

EXPERIMENT 4 (Organic Chemistry II) Pahlavan/Cherif

Properties of Alcohols: Structure, Reactions and Identification of Alcohols



Purpose

- Examine molecular models and observe some physical and chemical properties of selected alcohols.
- Relate the observed properties to the molecular structure. Identify an unknown alcohol.
- To learn some common properties of alcohols
- To distinguish phenols from the three types of alcohols by chemical tests.

Chemicals

Ethyl alcohol (ethanol)
Isopropyl alcohol (2-propanol)
t-butyl alcohol (2-methyl-2-propanol)
cyclohexanol
1-propanol (n-propanol)
1-butanol
2-butanol
unknown alcohols
acetic anhydride
glacial acetic acid
conc. H_2SO_4
dilute NaOH
Lucas reagent (ZnCl_2 in concentrated HCl)
Chromic acid reagent - 2% $\text{K}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 (oxidant)
Sodium metal
Phenolphthalein indicator

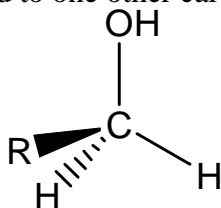
Materials

small test tubes (8 to 10)
stirring rod
hot plate
beakers (50, 400 mL)
test tube holder
test tube rack

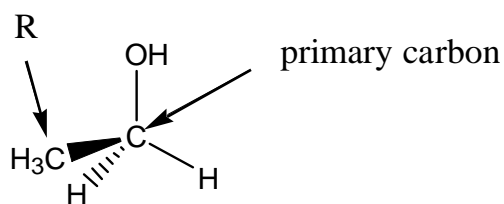
Introduction

Alcohols are organic compounds containing an -OH functional group bonded to a carbon atom. There are three classes (types) of alcohols: primary, secondary, and tertiary as shown below.

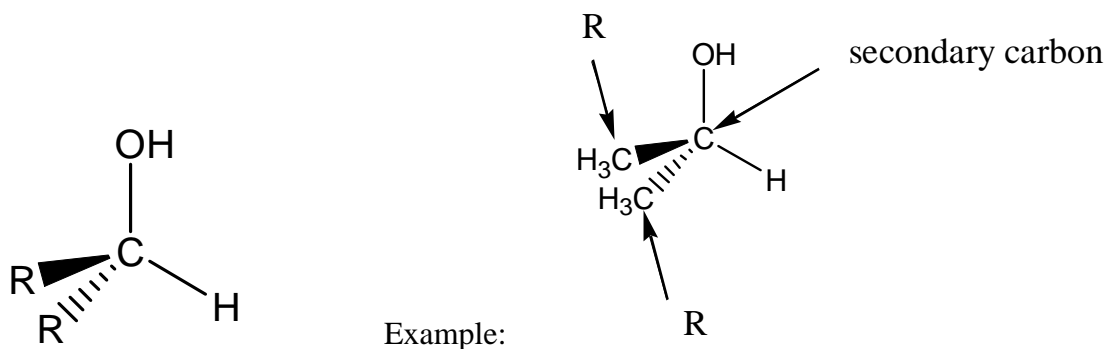
Primary alcohol: RCH_2OH the 'R', an alkyl group, and the -OH are attached to a primary carbon atom, a carbon bonded to one other carbon atom (highlighted).



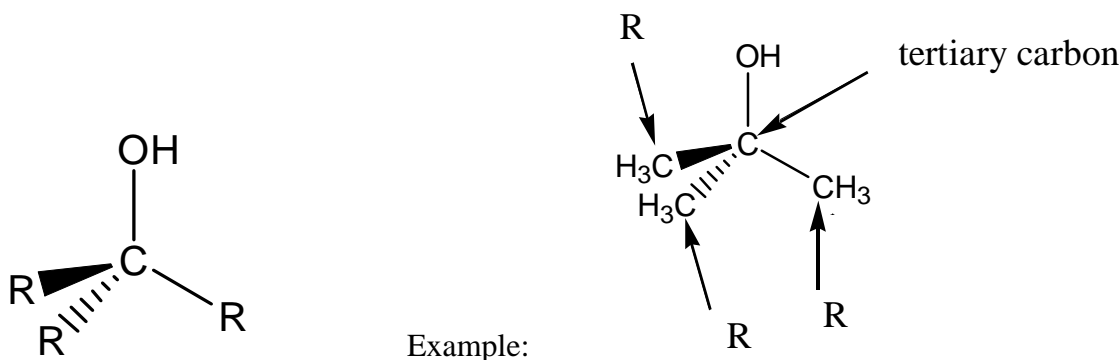
Example:



Secondary alcohol: R_2CHOH , the 2 'R' alkyl groups, and the -OH are attached to a secondary carbon atom, a carbon attached to two other carbon atoms from the 2 'R' (CH_3),



Tertiary alcohol: R_3COH the 3 'R' alkyl groups, and the -OH are attached to a tertiary carbon atom (highlighted), a carbon attached to three other carbon atoms from the 3 'R' (CH_3 -)



The International Union of Pure and Applied Chemistry (IUPAC) method of nomenclature for alcohols use the ending ol. Change the 'e' ending of an alkane to ol (i.e methane to methanol ethane to ethanol).

R = represents any alkyl group

Physical Properties

Molecular State- Straight-chain alcohols with up to 12 carbon atoms are liquids.

Solubility- Alcohols with a small organic part such as methanol or ethanol are much like water, thus miscible with water. Alcohols with a larger organic radical are more like alkanes and less like water. Alcohols with more than two -OH groups are more water soluble than similar alcohols with only one -OH group. In general each -OH group can solubilize four to five carbons

Melting (Fusion), Boiling points and Density- Straight-chain alcohols that have up to 12 carbons have boiling points that are considerably higher than the related alkanes, Alcohols with two or more -OH groups have higher boiling points.

Because the structural similarities between alcohols and water, their physical properties are also similar. Hydrogen bonding has a great influence on the physical properties of alcohols.

Alcohols with short carbon chains are quite **soluble in water**. Their solubility is due to **intermolecular hydrogen bonding** with water molecules, as shown in Figure 1(b). However, the **water solubility** of

alcohols begins to decrease as the length of the carbon chain increases. As the number of carbon atoms increases, the non-polarity of the larger hydrocarbon chain offsets the polarity of the –OH group. Alcohols with longer carbon chains are insoluble. Because they are less dense than water, insoluble alcohols will form a layer on top of the water surface.

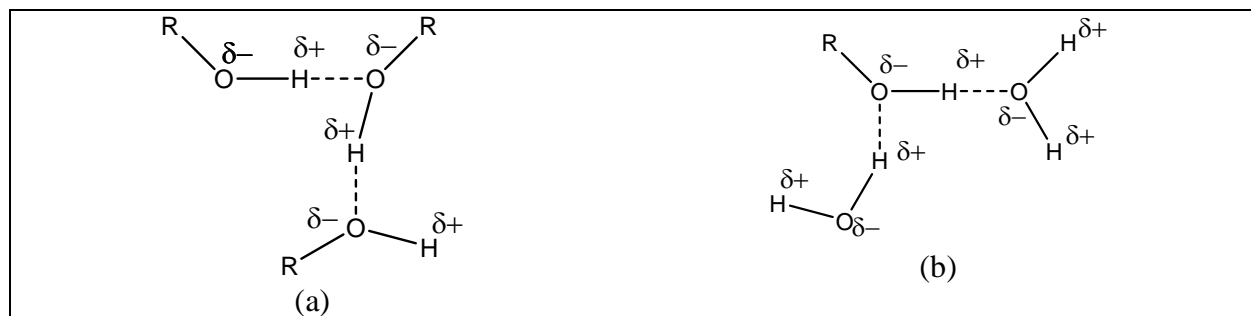


Figure 1- Hydrogen bonding between (a) alcohol molecules, and (b) alcohol and water molecules. Also, considering their molecular masses as compared to alkanes, alcohols have relatively **high boiling points**. Individual alcohol molecules are attracted to each other by **hydrogen bonds**. A higher temperature is necessary for these molecules to have sufficient energy to overcome these attractions. When enough energy breaks the hydrogen bonds, the alcohol converts from a liquid alcohol to a gaseous alcohol.

Viscosity refers to the resistance to flow. As the degree of intermolecular hydrogen bonding increases, the more viscous the liquid becomes. We commonly call viscous liquids “thick”.

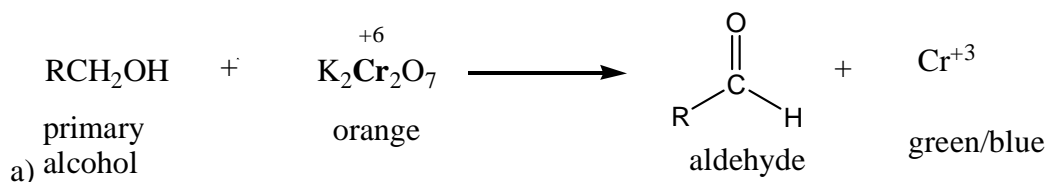
Many alcohols have characteristic odors that are readily detected. Particle size and hydrogen bonding both influence the ability of particles to escape from the liquid surface into the air. Greater size and greater intermolecular forces decrease the potential for alcohols to escape the liquid surface.

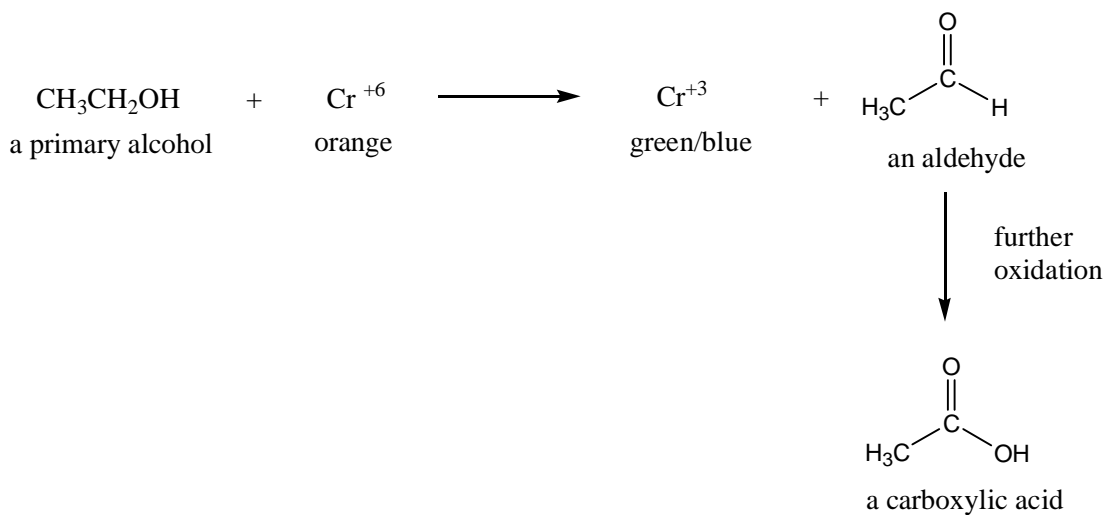
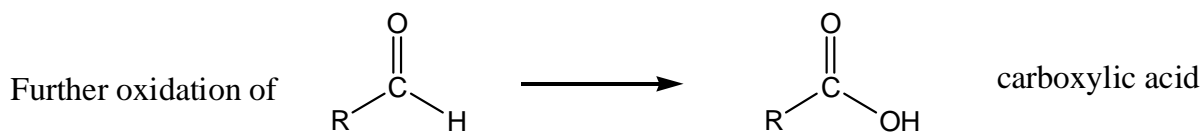
Main Uses- Some of the most common uses we have for alcohols are in medical clinics or at home for disinfecting things. Ethyl alcohol is classified for medical purposes as a “central nervous system depressant” this is the alcohol that people like to drink, and it is obtained by the fermentation of fruits. An other use that isn’t as popular is to synthesize other substances in laboratories.

Chemical Properties of Alcohols:

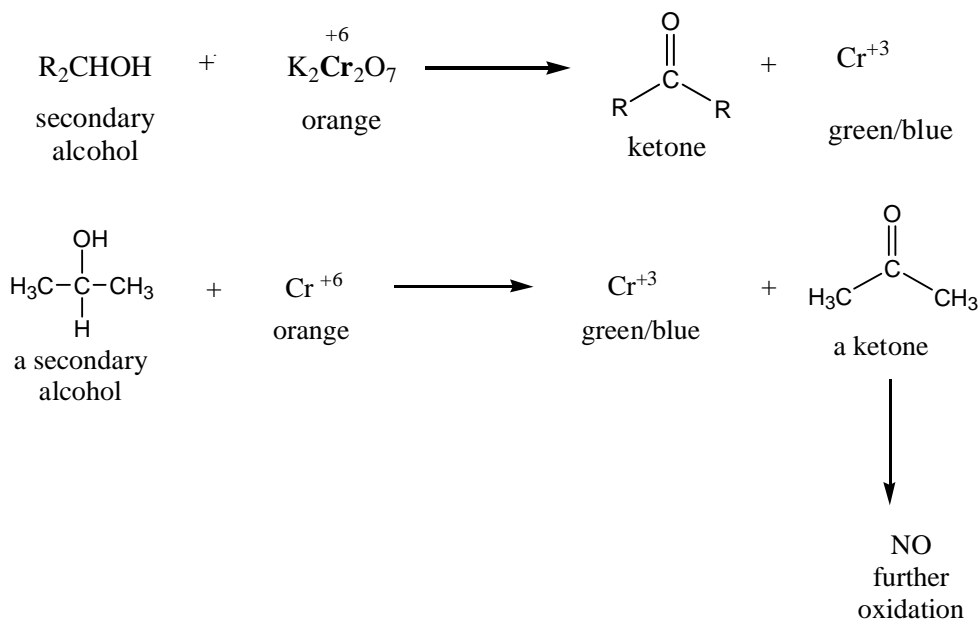
Alcohols are neutral compounds; the hydroxyl group does not ionize. However, the alcohol functional group is chemically reactive in other ways. Alcohols can be dehydrated. Depending upon the reaction conditions, loss of a water molecule forms either an ether or an alkene.

Oxidation of alcohols by strong oxidants such as $K_2Cr_2O_7$ in H_2SO_4 is possible, but differs depending on the degree of alcohol. Examples a, b, and c below show how a primary, secondary, and tertiary alcohol respectively respond to treatment of oxidants. If a reaction has occurred using $K_2Cr_2O_7$ in H_2SO_4 , there is a color change from orange to green.

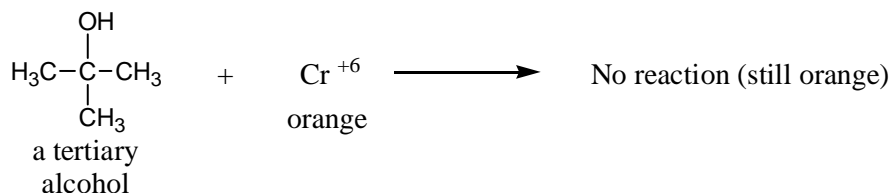




b)



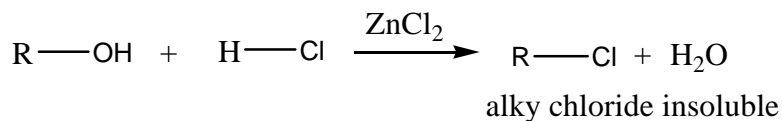
c) Tertiary alcohol: $\text{R}_3\text{COH} + \text{K}_2\text{Cr}_2\text{O}_7 \rightarrow \text{NO OXIDATION}$



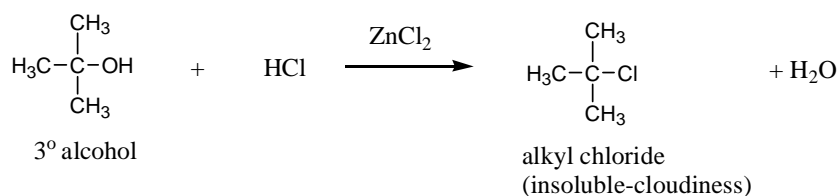
In this experiment, an acidic sodium dichromate solution, which is orange in color and contains Cr^{6+} , will be used to oxidize alcohols. As the alcohol is oxidized, the Cr^{6+} is reduced to Cr^{3+} , which turns the solution a blue-to-green color. The appearance of this blue-to-green color within one minute is considered a positive test for a primary or a secondary alcohol.

Lucas Test: This test is for low molecular weight alcohols and it distinguishes the rates of reaction of alcohols with the Lucas reagent (HCl and ZnCl₂). Positive indicator of the reaction is the formation of a water insoluble alkyl chloride as cloudiness or a precipitate. The formation of an alkyl chloride with tertiary alcohol is very rapid, followed by the secondary alcohol that may take from 5 to 20 minutes to form visible cloudiness. Primary alcohols do not react with Lucas reagent or it may show very little result in a very long time.

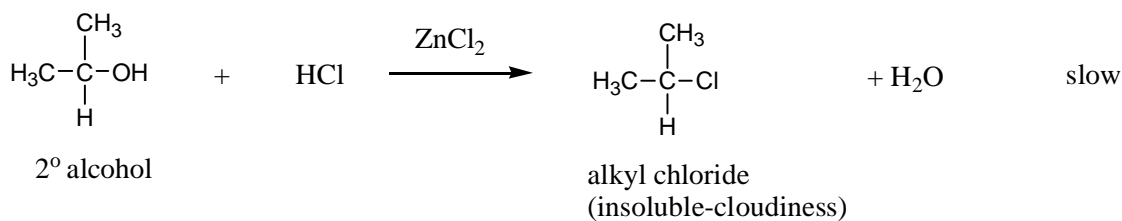
The chemical reaction involves replacing the –OH group of the alcohol with a chloride ion from hydrochloric acid (HCl), forming an alkyl chloride, as shown in the following equation.



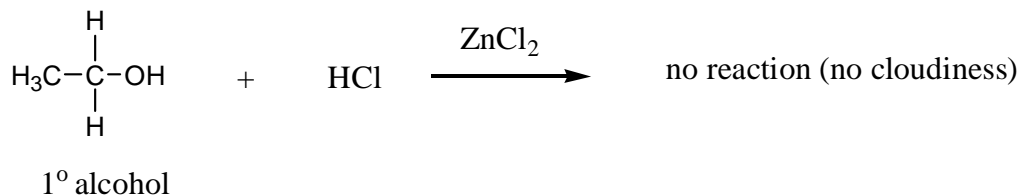
3° alcohol: R₃COH + HCl (ZnCl₂) → R₃Cl (alkyl chloride) + H₂O Very Fast
(insoluble/cloudiness)



2° alcohol: R₂CHOH + HCl (ZnCl₂) → R₂CHCl (alkyl; chloride) + H₂O Slow
(insoluble/cloudiness)



1° alcohol: RCH₂OH + HCl (ZnCl₂) → No reaction/very very slow



Zinc chloride (ZnCl₂) is a catalyst for this reaction, which is called the Lucas test. The resultant alkyl chloride is insoluble in water and separates from the Lucas reagent (ZnCl₂ in concentrated HCl), forming a cloudy mixture. Alcohols react at different rates, depending upon their structure. Tertiary alcohols form a cloudy mixture within 30 seconds at room temperature. Secondary alcohols react within 1–3 minutes, usually with slight heating. Primary alcohols require more than an hour to react.

Esterification :Esters are derivatives of organic acids. They can be prepared by the reaction of alcohols with carboxylic acids in the presence of a catalytic amount of mineral acid. Esters usually have pleasant, fruitlike odors and are responsible for flavors and fragrances of many fruits and flowers.

Note: • Record all your observations on your Data and Observations sheet. Dispose of your reaction mixtures according to your laboratory instructor's directions.

Safety Note

Caution: Wear departmentally approved safety goggles when doing this experiment. All chemicals are potentially harmful. Prevent contact with your eyes, skin, and clothing. Avoid ingesting any of the reagents. If you spill any reagents, immediately notify your laboratory instructor.

All the alcohols used are toxic, except glycerol. All the alcohols are flammable, except glycerol and ethylene glycol. Do not perform the experiment near an open flame.

Chromic acid reagent is toxic, corrosive, oxidant, and contains a suspected carcinogen.

Acetone is flammable and irritating. Do not use acetone near an open flame.

Lucas reagent (ZnCl_2 in concentrated HCl) is toxic and corrosive.

PROCEDURE

Part I – Reaction with sodium

Under the hood place a small piece of sodium metal in to a 50 mL beaker of half filled with **water**. Observe the reaction and after completion of the reaction, add 1 or 2 drops of phenolphthalein indicator to the solution in the beaker. Write a balance equation for the reaction of sodium and water.

Repeat the reaction of 2.0 mL alcohol with small piece of sodium metal in a large dry test tube. Note the reactivity of sodium metal with alcohol in compare (less or more reactive) to water. Test the resulting solution with phenolphthalein. Write the balance equations for reactions of sodium with **ethanol** and **1-butanol, phenol, and unknown**.

Part II – Solubility in water

Place 2.0 mL of water in a small test tube, dropwise add **ethanol** and shake the mixture. Count the number of drops until the alcohol is no longer soluble in water, but do not use more than 10 drops. Repeat the same procedure using **2-propanol, 1-butanol, cyclohexanol, phenol, and unknown**. Record your results as very soluble (for 6-10 drops), soluble (for 2-5 drops), and insoluble (1 drop).

Part III. Lucas Test

In a small test tube place 2.0 mL Lucas reagent, and add 4-5 drops of alcohol, shake the mixture well and observe the time required for the mixture to become cloudy or to form two different phases (layers). Try this test with **1-butanol, 2-butanol, 2-methyl-2-propanol (t-butyl alcohol), phenol, and unknown**. Based on your results of the Lucas test, determine the type of your unknown alcohols (1° , 2° , or 3°)

Part IV. Jones Reagent (Chromic acid test)

In a small test tube, place about 1.0 mL acetone, 1.0 mL alcohol, and 2 –3 drops of the Jones reagent. Observe the color change, clear, orange (formation of Cr^{+6} as CrO_3), or blue-green (formation of Cr^{3+}). Try this test with **1-butanol, 2-butanol, 2-methyl-2-propanol, phenol, and unknown**. Based on your results of the Chromic acid test determine the type of your unknown alcohol (1° , 2° , or 3°).

Part V. Esterification

- In a small test tube, mix ethanol (4-5 drops) and acetic acid (4-5 drops). Add one drop of concentrated sulfuric acid, warm the mixture in a hot water bath for about 5 minutes and then add 2.0 mL of cold water. Note the odor and write a complete equation for the reaction of ethanol and acetic acid.
- In a small test tube, mix 1-butanol (4-5 drops) and acetic anhydride (4-5 drops). Stir well, and warm the solution in hot water bath. Add 2.0 mL of cold water and make mixture slightly basic by adding 4-5 drops dilute NaOH. Note the odor and write a complete equation for the reaction of 1-butanol and acetic anhydride.

EXPERIMENT 4 (Organic Chemistry II)

Properties of Alcohols REPORT FORM

Name _____

Instructor _____

Date _____

Part I – Reaction with sodium

Compound	Observation
Water	
Ethanol	
1 -Butanol	
Phenol	
Unknown # _____	

Part II – Solubility in water

Alcohol	Observation
Ethanol	
2- propanol	
1- Butanol	
Cyclohexanol	
Phenol	
Unknown # _____	

Part III. Lucas Test

Alcohol	Observation
1-butanol	
2-butanol	
t-butyl alcohol 2-methyl-2-propanol	
Phenol	
Unknown # _____	

Jones Reagent (Oxidation Using Chromic Acid)

Alcohol	Observation
1-butanol	
2-butanol	
t-butyl alcohol (2-methyl-2-propanol)	
Phenol	
Unknown # _____	

Esterification – Ester Formation

a) Ethanol + acetic acid Odor _____

Reaction: _____

b) 1-Butanol + acetic anhydride Odor _____

Reaction: _____

UNKNOWN IDENTIFICATIONS (1°, 2°, or 3°)

Unknown Number _____ Identification _____

Pre-Laboratory Questions–EXP 4 Name:

Properties of Alcohols

Due before lab begins. Answer in space provided.

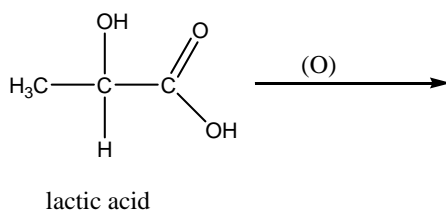
1. What are the specific hazards associated with the alcohols used in this experiment? What are the specific hazards associated with the chromic acid reagent?
2. Consider the alcohol hexyl alcohol (1-hexanol), $C_6H_{14}O$. Draw both a structural formula and a condensed structural formula for 1-hexanol. Identify 1-hexanol as a primary, secondary, or tertiary alcohol.
3. What would you expect to observe if you performed the chromic acid test on a sample of 1-hexanol?
4. What would you expect to observe if you performed the Lucas test on a sample of 1-hexanol?
5. Aqueous solutions of isopropyl alcohol are commonly sold as rubbing alcohol. The boiling point of isopropyl alcohol is $82.4\text{ }^{\circ}\text{C}$. It evaporates readily from the surface of the skin. Ethylene glycol (CH_2OHCH_2OH) is sold as antifreeze/antiboil. The boiling point of ethylene glycol is $198\text{ }^{\circ}\text{C}$. The molecular masses of isopropyl alcohol and ethylene glycol are similar. Provide an explanation for the observed difference in their boiling points.

Post-Laboratory Questions—EXP 4 Name: _____

Properties of Alcohols

Due after completing the lab.

1. Explain any differences observed between the solubility, viscosity, and the odor of ethyl alcohol and glycerol ($\text{CH}_2\text{OHCHOHCH}_2\text{OH}$)
2. Chromic acid oxidation is the basis of the Breathalyzer Test used by many police departments to detect ethyl alcohol in the breath of people suspected of driving under the influence. The amount of the green product is proportional to the amount of ethyl alcohol in the breath. Write structural formulas for the two oxidation products formed from ethyl alcohol. Name the oxidation products.
3. If you exercise strenuously without sufficient oxygen, lactic acid accumulates and contributes to muscle fatigue and soreness. When oxygen is later available, lactic acid must be oxidized to pyruvic acid. The structure of lactic acid is shown below.



- (a) Circle the alcohol functional group. Classify the alcohol as primary, secondary, or tertiary.
 - (b) Predict the solubility and chromic acid test results for lactic acid.
 - (c) Complete the reaction equation above. Draw the formula of the reaction product, pyruvic acid.
4. Containers of antifreeze contain such warnings as “Dispose of ethylene glycol properly” and “Keep out of the reach of children and animals”. Considering the chemical reactivity of alcohols, suggest a specific reason for these types of warnings.