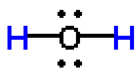
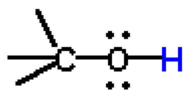
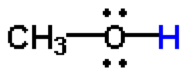
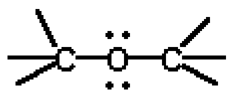
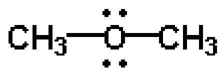
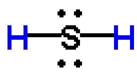
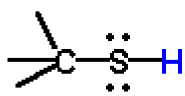
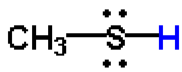
Alcohols

Contents

Structure

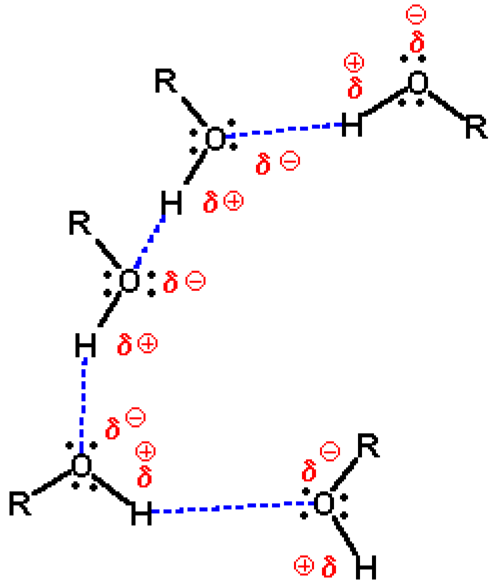
Alcohols can be considered as derivatives of water in which one hydrogen atom has been replaced by an alkyl or aryl group. In ethers, both hydrogen atoms of water have been replaced by organic groups. A third group of compounds, thiols, are derivatives of hydrogen sulfides, and since sulfur and oxygen are in the same family of the periodic table, they have some similar properties to alcohols.

Oxygen and Sulfur Functional Groups

Functional Group	Structure	Example
water		
alcohol		 methanol
ether		 dimethyl ether
hydrogen sulfide		
thiol		 methanethiol

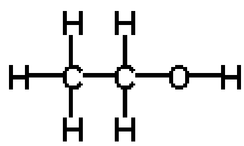
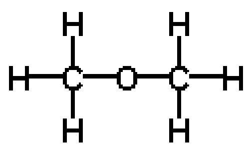
Physical properties of alcohols

The hydroxyl (-OH) group of water is polarized because of the high electronegativity of oxygen. This polarization leads to hydrogen bonding between alcohols and between alcohols and water.



The hydrocarbon group attached to the hydroxyl group is nonpolar. These disparate properties account for the decrease in water solubility of alcohols with increasing length of the carbon chain. Methanol and ethanol are completely water soluble, but higher alcohols like octanol are water insoluble. The ability of octanol and water to form two immiscible layers with different properties is exploited in studying the ability of drugs or potentially toxic chemicals to cross cell membranes. The octanol -water partition coefficient can be conveniently determined in the laboratory and used to assess how readily a chemical can diffuse across the nonpolar membranes of cells.

Hydrogen bonding gives alcohols high boiling points. Consider the isomers of C_2H_6O, ethanol and dimethyl ether. Even though they both have the same molecular weight, ethanol is capable of hydrogen-bonding and has a boiling point over 100^{o}C higher than dimethyl ether. Ethanol is also soluble in water while dimethyl ether is not.

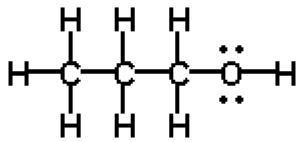
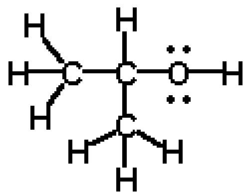
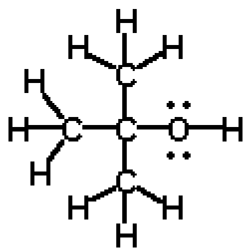
Comparison of Ethanol and Dimethyl Ether				
Name	Formula		Boiling Point	Water Solubility
Ethanol			78^{o} C	yes
Dimethyl ether			-24^{o} C	no

Classification of Alcohols

Alcohols are classified according to the nature of the carbon to which the -OH group is attached. This classification is very useful in categorizing the reactions of alcohols. Primary alcohols (designated 1^{o}) have the -OH group attached to a carbon atom bonded to only one nonhydrogen group. In secondary alcohols (2^{o}), the -OH group is attached to a carbon atom bonded to two nonhydrogen groups. In tertiary alcohols (3^{o}), the -OH group is attached to a carbon atom bonded to three nonhydrogen groups.

In the Chime representations, Compare how the electron density around the -OH group varies with the structure of the alcohol.

Classification of Alcohols

Classification	Example	
Primary 1^{o}	 1-propanol	
Secondary 2^{o}	 2-propanol	
Tertiary 3^{o}	 2-methyl-2-propanol	

Nomenclature of Alcohols

IUPAC Rules

I. Identify the parent hydrocarbon

Find the longest continuous chain of carbon atoms containing the hydroxyl group. The name of the straight-chain alkane with that number of carbon atoms is the parent name. Designate the -OH (hydroxyl) group by changing the family name (suffix) from -ane to -ol.

II. Number the parent chain

Number the parent chain starting from the end nearer the hydroxyl group.

If the hydroxyl group is the same distance from both ends, begin with the end nearer the first branch point, if there is one.

III. Assign each substituent a name and a number

Use the same rules as for branched-chain alkanes.

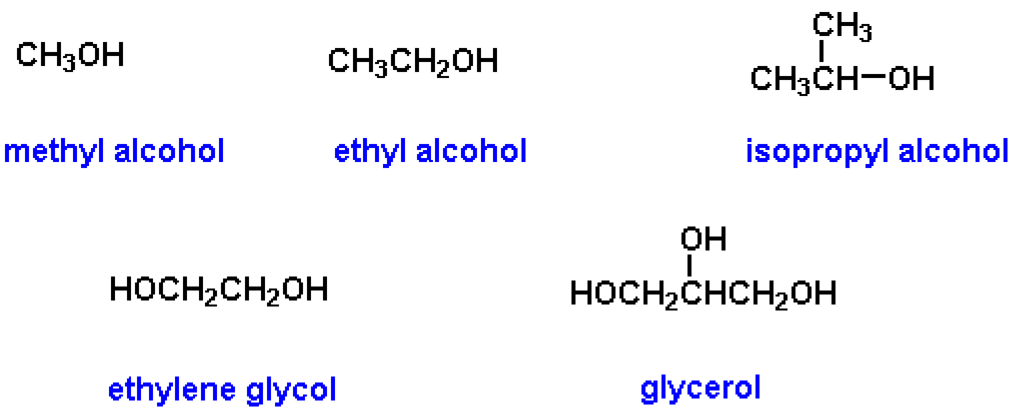
IV. Form a single word name for the alcohol

Combine the numbers and names of all substituents with the parent name to form one word. Use hyphens to separate numbers from names. Use comas to separate numbers.

- If two or more substituents are attached to the parent chain, write them in alphabetical order. If two or more substituents are identical, use prefixes di-, tri-, tetra-, penta-, etc. Each substituent must have a number, even if the numbers must be repeated. Do not use prefixes for alphabetizing.
- Indicate the position of the hydroxyl group by placing the number of the first carbon containing the -OH group before the -ol ending. If more than one hydroxyl group is present use the suffixes -diol, triol, etc.

Common Names

Simple alcohols have common names that are frequently used. These names use the name of the alkyl group plus the word alcohol. A few polyhydroxy compounds also have common names.



Preparation of Alcohols

Fermentation

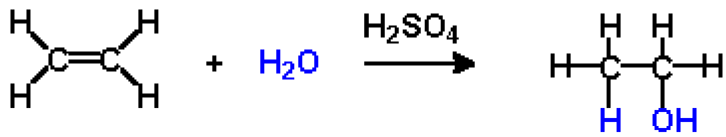
People have been producing ethanol by fermentation of sugar from fruits and grains for thousands of years. Today, fermentation is used to produce alcohol for beverages and as a fuel additive for gasoline.

$$C_6H_{12}O_6 \xrightarrow{\text{yeast}} 2\ CH_3CH_2OH + 2\ CO_2$$

glucose ethanol

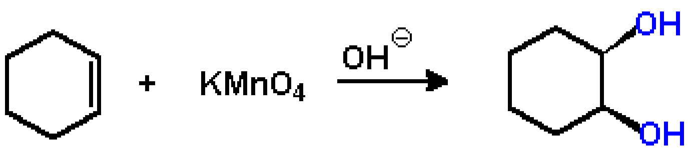
Hydration of Alkenes

Ethanol and other alcohols can also be produced by the acid catalyzed addition of water to alkenes. This addition reaction follows Markovnikov directed addition. Commercial ethanol has been produced by addition of water to ethylene, a byproduct of petroleum refining. Today, the relative high cost of crude oil and the low cost of corn, has made fermentation a more economic way to produce large quantities of ethanol.



ethylene ethanol

Cis-diols can be prepared by the oxidation of alkenes with alkaline potassium permanganate.



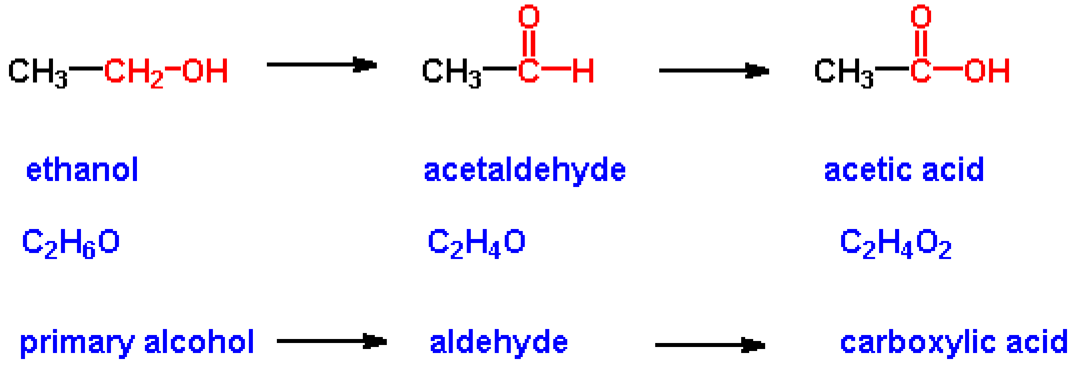
cyclohexene cis-1,2-cyclohexanediol

Reduction of carbonyl compounds is a very common way of preparing alcohols, and the addition of Grignard reagents to carbonyl compounds also leads to alcohols with larger carbon skeletons than the reactants.

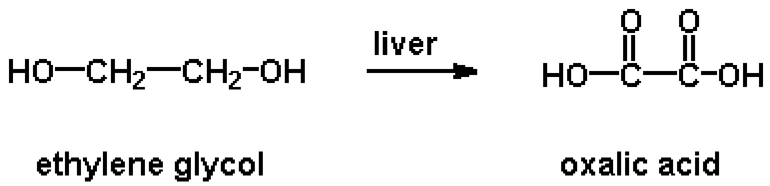
Oxidation of Alcohols

Ethanol is the alcohol least toxic to humans. Ingestion of methanol can lead to blindness and acidosis. Propanol and higher alcohols are more toxic than ethanol but are rarely abused. Ethylene glycol, a common ingredient in antifreeze, is also toxic. Deaths of animals and humans have occurred from drinking antifreeze containing ethylene glycol. The lower toxicity of ethanol is due to the body's ability to metabolize it into acetic acid, an important chemical in many biochemical processes in the body.

Ethanol is metabolized to acetaldehyde in the liver by an enzyme called alcohol dehydrogenase. Acetaldehyde is quite toxic and is rapidly metabolized to acetic acid by another enzyme (acetaldehyde dehydrogenase).



Acetic acid is used in the body as a building block for fats, carbohydrates, and as an energy source. The products of metabolism of other alcohols are responsible for their toxic effects. Methanol is metabolized to formaldehyde and formic acid, products that are responsible for toxicity. Ethylene glycol is metabolized to oxalic acid which binds calcium ions and is probably responsible for the kidney failure associated with ethylene glycol ingestion.



Organic chemists classify these transformations as oxidation reactions. Inorganic chemists usually think of oxidation as the loss of electrons and reduction as the gain of electrons. Organic chemists usually use operation definitions of oxidation and reduction based on changes in the composition of a molecule. While there are rules for calculating the oxidation number of an atom in an organic molecule, these numbers are usually not used by organic chemists. The ability to classify a reaction as an oxidation or reduction is more important in understanding the processes involved and in selecting reagents to accomplish a desired transformation.

oxidation	loss of H_2	gain of O, O_2, or
reduction	gain of H_2	loss of O, O_2, or X_2

X is a halogen.

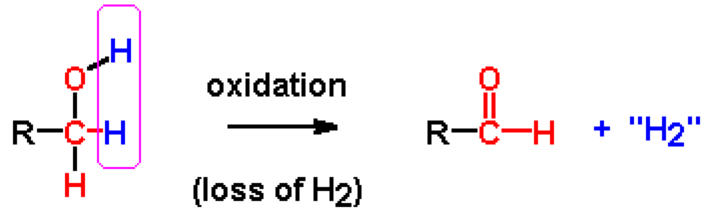
The loss or gain of H_2O, or HX are not considered oxidation-reduction reactions.

Exercise

Oxidation of Primary and Secondary Alcohols

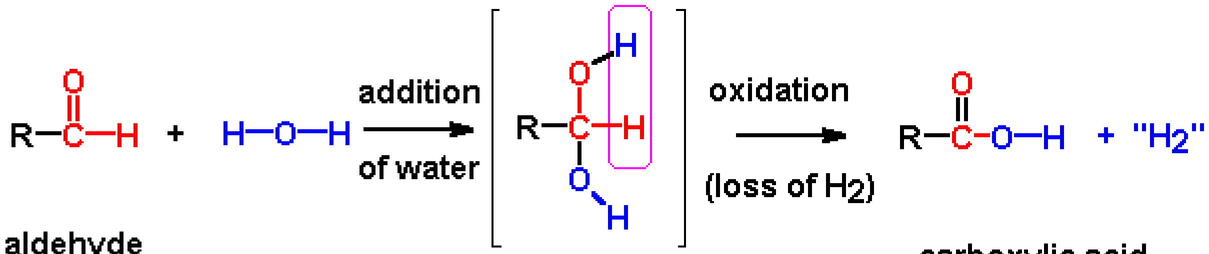
The fate of an alcohol in an oxidation reaction depends on its structure. Let's compare the reactivity of ethanol (a primary alcohol), 2-propanol (a secondary alcohol), and 2-methyl-2-propanol (a tertiary alcohol) toward chromic acid. The Cr (VI) ion in chromic acid is yellow. The solution turns to green reflecting the reduction to Cr(III).

In general, any primary alcohol can be oxidized to an aldehyde by removal of H_2.



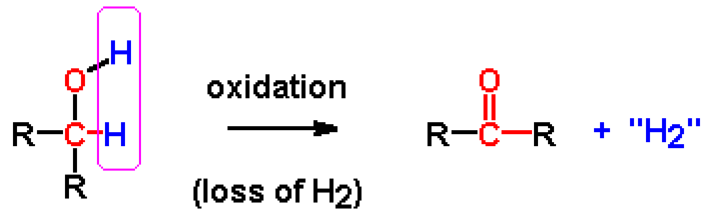
1° alcohol aldehyde

An aldehyde can be oxidized to a carboxylic acid. One way to visualize this process is to imagine that the aldehyde reacts with water to form a tetrahedral intermediate. This step is not an oxidation since H_2O was added. Elimination of H_2 , an oxidation, results in a carboxylic acid.



aldehyde carboxylic acid

A secondary alcohol such as 2-propanol can be oxidized to a ketone by elimination of H_2. Ketones usually resist further oxidation.



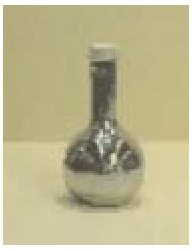
2° alcohol ketone

A tertiary alcohol such as 2-methyl-2-propanol, is resistant to oxidation because there are no hydrogen atoms on the carbon containing the -OH group.

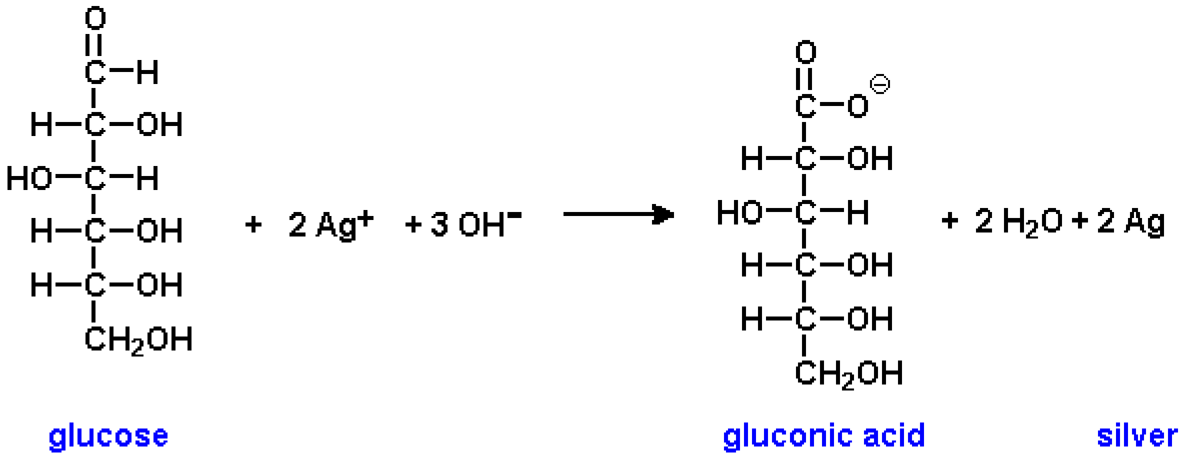
3° alcohol

Oxidation of Aldehydes

Aldehydes are readily oxidized to carboxylic acids by a variety of oxidizing agents. Tollens reagent, Ag_2O in a basic aqueous solution, is a very mild oxidizing agent which oxidizes aldehyde groups but not alcohols or carbon-carbon double bonds that would react with more vigorous oxidizing agents. The silver (I) oxide is reduced to metallic silver which can plate on the glass sides of the reaction vessel producing a mirror. This reaction is often used as a test to distinguish aldehydes from ketones which are not oxidized by this reagent.



Click the image for a video of the Tollens test for aldehydes

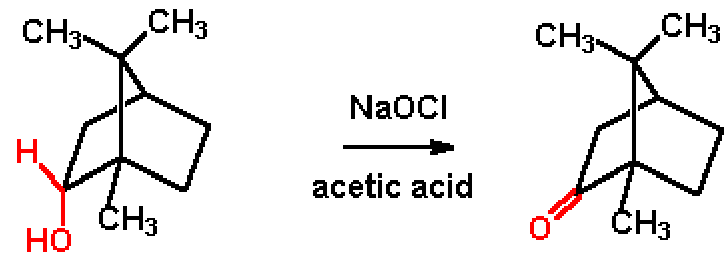


Oxidizing agents

Primary and secondary alcohols may be oxidized with a variety of reagents. The table shows the most common oxidizing agents and the active species.

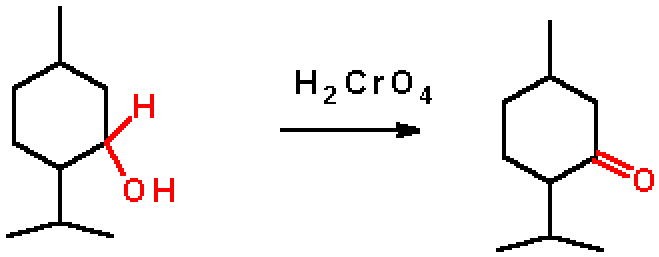
oxidizing agent	formula	active species
chromic acid	H_2CrO_4	Cr(VI)
potassium permanganate	$KMnO_4$	Mn(VII)
sodium hypochlorite	NaOCl	Cl(I)

Oxidation of secondary alcohols to ketones is easily accomplished using a variety of oxidizing reagents. For example, borneol can be oxidized to camphor using sodium hypochlorite (household bleach) in aqueous acetic acid.



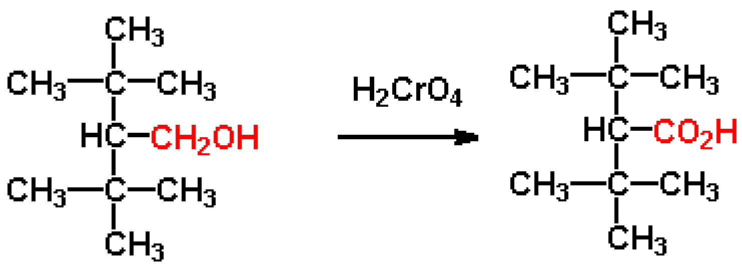
borneol **camphor**

Chromic acid is also commonly used. In this reaction the alcohol is oxidized to a ketone and the orange-red Cr(VII) is reduced to the green Cr(III).

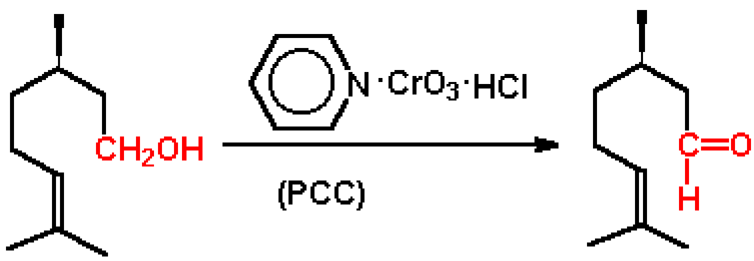


menthol **menthone**

Oxidation of primary alcohols to aldehydes is difficult because aldehydes are readily oxidized to carboxylic acids. Chromic acid usually oxidizes primary alcohols all the way to carboxylic acids.



The reagent of choice to prepare aldehydes from primary alcohols is pyridinium chlorochromate (PCC).



citronellol **citronellal**