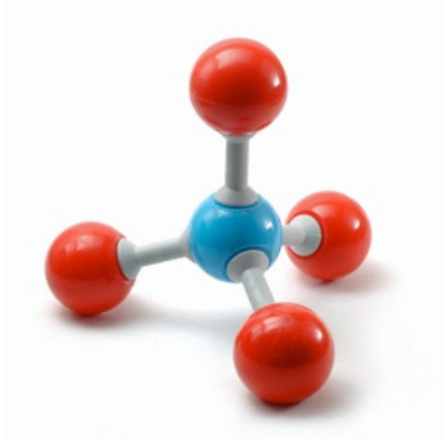
Ch09

Functional Groups

Building new utility onto carbon skeletons.

With small groups of atoms, featuring oxygen & sulfur.

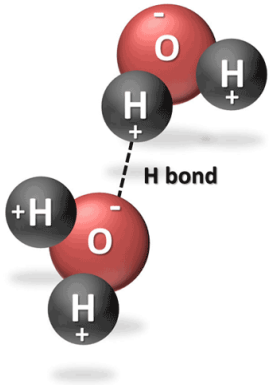


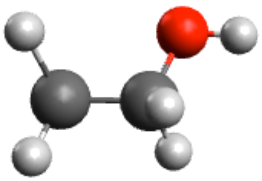
version 1.0

Ch09

Functional Groups

- What is a functional group?
  - Atoms responsible for utility
  - Starting with OXYGEN & SULFUR
    - The hydroxy group
- Alcohols
  - Structure
  - Properties
    - Hydrogen bonding
    - Solubility, m.p., b.p.
  - Sub classes
    - Primary, secondary or tertiary
- Naming Alcohols
  - Common names
  - IUPAC names
    - As a family
    - As a substituent





- Phenols & Thiols
  - Structure
    - Sulfur is like oxygen
  - Taste & Smell
  - Properties
    - Thiols: Harsh odors, bitter taste
    - Phenols: Pleasant odors, sweet taste
      - Antiseptics, & disinfectants
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- Ethers
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    - Doubling up on oxygen
    - Anesthetics
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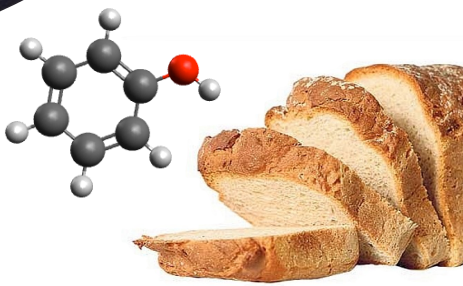

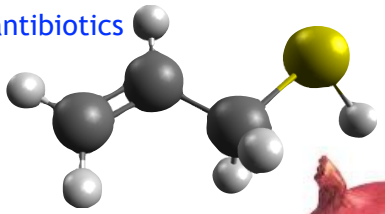

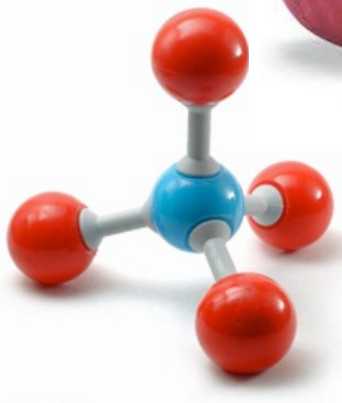

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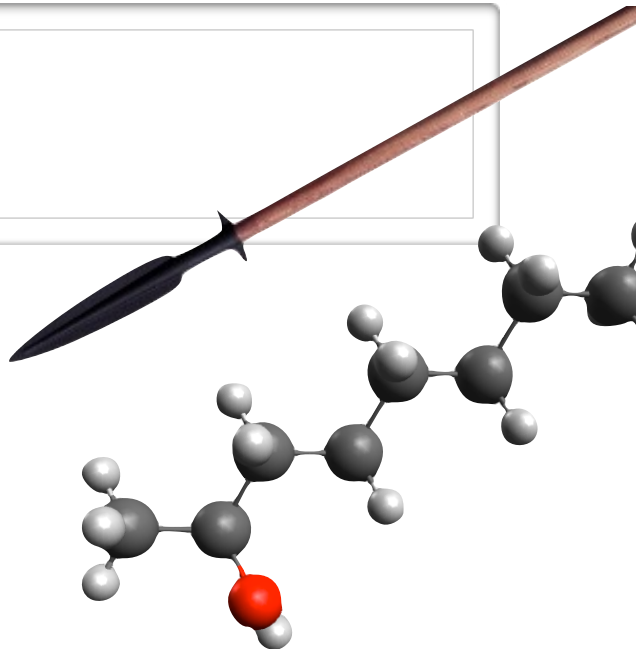
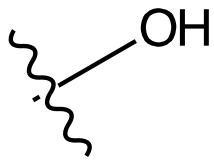
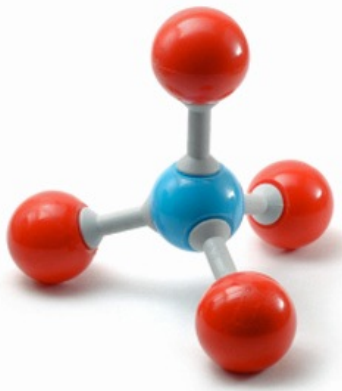


- Groups of atoms attached to hydrocarbons provide molecules with defining utility.
- Like a bronze head on a spear or a steel hook on the end of a fishing line, these small additions entirely change the function of the molecules that contain them.
- These groups are responsible for types of molecules having unique, powerful and predictable properties.
- A functional group is a group of atoms responsible for the characteristic reactions of a class (family) of compound.
  - The addition of these groups to a carbon structure defines it's chemical family.
- The first functional groups we'll discuss get their utility from incorporating OXYGEN & SULFUR atoms in unique ways.
- The first functional group we'll consider is the hydroxyl group.
  - Hydroxyl groups are one hydrogen paired with one oxygen atom (symbolized as -OH).
- Alkanes with hydroxyl groups are alcohols (alcohol family).
- Aromatics with hydroxyl groups are phenols (phenol family).





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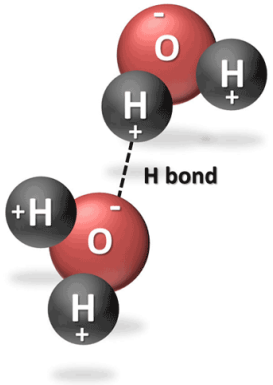

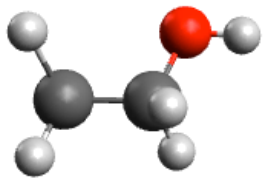

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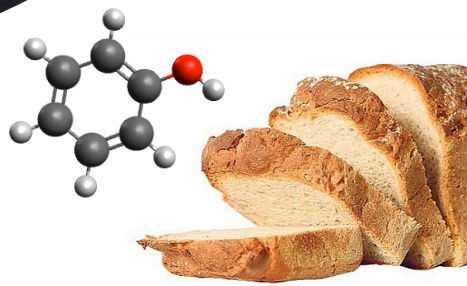
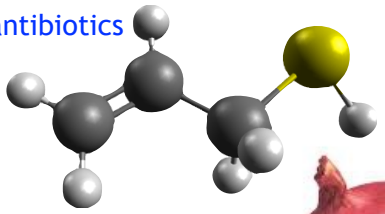
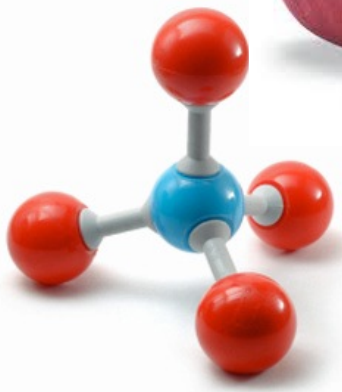
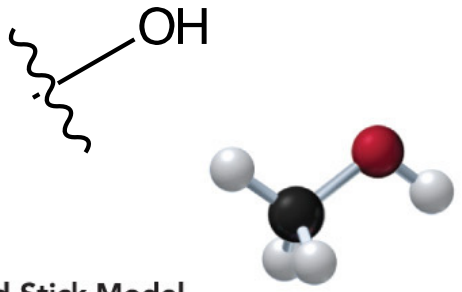






Alcohols

- Any compound which has a hydroxy group attached to it's backbone is a member of the class of compounds known as alcohols.
- The presence of the hydroxy functional group changes the chemical and physical properties of the substance.



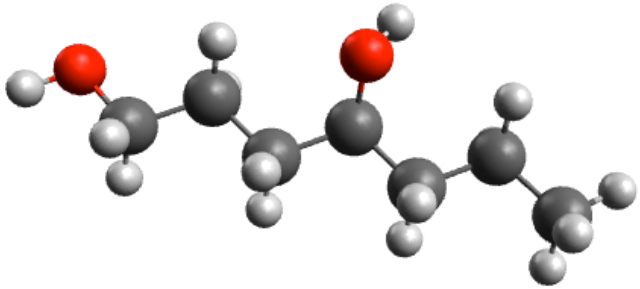
Ball-and-Stick Model

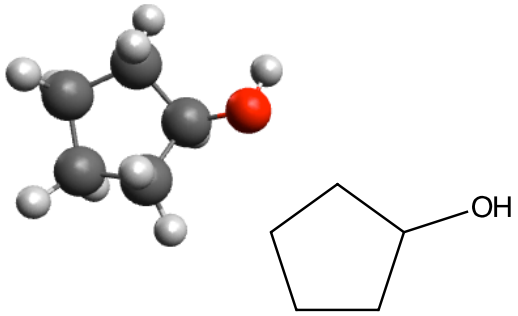
Condensed Structural Formula: CH_3OH

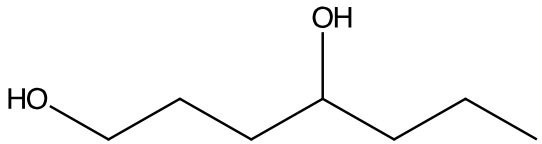
IUPAC Name: Methanol

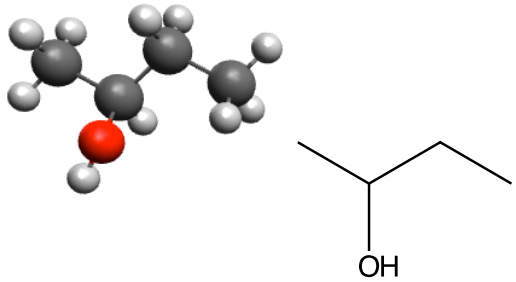
Family: Alcohol

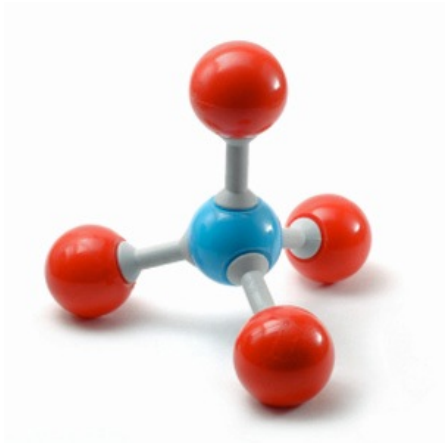
Functional Group: —OH





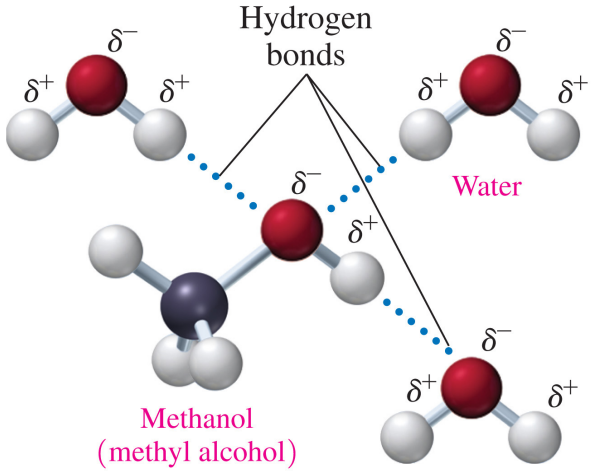


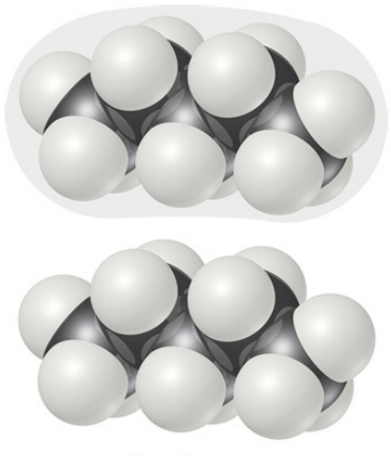


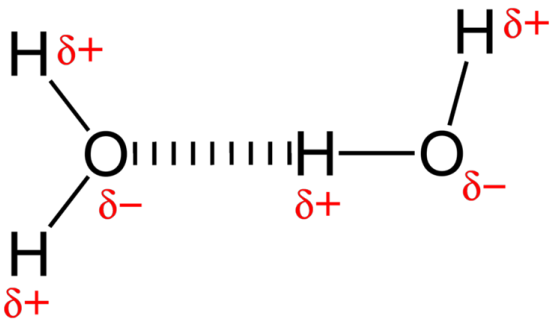


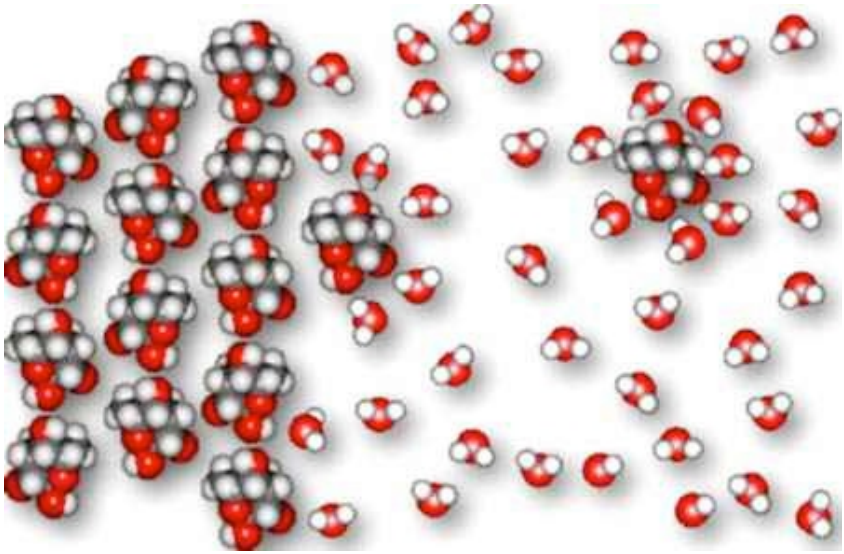
Properties of Alcohols

- Most hydrocarbons are not soluble in water.
- Hydrocarbons stick to each other primarily with non-polar London dispersion forces.
- Water molecules stick to each other primarily with hydrogen bonds.
- Nothing is gained by breaking those intermolecular binding forces to mix water and hydrocarbons.
- Because of the hydroxy functional group alcohols can take part in both kinds of intermolecular forces.
- Many alcohols are soluble in water.



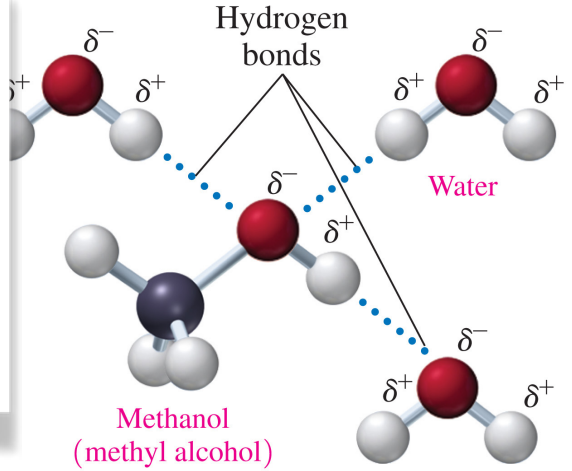




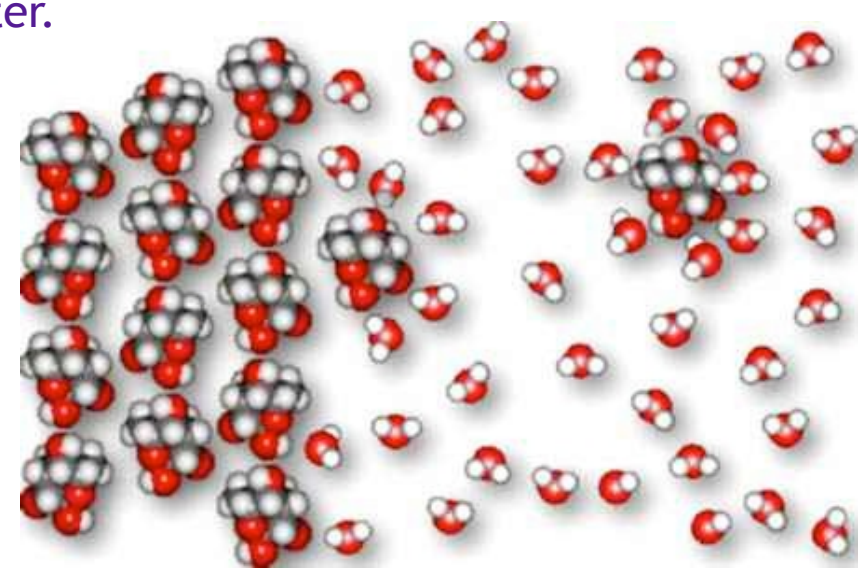


Properties of Alcohols

Compound	Condensed Structural Formula	Number of Carbon Atoms	Solubility in Water
Methanol	$CH_3—OH$	1	Soluble
Ethanol	$CH_3—CH_2—OH$	2	Soluble
1-Propanol	$CH_3—CH_2—CH_2—OH$	3	Soluble
1-Butanol	$CH_3—CH_2—CH_2—CH_2—OH$	4	Slightly soluble
1-Pentanol	$CH_3—CH_2—CH_2—CH_2—CH_2—OH$	5	Insoluble



- Because of the hydroxy functional group alcohols can take part in both kinds of intermolecular forces.
- Many alcohols are soluble in water.
- Alcohols with 1-3 carbons are infinitely soluble in water.
- Simple alcohols with more than 5 carbons are insoluble in water.
- Without water around, alcohols can hydrogen bond each other, increasing their intermolecular forces.
- Hydrogen bonding in alcohols increases the alcohols boiling point and melting point.



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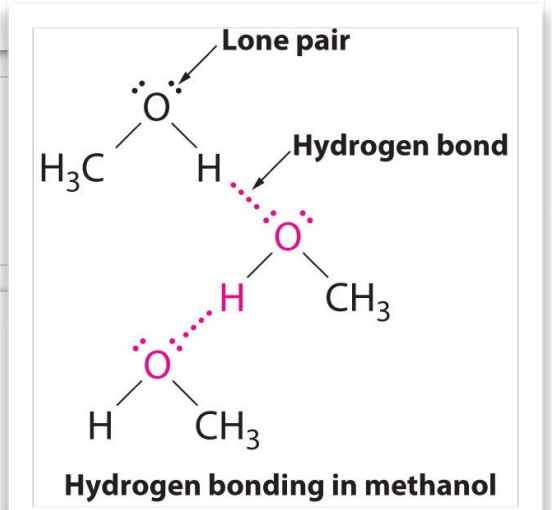
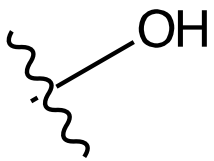
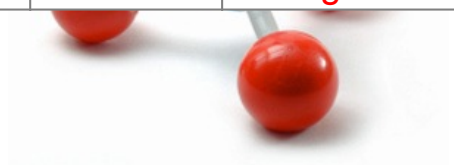


Hydrogen bonding in methanol

- The hydroxyl functional group changes many physical properties.
  - Solubility increases.
  - Boiling point increases.
  - Melting point increases.
- We'll see later that alcohols can undergo some chemical reactions *only* because they have the hydroxyl functional group.
- The hydroxyl functional group changes many chemical properties.
- This small group of atoms, fundamentally and predictably changes the function of the substances we call alcohols.

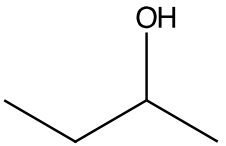


Compound	IUPAC Name	Melting Point (°C)	Boiling Point (°C)	Solubility in H_2O at 23°C
CH_3OH	Methanol	-97.8	65.0	Infinite
CH_3Cl	Chloromethane	-97.7	-24.2	0.74 g/100 mL
CH_4	Methane	-182.5	-161.7	3.5 mL (gas)/ 100 mL
CH_3CH_2OH	Ethanol	-114.7	78.5	Infinite
CH_3CH_2Cl	Chloroethane	-136.4	12.3	0.447 g/100 mL
CH_3CH_3	Ethane	-183.3	-88.6	4.7 mL (gas)/ 100 mL
$CH_3CH_2CH_2OH$	1-Propanol	-126.5	97.4	Infinite
$CH_3CH_2CH_3$	Propane	-187.7	-42.1	6.5 mL (gas)/ 100 mL
$CH_3CH_2CH_2CH_2OH$	1-Butanol	-89.5	117.3	8.0 g/100 mL
$CH_3(CH_2)_4OH$	1-Pentanol	-79	138	2.2 g/100 mL



Predicting Properties of Alcohols

- Which of the following is more soluble in water?



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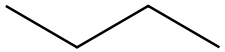

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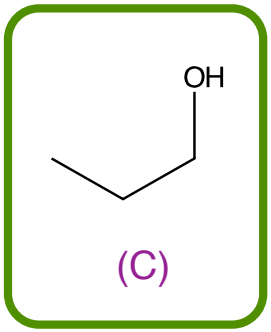

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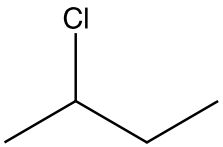
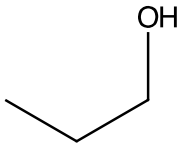


(D)

- Which of the following is most likely to be a solid at room temperature?



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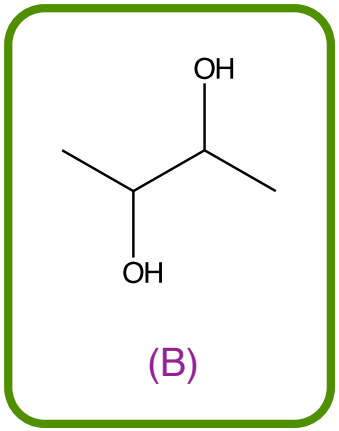

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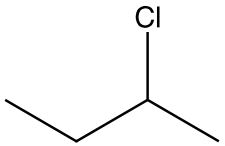

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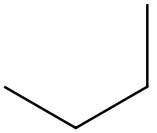

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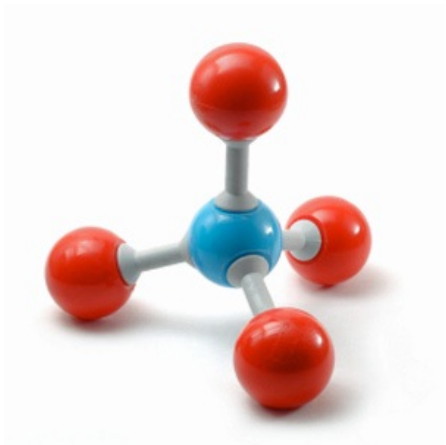
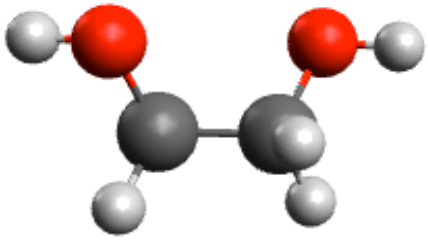
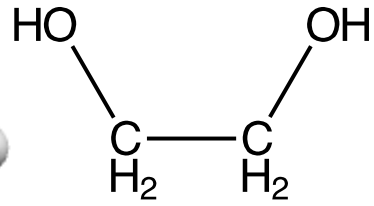


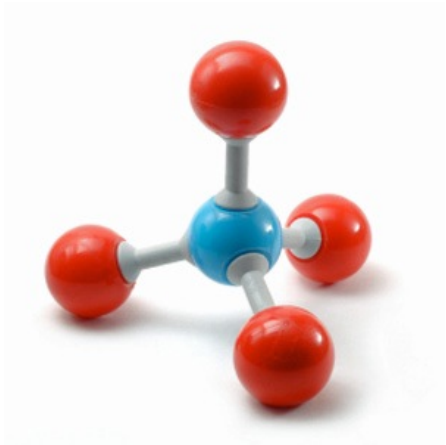
Applying the Properties of Alcohols

- We take advantage of two properties of alcohols to change the freezing point of water mixtures in our cold weather cars.
  - That alcohols have freezing points between that of pure hydrocarbons and water.
  - That alcohols have solubility in water.

- This allows us to “tune” to the freezing point of water mixtures by adding in the alcohol 1,2 ethane diol (also known as ethylene glycol or “antifreeze.”

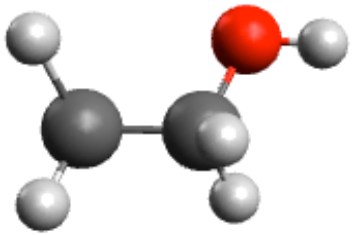


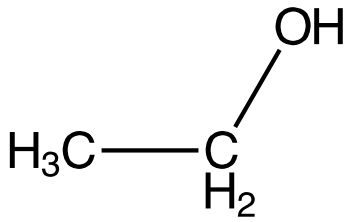


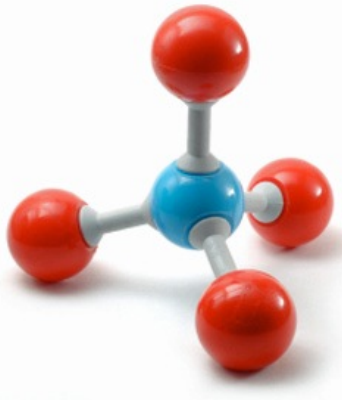


Applying the Properties of Alcohols

- Biological systems can get fooled by the structure of small alcohols.
- They can try absorb them, and use them like water.
  - But they don't quite work.
- This toxicity makes alcohols good disinfectants.
  - … and allows for other uses.







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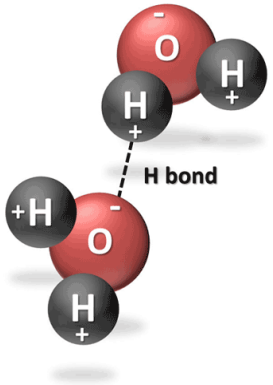

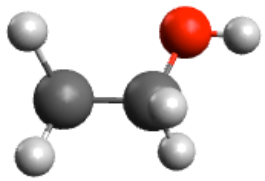

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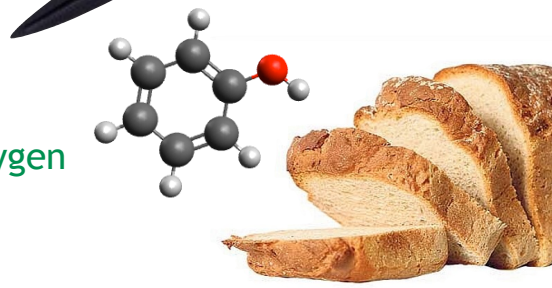
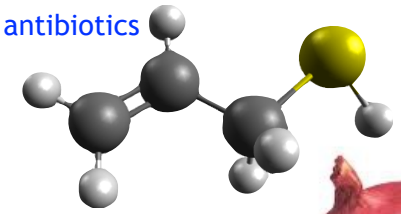
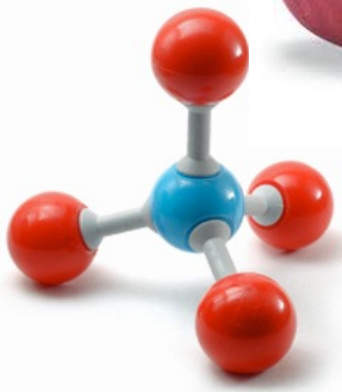
    - Anesthetics
  - Naming

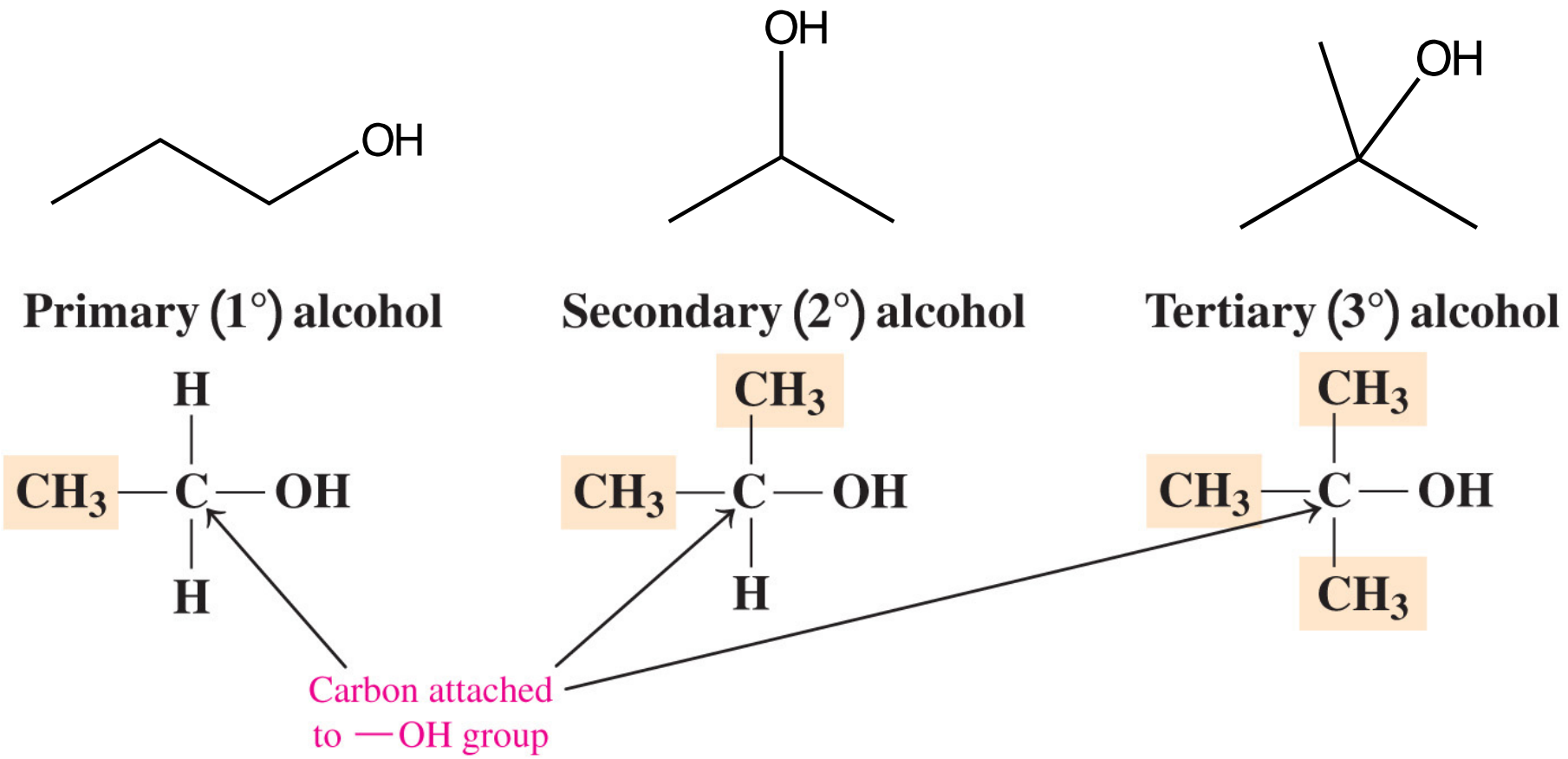






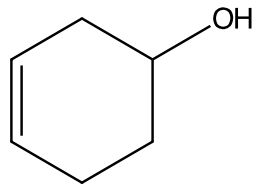
Subclasses of Alcohols

- The alcohol family is further sub classified by the number of alkyl groups attached to the carbon atom holding the hydroxyl group.
  - We'll see later that these subclasses of alcohol have very different chemical properties.
  - Some reactions that work for a primary alcohol do nothing to a tertiary alcohol.

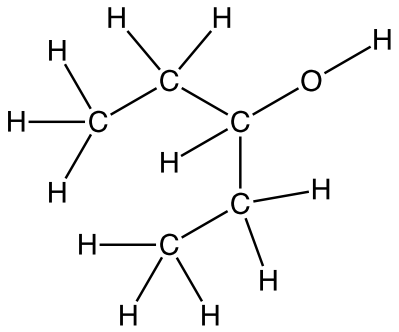


Subclasses of Alcohols

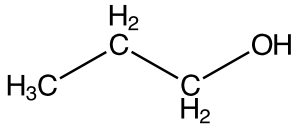
- Classify Each Alcohol as primary (1˚), secondary (2˚), or tertiary (3˚).



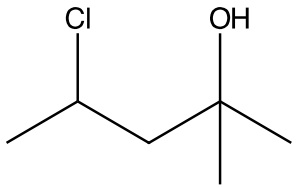
Secondary (2˚)



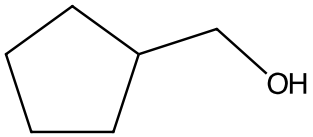
Secondary (2˚)



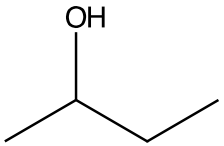
Primary (1˚)



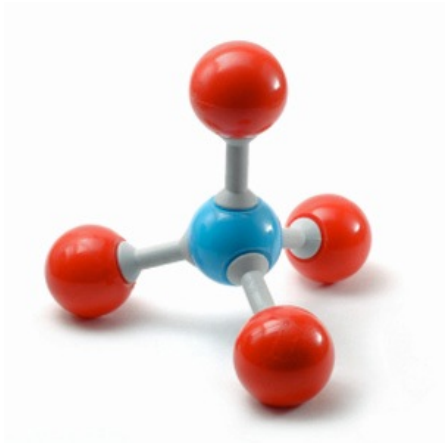
Tertiary (3˚)



Primary (1˚)

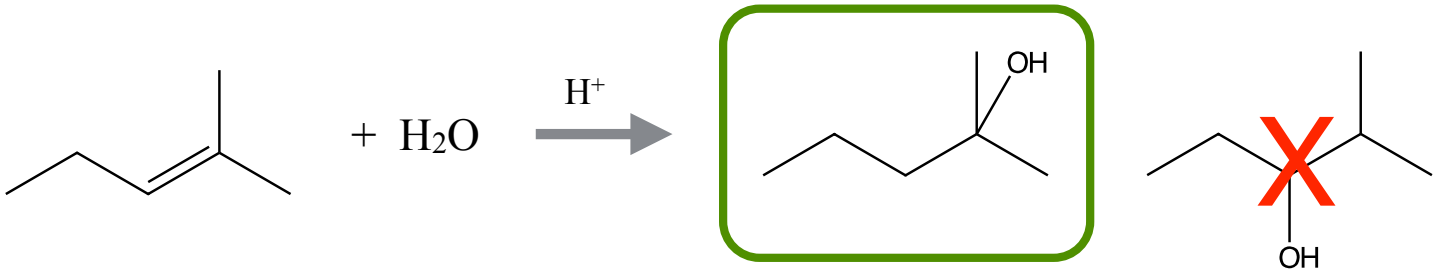


Secondary (2˚)

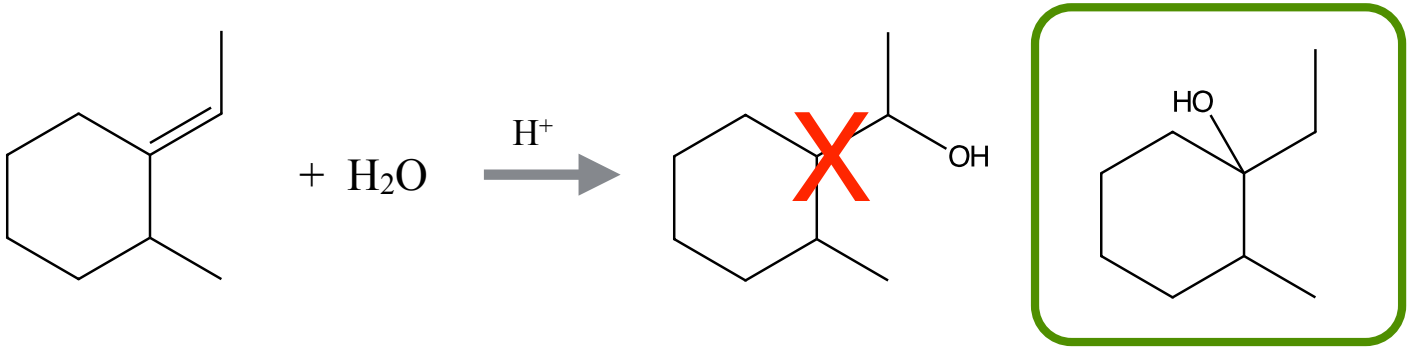


Subclasses of Alcohols

- You know water can be added across a double bond, to create an alcohol. As long as you have some acid to catalyze the reaction.
- If the two atoms of the double bond have different substitution, does this reaction prefer to form a secondary or tertiary alcohol?



Tertiary (3˚) Secondary (2˚)

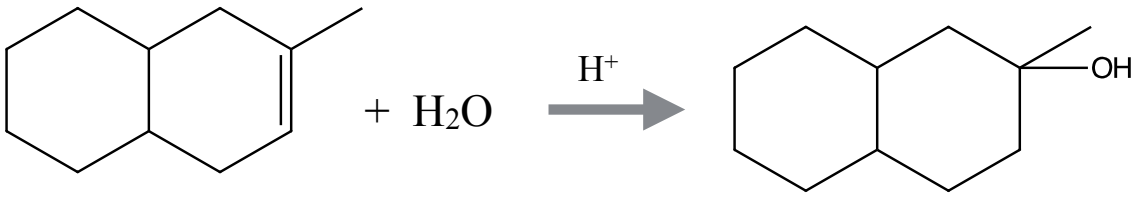


Secondary (2˚) Tertiary (3˚)

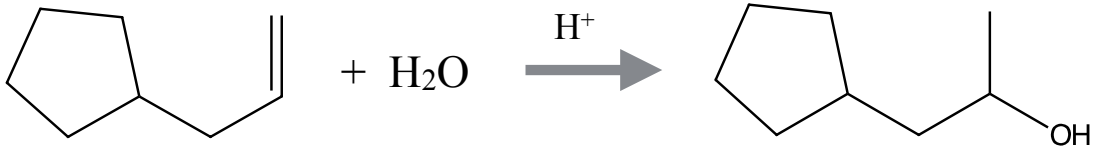
Acid + Water prefers to form $3^\circ > 2^\circ > 1^\circ$ Alcohols from double bonds.

Subclasses of Alcohols

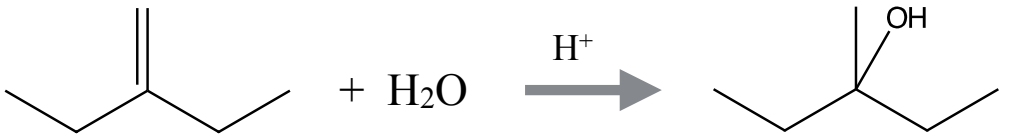
- Predict Which alcohol forms. Indicate whether it's a primary, secondary, or tertiary alcohol.



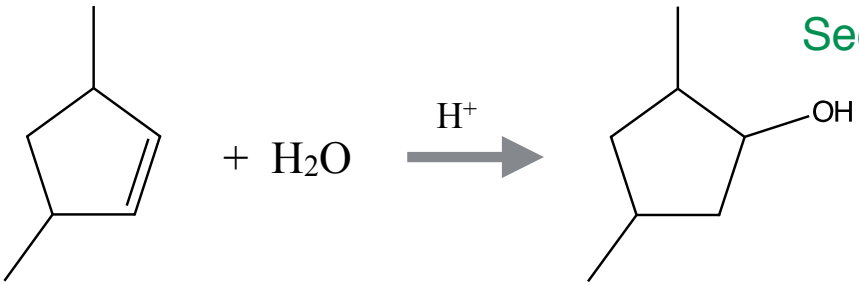
Tertiary (3˚)



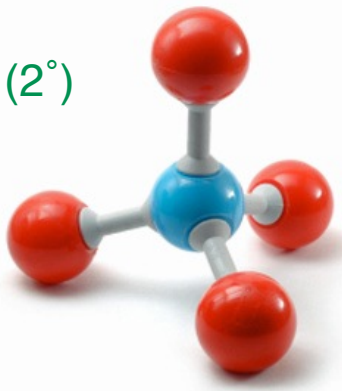
Secondary (2˚)



Tertiary (3˚)



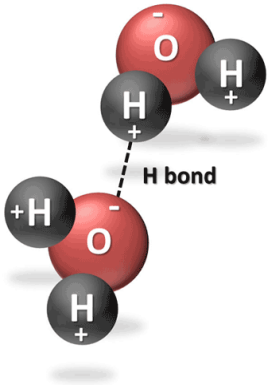
Secondary (2˚)

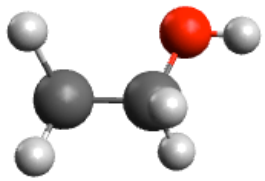


Ch09

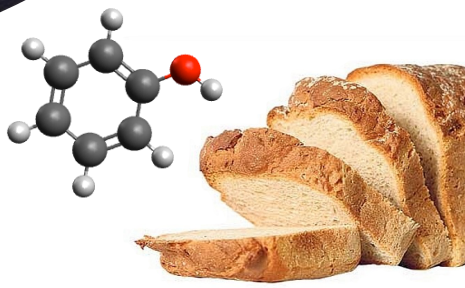
Functional Groups

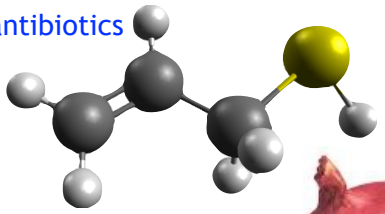
- What is a functional group?
  - Atoms responsible for utility
  - Starting with OXYGEN & SULFUR
    - The hydroxy group
- Alcohols
  - Structure
  - Properties
    - Hydrogen bonding
    - Solubility, m.p., b.p.
  - Sub classes
    - Primary, secondary or tertiary
- Naming Alcohols
  - Common names
  - IUPAC
    - As a family
    - As a substituent

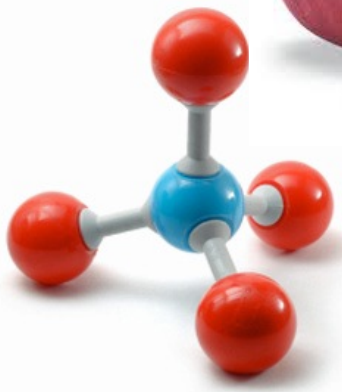




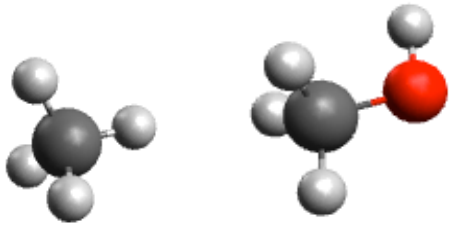
- Phenols & Thiols
  - Structure
    - Sulfur is like oxygen
  - Taste & Smell
  - Properties
    - Thiols: Harsh odors, bitter taste
    - Phenols: Pleasant odors, sweet taste
      - Antiseptics, & disinfectants
      - Replacement with antibiotics
  - Naming
- Ethers
  - Structure & Properties
    - Doubling up on oxygen
    - Anesthetics
  - Naming







Common Names



$CH_3—H$ $CH_3—OH$

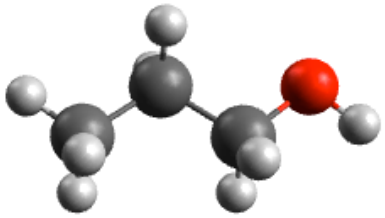
Methane Methyl Alcohol

- Simple alcohols are often named using common names.
- The common names is made by treating the alkane chain as if it were a branch off of an "alcohol" backbone.
  - This includes special branch names like isopropyl and *tert*-butyl.
  - "Ethyl alcohol" is to ethanol as "water" is to dihydrogen oxide.

Common names are **not** IUPAC names, but these are often used and you should recognize the substance from the name.

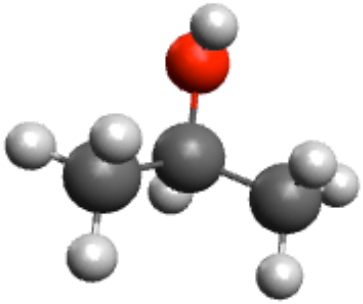
$CH_3—CH_2—H$ $CH_3—CH_2—OH$

Ethane Ethyl Alcohol



$CH_3—CH_2—CH_2—OH$

Propyl Alcohol



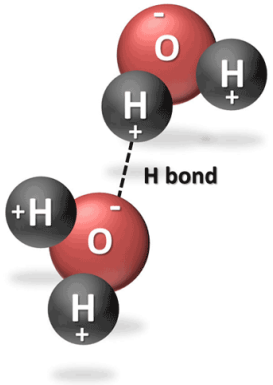
$CH_3—\underset{\displaystyle OH}{\underset{|}{CH}}—CH_3$

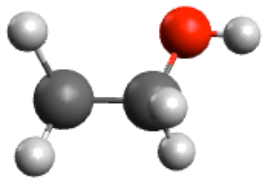
Isopropyl Alcohol

Ch09

Functional Groups

- What is a functional group?
  - Atoms responsible for utility
  - Starting with OXYGEN & SULFUR
    - The hydroxy group
- Alcohols
  - Structure
  - Properties
    - Hydrogen bonding
    - Solubility, m.p., b.p.
  - Sub classes
    - Primary, secondary or tertiary
- Naming Alcohols
  - Common names
  - IUPAC
    - As a family
    - As a substituent





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    - Sulfur is like oxygen
  - Taste & Smell
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  - Naming
- Ethers
  - Structure & Properties
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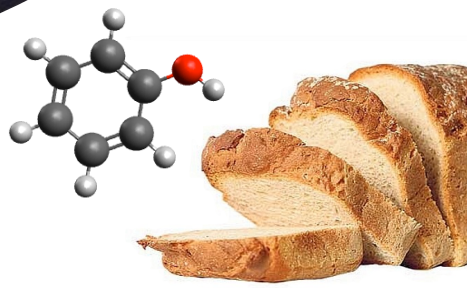
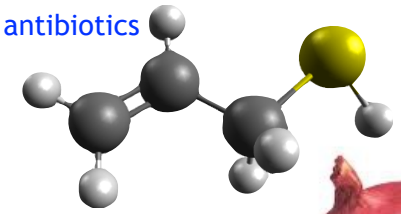
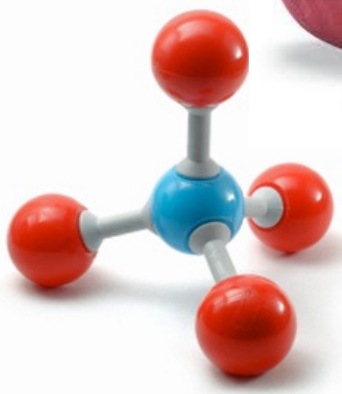
    - Anesthetics
  - Naming

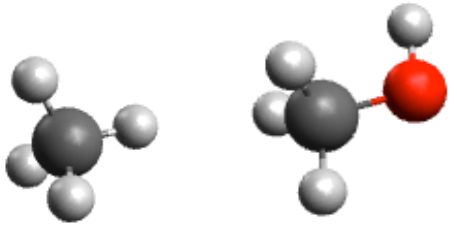






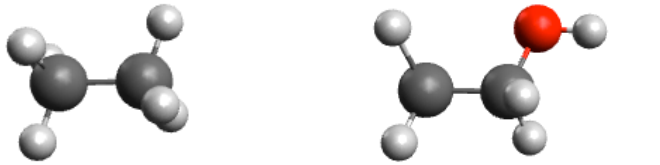
IUPAC Naming of Alcohols

- Substances with functional groups are not members of the hydrocarbon family.
- IUPAC names them with an identifying suffix.
- For alcohols add the suffix -ol to the **end** of the backbone.
  - This suffix is not part of the backbone (like -an-, -en-, and -yn- are).
  - -ol replaces the '-e' that would end the name.
- When addresses are needed, the backbone is numbered to give the functional group the lowest number.
- All other rules are the same as for hydrocarbons.



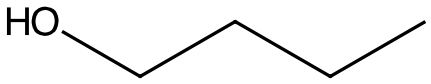
$CH_3—H$ Methane

$CH_3—OH$ Methanol (methyl alcohol)

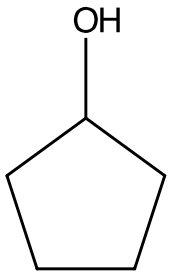


$CH_3—CH_2—H$ Ethane

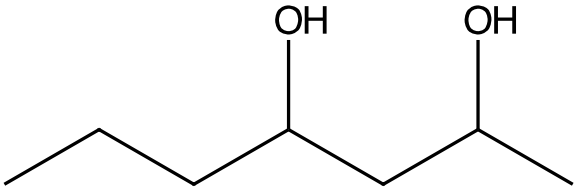
$CH_3—CH_2—OH$ Ethanol (ethyl alcohol)



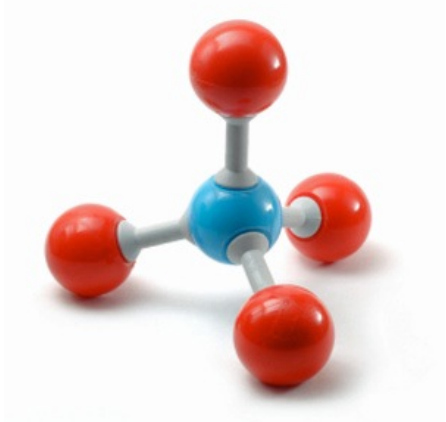
Butanol



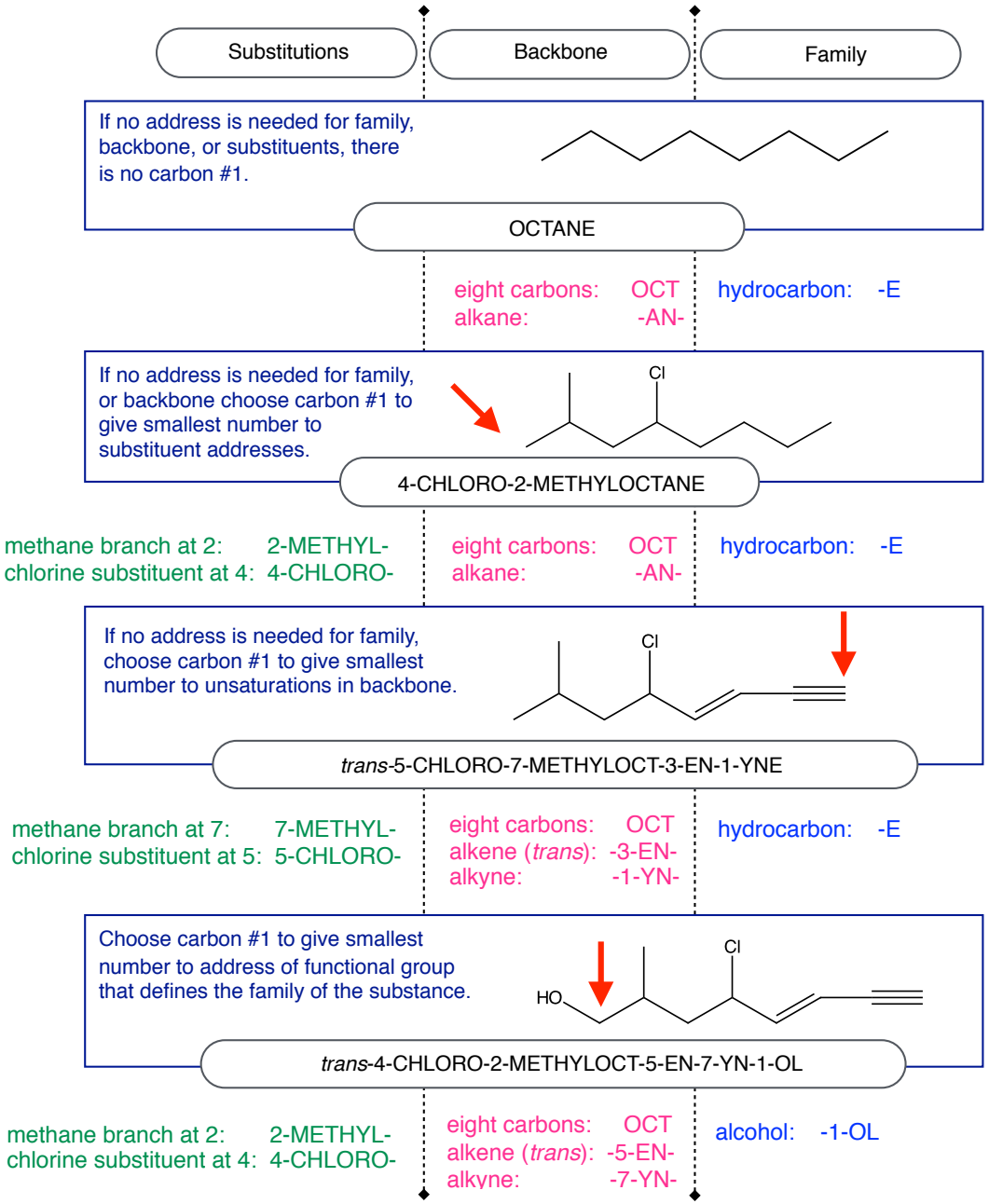
Cyclopentanol



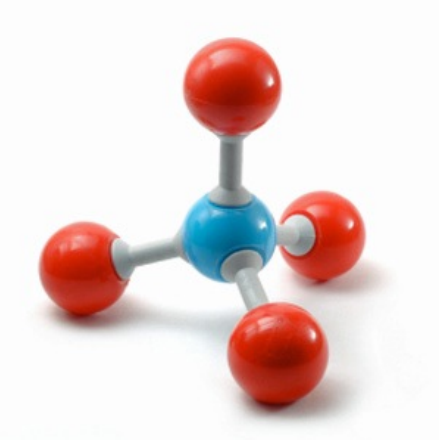
2,4-Heptanediol



Finding Carbon One

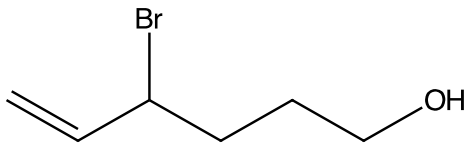


- The key to get the numbering right is remembering the priorities in finding that first carbon.
  - Priority one is the functional group(s).
  - Priority two is unsaturations.
  - Priority three is the substituents.



Finding Carbon One

Substitutions | Backbone | Family



4-Bromo-5-hexen-1-ol

substituents priority #3

backbone priority #2

family priority #1

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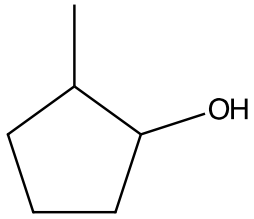
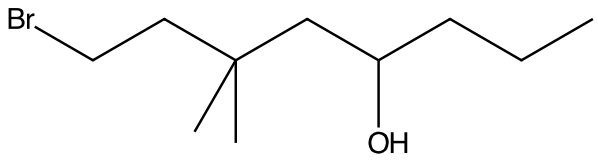
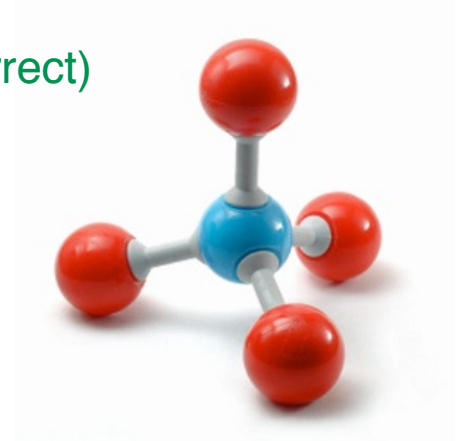


2-Methylcyclopentanol
(2-Methyl-1-cyclopentanol is also correct)



8-Bromo-6,6-dimethyl-4-octanol
(not 1-Bromo-2,3-dimethyl-5-octanol)



Finding Carbon One

Substitutions | Backbone | Family

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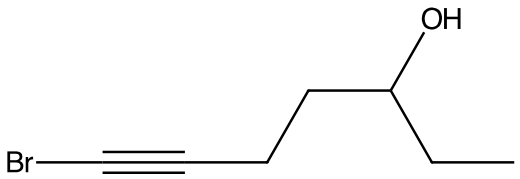
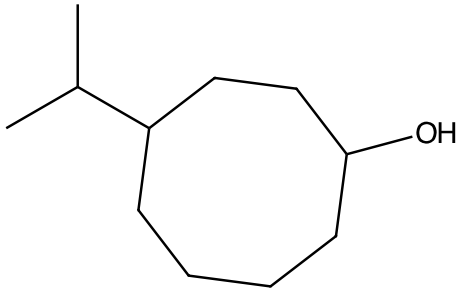
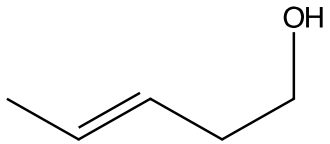


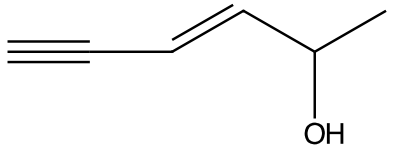
7-Bromo-6-heptyn-3-ol



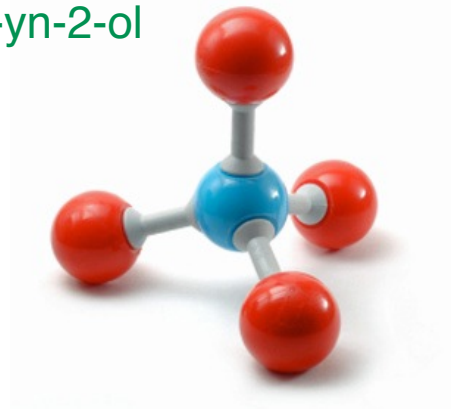
4-Isopropylcyclooctanol



trans-3-Penten-1-ol



trans-3-Hexen-5-yn-2-ol



Ch09

Functional Groups

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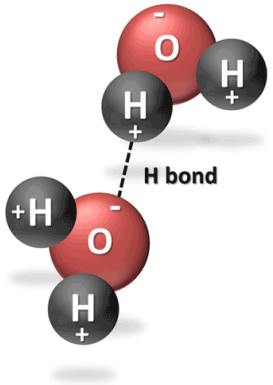
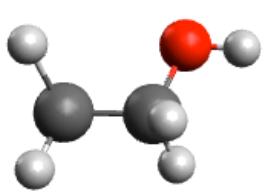
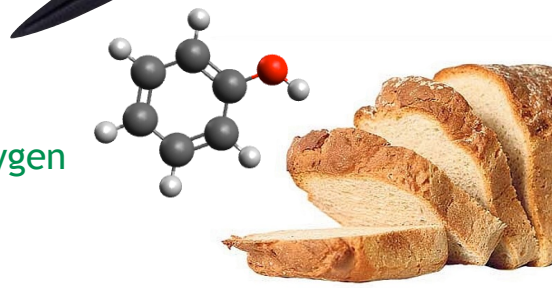
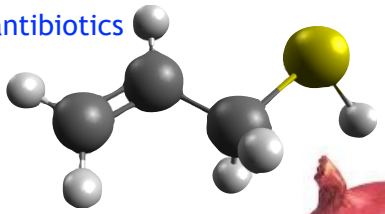
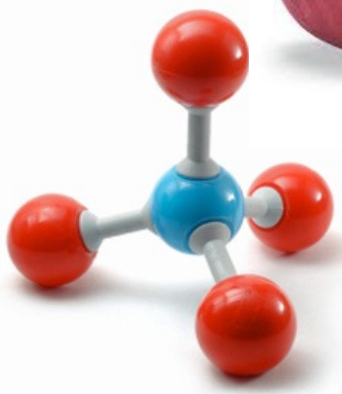




- Phenols & Thiols
  - Structure
    - Sulfur is like oxygen
  - Taste & Smell
  - Properties
    - Thiols: Harsh odors, bitter taste
    - Phenols: Pleasant odors, sweet taste
      - Antiseptics, & disinfectants
      - Replacement with antibiotics
  - Naming
- Ethers
  - Structure & Properties
    - Doubling up on oxygen
    - Anesthetics
  - Naming



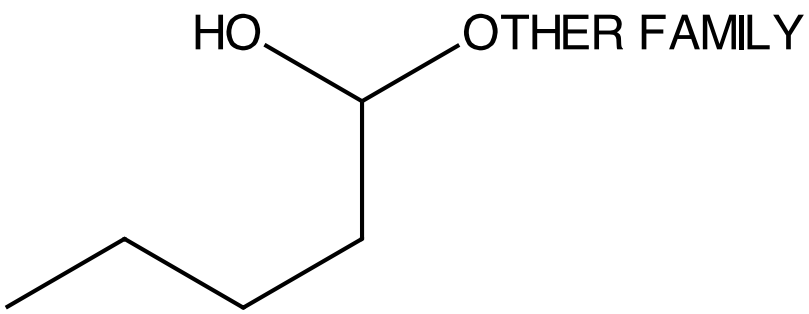


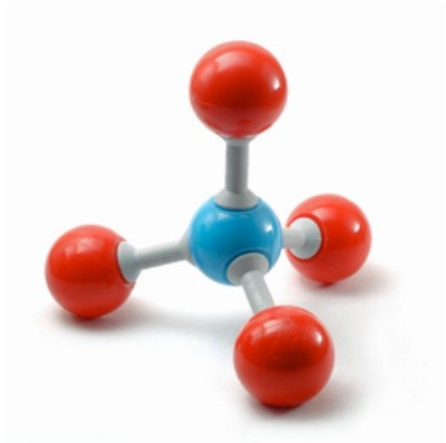


Alcohol Substituents

- If the substance belongs to another family, but has a hydroxyl group the substance is named using that families suffix. The hydroxyl groups treated as a "hydroxy" substituent.
- We'll talk about two families that take precedence over alcohols in in the next section (aldehydes and carboxylic acids).
- For now, just keep this in your back pocket:
  - …you can also describe an -OH as a "hydroxy" substituent if the compound isn't a simple alcohol.

2-Hydroxyhexan-(OTHER FAMILY SUFFIX)





Ch09

Functional Groups

- What is a functional group?
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  - Starting with OXYGEN & SULFUR
    - The hydroxy group
- Alcohols
  - Structure
  - Properties
    - Hydrogen bonding
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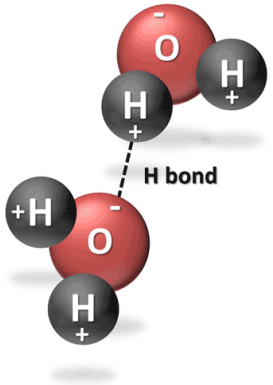

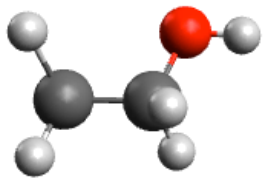

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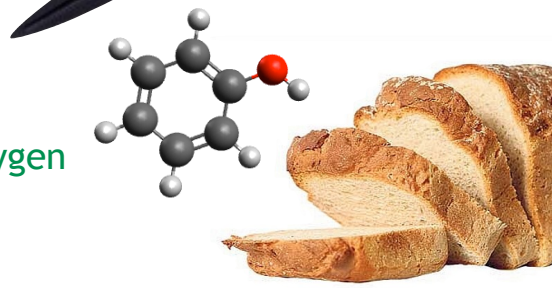
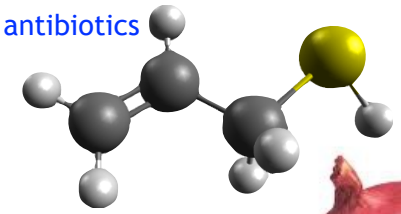
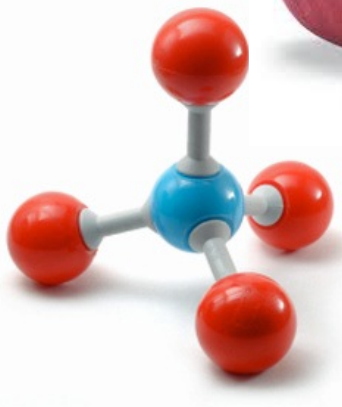
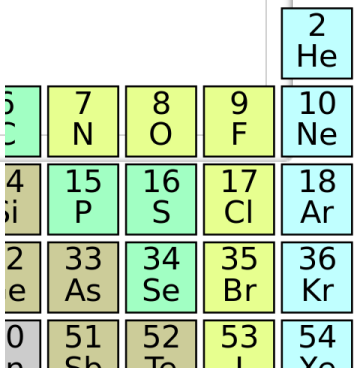


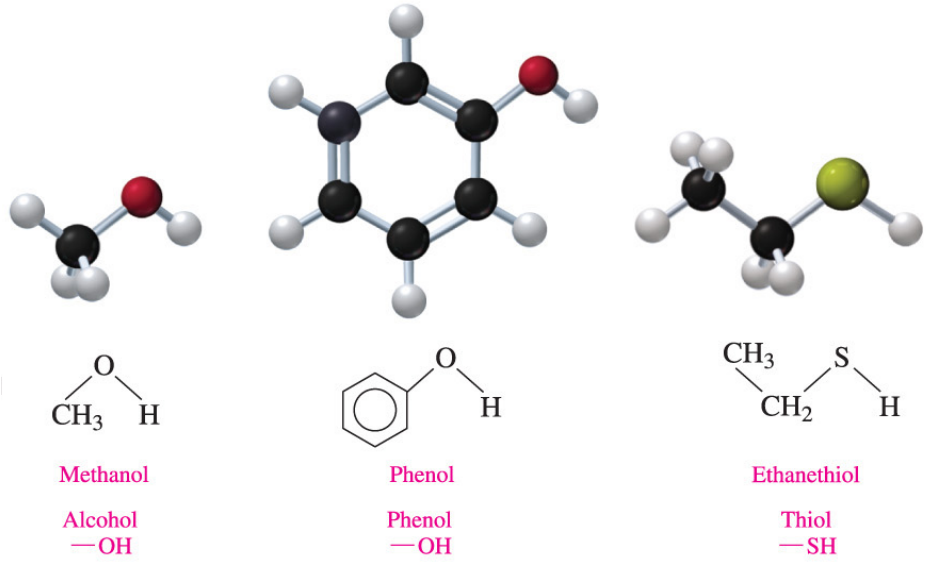


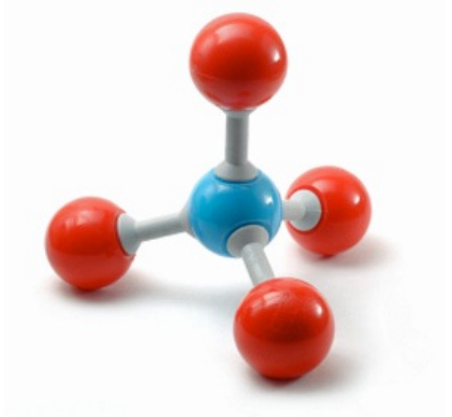


Phenols & Thiols



- Thiol and phenol families are related to alcohols.
- The phenol family is when the hydroxyl groups (-OH) exist on aromatic rings.
- The thiol (also called mercaptan) family of compounds is when thiol groups (-SH) exist on alkanes.
  - Sulfur and oxygen are both chalcogens and have similar atomic properties.
    - Resulting in similar chemical properties in alcohols and sulfides.





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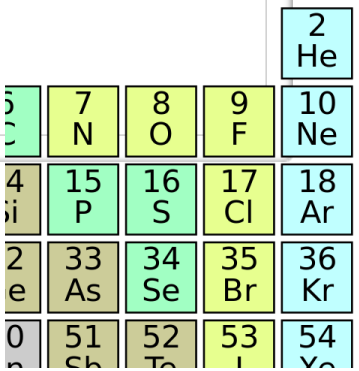

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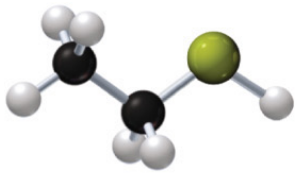
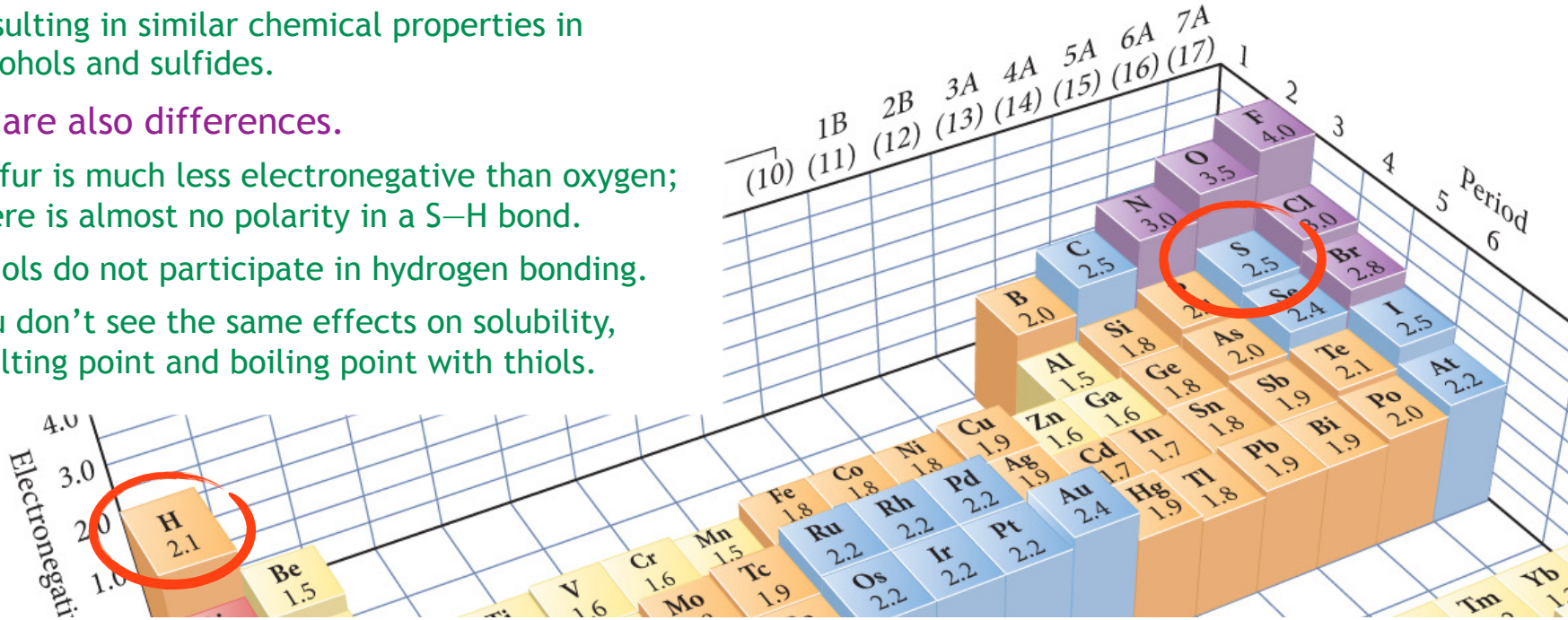
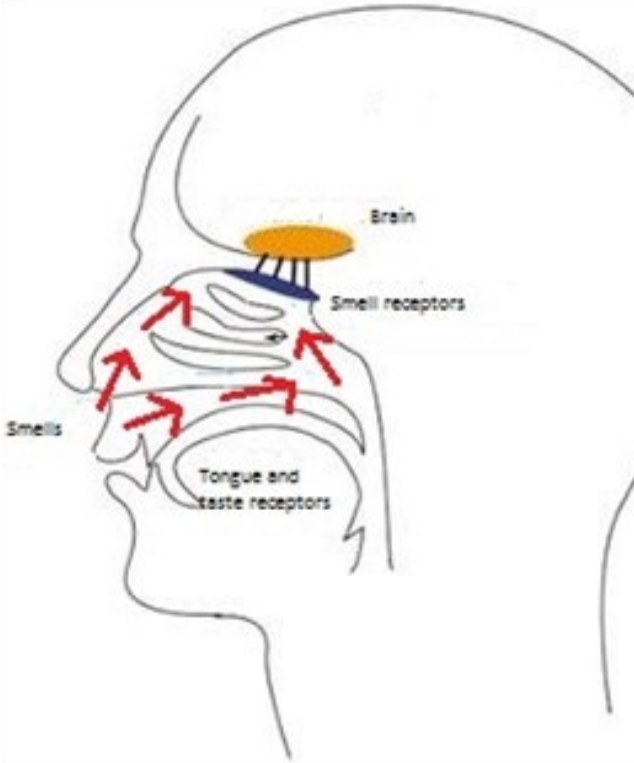


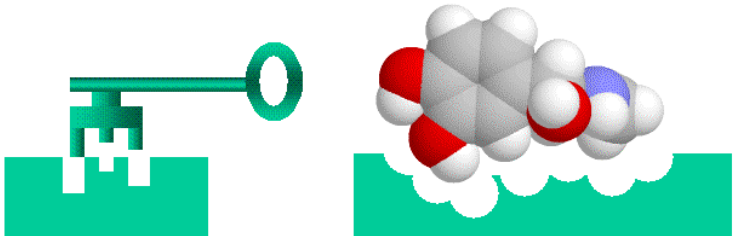
  - Sulfur and oxygen are both chalcogens and have similar atomic properties.
    - Resulting in similar chemical properties in alcohols and sulfides.
  - There are also differences.
    - Sulfur is much less electronegative than oxygen; there is almost no polarity in a S—H bond.
    - Thiols do not participate in hydrogen bonding.
    - You don't see the same effects on solubility, melting point and boiling point with thiols.

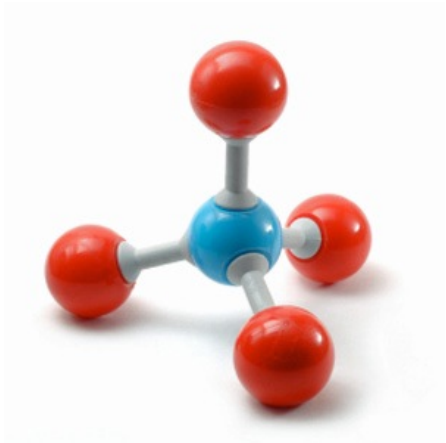


Taste & Smell

- Taste and smell are physical properties of a substance.
- Taste and smell are separate senses with their own receptor organs, yet they are entwined and similar.
  - Tastants, substances in foods, are detected by taste buds, which consist of special sensory cells.
    - These cells send signals to specific areas of the brain, which make us conscious of the perception of taste.
  - Olfactory cells in the nose pick up odorants, airborne odor molecules.
    - Odorants stimulate receptor proteins found on hairlike cilia at the tips of the sensory cells, a process that initiates a neural response.
- These organs are stimulated by a lock and key mechanism.
- The organs are triggered by the shape and location of functional groups in the molecule.

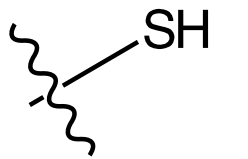


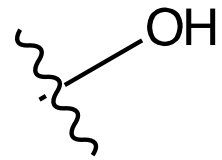


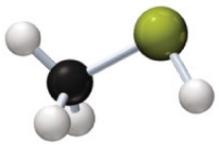


Properties of Thiols

- Thiols have a harsh odor and bitter taste.
  - Garlic, onions, oysters and many cheeses owe their odor and taste to molecules containing thiols.
- Thiols are added to hydrocarbon fuels to encourage reporting of spills and leaks.
  - Ethyl thiol is added to propane or other liquefied petroleum gases used as fuel gases.
  - tert-Butyl thiol is added as a blend of other components to natural gas used as fuel gas to to encourage reporting of gas leaks.
- Methyl thiol is a by product of purification, it's why rotting flesh or rotten eggs (and skunk odor) smell bad.

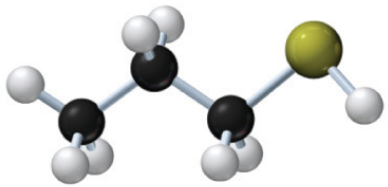






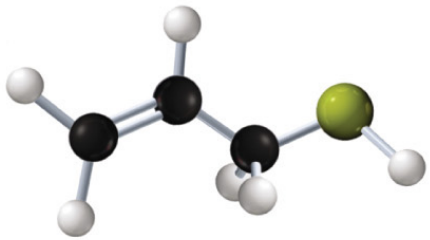
$CH_3—SH$

Methanethiol
(oysters and cheese)



$CH_3—CH_2—CH_2—SH$

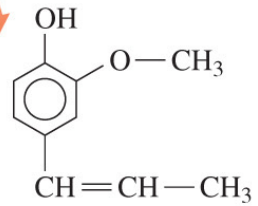
1-Propanethiol
(onions)



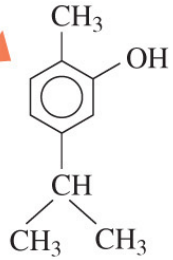
$H_2C=CH—CH_2—SH$

2-Propene-1-thiol
(garlic)

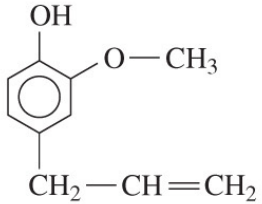
Properties of Phenols



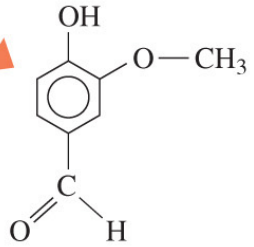
Tarragon



Thyme

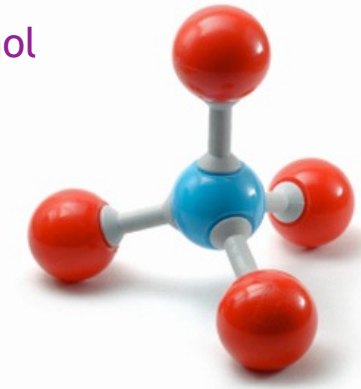


Clove



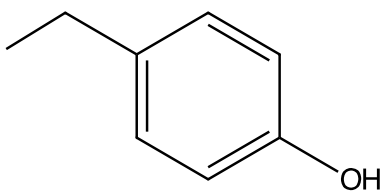
Vanilla

- In contrast, phenols trigger the "sweet" taste buds and olfactory organs.
  - Vanilla, Clove, Thyme, Tarragon all have phenol structures.

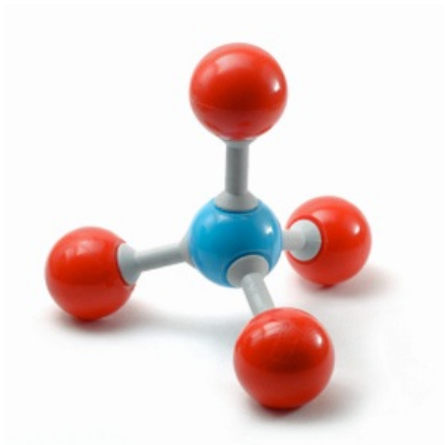


Properties of Phenols

- Phenols are found in hops, malt and produced by yeast.
- They contribute to the tastes in beers and smell of fresh bread.



4-ethylphenol



Ch09

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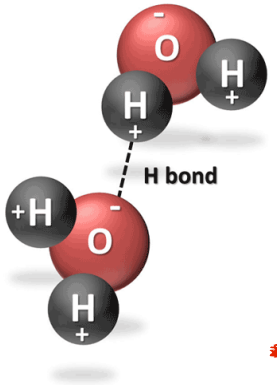

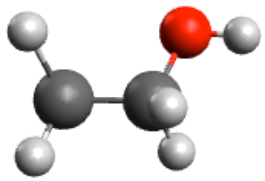

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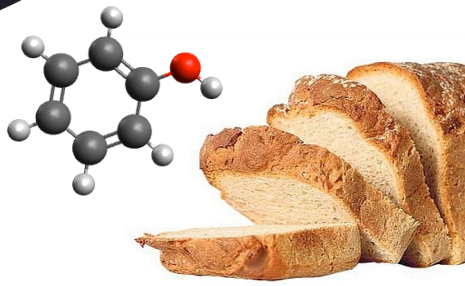

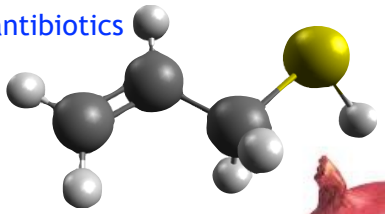

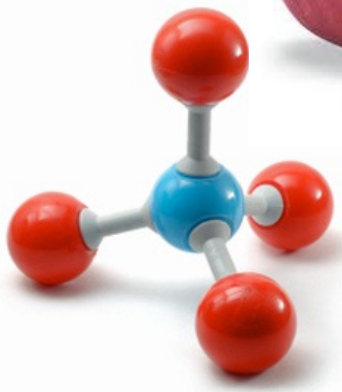

IUPAC Naming Thiols

- The family suffix for thiols is -thiol. Because the suffix starts with a consonant we retain the -e from the alkane backbone.
- Be sure to consider the position of the functional group when assigning addresses.
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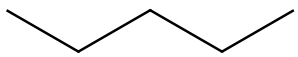
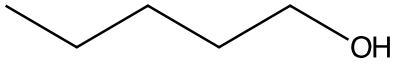
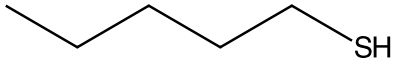


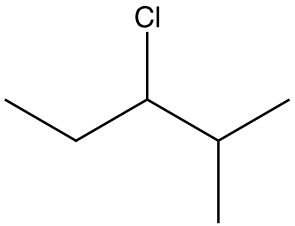
Pentane



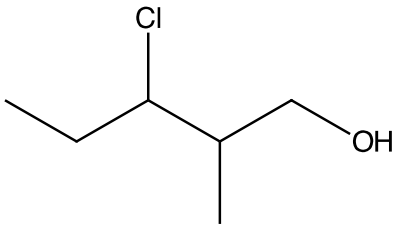
Pentanol



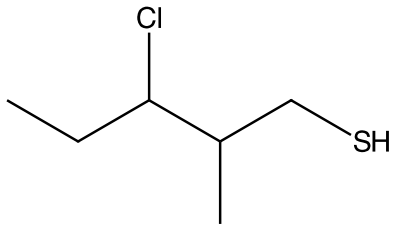
Pentanethiol



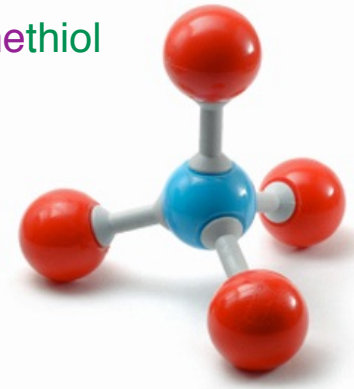
3-Chloro-2-methylpentane



3-Chloro-2-methylpentanol



3-Chloro-2-methylpentanethiol



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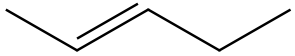
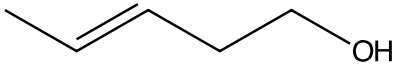
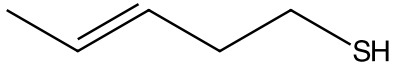


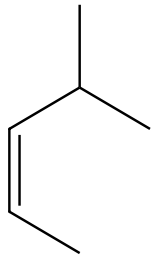
trans-2-Pentene



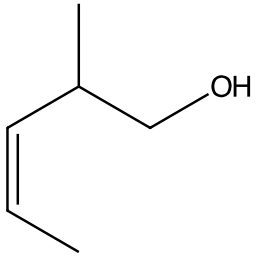
trans-3-Penten-1-ol



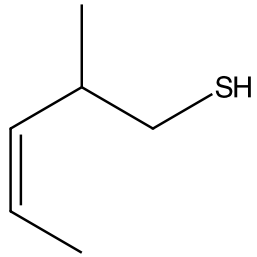
trans-3-Pentene-1-thiol



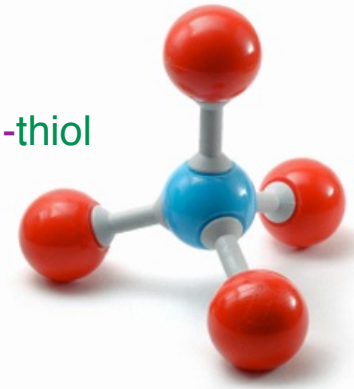
cis-4-Methyl-2-pentene



cis-2-Methyl-3-penten-1-ol

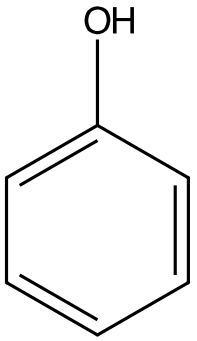


cis-2-Methyl-3-pentene-1-thiol

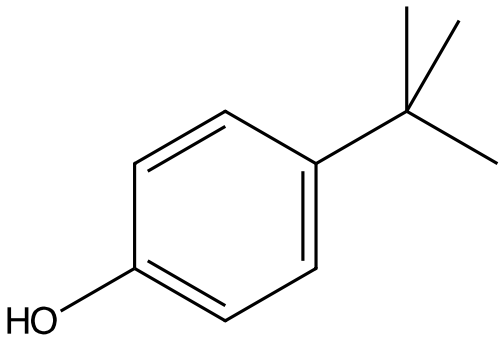


IUPAC Naming Phenols

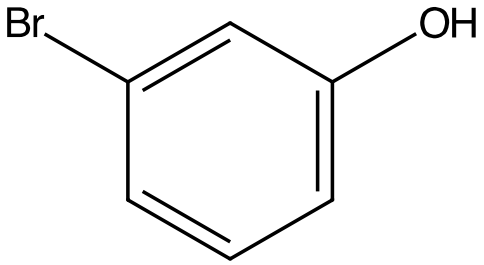
- With phenols we treat the atom attached to the hydroxyl group as carbon one of the phenol backbone.
  - All other rules are the same.



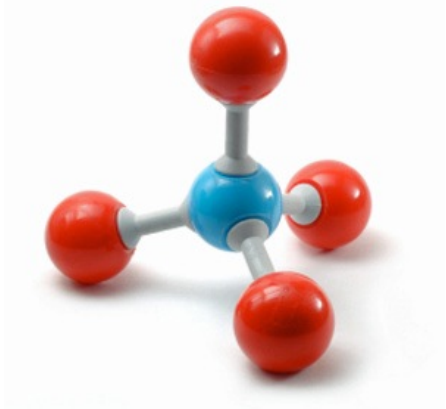
Phenol



4-*tert*-Butylphenol



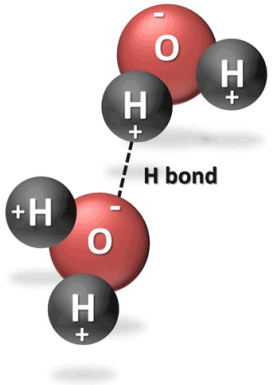
3-Bromophenol

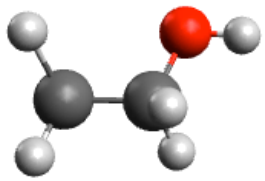


Ch09

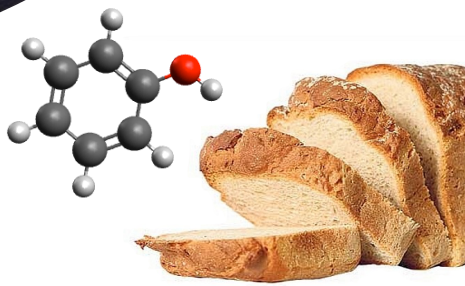
Functional Groups

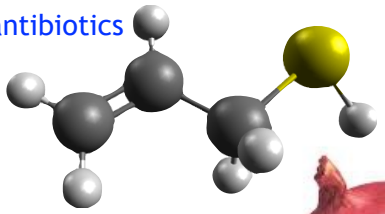
- What is a functional group?
  - Atoms responsible for utility
  - Starting with OXYGEN & SULFUR
    - The hydroxy group
- Alcohols
  - Structure
  - Properties
    - Hydrogen bonding
    - Solubility, m.p., b.p.
  - Sub classes
    - Primary, secondary or tertiary
- Naming Alcohols
  - Common names
  - IUPAC names
    - As a family
    - As a substituent



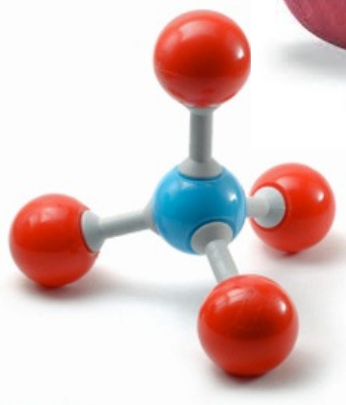


- Phenols & Thiols
  - Structure
    - Sulfur is like oxygen
  - Taste & Smell
  - Properties
    - Thiols: Harsh odors, bitter taste
    - Phenols: Pleasant odors, sweet taste
      - Antiseptics, & disinfectants
      - Replacement with antibiotics
  - IUPAC names



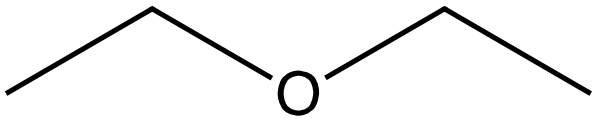


- Ethers
  - Structure & Properties
    - Doubling up on oxygen
    - Anesthetics
  - Common names

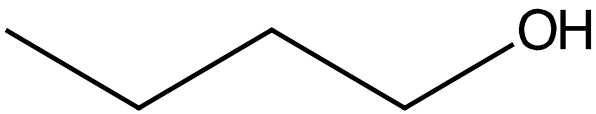


Properties of Ethers

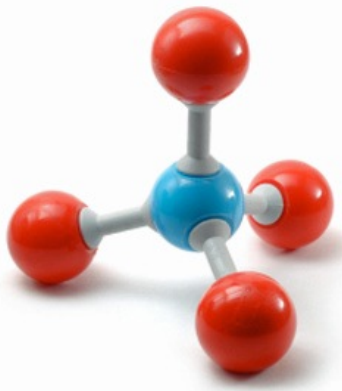
- An ether is two hydrocarbons connected to the same oxygen.
- Ethers cannot form hydrogen bonds, so they are more volatile than alcohols, thiols, and phenols.
  - Lower boiling points, melting points, and less soluble in water.
    - But often higher than alkanes with the same number of atoms.



$C_4H_{10}O$
molar mass 74.12 g/mol
b.p. 35 °C

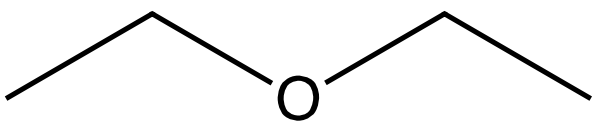


$C_4H_{10}O$
molar mass 74.12 g/mol
b.p. 117 °C

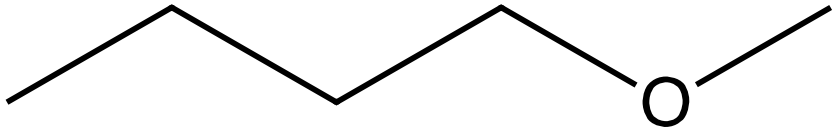


Naming Ethers

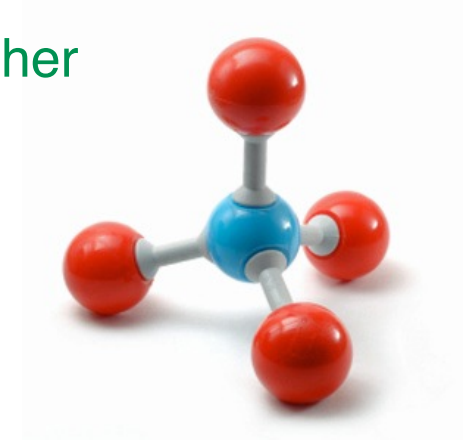
- We use common names to describe most ethers.
- Name both hydrocarbons attached to the ether in alphabetical order, and attach the word ether to the end.
- If both hydrocarbons are the same, use the prefix di-.



Diethylether

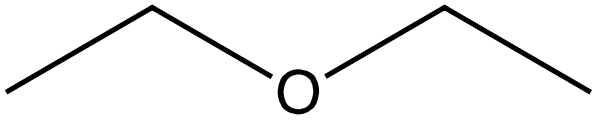


Butyl methyl ether

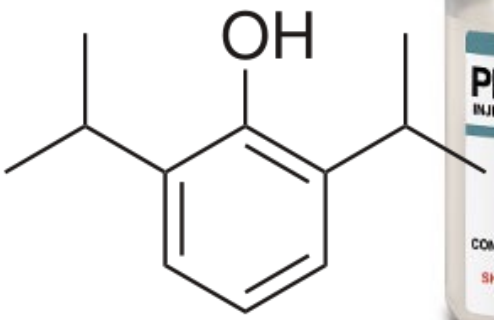


Use of Ethers

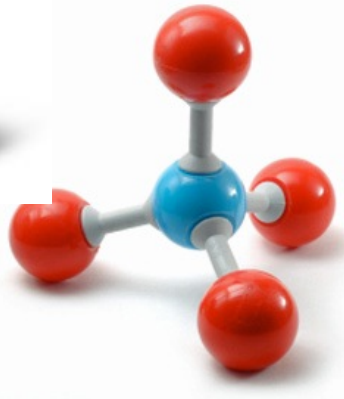
- Ethers have been used as anesthetics.
- Diethyl ether was first used as an anesthetic by the dentist William T. G. Morton in 1846.
- It was later used as a general anesthetic for surgery a few months later at Boston General hospital.
- Today diethyl ether is less preferred because prolonged use can result in undesirable side effects like nausea and vomiting.
- The substance known by the trade name Propofol™ is often preferred.



Diethylether



Propofol™
2,6 di-isopropyl-phenol



Ch09

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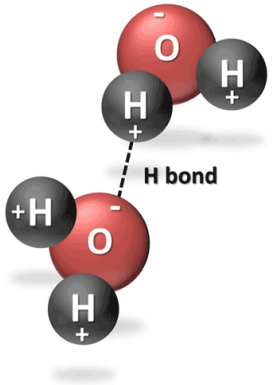

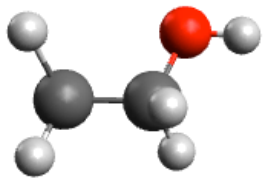

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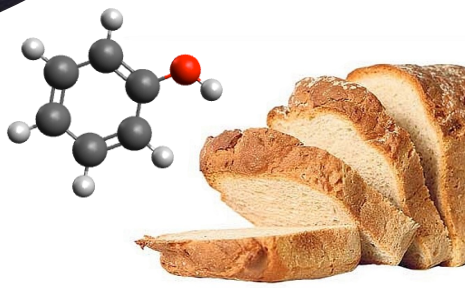

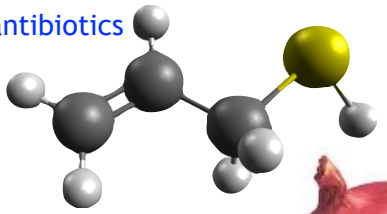

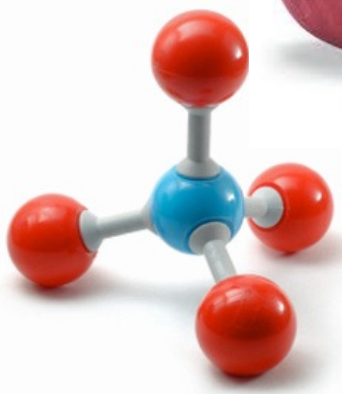

Questions?