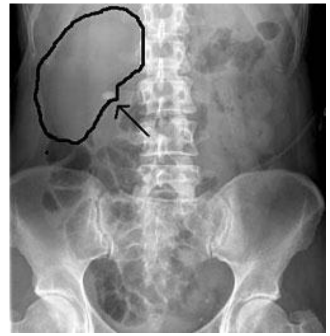
Alcohols, phenols and ethers

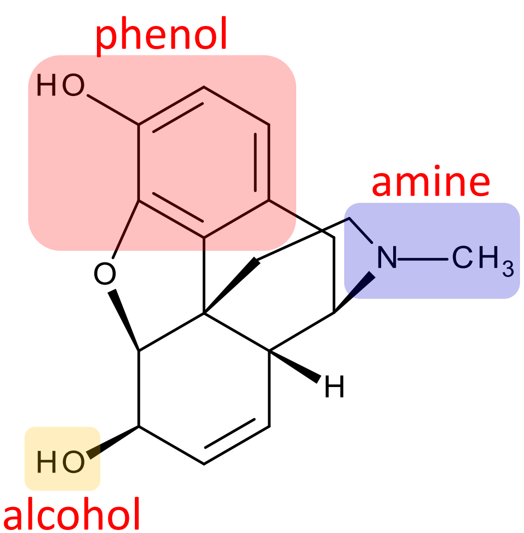
Chapter 14

H—O—H	R—O—H	R—O—R'
water	alcohol	ether

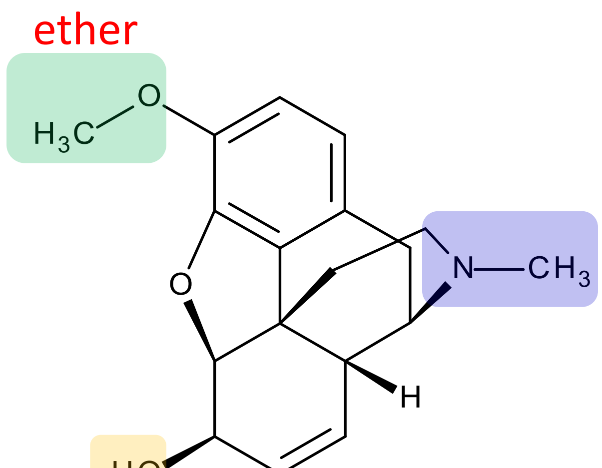
“without pain”

Opioid analgesics

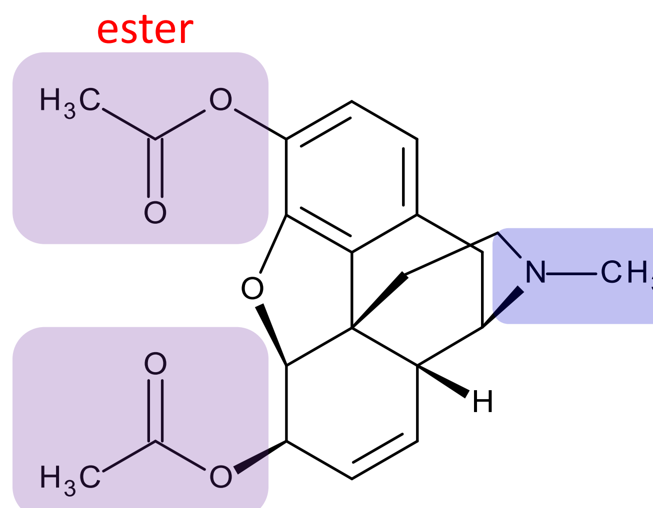




Morphine



Codeine

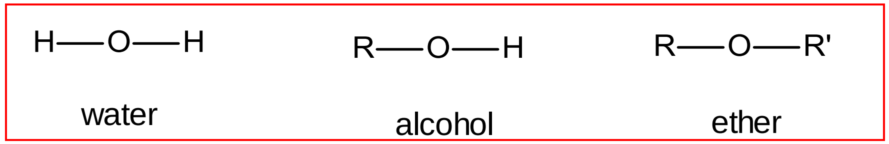


Heroin

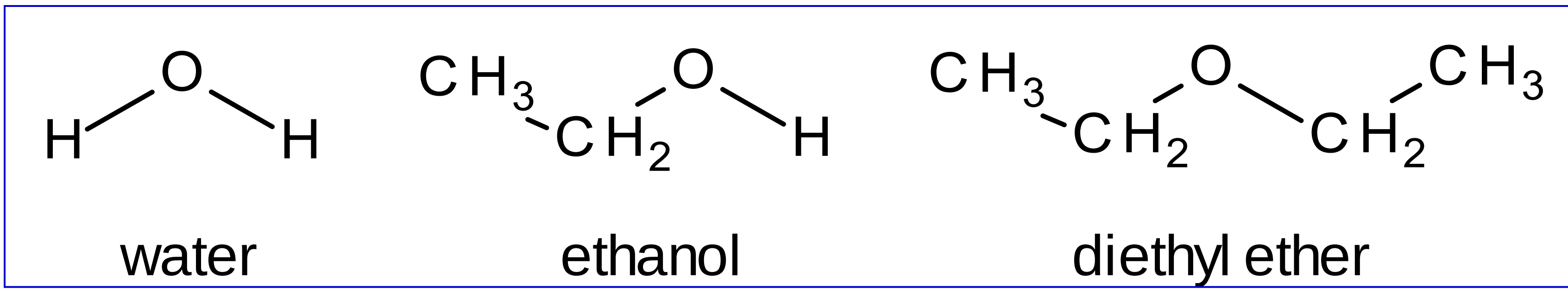
Functional groups: collections of atoms that define a molecule’s physical and chemical properties.

O as a functional group

- Water resembles ethers and alcohols



R = saturated carbon Component (e.g. CH_3-)

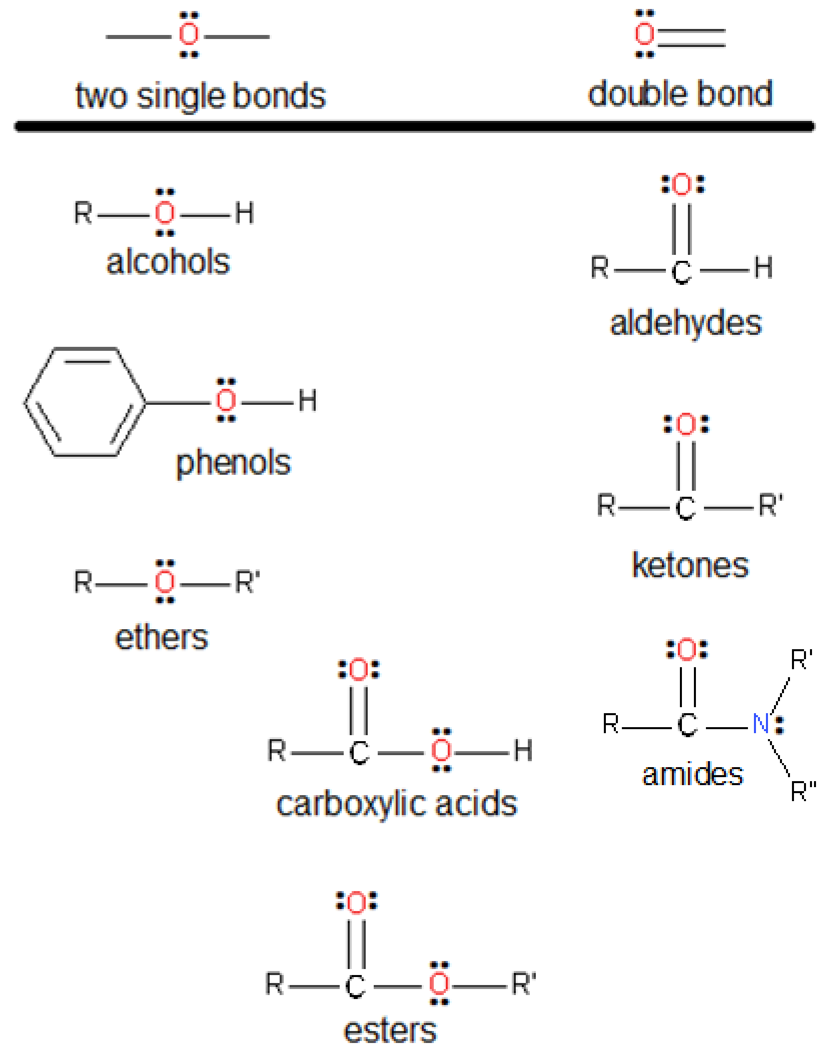


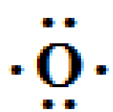
b.p. = 100°C   b.p. = 78°C   b.p. = 34°C

- The difference between water and these two organic substances is the presence of saturated carbons bound to the O-atom. (Ethers can also incorporate aromatic rings.)
- The slight changes in structure are accompanied by changes in their physical (e.g. boiling points) and chemical behavior.

Bonding for oxygen atoms in organic compounds

- Oxygen is commonly found in two forms in organic compounds:





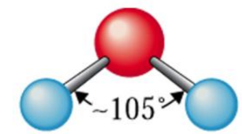
Oxygen is group 6A
Needs to form <u>two bonds</u>
to get an octet.

Structural characteristics of alcohols

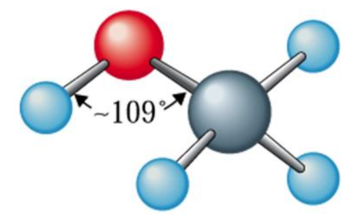
- Alcohols have the general formula:

R-OH

where "R" involves a saturated C-atom (bound to hydrogens and/or other carbons).

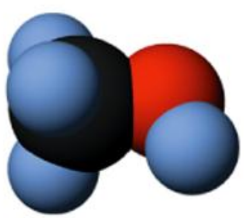


Water (HOH)



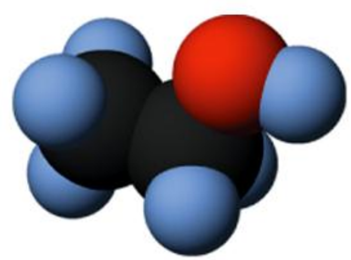
Methyl alcohol (CH_3OH)

- For example:



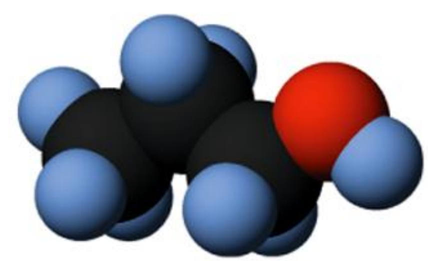
CH_3-OH

One-carbon alcohol



CH_3-CH_2-OH

Two-carbon alcohol



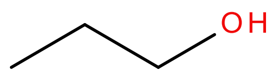
$CH_3-CH_2-CH_2-OH$

Three-carbon alcohol

Structural characteristics of alcohols

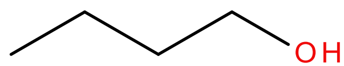
- Condensed structural formulas or line-angle structures are commonly used for depicting alcohols

IUPAC name



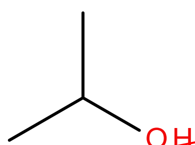
$CH_3-CH_2-CH_2-OH$

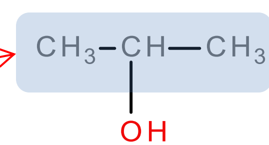
1-Propanol



$CH_3-CH_2-CH_2-CH_2-OH$

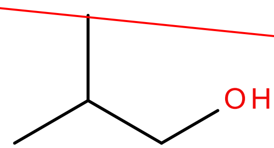
1-Butanol

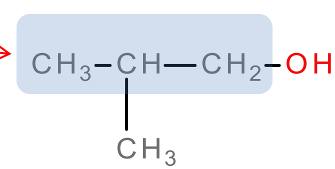




2-Propanol

Parent chain: identify longest C-chain which bears the OH group.





2-Methyl-1-propanol
(Isobutanol)

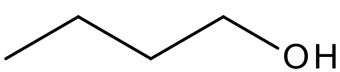
Nomenclature for alcohols

Common names for alcohols

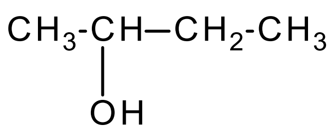
- Name the C-atoms of a single alkyl group as for alkanes.
- Add the word “alcohol” following a space after the alkyl name.

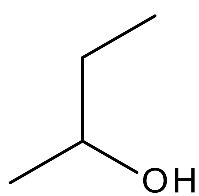
Like a butyl substituent

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$

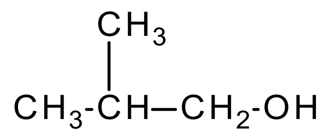


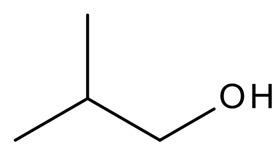
butyl alcohol



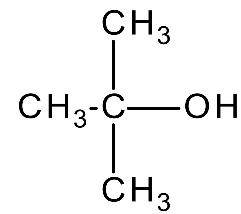


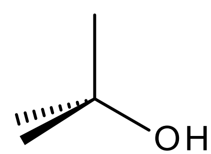
sec-butyl alcohol
sec-butanol





isobutyl alcohol
(isobutanol)



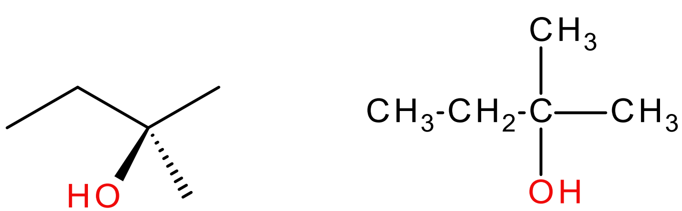


tert-butyl alcohol
tert-butanol

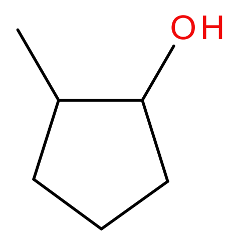
Nomenclature for alcohols

IUPAC Naming

- Find longest, continuous C-chain to which the OH group (hydroxyl) is bound. Number the chain in a way that gives the OH group the lowest numbering.
- Name and number other substituents present.
- The name for the corresponding alkane chain (e.g. for a 6-C chain, hexane) loses the "e" and picks up "ol" (hexanol).
- For cyclic alcohols, the OH group is understood to be attached to C-1.



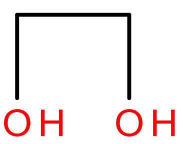
2-Methyl-2-butanol



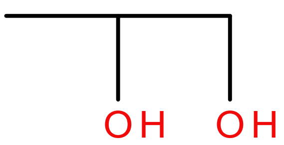
2-Methylcyclopentanol

Naming alcohols with more than one OH group

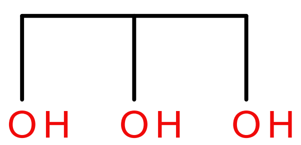
- Polyhydroxyl alcohols possess more than one OH group.
- Alcohols which possess two OH groups are called “diols” and those with three OH groups are called “triols”



1,2-Ethanediol



1,2-Propanediol



1,2,3-Propanetriol

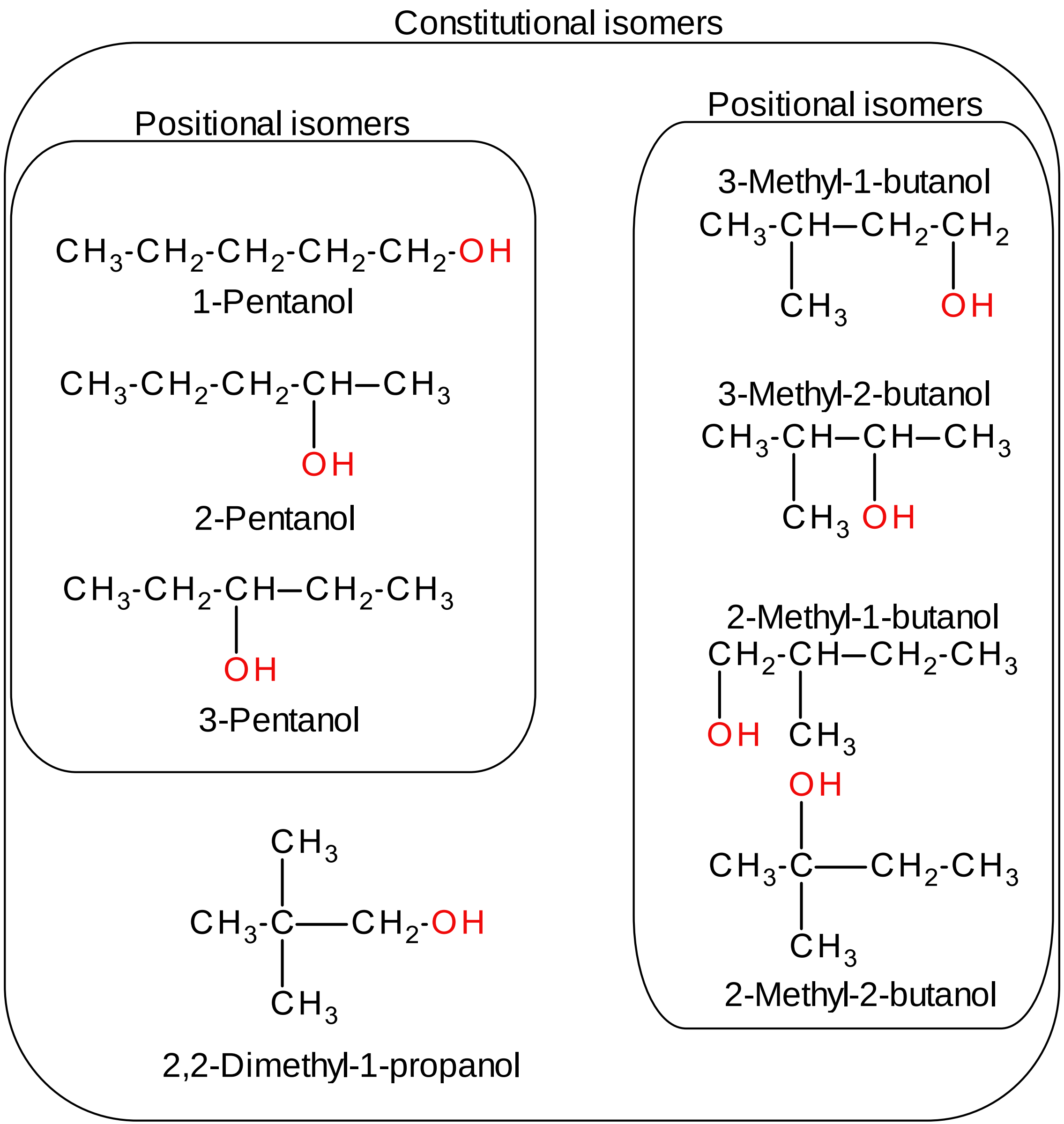
Alkane name + diol, “triol”, etc.

Isomerism

Formula	IUPAC Name	Common Name	
One carbon atom (CH_3OH)			CH_3OH
CH_3-OH	methanol	methyl alcohol	
Two carbon atoms (C_2H_5OH)			C_2H_5OH
CH_3-CH_2-OH	ethanol	ethyl alcohol	
Three carbon atoms (C_3H_7OH); two constitutional isomers exist			C_3H_7OH
$CH_3-CH_2-CH_2-OH$	1-propanol	propyl alcohol	
$CH_3-\underset{\underset{\displaystyle OH}{\vert}}{CH}-CH_3$	2-propanol	isopropyl alcohol	
Four carbon atoms (C_4H_9OH); four constitutional isomers exist			C_4H_9OH
$CH_3-CH_2-CH_2-CH_2-OH$	1-butanol	butyl alcohol	
$CH_3-\underset{\underset{\displaystyle CH_3}{\vert}}{CH}-CH_2-OH$	2-methyl-1-propanol	isobutyl alcohol	
$CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{\vert}}{CH}-OH$	2-butanol	*sec*-butyl alcohol	
$CH_3-\underset{\underset{\displaystyle CH_3}{\vert}}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}-OH$	2-methyl-2-propanol	*tert*-butyl alcohol	

Isomerism for alcohols

All have the formula $C_5H_{11}OH$

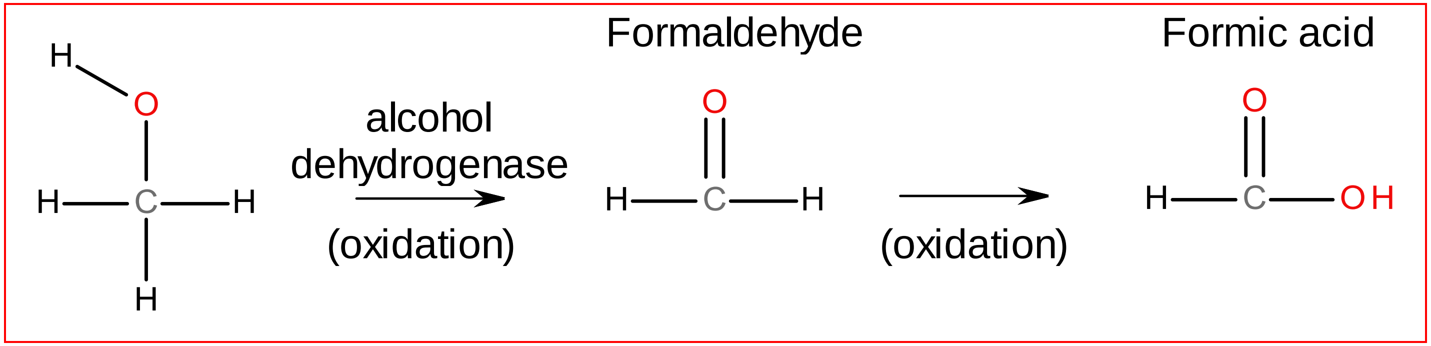


Commonly encountered alcohols

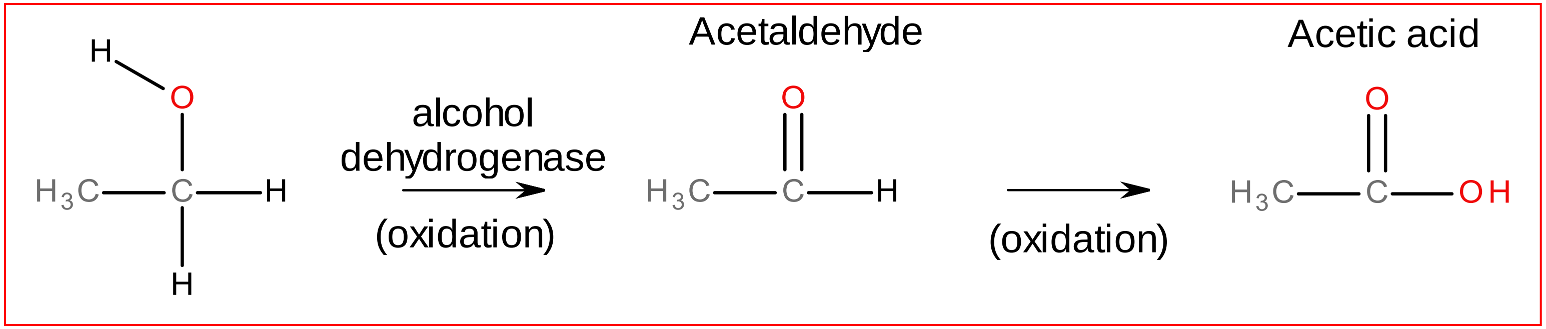
- You’ve probably used a few of the following alcohols:
  - Methyl alcohol — fuel
  - Ethyl alcohol — le booze
  - Isopropyl alcohol — rubbing alcohol
  - Ethylene glycol (1,2-Ethane diol) — antifreeze
  - Propylene glycol (1,2-Propane diol) — pharmaceuticals
  - Glycerol (1,2,3-Propane triol) — sweetner

Commonly encountered alcohols

- Drinking methanol is very bad for you. It is metabolized to formaldehyde and formic acid by the liver (alcohol dehydrogenase):



- Ethanol (CH_3CH_2OH) is also metabolized by the body, and this reaction produces acetaldehyde and acetic acid:

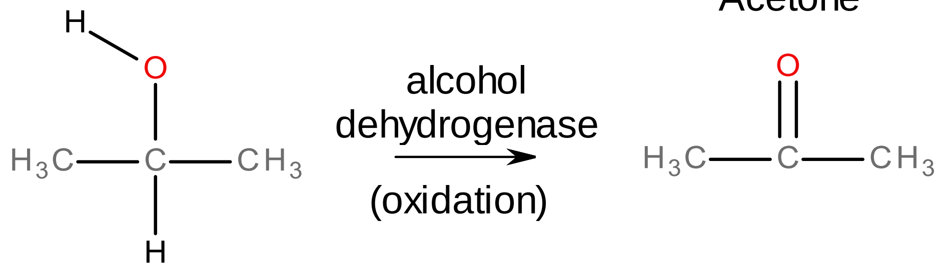


- Excessive drinking leads to liver cirrhosis, physiological addiction, loss of memory. Drinking during pregnancy poses risks for birth defects.

Commonly encountered alcohols

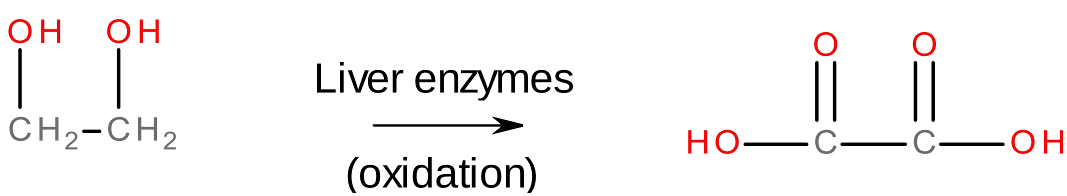
- Isopropyl alcohol is metabolized in the body to acetone:

Acetone



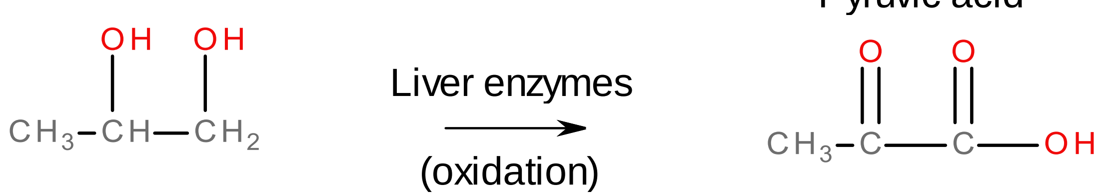
- Ethylene glycol is metabolized to oxalic acid, which causes renal problems:

Oxalic acid



- Propylene glycol is metabolized to pyruvic acid, which is non-toxic:

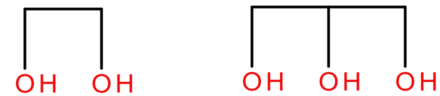
Pyruvic acid

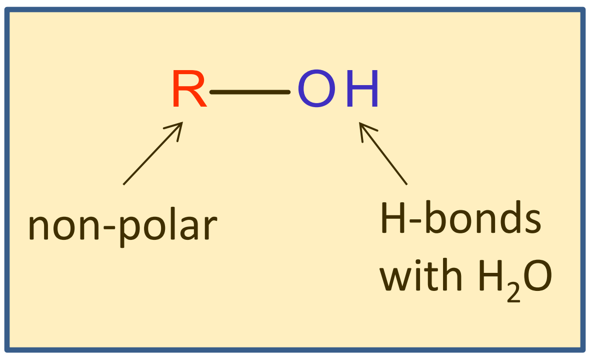


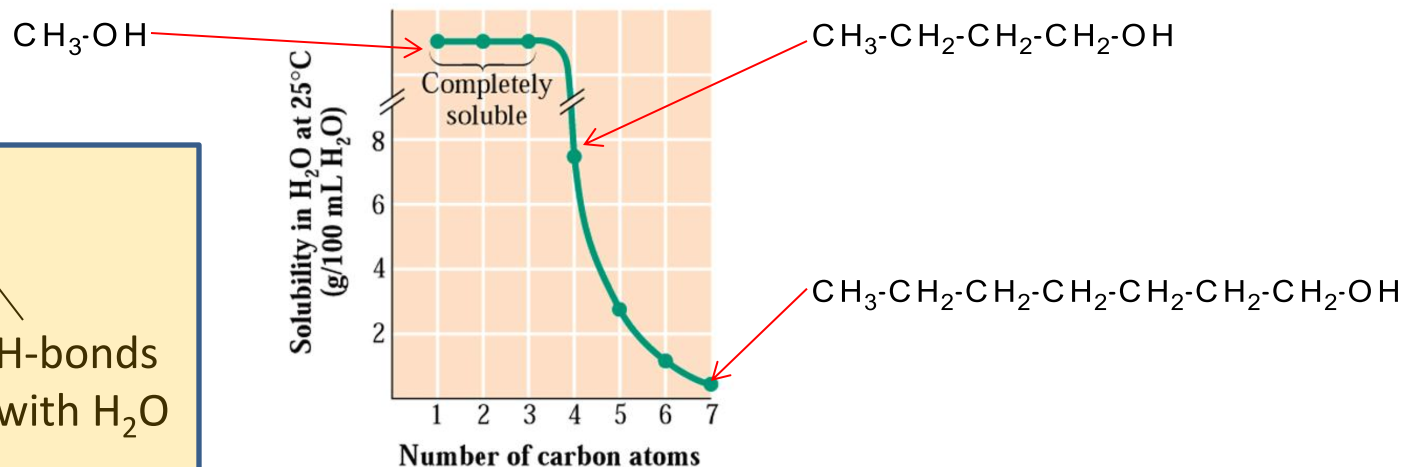
Physical properties of alcohols

Alcohol solubility

- Low molar mass alcohols are very water-soluble, because they can H-bond with water; heavier alcohols are less H_2O-soluble
- Polyhydroxyalcohols are <u>very</u> water soluble



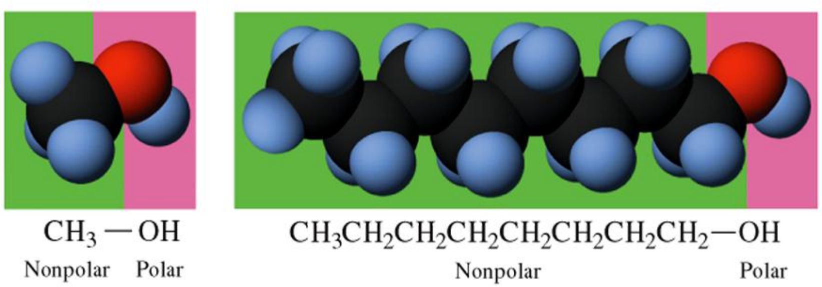




- As the C-chain component of an alcohol increases in size, water-solubility decreases
- As the number of OH groups on an alcohol increases, so does its water-solubility.

Physical properties of alcohols

- We already saw that the <u>boiling points</u> of alkanes increase with increasing chain length. The same is true for alcohols.
- Alcohols with more than one hydroxyl group (polyhydroxy alcohols) have higher boiling points than monoydroxy alcohols.



(a) Methanol **(b) 1- Octanol**

<u>Boiling points</u>

Ethane: **-89ºC** ← London forces

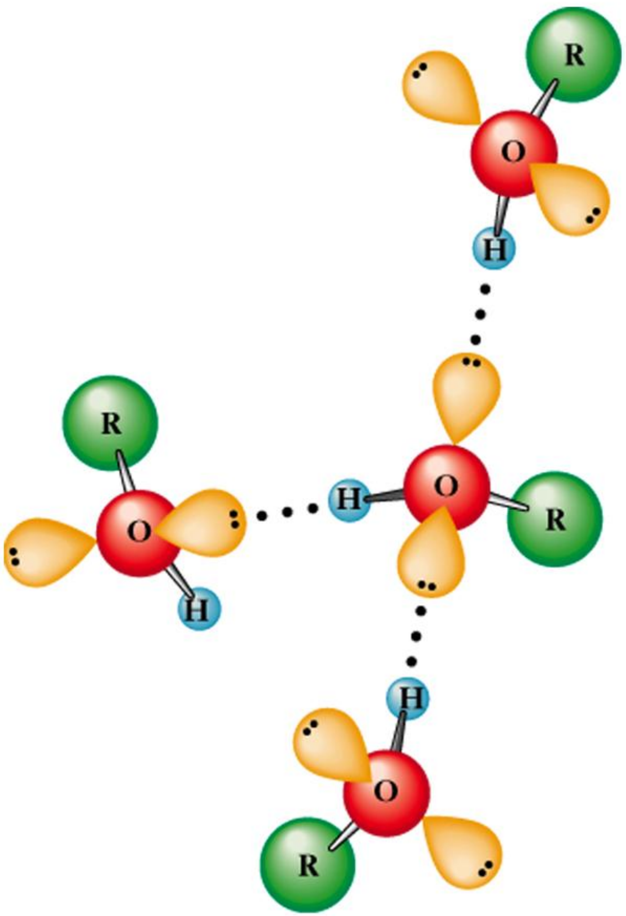
Methanol**: 65ºC** ← London + H-bonding

Ethanol: **78ºC** ← London + H-bonding

1,2-Ethane diol: **197ºC** ← London + more H-bonding

Physical properties of alcohols

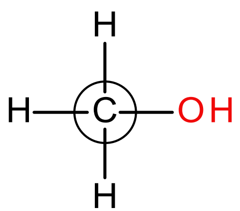
- Alcohols have higher boiling points than alkanes of the same chain length (because they hydrogen bond to each other; the intermolecular forces for alkanes are only London forces)
- Alcohols of a given chain length are far more water-soluble than alkanes.



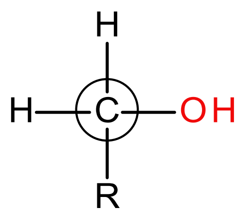
Remember: H-bonding is the strongest intermolecular force.
London forces are weak by comparison.

Classification of alcohols

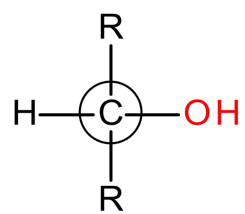
- Alcohols may be classified as 1°, 2°, or 3°, by considering the number of carbons *bound to the hydroxy-bearing <u>carbon</u>*.



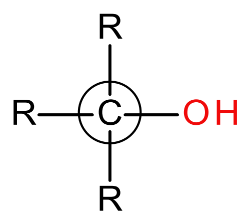
1° alcohol



1° alcohol



2° alcohol

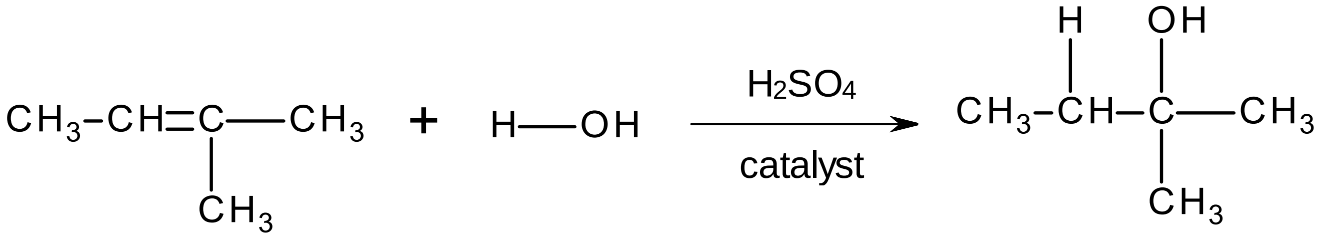


3° alcohol

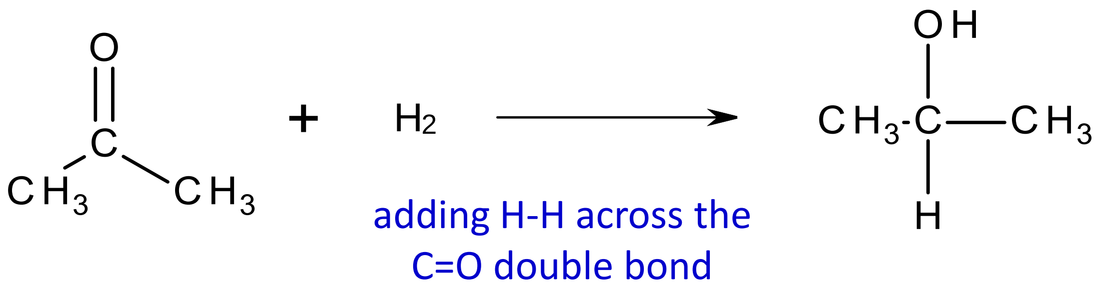
R = a saturated carbon group (e.g. alkyl substituent)

Preparation of alcohols

- Alcohols can be prepared by hydration of alkenes (as we saw in Chapter-13):



- They can also be prepared by the hydrogenation of C-O double bonds:



(Hydrogenation of this double bond is equivalent to a reduction in organic chemistry)

Chemical reactions of alcohols

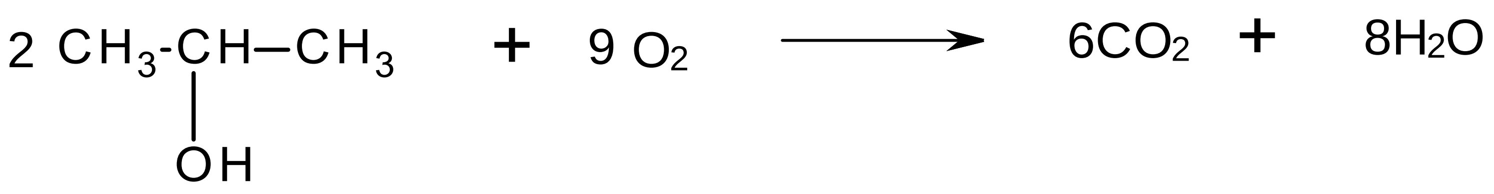
- Combustion – makes CO_2 and H_2O
- Dehydration (loss of water – intramolecular) – make an alkene
- Dehydration (loss of water – intermolecular) – makes an ether (not covered)
- Oxidation – makes aldehyde/ketone/carboxylic acid
- Halogenation – makes a halogenated alkane (not covered)

Chemical reactions of alcohols

Combustion reactions

- Any organic molecule can undergo a combustion reaction. In combustion reactions involving alcohols, CO_2 and H_2O are produced:
  - $CH_3OH + O_2 \rightarrow CO_2 + 2H_2O$
  - $CH_3CH_2OH + O_2 \rightarrow 2CO_2 + 3H_2O$

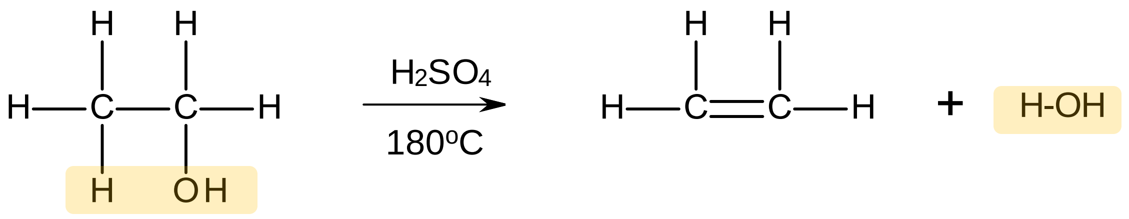
Or, for 2-Propanol:

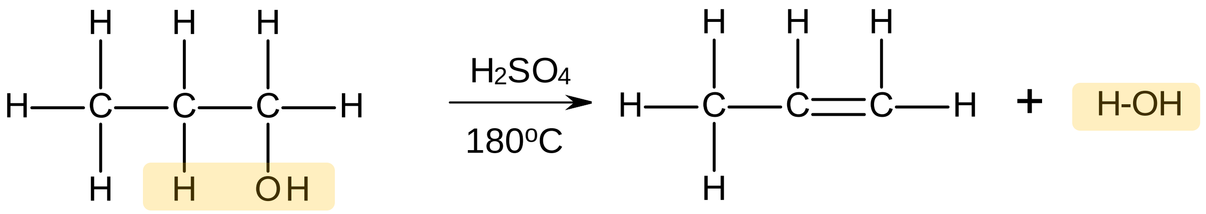


Chemical reactions of alcohols

Elimination reactions

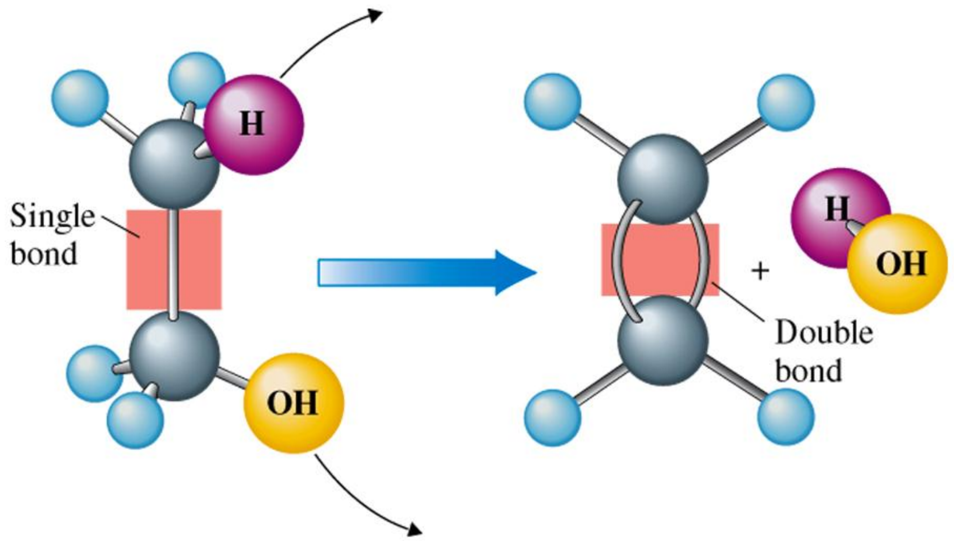
- In an intramolecular alcohol dehydration, a water molecule is lost (eliminated) from a single alcohol molecule.
- The elimination involved loss of the OH group and a H-atom from an adjacent C-atom (sometimes, there's more than one of these)





Chemical reactions of alcohols

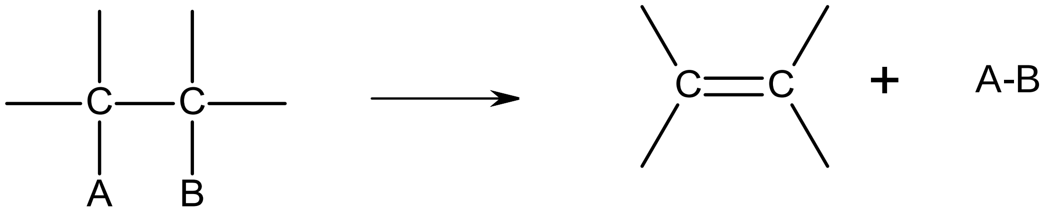
Elimination reactions



Chemical reactions of alcohols

Elimination reactions

- *In general*, these kinds of reactions (eliminations) proceed as follows:



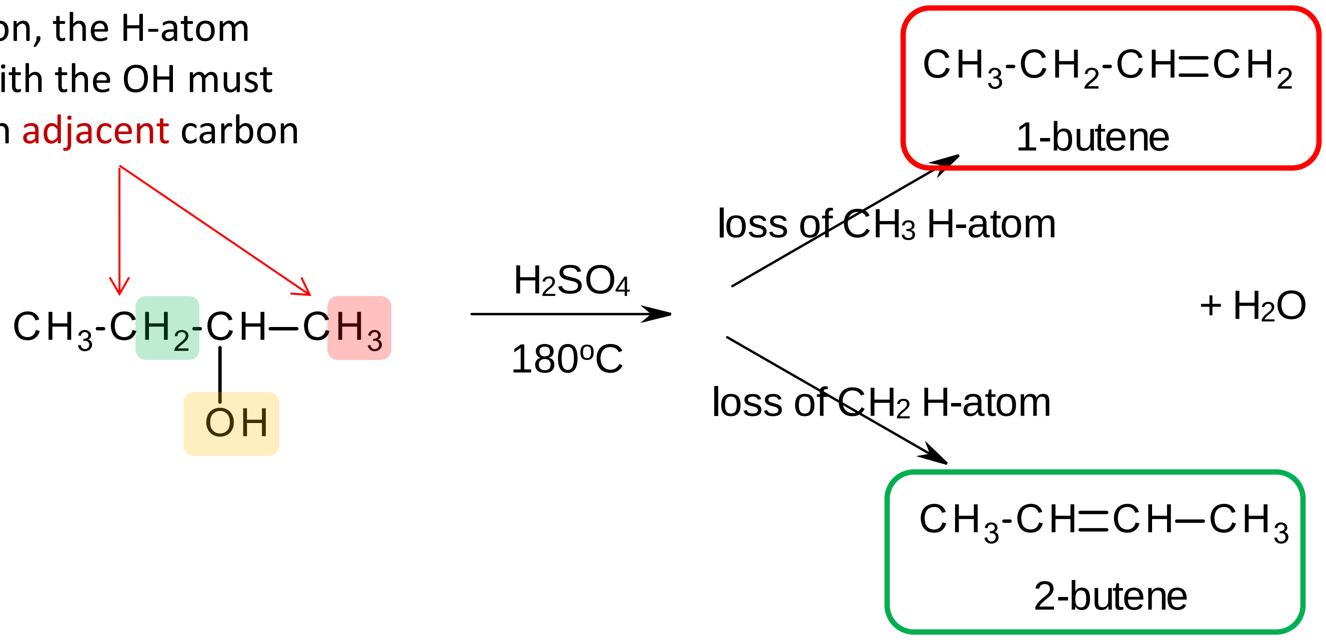
Two atoms (or groups of atoms) on neighboring carbons are removed, leaving a multiple bond between these carbon atoms

Chemical reactions of alcohols

Elimination reactions

- If there is more than one adjacent carbon atom from which loss of a H-atom can occur, there will be more than one possible alkene dehydration product:

For elimination, the H-atom that leaves with the OH must come from an adjacent carbon

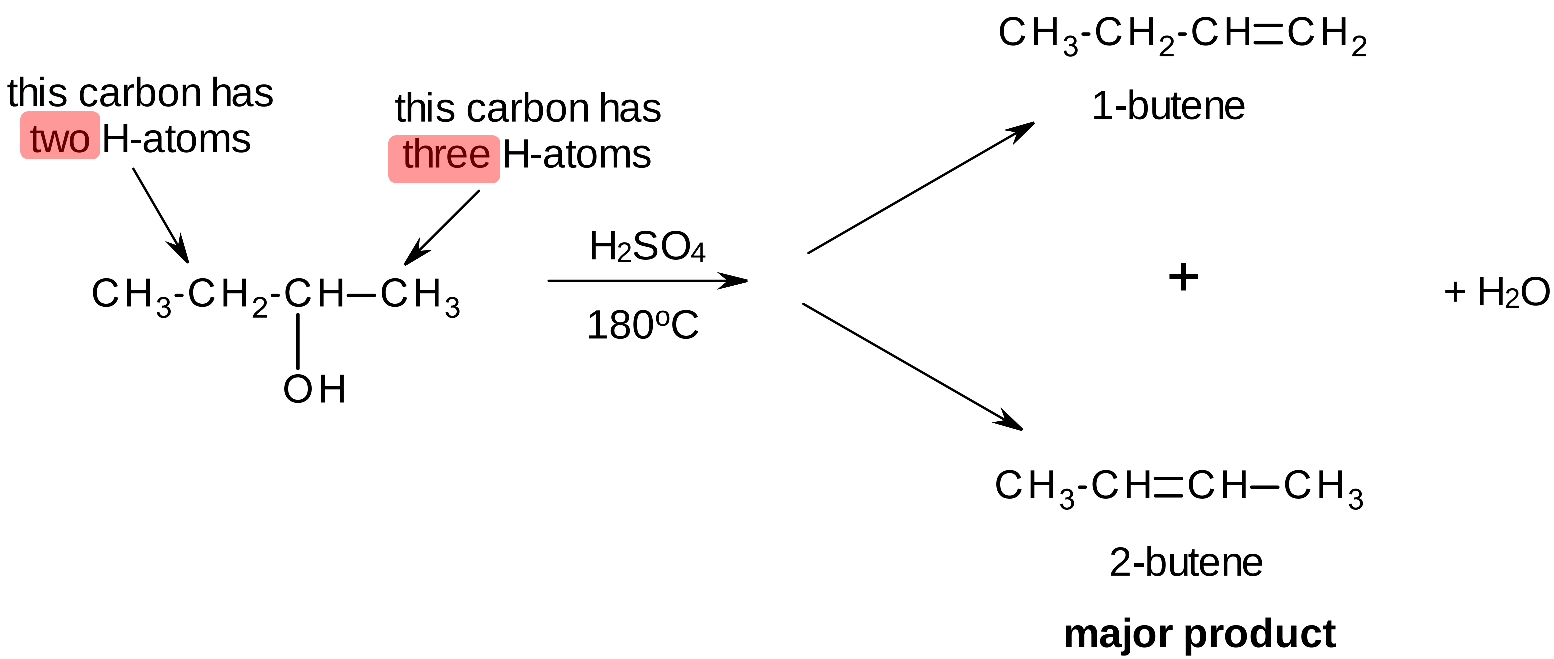


Use Zaitsev's Rule to predict which alkene will be produced in the greater amount

Chemical reactions of alcohols

Elimination reactions

- **Zaitsev’s Rule** (for alcohol dehydrations): for cases where more than one alkene product might be formed from an elimination reaction, the <u>hydrogen atom tends to be removed from the carbon that already possesses the *fewest* hydrogens</u>.



Chemical reactions of alcohols

- Example 14.3, pg. 414: identify the alcohol needed to produce each of the following alcohol dehydration products:

$$\text{alcohol} \xrightarrow[180^{o}C]{H_2SO_4} CH_3\text{-}CH{=}CH{-}CH_3$$

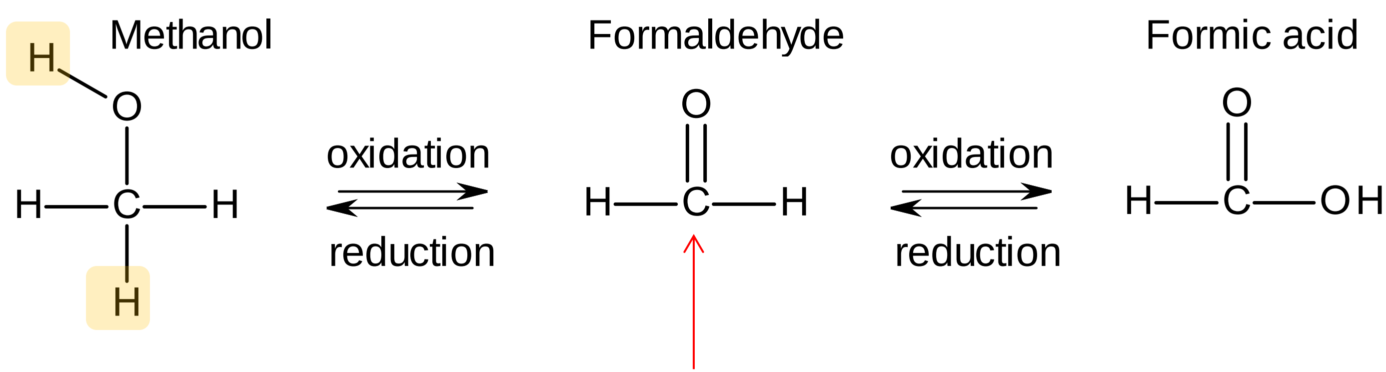
$$\text{alcohol} \xrightarrow[180^{o}C]{H_2SO_4} \begin{array}{l} CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_2\text{-}CH_3 \end{array}$$

Chemical reactions of alcohols

Oxidation reactions

- Oxidation/reduction reactions involving organic compounds result in a change in the number of H-atoms and/or the number of O-atoms bound to carbons in the molecule:
  - **Oxidations** increase the number of C-O bonds and/or decrease the number of C-H bonds in a molecule.
  - **Reductions** decrease the number of C-O bonds and/or increase the number of C-H bonds in a molecule.

Opposing reactions



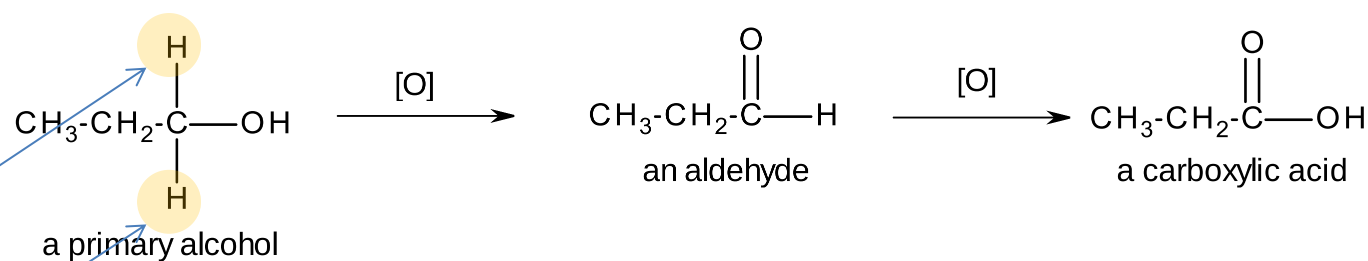
In order to increase # of C-O bonds here, a new O must be added

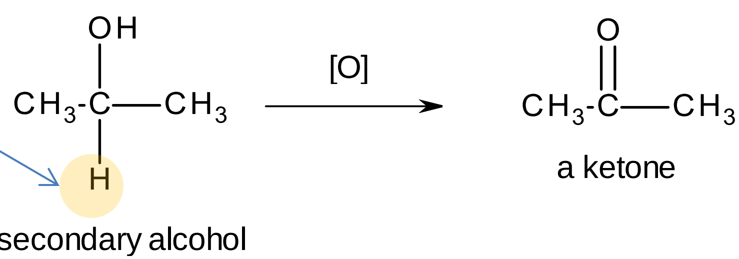
Chemical reactions of alcohols

Oxidation reactions

- Primary and secondary alcohols can be oxidized by mild oxidizing agents to produce compounds with C-O double bonds (aldehydes, ketones, carboxylic acids).

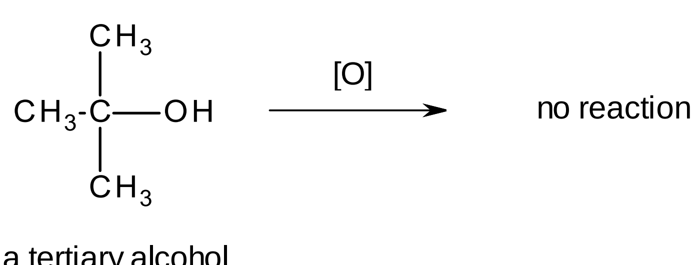
During oxidation, # of C-O bonds increases and # of C-H bonds decreases





mild oxidizing agent = [O]

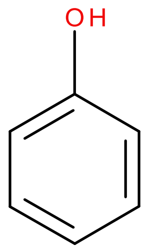
Tertiary alcohols can't be oxidized



No H on OH-bearing carbon to remove here. Can't be oxidized.

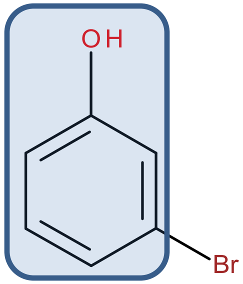
Structural characteristics of phenols

- Phenols are aromatic compounds that bear a OH group.

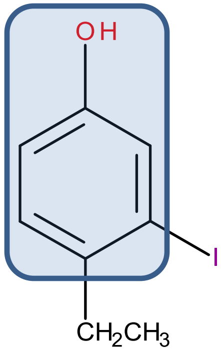


"phenol" = phenyl alcohol

- This is another "special case" compound as far as IUPAC naming goes. Hydroxyl groups have higher priority than CH_3 groups (or others we've seen so far) for ring-numbering.



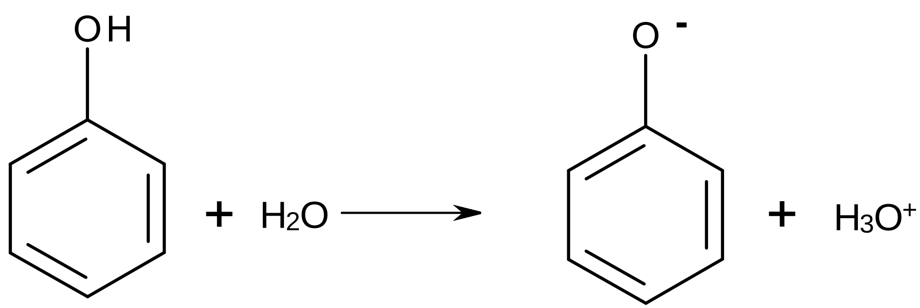
3-Bromophenol



4-Ethyl-3-iodophenol

Physical and chemical properties of phenols

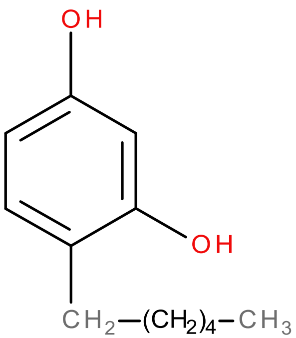
- Phenols are <u>weak acids</u> in water. They undergo deprotonation, as discussed in Ch-10:



$$\boxed{HA \quad + \quad H_2O \rightarrow \quad A^- \quad + \quad H_3O^+}$$

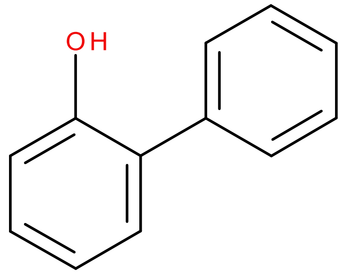
$K_a = 1.1 \times 10^{-10}$

Occurrence and uses of phenols

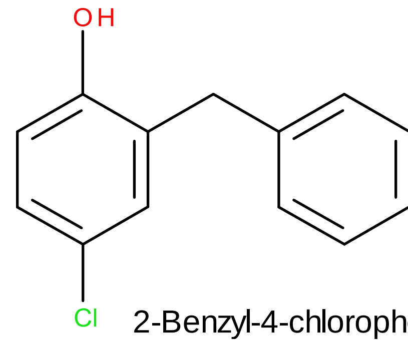


4-Hexylresorcinol

an antiseptic

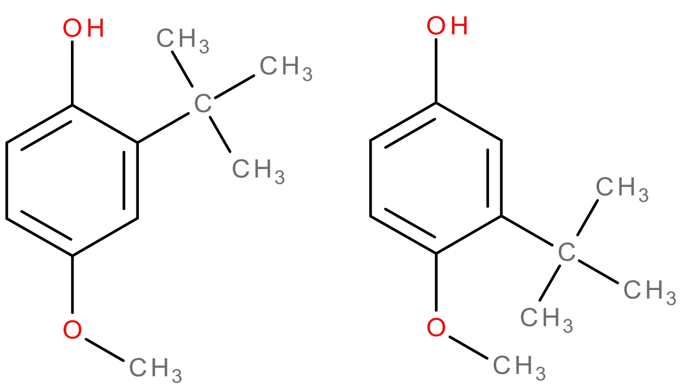


2-Phenylphenol

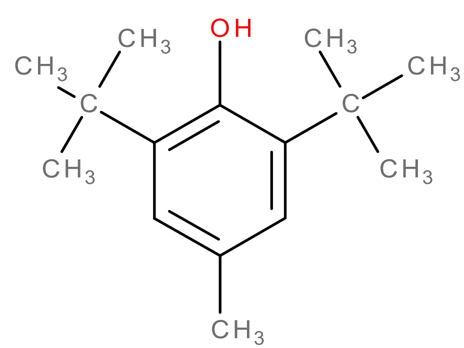


2-Benzyl-4-chlorophenol

disinfectants



BHAs (butylated hydroxyanilines)



BHT
(butylated hydroxytoluene)

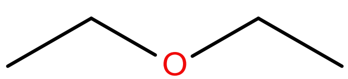
antioxidants

Nomenclature for ethers

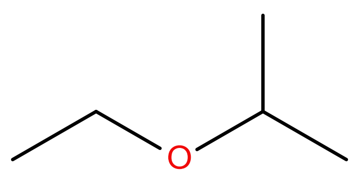
- **Ethers** are organic compounds in which two saturated carbon atoms are bound through a single oxygen atom.

$$R-O-R'$$

- Examples:



Diethyl ether



Ethyl isopropyl ether

$CH_3-O-CH_2-CH_2-CH_3$

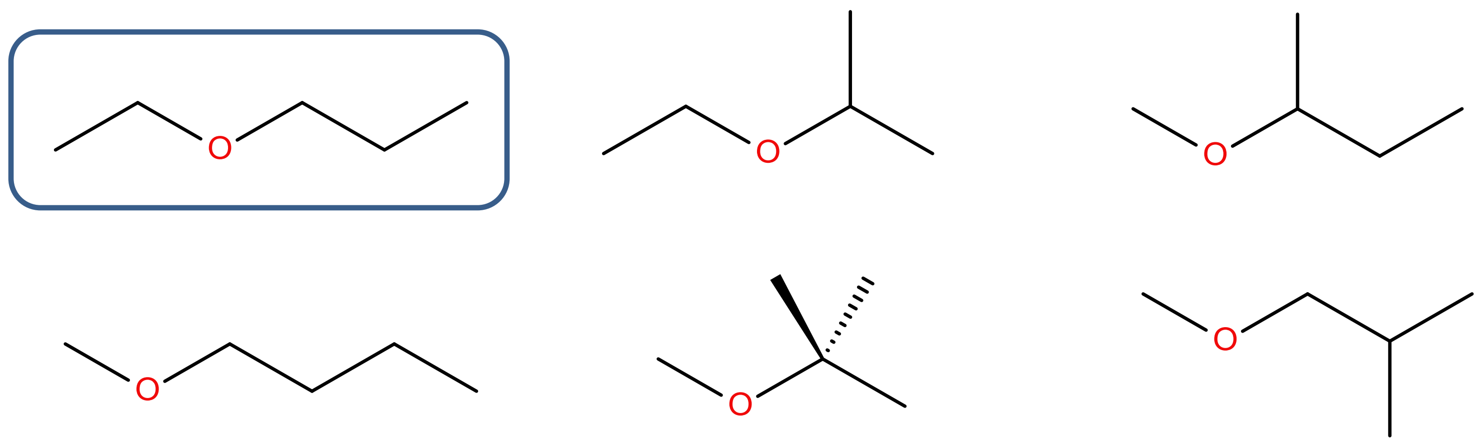
Methyl propyl ether

common names

Isomerism in ethers

- Because ethers contain C, H, and O atoms, the possibilities for isomers is greater than for hydrocarbons.
- For example, ethyl propyl ether will have the following constitutional isomers:

$C_5H_{12}O$

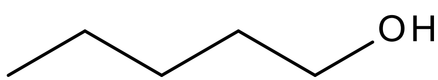


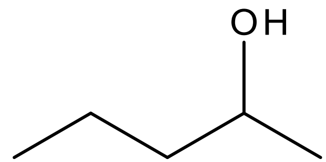
These constitutional isomer structures are all *skeletal* isomers

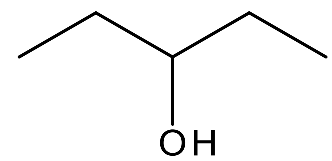
Remember: all isomers have the same molecular formula, **but**
Positional isomers have the same C-skeleton, different placement of functional group
Skeletal isomers have different C-skeletons

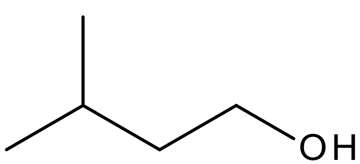
Isomerism in ethers

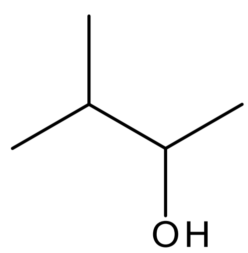
- …and then the following **functional group isomers** (ethers and alcohols having the same number of C-atoms are functional group isomers).

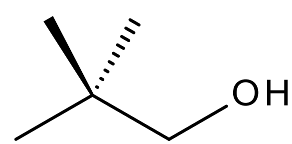


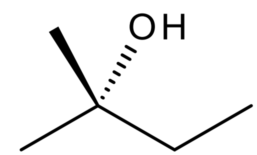








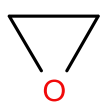




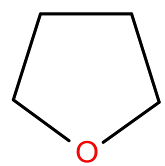
Functional group isomers: constitutional isomers that contain different functional groups

Cyclic ethers

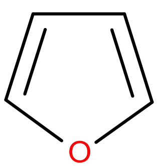
- Cyclic ethers are similar to cycloalkanes/cycloalkenes, but possess an O- atom as part of the ring.
- Cyclic organic compounds in which one or more carbon atoms of the ring have been replaced by atoms of other elements are called heterocyclic organic compounds.



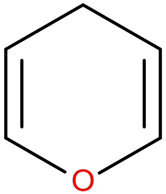
Ethylene oxide



Tetrahydrofuran (THF)



Furan



Pyran

Don’t memorize these names – just be able to recognize that they are ethers.

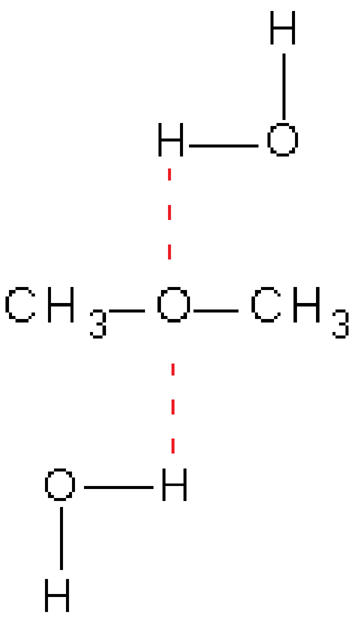
Physical and chemical properties of ethers

- Boiling points and melting points are dictated by intermolecular forces.
- Compared with alkanes of similar molar mass, an ether will have a similar boiling point.
- Compared to an alcohol of the same molar mass, the ether will have a much lower boiling point.

			Intermolecular force
alkane	CH_3-CH_2-CH_2-CH_2-CH_3	MM = 72 g/mol b.p. = 36°C	London forces
ether	CH_3-CH_2—O—CH_2-CH_3	MM = 74 g/mol b.p. = 35°C	London forces
alcohol	CH_3-CH_2-CH_2-CH_2-OH	MM = 74 g/mol b.p. = 117°C	London forces + H-bonding

Physical and chemical properties of ethers

- Ethers are more water-soluble than alkanes, because water molecules can H-bond with them.
- An ether and an alcohol of the same molar mass have about the same solubility in water.
- Some important chemical properties of ethers:
  - Ethers are **highly flammable**. The b.p. of diethyl ether is 35^{o}C and ether vapor ignites readily.



Water molecules H-bonding to an ether molecule