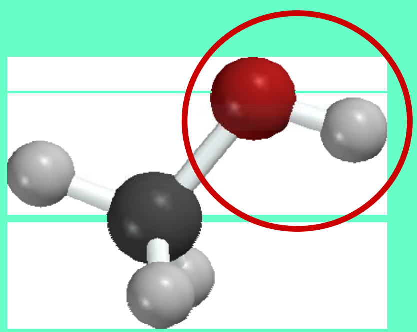
Chem101
General Chemistry

Lecture 12

Alcohols, Phenols and Ethers

Alcohols

- Alcohols are organic molecules containing a **hydroxy** functional group
  - 1. The hydroxy group is composed of an oxygen and a hydrogen atom (–O–H)

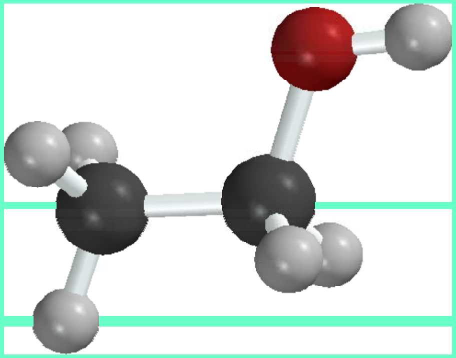


hydroxy group

$CH_3–OH$

Alcohols

- When the hydroxy group is attached to and alliphatic hydrocarbon (non-aromatic), it is called an **alcohol**.



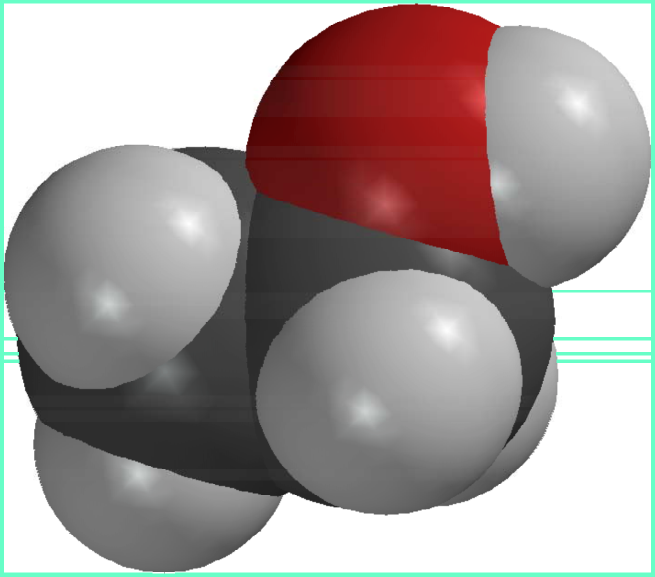
Ball-and-Stick model

$CH_3{-}CH_2{-}OH$

Ethyl alcohol or ethanol

Alcohols

- When the hydroxy group is attached to and alliphatic hydrocarbon (non-aromatic), it is called an **alcohol**.



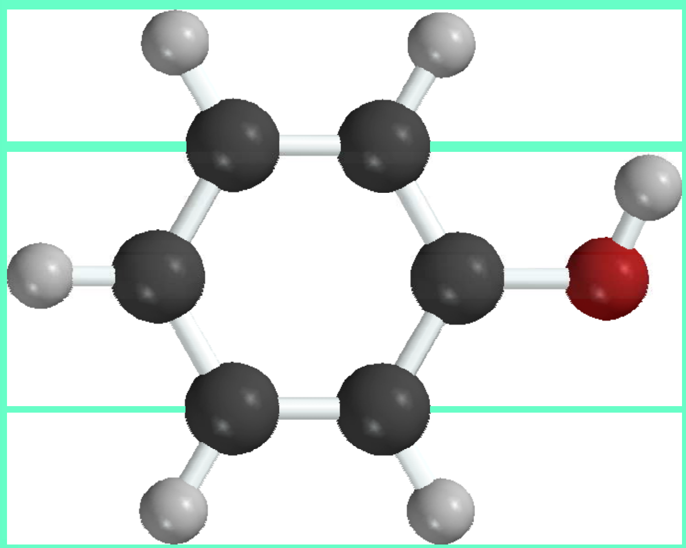
Space Filling model

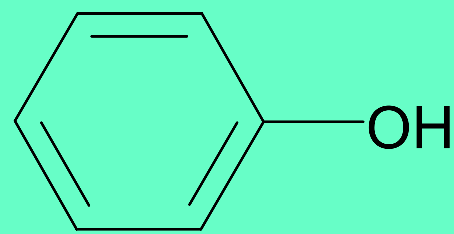
$CH_3{-}CH_2{-}OH$

Ethyl alcohol or ethanol

Alcohols

- When the hydroxy group is attached to aromatic hydrocarbon, it is called a **phenol**.





Phenol

Alcohols

- Some very important biological molecules that are alcohols:
  - Carbohydrates
    - √ Fuel
    - √ Structure, for example cellulose
    - √ Component of nucleic acids
  - Cholesterol
    - √ Component of cell membranes in animals
    - √ Implicated as a cause of heart disease
  - Ethanol
    - √ Product of alcoholic fermentation
  - Isopropanol
    - √ Antiseptic
  - Taxol
    - √ anticancer drug

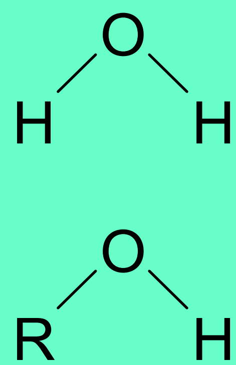
Phenols

- Some important biological molecules that are phenols:
  - Neurotransmitters
    - √ Epinephrine (adrenalin)
    - √ Dopamine

      The levels of dopamine are abnormally low in regions of the brains of people with Parkinson's disease
    - √ Serotonin

Alcohols

- The hydroxy group is a water molecule with one of its hydrogens substituted with a hydrocarbon.



When focusing our attention on the functional group of an organic molecule we often represent the hydrocarbon portion by the letter R, calling it an "R group".

Nomenclature of Alcohols

- Many of the simpler alcohols are referred to by common names:
  - Methyl alcohol (wood alcohol)

$$CH_3{-}OH$$

  - Ethyl alcohol (grain alcohol)

$$CH_3{-}CH_2{-}OH$$

  - Isopropyl alcohol (rubbing alcohol)

$$\begin{array}{c} CH_3 \\ | \\ CH_3{-}CH{-}OH \end{array}$$

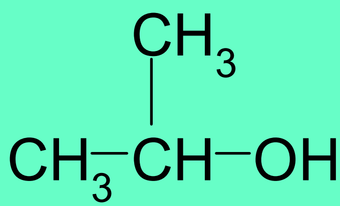
These common names give the name of the "R group" followed by the word "alcohol".

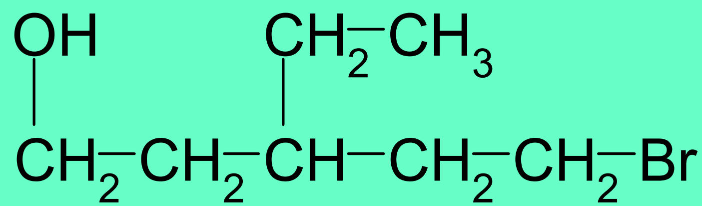
Nomenclature of Alcohols

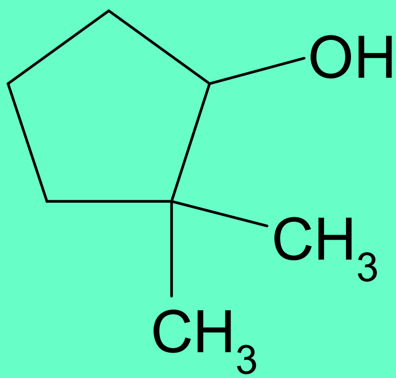
- IUPAC rules for naming alcohols:
  1. Name the longest chain to which the hydroxy group is attached. The chain name is obtained by dropping the final *–e* from the name of the hydrocarbon that contains the same number of carbons atoms, and adding the ending *–ol*.
  2. Number the longest chain to give the lower number to the carbon with the attached hydroxy group.
  3. Locate the position of the hydroxy group by the number of carbon atom to which it is attached.
  4. Locate and name any other groups attached to the longest chain.
  5. Combine the name and location for other groups, the hydroxy group location, and the longest chain into the final name.

Exercise 13.1 (p418)

Assign IUPAC names to the following alcohols:

a. 

c. 

d. 

Exercise 13.5 (p419)

Draw structural formulas for each of the following:

a. 2-methyl-1-butanol

c. 1-methylcyclopentanol

Classifications of Alcohols

- The outcome of reactions that alcohols participate in often depends on the number of hydrogens bonded to the carbon to which the hydroxy group is bonded to.
  - This becomes the basis for classifying alcohols

Classifications of Alcohols

- Primary alcohols have two or three hydrogens attached to the same carbon:

$CH_3{-}OH$

methanol

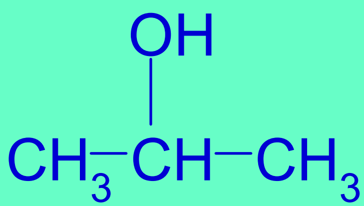
$CH_3{-}CH_2{-}OH$

ethanol

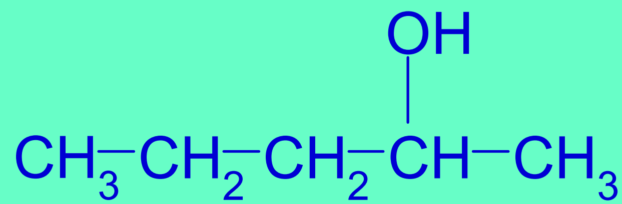
The hydroxy group is attached to carbon at the end of a chain

Classifications of Alcohols

- Secondary alcohols have only one hydrogen attached to the same carbon



2-propanol
(isopropanol)

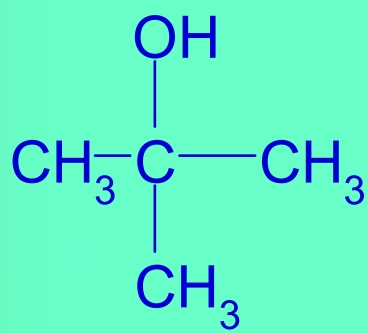


2-pentenol

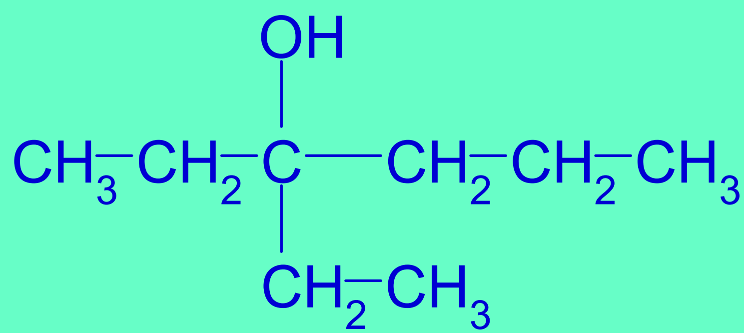
The hydroxy group is attached to a carbon in the middle of a chain

Classifications of Alcohols

- Tertiary alcohols have no hydrogens attached to the same carbon.



2-methyl-2-propanol

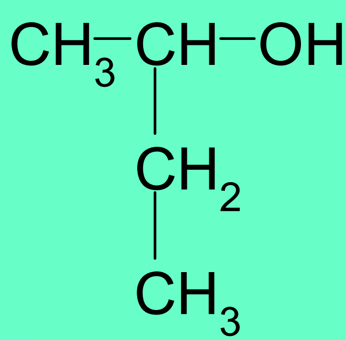


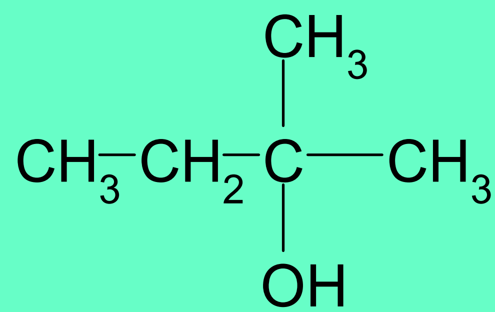
2-ethyl-2-hexanol

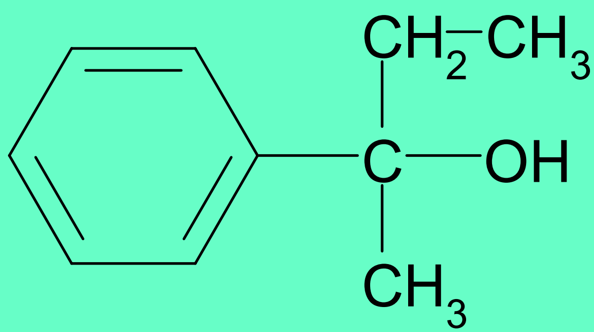
The hydroxy group is attached to a carbon at a branch point.

Exercise 13.13 (p418)

Classify the following alcohols as *primary*, *secondary*, or *tertiary*:

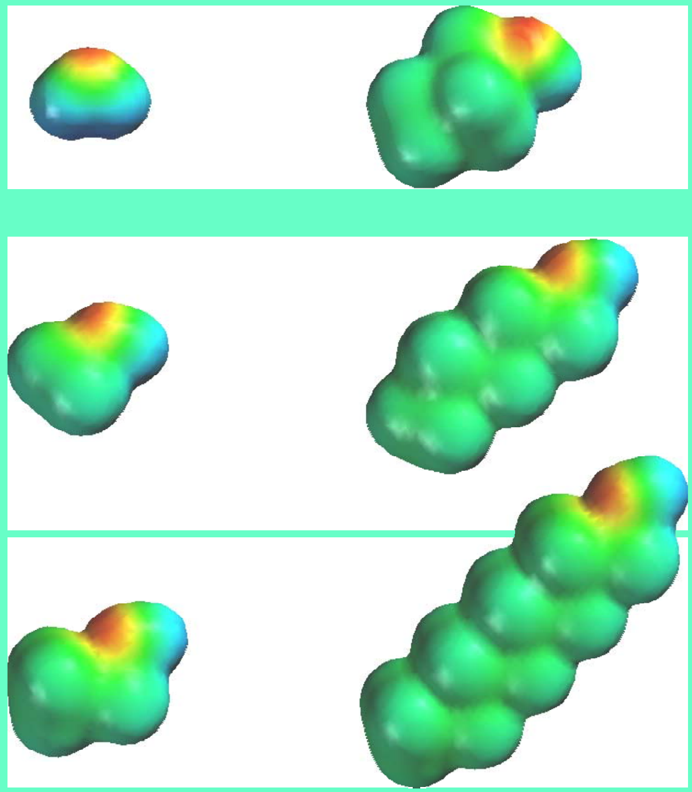
a. 

b. 

c. 

Physical Properties of Alcohols

- The hydroxy group imparts “water like” properties to an alcohol



water propanol

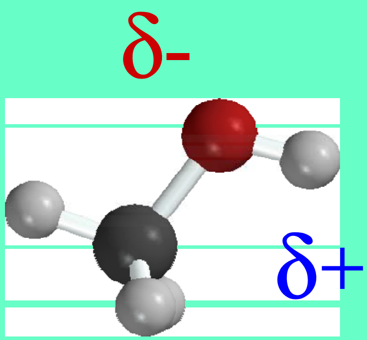
methanol pentanol

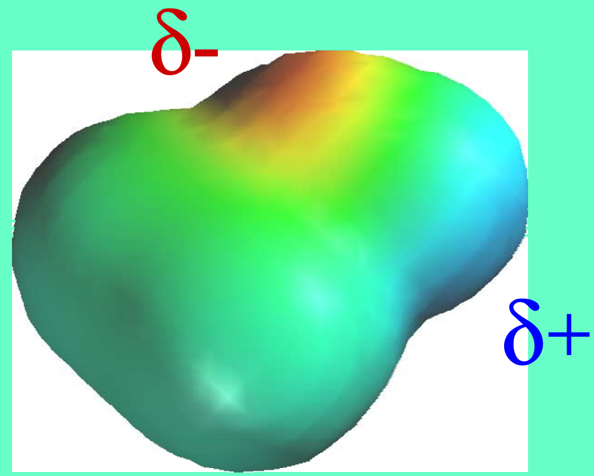
ethanol octanol

- The larger the “R group” the less “water like” and the more “alkane-like” the alcohol

Physical Properties of Alcohols

- The oxygen is more *electronegative* either carbon or hydrogen.
  - This makes C–O bonds and O–H polar



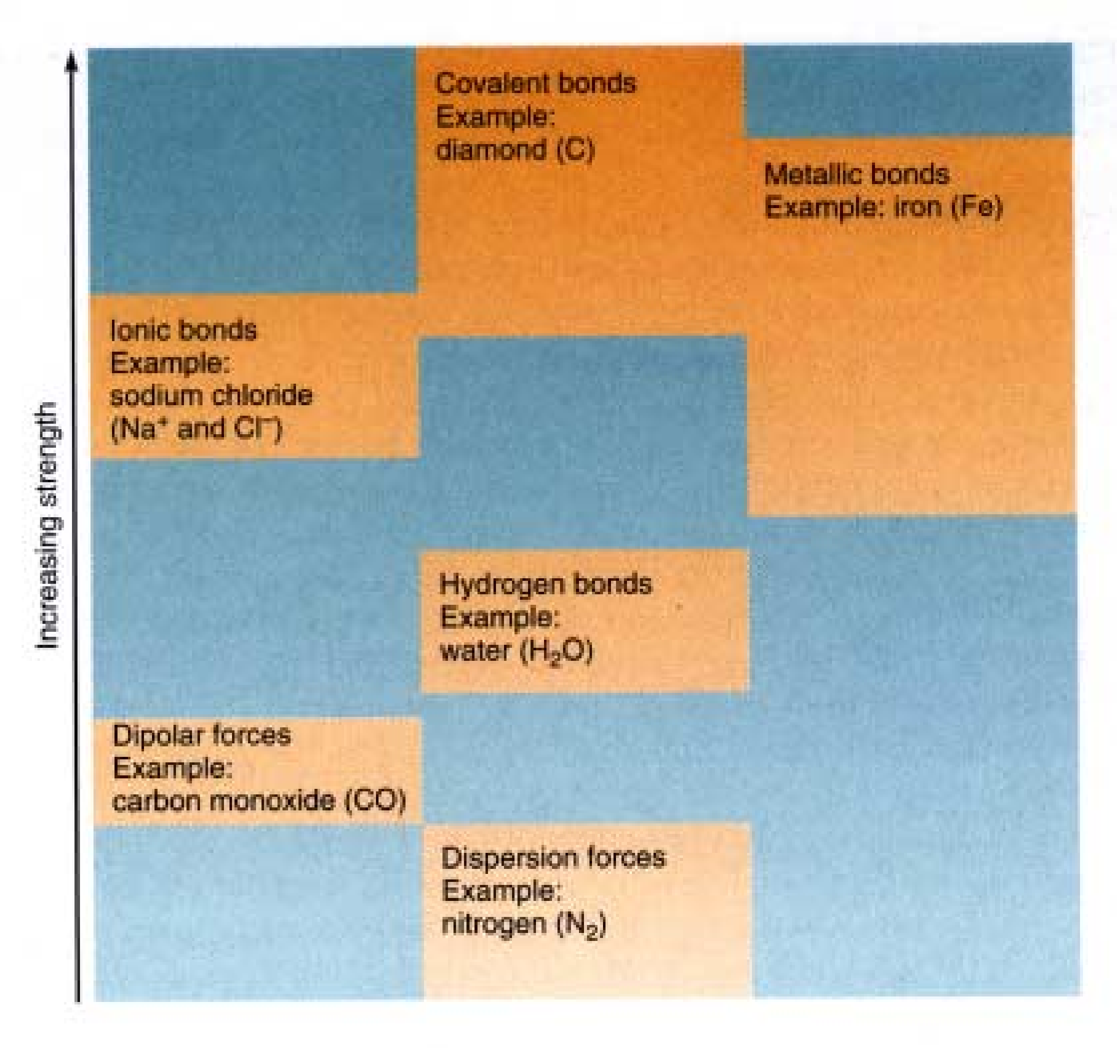


(See Chapter 4, p113 for a discussion on polarity)

Physical Properties of Alcohols

- Polar molecules can interact more strongly with themselves than non-polar molecules.

Figure 4.12
p124

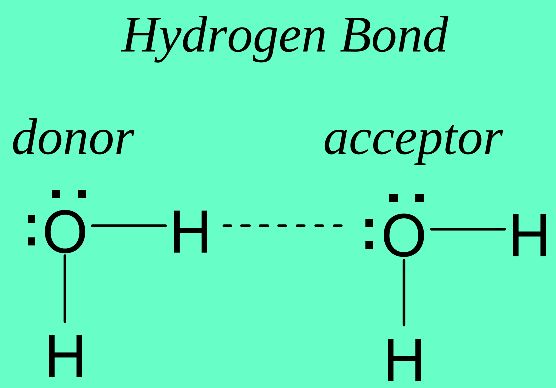


Physical Properties of Alcohols

- Water can also form hydrogen bonds with itself.
  - Hydrogen bonds can occur when a hydrogen is covalently bonded to an electronegative atom such as oxygen.
    - √ This electronegative atom is called the hydrogen bond donor
  - This hydrogen can be shared with another electronegative atom, which has a nonbonding pair of electrons.
    - √ This electronegative atom is called the hydrogen bond acceptor

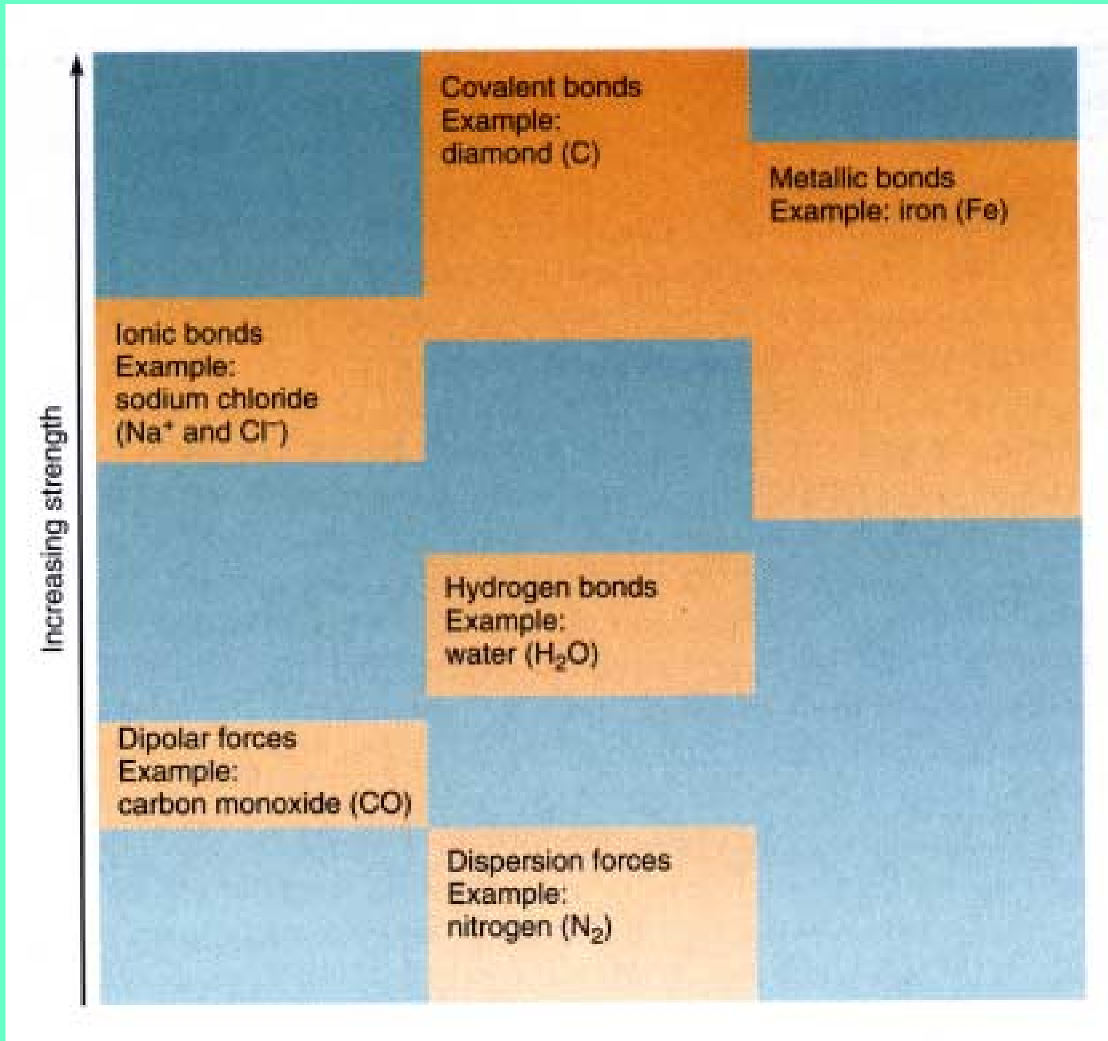
Physical Properties of Alcohols

- Water can also form hydrogen bonds with itself.



Physical Properties of Alcohols

- Hydrogen bonds are an even stronger interaction than dipole interactions.

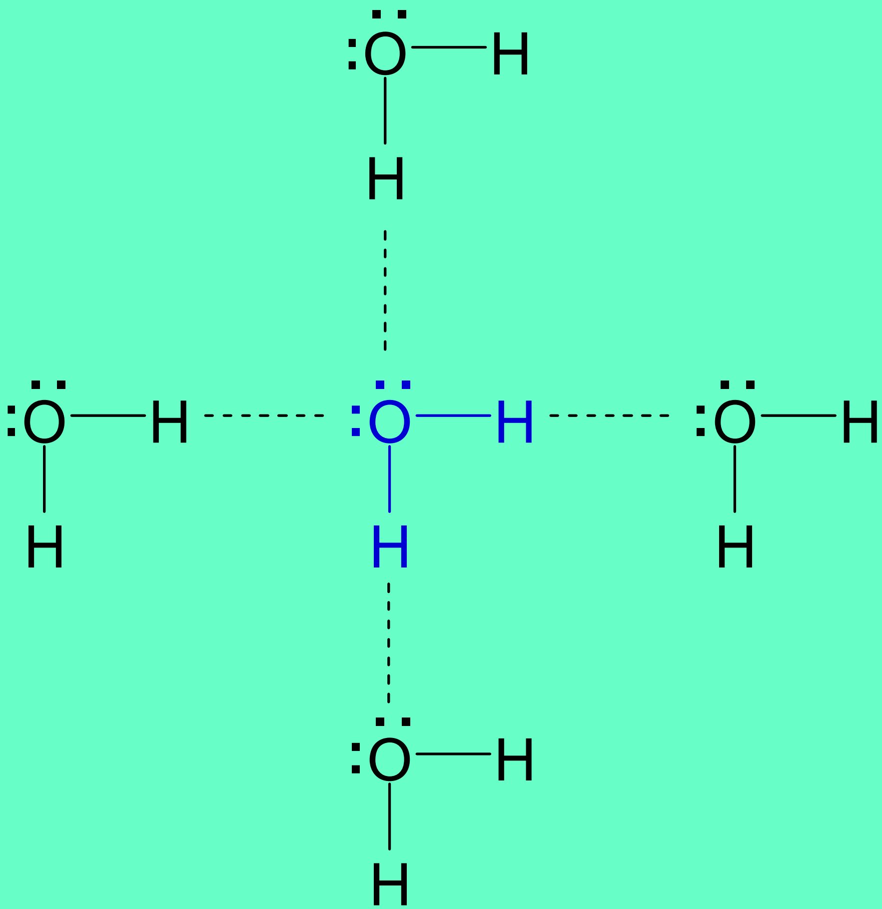


Physical Properties of Alcohols

- Water can also form hydrogen bonds with itself.
  - The oxygen is bonded to two hydrogens so it can serve as the donor in two hydrogen bonds.
  - This same oxygen also has two nonbonding pairs of electrons, so it can also serve as the acceptor in two hydrogen bonds.

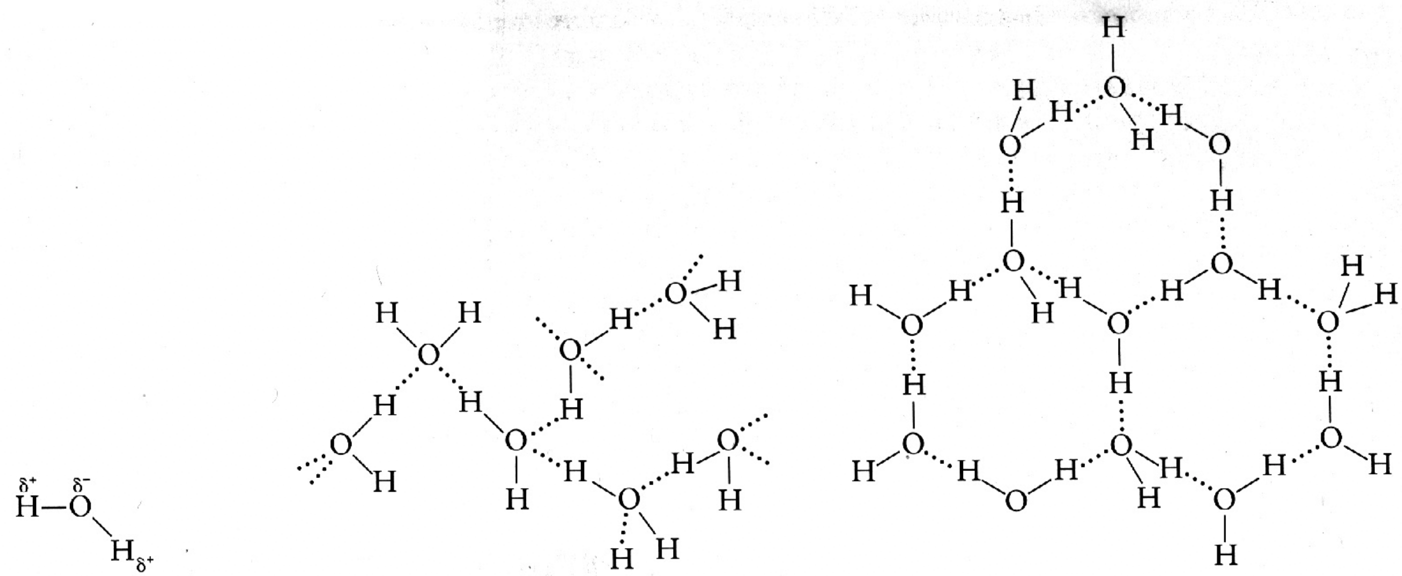
Physical Properties of Alcohols

- Water can also form hydrogen bonds with itself.



Physical Properties of Alcohols

- Water can also form hydrogen bonds with itself.
  - Tetrahedral geometry allows each water molecule in ice to form all four hydrogen bonds

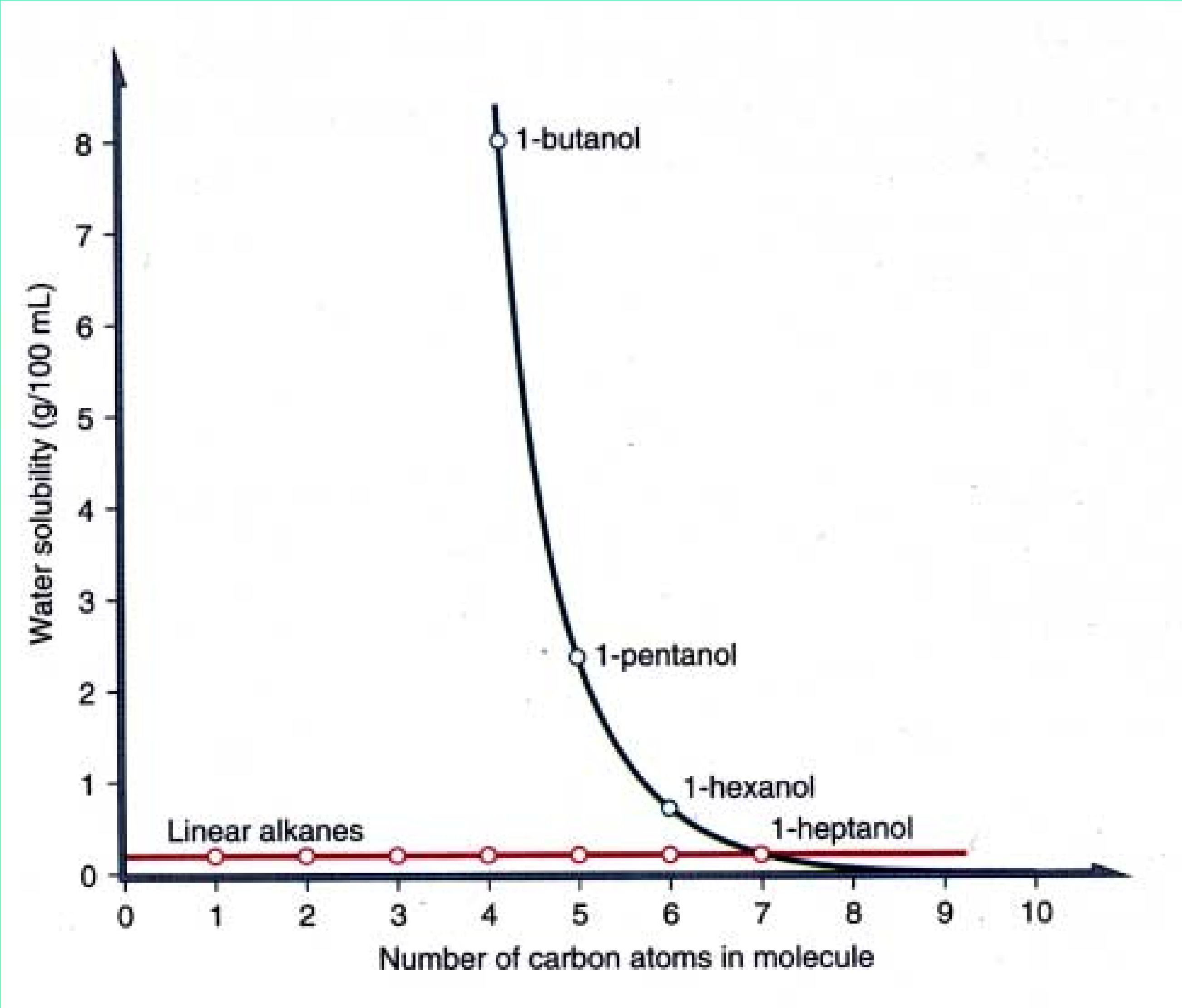


(a) Polar water molecule (b) Hydrogen bonding in liquid water (c) Hydrogen bonding in solid water

■ FIGURE 4.10 Hydrogen bonding in water. Hydrogen bonds are dotted, and covalent bonds are solid.

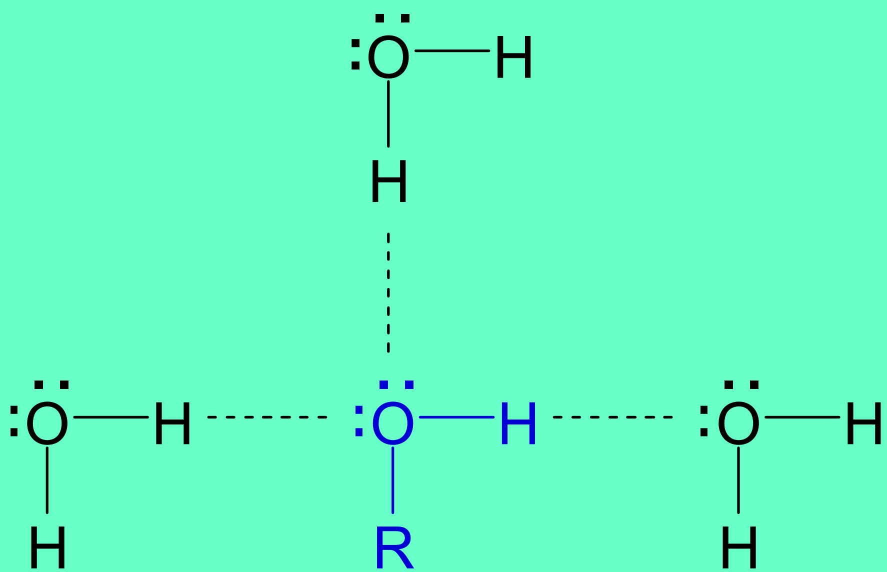
Physical Properties of Alcohols

- Solubility in water



Physical Properties of Alcohols

- Short-chain alcohols, such as *methanol*, *ethanol* and *propanol* are quite soluble in water.
  - This is because the hydroxy group can hydrogen bond to water.
  - It can serve as a donor in one hydrogen bond, and an acceptor in two hydrogen bonds.

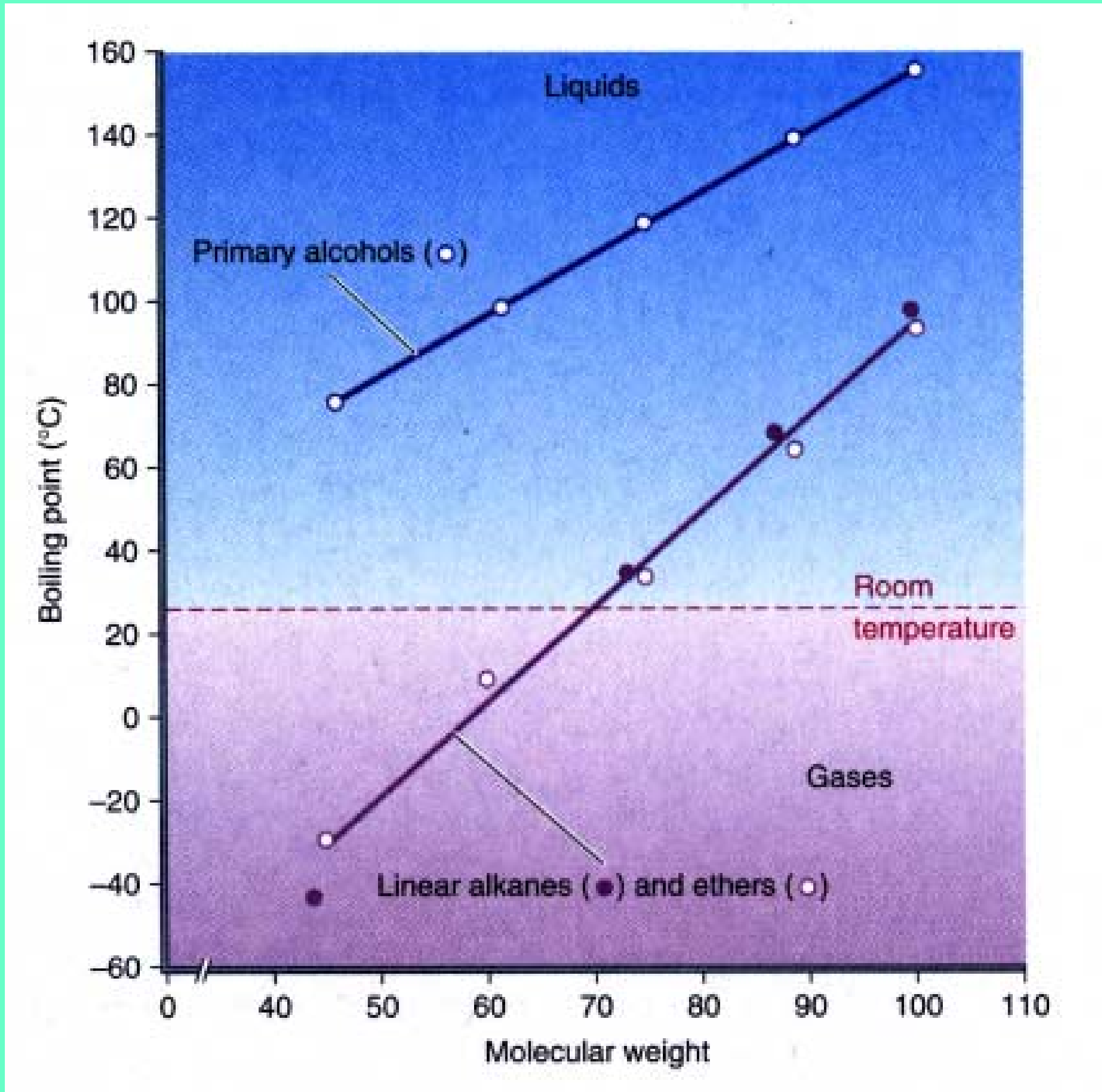


Physical Properties of Alcohols

- Longer chain alcohols are increasingly less soluble.
  - This is because the hydrocarbon portion of the molecule cannot hydrogen bond to water.
  - Substances that cannot interact favorably with water do not dissolve in water.

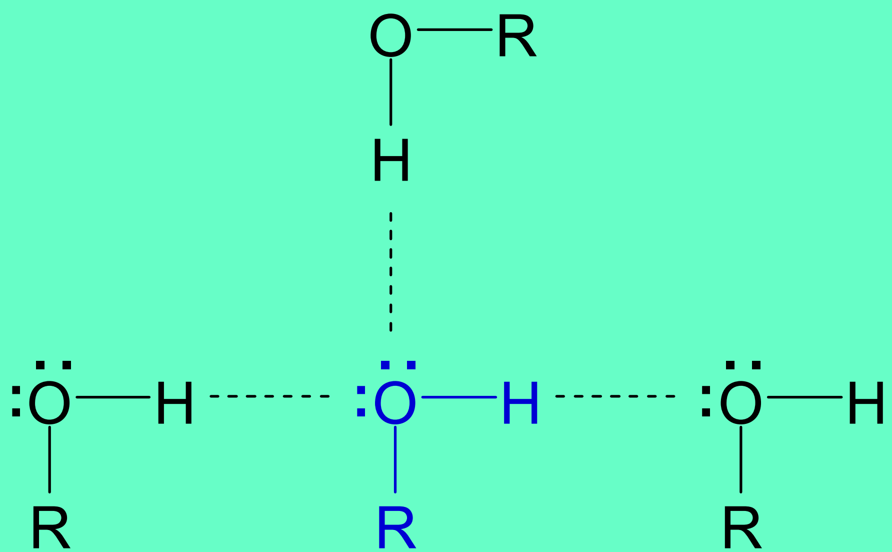
Physical Properties of Alcohols

- Boiling points of alcohols compared to alkanes



Physical Properties of Alcohols

- Hydrogen bonding can also explain why alcohols have higher boiling points than alkanes and other hydrocarbons.
  - Alcohols can hydrogen bond to themselves



Physical Properties of Alcohols

- There is a steady increase in boiling point with molecular weight that is observed for both alcohols and alkanes.
  - This is due to an increase in the attraction between molecules arising from dispersive interactions, which increase as the surface area of the molecules increase.

Reactions of Alcohols

- Alcohols undergo many reactions.
- We focus on just two of them.
  - Alcohol dehydration
  - Alcohol oxidation

Dehydration of Alcohols

- Alcohols can undergo two different dehydration (loss of water) reactions, depending on the temperature:
  - At 140°C, they undergo *intermolecular* dehydration to produce an ether plus water.
    - √ This is an important reaction in carbohydrate chemistry.
  - At 180°C, they undergo *intramolecular* dehydration to produce and alkene plus water
    - √ This is an important reaction in biochemistry, for example, it is found in the citric acid cycle.

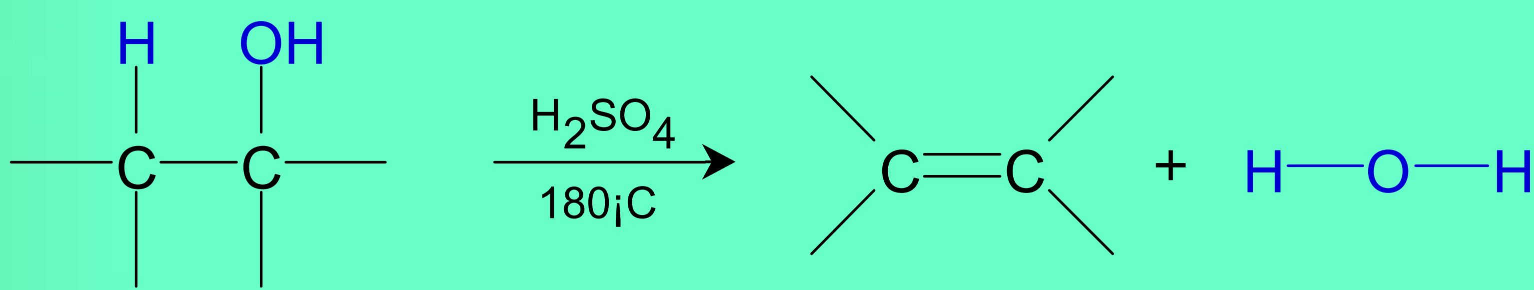
Dehydration of Alcohols

- At 140°C, they undergo *intermolecular* dehydration to produce an ether plus water:
  - The reaction is catalyzed by sulfuric acid (H_2SO_4).

$$\mathrm{R{-}O{-}H} + \mathrm{H{-}O{-}R} \xrightarrow[\text{140¡C}]{H_2SO_4} \underset{\textit{ether}}{\mathrm{R{-}O{-}R}} + \mathrm{H{-}O{-}H}$$

Dehydration of Alcohols

- At 180°C, they undergo *intramolecular* dehydration to produce and alkene plus water:
  - The reaction is also catalyzed by sulfuric acid (H_2SO_4).



alkene

Oxidation of Alcohols

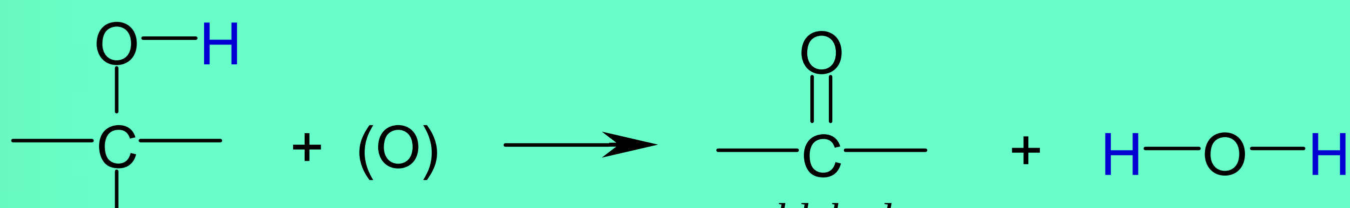
- By definition, oxidation *is a process that involves the removal of electrons from a molecule*.
  - The name comes from the fact that molecular oxygen, which has a high affinity for electrons, is particularly good at removing electrons from other molecules.
  - Oxidation reactions, though, do not require molecular oxygen, other agents that are good at taking away electrons will also work.
  - Examples of oxidizing agents that are often used include $K_2Cr_2O_7$ and $KMnO_4$.

Oxidation of Alcohols

- For the reactions with alcohols we will not stipulate the oxidizing agent being used.
  - We will simply represent the oxidizing agent as (O).
    - √ The "O" designates oxidizing agent, not oxygen.
- Consequently, we will not be able to write balanced chemical equations for oxidation reactions.

Oxidation of Alcohols

- Each alcohol class, *primary*, *secondary*, and *tertiary*, produces a different product when oxidized.
- The general reaction involves removing the hydrogen from the oxygen of the hydroxy group, along with a hydrogen from the carbon to which the hydroxy group is attached

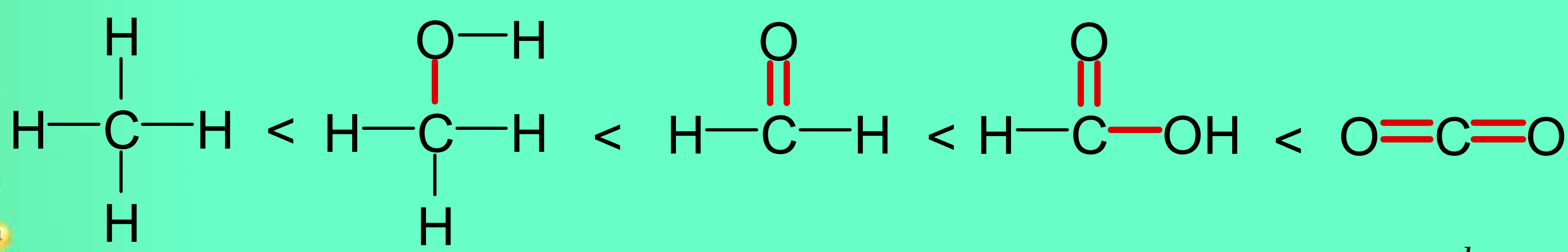


aldehyde or ketone

Oxidation of Alcohols

- The carbon is being oxidized in this reaction because the number of bonds it has to oxygens increases from one to two.
  - Oxygen has a stronger affinity for electrons than carbon
- Oxidation of carbon:

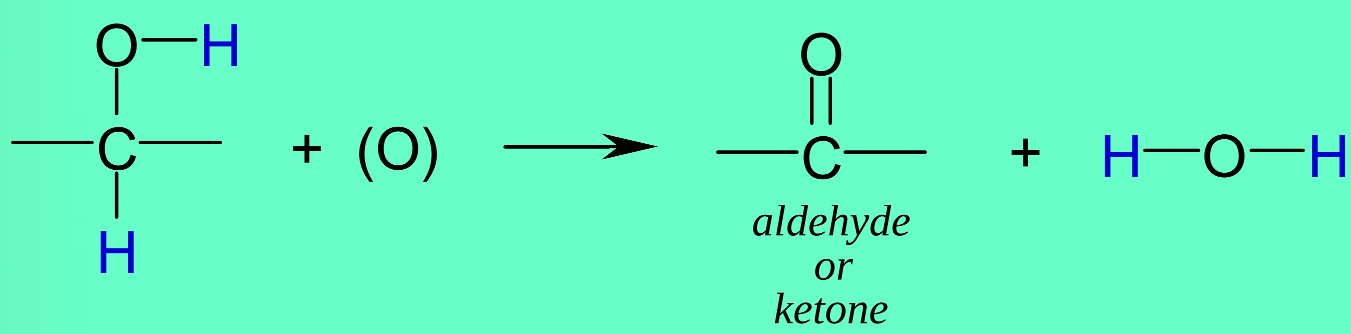
most reduced *most oxidized*



alkane *alcohol* *aldehyde* *carboxylic acid* *carbon dioxide*

Oxidation of Alcohols

- The carbon can be thought of as being oxidized in this reaction because the number of bonds it has to oxygens has increased from one to two.
- Primary alcohols produce aldehydes, while secondary alcohols produce ketones.



Oxidation of Primary Alcohols

- For example, the oxidation of ethanol:

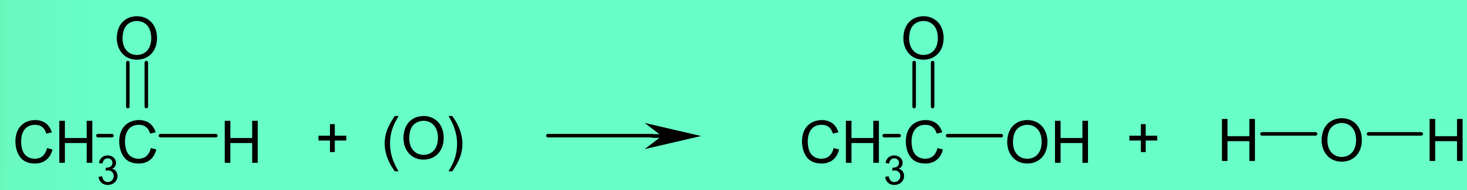
$$CH_3CH_2OH \;+\; (O) \longrightarrow CH_3\overset{\displaystyle O}{\overset{\|}{C}}{-}H \;+\; H{-}O{-}H$$

ethyl alcohol or ethanol → *acealdehyde or ethanal*

  - When ethanol is consumed, this reaction is carried out in the liver
    - √ If large quantities of ethanol are consumed, acetaldehyde levels build up in the blood, resulting nausea.
    - √ Acetaldehyde is the substance detected by breathalizer tests.

Oxidation of Primary Alcohols

- The aldehydes produced by the oxidation of primary alcohols can be further oxidized to carboxylic acids:



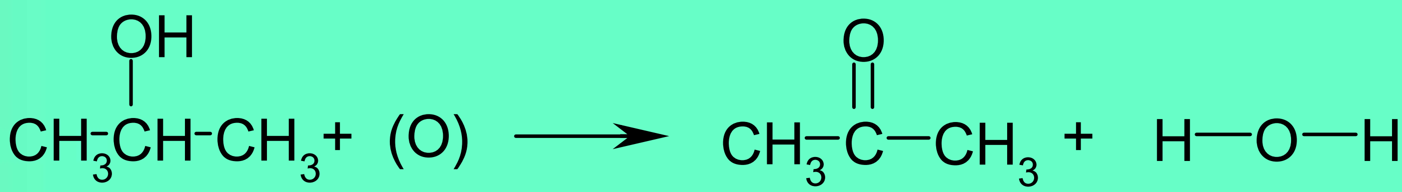
acealdehyde
or
ethanal

acetic acid
or
ethanoic acid

  - Note that an additional carbon–oxygen bond has formed
  - This is as far as the oxidation process goes when mild oxidizing agents, such as $K_2Cr_2O_7$ or $KMnO_4$ are used

Oxidation of Secondary Alcohols

- Secondary alcohols produce ketones when oxidized.
  - For example, 2-propanol is oxidized to 2-propanone (acetone):

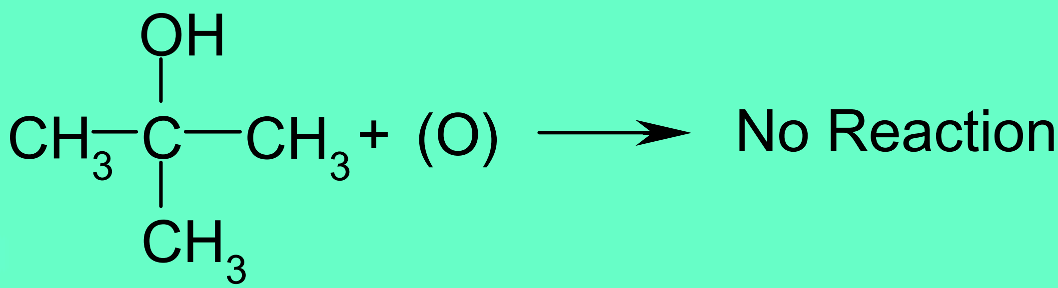


2-propanol *acetone or 2-propanone*

  - This is as far as the oxidation process goes when mild oxidizing agents, such as $K_2Cr_2O_7$ or $KMnO_4$ are used

Oxidation of Tertiary Alcohols

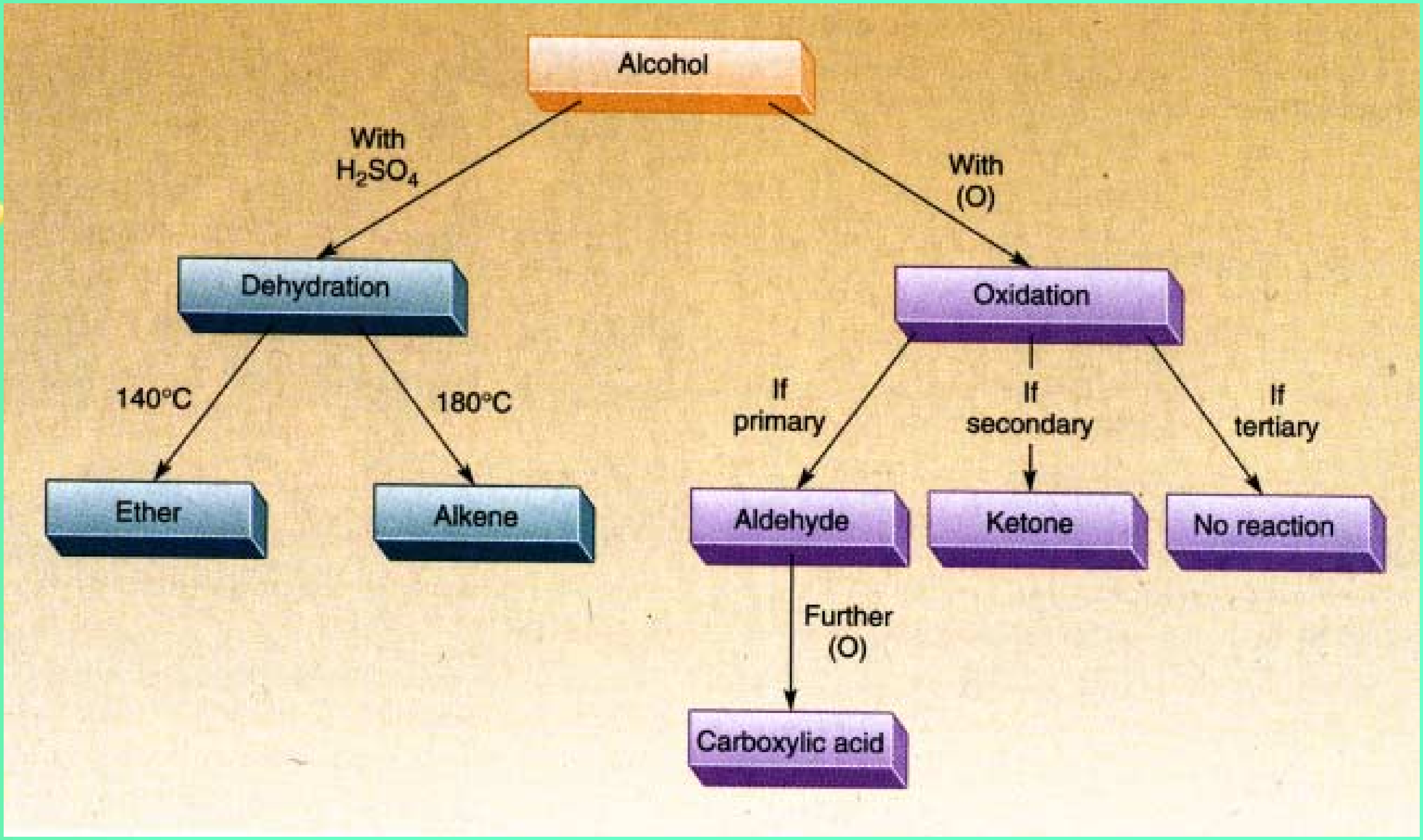
- Tertiary alcohols are not oxidized by mild agents, such as $K_2Cr_2O_7$ or $KMnO_4$.



2-methyl-2-propanol

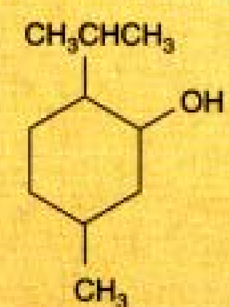
  - Oxidation seems to require that a hydrogen be bonded to the same carbon that the oxygen is bonded to.

Reactions of Alcohols



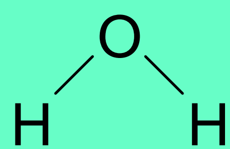
Some Important Alcohols

■ **TABLE 13.2** Examples of alcohols

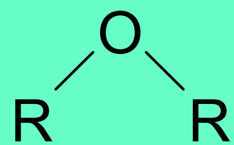
Name	Structural formula	Typical uses
methanol (methyl alcohol)	$CH_3—OH$	Solvent, making formaldehyde
ethanol (ethyl alcohol)	$CH_3CH_2—OH$	Solvent, alcoholic beverages
2-propanol (isopropyl alcohol)	$CH_3CH(OH)CH_3$	Rubbing alcohol, solvent
1-butanol (butanol)	$CH_3CH_2CH_2CH_2—OH$	Solvent, hydraulic fluid
1,2-ethanediol (ethylene glycol)	$HO—CH_2CH_2—OH$	Automobile antifreeze, polyester fibers
1,2-propanediol (propylene glycol)	$CH_3CH(OH)—CH_2(OH)$	Moisturizer in lotions and foods, automobile antifreeze
1,2,3-propanetriol (glycerin, glycerol)	$CH_2(OH)—CH(OH)—CH_2(OH)$	Moisturizer in foods, tobacco, and cosmetics
menthol		Cough drops, shaving lotion, mentholated tobacco

Ethers

- Ethers are obtained when both of the hydrogens of water are replaced with alkyl groups.



water



ether

Naming Ethers

- Ethers are usually referred to their common names.
  - Common names for ethers are constructed by naming each of the alkyl groups followed by *ether*.

$CH_3{-}O{-}CH_2CH_3$

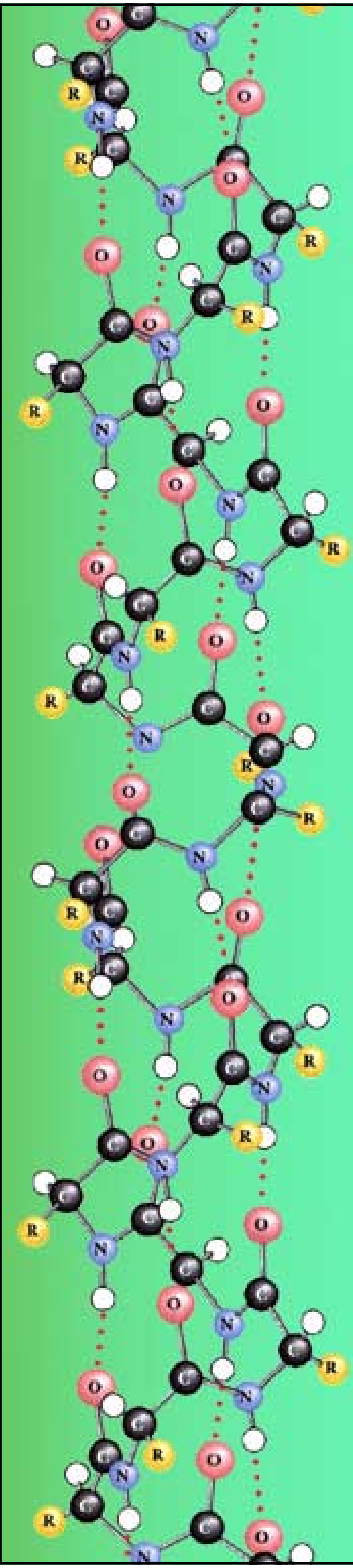
ethyl methyl ether

$CH_3{-}O{-}CH_3$

dimethyl ether

Ether

- Diethyl ether, which is often referred to as just *ether*, was in the 1850's one of the first general anesthetics discovered.

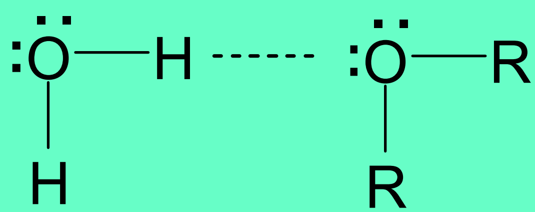


Physical Properties of Ethers

- Ethers can form hydrogen bond with water when they serve as the acceptor, however, they cannot serve as the donor in a hydrogen bond.

Hydrogen Bond

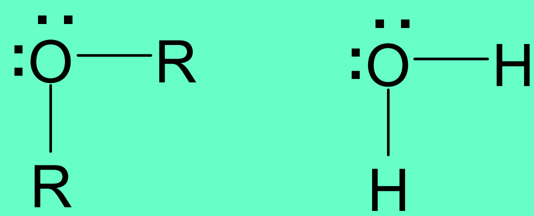
donor *acceptor*



water ether

No Hydrogen Bond can Form

no donor *acceptor*



ether water

Properties of Ethers

- Since ethers *can hydrogen bond to water*, they are somewhat soluble in water, like alcohols
- Since ethers *cannot hydrogen bond to themselves* their boiling points are more like those of alkanes than like alcohols.

Thiols

- Thiols are analogous to alcohol, where a sulfur atom is substituted for the oxygen

alcohol thiol

Thiols

- Thiols are analogous to alcohol, where a sulfur atom is substituted for the oxygen
- We will see that thiols are important in protein chemistry
- Thiols produce strong, often unpleasant, odors
  - Skunks, natural gas, rotten eggs, burning hair, chemicals used in perms, onions, garlic, coffee

Thiols

- The physical and chemical properties of thiols, however, are different than those for alcohols
  - Thiols are not as good at hydrogen bonding and therefore are less soluble in water.
  - Thiols are more reactive than alcohols

Reactions of Thiols

- Oxidation of thiols to produce a disulfide

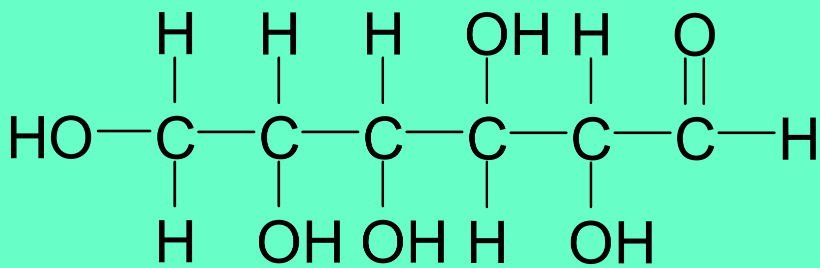
$$\underset{\textit{thiol}}{R\text{—}SH} + \underset{\textit{thiol}}{HS\text{—}R} + \underset{\textit{oxidizing agent}}{(O)} \longrightarrow \underset{\textit{disulfide}}{R\text{—}S\text{—}S\text{—}R} + H\text{—}O\text{—}H$$

- Reaction of thiols with heavy metals ions (Hg^{++}, Pb^{++}):

$$\underset{\textit{thiol}}{R\text{—}SH} + \underset{\textit{thiol}}{HS\text{—}R} + Hg^{++} \longrightarrow R\text{—}S\text{—}Hg\text{—}S\text{—}R + 2\,H\text{—}H$$

Polyfunctional Compounds

- Many organic molecules have more than one type of functional group
  - For example, glucose contains both hydroxy and aldehyde groups



glucose