Chapter 14: Alcohols, Phenols, and Ethers

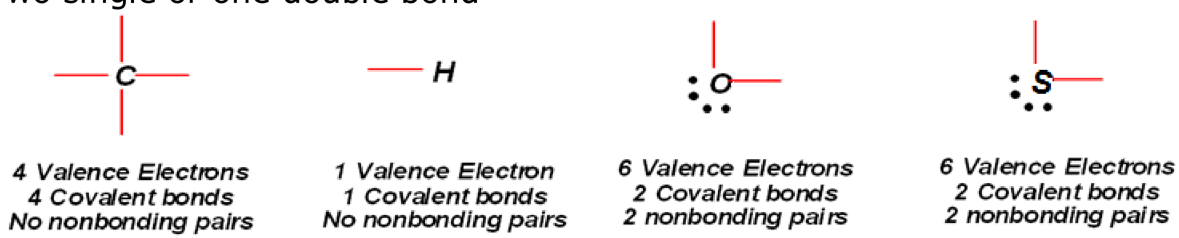
This chapter is the first of three that consider hydrocarbon derivatives with oxygen. This chapter is the first of three that consider hydrocarbon derivatives with o containing functional groups. Many biochemically important molecules contain carbon atoms bonded to oxygen atoms.

In this chapter we consider hydrocarbon derivatives whose functional groups contain one oxygen atom participating in two single bonds (alcohols, phenols, and ethers). Chapter 15 focuses on derivatives whose functional groups have one oxygen atom participating in a double bond (aldehydes and ketones), and in Chapter 16 we examine functional groups that contain two oxygen atoms, one participating in single bonds and the other in a double bond (carboxylic acids, esters, and other acid derivatives).

14.1 Bonding Characteristics of Oxygen and Sulfur Atoms in Organic Compounds

Oxygen and Sulfur are Group VIA Elements Has 6 valance electrons

- Two lone pairs
- Two bonding pairs, i.e., it can form two covalent bonds
- Two single or one double bond



14.2 Structural Characteristics of Alcohols

-OH unctional groups:

Alcohol: **R-O-H**

Phenols: **Ar-OH**

Alcohol: An organic compound in which an —OH group is bonded to a saturated carbon atom.

Saturated carbon atom: A carbon atom that is bonded to four other atoms.

General structure: R-OH (OH is functional group)

- Examples: CH_3OH, C_3H_7OH
- OH in alcohols is not ionic as in NaOH.

14.3 Nomenclature for Alcohols

Common names : Alcohols (C_1-C_4 alkyl groups).

- **Rule 1**: Name all of the carbon atoms of the molecule as a single alkyl group.
    - Example: Methyl (C_1), Ethyl (C_2), propyl (C_3) butyl (C_4)
- **Rule 2**: Add the word alcohol, separating the worlds with a space.
- Examples

The IUPAC Names:

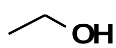
The **IUPAC system** deals with functional groups two different ways.
Modification of the hydrocarbon name to indicate the presence of a functional group.

• OH group takes priority (even over -ene or -yne)
- it must be in the parent chain
- the direction of numbering gives it the lowest possible number to carbon with –OH.

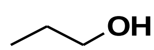
• -ol suffix with number designation
• name other substituents and multiple bonds as usual

alcohol, -OH use **-ol** ending.
ether: CH_3CH_2-O-CH_3 use **methoxy** **methoxy ethane**

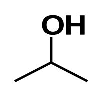
Examples:



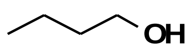
Ethanol
(Ethyl alcohol)



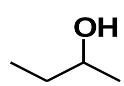
1-Propanol
(Propyl alcohol)



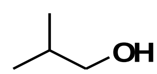
2-Propanol
(Isopropyl alcohol)



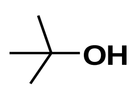
1-Butanol
(Butyl alcohol)



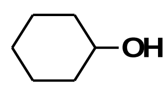
2-Butanol
(*sec*-Butyl alcohol)



2-Methyl-1-propanol
(Isobutyl alcohol)



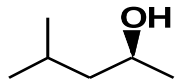
2-Methyl-2-propanol
(*tert*-Butyl alcohol)



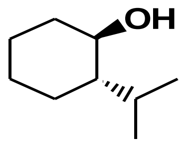
Cyclohexanol
(Cyclohexyl alcohol)

*Common names are in parenthesis

(a) $CH_3(CH_2)_6CH_2OH$ Octanol

(b) 

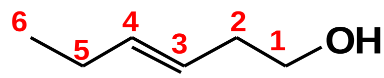
4-methyl-2-pentanol

(c) 

2-isopropyl cyclohexanol

IUPAC naming of unsaturated alcohols

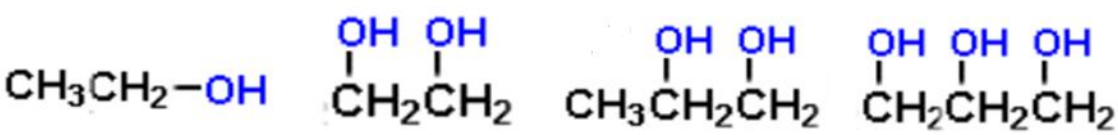
- the double bond is shown by the infix -en-
- the hydroxyl group is shown by the suffix -ol
- number the chain to give OH the lower number



***trans*-3-hexene-1-ol**
(*E*)-3-hexene-1-ol

Alcohol with More than one –OH group

Polyhydroxy alcohols—alcohols that possess more than one hydroxyl group—can b named with only a slight modification of the preceding IUPAC rules. An alcohol in which two hydroxyl groups are present is named as a diol, one containing three hydroxyl group is named as a triol, and so on. In these names for diols, trials, and so forth, the final -e c the parent allkane name is retained for pronunciation reasons.



1-Ethanol (ethyl alcohol)	1,2-Ethanediol (ethylene glycol)	1,2-Propanediol (propylene glycol)	1,2,3-Propanetriol (glycerol)

The first two of the preceding compounds have the common names ethylene glycol and propylene glycol. These two alcohols are synthesized, respectively, from the alkene ethylene and propylene (Section 13.3), hence the common names.

14.4 Isomerism for Alcohols (Constitutional Isomerism)

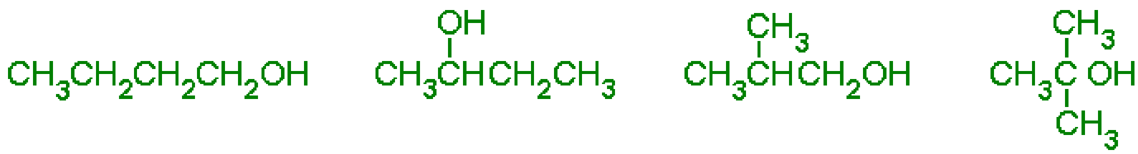
Isomerism in butanol

Constitutional isomerism is possible for alcohols containing three or more carbon atoms.

Two types of isomers

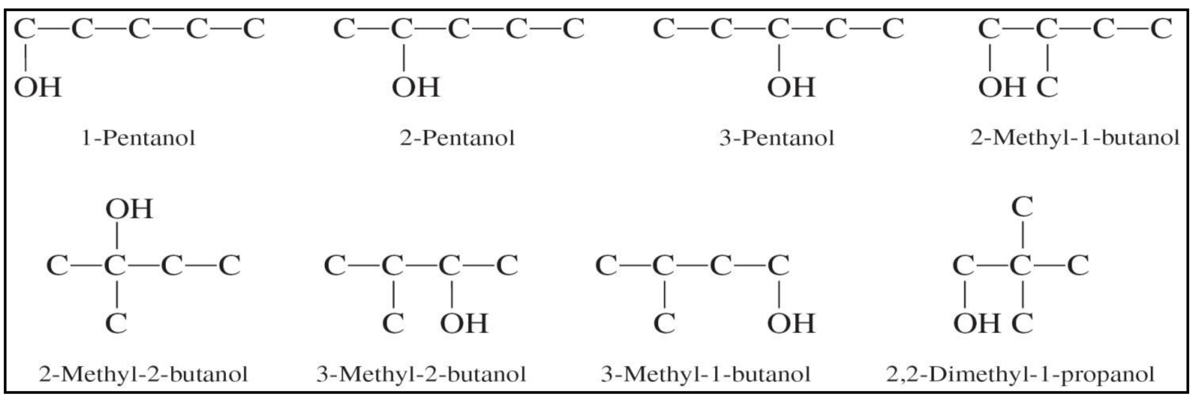
- Skeletal isomers
- Positional isomers

At with alkenes (Section 13.5), both skeletal isomers and **positional isomers** are possible. For monohydroxy saturated alcohols, there are two C3 isomers, four C4, and eight for C5 isomers.



1-butanol **2-butanol** **3-methyl-1-propanol** **2-methyl-2-propanol**

C5 isomers



14.5 Important Commoly Encountered Alcohols

Methyl Alcohol (Methanol)

- Good fuel and used as a solvent in paints
- Commonly called wood alcohol – original method of its preparation was by heating wood at high temperature in the absence of air.
- Currently, nearly all methyl alcohol is produced via the reaction between H_2 and CO.
- Toxic: oxidized by alcohol dehydrogenase in the body to toxic formaldehyde and formic acid – toxic to the eye and can cause blindness and/or optic nerve damage.
  - Treated with ethanol: Ethanol stops oxidation of methanol by competing with alcohol dehydrogenase enzyme.

Ethyl Alcohol (Ethanol)

- Also called grain alcohol as obtained by fermentation of grains like corn, rice and barley.
- Prepared by yeast fermentation of plant sugars by yeast
  - Maximum concentration of ethanol: 18% (yeast enzymes are inactivated at higher concentration of alcohol)
  - Excellent solvent and a fuel
  - Distributed as denatured Alcohol: Toxic substances such as methanol are added to prevent human consumption
  - Oxidized by body to acetaldehyde – toxic and causes hangover effects of alcohol
  - Consumption of alcohol during pregnancy can cause birth defects and fetal alcohol syndrome
  - Also know to cause liver damage, loss of memory and alcoholism (addiction to alcohol)

Isopropyl Alcohol (2-Propanol)

- Isopropyl alcohol is a three-carbon monohydroxy alcohol.
- A 70% isopropyl alcohol in water is marketed as rubbing alcohol (used to combat high body temperature by rubbing on the skin).
- Isopropyl alcohol has a bitter taste.
- Toxicity: Twice that of ethyl alcohol (often induces vomiting and thus doesn't stay down long enough to be fatal).
- In the body it is oxidized to acetone.

Glycerol (1,2,3-Propanetriol)

- Glycerol is a **triol** with three -OH groups attached on three adjacent carbon atoms.
- Clear thick liquid
- Byproduct of fat metabolism
- Used in skin lotions and soaps
- Used in shaving creams due to lubricating properties
- Often called biological antifreeze

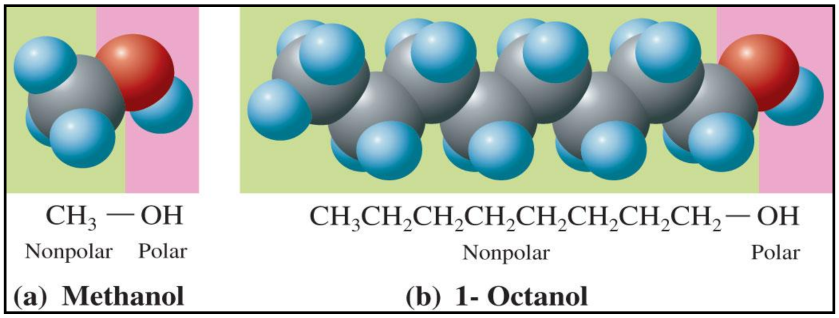
14.6 Physical Properties of Alcohols

Alcohol molecules have both **pola**r and **nonpolar** character.

- The hydroxyl group is polar part of the molecule
- The alkyl (R) group is nonpolar part of the molcule

The physical properties depend on which portion of the structure "dominates."

- Length of the nonpolar carbon chain
- Number of polar hydroxyl groups



Space-filling molecular models showing the nonpolar (green) and polar (pink) parts of methanol and 1-octanol.

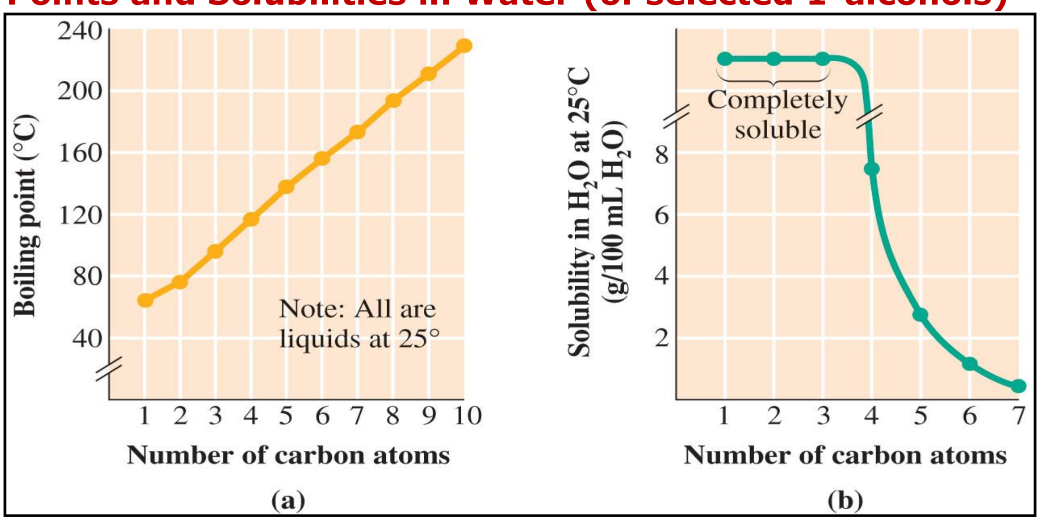
The polar **hydroxyl functional group** dominates the physical properties of methanol. The molecule is completely soluble in water (polar) but only partially so in hexane (nonpolar).

Conversely, the nonpolar portion of 1-octanol dominates its physical properties; it is infinitely soluble in hexane and has limited solubility in water.

Boiling Points and Water Solubilities

- The boiling points of 1-alcohols with an —OH group on an end carbon increases as the length of the carbon chain increases.
- Small monohydroxy alcohols are soluble in water in all proportions.
- As carbon chain length increases beyond three carbons, solubility in water rapidly decreases

Boiling Points and Solubilities in Water (of selected 1-alcohols)



Structural Formula	Name	Molecular Weight (g/mol)	Boiling Point (°C)	Solubility in Water
CH_3OH	methanol	32	65	infinite
CH_3CH_3	ethane	30	-89	insoluble
CH_3CH_2OH	ethanol	46	78	infinite
$CH_3CH_2CH_3$	propane	44	-42	insoluble
$CH_3CH_2CH_2OH$	1-propanol	60	97	infinite
$CH_3CH_2CH_2CH_3$	butane	58	0	insoluble
$CH_3CH_2CH_2CH_2CH_2OH$	1-pentanol	88	138	2.3 g/100 g
$HOCH_2CH_2CH_2CH_2OH$	1,4-butanediol	90	230	infinite
$CH_3CH_2CH_2CH_2CH_2CH_3$	hexane	86	69	insoluble

Alcohols and Hydrogen Bonding

The differences in physical properties between alcohols and alkanes

1. Alcohols have higher boiling points than alkanes of similar molecular mass.
2. Alcohols have much higher solubility in water than alkanes of similar molecular mass.

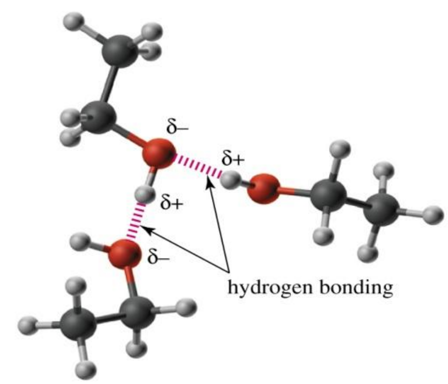


Figure shows the association of ethanol molecules in the liquid state (only two of the three possible hydrogen bonds to the upper oxygen are shown here).

Alcohols have higher boiling points and are more soluble in water than hydrocarbons

14.7 Preparation of Alcohols

14.8 Classification of Alcohols

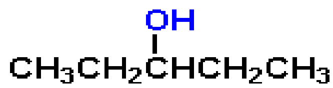
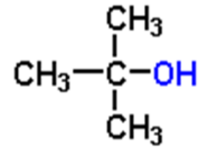
Alcohols are classified as **primary (1°), secondary (2°),** or **tertiary (3°)** alcohols

Primary alcohol (1°): Hydroxyl-bearing carbon atom is bonded to only one other carbon atom.

Secondary alcohol (2°): Hydroxyl bearing carbon atom is bonded to two other carbon atoms.

Tertiary alcohol (3°): Hydroxyl-bearing carbon atom is bonded to three other carbon atoms.

Reactions are dependent on the type of alcohol **1°, 2°,** or **3°**

Primary	Secondary	Tertiary
$CH_3CH_2CH_2CH_2-OH$		

14.9 Chemical Reactions of Alcohols

Combustion Reactions

Like other hydrocarbons alcohols are also flammable.
The combustion products are carbon dioxide and water.

$$2\ CH_3OH + 4O_2 \rightarrow 2CO_2 + 4\ H_2O$$

Alcohol Dehydration

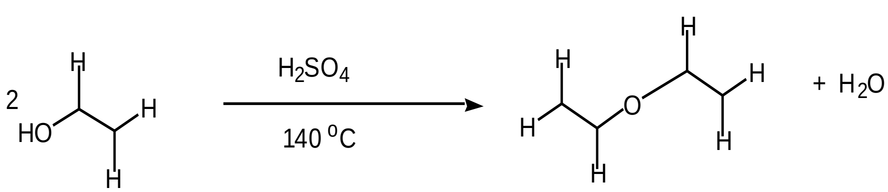
Intramolecular- Alcohol Dehydration

- A dehydration reaction in which the components of water (-H and -OH) are removed from a single reactant
- An alcohol can be converted to an alkene by elimination of H and OH from adjacent carbons (a β-elimination)

Intermolecular- Alcohol Dehydration

In this reaction, two molecules of alcohol combine to form an ether (Condensation reaction)

- Only true for **primary alcohols** and 140°C.

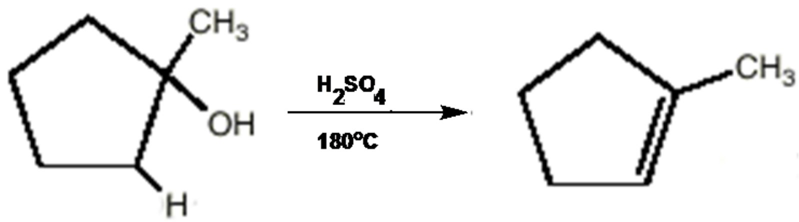


- **Secondary** and **tertiary** alcohols always give alkene.

Dehydration of an alcohol can result in more than one alkene product, because hydrogen loss can occur from either of the neighboring carbon atoms.

Example: Dehydration of 2-butanol produces two alkenes.

Zaitsev's rule (or the opposite of **Markovnikov's rule**) can be used determine the dominant product.



Oxidation of Alcohols

Addition of oxygen or removal of hydrogen
Mild Oxidizing Agents: $KMnO_4$, K_2Cr2O7, H2CrO4
Primary and Secondary Alcohols can be oxidized by mild oxidizing agents

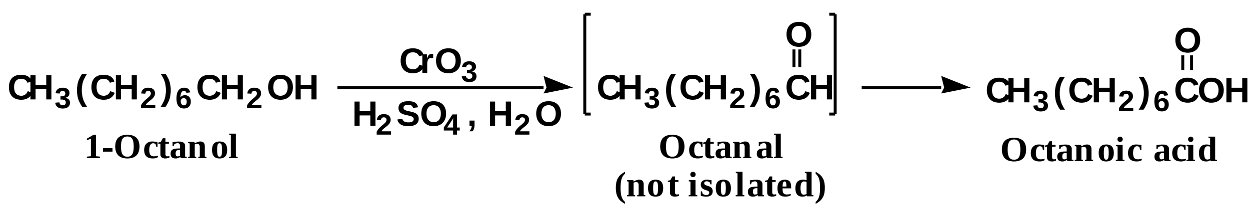
1° alcohol

Oxidation of a **1° alcohol** gives an **aldehyde** and then get oxidized to **carboxylic acid**, depending on the oxidizing agent and experimental conditions

- the most common oxidizing agent is chromic acid

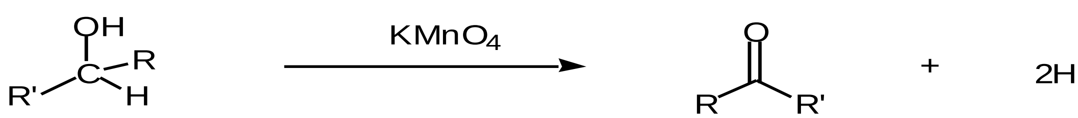
$$\underset{\text{Chromium(VI) oxide}}{CrO_3} + H_2O \xrightarrow{H_2SO_4} \underset{\text{Chromic acid}}{H_2CrO_4}$$

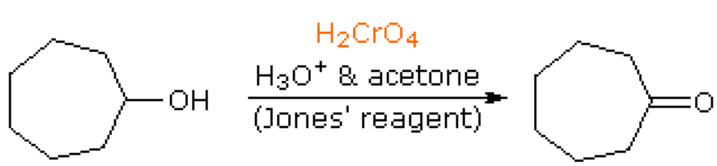
- chromic acid oxidation of 1-octanol gives octanoic acid



2° alcohol

Oxidation of a **2° alcohol** gives an **Ketone** the most common oxidizing agent is chromic acid.

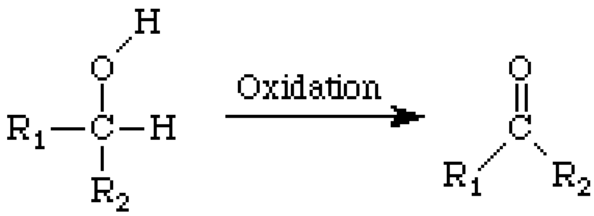




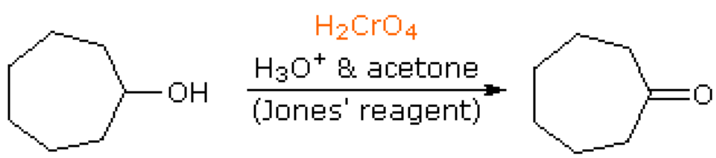
chromic acid oxidation of heptanol gives heptanone.

2° alcohol

Oxidation of a **2° alcohol** gives an **Ketone** the most common oxidizing agent is chromic acid.

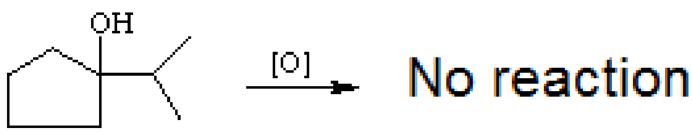


Chromic acid oxidation of heptanol gives heptanone.

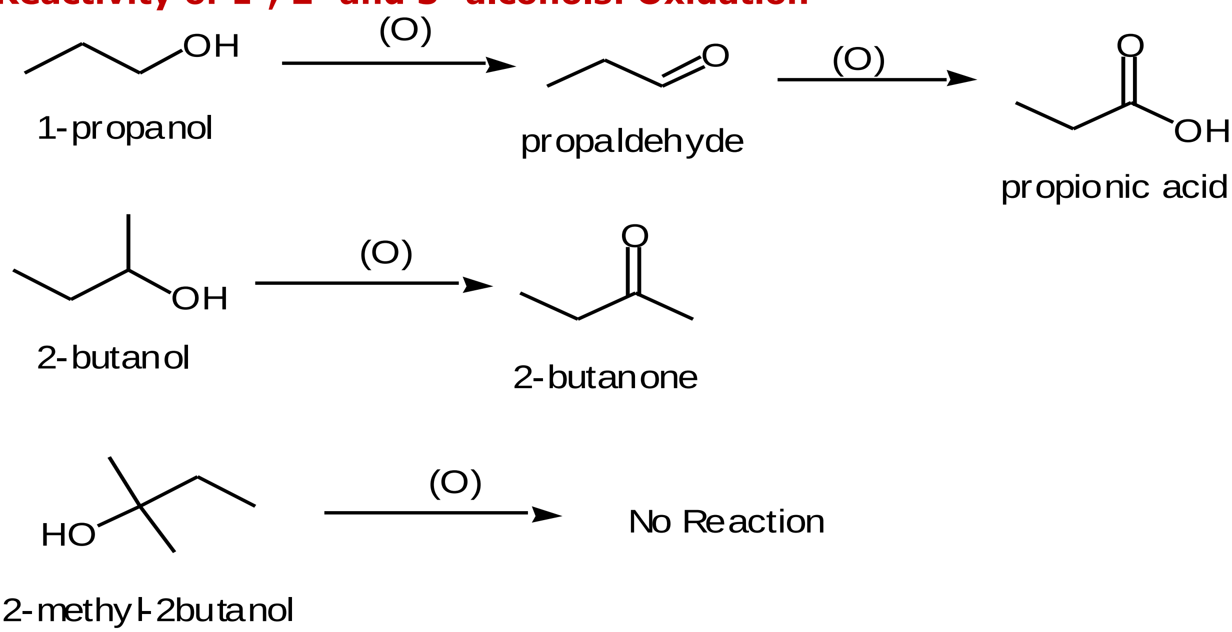


3° alcohol

Oxidation of a **3° alcohol** will not take place there is no hydrogen to be removed from a 3° carbon atom on a 3° alcohol.

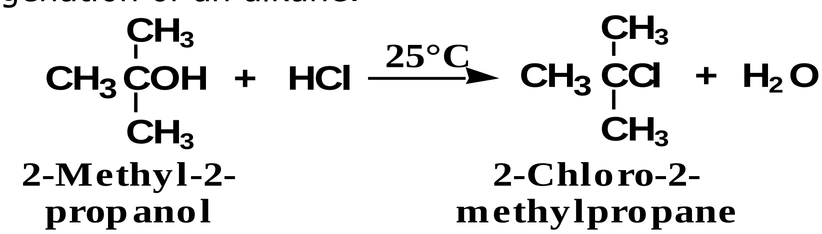


Reactivity of 1°, 2° and 3° alcohols: Oxidation



Halogenation of Alcohol

Alcohols undergo halogenation reactions. In this reaction a halogen atom is substituted for the hydroxyl group producing an alkyl halide.
Alkyl halide production by this reaction is superior to alkyl halide production through halogenation of an alkane.



$$3\,R{-}OH \quad + \quad PX_3 \longrightarrow 3\,R\text{-}X \quad + \quad H_3PO_4$$

(PX3: X is Cl or Br)

$$3\,CH_3CH_2OH \quad + \quad PCl_3 \longrightarrow 3\,CH_3CH_2Cl \quad + \quad H_3PO_4$$