point (highest = 4, lowest = 1)

7d) What is the primary intermolecular bonding force in each of the following compounds (H-bond, Dipole, Dispersion)?

\[\text{C}_2\text{H}_5\text{NH}_2\] \hspace{1cm} \text{cis 2,3-dichlorobutene}

\[\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{Br}\] \hspace{1cm} \text{C}_{12}\text{H}_{25}\text{COH}\]
Chem 240
Exam #1

CLOSED BOOK EXAM - No books or notes allowed. All work must be shown for full credit. You may use a calculator.

<table>
<thead>
<tr>
<th>Question</th>
<th>Credit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(12)</td>
<td></td>
</tr>
<tr>
<td>2(24)</td>
<td></td>
</tr>
<tr>
<td>3(12)</td>
<td></td>
</tr>
<tr>
<td>4(16)</td>
<td></td>
</tr>
<tr>
<td>5(8)</td>
<td></td>
</tr>
<tr>
<td>6(10)</td>
<td></td>
</tr>
<tr>
<td>7(18)</td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
</tr>
</tbody>
</table>

1) Please name or draw the structure of the following compounds.

Cis-1,2-dichlorocyclopentane

Bicyclo [4,1,0] heptane

4-ethyl-5-methyloctane

2R,3R-2,3-dichloropentane
2) Please draw the rotational energy diagram for the rotation of 2,2 dichloropentane around the C2-C3 bond.

Draw the molecule below, convert it to a Newman projection and then rotate it about the C2-C3 bond. Based on your rotations, draw the energy diagram above.

3) Please draw all of the isomers of C₃H₄Cl₂
4) Please answer the following questions concerning the molecule given below.

![Molecule Image]

a) How many pi and sigma bonds are in this compound?
   18 sigma and 4 pi

b) What is the hybridization on the following atoms;
   1: sp2  2: sp3  3: sp3  4: sp2  5: sp

5) Please draw the LEAST stable form of trans 1,2 dichlorocyclohexane.

![Least Stable Form Image]

6) Please predict the percentage of products made by the free radical chlorination of bicycle [4,2,0] octane.

![Bicycle Octane Image]

\[
\begin{align*}
\text{secondary} & \quad \frac{X}{100-X} = \frac{12}{2} \times \frac{3.5}{5} \\
X &= 80.77\% \text{ secondary} \\
19.23\% & \text{ tertiary}
\end{align*}
\]

7a) Hexane and cyclohexane both have six carbons but one has a higher boiling point than the other. Which one has the higher boiling point and why?

Hexane has the higher boiling point because it is longer and less compact than cyclohexane so it has more opportunity to exert dispersion forces on its neighbors.

7b) Rank the following compounds from highest to lowest boiling point (highest = 4, lowest = 1)

![Compound Images]

7d) What is the primary intermolecular bonding force in each of the following compounds (H-bond, Dipole, Dispersion)?

- \(\text{C}_2\text{H}_5\text{NH}_2\)  H-bond
- cis 2,3-dichlorobutene  Dispersion
- \(\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{Br}\)  Dipole-Dipole (borderline)
- \(\text{C}_{12}\text{H}_{25}\text{COH}\)  Dispersion (too big)
Exam II

SN1, E1, SN2, E2 Reactions
Markovnikov Addition
Ant-Markovnikov Addition
Reaction Mechanisms
Hoffman and Saytzeff Eliminations
Enantiomers and Diastereomers
**SN1 Reactions:**

**By-Products** - Whenever an SN1 reaction occurs there is always the possibility that an E1 by-product will form. This occurs if the nucleophile does not get to the carbocation soon enough. Therefore, if you see a reaction with SN1 conditions always assume that some E1 minor product will form.

**Racemic Mixtures** - In SN1 reactions you also have the possibility of making a racemic mixture of products – that is, left and right hand versions of the same molecule. Always check to see if the leaving group is on a chiral carbon, if so, then a racemic mixture will be made.

**Rearrangements** – It is also possible for SN1 reactions to rearrange. Carbocations want to be on the most stable carbon, and this means 3° if it is available. Therefore carbocations will rearrange themselves to place the positive charge onto the most stable carbon ONLY IF the most stable carbon is right next door.

![Rearrangement Diagram](image)

**E2 Reactions:**

**Big Bases** – For an E2 reaction to take place you must use a big base. Classically this means using the t-butoxide ion (t-ButO⁻) but other large bases can be used (more on this later). You do not want to use a base that is so small that an SN2 reaction could occur. If you look carefully, you will see that the conditions of an E2 and an SN2 reaction are nearly identical except for the size of the base. So large bases must be used for E2 reactions.

**Hoffman vs. Saytzeff** - E2 reactions make double and triple bonds by removing an HX from a molecule. But which HX? As can be seen below, you may have a couple of choices;

![E2 Reaction Diagram](image)
The Saytzeff is the “inner” product and the Hoffman is the “outer” product. Of the two, Saytzeff is the most stable because it produces a double bond with more carbons around it which can feed electrons to the double bond (by induction).

It is possible to select between Saytzeff and Hoffman products by selecting the proper sized base. Hoffman products are always made when very large bases like t-ButO⁻ are used. Large bases are simply too big to grab inner hydrogens and do an elimination. Big bases are force to attack on the outside of the molecule where there is less hinderance, thus the Hoffman product is formed.

To get the Saytzeff product a smaller base must be used, but not one that is so small that you risk the possibility of SN2 product formation. For this purpose EtO⁻ is often the base of choice. The EtO⁻ ion sits between the region of large and small bases and will do either E2 or SN2 reactions depending on the substrate used. As long as the substrate is hindered enough, E2 reactions will predominate, but there is always the risk of SN2 by-products.

Proper Orientation - Perhaps the most important aspect of E2 elimination is the need for proper orientation of the molecule. E2 reactions occur **anti** which means that the hydrogen being attacked and the halogen that is leaving must be on opposite sides of the molecule.

The reason why this orientation is important is that if the base is on the same side as the leaving group (**syn** attack) then the negative charge of the base, and the negative charge of the leaving group will repulse one another and keep a reaction from occurring. In addition, since the hydrogen and the halogen must be on opposite sides of the molecule, you may have more than one hydrogen to choose from when doing the elimination. Not all hydrogens are equal. In order to choose the right hydrogen, you must draw the most stable Newman projection of the molecule. Consider the molecule below.
Depending on the orientation of the molecule only one of the two possible products are formed, but which one? To know this, we must draw the Newman projection and then rotate the molecule so that the hydrogen is opposite the halogen.

By appropriate rotation and elimination you can see that the final product will be cis-3-methyl-2-butene (or Z-3-methyl-2-butene). You cannot predict whether the product will be cis or trans (E or Z) unless you draw the Newman projection and then do the elimination.

**E1 Reactions:**

E1 reactions are by the far the rarest reactions among this group. The reaction requires that there be a protic solvent and no nucleophile - a condition difficult, but not impossible, to satisfy.

Most protic solvents are also weak nucleophiles. As we have seen, solvents like water and alcohol can are nucleophilic enough to give SN1 by-products even under the best of conditions. The trick is to use a protic solvent that is also such a poor nucleophile that the nucleophile does not want to react. This can be done in two ways, make it big, and make it a very weak base. As it turns out, strong acids, like sulfuric acid ($\text{H}_2\text{SO}_4$) and phosphoric acid ($\text{H}_3\text{PO}_4$), fit this profile.

The sulfate and phosphate ions are very large and very poor nucleophiles as are the conjugate bases of most strong acids. Even relatively weak acids like acetic acid can be used, because the acetate ion is large and weakly basic. Most of the time, strong acids are used to do E1 eliminations. This is not exclusive of course – water and other protic solvents could be used, but you run the risk of making large amounts of SN1 by-product by using these solvents. As long as no strong nucleophile is present, solvents like water and alcohol could also be used. A typical E1 elimination is shown below. Note: The most stable product is always formed. For E1 reactions this always means trans.
About Solvents….

By now, I am sure that you are very confused about solvents and which solvent to use with which reaction. Some of it is common sense and some of it is experience, but there is much more to the common sense than the experience. Let me give you some examples.

Alcohols and Alkoxides

By far the most common solvent/nucleophile combination is the alcohol/alkoxide combination. Alkoxides (methoxide, ethoxide, t-butoxide, etc) are all made from their respective alcohols based on the following reaction:

\[ 2 \text{R}–\text{OH} + 2 \text{Na(s)} \rightarrow 2 \text{R}–\text{O}^– + \text{H}_2 \]

The point is that the alkoxide is always made from the alcohol so both are present in solution – the alcohol being the solvent and the alkoxide being the nucleophile/base. Common pairs are given below.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Nucleophile/base</th>
<th>Also known as;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃OH</td>
<td>CH₃ONa</td>
<td>(MeOH and MeO⁻)</td>
</tr>
<tr>
<td>C₂H₅OH</td>
<td>C₂H₅ONa</td>
<td>(EtOH and EtO⁻)</td>
</tr>
<tr>
<td>t-ButOH</td>
<td>t-ButOK</td>
<td>(t-ButOH and t-ButO⁻)</td>
</tr>
</tbody>
</table>

These solvent/base pairs are commonly used in SN₂, E₂, and even SN₁ reactions.

Strong Acids

Strong acids are common solvents used in E₁ reactions but they are also used in SN₁, and even SN₂ reactions (but never E₂). Now why would a strong protic solvent like H₂SO₄ be needed in a reaction that prefers aprotic solvents (like SN₂ reactions)? The answer is really very simple. Acids are commonly used to get rid of OH groups by turning them into good leaving groups (water!). So you frequently see acids used whenever the leaving group is an OH – even on SN₂ reactions as shown below.
### SN1, SN2, E1, and E2 Reaction Conditions

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Substrate</th>
<th>Nucleophile/Base</th>
<th>Solvent</th>
<th>Leaving Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN2</td>
<td>1\textsuperscript{a}, unhind 2\textsuperscript{o}</td>
<td>Small strong</td>
<td>Aprotic</td>
<td>Good LG</td>
</tr>
<tr>
<td>SN1</td>
<td>3\textsuperscript{o}, hind 2\textsuperscript{o}</td>
<td>Nuc\textsuperscript{-} present</td>
<td>Protic</td>
<td>Good LG</td>
</tr>
<tr>
<td>E2</td>
<td>1\textsuperscript{o}, 2\textsuperscript{o}, or 3\textsuperscript{o}</td>
<td>Large base</td>
<td>Aprotic</td>
<td>Good LG</td>
</tr>
<tr>
<td>E1</td>
<td>3\textsuperscript{o}, hind 2\textsuperscript{o}</td>
<td>No base or nuc\textsuperscript{-}</td>
<td>Protic</td>
<td>Good LG</td>
</tr>
</tbody>
</table>

#### Small Strong Bases
*(Nucleophiles):*

- OH\textsuperscript{-}
- CH\textsubscript{3}O\textsuperscript{-} (MeO\textsuperscript{-})
- C\textsubscript{2}H\textsubscript{5}O\textsuperscript{-} (EtO\textsuperscript{-})
- CH\textsubscript{3}\textsuperscript{+}
- C\textsubscript{2}H\textsubscript{5}\textsuperscript{-}
- I\textsuperscript{-}
- H\textsuperscript{+}
- NH\textsubscript{2}\textsuperscript{-}
- CH\textsubscript{3}NH\textsuperscript{-}

#### Big Bulky Bases:

- t-ButO\textsuperscript{-}
- isoPrO\textsuperscript{-}

#### Protic Solvents

- H\textsubscript{2}O
- Alcohols – MeOH, EtOH
- Organic Acids – HAC
- Inorganic Acids – H\textsubscript{2}SO\textsubscript{4}, H\textsubscript{3}PO\textsubscript{4}

#### Aprotic Solvents

- Acetone
- THF
- Diethyl ether
- DMSO
- Methylene Chloride
Mechanisms:

**SN2 Mechanism:**

**SN1 Mechanism:**

*Note: Racemic mixtures are possible*

**E1 Mechanism:**

*Note: Racemic mixtures are possible*

**E2 Mechanism:**

*Note: Walden inversion*
SN2 Reactions:

Solvent – SN2 reactions prefer the use of aprotic solvents but that does not mean that protic solvents cannot be used – it simply means that the reaction will go slower if a protic solvent is used, but that should not hinder its use. Many reactions will require the use of a protic solvent because of the nature of the nucleophile used.

A large number of nucleophiles are the conjugate bases of alcohols. These nucleophiles are made by adding pure sodium metal to the alcohol according to the following reaction:

\[ 2 \text{Na(s)} + 2 \text{ROH} \rightarrow 2 \text{RO}^- \text{Na}^+ + \text{H}_2 \]

The nucleophile (RO⁻) is produced in this reaction and then used to substitute for other poorer leaving groups. BUT because of the nature of the nucleophile, the solvent must be the alcohol from which it was made. Therefore you must use the corresponding alcohol for each of the following nucleophiles:

<table>
<thead>
<tr>
<th>Nuc-</th>
<th>Alcohol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃O⁻</td>
<td>CH₃OH</td>
</tr>
<tr>
<td>C₂H₅O⁻</td>
<td>C₂H₅OH</td>
</tr>
<tr>
<td>t-ButO⁻</td>
<td>t-ButOH</td>
</tr>
<tr>
<td>isoPrO⁻</td>
<td>isoPrOH</td>
</tr>
</tbody>
</table>

So, if you want to use a nucleophile that is made from an alcohol, you must use the alcohol as the solvent. The problem of course is that alcohols are protic, but this should not be cause for concern because they will work just fine even if they do slow down the reaction.

For other nucleophiles like OH⁻ (really NaOH), you can go into the stock room, get it, and throw it into any solvent you like (like THF or diethyl ether). This makes it easy. But most of the time this is not the case.
Markovnikov Additions to Alkenes

**HX Addition**

\[ \text{C} - \text{C} = \text{C} \xrightleftharpoons{\text{H}^+} \text{C} - \text{C} = \text{C} + \text{H} \xrightarrow{\text{Cl}^-} \text{C} - \text{C} = \text{C} + \text{H} \]\n
**Halogen Addition**

\[ \text{C} - \text{C} = \text{C} \xrightarrow{\text{Br}^+} \text{C} - \text{C} = \text{C} + \text{Br} \xrightarrow{\text{Br}^-} \text{C} - \text{C} = \text{C} + \text{Br} \]

**Hydration - Addition of Water**

\[ \text{C} - \text{C} = \text{C} \xrightarrow{\text{H}^+} \text{C} - \text{C} = \text{C} + \text{H} \xrightarrow{\text{H}_2\text{O}} \text{C} - \text{C} = \text{C} + \text{H} \]

**Alcohol Addition**

\[ \text{C} - \text{C} = \text{C} \xrightarrow{\text{H}^+} \text{C} - \text{C} = \text{C} + \text{H} \xrightarrow{\text{CH}_3\text{OH}} \text{C} - \text{C} = \text{C} + \text{H} \]

**Halohydrin Reaction**

\[ \text{C} - \text{C} = \text{C} \xrightarrow{\text{Br}^+} \text{C} - \text{C} = \text{C} + \text{Br} \xrightarrow{\text{OH}^-} \text{C} - \text{C} = \text{C} + \text{Br} \]

**Oxymercuration/Deoxymercuration**

\[ \text{C} - \text{C} = \text{C} \xrightarrow{\text{HgOAc}^+} \text{C} - \text{C} = \text{C} + \text{HgOAc}^+ \xrightarrow{\text{H}_2\text{O}} \text{C} - \text{C} = \text{C} + \text{HgOAc} \]

**Alkoxymercuration/Dealkoxymercuration**

\[ \text{C} - \text{C} = \text{C} \xrightarrow{\text{HgOAc}^+} \text{C} - \text{C} = \text{C} + \text{HgOAc}^+ \xrightarrow{\text{CH}_3\text{OH}} \text{C} - \text{C} = \text{C} + \text{HgOAc} \]

**Epoxide Ring Opening - Acid**

\[ \text{C} - \text{C} = \text{C} \xrightarrow{\text{H}^+} \text{C} - \text{C} = \text{C} + \text{H} \xrightarrow{\text{H}_2\text{O}} \text{C} - \text{C} = \text{C} + \text{H} \]

**Epoxide Ring Opening - Base**

\[ \text{C} - \text{C} = \text{C} \xrightarrow{\text{OH}^-} \text{C} - \text{C} = \text{C} + \text{H} \xrightarrow{\text{H}_2\text{O}} \text{C} - \text{C} = \text{C} + \text{H} \]
Anti-Markovinikov Additions

Anti-Markovinikov HX Addition

Chain Initiation

\[
\begin{align*}
\text{OCCO} & \xrightarrow{\text{Heat or Light}} \text{OCCO}^* \\
\text{Cl} & + \text{Cl} \\
\text{meta-chloroperoxybenzoic acid (MCPBA)} & \\
\cdot \text{OH} & + \text{HBr} \rightarrow \text{H}_2\text{O} & + \text{Br}^*
\end{align*}
\]

Chain Propagation

\[
\begin{align*}
\text{C} & \text{C} & \text{C} & \xrightarrow{\text{HBr}} & \text{C} & \text{C} & \cdot \text{C} & \text{Br} \\
\text{C} & \text{C} & \cdot \text{C} & \text{Br} & \xrightarrow{\text{HBr}} & \text{C} & \text{C} & \cdot \text{C} & \text{Br} + \text{Br}^*
\end{align*}
\]

Chain Termination - Any two radicals (not shown)

Hydroboration

\[
\begin{align*}
\text{C} \text{C} & \text{C} & \xrightarrow{\text{BH}_3} & \text{C} \text{C} & \text{C} \\
\text{C} & \text{C} & \text{C} & \xrightarrow{\text{H}_3\text{BH}} & \text{C} \text{C} & \text{C} & \xrightarrow{\text{H}_3\text{BH}} & \text{C} \text{C} & \text{C} \text{C} \\
\text{H} & \text{B} & \text{H} & \xrightarrow{\text{C} \text{C} \text{C} \text{C}} & \text{H} & \text{B} & \text{H} & \xrightarrow{\text{C} \text{C} \text{C} \text{C}} & \text{C} \text{C} & \text{C} \text{C} \text{C} \\
\text{H} & \text{B} & \text{H} & \xrightarrow{\text{C} \text{C} \text{C} \text{C}} & \text{H} & \text{B} & \text{H} & \xrightarrow{\text{C} \text{C} \text{C} \text{C}} & \text{C} \text{C} & \text{C} \text{C}
\end{align*}
\]

\[
\text{H}_2\text{O}, \text{NaOH}, \text{H}_3\text{O} \rightarrow 3 \times \text{C} \text{C} \text{C} + \text{H}_3\text{BO}_3
\]
Other Alkene Reactions

Epoxide Formation

\[
\text{meta-chloroperoxycarboxylic acid} \rightarrow \text{Epoxide}
\]

Carbene Addition

\[
	ext{Carbene Addition}
\]

Catalytic Hydrogenation

\[
\text{Catalytic Hydrogenation}
\]
Substrate

Solvent Combinations

Strong Acids Only

Strong Acid and Halide

Nucleophile and Apotic Solvent

Base and Protic Solvent

Protic Solvent Only

1° Unhind 2°

Halide

Nucleophile and Apotic Solvent

Base and Protic Solvent

Protic Solvent Only

Halide

Nucleophile and Apotic Solvent

Base and Protic Solvent

Protic Solvent Only

Alcohol

Sn2

Nucleophile and Apotic Solvent

Base and Protic Solvent

Protic Solvent Only

Hind. 2° 3°

Sn1

E2

E2

E1 (Sn1)

E1 (Sn1)
1) Please supply the product for each of the following reactions.

- \( \text{C}=\text{C} \rightarrow \text{HCl} \rightarrow \text{H}_{2}\text{O}, \text{Br}_2 \)
- \( \text{C}-\text{C}-\text{C}-\text{C} \rightarrow \text{EtO}^+\text{EtOH} \rightarrow \text{NaEIO}_4\text{EtOH} \)
- \( \text{Hg}^2+\). \text{hv} \)
- \( \text{HBr}, \text{MCPBA} \)
- \( \text{O}_3, (\text{CH}_3)_2\text{S} \)
- \( \text{OsO}_4, \text{H}_2\text{O}_2 \rightarrow \text{HAc}, \text{Heat} \)
- \( \text{con. H}_2\text{SO}_4 \)

2) Circle the type of reaction occurring in each of the following. If more than one reaction type occurs label the major and minor product.

- \( \text{Kl, Ether} \rightarrow \text{SN1, SN2, E1, E2} \)
- \( \text{CH}_3\text{ONa, CH}_2\text{OH} \rightarrow \text{SN1, SN2, E1, E2} \)
- \( \text{MeOH, Heat} \rightarrow \text{SN1, SN2, E1, E2} \)
- \( \text{HI} \rightarrow \text{SN1, SN2, E1, E2} \)
- \( \text{POCl}_3 \rightarrow \text{SN1, SN2, E1, E2} \)
- \( \text{EtOH, NaEtO} \rightarrow \text{SN1, SN2, E1, E2} \)
- \( \text{MeOH, MeOK} \rightarrow \text{SN1, SN2, E1, E2} \)
- \( \text{HAc, Heat} \rightarrow \text{SN1, SN2, E1, E2} \)
- \( \text{H}_2\text{SO}_4, \text{H}_2\text{O} \rightarrow \text{SN1, SN2, E1, E2} \)
- \( \text{KOH, EtOH} \rightarrow \text{SN1, SN2, E1, E2} \)
- \( \text{tBuOH, Heat} \rightarrow \text{SN1, SN2, E1, E2} \)
3) Please give the R,S and D, L designation for each of the following compounds,

\[
\begin{align*}
\text{COOH} & \quad \text{CH}_3 \\
\text{H} & \quad \text{C} \quad \text{CH}_3 \\
\text{Cl} & \quad \text{C} \quad \text{OH} \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{CH}_3 & \\
\text{H} & \quad \text{C} \quad \text{COOH} \\
\text{Cl} & \quad \text{C} \quad \text{CH}_3 \\
\text{OH} & \\
\text{Cl} & \\
\text{HOOC} & \quad \text{C} \quad \text{CH}_3 \\
\text{HO} & \quad \text{C} \quad \text{CH}_3 \\
\text{Cl} & \\
\end{align*}
\]

R, S _______                _______                _______                _______
D, L _______                _______                _______

3b) Which are enantiomers and which are diastereomers?

Enantiomers = Diastereomers =

4) Please draw the complete mechanism for the Markovnikov addition of HCl to 3-methyl butene.

5) Please give the complete mechanism of the halohydrin reaction caused by reacting 3-methylbutene with water and bromine.

6a) Please draw the product of the Saytzeff elimination of 3R, 4S 3-chloro-4-methyl hexane.

7) Please give the product of the Saytzeff elimination of HBr from the following compound. Show your work.

\[
\begin{align*}
\text{CH}_3 & \quad \text{C}_2\text{H}_5 \\
\text{C}_2\text{H}_5 & \quad \text{C} \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{Br} \\
\end{align*}
\]

8) Please draw the complete mechanism of the E1 elimination of 2-methylcyclohexanol using H$_3$PO$_4$ and heat.

9) Please draw the complete mechanism of the acid catalyzed addition of ethanol to 3-methyl pentene.

10) Please give the complete mechanism of the anti-Markovnikov addition of HBr to butene.

11) Please give the mechanism for the formation of both products made by the reaction of t-butyl alcohol with HCl.
12) Please draw all of the products from the reaction of trans 2 butene with water and bromine (Halohydrin reaction).

13) Please give the complete mechanism of acid catalyzed epoxide ring opening using epoxy propane.

14) Please draw the reaction diagram for the anti-Markovnikov addition of HCl with PBA to butene, showing all reactants, products, intermediates and transition states. Do not show any chain termination steps. The first step is endothermic and all subsequent steps are exothermic.

15) Please draw the reaction diagram including all reactants, products, intermediates, and transition states for the SN1 reaction that occurs between cyclohexanol and HCl. The reaction is overall exothermic and the first step is rate determining.

16) Please draw the complete mechanism of the acid catalyzed addition of ethanol to propene. When you are finished draw the reaction diagram below.

17) What is the ratio of products formed by the free radical halogenation of hexane? Set it up. You do not have to solve it.

18) Please calculate the percentage of 1º and 2º products formed by the free radical chlorination of butane.

19) Predict the percentage of products made by the free radical chlorination of 1,1,4,4 tetramethylcyclohexane
1) Please supply the product for each of the following reactions.
2) Circle the type of reaction occurring in each of the following. If more than one reaction type occurs label the major and minor product.

- **Kl, Ether**
  - Major: SN1
  - Minor: SN2
  - E1
  - E2

- **CH₄ONa, CH₂OH**
  - Major: SN1
  - Minor: SN2
  - E1
  - E2

- **MeOH, Heat**
  - Major: SN1
  - Minor: SN2
  - E1
  - E2

- **H₂SO₄, H₂O**
  - Major: SN1
  - Minor: SN2
  - E1
  - E2

- **KOH, EtOH**
  - Major: SN1
  - Minor: SN2
  - E1
  - E2

- **tButOH, Heat**
  - Major: SN1
  - Minor: SN2
  - E1
  - E2
3) Please give the R,S and D, L designation for each of the following compounds,

\[
\begin{align*}
\text{COOH} & \quad \text{CH}_3 \\
\text{H} - \text{C} - \text{CH}_3 & \quad \text{H} - \text{C} - \text{COOH} \\
\text{Cl} - \text{C} - \text{OH} & \quad \text{Cl} - \text{C} - \text{CH}_3 \\
\text{CH}_3 & \quad \text{OH} & \quad \text{HOOC} - \text{C} - \text{CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{R, S} & \quad \text{S, S} & \quad \text{R, R} & \quad \text{R, S} \\
\text{D, L} & \quad \text{D} & \quad \text{L} & \quad \text{D} \\
\end{align*}
\]

3b) Which are enantiomers and which are diastereomers?

Enantiomers = AB  
Diastereomers = AC, BC

4) Please draw the complete mechanism for the Markovnikov addition of HCl to 3-methyl butene.

\[
\begin{align*}
\text{C} = \text{C} - \text{C} - \text{C} - \text{CH}_3 & \quad \text{H} + \text{H}_2\text{C} - \text{C} - \text{C} - \text{CH}_3 \\
\text{H} & \quad \text{H} + \text{H}_2\text{C} - \text{C} - \text{C} - \text{CH}_3 \\
\text{Cl} - \text{C} - \text{OH} & \quad \text{Cl} - \text{C} - \text{CH}_3 \\
\text{CH}_3 & \quad \text{Cl} - \text{C} - \text{CH}_3 \\
\end{align*}
\]

5) Please give the complete mechanism of the halohydrin reaction caused by reacting 3-methylbutene with water and bromine.

\[
\begin{align*}
\text{C} = \text{C} - \text{C} - \text{C} - \text{CH}_3 & \quad \text{Br} + \text{H}_2\text{C} - \text{C} - \text{C} - \text{CH}_3 \\
\text{H} & \quad \text{H} + \text{H}_2\text{C} - \text{C} - \text{C} - \text{CH}_3 \\
\text{Cl} - \text{C} - \text{OH} & \quad \text{Cl} - \text{C} - \text{CH}_3 \\
\text{CH}_3 & \quad \text{Cl} - \text{C} - \text{CH}_3 \\
\end{align*}
\]

6) Please draw the product of the Saytzeff elimination of 3R, 4S 3-chloro-4-methyl hexane.

\[
\begin{align*}
\text{C} = \text{C} - \text{C} - \text{C} - \text{C} - \text{C} & \quad \text{Cl} - \text{H} - \text{CH}_3 \\
\text{Cl} & \quad \text{Cl} - \text{H} - \text{CH}_3 \\
\end{align*}
\]

The chlorine and the hydrogen must be opposite one another
7) Please give the product of the Saytzeff elimination of HBr from the following compound. Show your work.

8) Please draw the complete mechanism of the E1 elimination of 2-methylcyclohexanol using H$_3$PO$_4$ and heat.

9) Please draw the complete mechanism of the acid catalyzed addition of ethanol to 3-methyl pentene.

10) Please give the complete mechanism of the anti-Markovnikov addition of HBr to butene.
11) Please give the mechanism for the formation of both products made by the reaction of t-butyl alcohol with HCl.

12) Please draw all of the products from the reaction of trans 2 butene with water and bromine (Halohydrin reaction).

13) Please give the complete mechanism of acid catalyzed epoxide ring opening using epoxy propane.
14) Please draw the reaction diagram for the anti-Markovnikov addition of HCl with PBA to butene, showing all reactants, products, intermediates and transition states. Do not show any chain termination steps. The first step is endothermic and all subsequent steps are exothermic.

15) Please draw the reaction diagram including all reactants, products, intermediates, and transition states for the SN1 reaction that occurs between cyclohexanol and HCl. The reaction is overall exothermic and the first step is rate determining.
16) Please draw the complete mechanism of the acid catalyzed addition of ethanol to propene. When you are finished draw the reaction diagram below.

17) What is the ratio of products formed by the free radical chlorination of hexane? Set it up. You do not have to solve it.

\[
\frac{X}{100-X} = \frac{6 \text{ (1°)} \times 1.0}{8 \text{ (2°)} \times 3.5}
\]

\[
X = 17.65\% \text{ 1° and 82.35\% 2°}
\]

18) Please calculate the percentage of 1° and 2° products formed by the free radical chlorination of butane.

\[
\frac{X}{100-X} = \frac{6 \text{ (1°)} \times 1.0}{4 \text{ (2°)} \times 3.5}
\]

\[
X = 30\% \text{ 1° and 70\% 2°}
\]

19) Predict the percentage of products made by the free radical chlorination of 1,1,4,4 tetramethylcyclohexane

\[
\frac{X}{100-X} = \frac{12 \text{ (1°)} \times 1.0}{8 \text{ (2°)} \times 3.5}
\]

\[
X = 30\% \text{ 1° and 70\% 2°}
\]
Closed Book Exam - No books or notes allowed. All work must be shown for full credit. You may use a calculator.

<table>
<thead>
<tr>
<th>Question</th>
<th>Credit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(12)</td>
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<td>2(28)</td>
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<td>6(14)</td>
<td></td>
</tr>
<tr>
<td>TOTAL</td>
<td></td>
</tr>
</tbody>
</table>

1) Please name or draw the structure of the following compounds.

D - 2 hydroxy propanoic acid
2) Please supply the product for each of the following reactions. If there is no reaction, write “No Reaction.”

```
C—C—C≡C  Br₂, H₂O

H
C

CH₃

1) Br₂, hv
2) EtO⁻, EtOH
3) NBS

H
CH₃

CH₃

H₂SO₄, KBr

OH
C—C—C  EtOH, Δ

C

OH

C—C—C  P/I₂

OH

C

H₂SO₄, CH₃OH

H₂O, NaOH, H₂O

H₂O

H₂O

1) PBA
2) H₂SO₄, CH₃OH
```
3) Circle the type of reaction occurring in each of the following. If more than one reaction type occurs label the major and minor product.

- \( \text{C} = \text{C} - \text{C} \) with \( \text{POCl}_3 \) → SN1 SN2 E1 E2
- \( \text{C} - \text{C} \) with \( \text{EtOH} \) \( \text{NaEtO} \) → SN1 SN2 E1 E2
- \( \text{C} - \text{C} \) with \( \text{MeOH} \) \( \text{MeOK} \) → SN1 SN2 E1 E2
- \( \text{C} = \text{C} \) with MeOH, Heat → SN1 SN2 E1 E2

4) Please draw the complete mechanism of the acid catalyzed addition of ethanol to propene. When you are finished draw the reaction diagram below.
5) Please label the following compounds as R and S. Also, draw and label the missing diastereomer/enantiomer.

\[
\begin{align*}
\text{A} &: \text{COOH} \quad \text{H} - \text{C} - \text{Cl} \\
\text{B} &: \text{Cl} \quad \text{H} - \text{C} - \text{COOH} \\
\text{C} &: \text{Cl} \quad \text{H} - \text{C} - \text{Cl} \\
\text{D} &: \text{H} - \text{C} - \text{Cl} \\
\end{align*}
\]

R,S ______  ______  ______  ______  ______

5) Please indicate the enantiomer/diastereomer pairs below.

Diastereomers =

Enantiomers =

6) Using alkanes as your only carbon source please gives all steps in the synthesis of methyl ethyl ketone (2 butanone).
1) Please name or draw the structure of the following compounds.

Meso-2,3-dichlorobutane

R-chloroethanol

2R,33-2-chloro-3-methylpentane

D - 2 hydroxy propanoic acid
2) Please supply the product for each of the following reactions. If there is no reaction, write “No Reaction.”

\[
\text{C} = \text{C} - \text{C} = \text{C} \quad \xrightarrow{\text{Br}_2, \text{H}_2\text{O}} \quad \text{C} - \text{C} - \text{C} = \text{C} \quad \xrightarrow{\text{Br}} \quad \text{C} - \text{C} - \text{C} - \text{OH}
\]

\[
\text{C} \quad \xrightarrow{\text{H}_2\text{SO}_4, \text{KBr}} \quad \text{C}
\]

Three possible products

\[
\text{C} - \text{C} - \text{C} \quad \xrightarrow{\text{EtOH, } \Delta} \quad \text{No Reaction}
\]

\[
\text{C} - \text{C} - \text{C} \quad \xrightarrow{\text{P/I}_2} \quad \text{C} - \text{C} - \text{C}
\]

\[
\text{dil KMnO}_4, \text{NaOH, } \text{H}_2\text{O} \quad \xrightarrow{\text{H}} \quad \text{OH} \quad \text{OH}
\]

\[
\triangle \quad \xrightarrow{1) \text{PBA}} \quad \text{OH} \quad \text{H} \quad \text{OCH}_3 \quad \xrightarrow{2) \text{H}_2\text{SO}_4, \text{CH}_3\text{OH}} \quad \text{OH} \quad \text{H} \quad \text{OCH}_3
\]
3) Circle the type of reaction occurring in each of the following. If more than one reaction type occurs label the major and minor product.

\[
\begin{align*}
&\text{OH} \quad \text{POCl}_3 \quad \text{SN1} \quad \text{SN2} \quad \text{E1} \quad \text{E2} \\
&\text{Cl} \quad \text{EtOH} \quad \text{NaEtO} \quad \text{SN1} \quad \text{SN2} \quad \text{E1} \quad \text{E2} \\
&\text{CH}_3 \quad \text{MeOH} \quad \text{MeOK} \quad \text{SN1} \quad \text{SN2} \quad \text{E1} \quad \text{E2} \\
&\text{Br} \quad \text{MeOH, Heat} \quad \text{SN1} \quad \text{SN2} \quad \text{E1} \quad \text{E2}
\end{align*}
\]

4) Please draw the complete mechanism of the acid catalyzed addition of ethanol to propene. When you are finished draw the reaction diagram below.
5) Please label the following compounds as R and S. Also, draw and label the missing diastereomer/enantiomer.

\[
\begin{array}{cccc}
\text{A} & \text{B} & \text{C} & \text{D} \\
\text{COOH} & \text{Cl} & \text{H} & \text{COOH} \\
\text{H} & \text{C} & \text{Cl} & \text{H} & \text{C} & \text{Cl} \\
\text{Cl} & \text{C} & \text{H} & \text{H}_3\text{C} & \text{C} & \text{Cl} \\
\text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 \\
\end{array}
\]

R,S  \quad 2S, 3S  \quad 2R, 3S  \quad 2R, 3R  \quad 2S, 3R

5) Please indicate the enantiomer/diastereomer pairs below.

Diastereomers = AB, AD, BC, CD

Enantiomers = AC, BD

6) Using alkanes as your only carbon source please gives all steps in the synthesis of methyl ethyl ketone (2 butanone).

\[
\begin{align*}
\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} \\
\text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} & \quad \text{Br} \\
\text{t-ButO} & \quad \text{t-ButO} & \quad \text{t-ButO} & \quad \text{t-ButO} & \quad \text{t-ButO} & \quad \text{t-ButO} & \quad \text{t-ButO} & \quad \text{t-ButO} & \quad \text{t-ButO} \\
\text{O}_2 & \quad \text{O}_2 & \quad \text{O}_2 & \quad \text{O}_2 & \quad \text{O}_2 & \quad \text{O}_2 & \quad \text{O}_2 & \quad \text{O}_2 & \quad \text{O}_2 \\
\end{align*}
\]
Chem 240
Exam #2
Name___________________
November 22, 2000

CLOSED BOOK EXAM - No books or notes allowed. All work must be shown for full credit. You may use a calculator.

<table>
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<tr>
<td>1(20)</td>
<td></td>
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<tr>
<td>2(32)</td>
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<td>3(16)</td>
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<td>4(12)</td>
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<td>5(20)</td>
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</tr>
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<td>TOTAL</td>
<td></td>
</tr>
</tbody>
</table>

1a) Please draw the complete mechanism of the acid catalyzed addition of ethanol to 3-methyl butene.

1b) Please draw the product of the Saytzeff elimination of HBr from the following compound. Two products are possible, but only one is made. Show how both could be made and EXPLAIN which one is possible and why.

```
Br   H  
H₃C—C—C—H
    |    
    H  C₂H₅
```
3) Circle the type of reaction occurring in each of the following. If more than one reaction type occurs label the major and minor product.

- \[
\begin{array}{c}
\text{C} \quad \text{C} \quad \text{C} \\
\text{Cl} \quad \text{HCl, H}_2\text{O} \\
\text{C} \quad \text{C} \quad \text{C}
\end{array}
\]

- \[
\begin{array}{c}
\text{C} \quad \text{C} \quad \text{C} \\
\text{Cl} \quad \text{CH}_3\text{ONa, CH}_3\text{OH} \\
\text{C} \quad \text{C} \quad \text{C}
\end{array}
\]

- \[
\begin{array}{c}
\text{H} \quad \text{H}_2\text{SO}_4, \text{H}_3\text{PO}_4 \\
\text{OH} \\
\end{array}
\]

- \[
\begin{array}{c}
\text{Cl} \quad \text{tButOK, tButOH} \\
\text{C} \quad \text{C} \quad \text{C}
\end{array}
\]

4) The reactions using HBr and Br\(_2\)/dark to alkenes are both Markovnikov additions. Please show how the presence of H\(^+\) or Br\(^+\) changes the product when each of them reacts with 3 methyl butene.

5) Synthesize any two of the following compounds using alkanes as your only carbon source. The number of steps required to make each compound is given.

- Methyl ethyl ketone (2 butanone) (3 steps)
- Propene-3-ol (4 steps)
- Methyl ethyl ether (5 steps)
1a) Please draw the complete mechanism of the acid catalyzed addition of ethanol to 3-methyl butene.

\[
\begin{align*}
\text{C} &= \text{C} - \text{C} - \text{C} \\
& \quad \quad \downarrow \quad \quad \downarrow \quad \quad \downarrow \\
\text{H} & \quad \quad \quad \text{H} & \quad \quad \quad \text{H} & \quad \quad \quad \text{H} \\
& \quad \quad \quad \quad \quad \downarrow \quad \quad \quad \downarrow \\
\text{C} & \quad \quad \quad \text{C} & \quad \quad \quad \text{C} & \quad \quad \quad \text{C} \\
& \quad \quad \quad \quad \quad \downarrow \quad \quad \quad \downarrow \\
\text{H} & \quad \quad \quad \text{H} & \quad \quad \quad \text{H} & \quad \quad \quad \text{H} \\
& \quad \quad \quad \quad \quad \downarrow \quad \quad \quad \downarrow \\
\text{C} & \quad \quad \quad \text{C} & \quad \quad \quad \text{C} & \quad \quad \quad \text{C} \\
& \quad \quad \quad \quad \quad \downarrow \quad \quad \quad \downarrow \\
\text{H} & \quad \quad \quad \text{H} & \quad \quad \quad \text{H} & \quad \quad \quad \text{H} \\
& \quad \quad \quad \quad \quad \downarrow \quad \quad \quad \downarrow \\
\text{C} & \quad \quad \quad \text{C} & \quad \quad \quad \text{C} & \quad \quad \quad \text{C} \\
& \quad \quad \quad \quad \quad \downarrow \quad \quad \quad \downarrow \\
\text{H} & \quad \quad \quad \text{H} & \quad \quad \quad \text{H} & \quad \quad \quad \text{H} \\
& \quad \quad \quad \quad \quad \downarrow \quad \quad \quad \downarrow \\
\text{C} & \quad \quad \quad \text{C} & \quad \quad \quad \text{C} & \quad \quad \quad \text{C} \\
& \quad \quad \quad \quad \quad \downarrow \quad \quad \quad \downarrow \\
\text{H} & \quad \quad \quad \text{H} & \quad \quad \quad \text{H} & \quad \quad \quad \text{H} \\
& \quad \quad \quad \quad \quad \downarrow \quad \quad \quad \downarrow \\
\text{C} & \quad \quad \quad \text{C} & \quad \quad \quad \text{C} & \quad \quad \quad \text{C} \\
& \quad \quad \quad \quad \quad \downarrow \quad \quad \quad \downarrow \\
\text{H} & \quad \quad \quad \text{H} & \quad \quad \quad \text{H} & \quad \quad \quad \text{H} \\
& \quad \quad \quad \quad \quad \downarrow \quad \quad \quad \downarrow \\
\text{C} & \quad \quad \quad \text{C} & \quad \quad \quad \text{C} & \quad \quad \quad \text{C} \\
& \quad \quad \quad \quad \quad \downarrow \quad \quad \quad \downarrow \\
\text{H} & \quad \quad \quad \text{H} & \quad \quad \quad \text{H} & \quad \quad \quad \text{H} \\
& \quad \quad \quad \quad \quad \downarrow \quad \quad \quad \downarrow \\
\text{C} & \quad \quad \quad \text{C} & \quad \quad \quad \text{C} & \quad \quad \quad \text{C} \\
& \quad \quad \quad \quad \quad \downarrow \quad \quad \quad \downarrow
\end{align*}
\]

1b) Please draw the product of the Saytzeff elimination of HBr from the following compound. Two products are possible, but only one is made. Show how both could be made and explain which one is possible and why.

The most stable Newman projection puts the C\textsubscript{2}H\textsubscript{5} and the CH\textsubscript{3} opposite each other which forces the product to be trans.
2) Please supply the product for each of the following reactions. If there is no reaction, write “No Reaction.”

\[
\begin{align*}
\text{C} &= \text{C} \quad \text{HBr, PBA} \quad \text{Br-C} = \text{C} \\
\text{C} &= \text{C} \quad \text{H}_2\text{O}, \text{Br}_2 \quad \text{H} \quad \text{Br} \quad \text{C} \quad \text{C} \\
\text{C} &= \text{C} \quad \text{1. Br}_2, \text{light} \quad \text{1. PBA} \\
& \quad \text{2. tBuOK, tBuOH} \quad \text{2. H}_2\text{SO}_4, \text{CH}_3\text{OH} \quad \text{1. Hg(\text{OAc})}_2 \\
& \quad \text{3. O}_3, (\text{CH}_3)_2\text{S} \\
\text{C} &= \text{C} \quad \text{Acetic Acid, Heat} \\
\text{Br} &= \text{C} \quad \text{CH}_3\text{ONa, CH}_3\text{OH} \\
\text{Br} &= \text{C} \quad \text{CH}_3\text{ONa, CH}_3\text{OH} \\
\text{OH} &= \text{C} \quad \text{Hi, DMSO} \\
\text{CH}_3 &= \text{C} \\
\end{align*}
\]
3) Circle the type of reaction occurring in each of the following. If more than one reaction type occurs label the major and minor product.

\[ \text{OH} \quad \text{HCl, H}_2\text{O} \quad \text{SN1} \quad \text{SN2} \quad \text{E1} \quad \text{E2} \]

\[ \text{Cl} \quad \text{CH}_3\text{ONa, CH}_3\text{OH} \quad \text{SN1} \quad \text{SN2} \quad \text{E1} \quad \text{E2} \]

\[ \text{H} \quad \text{H}_2\text{SO}_4, \text{H}_3\text{PO}_4 \quad \text{SN1} \quad \text{SN2} \quad \text{E1} \quad \text{E2} \]

\[ \text{Cl} \quad \text{tButOK, tButOH} \quad \text{SN1} \quad \text{SN2} \quad \text{E1} \quad \text{E2} \]

4) The reactions using HBr and Br$_2$/dark to alkenes are both Markovnikov additions. Please show how the presence of H$^+$ or Br$^+$ changes the product when each of them reacts with 3 methyl butene.

\[ \text{C} = \text{C} - \text{CH}_3 \quad \text{H}^+ \quad \text{H}^+ \quad \text{Br}^- \quad \text{Br}^- \]

5) Synthesize any two of the following compounds using alkanes as your only carbon source. The minimum number of steps needed to make each compound is given.

Methyl ethyl ketone (3 steps)
Propene-3-ol (4 steps)
Methyl ethyl ether (5 steps)
Exam III

Alcohol Synthesis
Alcohol Reactions
Acetal Reaction
Fisher Ester forwards and backwards
Oxidation of Alcohols
Reduction of Aldehydes, Ketones, Acids
Grignard Reactions
Alcohol and Epoxide Syntheses

Oxymercuration/Deoxymercuration

\[ \text{C-C=C} \xrightarrow{\text{HgOAc}^+} \text{C-C=C} \xrightarrow{\text{H}_2\text{O}} \text{C-C=C} \xrightarrow{\text{NaBH}_4} \text{C-C=C} \]

Alkoxymercuration/Dealkoxymercuration

\[ \text{C-C=C} \xrightarrow{\text{HgOAc}^+} \text{C-C=C} \xrightarrow{\text{OH}_2\text{H}} \text{C-C=C} \xrightarrow{\text{NaBH}_4} \text{C-C=C} \]

Epoxide Ring Opening - Acid

\[ \text{C-C-C} \xrightarrow{\text{H}^+} \text{C-C=C} \xrightarrow{\text{H}_2\text{O}} \text{C-C-C} \xrightarrow{\text{OH}^-} \text{C-C-C} \]

Epoxide Ring Opening - Base

\[ \text{C-C-C} \xrightarrow{\text{OH}^-} \text{C-C=C} \xrightarrow{\text{H}_2\text{O}} \text{C-C-C} + \text{OH}^- \]

Hydration - Addition of Water

\[ \text{C-C=C} \xrightarrow{\text{H}^+} \text{C-C=C} \xrightarrow{\text{H}_2\text{O}} \text{C-C-C} + \text{H}^+ \]

Alcohol Addition

\[ \text{C-C=C} \xrightarrow{\text{H}^+} \text{C-C=C} \xrightarrow{\text{CH}_2\text{OH}} \text{C-C-C} + \text{H}^+ \]

Halohydrin Reaction

\[ \text{C-C=C} \xrightarrow{\text{Br}^+} \text{C-C=C} \xrightarrow{\text{OH}^-} \text{C-C-C} \]

Hydroboration

\[ \text{C-C=C} \xrightarrow{\text{BH}_3} \text{C-C-C} \xrightarrow{\text{H}_2\text{O} \cdot \text{NaOH} \cdot \text{H}_2\text{O}} \text{C-C-C} \]

\[ 3 \times \text{C-C-C} + \text{H}_3\text{BO}_3 \]
Alcohol Oxidations

\[
\begin{align*}
\text{PCC} & : \text{CH}_2\text{O}_2 \\
\text{OH} & \quad \text{PCC} \quad \text{CH}_2\text{O}_2 \\
\text{OH} & \quad \text{KMnO}_4, \text{H}^+, \text{H}_2\text{O} \\
\text{OH} & \quad \text{K}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4, \text{Heat} \\
\text{OH} & \quad \text{KMnO}_4, \text{H}^+, \text{H}_2\text{O} \\
\text{OH} & \quad \text{K}_2\text{Cr}_2\text{O}_7, \text{H}_2\text{SO}_4, \text{Heat}
\end{align*}
\]

Reductions that make alcohols

\[
\begin{align*}
\text{HCN} & : \quad \text{C} - \text{C} - \text{C} \\
\text{CH}_3\text{OH} & : \quad \text{C} - \text{C} - \text{C} \\
1. \text{C}_2\text{H}_5\text{MgBr} & \\
2. \text{H}_2\text{O}, \text{H}^+ & \\
\text{LiAlH}_4, \text{H}_2\text{O} & \\
\text{NaBH}_4, \text{H}_2\text{O} & \\
\end{align*}
\]
Fisher Ester Forwards

\[ \begin{align*}
\text{O} & \quad \text{H}^+ \\
\text{C} = \text{C} - \text{OH} & \quad \rightarrow \quad + \text{O} - \text{H} \\
& \quad \rightarrow \quad \text{C} - \text{C} - \text{OH} \\
& \quad \rightarrow \quad \text{C} - \text{C} - \text{OH} \\
& \quad \rightarrow \quad \text{C} - \text{C} - \text{OH} \\
& \quad \rightarrow \quad \text{C} - \text{C} - \text{OH} \\
& \quad \rightarrow \quad \text{C} - \text{C} - \text{OH} \\
& \quad \rightarrow \quad \text{OH} \\
& \quad \rightarrow \quad \text{H}_2\text{O} + \\
& \quad \rightarrow \quad \text{C} - \text{C} - \text{O} - \text{C} - \text{C} + \text{H}^+ 
\end{align*} \]

Fisher Ester Backwards

\[ \begin{align*}
\text{O} & \quad \text{H}^+ \\
\text{C} = \text{C} - \text{O} - \text{C} - \text{C} & \quad \rightarrow \quad + \text{O} - \text{H} \\
& \quad \rightarrow \quad \text{C} - \text{C} - \text{O} - \text{C} - \text{C} \\
& \quad \rightarrow \quad \text{C} - \text{C} - \text{O} - \text{C} - \text{C} \\
& \quad \rightarrow \quad \text{C} - \text{C} - \text{O} - \text{C} - \text{C} \\
& \quad \rightarrow \quad \text{C} - \text{C} - \text{O} - \text{C} - \text{C} \\
& \quad \rightarrow \quad \text{C} - \text{C} - \text{O} - \text{C} - \text{C} \\
& \quad \rightarrow \quad \text{C} - \text{C} - \text{O} - \text{C} - \text{C} \\
& \quad \rightarrow \quad \text{C} - \text{C} - \text{O} - \text{C} - \text{C} \\
& \quad \rightarrow \quad \text{O} \\
& \quad \rightarrow \quad \text{H}_2\text{O} + \\
& \quad \rightarrow \quad \text{C} - \text{C} - \text{O} - \text{C} - \text{C} + \text{H}^+ 
\end{align*} \]
Acetal Formation

\[
\begin{align*}
\text{Acetal Formation} & \quad \text{Acetal Cleavage} \\
\text{If using 1,2 propadiol as your alcohol} & \quad \text{If using two methanols as your alcohol}
\end{align*}
\]

This makes the oxygen a good leaving group...

...but it has to be pushed off by H_2O

Now we make the other oxygen a good leaving group...

...but it has to be pushed off too.
SOCl₂ Mechanism

\[
\text{C} - \text{C} - \text{OH} \quad \xrightarrow{\text{Cl}_2\text{SO}_2} \quad \text{C} - \text{C} - \hat{\text{O}} - \text{S} - \text{O}^\bullet \quad \xrightarrow{\text{Cl}^-} \quad \text{C} - \text{C} - \hat{\text{O}} - \text{S} = \text{O} + \text{Cl}^-
\]

\[
\text{H}^+ + \text{O}=\text{S}=\text{O} \quad \xrightarrow{} \quad \text{H}_2\text{O}=\text{S}=\text{O} \quad \text{C} - \text{C} - \text{Cl}
\]

PCl₃ Mechanism

\[
\text{C} - \text{C} - \text{OH} \quad \xrightarrow{\text{PCl}_3} \quad \text{C} - \text{C} - \hat{\text{O}} - \text{P} - \text{Cl} \quad \xrightarrow{\text{Cl}^-} \quad \text{C} - \text{C} - \hat{\text{O}} - \text{P} - \text{Cl} + \text{Cl}^-
\]

\[
\text{C} - \text{C} - \text{Cl} \quad + \quad \text{HO} - \text{P} - \text{Cl} \quad \text{Cl}
\]

POCl₃ Mechanism

\[
\text{C} - \text{C} - \text{OH} \quad \xrightarrow{\text{Cl}_2\text{O} - \text{P} - \text{Cl}} \quad \text{C} - \text{C} - \hat{\text{O}} - \text{P} - \text{Cl} \quad \xrightarrow{\text{Cl}^-} \quad \text{C} - \text{C} - \hat{\text{O}} - \text{P} - \text{Cl} + \text{Cl}^-
\]

\[
\text{C} - \text{C} - \text{Cl} \quad + \quad \text{HO} - \text{P} - \text{Cl} \quad \text{Cl}
\]
Grignard are not mysterious. They are made using the following reaction,

\[ \text{C-C-C-Br} + \text{Mg(s)} \rightarrow \text{C-C-C-Mg-Br} \] (a Grignard)

If we account for all of the charges in the Grignard, Mg has a 2+ charge \((\text{Mg}^{2+})\) and since the charges must balance, the Br is negative \((\text{Br}^-)\) and the carbons must be negative also \((\text{CH}_3\text{CH}_2\text{CH}_2^-)\). This makes the carbon portion of the compound a very powerful nucleophile that tends to attack C=O's to make alcohols. See the following reaction;

\[
\begin{align*}
\text{C-C-C-Br} & \overset{\text{Mg(s)}}{\longrightarrow} \text{C-C-C-MgBr} \\
& \rightarrow \text{C-C-C-} + \text{OMgBr} \\
& \rightarrow \text{H}^+, \text{H}_2\text{O} \\
& \rightarrow \text{C-C-C-C-C} + \text{Mg(OH)Br}
\end{align*}
\]

The point is that Grignards generally make alcohols although other compounds can be made. See the following reactions;

\[
\begin{align*}
\text{C-C-C-MgBr} & \overset{\text{H-}}{\longrightarrow} \text{C-C-C-} + \text{OH} \\
& \rightarrow \text{C-C-C-} + \text{C} \\
& \rightarrow \text{C-C-C-} + \text{OH} \\
& \rightarrow \text{C-C-C-} + \text{C} \\
& \rightarrow \text{C-C-C-} + \text{C} \\
& \rightarrow \text{C-C-C-} + \text{C} \\
& \rightarrow \text{C-C-C-} + \text{C}
\end{align*}
\]
## Reducing Agents and Their Products

<table>
<thead>
<tr>
<th>Reducing Agent</th>
<th>C=C</th>
<th>C=O Ket</th>
<th>C=O Ald</th>
<th>COOH</th>
<th>COOR</th>
<th>COCl</th>
<th>C≡N</th>
<th>CONH₂</th>
<th>Benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiAlH₄, H₂O</td>
<td>No Rxn</td>
<td>C-OH</td>
<td>C-OH</td>
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<td>C-OH</td>
<td>C-OH</td>
<td>C-NH₂</td>
<td>C-NH₂</td>
<td>No Rxn</td>
</tr>
<tr>
<td>NaBH₄</td>
<td>No Rxn</td>
<td>C-OH</td>
<td>C-OH</td>
<td>No Rxn</td>
<td>No Rxn</td>
<td>No Rxn</td>
<td>No Rxn</td>
<td>No Rxn</td>
<td></td>
</tr>
<tr>
<td>DIBAH, -78°C</td>
<td>No Rxn</td>
<td></td>
<td>C≡O</td>
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<td></td>
<td></td>
<td></td>
<td>No Rxn</td>
</tr>
<tr>
<td>Raney Ni / H₂</td>
<td>C-C</td>
<td>C-OH</td>
<td>C-OH</td>
<td>C-OH</td>
<td>C-OH</td>
<td>C-OH</td>
<td>C-NH₂</td>
<td>No Rxn</td>
<td></td>
</tr>
<tr>
<td>Zn(Hg) HCl</td>
<td>No Rxn</td>
<td>Alkane</td>
<td>Alkane</td>
<td>No Rxn</td>
<td>No Rxn</td>
<td>Alkane</td>
<td>No Rxn</td>
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<td></td>
</tr>
<tr>
<td>N₂H₄, KOH, Heat</td>
<td>No Rxn</td>
<td>Alkane</td>
<td>Alkane</td>
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<td>No Rxn</td>
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<td>No Rxn</td>
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<td></td>
</tr>
<tr>
<td>Li(tButO)₃Al H</td>
<td>No Rxn</td>
<td>No Rxn</td>
<td>No Rxn</td>
<td>No Rxn</td>
<td>No Rxn</td>
<td>C≡O</td>
<td>No Rxn</td>
<td>No Rxn</td>
<td></td>
</tr>
<tr>
<td>H₂, 1000psi, Pt, Pd, Ni, Ru, or Rh</td>
<td>C-C</td>
<td>C-OH</td>
<td>C-OH</td>
<td>C-OH</td>
<td>C-OH</td>
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<td>C-NH₂</td>
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<td>B₂H₆, Diglyme</td>
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<tr>
<td>H₂/Pd/BaSO₄/Quinoline</td>
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<td>C-OH</td>
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<td></td>
<td></td>
<td></td>
<td>C≡O</td>
<td></td>
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</tr>
</tbody>
</table>
1) Please supply the product for each of the following reactions.
2) Suppose you wanted to carry out the following reaction using HBr as your reagent. Why would this be a poor choice of reagent to carry out this reaction?

\[
\text{CH}_3\text{OH} + \text{Br}^- \rightarrow \text{CH}_3\text{Br}
\]

3) Two students are assigned the synthesis of t-butyl ethyl ether. One uses process number one below, and the other uses process number two. Only one student obtains the desired product. Which one was it and why?

\[\begin{align*}
\text{#1} & \quad \text{C} & \quad \text{Na} & \quad \text{C} & \quad \text{C} \quad \text{C} & \quad \text{O} \\
\text{#2} & \quad \text{C} & \quad \text{Na} & \quad \text{C} & \quad \text{C} \quad \text{C} & \quad \text{O} \\
\end{align*}\]

4) There are a number of ways of substituting a halogen for an alcohol group, but some ways are better than others. What advantage is there in using PCl\(_3\) rather than HCl in the chloride substitution reactions? Give an example.

5) Esters do not have to be made from alcohols and acids. It is possible to make an ester using a ketone and acid instead. Please give the mechanism for the formation of the following ester in a base;

\[
\text{C} \quad \text{C} \quad \text{C} \quad + \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{O} \quad \text{NaOH} \quad \text{Catalyst} \quad \rightarrow \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{C} \quad + \quad \text{H}_2\text{O}
\]

6) Please draw all of the steps for the acid catalyzed cleavage of propyl acetate.

7) What is the mechanism for the reaction between ethanol and thionyl chloride (SOCl\(_2\))?
8) 3-bromo-1,2-epoxybutane reacts with sodium methoxide to give a new oxirane, 1-methoxy-2,3-epoxybutane. Suggest a mechanism for this reaction.

\[
\text{Br} \quad \text{CH}_3\text{ONa} \quad \text{H}_3\text{C} - \underset{\text{O}}{\text{C}} - \underset{\text{C}}{\text{C}} - \underset{\text{OCH}_3}{\text{C}} + \text{Br}^-
\]

9) Please give the mechanism for the formation of the hemiacetal made when ethanol and acetone are combined in the presence of H\(_2\)SO\(_4\).

10) Please show the mechanism for the reaction between methyl cyclohexene, bromine, and water. Four products are formed during this reaction. Give the complete mechanism for just one product but show how each product is formed and label them R,S appropriately.

11) Esters do not have to be made from alcohols and acids. It is possible to make an ester using a ketone and acid instead. Please give the mechanism for the formation of the following ester in a base;

\[
\text{NaOH Catalyst} \quad \text{C} - \underset{\text{OH}}{\text{C}} + \text{C} - \underset{\text{O}}{\text{C}}' \quad \text{O} \quad \text{C} - \underset{\text{O}}{\text{C}} - \underset{\text{C}}{\text{C}} + \text{H}_2\text{O}
\]

12) The peptide bond that links amino acids in proteins is a type of ester bond. This bond is easily broken in acidic environments but not in basic environments. Please show how the breakdown of this bond in an acidic environment and discuss why it would not easily be broken down under basic conditions.

\[
\text{R} \quad \text{H} \quad \text{R} \quad \text{H} \quad \text{H}^+ \quad \text{H}_2\text{O} \quad \text{2} \quad \text{R} \quad \text{H} \quad \text{H} \quad \text{O} \quad \text{H}
\]

13) A grad student wanted to make diphenyl methanol using a Grignard reaction between phenyl magnesium bromide and benzaldehyde. To make sure his yield was good he added twice as much benzaldehyde as Grignard reagent and got a lot of white crystalline product. When he analyzed his product he found that he had not made diphenyl methanol, but diphenyl methanal (also called benzophenone) instead. When he asked his research director about it he was told that he should have used equivalent amounts of benzaldehyde and Grignard instead. Doing so, he obtained his desired product. Please explain, using reactions, what had gone wrong with the original synthesis and why the product changed when the amount of benzaldehyde changed. Show the mechanism of each reaction. Hint: One step of this reaction produces a very unusual leaving group.
14) Please draw the complete mechanism for the base catalyzed cleavage of an ester. The overall reaction should be,

\[
\begin{align*}
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{O} \\
\text{O} & \text{H}\text{H}_2\text{O} \\
\rightarrow & \\
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{OH} \\
\text{OH} & \text{C} \\
\end{align*}
\]

15) Please give an example of a reaction where an alcohol is acting like an acid, and another where it is acting like a base.

16) Using any alkane that is four carbons or less, synthesize methyl cyclohexane.

17) Starting with alcohols of two carbons or less synthesize 4 bromobutanol.

18) Please label as R and S all the products formed by the halohydrin addition of Br₂ and water to cis 2 pentene. There are four products in all.

19) Using any alkane that is four carbons or less synthesize the following:

20) Using compounds of two carbons or less, synthesize the following compounds.

21) The SN2 reaction between ethanol and methoxide is doomed to failure even though methoxide is a stronger nucleophile than hydroxide. Why does this reaction fail?

\[
\text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{O}^- \rightarrow \text{C}_2\text{H}_5\text{OCH}_3 + \text{OH}^- \quad \text{(does not occur)}
\]

21b) Since the above reaction does not occur we tend to use compounds like TosCl to help the reaction along. What exactly does the TosCl do to help the reaction occur? (Two things).
22) Please supply the R,S configuration for each of the following compounds.

\[
\begin{array}{cccc}
A & B & C & D \\
\text{COOH} & \text{Cl} & \text{H} & \text{H} \\
\text{H} & \text{C} & \text{Cl} & \text{Cl} \\
\text{Cl} & \text{C} & \text{CH}_3 & \text{C} & \text{COOH} \\
\text{Cl} & \text{C} & \text{H} & \text{H} & \text{Cl} \\
\text{H} & \text{C} & \text{Cl} & \text{CH}_3 \\
\end{array}
\]

22b) Draw the R,S configuration of the enantiomers/diastereomers missing from the above set of compounds.

23) Please label the following compounds as R and S. Also, draw and label the missing diastereomer/enantiomer.

\[
\begin{array}{cccc}
A & B & C & D \\
\text{CH}_3 & \text{Cl} & \text{Cl} & \text{H} \\
\text{Cl} & \text{C} & \text{H} & \text{C} & \text{CH}_3 \\
\text{Cl} & \text{C} & \text{CH}_3 & \text{H} & \text{C} & \text{CH}_3 \\
\text{H} & \text{C} & \text{Cl} & \text{CH}_3 \\
\end{array}
\]

Please indicate the enantiomer/diastereomer pairs below.

Diastereomers =
Enantiomers =
Meso Pairs =
1) Please supply the product for each of the following reactions.
2) Suppose you wanted to carry out the following reaction using HBr as your reagent. Why would this be a poor choice of reagent to carry out this reaction?

\[ \text{HBr should not be used because it would also attack the double bond. A better reagent would be PBr}_3 \text{ because it does not attack double bonds.} \]

3) Two students are assigned the synthesis of t-butyl ethy ether. One uses process number one below, and the other uses process number two. Only one student obtains the desired product. Which one was it and why?

\[ \begin{align*}
\text{#1} & \quad \text{C} \quad \text{C} \quad \text{OH} \quad \xrightarrow{\text{Na}} \quad \text{C} \quad \text{C} \quad \text{O} \quad \xrightarrow{\text{C} \quad \text{C} \quad \text{Br}} \quad \text{C} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{C} \\
\text{#2} & \quad \text{C} \quad \text{C} \quad \text{OH} \quad \xrightarrow{\text{Na}} \quad \text{C} \quad \text{C} \quad \text{O} \quad \xrightarrow{\text{C} \quad \text{C} \quad \text{Br}} \quad \text{C} \quad \text{C} \quad \text{O} \quad \text{C} \quad \text{C}
\end{align*} \]

\[ \text{Although the general rule is to use the larger nuc- and the smaller substrate, doing so in this case would only lead to E2 elimination on #2. By using the smaller nuc- and larger substrate in #1 the reaction would go SN1 which would mean that you would get a lot of by-products but you would end up getting more product also (SN1 major, E1 minor).} \]

4) There are a number of ways of substituting a halogen for an alcohol group, but some ways are better than others. What advantage is there in using PCl\(_3\) rather than HCl in the chloride substitution reactions? Give an example.

\[ \text{HCl can react with double bonds and PCl}_3 \text{ cannot, so in some cases only PCl}_3 \text{ can be used. See below;} \]

\[ \begin{align*}
\text{OH} \quad \xrightarrow{\text{HCl}} & \quad \text{Cl} \\
\text{Cl} \quad \xrightarrow{\text{PCl}_3} & \quad \text{Cl} \quad \text{Cl}
\end{align*} \]
5) Esters do not have to be made from alcohols and acids. It is possible to make an ester using a ketone and acid instead. Please give the mechanism for the formation of the following ester in a base:

\[
\text{C-C-C} + \text{C-C-O} \xrightarrow{\text{NaOH Catalyst}} \text{C-C-O-C=C} + \text{H}_2\text{O}
\]

6) Please draw all of the steps for the acid catalyzed cleavage of propyl acetate.

7) What is the mechanism for the reaction between ethanol and thionyl chloride (SOCl\(_2\))?
8) 3-bromo-1,2-epoxybutane reacts with sodium methoxide to give a new oxirane, 1-methoxy-2,3-epoxybutane. Suggest a mechanism for this reaction.

\[
\begin{align*}
\text{H}_3\text{C} & \text{C} - \text{C} - \text{C} - \text{C} \quad \text{Br} \\
& \xrightarrow{\text{CH}_3\text{ONa}} \quad \text{H}_3\text{C} - \text{C} - \text{C} - \text{C} - \text{OCH}_3 + \text{Br}^- \\
& \xrightarrow{\text{CH}_3\text{O}^-} \quad \text{H}_3\text{C} - \text{C} - \text{C} - \text{C} - \text{OCH}_3 \quad \xrightarrow{\Theta} \quad \text{H}_3\text{C} - \text{C} - \text{C} - \text{C} - \text{OCH}_3 + \text{Br}^-
\end{align*}
\]

9) Please give the mechanism for the formation of the hemiacetal made when ethanol and acetone are combined in the presence of H\textsubscript{2}SO\textsubscript{4}

\[
\begin{align*}
\text{C} - \text{C} - \text{C} - \Theta & \xrightarrow{\text{H}^+} \quad \text{C} - \text{C} - \text{C} - \Theta \\
& \xrightarrow{\Theta} \quad \text{C} - \text{C} - \text{C} - \Theta \quad \xrightarrow{\Theta} \quad \text{C} - \text{C} - \text{C} - \Theta \\
& \xrightarrow{\Theta} \quad \text{C} - \text{C} - \text{C} - \Theta \\
& \xrightarrow{\Theta} \quad \text{C} - \text{C} - \Theta + \text{C} - \Theta - \text{C} \quad \xrightarrow{\Theta} \quad \text{C} - \Theta - \text{C} - \Theta \\
\end{align*}
\]

10) Please show the mechanism for the reaction between methyl cyclohexene, bromine, and water. Four products are formed during this reaction. Give the complete mechanism for just one product but show how each product is formed and label them R,S appropriately.
12) The peptide bond that links amino acids in proteins is a type of ester bond. This bond is easily broken in acidic environments but not in basic environments. Please show how the breakdown of this bond in an acidic environment and discuss why it would not easily be broken down under basic conditions.

\[
\begin{align*}
\text{HO-C} & \text{-C-N-C-C-NH}_2 \\
& \xrightarrow{H^+, H_2O} 2 \text{HO-C} \text{-C-N-H} \\
\end{align*}
\]
13) A grad student wanted to make diphenyl methanol using a Grignard reaction between phenyl magnesium bromide and benzaldehyde. To make sure his yield was good he added twice as much benzaldehyde as Grignard reagent and got a lot of white crystalline product. When he analyzed his product he found that he had not made diphenyl methanol, but diphenyl methanal (also called benzophenone) instead. When he asked his research director about it he was told that he should have used equivalent amounts of benzaldehyde and Grignard instead. Doing so, he obtained his desired product. Please explain, using reactions, what had gone wrong with the original synthesis and why the product changed when the amount of benzaldehyde changed. Show the mechanism of each reaction. Hint: One step of this reaction produces a very unusual leaving group.

Without the extra benzaldehyde present, the H would have nothing to attack except the benzophenone converting it to diphenyl methanol, the desired product.

14) Please draw the complete mechanism for the based catalyzed cleavage of an ester. The overall reaction should be,

```latex
\begin{align*}
C\equivC\equivO\equivC\equivC & \overset{\text{OH}, \text{H}_2\text{O}}{\rightarrow} C\equivC\equivO\equivC\equivC + \text{HO-C=C} \\
C\equivC\equivO\equivC\equivC & \overset{\text{OH}^-}{\rightarrow} C\equivC\equivO\equivC\equivC \overset{\text{OH}}{\rightarrow} C\equivC\equivO\equivC\equivC \overset{\text{H}_2\text{O}}{\rightarrow} \text{HO-C=C} + \text{OH}^-
\end{align*}
```
15) Please give an example of a reaction where an alcohol is acting like an acid, and another where it is acting like a base.

*Water behaves like an acid any time it gives off an $H^+$ like when a nucleophile takes a hydrogen off of water.*

*Water behaves like a base when the oxygen in water attacks something like carbon with a $+\text{ charge}$.*

16) Using any alkane that is four carbons or less, synthesize methyl cyclohexane.

\[
\begin{align*}
\text{C} & \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{C} & \quad \text{C} \quad \text{C} \\

\text{1. Br}_2, \text{hv} & \quad \text{2. EtO}^-, \text{EtOH} \\
\text{3. Br}_2, \text{dark} & \quad \text{4. } \text{tButO}^-, \text{tButOH}
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{C} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{C} \quad \text{C} \\

\text{1. Br}_2, \text{hv} & \quad \text{2. EtO}^-, \text{EtOH} \\
\text{3. Br}_2, \text{dark} & \quad \text{4. } \text{tButO}^-, \text{tButOH}
\end{align*}
\]

17) Starting with alcohols of two carbons or less synthesize 4 bromobutanol.

\[
\begin{align*}
\text{C} & \quad \text{C} \quad \text{C} \quad \text{OH} \\
\text{H}_3\text{C} & \quad \text{OH} \\

\text{1. SOCl}_2 & \quad \text{2. Mg(s), dry ether} \\
\text{2. LiAlH}_4 & \quad \text{3. NBS}
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C} \quad \text{C} \\
\text{Br} & \quad \text{C} \quad \text{C} & \quad \text{OH} \\

\text{1. H}^+, \text{H}_2\text{O}, \Delta & \quad \text{Br} \\
\text{2. tButO}^-, \text{tButOH} & \quad \text{3. NBS}
\end{align*}
\]

18) Please label as R and S all the products formed by the halohydrin addition of Br$_2$ and water to cis 2 pentene. There are four products in all.

\[
\begin{align*}
\text{C} & \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{Br} & \quad \text{OH} \\

\text{H}_3\text{C} & \quad \text{OH} \\
\text{C}_2\text{H}_5 & \quad \text{Br} \quad \text{left} \\
\text{Top} & \quad \text{OH} \\
\text{Br} & \quad \text{OH} \\
\text{Bottom} & \quad \text{OH} \\
\text{Br} & \quad \text{OH} \\
\text{Same} & \quad \text{OH}
\end{align*}
\]
19) Using any alkane that is four carbons or less synthesize the following:

\[
\begin{align*}
\text{C} - \text{C} - \text{C} - \text{C} & \xrightarrow{1. \text{Br}_2, \text{hv}} \text{C} - \text{C} - \text{C} - \text{C} \\
\text{C} - \text{C} - \text{C} & \xrightarrow{2. \text{EtO}, \text{EtOH}} \text{C} - \text{C} - \text{C} - \text{C} \\
\text{C} - \text{C} - \text{C} & \xrightarrow{3. \text{Br}_2, \text{dark}} \text{C} - \text{C} - \text{C} - \text{C} \\
\text{C} - \text{C} - \text{C} & \xrightarrow{4. \text{tButO}, \text{tButOH}} \text{C} - \text{C} - \text{C} - \text{C} \\
\text{C} - \text{C} & \xrightarrow{5. \text{BH}_3, \text{H}_2\text{O}_2, \text{NaOH}, \text{H}_2\text{O}} \text{C} - \text{C} - \text{C} - \text{C} \\
\text{H}_2\text{C} - \text{C} & \xrightarrow{6. \text{PCC}} \text{C} - \text{C} - \text{C} - \text{C} - \text{C} \\
\end{align*}
\]
20) Using compounds of two carbons or less, synthesize the following compounds.

\[
\text{CH}_4 \xrightarrow{1. \text{Br}_2, \text{hv} \atop 2. \text{KOH, Ether}} \text{CH}_3\text{OH}
\]

\[
\text{C} - \text{C} \xrightarrow{1. \text{Br}_2, \text{hv} \atop 2. \text{KOH, Ether}} \text{CH}_3\text{OH}
\]

\[
\text{C} - \text{C} \xrightarrow{1. \text{Br}_2, \text{hv} \atop 2. \text{Mg(s)} \atop 3. \text{CO}, \text{HCl} \atop 4. \text{LiAlH}_4 \atop 5. \text{PBr}_3} \text{C} - \text{C} - \text{Br} \xrightarrow{\text{H}_2\text{SO}_4, \text{Heat}} \text{C} - \text{C} - \text{C} - \text{O} - \text{CH}_3
\]

\[
\text{CH}_4 \xrightarrow{1. \text{Br}_2, \text{hv} \atop 2. \text{KOH, Ether}} \text{CH}_3\text{OH}
\]

\[
\text{C} - \text{C} \xrightarrow{1. \text{Br}_2, \text{hv} \atop 2. \text{Mg(s)} \atop 3. \text{CO}, \text{HCl} \atop 4. \text{LiAlH}_4 \atop 5. \text{PBr}_3} \text{C} - \text{C} - \text{Br} \xrightarrow{\text{H}_2\text{SO}_4, \text{Heat}} \text{C} - \text{C} - \text{C} - \text{O} - \text{CH}_3
\]

\[
\text{C} - \text{C} \xrightarrow{1. \text{Br}_2, \text{hv} \atop 2. \text{EtO}^-, \text{EtOH} \atop 3. \text{O}_3, (\text{CH}_3)_2\text{S}} \text{C} - \text{C} - \text{C} - \text{Br} \xrightarrow{\text{H}^+} \text{C} - \text{C} - \text{C} - \text{C} - \text{OH}
\]

\[
\text{C} - \text{C} \xrightarrow{1. \text{Br}_2, \text{hv} \atop 2. \text{Mg(s), dry ether} \atop 3. \text{CO}, \text{HCl} \atop 4. \text{PBr}_3} \text{C} - \text{C} - \text{C} - \text{Br} \xrightarrow{\text{KOH, ether (3x)}} \text{C} - \text{C} - \text{C} - \text{C}
\]

21) The SN2 reaction between ethanol and methoxide is doomed to failure even though methoxide is a stronger nucleophile than hydroxide. Why does this reaction fail?

\[\text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{O}^- \rightarrow \text{C}_2\text{H}_5\text{OCH}_3 + \text{OH}^- \text{ (does not occur)}\]

*It fails because alcohols are really acids, so they donate their hydrogen to the MeO- in an acid/base neutralization.*
21b) Since the above reaction does not occur we tend to use compounds like TosCl to help the reaction along. What exactly does the TosCl do to help the reaction occur? (Two things).

*TosCl is just a fancy SOCl₂, so it does two things,

a) it turns the OH into a good leaving group (main thing)

b) it is large so it does not do any SN2 reactions.

22) Please supply the R,S configurartion for each of the following compounds.

\[
\begin{array}{cccc}
& \text{COOH} & \text{Cl} & H & H \\
\text{H} & \text{Cl} & \text{H} & \text{Cl} & \text{H} \\
\text{Cl} & \text{H} & \text{Cl} & \text{H} & \text{Cl} \\
\text{H} & \text{Cl} & \text{H} & \text{Cl} & \text{H} \\
\text{S, R} & \text{R, S} & \text{R, R} & \text{S, R} \\
\end{array}
\]

A  B  C  D

22b) Draw the R,S configuration of the enantiomers/diastereomers missing from the above set of compounds.

The S, S version is missing =>

\[
\begin{array}{c}
\text{H} \\
\text{Cl} \\
\text{H}
\end{array}
\]

23) Please label the following compounds as R and S. Also, draw and label the missing diastereomer/enantiomer.

\[
\begin{array}{cccc}
& \text{CH₃} & \text{Cl} & \text{Cl} & \text{CH₃} \\
\text{Cl} & \text{C} & \text{H} & \text{C} & \text{CH₃} \\
\text{Cl} & \text{C} & \text{CH₃} & \text{C} & \text{CH₃} \\
\text{H} & \text{CH₃} & \text{Cl} & \text{Cl} & \text{H} \\
\text{A} & \text{B} & \text{C} & \text{D} \\
\text{R, R} & \text{S, R} & \text{R, S} & \text{S, S} \\
\end{array}
\]

Please indicate the enantiomer/diastereomer pairs below.

Diastereomers = AB, AC, BD, CD
Enantiomers = AD, BC
Meso Pairs = B & C are meso to each other
1) Please discuss, and give examples, of the relative acidity of 1°, 2°, and 3° alcohols. Why is one more acidic than another?

2) Please give the mechanism of an acid halide with an alcohol to form an ester. Use the following reactants:

\[
\begin{array}{c}
\text{C} - \text{C} - \text{OH} \\
\text{C} - \text{C} - \text{OH}
\end{array}
\]
3a) It is well known that Grignards cannot be made when there is water or any other compound that can provide an $H^+$ present. Why is this so?

3b) Grignard cannot be made in the presence of aldehydes or ketones either. Somehow these compounds provide $H^+$ to the solution. How does this happen?

4) Please give the complete mechanism for the cleavage of the ester, ethyl acetate, with $H^+$ and water. Note: Some people try to draw the forward reaction (making of the ester) and then draw all the arrows backwards. Please refrain from doing so. Besides, it doesn’t work.
5) Please supply the product for each of the following reactions. If there is no product, write “No Rxn.”

1. \( \text{O}_3, (\text{CH}_3)_2\text{S} \)
2. \( \text{LiAlH}_4 \)

1. \( \text{KMnO}_4, \text{H}^+, \text{H}_2\text{O}, \text{heat} \)
2. \( \text{CH}_3\text{OH}, \text{H}_2\text{SO}_4 \)

1. \( \text{Hg(OAc)}_2 \)
2. \( \text{C}_2\text{H}_5\text{OH} \)
3. \( \text{NaBH}_4 \)

cold dil. \( \text{KMnO}_4, \text{OH}^- \)

\( \text{H}_2\text{SO}_4, \text{CH}_3\text{OH} \)

\( \text{Br}_2, \text{H}_2\text{O} \)

\( \text{BH}_3, \text{H}_2\text{O}_2, \text{NaOH}, \text{H}_2\text{O} \)
6) Starting with any compound that is three carbons or less, synthesize the following compounds.

- \( \text{CH}_3 \text{Cl} \)
- \( \text{C}=\text{C} \text{O} \)
- \( \text{C}=\text{C} \text{C} \text{O} \text{C} \text{C} \)

You MUST use Grignard (do not use ozonolysis)

- \( \text{C}=\text{C} \text{C} \text{O} \text{C} \text{C} \)
- \( \text{C}=\text{C} \text{C} \equiv \text{O} \)
- \( \text{C}=\text{C} \text{C} \equiv \text{O} \)

Use two different methods

| \( \text{H}_2\text{C} \text{C} \text{C} \text{C} \text{O} \text{H} \text{H} \text{H} \text{C} \text{C} \text{CH}_2 \) | \( \text{H}_2\text{C} \text{CH} \text{CH}_2 \) | Do not use Grignard or ozonolysis

- \( \text{C}=\text{C} \text{C} \equiv \text{O} \text{C} \text{C} \text{O} \text{C} \text{C} \)


1) Please discuss, and give examples, of the relative acidity of $1^\circ$, $2^\circ$, and $3^\circ$ alcohols. Why is one more acidic than another?

The more acidic alcohol is the smaller alcohol (ie: $1^\circ$). They have the fewest methyl groups pushing into the OH group. This causes the oxygen to pull as many electrons from the surrounding atoms as possible making the hydrogen more acidic (it leaves easier). As methyl groups are added the entire OH group become a good leaving group and the compound actually becomes more basic. Therefore $1^\circ > 2^\circ > 3^\circ$ in terms of acidity.

2) Please give the mechanism of an acid halide with an alcohol to form an ester. Use the following reactants:

```
\[\text{C} - \text{C} + \text{O} - \text{C} - \text{C} - \text{OH} \rightarrow \text{C} - \text{C} - \text{Cl} + \text{O} - \text{C} - \text{C} - \text{H} \]
\[
\text{C} - \text{C} - \text{Cl} \rightarrow \text{C} - \text{C} + \text{Cl}^+ \rightarrow \text{C} - \text{C} + \text{H}^+ \]
\[\text{C} - \text{C} - \text{OH} \rightarrow \text{C} - \text{C} - \text{O} - \text{C} - \text{C} \]
```
3a) It is well known that Grignards cannot be made when there is water or any other compound that can provide an H⁺ present. Why is this so?

Grignards are powerful nucleophiles (bases) and are easily neutralized in the presence of H⁺, therefore no H⁺ can be present when making a Grignard.

3b) Grignard cannot be made in the presence of aldehydes or ketones either. Somehow these compounds provide H⁺ to the solution. How does this happen?

This happens because of keto-enol tautomerism. The enol form of the tautomer is an alcohol which provides the H⁺ ions that destroy the Grignard. See below;

4) Please give the complete mechanism for the cleavage of the ester, ethyl acetate, with H⁺ and water. Note: Some people try to draw the forward reaction (making of the ester) and then draw all the arrows backwards. Please refrain from doing so. Besides, it doesn’t work.
5) Please supply the product for each of the following reactions. If there is no product, write “No Rxn.”
6) Starting with any alcohol or alkyl halide that is two carbons or less, synthesize the following compounds.

\[
\begin{align*}
\text{CH}_3 & \quad \text{Cl} \\
& \quad \text{You MUST use Grignard (do not use ozonolysis)}
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{C} & \quad \text{C} \\
\text{O} & \quad \text{C} & \quad \text{C} \\
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{O} & \quad \text{C} & \quad \text{C} \\
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{O} & \quad \text{C} & \quad \text{C} \\
\text{Use two different methods} & \\
\end{align*}
\]

\[
\begin{align*}
\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{O} & \quad \text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{O} & \quad \text{C} & \quad \text{C} \\
\text{Do not use Grignard or ozonolysis} & \\
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{H}_2\text{C} & \quad \text{C} & \quad \text{CH}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \quad \text{OH} & \quad \text{OH} \\
\text{H}_2\text{C} & \quad \text{CH} & \quad \text{CH}_2 \\
\end{align*}
\]
Closed Book Exam - No books or notes allowed. All work must be shown for full credit. You may use a calculator.

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1) Please name each of the following compounds.

![Compounds](image1.png)

2) Suppose you wanted to carry out the following reaction using HBr as your reagent. Why would this be a poor choice of reagent to carry out this reaction?

![Reaction](image2.png)
3) Please supply the product for each of the following reactions.

\[
\begin{align*}
\text{C} & \quad \text{C} \quad \text{C} \quad \text{OH} & \quad \text{HI} \\
\text{C} & \quad \text{C} \quad \text{C} & \quad \text{BH}_3, \text{H}_2\text{O}_2, \text{H}_2\text{O}, \text{KOH} \\
\text{CH}_3 & \quad \text{CH}_3 & \quad 1. \text{PBA} \\
& & \quad 2. \text{C-C-MgCl} \\
& & \quad 3. \text{H}_2\text{O} \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{OsO}_4, \text{H}_2\text{O}_2, \text{H}_2\text{O} \\
\text{C} & \quad \text{C} \quad \text{C} & \quad \text{KOH}, \text{Ether} \\
\text{OH} & \quad \text{C} & \quad \text{C} & \quad 1. \text{PCC} \\
& & \quad 2. \text{C-C-MgCl} \\
& & \quad 3. \text{H}_2\text{O}, \text{H}^+ \\
\text{C} & \quad \text{C} \quad \text{CMgCl} & \quad \text{CO}_2, \text{HCl} \\
\text{OH} & \quad \text{C} & \quad \text{C} & \quad \text{SOCl}_2 \\
\text{C} & \quad \text{C} \quad \text{C} & \quad \text{H}_2\text{SO}_4 \\
\text{C} & \quad \text{C} \quad \text{C} & \quad 1. \text{Ag}_2\text{O} \\
& & \quad 2. \text{C-C-OH} 
\end{align*}
\]
5a) What is the mechanism for the reaction between ethanol and thionyl chloride (SOCl$_2$)?

5b) There are a number of ways of substituting a halogen for an alcohol group, but some ways are better than others. What advantage is there in using PCl$_3$ rather than HCl in the chloride substitution reactions? Give an example.

6) Two students are assigned the synthesis of t-butyl ethy ether. One uses process number one below, and the other uses process number two. Only one student obtains the desired product. Which one was it and why?

\[ \begin{align*}
\text{#1} & \quad \text{C—C—OH} \xrightarrow{\text{Na}} \text{C—C—O}^- \xrightarrow{\text{C—C—Br}} \text{C—C—O—C—C} \\
\text{#2} & \quad \text{C—C—OH} \xrightarrow{\text{Na}} \text{C—C—O}^- \xrightarrow{\text{C—C—Br}} \text{C—C—O—C—C}
\end{align*} \]
7) Using any compound of two carbons or less, synthesize methyl ethyl ketone (2-butanone).

Extra Credit - Esters are usually made by reacting an alcohol with an acid but they do not have to be. It is possible to make an ester using a ketone and acid instead. Please give the mechanism for the formation of the following ester in a base:

$$\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{NaOH Catalyst}} \text{CH}_3\text{CO}_2\text{CH}_3 + \text{H}_2\text{O}$$
Chem 240 Name__Answer Key____
Exam #3 December 9, 2002

**Closed Book Exam** - No books or notes allowed. All work must be shown for full credit. You may use a calculator.

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1) Please name each of the following compounds.

- Tetrahydrofuran
- 1,3-dioxane
- 15 crown 5
- 1,2,4-pentatriol

2) Suppose you wanted to carry out the following reaction using HBr as your reagent. Why would this be a poor choice of reagent to carry out this reaction?

Because the HBr would also react with the double bond to give the addition product also.
3) Please supply the product for each of the following reactions.

\[
\begin{align*}
\text{C–C–C–OH} & \xrightarrow{\text{HI}} \text{C–C–C–I} \\
\text{C≡C–C} & \xrightarrow{\text{BH}_3, \text{H}_2\text{O}_2, \text{H}_2\text{O}, \text{KOH}} \text{HO–C–C–C} \\
\text{C–C–C–Cl} & \xrightarrow{\text{KOH, Ether}} \text{C–C–C–OH} \\
\text{C–C–C} & \xrightarrow{1. \text{PBA} \\
2. \text{C–C–MgCl} \\
3. \text{H}_2\text{O}, \text{H}^+} \text{C–C–C–C} \\
\text{C–C–CMgCl} & \xrightarrow{\text{CO, HCl}} \text{C–C–C–C} \\
\text{C–C–C} & \xrightarrow{\text{SOCl}_2} \text{C–C–C} \\
\text{C–C–C–OH} & \xrightarrow{\text{H}_2\text{SO}_4} \text{C–C–C} \\
\text{C–C–C} & \xrightarrow{1. \text{Ag}_2\text{O} \\
2. \text{C–C–OH}} \text{C–C–C–Cl}
\end{align*}
\]

5a) What is the mechanism for the reaction between ethanol and thionyl chloride (SOCl\(_2\))? 

\[
\begin{align*}
\text{C–C–OH} & \xrightarrow{\text{Cl}_2} \text{C–C–O}^+\text{S}^–\text{O}^- & \text{C–C–O}^+\text{S}^–\text{O}^- & \text{SO}_2 + \text{HCl} + \text{C–C–Cl} \\
& \xrightarrow{\text{Cl}} \text{C–C–O}^+\text{S}^–\text{O}^- + \text{Cl}^– \\
& \xrightarrow{\text{Cl}^-} \text{C–C–O}^+\text{S}^–\text{O}^- + \text{H}^+
\end{align*}
\]
5b) There are a number of ways of substituting a halogen for an alcohol group, but some ways are better than others. What advantage is there in using PCl₃ rather than HCl in the chloride substitution reactions? Give an example.

PCl₃ does not allow rearrangements to occur and it is OH specific. HCl allows for rearrangements and can add to double bonds. For example:

6) Two students are assigned the synthesis of t-butyl ethy ether. One uses process number one below, and the other uses process number two. Only one student obtains the desired product. Which one was it and why?

Although the general rule is to use the larger nuc- and the smaller substrate, doing so in this case would only lead to E₂ elimination on #2. By using the smaller nuc- and larger substrate in #1 the reaction would go SN₁ which would mean that you would get a lot of by-products but you would end up getting more product also (SN₁ major, E₁ minor).
7) Using any compound of two carbons or less, synthesize methyl ethyl ketone (2 butanone).

\[
\begin{align*}
\text{C} &= \text{C}=\text{O} \quad \xrightarrow{\text{C-C-MgCl}} \quad \text{C} &= \text{C} - \text{C} - \text{Cl} \\
\text{C} &= \text{C} - \text{OH} \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{C} &= \text{C} - \text{O} - \text{C} = \text{C} \quad \xrightarrow{\text{PCC}} \quad \text{C} &= \text{C} - \text{C} - \text{Cl}
\end{align*}
\]

Extra Credit - Esters are usually made by reacting an alcohol with an acid but they do not have to be. It is possible to make an ester using a ketone and acid instead. Please give the mechanism for the formation of the following ester in a base;

\[
\begin{align*}
\text{C} &= \text{C} - \text{C} \quad + \quad \text{C} &= \text{C} - \text{OH} \quad \xrightarrow{\text{NaOH Catalyst}} \quad \text{C} &= \text{C} - \text{O} - \text{C} = \text{C} \quad + \quad \text{H}_2\text{O}
\end{align*}
\]
Final Exam

Comprehensive Exam
CLOSED BOOK EXAM - No books or notes allowed. All work must be shown for full credit. You may use a calculator.

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I want my final to count for 300 pts. ______________________________
(This will drop your lowest exam) ________________________________

Signature

1) Please name or draw the structure of the following compounds.

![Chemical structures](image1)

![Chemical structures](image2)
2) Please draw the most stable form of trans-1,3-dimethyl cyclohexane.

3) Please draw the complete mechanism of the acid catalyzed addition of ethanol to 3-methyl butene and then draw the reaction diagram.

4) Please draw the product of the Saytzeff elimination of HBr from the following compound. Two products are possible, but only one is made. Show how both could be made and \textbf{EXPLAIN} which one is possible and why.
5) Circle the type of reaction occurring in each of the following reactions. If more than one reaction type occurs label the major and minor product.

\[
\begin{align*}
\text{H} & \quad \text{HI, Ether} \quad \xrightarrow{\text{SN}_1, \text{SN}_2, \text{E}_1, \text{E}_2} \quad \text{OH} \\
\text{C} & \quad \text{C} & \quad \text{O} & \quad \text{C} & \quad \text{C} \quad \xrightarrow{\text{H}_2\text{SO}_4, \text{CH}_3\text{OH}} \quad \text{SN}_1, \text{SN}_2, \text{E}_1, \text{E}_2 \\
\text{H} & \quad \text{EtOH, Heat} \quad \xrightarrow{\text{SN}_1, \text{SN}_2, \text{E}_1, \text{E}_2} \quad \text{Cl} \\
\text{C} & \quad \text{C} & \quad \text{C} & \quad \text{C} \quad \xrightarrow{\text{IsoPrO}^-, \text{IsoPrOH}} \quad \text{SN}_1, \text{SN}_2, \text{E}_1, \text{E}_2 \\
\end{align*}
\]

6) There are three forces that hold liquids together. Please explain how each of these contributes to the overall bonding in liquids and order them according to relative strength.

7) Label each of the following compounds R,S.

\[
\begin{align*}
\text{CH}_3 & \quad \text{Cl} & \quad \text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} & \quad \text{Cl} & \quad \text{H} & \quad \text{Cl} & \quad \text{C} & \quad \text{Cl} & \quad \text{H} & \quad \text{C} & \quad \text{Cl} \\
\text{Cl} & \quad \text{C} & \quad \text{H} & \quad \text{H} & \quad \text{C} & \quad \text{C} & \quad \text{H} & \quad \text{H} & \quad \text{C} & \quad \text{Cl} & \quad \text{CH}_3 \\
\text{H} & \quad \text{CH}_3 & \quad \text{Cl} & \quad \text{Cl} & \quad \text{H} & \quad \text{CH}_3 & \quad \text{Cl} & \quad \text{Cl} & \quad \text{H} & \quad \text{CH}_3 \\
\end{align*}
\]

A \quad B \quad C \quad D

7b) Which are enantiomers and diastereomers, and which compound (if any) is meso?
8) Please give the product for each of the following reactions.

- \( \text{C} = \text{C} \) \( \xrightarrow{\text{BH}_3, \text{H}_2\text{O}_2} \) \( \text{H}_2\text{O}, \text{KOH} \)
- \( \text{CH}_3 \) \( \xrightarrow{\text{HCl}} \) \( \text{Peroxide} \)
- \( \text{C} = \text{C} - \text{C} - \text{C} = \text{C} \) \( \xrightarrow{\text{EtOH, Heat}} \)
- \( \text{CH}_3 \) \( \xrightarrow{\text{H}_2\text{SO}_4, \text{H}_2\text{O}} \)
- \( \text{Cl} \) \( \xrightarrow{\text{KMnO}_4} \) \( \text{H}_2\text{O}, \text{KOH} \)
- \( \text{PBA} \)
- \( \text{Cl} \) \( \xrightarrow{\text{KI}} \)
- \( \text{Cl} \) \( \xrightarrow{1) \text{Mg} \atop 2) \text{H}_2\text{O}} \)
- \( \text{OH} \) \( \xrightarrow{\text{P} / \text{I}_2} \)
- \( \text{O}_3\text{S}_4 \) \( \xrightarrow{\text{H}_2\text{O}_2, \text{H}_2\text{O}} \)
- \( \text{C} = \text{C} \) \( \xrightarrow{\text{Hg(\text{OAc})}_2} \) \( \text{CH}_3\text{OH}, \text{NaBH}_4 \)
- \( \text{C} - \text{C} - \text{OH} \) \( \xrightarrow{\text{H}_2\text{SO}_4, \text{Heat}} \)
9a) Please show all the steps in the free radical chlorination of 2 methyl butane. It is important for the chlorine to become attached to the proper carbon so be careful of which carbon you choose to halogenate.

9b) Please give the ratio of products made in the free radical chlorination of 1,1 dimethyl cyclohexane.

10) Please draw the Lewis structure of C\textsubscript{4}H\textsubscript{4}O\textsubscript{4}
11) Please give all the steps in the Fisher ester synthesis of ethyl acetate.

12) Starting with alkanes of two carbons or less synthesize any two of the following:

![Chemical structures](image)
Chem 240
Final Exam

CLOSED BOOK EXAM - No books or notes allowed. All work must be shown for full credit. You may use a calculator.

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I want my final to count for 300 pts. ______________________________
(This will drop your lowest exam)  
Signature

1) Please name or draw the structure of the following compounds.

E 3-chloro-2-iodo-2-propene-1-ol

1R,2R,3S-4-chloro-2-bromo-cyclopentanol

3-ethyl-4-methyl-heptane

3R,4R-4-chloro-3-pentanol

E,Z-3-bromo-4-methyl-2,4-hexadiene
cyclopentyl(sec-butyl) ether
2) Please draw the most stable form of trans-1,3-dimethyl cyclohexane.

![trans-1,3-dimethyl cyclohexane](image)

3) Please draw the complete mechanism of the acid catalyzed addition of ethanol to 3-methyl butene and then draw the reaction diagram.

![Reaction Coordinate](image)

4) Please draw the product of the Saytzeff elimination of HBr from the following compound. Two products are possible, but only one is made. Show how both could be made and explain which one is possible and why.

![Saytzeff elimination](image)
5) Circle the type of reaction occurring in each of the following reactions. If more than one reaction type occurs label the major and minor product.

\[
\begin{align*}
\text{H} & \quad \text{HI} \\
\text{OH} & \quad \text{Ether} \\
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{CH}_3 \text{OH} \\
\text{EtOH, Heat} & \\
\text{Cl} & \quad \text{Cl} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{IsoPrO}^- \\
\text{H} & \quad \text{CH}_3
\end{align*}
\]

6) There are three forces that hold liquids together. Please explain how each of these contributes to the overall bonding in liquids and order them according to relative strength.

1. Hydrogen Bonding – it is the strongest bond. It is a sharing of H’s in compound with OH or NH bonds.

2. Dipole-Dipole – the second strongest bond. It is the attraction between + and – in molecules with dipoles.

3. Diserson/London Forces – the weakest of the forces. Transient dipoles are made when molecules bump into each other, and these weak dipoles attract one another.

7) Label each of the following compounds R,S.

\[
\begin{align*}
\text{CH}_3 & \quad \text{Cl} \\
\text{H} & \quad \text{Cl} \\
\text{Cl} & \quad \text{H} \\
\text{H} & \quad \text{Cl} \\
\text{H} & \quad \text{H} \\
\text{Cl} & \quad \text{C} \\
\text{C} & \quad \text{H} \\
\text{CH}_3 & \quad \text{Cl} \\
\text{H} & \quad \text{CH}_3 \\
\text{2S, 3R} & \quad \text{2R, 3S} \\
\text{A} & \quad \text{B} \\
\text{2R, 3R} & \quad \text{2S, 3R} \\
\text{C} & \quad \text{D}
\end{align*}
\]

7b) Which are enantiomers and diastereomers, and which compound (if any) is meso?
A B, and D are the same compound – these are all meso so there are no enantiomers. C and (A,B,D) are diastereomers.
8) Please give the product for each of the following reactions.
9a) Please show all the steps in the free radical chlorination of 2 methyl butane. It is important for the chlorine to become attached to the proper carbon so be careful of which carbon you choose to halogenate.

Initiation

\[ \text{Cl}_2 \xrightarrow{\text{hv}} 2 \text{Cl}^\bullet \]

Propagation

\[ \begin{align*}
\text{C} &-\text{C} &-\text{C} &-\text{C} &+ \text{Cl}^\bullet &\rightarrow &\text{C} &-\text{C} &-\text{C} &-\text{C} &+ \text{HCl} \\
\text{C} &-\text{C} &-\text{C} &-\text{C} &+ \text{Cl}_2 &\rightarrow &\text{C} &-\text{C} &-\text{C} &-\text{C} &+ \text{Cl}^\bullet \\
\end{align*} \]

Termination

\[ 2 \text{Cl}^\bullet \rightarrow \text{Cl}_2 \]

\[ \begin{align*}
\text{C} &-\text{C} &-\text{C} &-\text{C} &+ \text{Cl}^\bullet &\rightarrow &\text{C} &-\text{C} &-\text{C} &-\text{C} \\
2 \text{C} &-\text{C} &-\text{C} &-\text{C} &\rightarrow &\text{C} &-\text{C} &-\text{C} &-\text{C} \\
\end{align*} \]

9b) Please give the ratio of products made in the free radical chlorination of 1,1 dimethyl cyclohexane.

\[ \begin{align*}
\text{CH}_3 &\text{CH}_3 \\
\text{CH}_3 &\text{CH}_3 \\
\end{align*} \]

\[ \begin{align*}
\begin{array}{c}
1^\circ \\
2^\circ \\
100 - X
\end{array} & \begin{array}{c}
X \\
100 - X
\end{array} = \frac{6}{10} \times \frac{1}{3.5} \\
35X = 600 - 6X \\
41X = 600 \\
X = 14.63\%
\end{align*} \]
10) Please draw the Lewis structure of C₄H₄O₄

11) Please give all the steps in the Fisher ester synthesis of ethyl acetate.

12) Starting with alkanes of two carbons or less synthesize any two of the following: