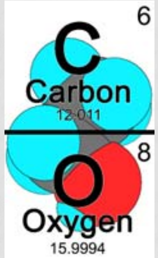
Chapter 3
Alcohols, Phenols, and Ethers

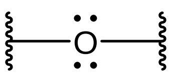


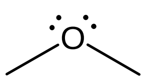
Chapter Objectives:

- Learn to recognize the alcohol, phenol, and ether functional groups.
- Learn the IUPAC system for naming alcohols, phenols, and ethers.
- Learn the important physical properties of the alcohols, phenols, and ethers.
- Learn the major chemical reaction of alcohols, and learn how to predict the products of dehydration and oxidation reactions.
- Learn to recognize the thiol functional group.

Introduction

- In this chapter, we will start looking at organic molecules that incorporate C—O bonds.
- Oxygen is in Group 6A of the periodic table, and in most of its compounds, contains two single bonds and two lone pairs (or one double bond and two lone pairs), and is sp^3-hybridized with a **bent** molecular shape:

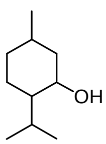




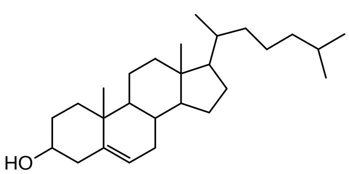
- The **alcohol**, **phenol**, and **ether** functional groups are found in a number of important naturally occurring molecules:

CH_3CH_2OH
Ethanol

$CH_3CH_2OCH_2CH_3$
Diethyl ether



Menthol



Cholesterol

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Alcohols

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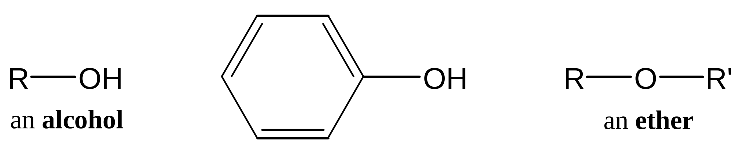
The Hydroxy (—OH) Functional Group

- The **hydroxyl group** (**—OH**) is found in the **alcohol** and **phenol** functional groups. (***Note:*** that's not the same as hydroxide, OH^-, which is ionic.)
  - in **alcohols**, a hydroxyl group is connected to a carbon atom.
  - in **phenols**, —OH is connected to a benzene ring. (The "parent" molecule of this class is also named phenol: PhOH or C_6H_5OH.)
- When two carbon groups are connected by single bonds to an oxygen, this is classified as the **ether** functional group.



an **alcohol**   a **phenol**   an **ether**

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Where Does the Word "Alcohol" Come From?

- The word "alcohol" comes from the Arabic term *al kohl* meaning "the fine powder." Originally, this referred to an antimony sulfide (Sb_2S_3)compound used for eye shadow, which was ground up to form a fine powder, but then later came to refer to any finely divided powder. In the Middle Ages, this term came to mean the "essence" of anything.
- When the Europeans took up alchemy in the Middle Ages, they referred to vapors from evaporating or boiling compounds as "spirits," since they did not believe them to be material in the same sense that solids and liquids were. Alchemists began referring to "spirits of wine," and since an alcohol when it boils away seems to powder away to nothing, they also began to refer to "alcohol of wine" and then simply "alcohol".

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Some Common Alcohols

CH_3OH

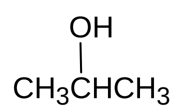
methanol
methyl alcohol
(wood alcohol)
("methy" = wine, "hule" = wood)
Found in wood smoke; contributes to the bouqet of new wine; metabolized in the body to formaldehyde and formic acid, and can cause blindness or death (> 50 mL)

CH_3CH_2OH

ethanol
ethyl alcohol
(grain alcohol)
The acohol of alcoholic beverages; the fermentation of honey, grain, or fruit juices to yield beers and wines was probably the first chemical reaction to be discovered; metabolized in the body to produce acetaldehyde

$CH_3CH_2CH_2OH$

1-propanol
n-propyl alcohol



2-propanol
isopropyl alcohol
Rubbing alcohol is 70% isopropyl alcohol and 30% water

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Nomenclature of Alcohols and Phenols

- **Step 1.** Name the longest chain to which the hydroxyl (—OH) group is attached. The name for this chain is obtained by dropping the final **-e** from the name of the hydrocarbon parent name and adding the ending **-ol**.
- **Step 2.** Number the longest chain to give the lowest possible number to the carbon bearing the hydroxyl group.
- **Step 3.** Locate the position of the hydroxyl group by the number of the C to which it is attached.
- **Step 4.** Locate and name any other substituents.
- **Step 5.** Combine the name and location for other groups, the hydroxyl group location, and the longest chain into the final name.

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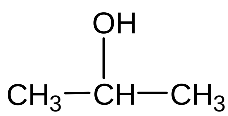
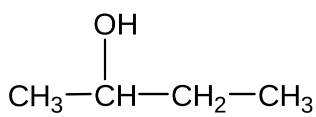
Examples: Naming Alcohols and Phenols

- Provide acceptable IUPAC names for the following compounds:

CH_3-OH CH_3-CH_2-OH $CH_3-CH_2-CH_2-OH$





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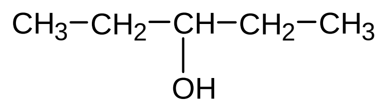
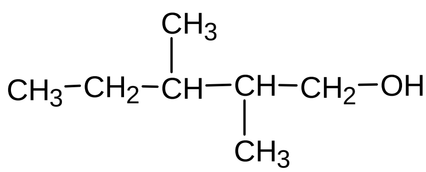
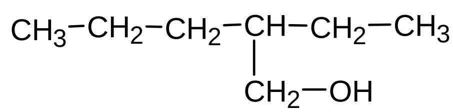
Examples: Naming Alcohols and Phenols

- Provide acceptable IUPAC names for the following compounds:

$CH_3-CH_2-CH_2-CH_2-CH_2-OH$







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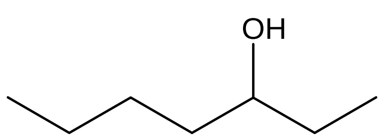
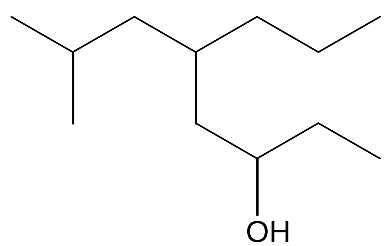
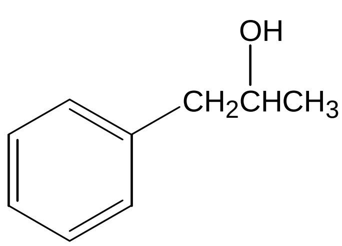
Examples: Naming Alcohols and Phenols

- Provide acceptable IUPAC names for the following compounds:







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Examples: Naming Alcohols and Phenols

- Draw and name all of the possible isomers of butanol ($C_4H_{10}O$)

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Nomenclature of Alcohols and Phenols

- If there is more than one OH group, a counting prefix (di-, tri-, tetra-, etc.) is placed immediately in front of the suffix **-ol** (*di*ol, *tri*ol, *tetra*ol, etc.).
  - Usually, the final "e" of the parent hydrocarbon is not dropped (e.g., 1,2-propanediol).
  - The position of each alcohol group is indicated by carbon number, separated by commas (e.g., *1,3*-butanediol).
- For cyclic alcohols, the carbon bearing the OH is numbered as "1."
- Phenols are named after the parent compound **phenol**; the C bearing the OH is numbered as "1."

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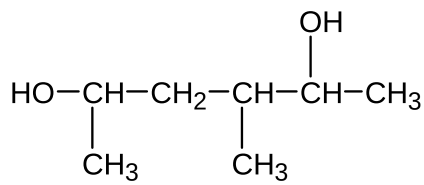
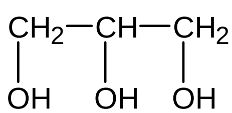
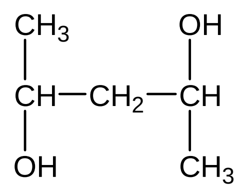
Examples: Naming Alcohols and Phenols

- Provide acceptable IUPAC names for the following compounds:

$HO-CH_2-CH_2-OH$







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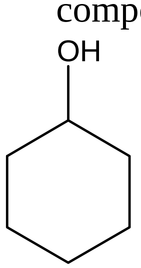
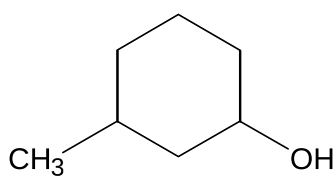
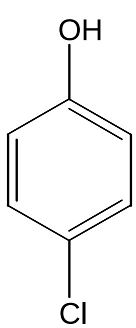
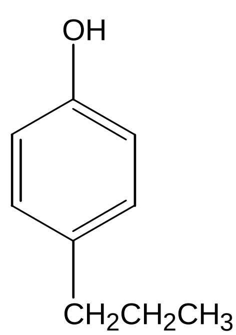
Examples: Naming Alcohols and Phenols

- Provide acceptable IUPAC names for the following compounds:









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Examples: Nomenclature of Alcohols

- Draw structural formulas for the following molecules:
  - 3-methyl-2-pentanol
  - 2,4,4,5-tetramethyl-2-heptanol
  - 1-ethyl-1-hexanol (what's wrong with this name?)

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Examples: Nomenclature of Alcohols

- Draw structural formulas for the following molecules:
  - 3-ethylcyclopentanol
  - 3-ethylphenol
  - 3-methyl-2,4-pentanediol

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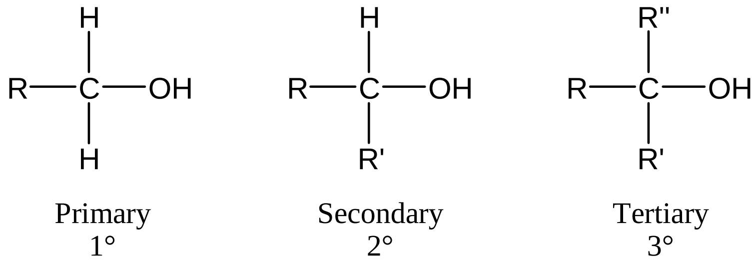
Classification of Alcohols

- Alcohols are classified as **primary (1°)**, **secondary (2°)**, or **tertiary (3°)** according to how many carbon groups are attached to the carbon bearing the OH group:



- The number of hydrogens on the carbon bearing the OH group does affect some chemical properties.

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Physical Properties of Alcohols

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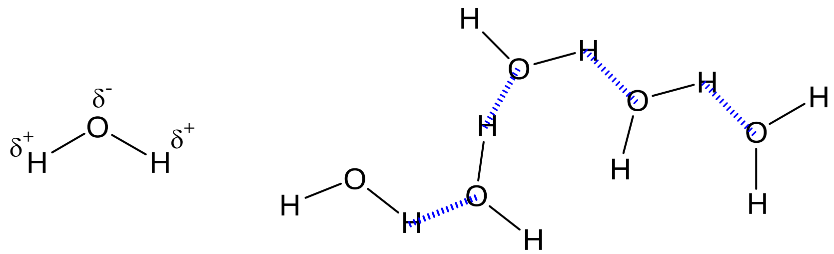
Hydrogen Bonding

- The oxygen-hydrogen bond is an especially polar bond because oxygen is much more electronegative than hydrogen is.



- The O—H bond is therefore a **polar bond**, and any molecule which contains an O—H bond (like an alcohol) is a **polar** molecule.

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Physical Properties of Alcohols

- The general rule in solubility is "like dissolves like."
- Since the OH group makes alcohols polar, they will mix with polar solvents like water — as long as the carbon chain is fairly short.
  - The longer the carbon chain, the less soluble the alcohol is.

Water solubility

Soluble ⟷ Insoluble

Short chain alcohols methanol ethanol isopropanol	butanol	pentanol	**Long chain alcohols** hexanol heptanol etc.

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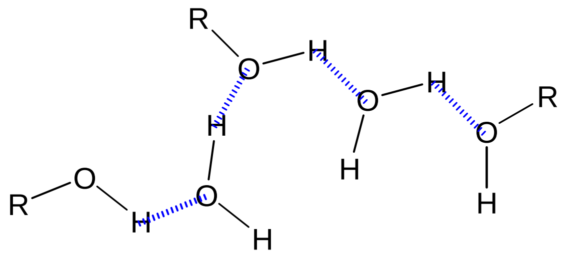
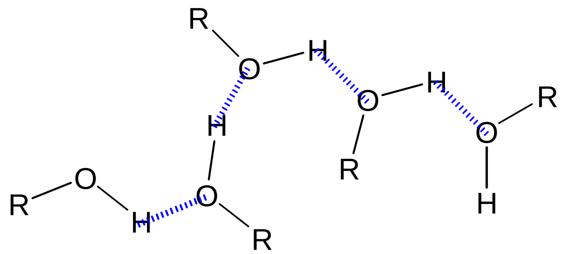
Hydrogen Bonding of Alcohols

- Alcohols hydrogen-bond to water:



- Alcohols also hydrogen-bond to each other:



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Boiling Points of Alcohols

- Because alcohols hydrogen bond to each other, they have higher boiling points than alkanes of the same molecular weight.
- The boiling point of alcohols increases as the molecules become larger.

Name	Structure	Molecular Weight	Boiling Point
propane	$CH_3CH_2CH_3$	44.09 g/mol	-42.1°C
dimethyl ether	CH_3OCH_3	46.07 g/mol	-24°C
ethanol	CH_3CH_2OH	46.07 g/mol	78.3°C

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Examples: Physical Properties of Alcohols

- Arrange the following substances in order of increasing boiling point and increasing solubility in water:
  - 2-butanol
  - 2-propanol
  - 2-methylpropane
  - 2-pentanol

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Reactions of Alcohols

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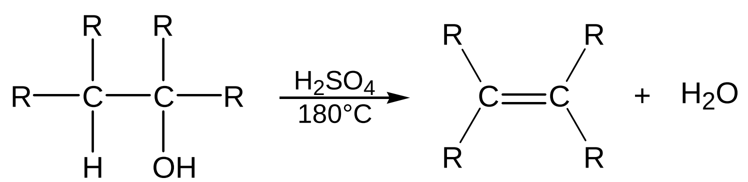
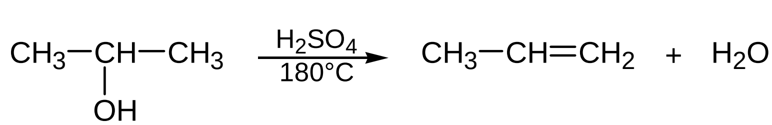
Dehydration of Alcohols to Produce Alkenes

- Heating alcohols in concentrated sulfuric acid (**H_2SO_4**) at **180°C** removes the OH group and a H from an adjacent carbon to produce an **alkene**, with water as a by-product. Since water is "removed" from the alcohol, this reaction is known as a **dehydration reaction** (or an *elimination reaction*):





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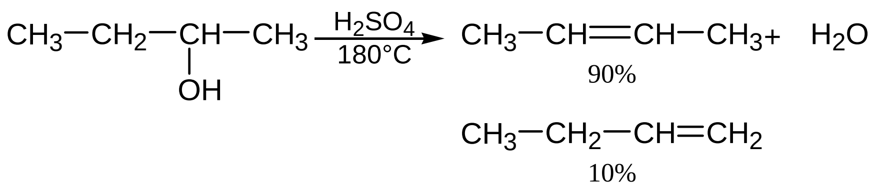
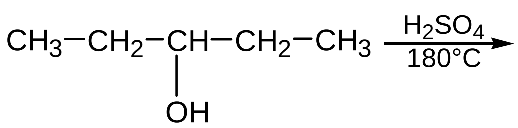
Dehydration of Alcohols to Produce Alkenes

- If there is more than one possible product of a dehydration reaction, the major product can be predicted from Zaitsev's Rule:
- **Zaitsev's Rule** — when an alkene is produced in an elimination reaction, the major product is the one with the more highly substituted double bond.





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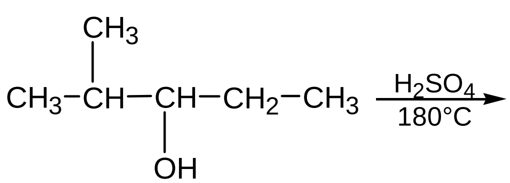
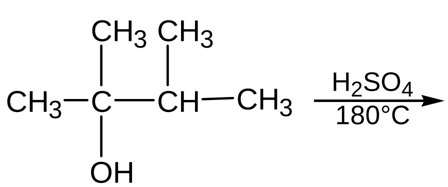
Examples: Dehydration of Alcohols

- Complete the following reactions:





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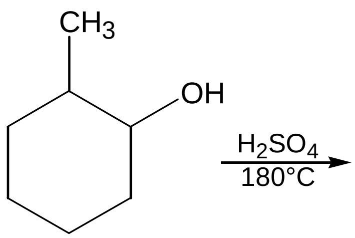
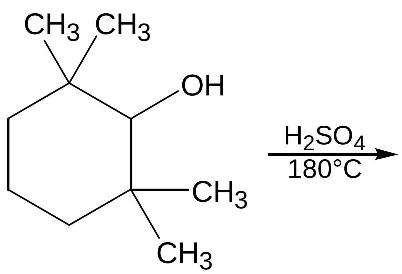
Examples: Dehydration of Alcohols

- Complete the following reactions:





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Dehydration of Alcohols to Produce Ethers

- Heating alcohols (R—OH) in concentrated sulfuric acid (**H_2SO_4**) at **140°C** removes a molecule of water from two alcohol molecules, causing the two “R” groups to become attached to an oxygen atom, forming an **ether** functional group:

$$R{-}OH + R{-}OH \xrightarrow[140°C]{H_2SO_4} R{-}O{-}R + H_2O$$

$$CH_3CH_2OH + CH_3CH_2OH \xrightarrow[140°C]{H_2SO_4} CH_3CH_2OCH_2CH_3$$

diethyl ether

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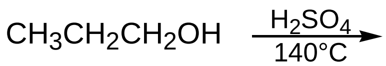
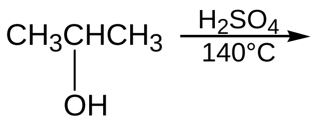
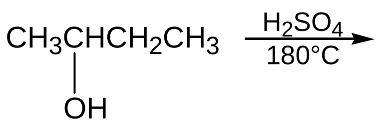
Examples: Dehydration of Alcohols

- Complete the following reactions:







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Oxidation of Alcohols to Carbonyl Compounds

- An oxidation reaction occurs when a molecule *loses electrons*. This is usually manifested as an *increase in the number of oxygen atoms* or a *decrease in the number of hydrogen atoms*.
- Some common oxidizing agents include potassium permanganate ($KMnO_4$), chromic acid (H_2CrO_4), sodium dichromate ($Na_2Cr_2O_7$), and other Cr^{6+} salts.
- Alcohols can be oxidized by removing two H atoms from the molecule; the exact products of the reaction will depend on the type of alcohol.
- Representation in book:

$$R_2CHOH + (O) \rightarrow R_2C{=}O + H_2O$$

- [O] = oxidation

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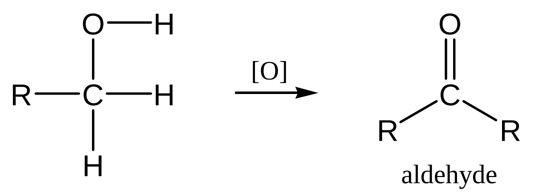
Oxidation of Alcohols to Carbonyl Compounds

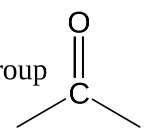
- Primary or secondary alcohols can be oxidized to produce compounds containing the carbonyl group (a carbon-oxygen double bond, C=O):



1° or 2° alcohol

aldehyde or ketone

carbonyl group



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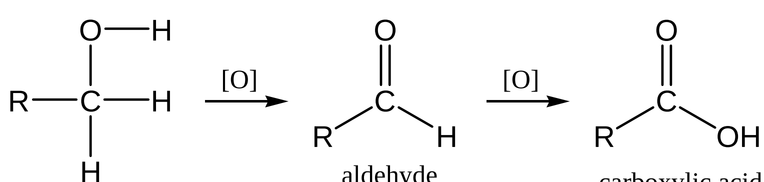
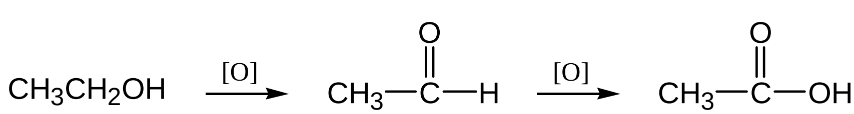
Oxidation of 1° Alcohols

- Primary alcohols are oxidized first to **aldehydes**, but the aldehydes are then usually oxidized into **carboxylic acids**.



1° alcohol

carboxylic acid



ethanol

acetaldehyde

acetic acid

In the body, oxidation of ethanol to acetaldehyde takes place in the liver; the acetaldehyde is further oxidized to acetyl coenzyme A, which can be used to synthesize fat or eventually be oxidized to water and carbon dioxide.

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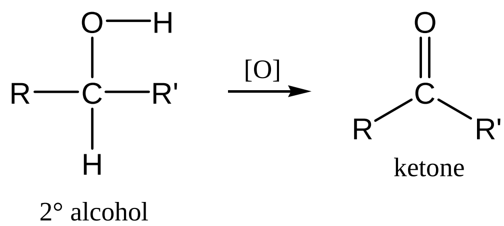
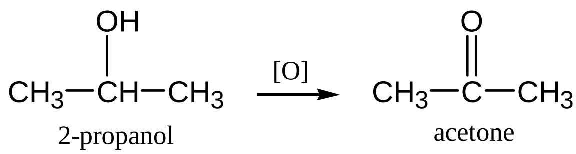
Oxidation of 2° Alcohols

- Secondary alcohols are oxidized to **ketones**, which cannot be oxidized any further:





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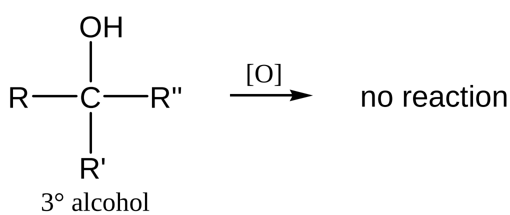
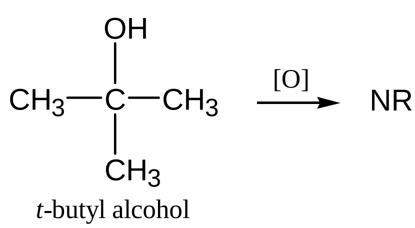
Oxidation of 3° Alcohols

- Tertiary alcohols, because there is by definition no hydrogen on the alcoholic carbon, cannot be oxidized:





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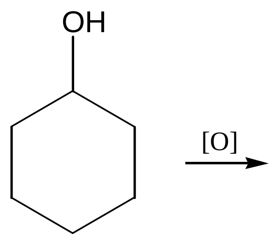
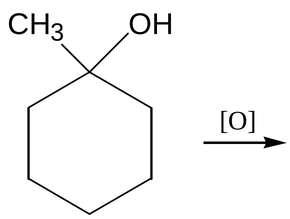
Examples: Oxidation of Alcohols

- Complete the following reactions:





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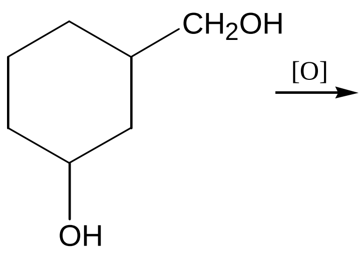
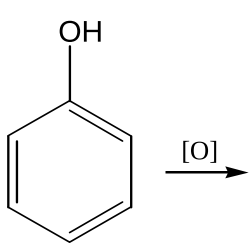
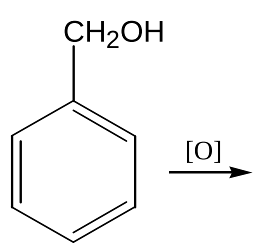
Examples: Oxidation of Alcohols

- Complete the following reactions:







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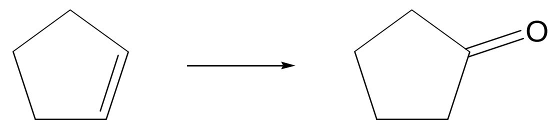
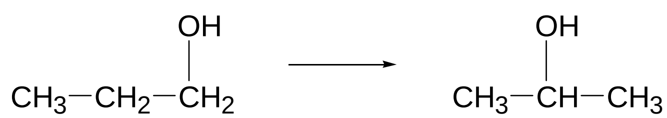
Examples: Multistep Reactions

- Often, transformations on organic molecules must take place in more than one step.





$CH_2{=}CH_2 \longrightarrow CH_3CH_2-O-CH_2CH_3$

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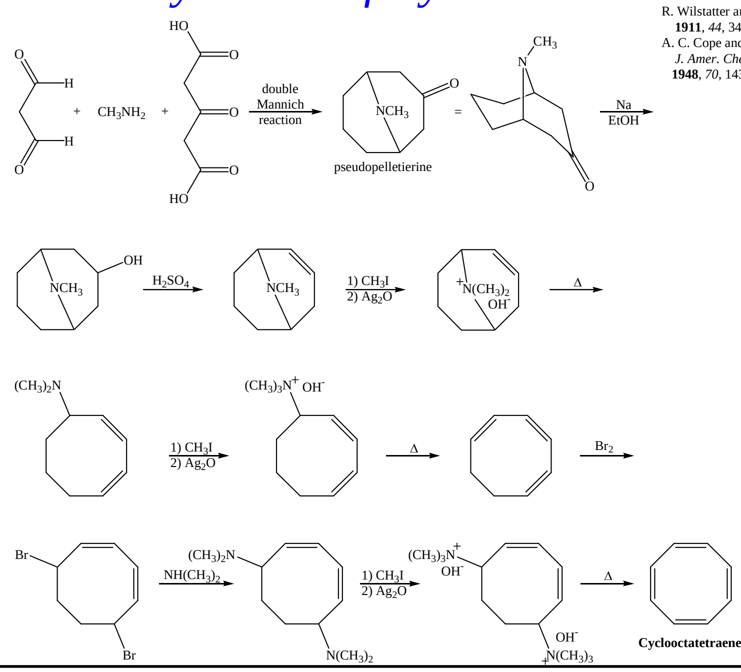
Total Synthesis of Cyclooctatetraene

R. Wilstatter and E. Waser, *Ber.*, **1911**, *44*, 3423
A. C. Cope and C. G. Overberger, *J. Amer. Chem. Soc.*, **1947**, *69*, 976; **1948**, *70*, 1433



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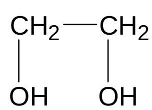
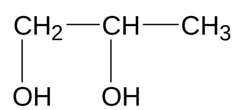
Some Important Alcohols

41

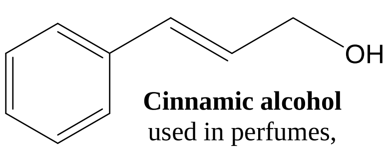
Some Important Alcohols



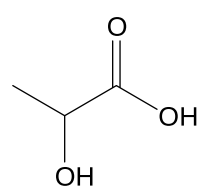
Ethylene glycol
antifreeze — pure ethylene glycol freezes at 11°F, but a 50:50 mixture of ethylene glycol and water freezes at -37°F; airplane de-icer; humectant (keeps other substances moist), used in ball point pen inks



Propylene glycol
antifreeze, moisturizer in lotions and foods



Cinnamic alcohol
used in perfumes, particularly in lilac and other floral scents; flavoring agent, soaps, cosmetics



Lactic acid
produced from fermentation of sugars during anaerobic conditions; sour taste, found in sourdough bread, pickles, sauerkraut, sweat, etc.

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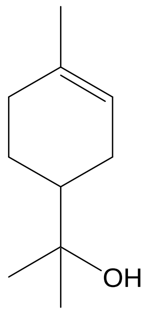
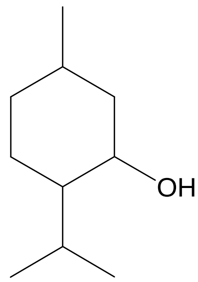
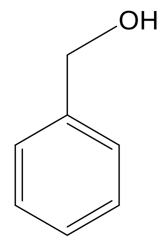


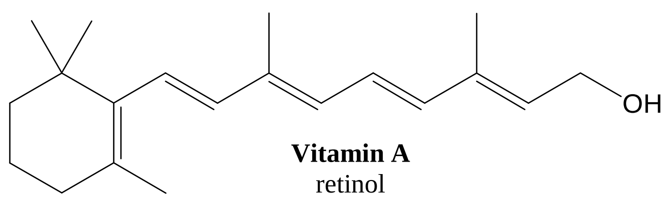
α-Turpineol
pine oil; perfume and bactericide used in domestic cleaners



Menthol
oil of mint; has a cooling taste; found in cough drops, shaving lotion, and mentholated tobacco

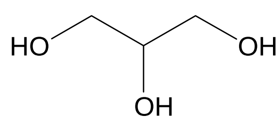


Benzyl alcohol
used in perfumes and flavors, cosmetics, ointments, ball point pen inks

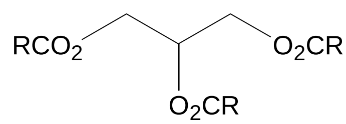


Vitamin A
retinol

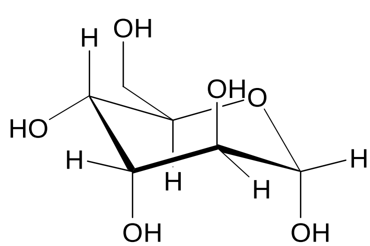
43



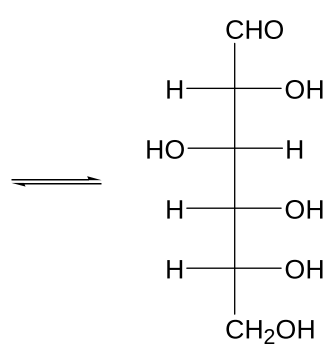
Glycerol / glycerin
softening agent and moisturizer found is cosmetics and many foods; used to keep toothpaste moist



A **triglyceride**
fats and oils



α-D-glucose



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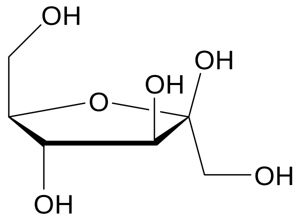
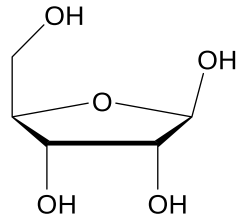
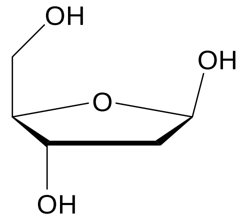
A Few Sugars



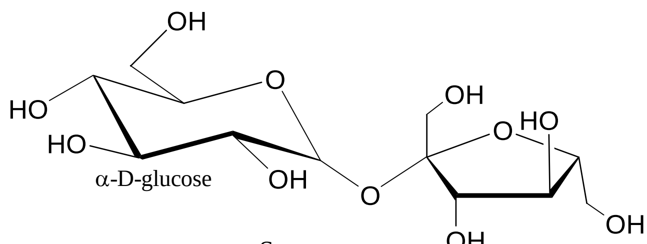
β-D-fructose



β-D-ribose



β-D-deoxyribose



α-D-glucose

β-D-fructose

Sucrose
(a **disaccharide**)

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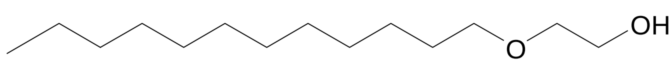
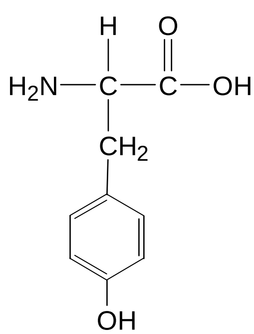
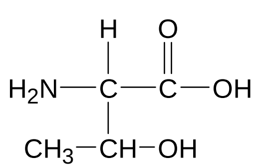


Polyoxyethylene
a *nonionic detergent*; produces less foam, and is more effective at lower temperatures than many other detergents

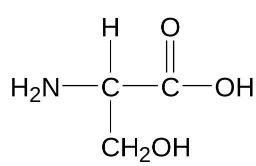
Amino Acids containing alcohols



Tyrosine (Tyr)



Threonine (Thr)



Serine (Ser)

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Phenols

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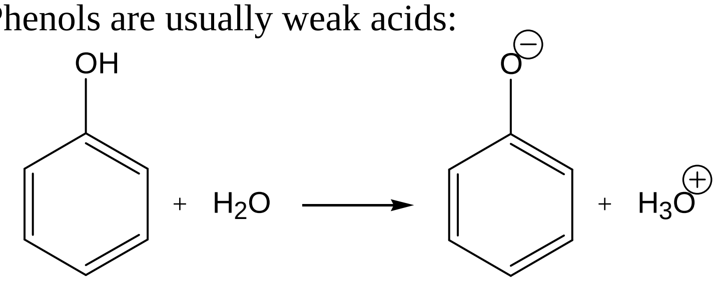
Characteristics and Uses of Phenols

- Phenols are usually weak acids:



- A solution of phenol in water (carbolic acid) can be used as an antiseptic and disinfectant. Joseph Lister introduced the use of phenol as a hospital antiseptic in 1867, which cut down drastically on deaths due to complications resulting from the use of unsterile equipment.

"Lister and his carbolic acid ... succeeded in converting hospitals into something more than elaborate pauses on the way to the grave." (Isaac Asimov, *Isaac Asimov's Biographical Encyclopedia of Science and Technology*, 1972).

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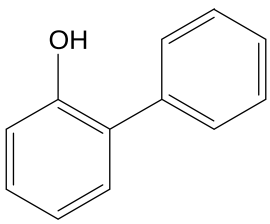
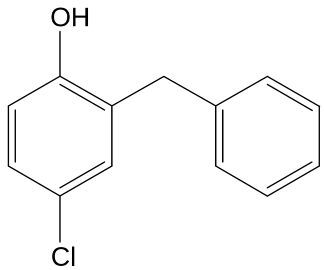
Important Phenols

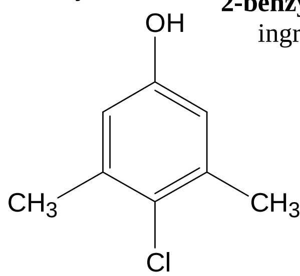


***ortho*-phenylphenol**
ingredient in Lysol

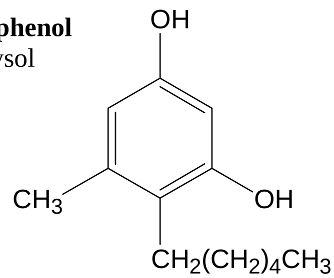


2-benzyl-4-chlorophenol
ingredient in Lysol

Other phenols are also present in Lysol; they interfere with oxidation reactions to prevent the spoiling of food.



4-chloro-3,5-dimethylphenol
topical antiseptic



4-n-hexylresorcinol
found in mouthwash, throat lozenges

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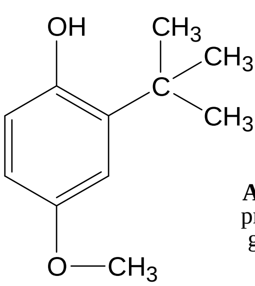
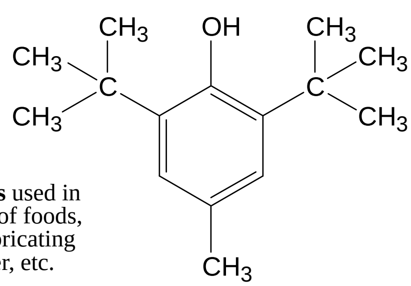
Phenols as Preservatives

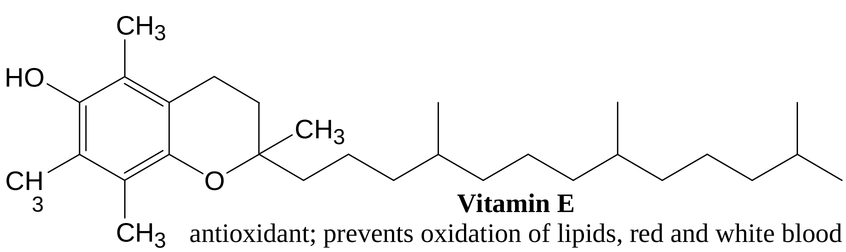


BHA (butylated hydroxy anisole)
2-*t*-butyl-4-methoxyphenol

Antioxidants used in preservation of foods, gasoline, lubricating oils, rubber, etc.



BHT (butylated hydroxy toluene)
2,6-di-*t*-butyl-4-methylphenol



Vitamin E
antioxidant; prevents oxidation of lipids, red and white blood cells, polyunsaturated fatty acids, lung tissue; prevents oxidation in lungs of pollutants such as NO_2 and O_3

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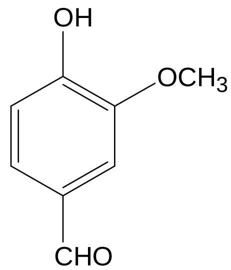
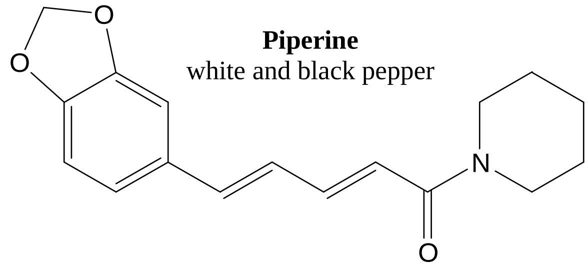
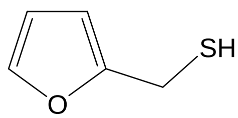
Phenols in Flavors and Fragrances



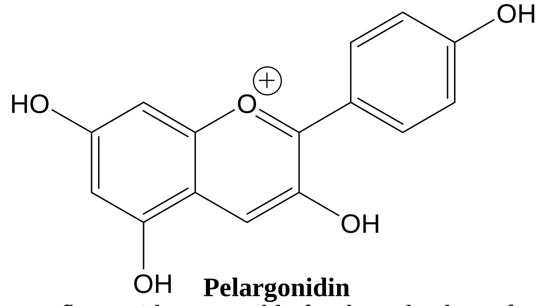
Vanillin
oil of vanilla



Piperine
white and black pepper



2-Furylmethanethiol
odor of coffee



Pelargonidin
a *flavonoid*; responsible for the red colors of geraniums, ripe raspberries, and strawberries

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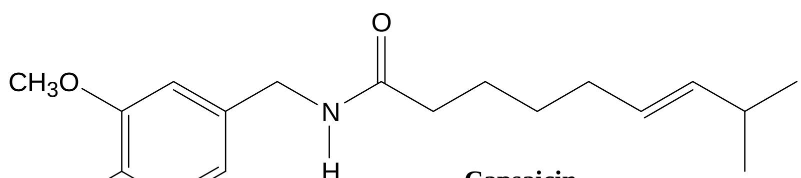
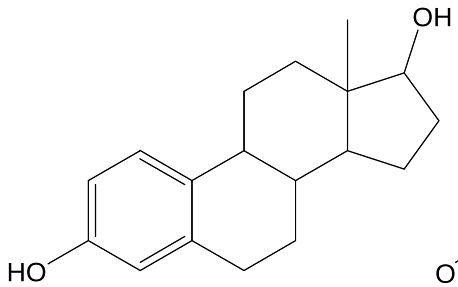
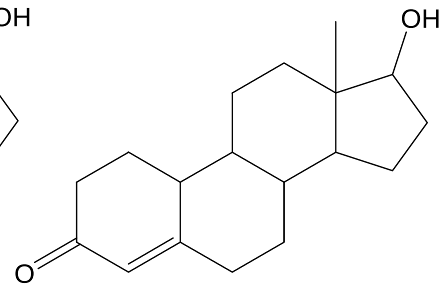


Capsaicin
active component of red and green chili peppers, paprika



Estradiol



Testosterone

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Ethers

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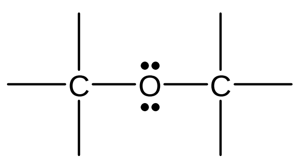
Ethers

- In the **ether** functional group, two carbon groups are connected to a single oxygen.

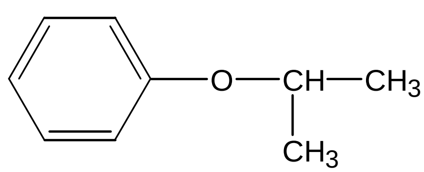


an **ether**

$CH_3—O—CH_3$

$CH_3CH_2—O—CH_2CH_3$

$CH_3—O—CH_2CH_3$



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Ether Nomenclature

- Common names for ethers are obtained by first naming the two carbon groups attached to the oxygen (in alphabetical order) and then adding the word "ether" to the end. If the two groups are the same, the prefix "di-" is used, although sometimes this is simply dropped ("ethyl ether").

- In the IUPAC system, ethers are named as **alkoxy** substituents (—OR = alkoxy group). The *-yl* ending of alkyl substituents is replaced by ***-oxy***

$—CH_3$	methyl	$—OCH_3$	methoxy
$—CH_2CH_3$	ethyl	$—OCH_2CH_3$	ethoxy

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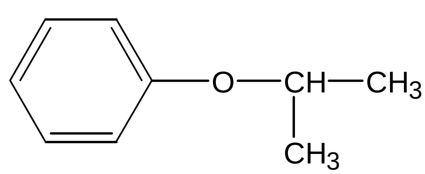
Examples: Nomenclature of Ethers

- For the following compounds, provide IUPAC names and trivial names (where possible).

$CH_3—O—CH_3$ $CH_3CH_2—O—CH_3$

$CH_3CH_2—O—CH_2CH_3$



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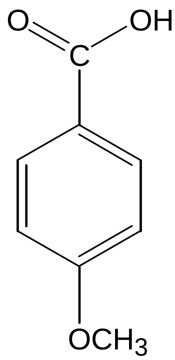
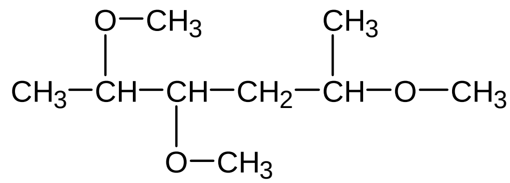
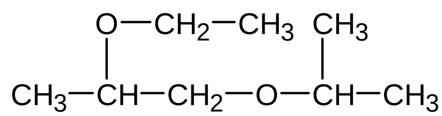
Examples: Nomenclature of Ethers

- Name the following compounds:







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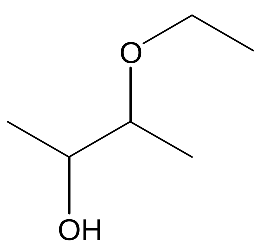
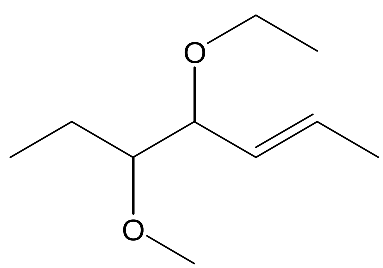
Examples: Nomenclature of Ethers

- Name the following compounds:





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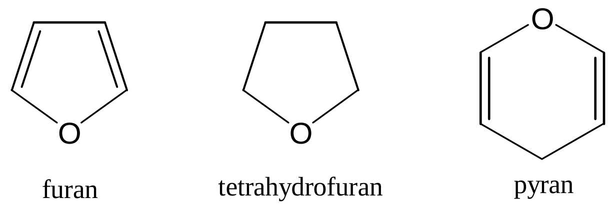
Cyclic Ethers

- Some ethers are found in cyclic structures. (A ring that contains elements other than carbon is called a *heterocyclic ring*.)



- Tetrahydrofuran (THF) is a common solvent in organic reactions, often used in place of diethyl ether; furan and pyran turn up frequently in carbohydrate chemistry.

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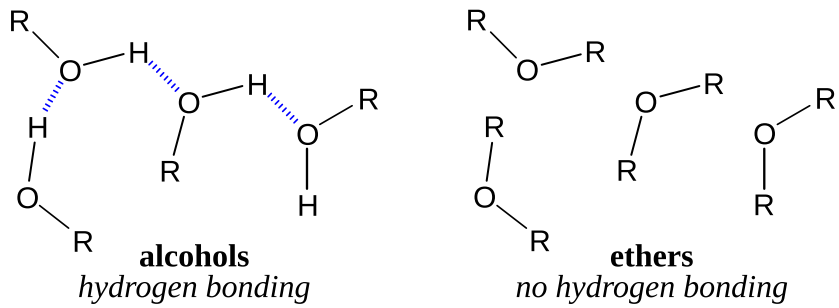
Physical Properties of Ethers

- Alcohols hydrogen-bond to each other because they have highly polar O—H bonds.
- Ethers do not have O—H bonds, and so do **not** hydrogen-bond to each other.



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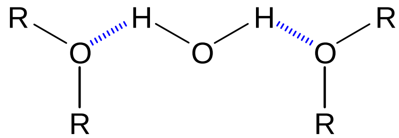
Physical Properties of Ethers

- Ethers are slightly polar, and **can** hydrogen-bond to water, although very weakly, through the oxygen atom:



- Ethers therefore have low boiling points, and a higher solubility in water than hydrocarbons.
- Ethers are inert to most reagents, so they make good solvent for chemical reactions.
- Some ethers make good anesthetics.

boiling point: alcohols > ethers > alkanes

water solubility: alcohols > ethers > alkanes

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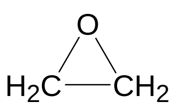
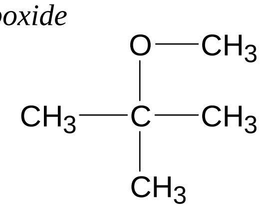
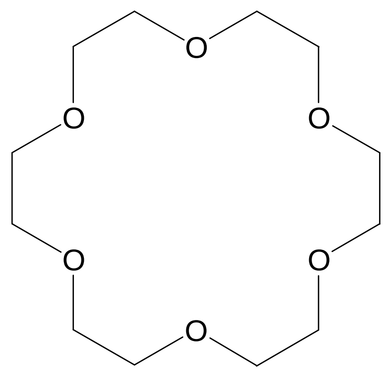
Some Important Ethers



Ethylene oxide
an *epoxide*



methyl t-butyl ether (MTBE)
A common gasoline additive used as an octane booster to oxygenate the gas, and make it burn with less "knocking." It has been used since 1979 as a replacement for tetraethyl lead (leaded gasoline). This additive is the subject of intense debate because of potential health hazards of drinking water contaminated with MTBE



18-crown-6
A "crown ether" (Charles J. Pedersen, Donald J. Cram, and Jean-Marie Lehn, Nobel Prize, 1987), which is capable of binding metal ions

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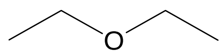
Anesthetics

N_2O

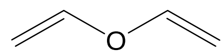
Nitrous oxide
laughing gas
first chemical anesthetic
(Sir Humphrey Davy, 1800)

$CHCl_3$

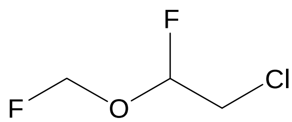
Chloroform
(James Young Simpson, 1846; first to use anesthesia during childbirth)



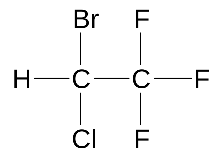
Diethyl ether
first common anesthetic
(Crawford W. Long, 1842
William T. G. Morton,
Charles T. Jackson, 1844)



Divinyl ether
faster acting and less nauseating than diethyl ether



Enflurane



Halothane

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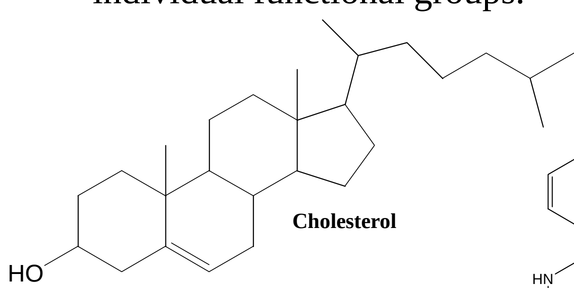
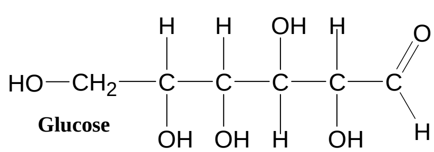
Polyfunctional Compounds

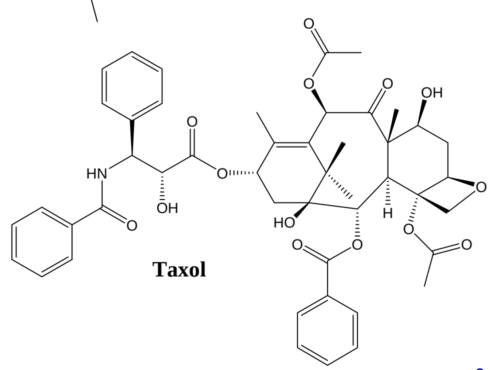
- Compounds with more than one functional group are very common in nature; these polyfunctional molecules possess all of the reactivity of their individual functional groups.



Cholesterol



Glucose



Taxol

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Thiols

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Thiols

- Sulfur is in the same group on the periodic table as oxygen, and so forms many compounds which are similar to oxygen:

R—OH	R—SH	R—S—S—R
an **alcohol**	a **thiol**	a **disulfide**

- Many thiols have strong, unpleasant odors. Ethanethiol, for instance, is added to natural gas to make it possible to detect gas leaks:

CH_3CH_2SH

ethanethiol

66

A Few Interesting Thiols

$CH_3CH_2CH_2SH$

Propanethiol
lachrymator produced when onions are cut

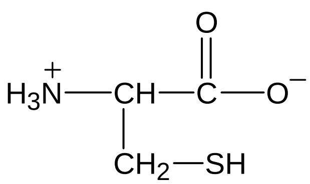
$CH_2{=}CHCH_2SH$

Allyl thiol

$CH_2{=}CHCH_2{-}S{-}CH_2CH{=}CH_2$

Allyl sulfide

These compounds are partially responsible for the odor and flavor of garlic.



Cysteine (Cys)

The amino acid cysteine is found in many proteins; the SH group can link with other SH groups to form disulfide bridges.

- Disulfide linkages are important structural features of some proteins, especially those of hair.
- Enzymes containing SH groups can be damaged by complexation with heavy metals such as lead and mercury.

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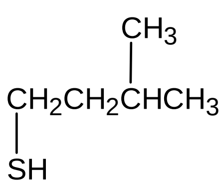
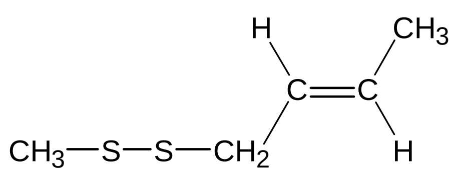
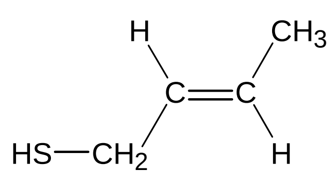
A Few Interesting Thiols







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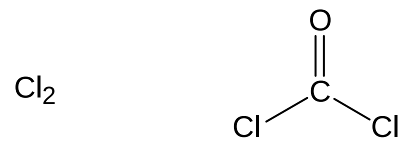
Gas Warfare



Chlorine Phosgene

Chlorine gas and **phosgene** are among the first agents to have been used in gas warfare. Molecular chlorine is a gas at room temperature, and heavier than air; breathing chlorine gas causes pulmonary edema (swelling from excess fluid in tissues).

Phosgene is a particularly insidious poison, since symptoms may take from one to three days to appear. The gas does not have as obvious an odor as chlorine, and when inhaled, is hydrolyzed in the lungs to produce hydrochloric acid, which dissolves the membranes in the lungs. This can result in edema, blood loss, shock, and respiratory failure. Phosgene must be inhaled to be "effective," since it cannot be absorbed through the skin.

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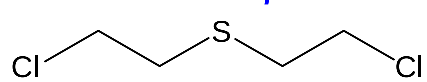
Gas Warfare



Mustard gas

Mustard gas is a chemical weapon first used in 1917 during World War I at the battle of Ypres. It has a sweet, agreeable odor, similar to that of mustard, but the similarity ends there.

It forms painful blisters on the skin (a *vesicant*) on contact, and in the lungs when inhaled; symptoms usually develop anywhere from 4 to 24 hours after exposure. Exposure produces deep, itching or burning blisters, swelling of the eyelids, and possibly blindness; inhalation at high concentrations damages the mucous membranes, causing bleeding and blistering within the lungs, leading to pulmonary edema. It is also carcinogenic and mutagenic (causes damage to DNA).

Mustard gas is not very soluble in water but is very soluble in fat, contributing to its rapid absorption into the skin. It easily penetrated the early forms of protective clothing and gas masks.

Modern "improvements" include using longer carbon chains to make the molecule more hydrocarbon-like (and thus more fat-soluble). *Nitrogen mustards* have nitrogen atoms in place of the sulfur atom.

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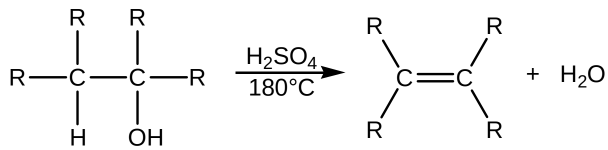
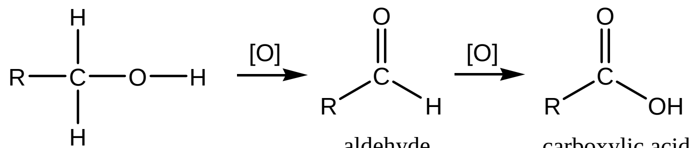
Reactions of Alcohols

1. Dehydration of alcohols to give alkenes:



2. Dehydration of alcohols to give ethers:

3. Oxidation of a primary alcohol to give an aldehyde or carboxylic acid:



1° alcohol aldehyde carboxylic acid

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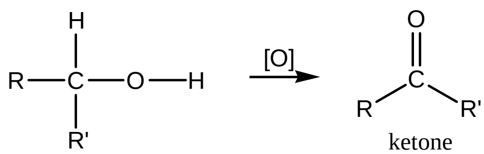
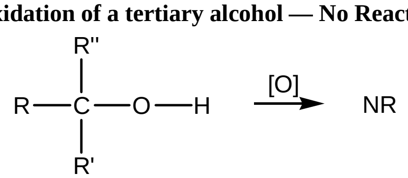
4. Oxidation of a secondary alcohol to give a ketone:



2° alcohol ketone

5. Oxidation of a tertiary alcohol — No Reaction:



3° alcohol

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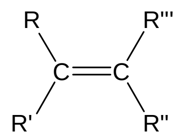
Functional Groups

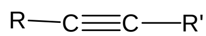
R = a carbon group

$CH_3CH_2CH_3$

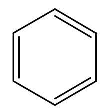
alkane



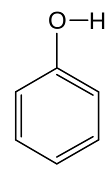
alkene



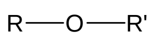
alkyne



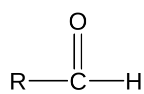
aromatic ring



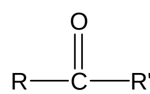
phenol



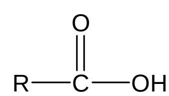
ether



aldehyde



ketone



carboxylic acid

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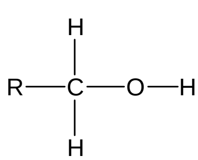
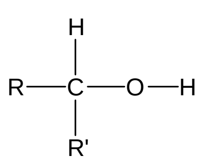
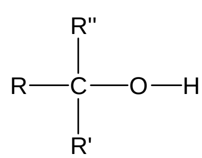


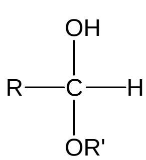
primary (1°)
alcohol



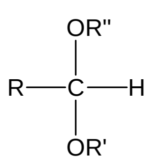
secondary (2°)
alcohol



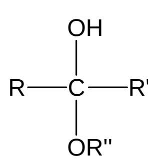
tertiary (3°)
alcohol



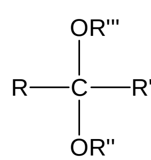
hemiacetal



acetal



hemiketal



ketal

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Chapter 4
Aldehydes and Ketones

Chapter Objectives:

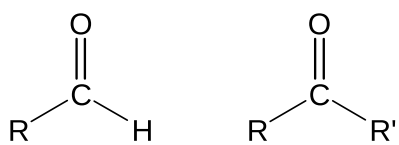
- Learn to recognize the aldehyde and ketone functional groups.
- Learn the IUPAC system for naming aldehydes and ketones.
- Learn the important physical properties of the aldehydes and ketones.
- Learn the major chemical reaction of aldehydes and ketones, and learn how to predict the products of hydrogenation, oxidation, and addition of alcohol reactions.
- Learn to recognize the acetal, hemiacetal, ketal, and hemiketal group, and how these are related to aldehydes and ketones.

The Carbonyl Group

The Carbonyl Group

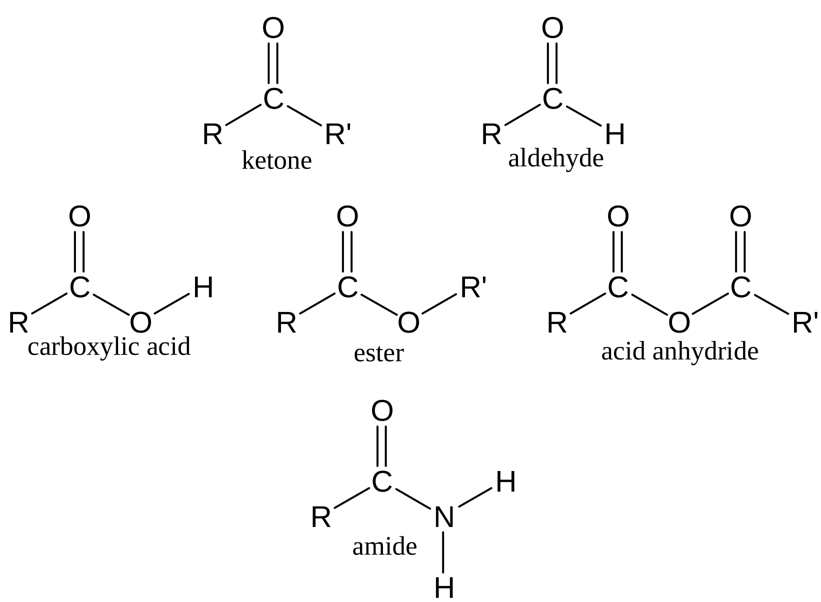
- The **carbonyl group** (C=O) is found in **aldehydes**, **ketones**, and many other organic functional groups.
- The carbon and oxygen in the carbonyl group are sp^2-hybridized, with bond angles of 120°.

- In **ketones**, two carbon groups are attached to the carbonyl carbon, while in **aldehydes** at least one hydrogen is attached to the carbon.



aldehyde **ketone**

Functional Groups Containing Carbonyls



Nomenclature of Aldehydes and Ketones

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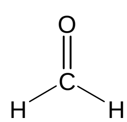
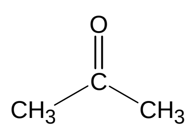
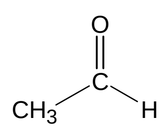
Some Common Aldehydes and Ketones



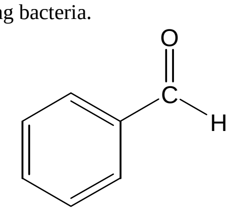
Methanal
(Formaldehyde)
Gas at room temperature; 35-40% solution in water, called **formalin**, used to preserve biological specimens, sterilize instruments, and embalm cadavers; present in wood smoke, and helps to preserve smoked meats by killing bacteria.



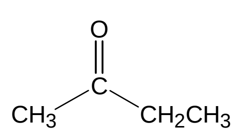
2-Propanone
(Acetone)
1 billion pounds used annually in U.S.; good solvent for most organic compounds, and is also soluble in water; solvent for coatings such as fingernail polish and enamel paints, etc.



Ethanal
(Acetaldehyde)
Product of oxidation of ethanol in the liver; consuming large quantities of ethanol causes acetaldehyde to build up in bloodstream faster than it can be consumed in the liver to make other products, leading to nausea, sweating, reduced blood pressure, etc.



Benzaldehyde
Causes the odor of almonds and cherries, and is also found in apricots and peaches.

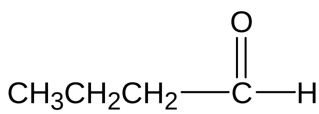


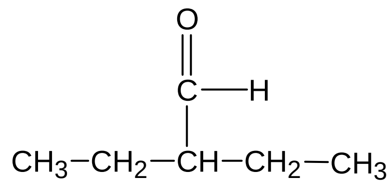
2-Butanone
(Methyl ethyl ketone, MEK)
Common industrial solvent

6

Nomenclature of Aldehydes

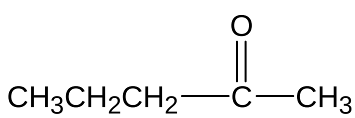
- Select the longest carbon chain *containing the carbonyl carbon*.
- The **-e** ending of the parent alkane name is replaced by the suffix **-al**.
- The carbonyl carbon is always numbered "1." (It is not necessary to include the number in the name.)
- Name the substituents attached to the chain in the usual way.

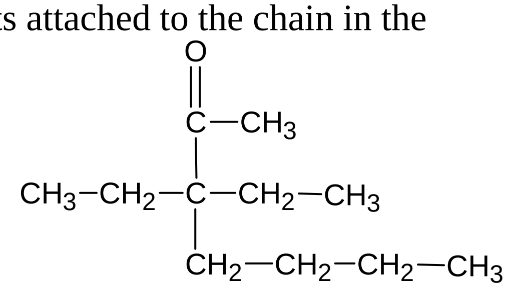




Nomenclature of Ketones

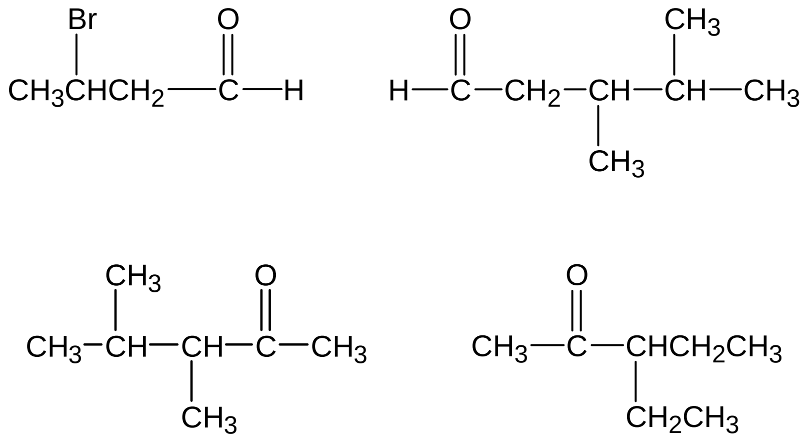
- Select the longest carbon chain *containing the carbonyl carbon*.
- The **-e** ending of the parent alkane name is replaced by the suffix **-one**.
- Number the chain starting with the end closest to the ketone group (the carbonyl carbon should have the lowest possible number). The location # for the ketone group precedes the name for the longest chain.
- Name the substituents attached to the chain in the usual way.





Examples: Naming Aldehydes and Ketones

- Name the following compounds:



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Other Nomenclature Rules

- In cyclic ketones, the carbonyl group is always numbered “1”; this does not need to be included in the name. The numbering continues clockwise or counterclockwise to give the lowest number for the next substituent.
- Molecules with more than one ketone group are named by preceding the suffix with a counting prefix (*di*one, *tri*one, etc.); position numbers must be used for each ketone group.
- Aromatic aldehydes (containing an aldehyde group directly attached to a benzene ring) are named after the parent compound **benzaldehyde**. (The carbon to which the aldehyde group is attached is carbon “1”).

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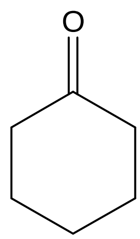
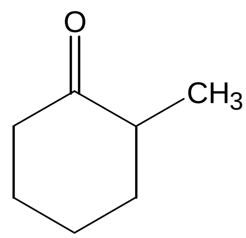
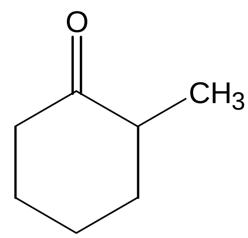
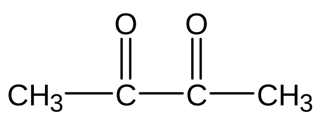
Examples: Naming Aldehydes and Ketones

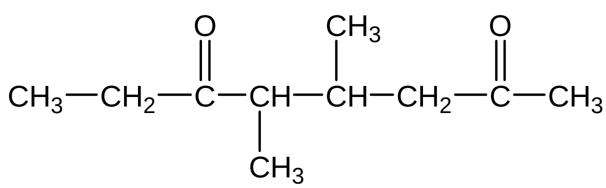
- Name the following compounds:





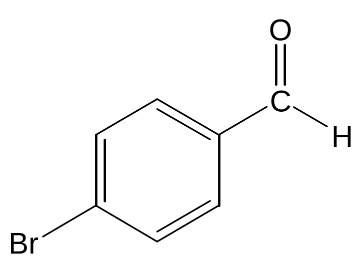


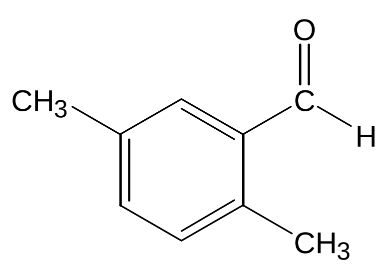


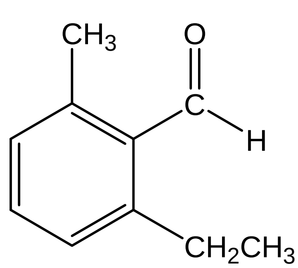


Examples: Naming Aldehydes and Ketones

- Name the following compounds:







Examples: Naming Aldehydes and Ketones

- Draw structural formulas for the following molecules:
  - 3-ethyl-2-pentanone
  - 2,4,6-trimethylheptanal
  - 3-ethylcyclopentanone

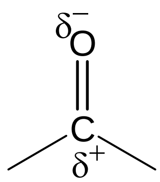
Examples: Naming Aldehydes and Ketones

- Draw structural formulas for the following molecules:
  - 4-chloro-2-phenylpentanal
  - para-nitrobenzaldehyde
  - 3-ethyl-2-butanone (what's wrong with this name?)

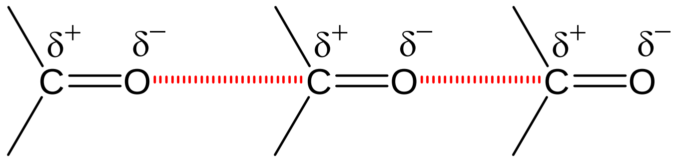
Physical Properties of Aldehydes and Ketones

The Polarity of the Carbonyl Group

- Carbonyl compounds are polar, containing a dipole along the carbon-oxygen double bond.



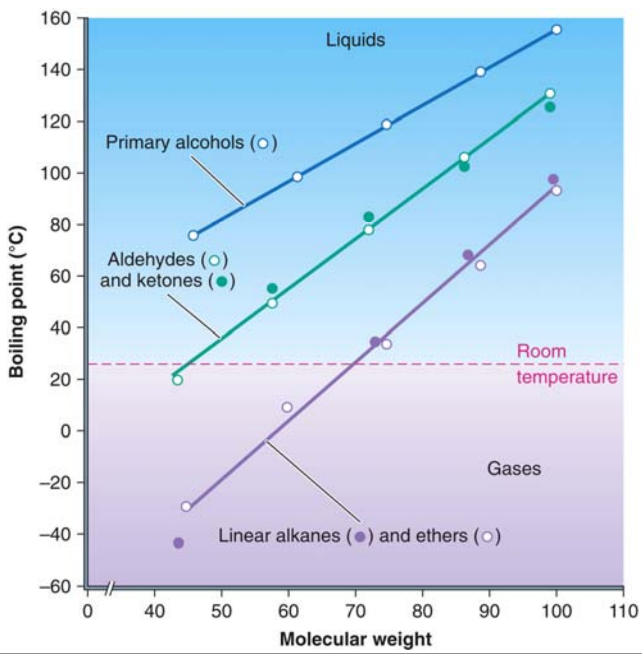
- This creates weak attractive forces between carbonyl compounds, but these attractions are not as strong as those that result from hydrogen-bonding.



The Boiling Points of Aldehydes and Ketones

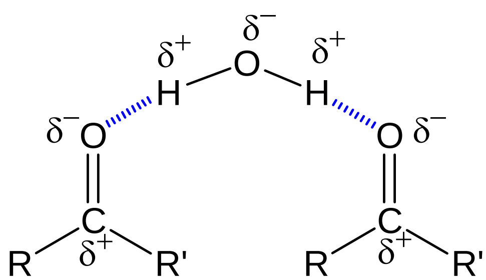
- Since there is no hydrogen on the carbonyl oxygen, aldehydes and ketones *do not form hydrogen bonds with themselves*.
- Aldehydes and ketones therefore have boiling points that are in between those of alcohols and hydrocarbons of the same molecular weight:
  - Alcohols form hydrogen bonds, and have high boiling points.
  - Hydrocarbons are nonpolar, and have low boiling points.
  - Aldehydes and ketones are polar, so they have higher boiling points than hydrocarbons, but they are not as polar as molecules which can hydrogen bond.

The Boiling Points of Aldehydes and Ketones



Physical Properties of Aldehydes and Ketones

- Carbonyl compounds cannot hydrogen-bond to each other, but they can hydrogen-bond to water through the carbonyl oxygen.
- Low-molecular weight aldehydes and ketones are water-soluble; water solubility decreases as the size of the molecule increases.



Physical Properties of Aldehydes and Ketones

Boiling Points:

Alcohols
Aldehydes/Ketones
Ethers
Alkanes

Water Solubility:

Alcohols
Aldehydes/Ketones
Ethers
Alkanes

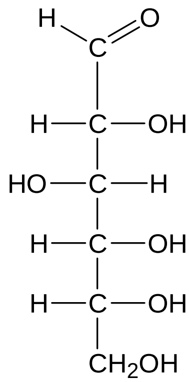
Name	Molecular weight	Boiling point	Solubility in water
butane	58 g/mol	0°C	Insoluble
propanal	58 g/mol	49°C	Soluble
acetone	58 g/mol	56°C	Soluble
1-propanol	60 g/mol	97°C	Soluble

Examples: Predicting Boiling Points

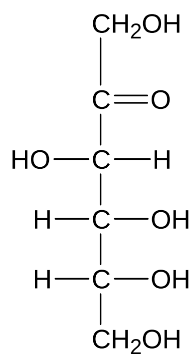
- Arrange the following compounds in order of increasing boiling point:
  - 2-pentanone
  - 2-methylpentane
  - 2-pentanol

Some Important Aldehydes and Ketones

Important Aldehydes and Ketones

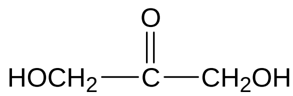


Glucose
One of the most important of the **carbohydrates**, which are *polyhydroxy aldehydes and ketones*; the metabolism of glucose is a major source of energy for living organisms

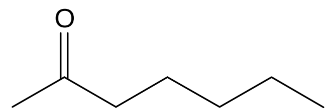


Fructose
Another important carbohydrate; a major component of corn syrup; found in honey, syrups, and preserves; in combination with glucose it forms the disaccharide **sucrose**.

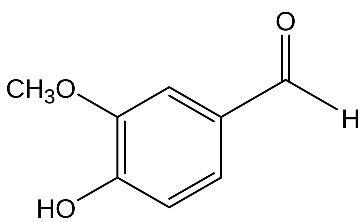
Important Aldehydes and Ketones



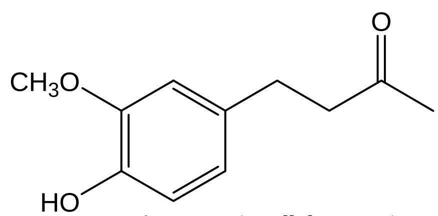
Dihydroxyacetone
Active ingredient in "bronzers" that provide fake suntan coloration; reacts with dead, outer skin cells to produce a darker color; fades as the dead skin cells slough off.



2-Heptanone
Found in oil of clove; also present in the odor of many fruits and dairy products, and is also responsible for the odor of blue cheese.



Vanillin
flavoring in Vanilla beans
(parent compound of the *vanniloids*)



Zingerone (vanillyl acetone)
The pungent, hot component of ginger

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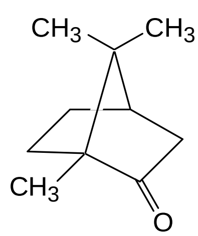
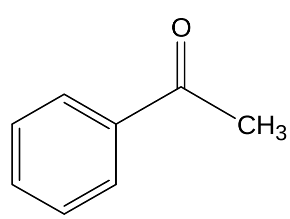
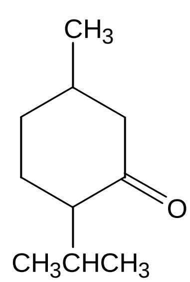


Camphor
Isolated by steam distillation from the camphor tree of China and Japan. Camphor is a counter-irritant (produces a superficial inflammation to reduce deeper inflammation) and antipruritic (anti-itching) medication; it appears to selectively stimulate cold sensors. It also stimulates the respiratory systems and inspires deep breathing, but can cause convulsions and respiratory collapse in larger doses.



Acetophenone
Used in perfurmery, and as an organic solvent; also used in the synthesis of some pharmeceuticals



Menthone

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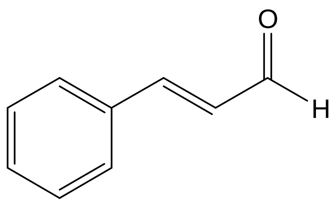
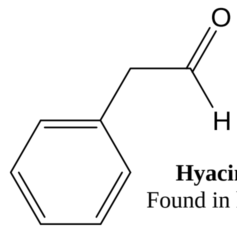
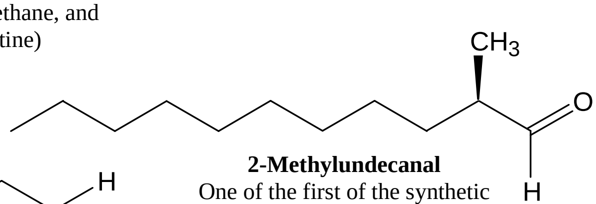


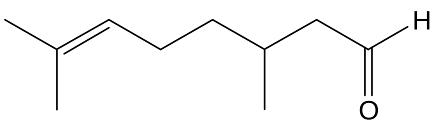
Cinnamaldehyde
The flavoring in oil of cinnamon; obtained by steam distillation from the bark of the cinnamon tree; has a *carminative* action (releases hydrogen sulfide, methane, and hydrogen from the intestine)



Hyacinthin
Found in hyacinth



2-Methylundecanal
One of the first of the synthetic perfumes, introduced by Coco Chanel in 1921 as *Chanel No. 5*



Citronellal
Found in citronella oil; used as an insect repellant

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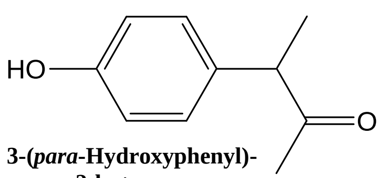
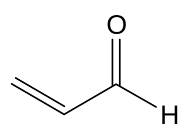
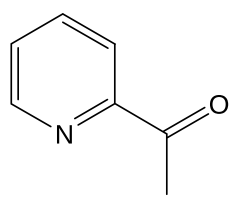


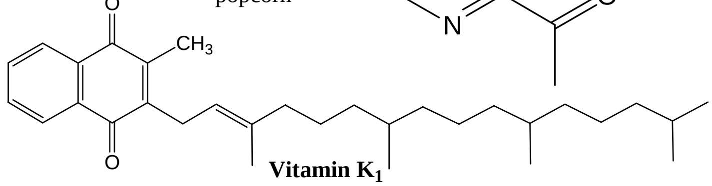
3-(*para*-Hydroxyphenyl)-2-butanone
Responsible for the odor of ripe raspberries.



Acrolein
Produced from the breakdown of triglycerides in meat during cooking; the acrid smell of this compound is obvious during barbeques. It also contributes to the taste of caramel, where it is produced by decomposing sucrose

Methyl 2-pyridyl ketone
Found in the odor of popcorn





Vitamin K_1
A fat soluble vitamin btained from green leafy vegetables, cabbage, cauliflower, kale, spinach, pork liver; also made by intestinal bacteria. Essential for blood clotting.

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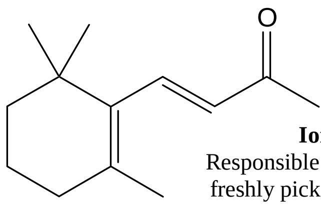
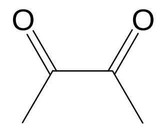
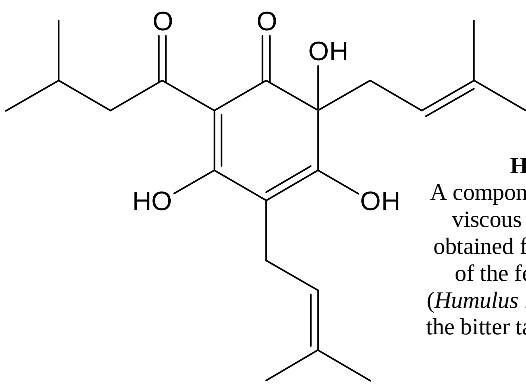


Ionone
Responsible for the odor of freshly picked raspberries, violets (and the extract, oil of violets), and sun-dried hay.

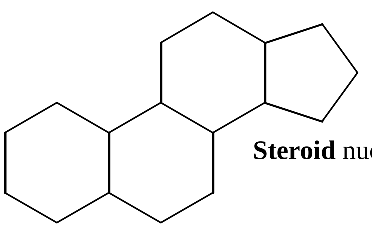


Butanedione
A volatile yellow liquid compound with the odor of cheese; gives butter its characteristic flavor. It also contributes to the odor of armpits and unwashed feet by the action of bacteria which ferment the compounds in perspiration.

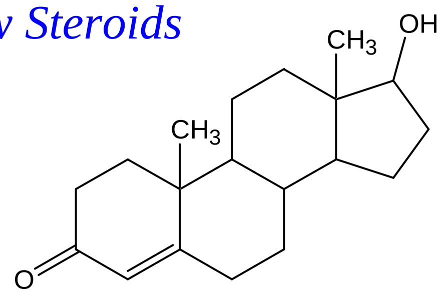


Humulone
A component of hop resin, a viscous yellow material obtained from the blossoms of the female hop plant (*Humulus lupulus*); it adds to the bitter taste of some beers.

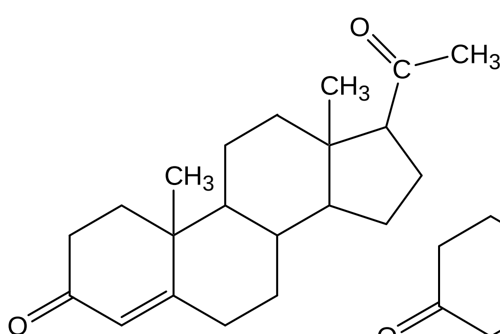
A Few Steroids



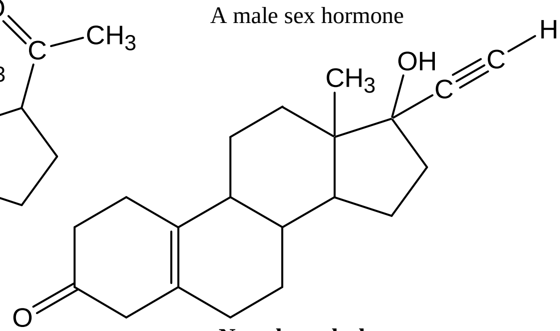
Steroid nucleus



Testosterone
A male sex hormone



Progesterone
A female sex hormone

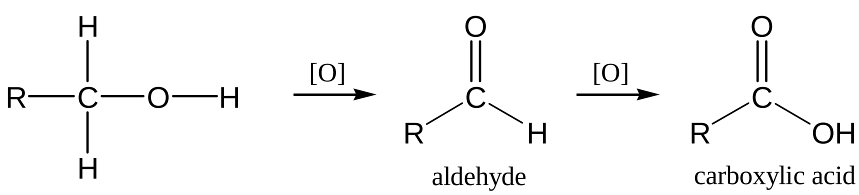


Norethynodrel
Active ingredient in birth-control pills

Reactions of Aldehydes and Ketones

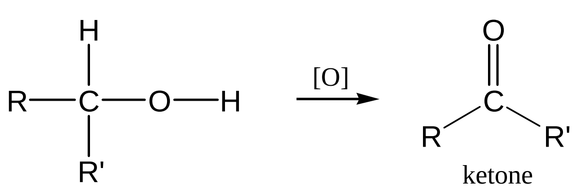
Oxidation of Alcohols to Produce Carbonyls

- Aldehydes, like primary alcohols, can be oxidized to produce carboxylic acids:



1° alcohol aldehyde carboxylic acid

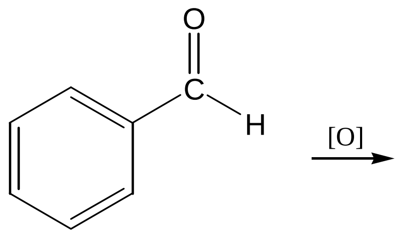
- Secondary alcohols can be oxidized to produce ketones, which are not further oxidized:

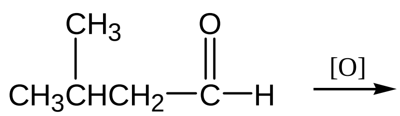


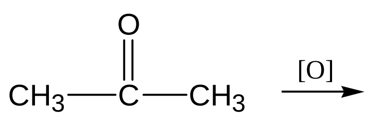
2° alcohol ketone

Examples: Oxidation Reactions

- Complete the following reactions:







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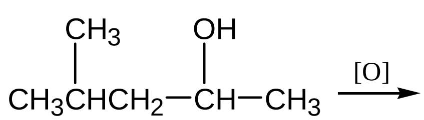
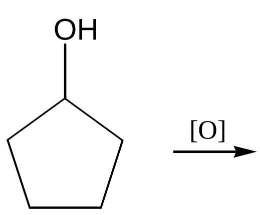
Examples: Oxidation Reactions

- Complete the following reactions:





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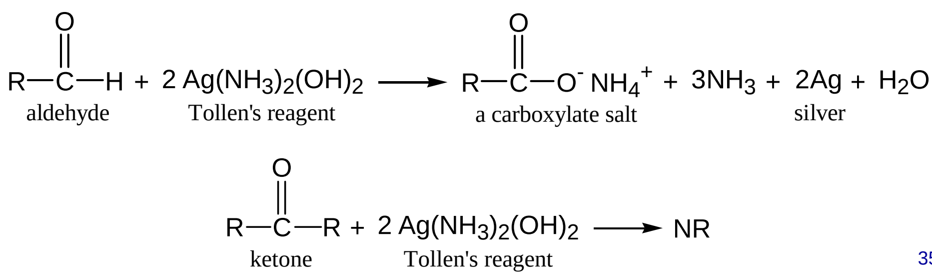
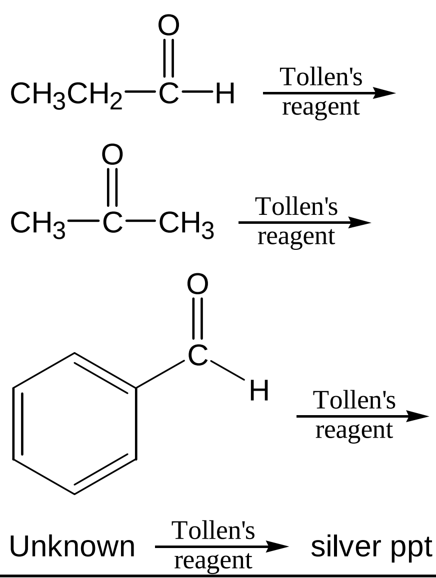
Oxidation of Aldehydes: The Tollens' Test

- **Tollens' reagent** is a mild oxidizing agent composed of silver ions in an aqueous basic solution of ammonia.
- Aldehydes are oxidized to carboxylate salts (since the solution is basic), and the silver ions are reduced to solid silver, which coats the bottom of the test tube with a "silver mirror."
- Ketones are not oxidized, so no silver mirror forms.



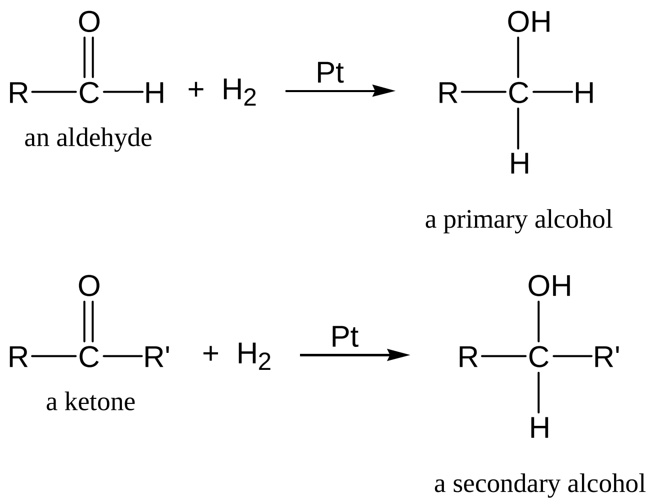
Examples: The Tollens' Test

- What observations would be made in the following reactions?



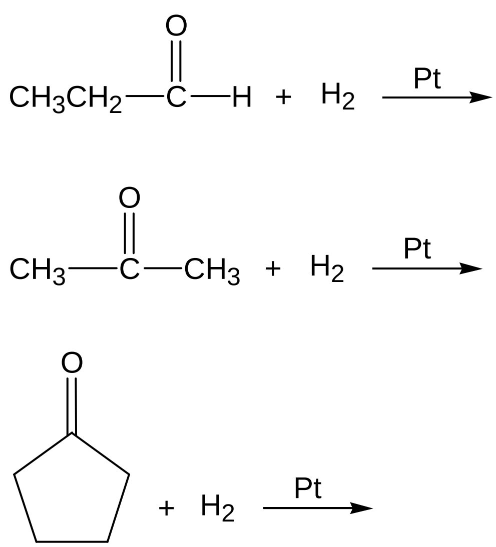
Hydrogenation of Aldehydes and Ketones

- **Hydrogenation** of aldehydes and ketones with hydrogen gas and a platinum catalyst produces alcohols:



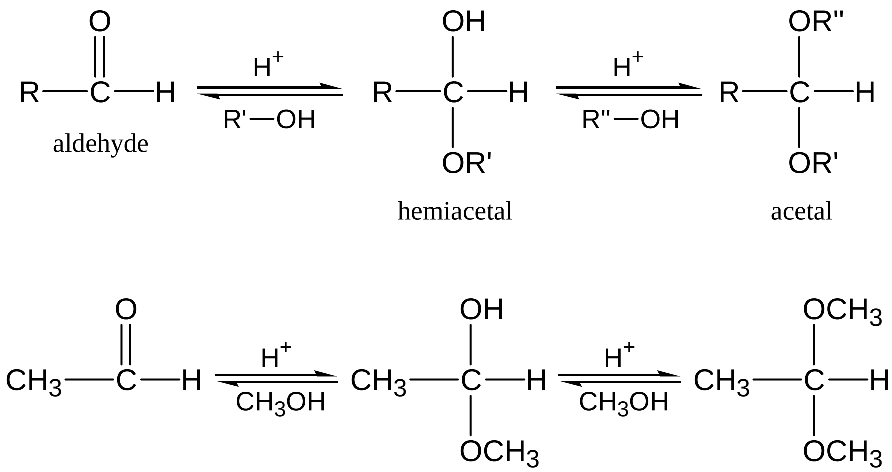
Examples: Hydrogenation Reactions

- Complete the following reactions:



Addition of Alcohols to Aldehydes

- Aldehydes react with alcohols first to form **hemiacetals**, which then react with excess alcohol to produce **acetals**.



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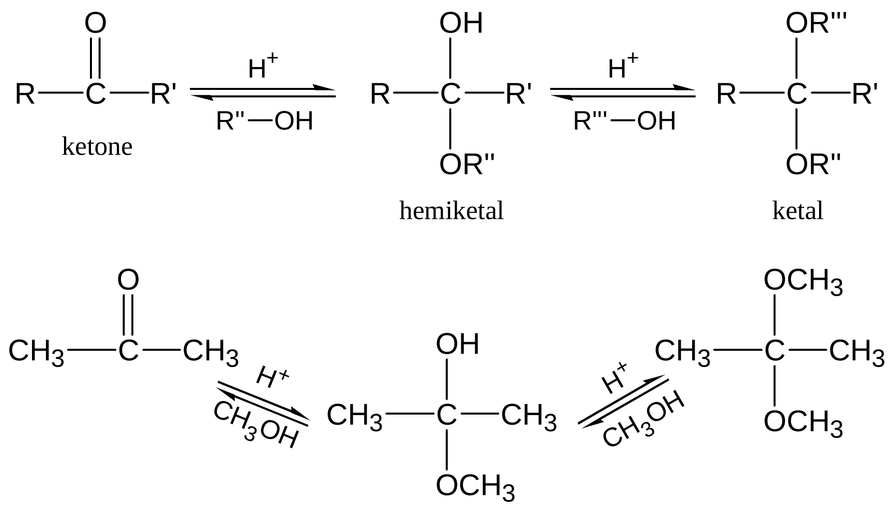
Addition of Alcohols to Ketones

- Ketones react with alcohols first to form **hemiketals**, which then react with excess alcohol to produce **ketals**.



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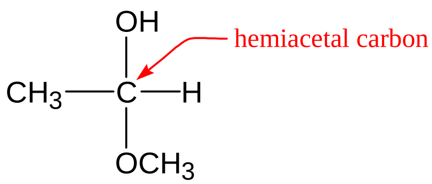
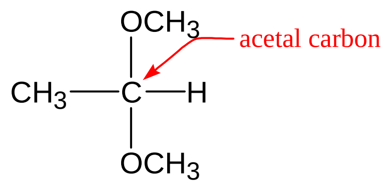
Hemiacetals, Acetals, Hemiketals, and Ketals

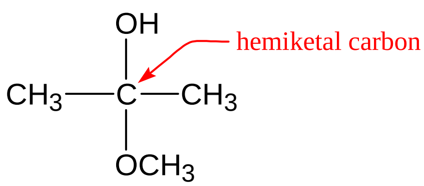
(oh my)



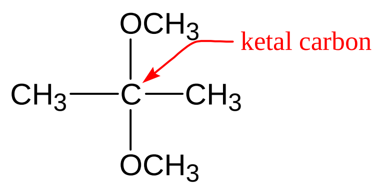
a **hemiacetal**



an **acetal**



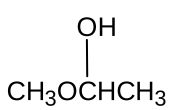
a **hemiketal**



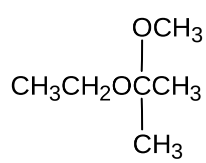
a **ketal**

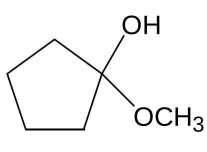
Examples: Identifying Acetals and Ketals

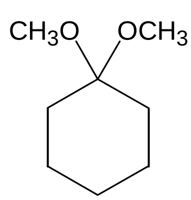
- Identify the following compounds as being acetals, ketals, hemiacetals, or hemiketals.

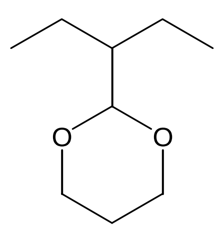


$CH_3OCH_2CH_2OH$



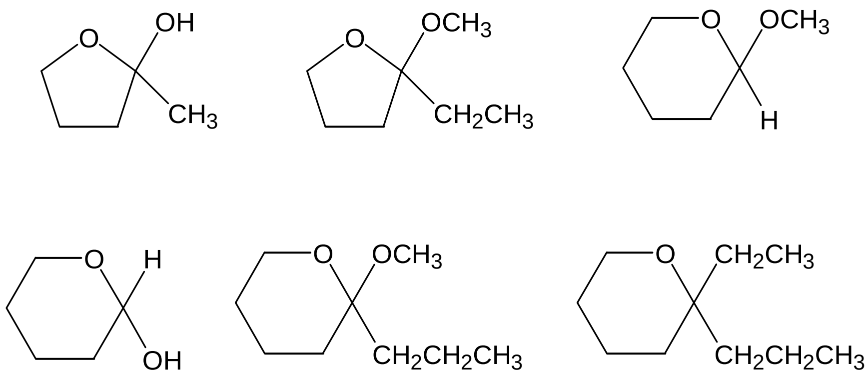






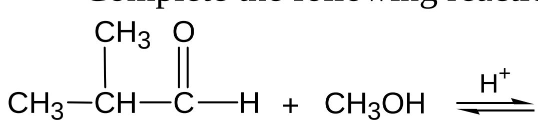
Examples: Identifying Acetals and Ketals

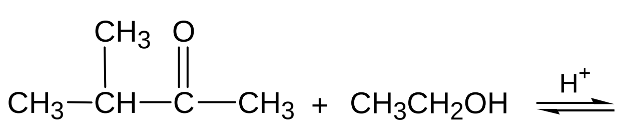
- Identify the following compounds as being acetals, ketals, hemiacetals, or hemiketals.



Examples: Formation of Acetals and Ketals

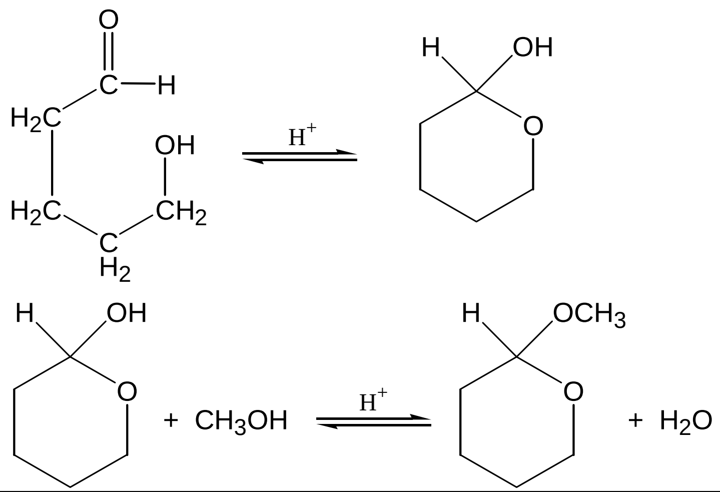
- Complete the following reactions.





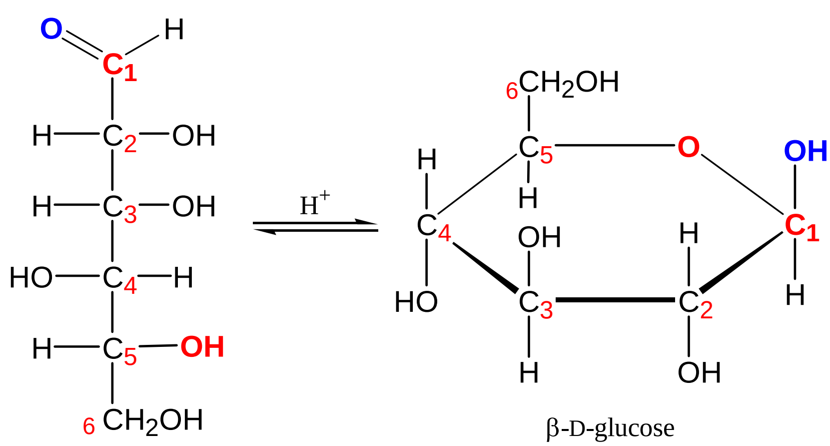
Intramolecular Addition Reactions

- In molecules which have both OH and C=O groups on different carbon atoms, an *intramolecular* addition reaction can occur, producing a cyclic hemiacetal or hemiketal:



Intramolecular Addition Reactions

- These kinds of reactions are very important in carbohydrate chemistry:

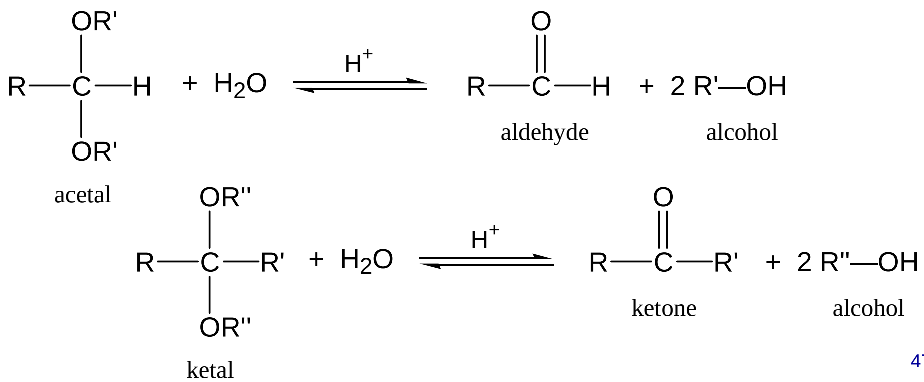


D-glucose

β-D-glucose

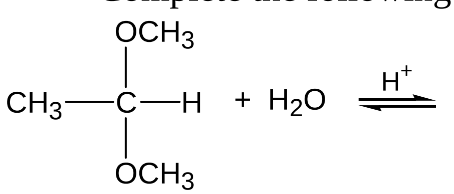
Hydrolysis of Acetals and Ketals

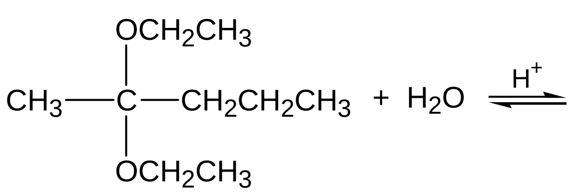
- Under acidic conditions, water can be used to reverse the previous reaction, and regenerate the original aldehyde or ketone from the acetal or ketal.
- This is an example of a **hydrolysis** reaction, in which water causes a compound to be split into its component substances.



Examples: Hydrolysis of Acetals and Ketals

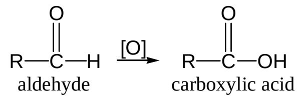
- Complete the following reactions.



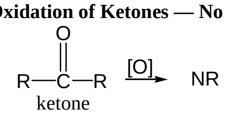


Reactions of Aldehydes and Ketones

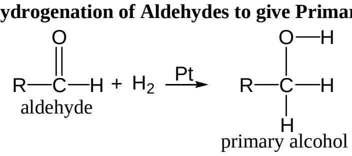
1. Oxidation of Aldehydes to give Carboxylic Acids



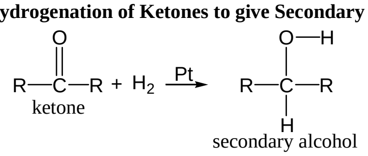
2. Oxidation of Ketones — No Reaction



3. Hydrogenation of Aldehydes to give Primary Alcohols



4. Hydrogenation of Ketones to give Secondary Alcohols



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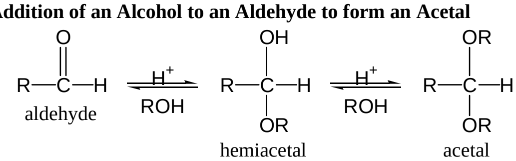
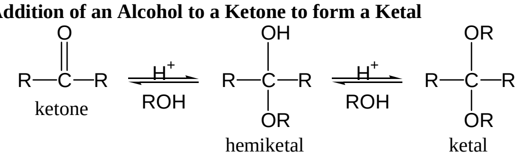
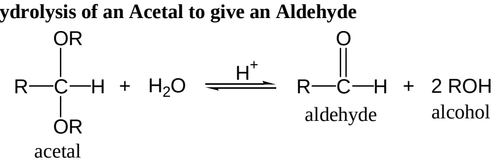
5. Addition of an Alcohol to an Aldehyde to form an Acetal



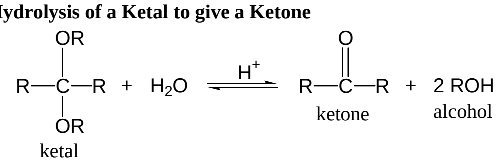
6. Addition of an Alcohol to a Ketone to form a Ketal



7. Hydrolysis of an Acetal to give an Aldehyde



8. Hydrolysis of a Ketal to give a Ketone



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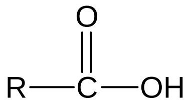
Chapter 5
Carboxylic Acids and Esters

Chapter Objectives:

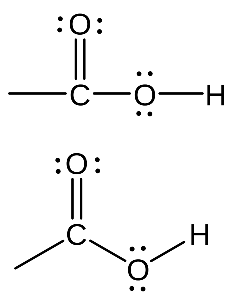
- Learn to recognize the carboxylic acid, ester, and related functional groups.
- Learn the IUPAC system for naming carboxylic acids and esters.
- Learn the important physical properties of the carboxylic acids and esters.
- Learn the major chemical reaction of carboxylic acids and esters, and learn how to predict the products of ester synthesis and hydrolysis reactions.
- Learn some of the important properties of condensation polymers, especially the polyesters.

Carboxylic Acids

- **Carboxylic acids** are weak organic acids which contain the **carboxyl group** (RCO_2H):



a **carboxylic acid**



the **carboxyl** group

RCOOH RCO_2H

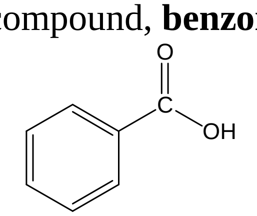
condensed ways of writing the carboxyl group

- The tart flavor of sour-tasting foods is often caused by the presence of carboxylic acids.

Nomenclature of Carboxylic Acids

Nomenclature of Carboxylic Acids

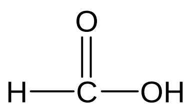
- Select the longest carbon chain containing the carboxyl group. The **-e** ending of the parent alkane name is replaced by the suffix **-oic acid**.
- The carboxyl carbon is always numbered "1" but the number is not included in the name.
- Name the substituents attached to the chain in the usual way.
- Aromatic carboxylic acids (i.e., with a CO_2H directly connected to a benzene ring) are named after the parent compound, **benzoic acid**.

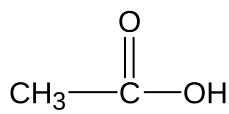


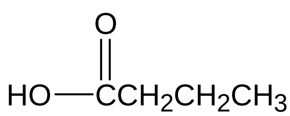
Benzoic acid

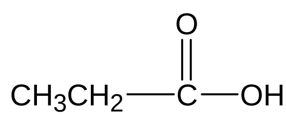
Examples: Naming Carboxylic Acids

- Name the following compounds:









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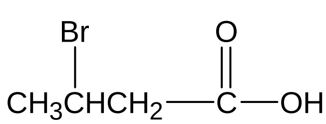
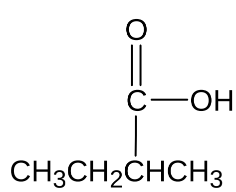
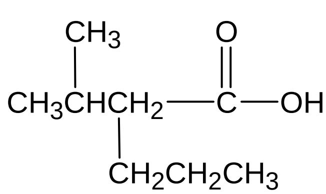
Examples: Naming Carboxylic Acids

- Name the following compounds:







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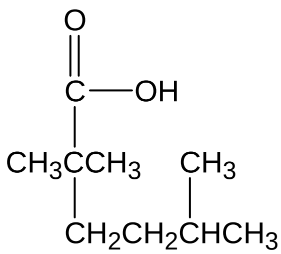
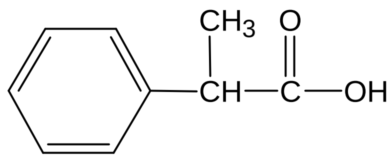
Examples: Naming Carboxylic Acids

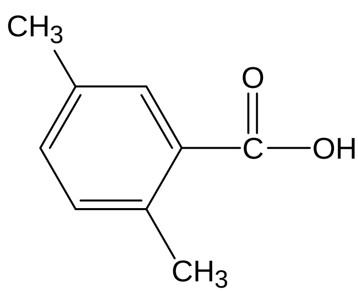
- Name the following compounds:

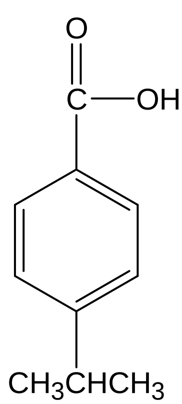


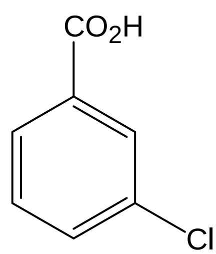


Examples: Naming Carboxylic Acids

- Name the following compounds:

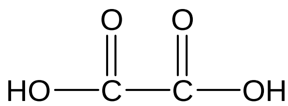


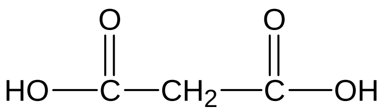


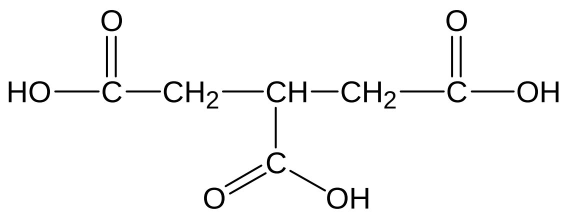


More Complicated Acids

- For molecules with two carboxylic acid groups the carbon chain in between the two carboxyl groups (including the carboxyl carbons) is used as the longest chain; the suffix **-dioic acid** is used.
- For molecules with more than two carboxylic acid groups, the carboxyl groups are named as *carboxylic acid substituents*.


ethanedioic acid


propanedioic acid


propane-1,2,3-tricarboxylic acid

Examples: Drawing Carboxylic Acids

- Draw structural formulas for the following molecules:
  - 2-methylpropanoic acid
  - 2,2,5-trimethylhexanoic acid
  - 4,5-dimethyl-3-nitrooctanoic acid

Examples: Drawing Carboxylic Acids

- Draw structural formulas for the following molecules:
  - *para*-bromobenzoic acid
  - 2,4,6-trinitrobenzoic acid
  - 4-ethylpentanedioic acid (what's wrong with this name?)

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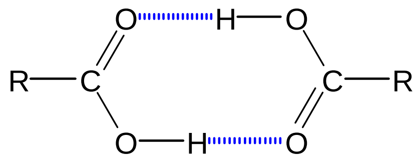
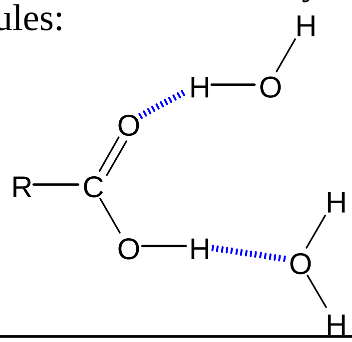
Physical Properties of Carboxylic Acids

Physical Properties of Carboxylic Acids

- Carboxylic acids hydrogen bond to themselves to form a **dimer**:



- Carboxylic acids also form hydrogen bonds to water molecules:



Physical Properties of Carboxylic Acids

- Since carboxylic acids can form more than one set of hydrogen bonds, their boiling points are usually higher than those of other molecules of the same molecular weight (MW).
- Low-MW carboxylic acids are generally liquids at room temp. (often, they are somewhat oily); higher-MW carboxylic acids are generally waxy solids.
- Carboxylic acids with 12 to 20 carbon atoms are often referred to as **fatty acids**, since they are found in the triglycerides in fats and oils (more later).
- Short-chain carboxylic acids are also generally more soluble in water than compounds of similar MW, since they can hydrogen bond to more than one water molecule.

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Physical Properties of Carboxylic Acids

- As the number of carbons in a carboxylic acid series becomes greater, the boiling point increases and the solubility in water decreases.
- Many carboxylic acids that are liquids at room temperature have characteristically sharp or unpleasant odors.
  - Ethanoic acid/acetic acid is the main ingredient in vinegar.
  - Butanoic acid is partially responsible for the odor of locker rooms and unwashed socks.
  - Hexanoic acid is responsible for the odor of Limburger cheese.
- Like most acids, carboxylic acids tend to have a sour taste (e.g., vinegar, citric acid, etc.)

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Table 5.2 Physical properties of some carboxylic acids

Common Name	Structural Formula	BP (°C)	MP (°C)	Solubility (g/100 mL H_2O)
Formic acid	$H—CO_2H$	101	8	Infinite
Acetic acid	$CH_3—CO_2H$	118	17	Infinite
Propionic acid	$CH_3CH_2—CO_2H$	141	-21	Infinite
Butyric acid	$CH_3(CH_2)_2—CO_2H$	164	-5	Infinite
Valeric acid	$CH_3(CH_2)_3—CO_2H$	186	-34	5
Caproic acid	$CH_3(CH_2)_4—CO_2H$	205	-3	1
Caprylic acid	$CH_3(CH_2)_6—CO_2H$	239	17	Insoluble
Capric acid	$CH_3(CH_2)_8—CO_2H$	270	32	Insoluble
Lauric acid	$CH_3(CH_2)_{10}—CO_2H$	299	44	Insoluble
Myristic acid	$CH_3(CH_2)_{12}—CO_2H$	Dec.	58	Insoluble
Palmitic acid	$CH_3(CH_2)_{14}—CO_2H$	Dec.	63	Insoluble
Stearic acid	$CH_3(CH_2)_{16}—CO_2H$	Dec.	71	Insoluble

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Boiling Points of Various Functional Groups

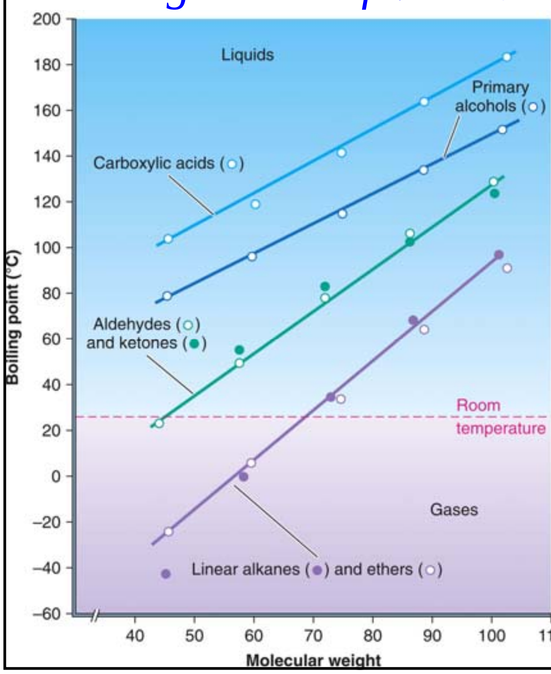

Figure 5.4
The boiling points of carboxylic acids compared to 1° alcohols, aldehydes and ketones, ethers and alkanes.

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Comparing Physical Properties

Boiling Point:
- Carboxylic acid
- Alcohols
- Aldehydes/Ketones
- Ethers
- Alkanes

Water Solubility:
- Carboxylic acid
- Alcohols
- Aldehydes/Ketones
- Ethers
- Alkanes

Name	Molecular weight	Boiling point	Solubility in water
Pentane	72 g/mol	35°C	Insoluble
Diethyl ether	74 g/mol	35°C	Insoluble
Butanal	72 g/mol	76°C	7.1 g / 100 mL H_2O
1-Butanol	74 g/mol	118°C	9.1 g / 100 mL H_2O
Propanoic acid	74 g/mol	141°C	Infinite

Examples: Predicting Physical Properties

- Arrange the following compounds in order of increasing boiling point. (All of the compounds have about the same molecular weight.)
  - 1-pentanol
  - hexane
  - butanoic acid
  - pentanal
- Which member of each of the following pairs of compounds would you expect to have a higher solubility in water?
  - 2-butanone *or* propanoic acid
  - hexanoic acid *or* ethanoic acid

Some Important Carboxylic Acids

Important Carboxylic Acids

$H-\overset{\overset{O}{||}}{C}-OH$

Methanoic acid
(Formic acid)
(from Latin *formica,* ant)
A component of the venom of ants and caterpillars; produced in the body when methanol is consumed

$CH_3-\overset{\overset{O}{||}}{C}-OH$

Ethanoic acid
(Acetic acid)
(from Latin *acetum*, vinegar)
Vinegar is a 5% solution of acetic acid dissolved in water; acetic acid is also responsible for the taste of sour wine (from the oxidation of ethanol) and sourdough bread

$CH_3CH_2-\overset{\overset{O}{||}}{C}-OH$

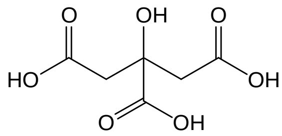
Propanoic acid
(Propionic acid)
Found in Swiss cheese; salts of this acid are used as mold inhibitors

$CH_3CH_2CH_2-\overset{\overset{O}{||}}{C}-OH$

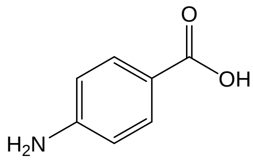
Butanoic acid
(Butyric acid)
(from Latin *butyrum,* butter)
This acid has a foul, rancid odor; produced from the breakdown of soft triglycerides in butter

$CH_3CH_2CH_2CH_2CH_2-\overset{\overset{O}{||}}{C}-OH$

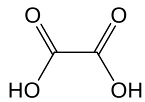
Hexanoic acid
(Caproic acid)
Responsible for the odor of Limburger cheese.



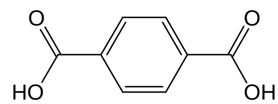
2-hydroxy-1,2,3-propanetricarboxylic acid (Citric acid)
Found in citrus fruits (lemons, grapefruit, oranges, etc.); commonly used in buffering solutions with sodium citrate



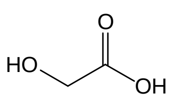
para-Aminobenzoic aid (PABA)
Used in sunscreens; absorbs short-wavelength UV light. It is also required by bacteria for the production of folic acid, needed to maintain the growth of healthy cell walls; sulfa drugs block the uptake of PABA by bacteria, causing them to be unable to manufacture folic acid, and thus preventing the bacteria from multiplying



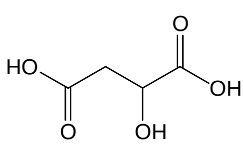
Oxalic acid
Found in many leafy green plants such as rhubarb and spinach; combines with calcium ions in the body to produce insoluble salts, which form kidney stones



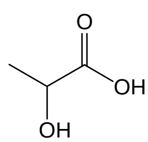
Terephthalic acid
A white, crystalline solid; used in the manufacture of some polyesters



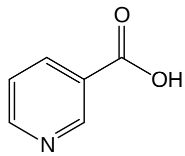
Glycolic acid
An **alpha-hydroxy acid** used in cosmetics and skin creams; alpha-hydroxy acids are thought to loosen the cells of the epidermis and accelerate the flaking off of dead skin; however these compounds can increase the skin's sensitivity to UV light



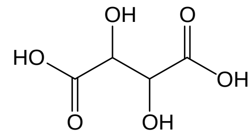
Malic acid
Responsible for the sharp taste of apples (genus *Malus*)



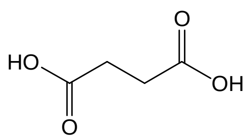
2-hydroxypropanoic acid (Lactic acid)
Produced from the fermentation of sugars under anaerobic conditions; found in sweat, sour milk, fermented pickles, sauerkraut, and yogurt; produced in muscles from glucose under anaerobic conditions (the buildup of lactic acid leads to a heavy, weak feeling, and muscle cramps); produced after death during the breakdown of sugars in the body by bacteria, inactivating the enzymes that allow the transport of calcium ions, causing rigor mortis



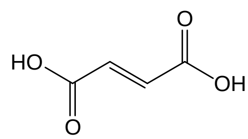
Niacin
A water-soluble, B-Complex vitamin obtained from fish, green vegetables, lean meat, poultry, whole-grain and enriched bread and cereal; produced in the body from tryptophan; essential for growth, healthy tissues, the production of energy from carbohydrates, and the production of fats



Tartaric acid
Found naturally in wine, and is responsible for some of the sharp taste of wine; it is added to many sour-tasting sweet foods. The potassium salt, *cream of tartar*, has many cooking applications; the potassium-sodium salt, *Rochelle salt*, is a mild laxative.



Succinic acid
An intermediate along the citric acid cycle



Fumaric acid
Occurs naturally in many plants, and is essential for vegetable and animal tissue respiration; used in baking powders, and in some fruit drinks as a replacement for citric acid

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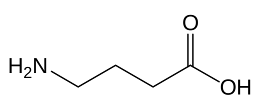
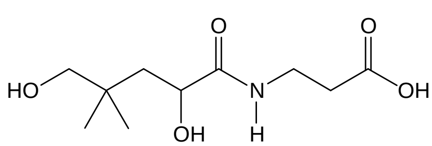
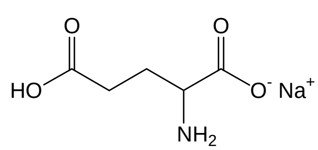


Gamma-aminobutanoic acid (GABA)
A *inhibitory neurotransmitter*; ethanol binds to the same protein as GABA at a neighboring location, distorting the protein so that GABA binds more easily, further inhibiting the cell from firing; benzodiazepines such as Valium also bind to the same protein but at a different site, inhibiting the cell still further, and sometimes with deadly consequences



Pantothenic acid
A water-soluble B-complex vitamin; converted by the body into Coenzyme A, which helps the body produce energy from food



Monosodium Glutamate (MSG)
The sodium salt of the amino acid glutamate; produced in meat during the decomposition of proteins; with inosine monophosphate (IMP), one of the major substances responsible for the flavor of meat; MSG is also added to some foods to enhance their meaty flavor

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Chemical Properties of Carboxylic Acids

Acids and Bases

- **Acids:**
  - have a sour taste.
  - react with active metals to produce H_2 gas.
  - turn blue litmus red.
- **Bases:**
  - have a bitter taste and a slippery feel.
  - turn red litmus blue.
- When they react with each other, acids and bases cancel each others properties in a **neutralization reaction**:

$$\text{acid} + \text{base} \rightarrow \text{salt} + \text{water}$$

Acids

- An **acid** gives a **proton (H^+)** to another species. Acids produce **hydronium ions, H_3O^+**, when they are dissolved in water:

$$H{-}A + H_2O \rightarrow A^- + H_3O^+$$

- A **strong acid** is one that *completely dissociates* in water (i.e., every molecule of the acid splits apart):

$$H{-}Cl + H_2O \rightarrow Cl^- + H_3O^+$$

- A **weak acid** is one in which only a small percentage of the molecules are dissociated at any one time (in other words, there is also a backwards reaction, where the acid molecule is regenerated):

$$H{-}F + H_2O \rightleftharpoons F^- + H_3O^+$$

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The pH Scale

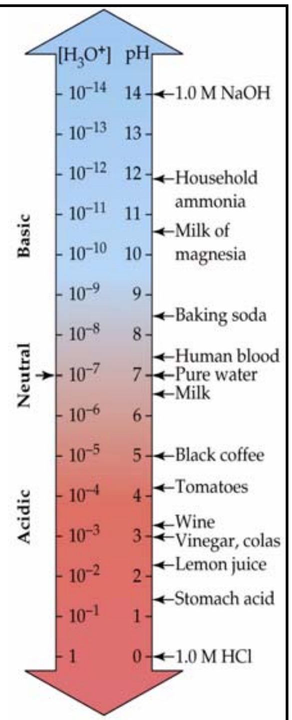
- The acidity of a solution is measured using the **pH scale**. The pH of a solution is defined as

$$\mathbf{pH = -\log[H_3O^+]}$$

Acidic: **pH < 7.00** $[H_3O^+] > [OH^-]$

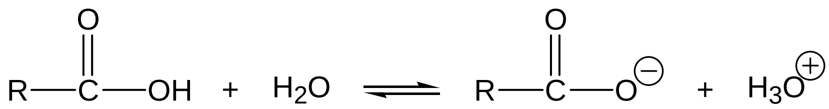
Basic: **pH > 7.00** $[H_3O^+] < [OH^-]$

Neutral: **pH = 7.00** $[H_3O^+] = [OH^-]$



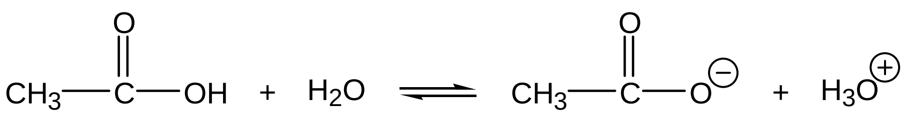
The Acidity of Carboxylic Acids

- Carboxylic acids are weak acids; in water, they dissociate to produce hydronium ions and **carboxylate ions**:



carboxylic acid — **carboxylate ion**

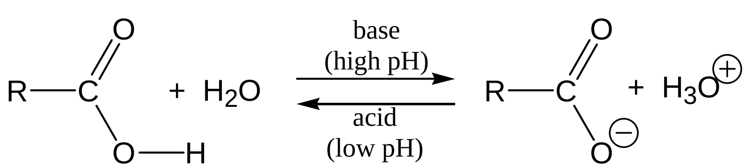
- A 1.0 *M* solution of acetic acid is about 0.5% dissociated into hydronium and **acetate** ions:



acetic acid — acetate ion

The Acidity of Carboxylic Acids

- The dissociation of a carboxylic acid is a reversible reaction, and the position of the equilibrium can be affected by the addition of acid (low pH) or by adding base (high pH):



carboxylic acid — carboxylate ion

- At the *physiological pH* of 7.4 (the pH of most body fluids) the carboxylate form of most carboxylic acids is the predominate form.

Carboxylate Salts

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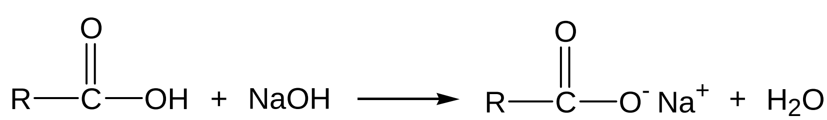
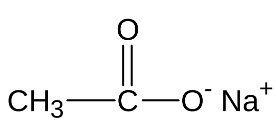
Carboxylate Salts

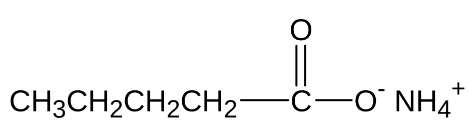
- Carboxylic acids react with strong bases such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) to produce **carboxylate salts**.
- Carboxylate salts are named by naming the metal first, and changing the **-ic acid** ending of the carboxylic acid name to **-ate**.



carboxylic acid base metal carboxylate



sodium ethanoate
(sodium acetate)



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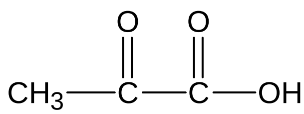
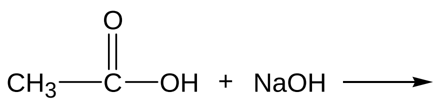
Examples: Carboxylate Salts

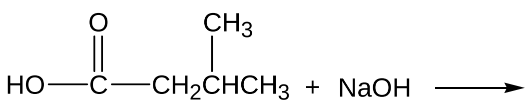
- Draw the structure of pyruvate, the form of pyruvic acid which is found as an intermediate in energy conversion reactions in living organisms.



pyruvic acid

- Complete the following reactions and name the carboxylate salt products.

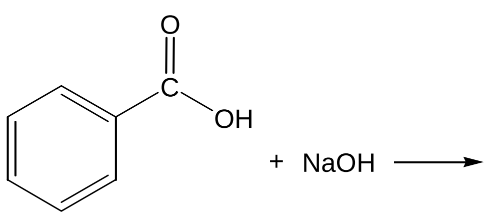


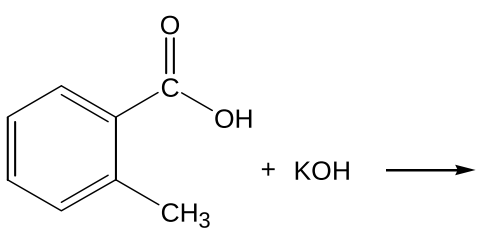


35

Examples: Carboxylate Salts

- Complete the following reactions and name the carboxylate salt products.





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Physical Properties of Carboxylate Salts

- Carboxylate salts are ionic compounds, and are typically solids at room temperature.
- Because they contain charges, carboxylate salts are typically much more soluble in water than the carboxylic acids from which they are derived.
  - This is important in the formation of *soaps* (more later).

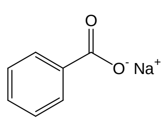
$$CH_3(CH_2)_{16}C(=O){-}OH + NaOH \longrightarrow CH_3(CH_2)_{16}C(=O){-}O^- Na^+ + H_2O$$

Stearic acid
(octadecanoic acid)
insoluble in water
found in beef fat and
some butters

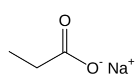
Sodium stearate
(sodium octadecanoate)
soluble in water

37

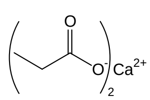
Important Carboxylate Salts



Sodium benzoate
Found in cranberries and prunes; commonly used as a preservative in baked goods, ketchup, carbonated beverages, etc.

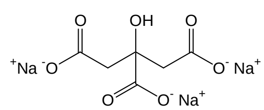


Sodium propanoate

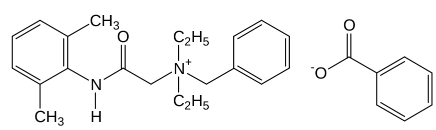


Calcium propanoate

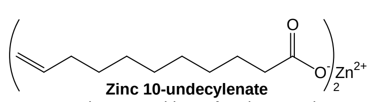
Commonly used preservatives; found in bread, cakes, and cheeses



Sodium citrate
The sodium salt of citric acid, sodium citrate, is used in buffers with citric acid to maintain desirable characteristics of foams and gels (jelly, ice cream, candy, whipped cream, etc.) by controlling the pH of the product; also used in medicines and blood for transfusions; also functions as an anticoagulant in blood



Denatonium benzoate ('Bitrex')
Benzyl diethyl ((2,6-xylylcarbamoyl)methyl) ammonium benzoate
Discovered in 1958, this is the bitterest-tasting compound known; as little as ten parts per million make substances unbearably bitter to most humans. It is used as an *aversive agent*, an additive that prevents accidental ingestion of a toxic substance. It is used to denature ethanol, methanol, and rubbing alcohol, and well as solvents, paints, arnishes, antifreeze, etc.



Zinc 10-undecylenate
Used to treat athlete's foot (Desenex)

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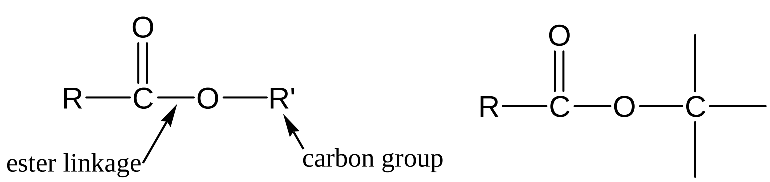
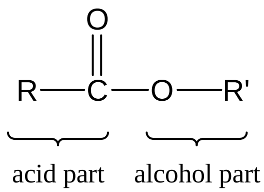
Esters

Esters

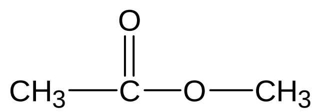
- An **ester** ("carboxylic ester" in the textbook) is a derivative of a carboxylic acid in which there is a carbon group connected to the single-bonded oxygen:

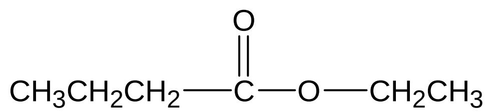


Nomenclature of Esters



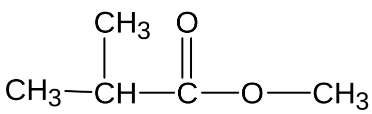
- Name the alkyl or aromatic portion contributed by the “alcohol part” first.
- The “acid part” is named as a carboxylic acid, with the **-ic acid** suffix changed to **-ate**.

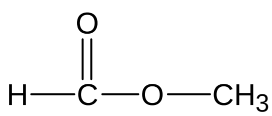


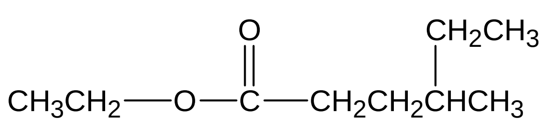


Examples: Ester Nomenclature

- Name the following compounds:

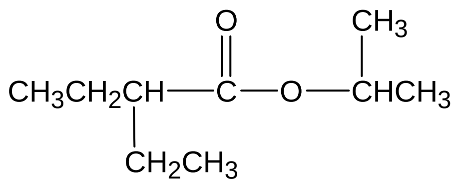


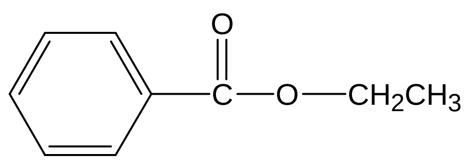




Examples: Ester Nomenclature

- Name the following compounds:





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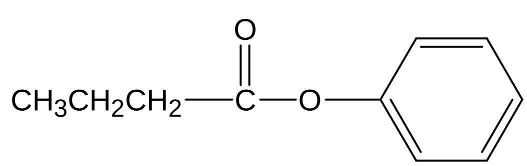
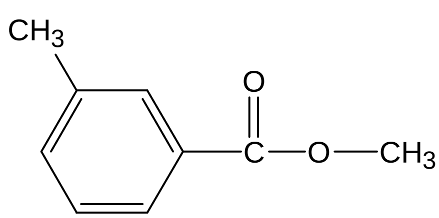
Examples: Ester Nomenclature

- Name the following compounds:





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Examples: Drawing Esters

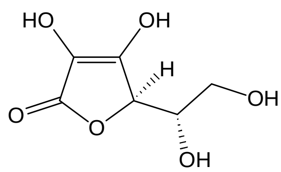
- Draw structural formulas for the following molecules:
  - methyl butanoate
  - ethyl 2-methylpropanoate
  - methyl 2,4-dimethylhexanoate

Examples: Drawing Esters

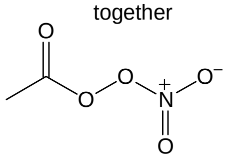
- Draw structural formulas for the following molecules:
  - propyl 2,2,3,4-tetramethylhexanoate
  - isopropyl benzoate
  - methyl *para*-nitrobenzoate

Some Important Esters

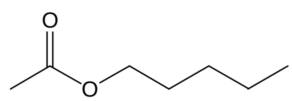
Important Esters



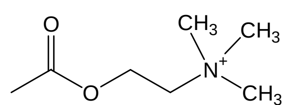
Vitamin C (ascorbic acid)
A water-soluble vitamin found in citrus fruits; prevents scurvy; essential for healthy blood vessels, bones, and teeth; helps form collagen, a protein that holds tissues together



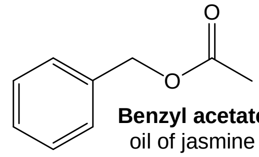
Peroxyacetyl nitrate (PAN)
Produced by the action of sunlight on fragments of unburnt hydrocarbon fuel, oxygen, and nitrogen dioxide; one of the irritants (lachrymator) found in photochemical smog



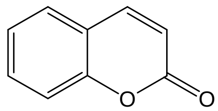
Amyl acetate
Also known as banana oil and pear oil; the commercially available compound is a mixture of amyl (pentyl) isomers



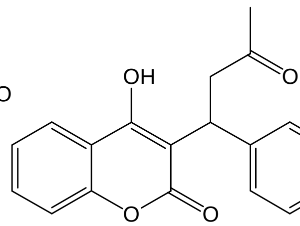
Acetylcholine
an important neurotransmitter



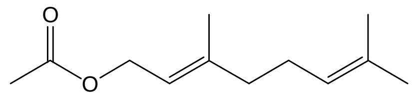
Benzyl acetate
oil of jasmine



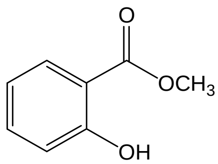
Coumarin
Found in lavender oil, sweet clover and tonka beans



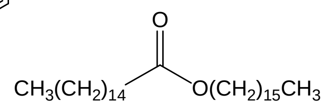
Warfarin
A potent rodenticide



Geranyl acetate
geranium oil

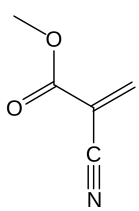


Methyl salicylate
Also known as oil of wintergreen and betula oil; used as a flavoring and as an ingredient in deep heating rubs. It also fluoresces under ultraviolet light, producing visible blue light. This is most apparent in Wint-O-Green Lifesavers, which contain methyl salicylate as their flavoring. It is also used in some sunscreen lotions

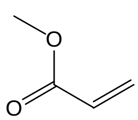


Spermaceti
Also known as *cetyl palmitate*; found in the spermaceti organ or case above the skull of the sperm whale (*Physeter macrocephalus*). Its exact function is not known but it may be used as "cushioning," allowing the whale's head to be used as a battering ram in fights between males (see *Moby Dick*), as a regulator of the whale's buoyancy in water, or as an aid in echolocation in focusing sound waves. Spermaceti was highly sought by whalers in the 18th and 19th centuries, and was widely used commercially.

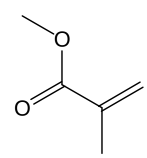
Polymers with Ester Groups



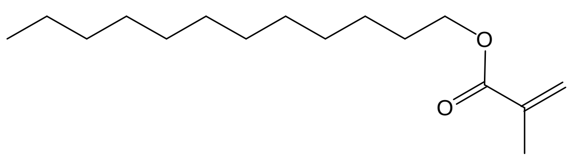
Methyl cyanoacrylate
Polymerizes on contact with surfaces containing trace amounts of water and alcohols to form Superglue; superglue is also used in surgery in place of sutures, and by morticians to seal the eyes and lips of their clients



Methyl acrylate (vinyl acetate)
Polymerizes to form polyvinyl acetate; used in acrylic paints in combination with pigments and a surfactant which causes the polymer to be suspended in an emulsion; also used in safety glass (a layer of PVA sandwiched between two layers of glass) and chewing gum



Methyl methacrylate
Polymerizes to form poly(methyl methacrylate); trade names are Lucite, Plexiglass, and Perspex; the bulky methyl and methyl ester groups cause the polymer to be oriented chaotically within the solid polymer, allowing light to pass through without scattering, rendering the plastic transparent



Lauryl methacrylate
Used to make the polymer poly(lauryl methacrylate); used as an additive in viscostatic engine oils, which keeps the oild viscous at high temperatures

Reactions of Esters

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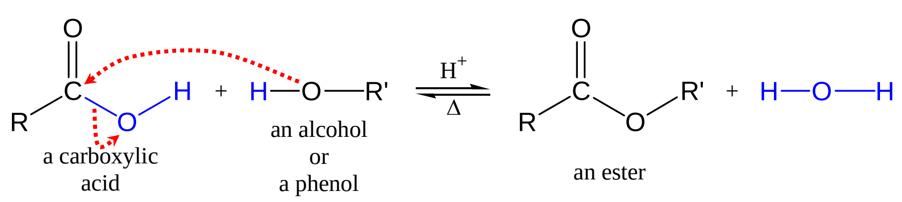
Synthesis of Esters: Esterification Reactions

- The simplest way to synthesize an ester is to heat a carboxylic acid with an alcohol or phenol (plus an acid catalyst); the oxygen of the alcohol adds to the carboxyl group, splitting out a molecule of water in the process (an *esterification reaction*).



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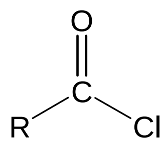
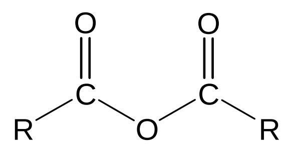
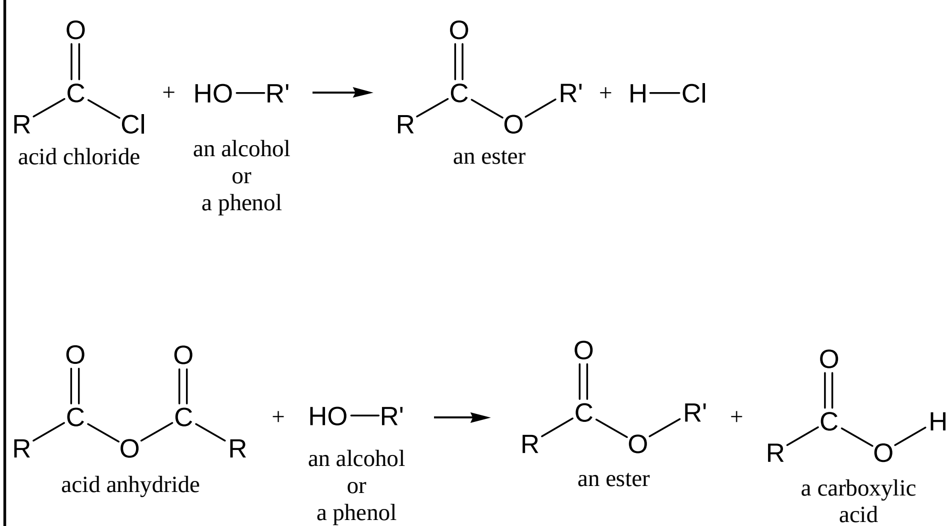
Synthesis of Esters: Esterification Reactions

- Since this reaction is a reversible reaction, it often reaches an equilibrium with a large amount of unreacted starting material still present.
- Better yields are obtained using either **acid chlorides** or **acid anhydrides** as starting materials. These reactions are nonreversible.



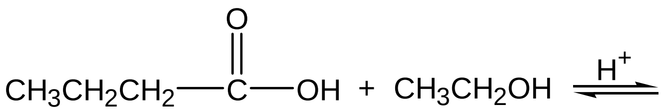


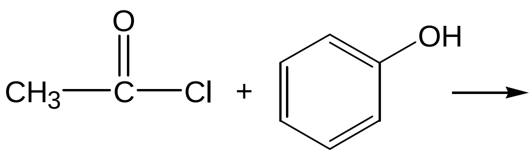
Synthesis of Esters: Esterification Reactions



Examples: Esterification Reactions

- Write both products of the following reactions:





Examples: Esterification Reactions

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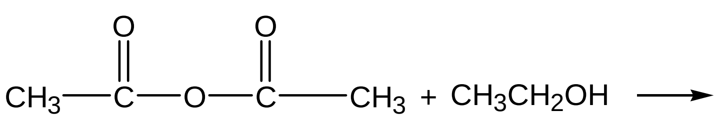
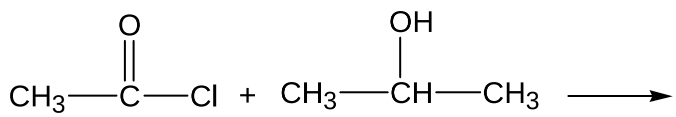


Examples: Esterification Reactions

- Write both products of the following reactions:



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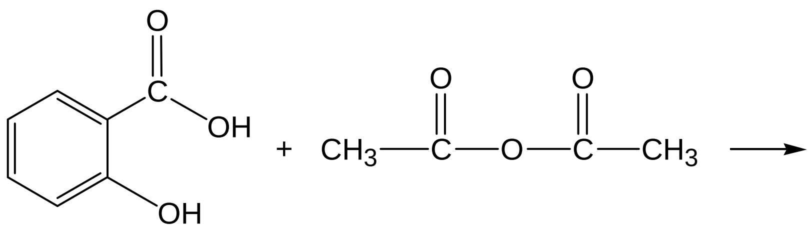
Examples: Esterification Reactions

- Write both products of the following reactions:



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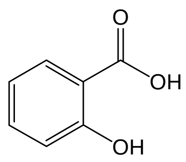
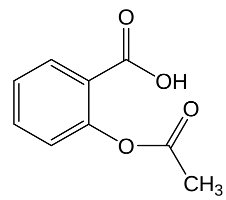
Pain, Pain, Go Away



Salicylic acid
Found in the bark of the willow tree (*Salix*); a tea brewed from the bark reduces fever and relives pain and inflammation, but is very acidic, and causes irritation of the mucous membranes in the mouth, throat, and stomach, and can cause painful ulcers and stomach bleeding



Aspirin (acetylsalicylic acid)
Produced by reacting salicylic acid with acetic anhydride, giving a compound which is less acidic, and does not cause as much irritation, but still retains all of the beneficial medical properties; aspirin seems to work by blocking the production of prostaglandins, hormones which may be responsible for producing pain, fever and inflammation; one of the most commonly used pharmaceutical drugs; over 40 million pounds are produced in the United States per year

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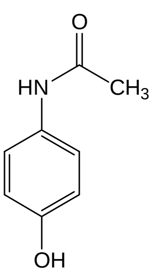
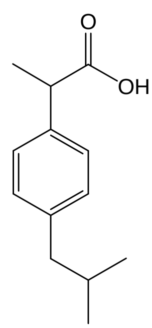
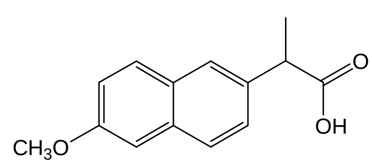
More Pain Relievers



Acetominophen
Does not cause stomach irritation, and has analgesic and antipyretic properties that are similar to aspirin, but no anti-inflammatory functions; available under the trade names Tylenol, Excedrin Aspirin Free, Panadol, and Anacin-3



Ibuprofen
An analgesic, antipyretic, and anti-inflammatory drug; it is also not irritating to the stomach lining; available under the trade names Motrin, Advil, Ibuprin, Nuprin, and Mediprin



Naproxen
An analgesic, anti-pyretic, and anti-inflammatory drug; active ingredient in Aleve

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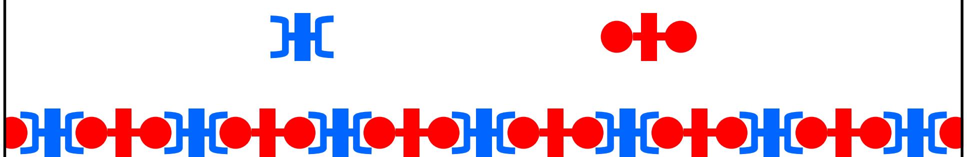
Condensation Polymers: Polyesters

- **Condensation polymers** are polymers which form with the loss of a small molecule (typically water or HCl).
- Condensation polymers, such as *polyesters* and *polyamides* (Nylon, Ch. 6), form when each of the monomers contain two of the same functional group, so the reaction can take place at both ends.



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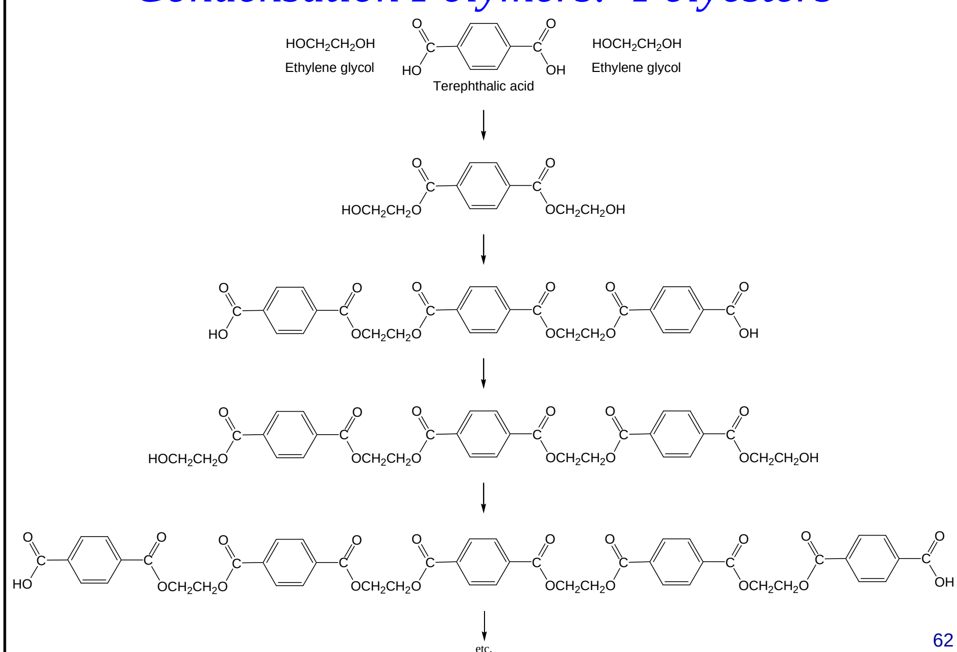
Condensation Polymers: Polyesters



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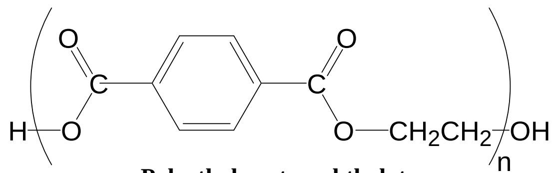
Condensation Polymers: Polyesters



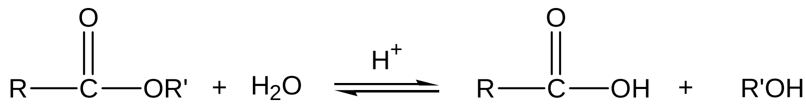
PETE

Polyethylene terephthalate
(PET)
A **polyester**

Over 3 billion pounds of PET are made every year. It forms a very linear chain, and is very inert. It can be melted and pulled through spinnerettes to make fibers, threads, or yarn (Dacron, Fortrel, Terylene), where it can be used in automobile tire cord, permanent press clothing, sutures, replacements for damaged sections of blood vessels and the esophagus, etc. PET melts can also be forced through narrow slits to produce thin sheets or ribbons known as Mylar; this form is used as the support medium in audio and video tape.

Reactions of Esters: Ester Hydrolysis

- Esters may be broken apart under *acidic conditions* by water (a **hydrolysis** reaction) to form a carboxylic acid and an alcohol.

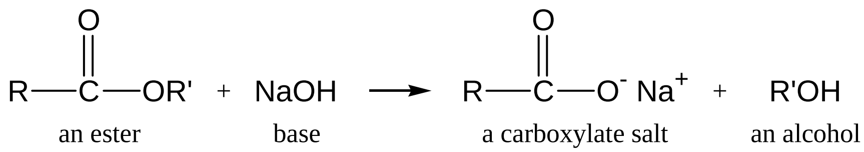


an ester　　a carboxylic acid　　an alcohol

- This is essentially the reverse reaction of the synthesis of esters from carboxylic acids and alcohols.

Reactions of Esters: Saponification

- Esters may be broken apart under *basic conditions* by sodium hydroxide (lye) or potassium hydroxide to form carboxylate salts and alcohols.

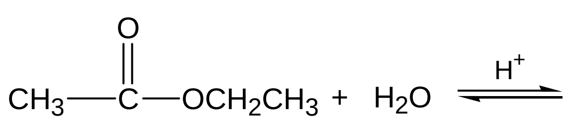


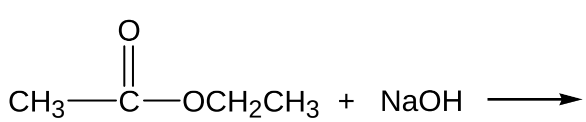
- This reaction is important in the production of **soaps**.

Examples: Splitting Esters

(Because Breaking Up Is Hard To Do)

- Complete the following reactions:

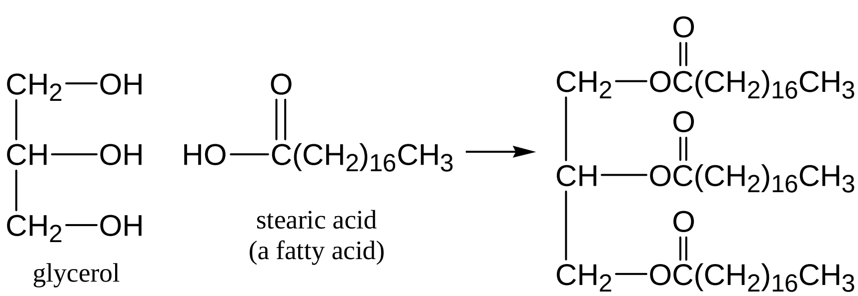




Triglycerides and Soaps

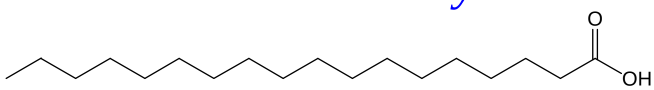
Triglycerides

- Long-chain carboxylic acids, often referred to as *fatty acids*, are stored by living organisms by combining them with glycerol to produce tri-esters called **triglycerides**.
- Triglycerides at room temperature are usually either solids or semi-solids (**fats**), or viscous liquids (**oils**).

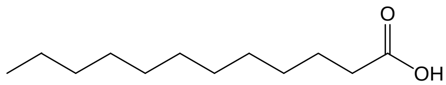


glyceryl tristearate (tristearin)
a **triglyceride**

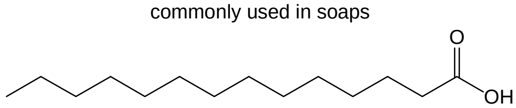
Some Saturated Fatty Acids



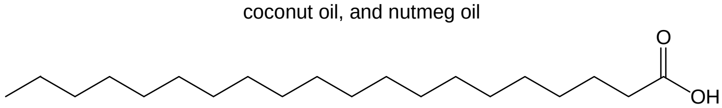
Stearic acid
A saturated fatty acid found in lard, beef fat, butterfat, cottonseed oil; the sodium salt, produced by heating lard with sodium hydroxide, can be used as a soap



Lauric acid
Found in coconut oil; commonly used in soaps



Myristic acid
A fatty acid found in butterfat, coconut oil, and nutmeg oil



Arachidic acid
A fatty acid found in peanut oil

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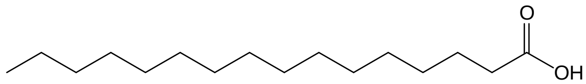
Some Saturated Fatty Acids



Palmitic acid
A fatty acid, found in lard, beef fat, butterfat, and cottonseed oil; the triglycerides in cocoa butter have oleic acid attached to the central oxygen, with stearic acid or palmitic acid on the other oxygens; this more regular composition gives cocoa butter a much sharper melting point than is usually observed in fats, and chocolate remains brittle almost up to its melting point of 34°C (just below body temperature); the sudden melting of chocolate in the mouth gives it a pleasant feeling of coolness

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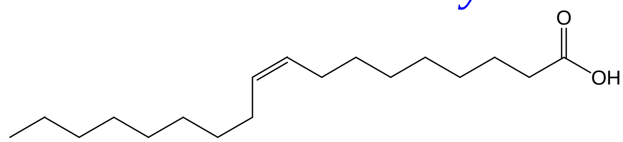
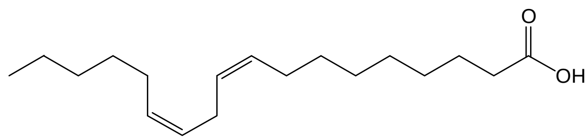
Some Unsaturated Fatty Acids



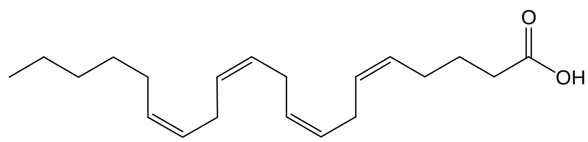
Oleic acid

An unsaturated fatty acid; the chain is much less flexible than that of stearic acid because of the double bond, and cannot pack as tightly, so the triglycerides it forms are oils and not fats; found in olive oil, cocoa butter and chocolate, beef fat, lard, and peanut oil



Linolenic acid

A omega-6 polyunsaturated fatty acid found in linseed oil and corn oil



Arachidonic acid

An omega-6 polyunsaturated fatty acid found in corn oil, linseed oil, animal tissues

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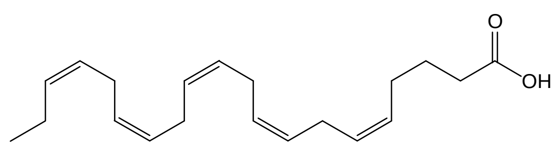
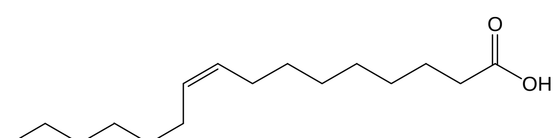
Some Unsaturated Fatty Acids



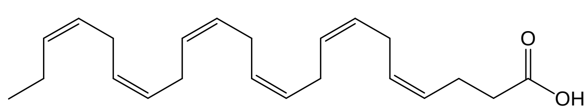
Eicosapentaenoic acid

A omega-3 polyunsaturated fatty acid found in fish oil and seafoods; omega-3 fatty acids may, according to some studies, help to lower the risk of heart disease



Palmitoleic acid

An unsaturated fatty acid found in butterfat and cod liver oil



Docosahexaenoic acid

An omega-3 polyunsaturated fatty acid found in fish oil and seafoods

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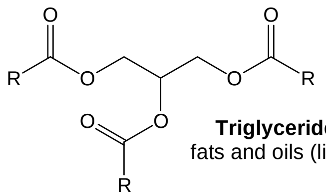
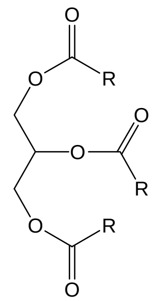
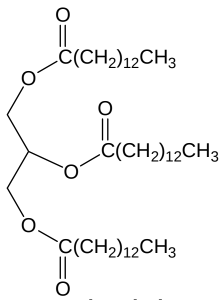
Triglycerides (Fats and Oils)



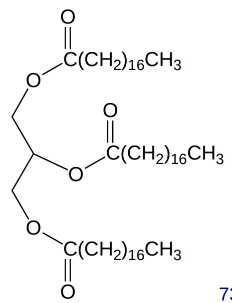


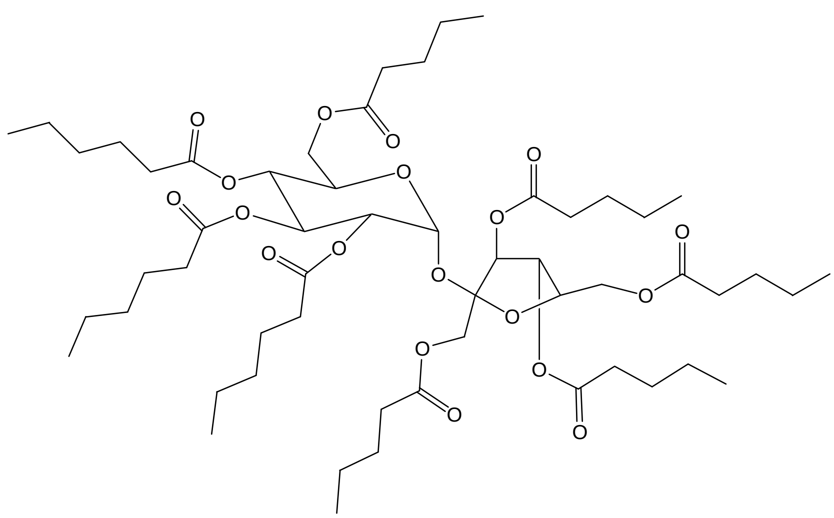
Triglycerides
fats and oils (lipids)



Trimyristin
Found in nutmeg, a spice obtained from the seed of the nutmeg tree, found in Indonesia and the West Indies, and other tropical areas

Tristearin
One of the principle compounds in beef fat and cocoa butter; triglycerides such as this lubricate meat fibers, and make the meat more tender when cooked; the yellow color of beef fat comes from carotene dissolved in tristearin.

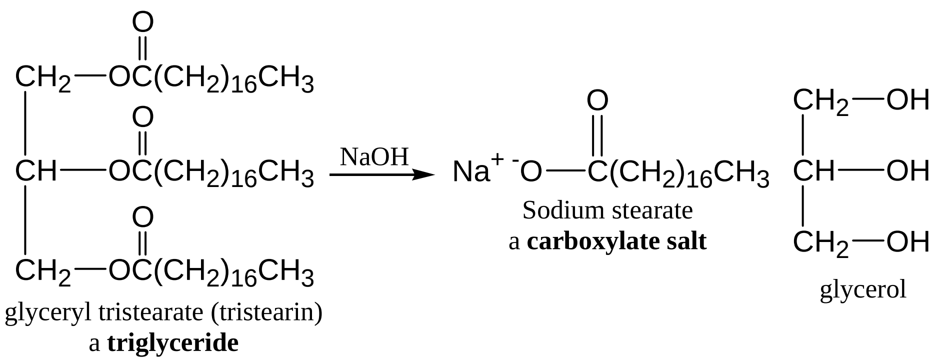




Olestra
A substitute for dietary fats developed by Procter & Gamble after 30 years and $200 million dollars worth of research; it is a combination of sucrose and fatty acids obtained from soybean oil and cottonseed oil; it is too hindered for digestive enzymes to react with; can carry small amounts of fat-soluble vitamins out of intestinal tract

Saponification of Triglycerides

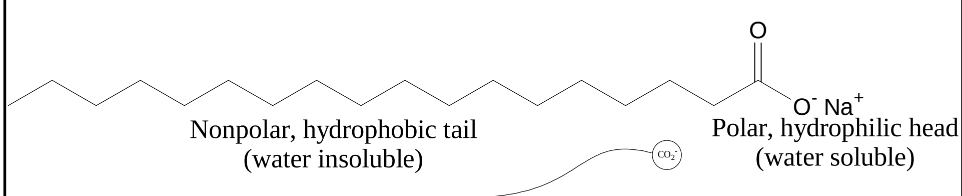
- Triglycerides can be broken apart under basic conditions (a saponification reaction) to produce long-chain carboxylate salts.



- Unlike their carboxylic acid forms, the carboxylate salts are at least somewhat soluble in water.

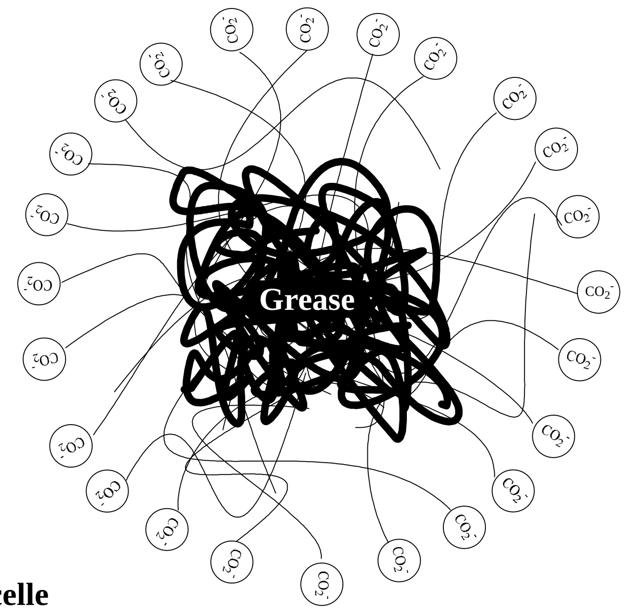
Fatty Acid Salts

- Salts of fatty acids combine two different solubility characteristics:
  - a long, nonpolar, water-insoluble (*hydrophobic*) hydrocarbon "tail."
  - a charged, water-soluble (*hydrophilic*) "head."



- When these substances are placed in water, their "tails" become tangled, thereby dissolving each other, leaving the charged, hydrophilic portions sticking out into the solution, allowing the whole **micelle** to dissolve in water, acting as a **soap**.

Soap



a **soap micelle**

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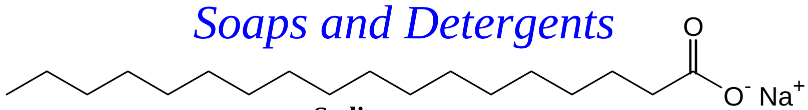
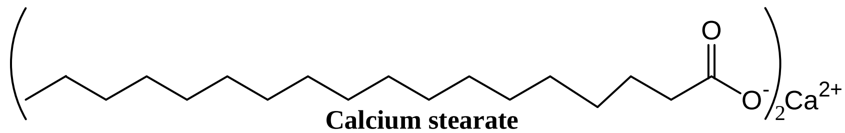
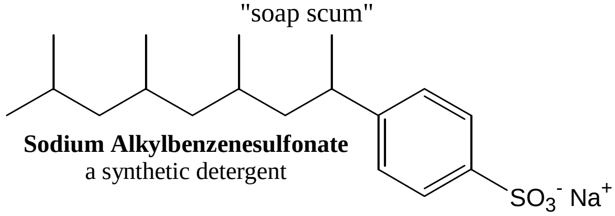
Soaps and Detergents



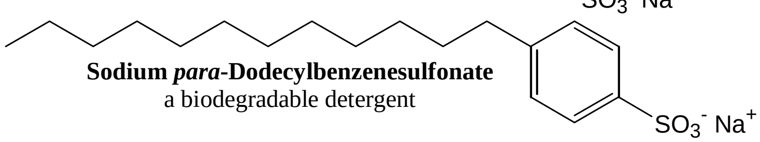
Sodium stearate



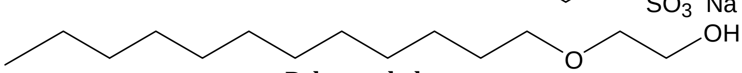
Calcium stearate
"soap scum"



Sodium Alkylbenzenesulfonate
a synthetic detergent



Sodium *para*-Dodecylbenzenesulfonate
a biodegradable detergent



Polyoxyethylene
A nonionic synthetic detergent; causes less foaming.

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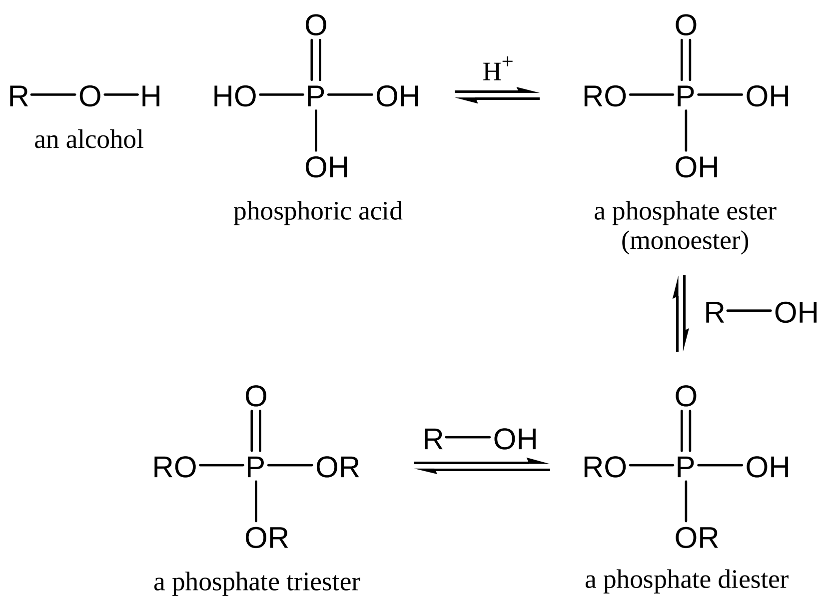
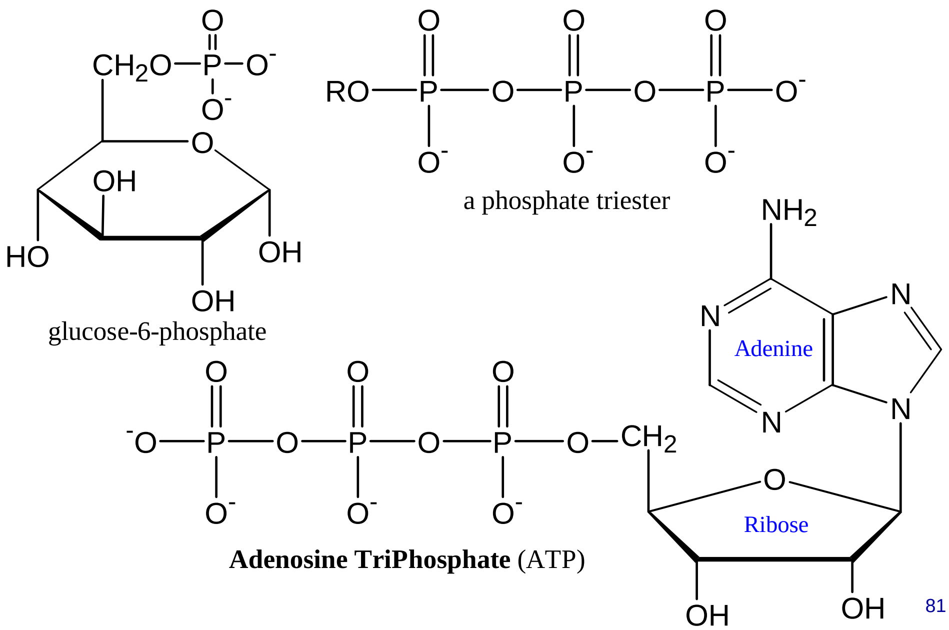
Esters of Inorganic Acids

Esters of Inorganic Acids



Some Important Phosphate Esters



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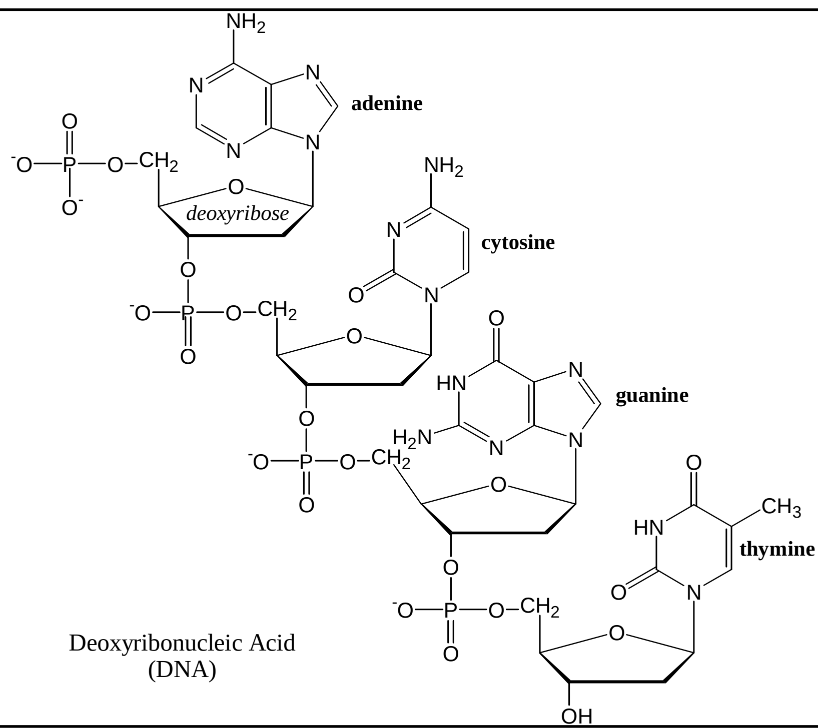

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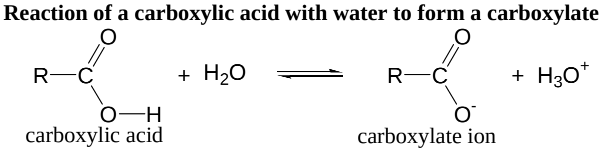
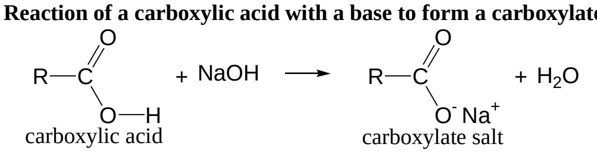
Reactions of Carboxylic Acids

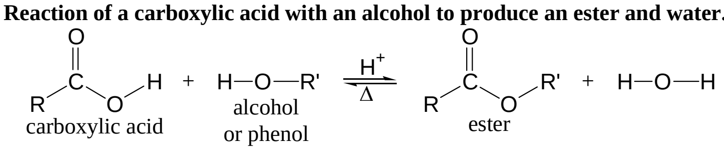
1. Reaction of a carboxylic acid with water to form a carboxylate ion.



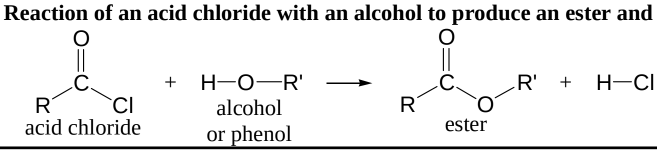
2. Reaction of a carboxylic acid with a base to form a carboxylate salt and water.



3. Reaction of a carboxylic acid with an alcohol to produce an ester and water.



4. Reaction of an acid chloride with an alcohol to produce an ester and HCl.



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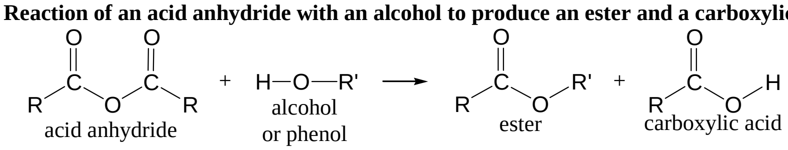
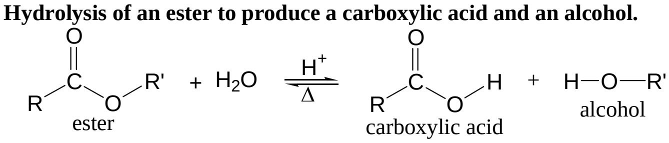
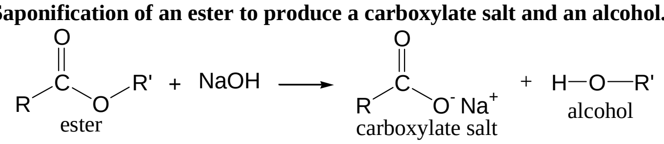
5. Reaction of an acid anhydride with an alcohol to produce an ester and a carboxylic acid.



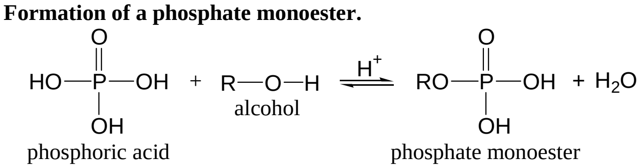
6. Hydrolysis of an ester to produce a carboxylic acid and an alcohol.



7. Saponification of an ester to produce a carboxylate salt and an alcohol.



8. Formation of a phosphate monoester.



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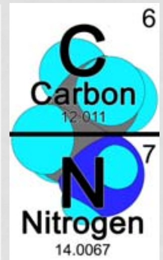
Chapter 6
Amines and Amides

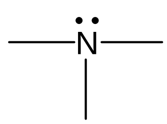


Chapter Objectives:

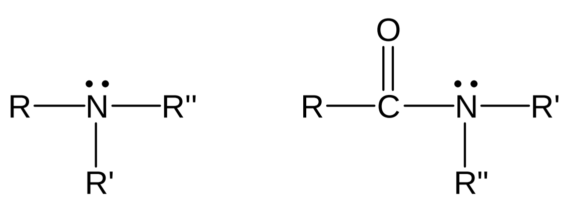
- Learn to recognize the amine and amide functional groups.
- Learn the IUPAC system for naming amines and amides.
- Learn the important physical properties of the amines and amides.
- Learn the major chemical reactions of amines and amides, and learn how to predict the products of amide synthesis and hydrolysis reactions.
- Learn some of the important properties of condensation polymers, especially the polyamides.

Nitrogen-Containing Functional Groups

- Nitrogen is in Group V of the periodic table, and in most of its compounds, it has three single bonds and one lone pair:



- In this chapter, we will take a look at two functional groups which contain nitrogen atoms connected to carbons: the **amines** and the **amides**.

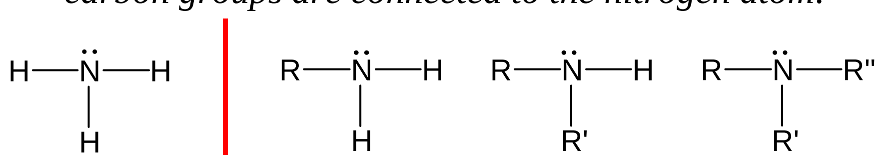


Amine **Amide**

Classification and Nomenclature of Amines

Amines

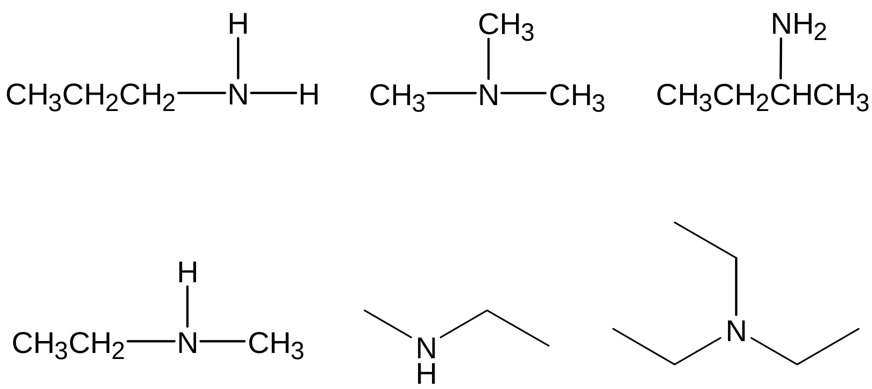
- Amines and amides are abundant in nature. They are a major component of proteins and enzymes, nucleic acids, alkaloid drugs, etc. (*Alkaloids* are N-containing, weakly basic organic compounds; thousands of these substances are known.)
- **Amines** are organic derivatives of ammonia, NH_3, in which one or more of the three H's is replaced by a carbon group.
- Amines are classified as **primary** (**1°**), **secondary** (**2°**), or **tertiary** (**3°**), depending on *how many carbon groups are connected to the nitrogen atom*.



Ammonia | **1° Amine** | **2° Amine** | **3° Amine**

Examples: Classifying Amines

- Classify the following amines as primary (1°), secondary (2°), or tertiary (3°).



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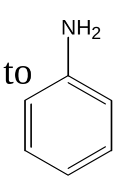
Nomenclature of Amines

- **Simple 1°, 2°, and 3° amines:** common (trivial) names are obtained by alphabetically arranging the names of the alkyl substituents on the nitrogen and adding the suffix **-amine** (e.g., ethylmethylamine).
- **Amines in the IUPAC system:** the "e" ending of the alkane name for the longest chain is replaced with **–amine**. The amine group is located by the position number. Groups that are attached to the nitrogen atom are located using "N" as the position number. More complex primary amines are named with —NH_2 as the *amino* substituent.
- **Aromatic amines:** named as derivatives of the parent compound **aniline**. Substituents attached to the nitrogen are indicated by using "N-" as the location number.



aniline

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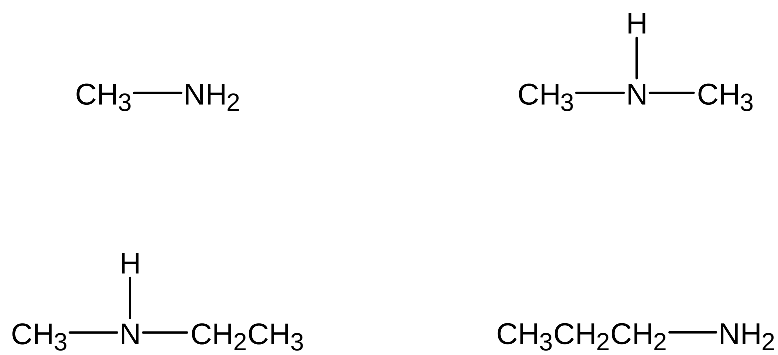
Examples: Nomenclature of Amines

- Provide common names for the following 2° and 3° amines; for 1° amines, provide common and/or IUPAC names where possible.



Examples: Nomenclature of Amines

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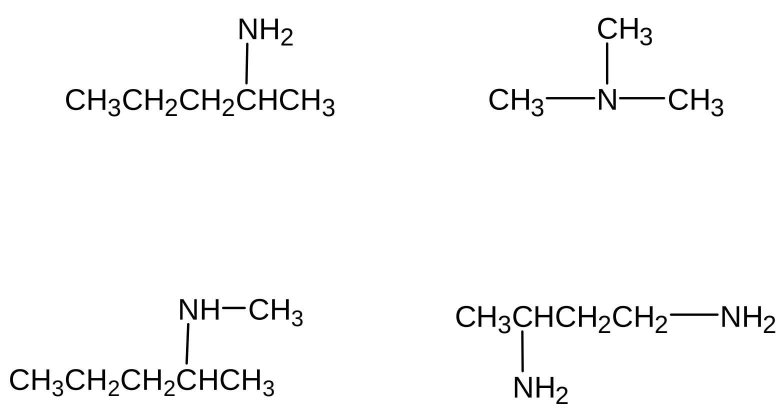

Examples: Nomenclature of Amines

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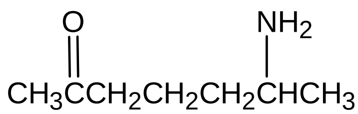
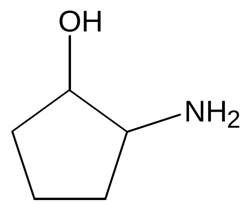
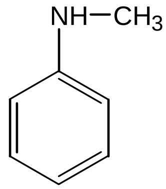
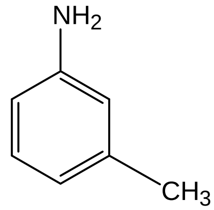


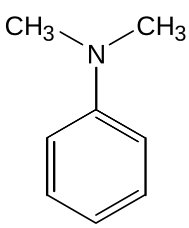


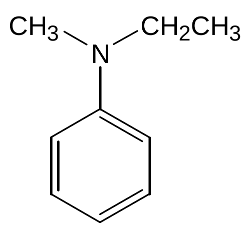
Examples: Nomenclature of Amines

- Provide names for the following aromatic amines.



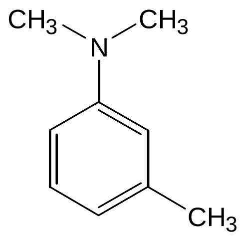


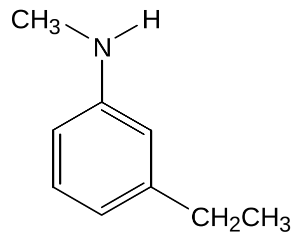


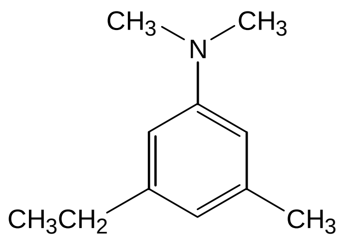


Examples: Nomenclature of Amines

- Provide names for the following aromatic amines.







Examples: Nomenclature of Amines

- Draw structural formulas for the following molecules:
  - ethylisopropylamine
  - tert-butylamine
  - 2-pentanamine

Examples: Nomenclature of Amines

- Draw structural formulas for the following molecules:
  - N-methyl-2-propanamine
  - 1,6-diaminohexane
  - 3-amino-1-propanol

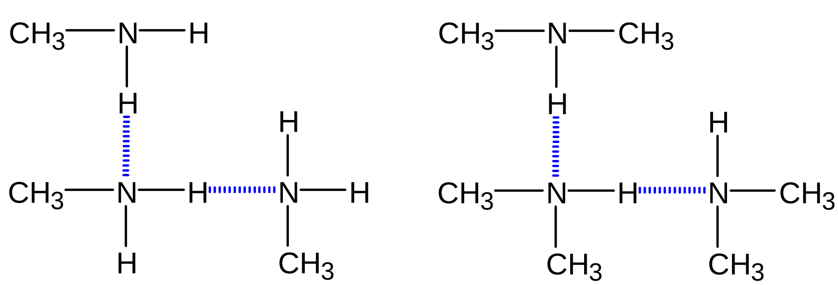
Examples: Nomenclature of Amines

- Draw structural formulas for the following molecules:
  - N-methyl-2-chloroaniline
  - N,3-diethylaniline
  - N,N-dimethylaniline

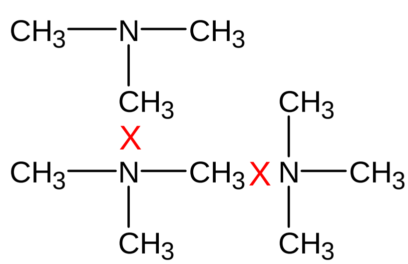
Physical Properties of Amines

Physical Properties of Amines: H-Bonding

- 1° and 2° amines can hydrogen bond to each other:



- 3° amines cannot hydrogen bond to each other:



Physical Properties of Amines: Boiling Points

- Nitrogen is less electronegative than oxygen, so the N—H bond is not quite as polar as the O—H bond.
  - Hydrogen bonds from N—H's are not as strong as those resulting from O—H's.
  - Hydrogen bonding between 1° and 2° amines is not as strong as those found in alcohols or carboxylic acids.
- 1° and 2° amines have lower boiling points than alcohols of similar molecular weight.
- 3° amines, since they do not hydrogen bond to each other, have boiling points similar to hydrocarbons of the same molecular weight.

Physical Properties of Amines: Boiling Points

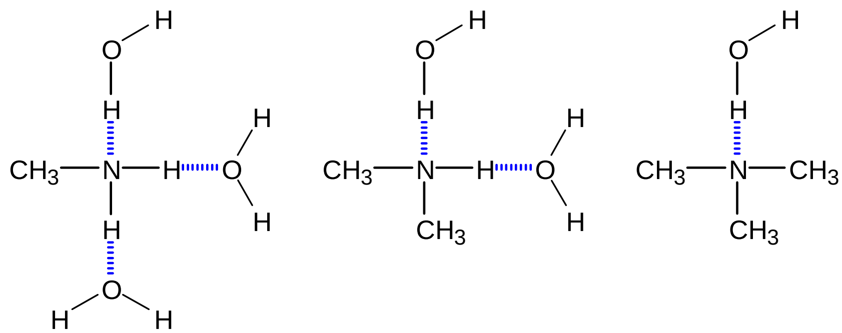
Boiling Point:

↑ Carboxylic acid
Alcohols
1°/2° Amines
3° Amines/Alkanes

Name	**Molecular weight**	**Boiling point**
Acetic acid	60.0 g/mol	118°C
1-propanol	60.1 g/mol	97°C
propyl amine	59.1 g/mol	48°C
ethylmethylamine	59.1 g/mol	36°C
trimethylamine	59.1 g/mol	2.9°C
butane	58.1 g/mol	-0.5°C

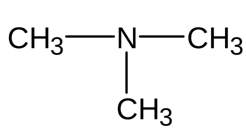
Physical Properties of Amines: Water Solubility

- 1°, 2°, and 3° amines can all form hydrogen bonds with water.
- Low-molecular weight amines are generally water-soluble.

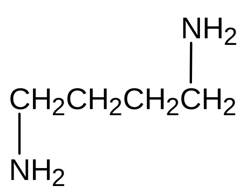


Physical Properties of Amines: Odor

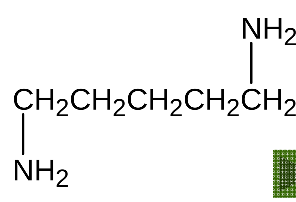
- Low molecular-weight amines tend to have sharp, penetrating odors similar to ammonia
- Higher molecular-weight amines often smell like rotting fish, and are often found in decaying animal tissues.



Trimethylamine
Responsible for the odor of rotting fish



1,4-Diaminobutane (Putrescine)
A poisonous oil present in rotting flesh; produced during the decomposition of the amino acid arginine; also partially responsible for the odor of urine and bad breath



1,5-Diaminopentane (Cadaverine)
A poisonous, viscous liquid present in rotting flesh; produced during the decomposition of the amino acid lysine; also partially responsible for the odor of urine and bad breath

Examples: Predicting Physical Properties

- Arrange the following compounds in order of increasing boiling point. (All of the compounds have about the same molecular weight.)

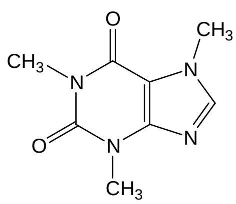
propanoic acid, diethylamine, 1-butanol, ethyldimethylamine

Examples: Predicting Physical Properties

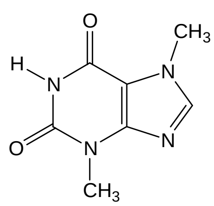
- Which member of each of the following pairs of compounds would you expect to have a higher boiling point?
  - 2-aminopropane *or* 2-aminohexane
  - triethylamine *or* 1-aminohexane
  - propanoic acid *or* diethylamine
  - 1-pentanol *or* 1-aminopentane

Some Important Alkaloids

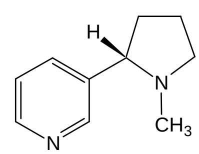
Important Alkaloids



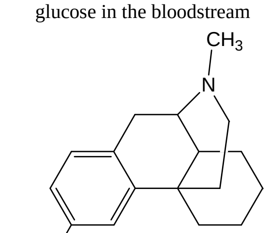
Caffeine
Found in the seeds of *Coffea arabica*, roasted coffee beans; inhibits the action of phosphodiesterase, an enzyme which inhibits cyclic adenosine monophosphate (AMP), which is responsible for forming glucose in the bloodstream



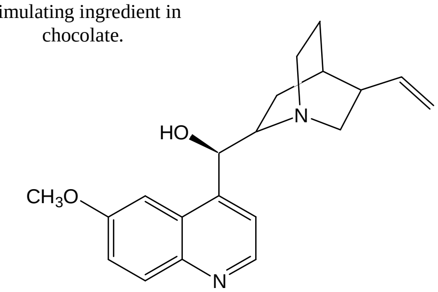
Theobromine
Found in the seeds of *Theobroma cacao*; the stimulating ingredient in chocolate.



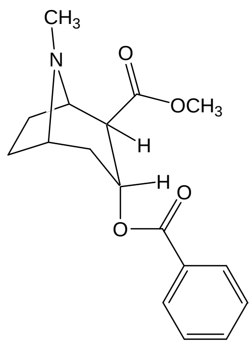
Nicotene
Found in tobacco plants; mild stimulant in small doses; addictive, but not especially harmful itself



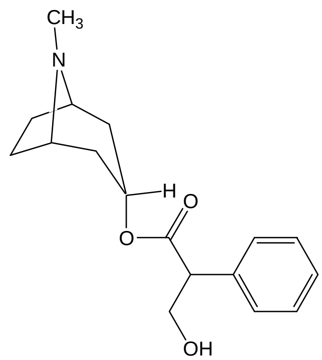
Dextromethorphan
Ingredient in cough suppressants.



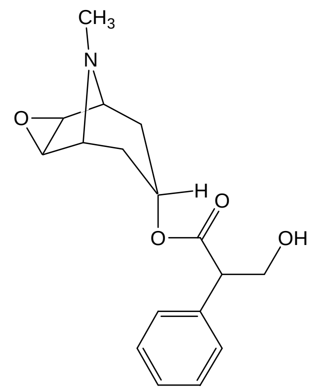
Quinine
Antimalarial drug from *cinchona* tree



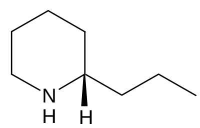
Cocaine
The form which is "snorted" is the hydrochloride salt; the free-base "crack" form is burned and inhaled, and reaches the brain in 15 seconds.



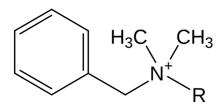
Atropine
relaxes muscles and reduces secretion of saliva during surgery; used to dilate pupils for eye examinations.



Scopolamine
used in treatment of motion sickness



Coniine
Poison from hemlock



Zephiran chloride
(benzalkonium chloride)
Antiseptic compound that kills bacteria and fungi on contact

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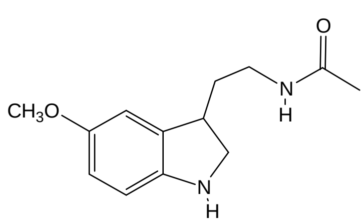
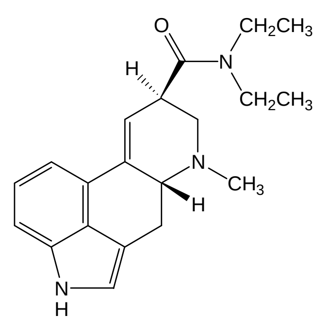
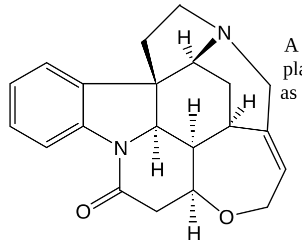


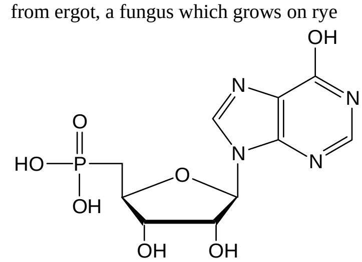
Melatonin
A naturally occuring hormone produced in the pineal gland; its production is triggered by the absence of light; causes drowsiness in humans at night, triggers birds to migrate, and signals dogs to shed their winter coats; sold as a treatment for jet lag.



Lysergic acid diethylamide (LSD)
A synthetic hallucinogen from alkaloids obtained from ergot, a fungus which grows on rye



Strychnine
A poison from strychnos plant (*Nux vomica*); used as a rat and mouse poison



Inosine Monophosphate (IMP)
With monosodium glutamate (MSG), one of the major substances responsible for the flavor of meat

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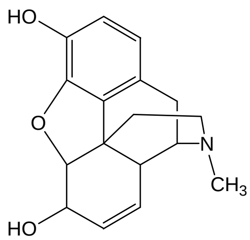
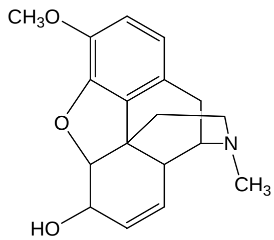
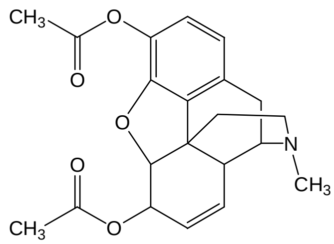


Morphine
Found in the opium poppy; a CNS depressant; very effective painkiller



Codeine
Used in some cough syrups to depress the action of the cough center of the brain



Heroin
More fat-soluble than morphine, and must be injected directly into the bloodstream, but crosses the blood-brain barrier more readily, causing it to be more potent than morphine

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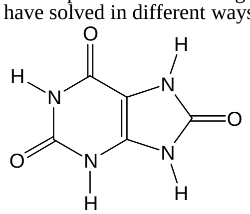
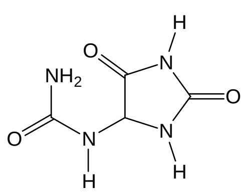
Nitrogen Wastes

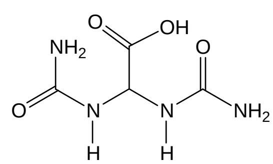
The disposal of waste nitrogen from the body is a problem which different species of animals have solved in different ways:



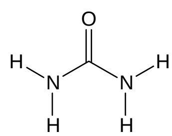
Uric acid
Birds, reptiles and insects excrete nigrogen wastes in the form of uric acid. Uric acid can be eliminated directly in the solid form, without being dissolved in water. It is produced in the body from foods and beverages rich in purines, such as claret and port. Lactic acid inhibits the removal of salts of uric acid in the urine; these salts instead deposit in the joints, causing gout. Dalmations have been bred to have black spots with no white hairs in them on their coats; however, the gene which determines the presence of white hairs is linked to the gene which codes the enzyme which breaks down uric acid into allantoin. Dalmations thus excrete uric acid instead of allantoin, and are very susceptible to gout.



Allantoin
Most mammals contain enzymes which metabolyze uric acid into allantoin.



Allantoic acid
Marine vertebrates further metabolyze allantoin into allantoic acid.



Urea
Urea is the major organic component of urine; about 25 g are excreted every day by humans. Cartilaginous fish and amphibians also excrete urea.

NH_4^+ X^-
Marine invertebrates excrete ammonium salts.

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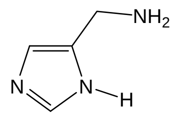
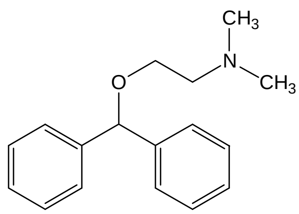
Antihistamines



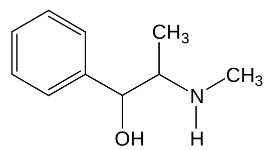
Histamine

People who are allergic to pollen produce histamine, which causes blood vessels to dilate and leak, releasing fluid into surrounding tissues, causing watery eyes, sniffles, congestion, and other symptoms of hay fever (*allergic rhinitis*); also causes the symptoms of the common cold and swelling after insect bites.



Diphenylhydramine

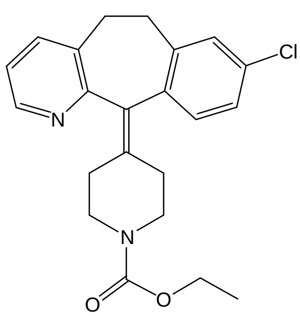
an *antihistamine*; active ingredient in Benadryl; sometimes used in sleeping pills



Ephedrine / Pseudoephedrine

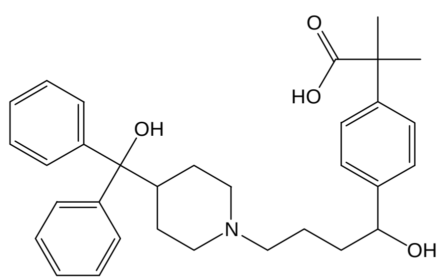
found in the Chinese ma-huang plant; a decongestant used in many cold remedies

Antihistamines



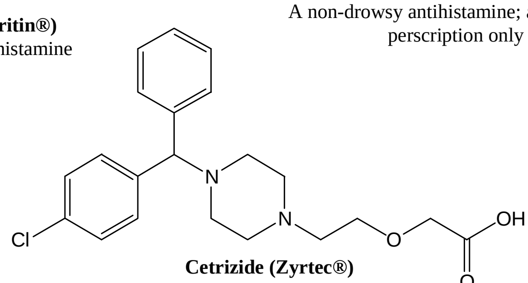
Loratadine (Claritin®)

A non-drowsy antihistamine



Fexofenadine (Allegra®)

A non-drowsy antihistamine; available by perscription only



Cetrizide (Zyrtec®)

A stronger antihistamine than Allegra or Claritin, but causes drowsiness in some people

Reactions of Amines

Bases

- A **base** takes a **proton (H^+)** from another species. A base produces **hydroxide ions**, **$OH^–$**, when dissolved in water:

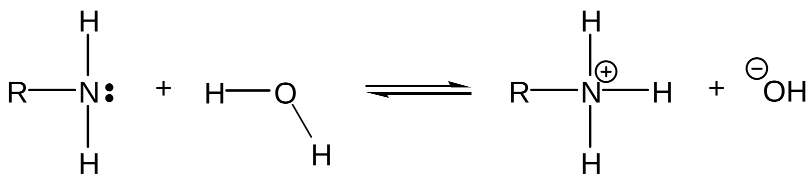
$$B + H_2O \rightarrow BH^+ + OH^-$$

- A **strong base** is one that *completely dissociates* in water (i.e., every molecule of the acid splits apart).
- A **weak base** is one in which only a small percentage of the molecules are dissociated at any one time.

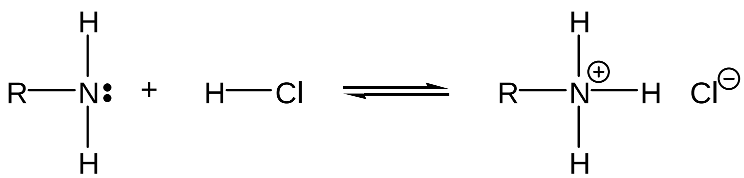
- **Acidic** solution: **pH < 7.00** ($[H_3O^+] > [OH^-]$)
- **Basic** solution: **pH > 7.00** ($[H_3O^+] < [OH^-]$)
- **Neutral** solution: **pH = 7.00** ($[H_3O^+] = [OH^-]$)

Chemical Properties of Amines: Basicity

- Amines are weak organic **bases**. They react with water to produce *alkylammonium ions* and hydroxide anions:

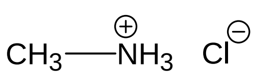


- and with acids to produce *alkylammonium salts*:

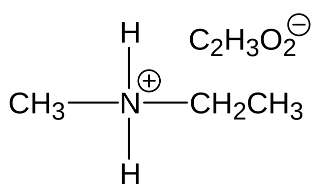


Alkylammonium Salts

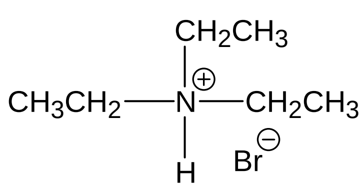
- Salts of amines are named by changing "amine" to "ammonium" and adding the name of the negative ion to the end of the word:



methylammonium chloride



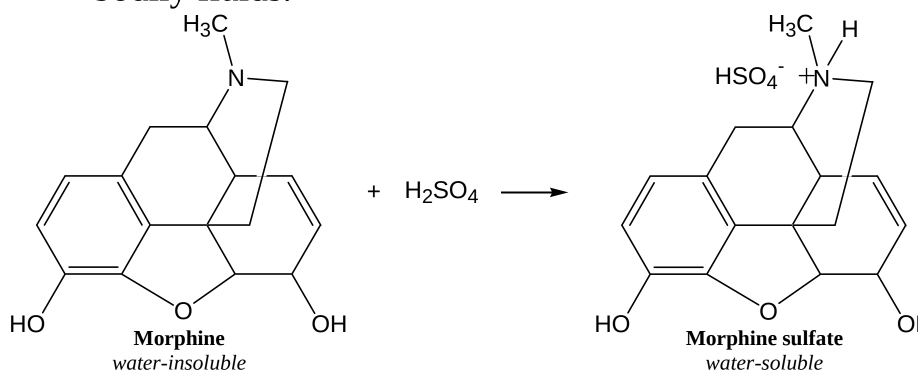
ethylmethylammonium acetate



triethylammonium bromide

Alkylammonium Salts

- Salts of amines are generally white crystalline solids with high melting points.
- The ionic charges makes these salts more soluble in water than the neutral amines. Many amine-containing drugs are administered in the form of alkylammonium salts to increase their solubility in bodily fluids.



Chemical Properties of Amines: Basicity

- Ammonium salts may be converted back into neutral amines by a strong base:

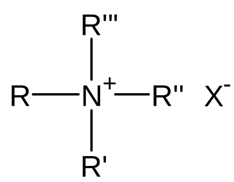
$$R—NH_3^+\ Cl^- \ + \ NaOH \longrightarrow R—NH_2 \ + \ H_2O \ + \ NaCl$$

- Thus, by adjusting the pH of the solution, it is possible to influence whether an amine is present in the neutral form or as its ammonium cation form:

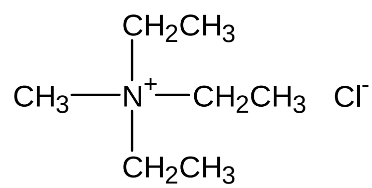
$$\underset{\text{amine}}{R—NH_2} \ + \ H_2O \ \underset{\text{base (high pH)}}{\overset{\text{acid (low pH)}}{\rightleftharpoons}} \ \underset{\text{alkylammonium ion}}{R—NH_3^+} \ + \ {}^-OH$$

Quaternary Ammonium Salts

- In addition to salts of 1°, 2°, and 3° amines, it is possible to have amine cations which contain four alkyl groups attached to a nitrogen atom, which will *always* carry a positive charge, regardless of the pH of the surrounding solution. These are known as **quaternary ammonium salts**.



quaternary ammonium salt



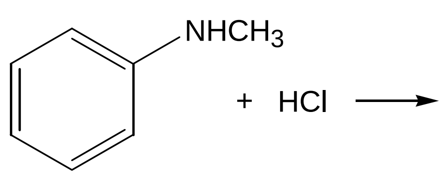
triethylmethylammonium chloride

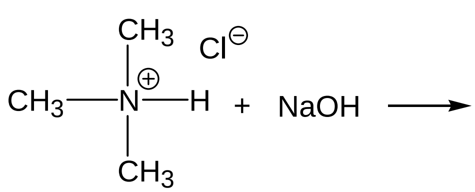
- These salts are present in many antiseptics and antibacterial agents.

Examples: Basicity of Amines

- Complete the following reactions:

$$CH_3NH_2 + HCl \longrightarrow$$

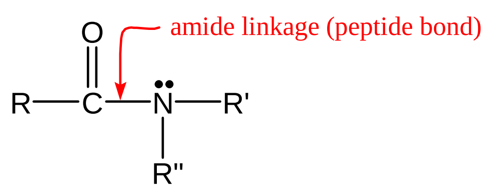




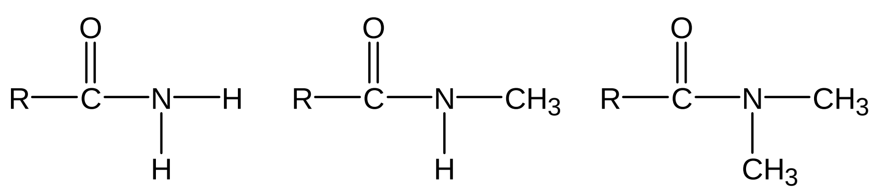
Amides

Amides

- **Amides** contain a nitrogen which is directly attached to a carbon in a carbonyl group:

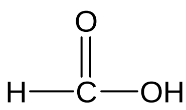


Amide

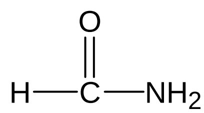


Nomenclature of Amides

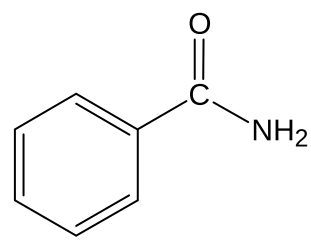
- Amides are named by changing the *-oic acid* ending of the corresponding carboxylic acid to **-amide**. If alkyl groups are attached to the nitrogen, they are named as N-alkyl substituents.



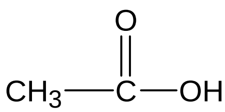
methanoic acid
(formic acid)



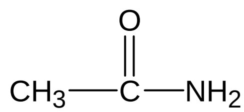
methanamide
(formamide)



benzamide



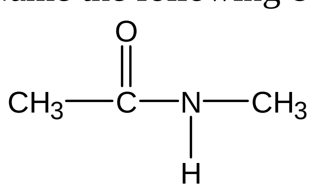
ethanoic acid
(acetic acid)

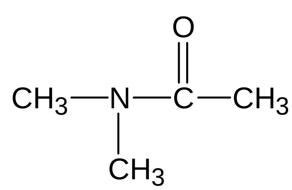


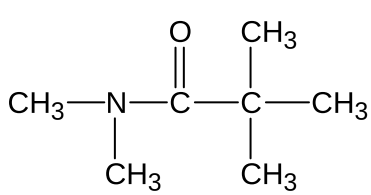
ethanamide
(acetamide)

Examples: Nomenclature of Amides

- Name the following compounds:

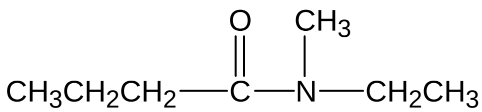


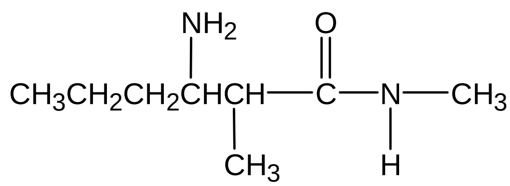




Examples: Nomenclature of Amides

- Name the following compounds:





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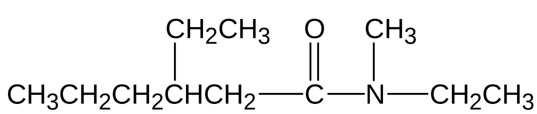
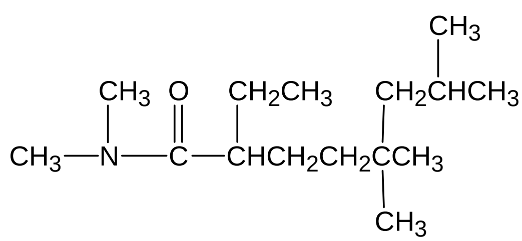
Examples: Nomenclature of Amides

- Name the following compounds:





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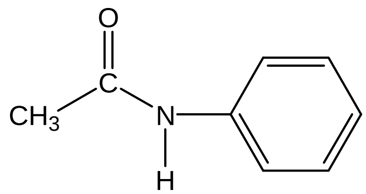
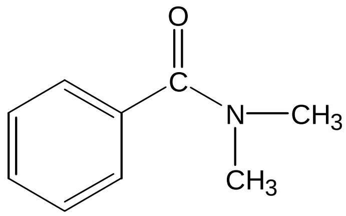
Examples: Nomenclature of Amides

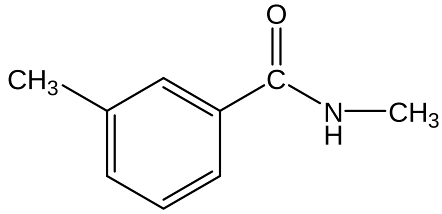
- Name the following compounds:

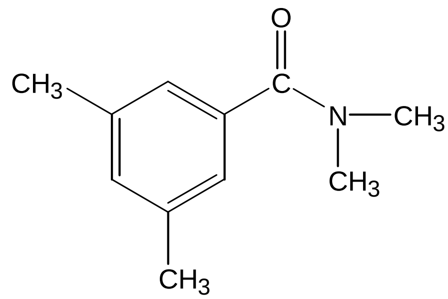




Examples: Nomenclature of Amides

- Name the following compounds:





Examples: Nomenclature of Amides

- Draw structural formulas for the following molecules:
  - 2-methylpropanamide
  - N,2,4-trimethylpentanamide
  - N-ethyl-N-methylacetamide

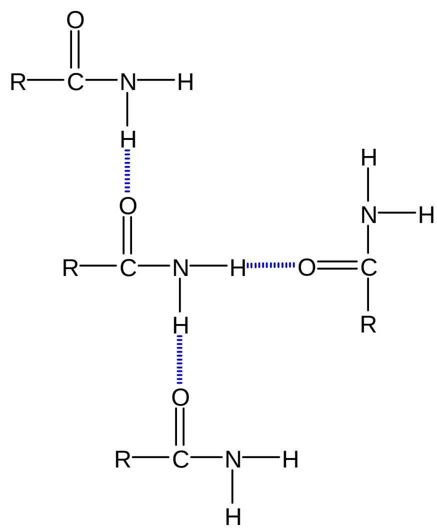
Examples: Nomenclature of Amides

- Draw structural formulas for the following molecules:
  - N,2-diethylbenzamide
  - N,N,2,3,4-pentamethylbenzamide
  - N,N,4,4-tetramethylbutanamide (what's wrong with this name?)

Physical Properties of Amides

Physical Properties of Amides

- N,N-unsubstituted amides can form a complex network of hydrogen bonds. They tend to have high melting points and also high boiling points.



Physical Properties of Amides

- N-substituted amides often have lower melting points and boiling points than N,N-unsubstituted amides because fewer hydrogen bonds can form.
- N,N-disubstituted amides cannot form hydrogen bonds, and have even lower melting points and boiling points.
- All amides can hydrogen bond with water, so low-molecular weight amides are water-soluble.

Boiling Point:

↑ N,N-unsubstituted amides
N-substituted amides
N,N-disubstituted amides

Examples: Predicting Physical Properties

- Arrange the following compounds in order of increasing boiling point. (All of the compounds have about the same molecular weight.)

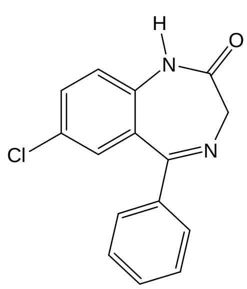
N-ethylethanamide

butanamide

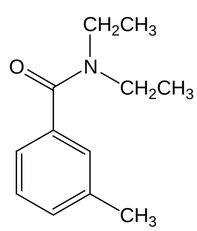
N,N-dimethylethanamide

Important Amides

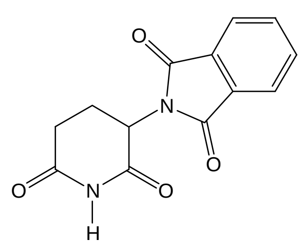
Important Amides



Diazepam (Valium)
A benzodiazepene tranquilizer; acts by enhancing the inhibitory neurotransmitter GABA; since it binds to the same protein as ethanol, combinations of valium and ethanol can be deadly

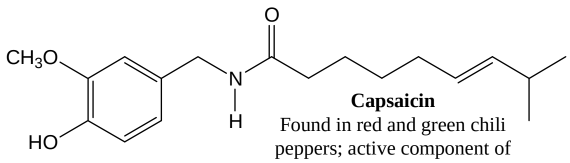


***N,N*-Diethyl-*m*-toluamide**
Active ingredient in OFF

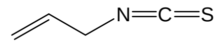


Thalidomide
Until 1956, a very popular, safe sedative; the largest market was for pregnant women who were experiencing morning sickness. However, it caused massive birth defects in women who used it in the early states of pregnancy, and was banned in Europe; it was never authorized for sale in the U.S.

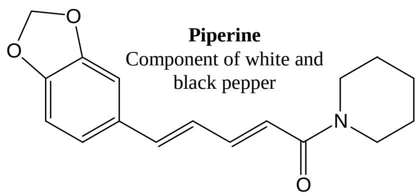
Hot Stuff



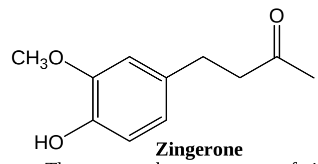
Capsaicin
Found in red and green chili peppers; active component of paprika



Allyl isocyanate
Used in horseradish flavor, mustard oil, pickles, salad dressings and sauces; mustard plasters, medications and fumigants



Piperine
Component of white and black pepper



Zingerone
The pungent, hot component of ginger

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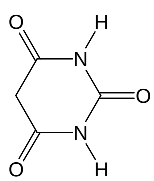
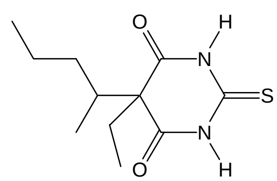
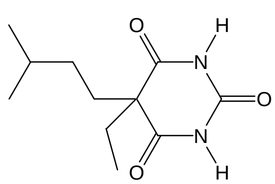
Barbiturates



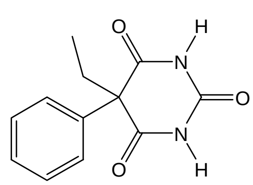
Barbituric acid
First synthesized by Adolf von Baeyer in 1864; barbiturates are soporifics, and are used as tranquilizers and anesthetics; many are also addictive, and overdoses can be fatal. (Other barbiturates include Seconal, Veronal, Phenobarbitol, Thiopental, Amobarbitol, etc.)



Thiopental (Pentothal)
An intravenous anesthetic



Amobarbital (Amytal)
Used in the treatment of insomnia



Phenobarbitol
Anti-seizure medication, sedative

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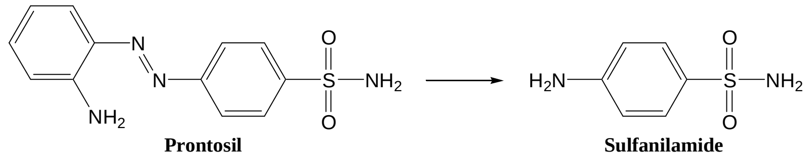
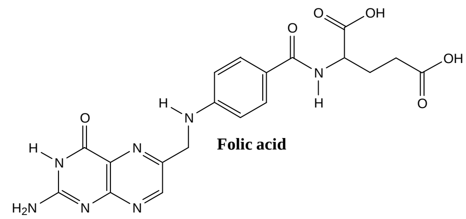
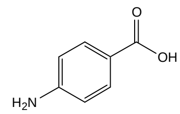
Sulfa Drugs







para-Aminobenzoic aid (PABA)

Sulfanilamide, the first **antibiotic**, was discovered by Gerhard Damagk (Nobel Prize, 1939), who observed the antibacterial action of the red dye Protonsil; further researched showed that it was the metabolic byproduct, sulfanilamide, which was the active form. It prevents bacteria from synthesizing folic acid, which they need in order to grow. Bacterial enzymes synthesize folic acid using *para*-aminobenzoic acid (PABA); sulfanilamide fits into the enzyme more tightly, blocking it from taking up PABA, and thus blocking folic acid synthesis. The bacterium cannot grow, and eventually dies. Humans obtain folic acid from their diet (an **essential vitamin**), so sulfa drugs do not harm people in this way (although they can cause allergic reactions).

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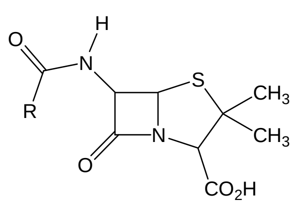
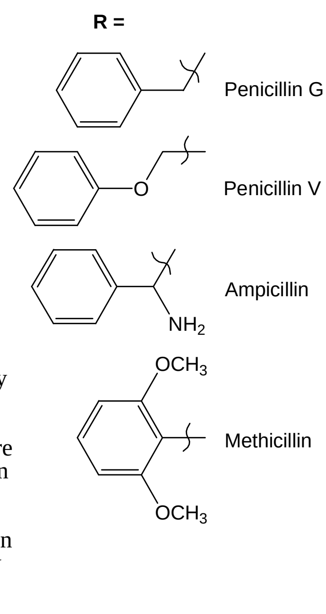
Penicillin



Penicillin



Penicillin is an antibiotic compound produced by the molds *Penicillium notatum* and *Penicillium chrysogenum*; it was discovered by Alexander Fleming in 1928 in a culture of bread mold. There are several varieties: Penicillin G and Methicillin are administered by injection; Penicillin V is an oral form which is not broken down in the stomach; Ampicillin is a broad spectrum penicillin which can be administered by injection or orally

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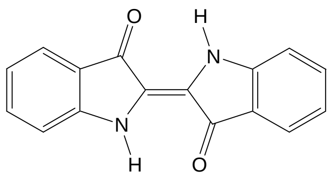
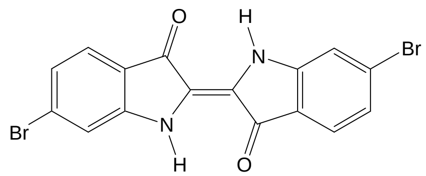
Molecules To Dye For

- **Dyes** are compounds that can be used to color other materials, such as clothing, paper, hair, etc.
- Many organic dyes contain a long series of double bonds that are close together. If the chain of double bonds is long enough, these molecules can absorb low-energy light in the visible region of the electromagnetic spectrum, resulting in colors that are visible to the human eye.

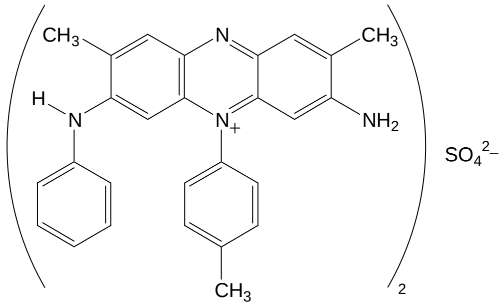


Indigo
A naturally occurring blue dye which has been used for thousands of years. It is obtained from an Indian plant (*Indigofera tinctoria*) and the European woad (*Isatis tinctoria*). Today, indigo can be made synthetically, and is used in dyeing denim to make blue jeans.



Tyrian purple
6,6'-dibromoindigo
Tyrian purple, or "royal purple," is a purple dye originally obtained from a species of mollusk (*Murex*) found near the cities of Tyre and Sidon in ancient Phoenicia. It took about 9,000 mollusk shells to obtain one gram of the dye, making it very expensive. This dye was used by royalty (hence the name "royal purple") and the Roman aristocracy.

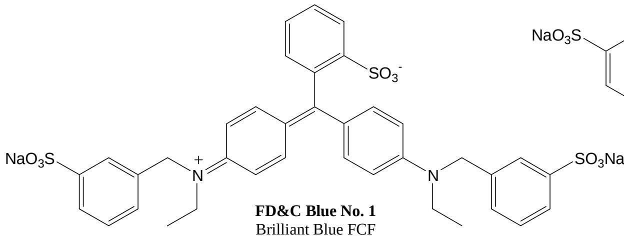
Molecules To Dye For



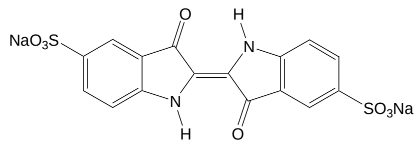
Mauve
This is the first of the synthetic dyes. It was discovered by the 18-year-old English chemist William Henry Perkin in his home laboratory, while attempting to synthesize quinine (the only known treatment for malaria at that time). While cleaning up the sludge from one of his failed attempts, he noticed that the sludge was turning the water in his sink violet, and that cloth would pick up this purple color. Perkin patented his serendipitous discovery, and went into business making dyes, becoming so successful that he was able to retire at the age of 36 to focus his attention on chemical research.

FD&C Dyes

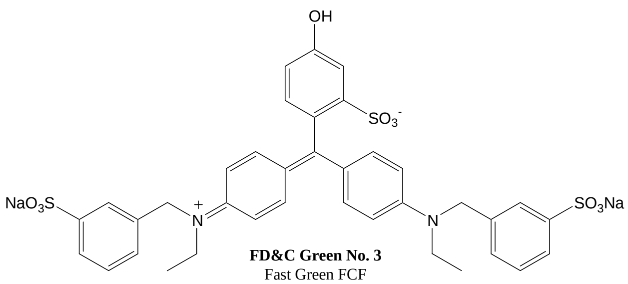
These color additives are approved by the Food and Drug Administration (FDA) under the Federal Food, Drug, and Cosmetic Act (FD&C, 1938, amended 1997) for use in foods.



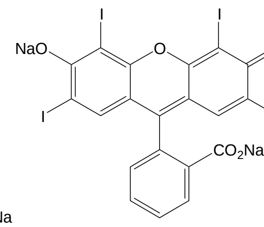
FD&C Blue No. 1
Brilliant Blue FCF



FD&C Blue No. 2
Indigo Carmine, Indigotine

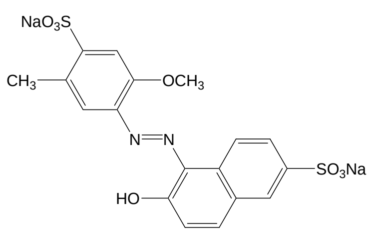


FD&C Green No. 3
Fast Green FCF

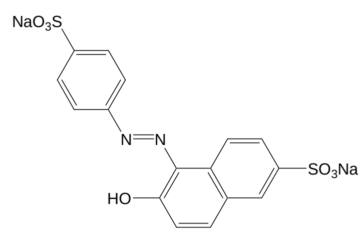


FD&C Red No. 3
Erythrosine

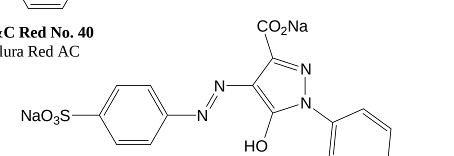
FD&C Dyes



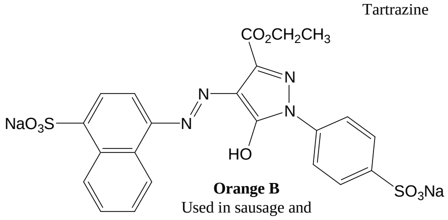
FD&C Red No. 40
Allura Red AC



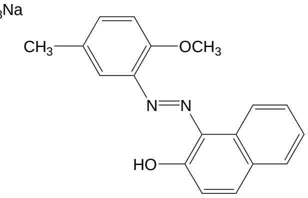
FD&C Yellow No. 6
Sunset Yellow FCF



FD&C Yellow No. 5
Tartrazine

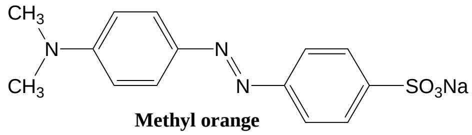


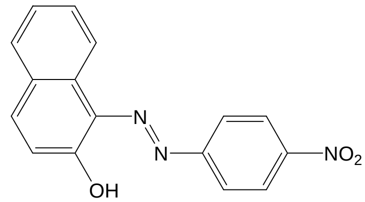
Orange B
Used in sausage and frankfurter casings

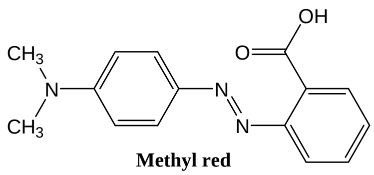


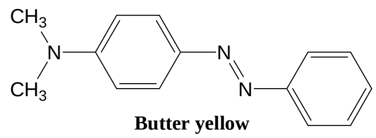
Citrus Red No. 2
Used to color orange skins

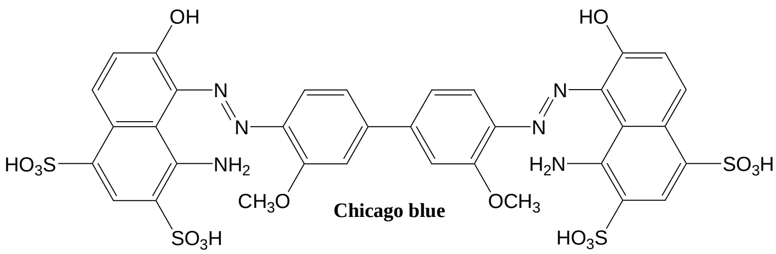
Molecules To Dye For


Methyl orange


Para red


Methyl red


Butter yellow


Chicago blue

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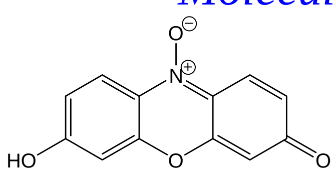
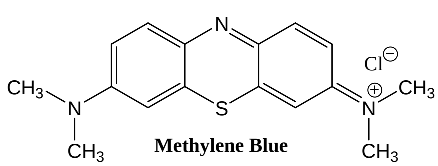
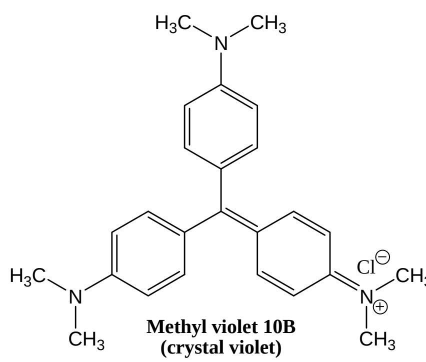
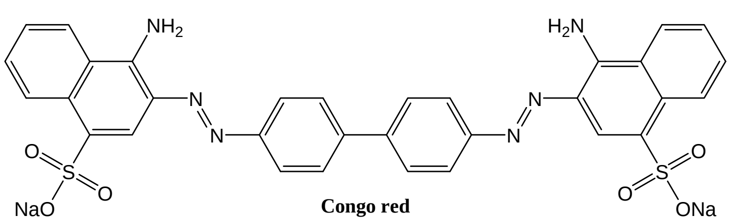
Molecules To Dye For


Resazurin


Methylene Blue


Methyl violet 10B (crystal violet)


Congo red

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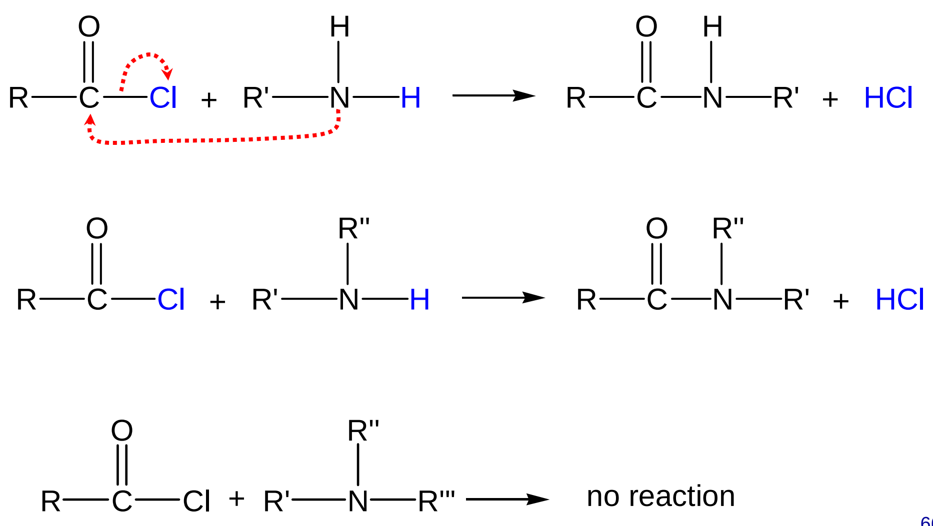
Reactions of Amides

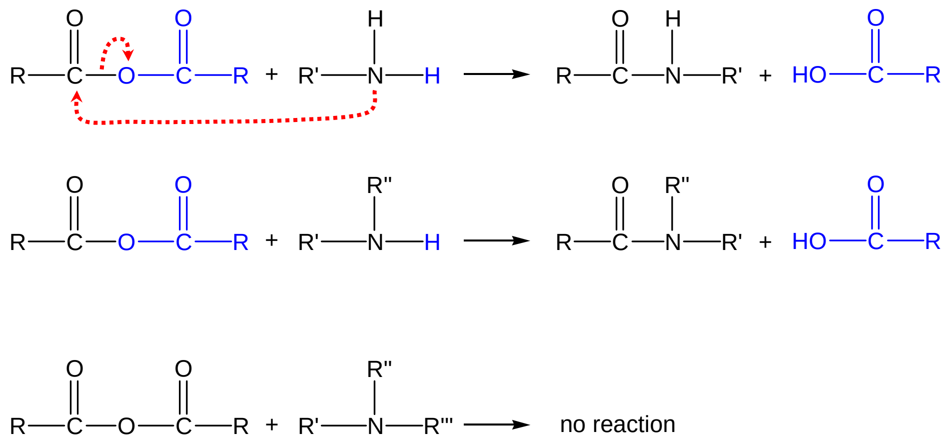
Amide Formation

- Amides are formed when acid chlorides react with 1° or 2° amines; 3° amines cannot form amides:



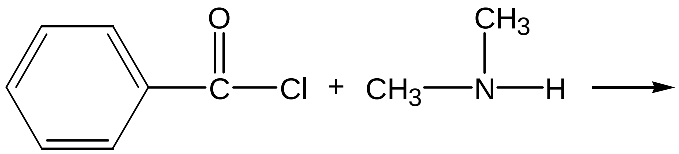
Amide Formation

- Amides are also formed when acid anhydrides react with 1° or 2° amines.



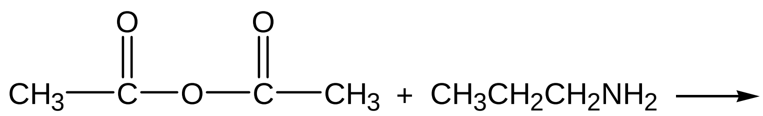
Examples: Formation of Amides

- Complete the following reactions:



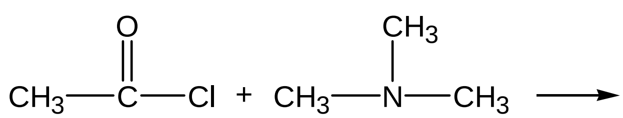
Examples: Formation of Amides

- Complete the following reactions:



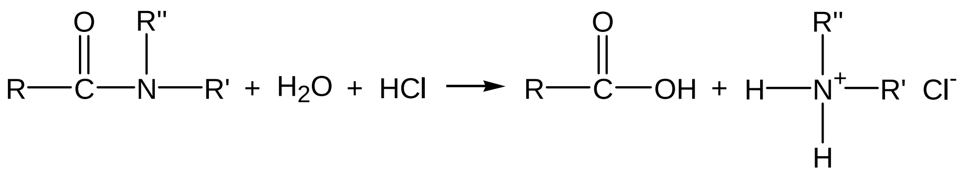
Examples: Formation of Amides

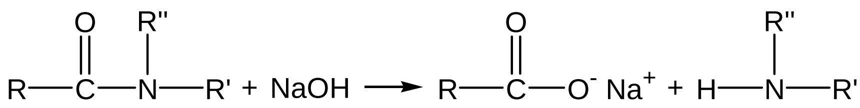
- Complete the following reactions:



Chemical Properties of Amides

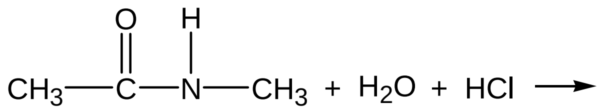
- Unlike amines, amides are not basic.
- Amide hydrolysis can take place under acidic or basic conditions:

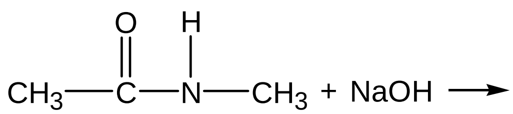




Examples: Reactions of Amines and Amides

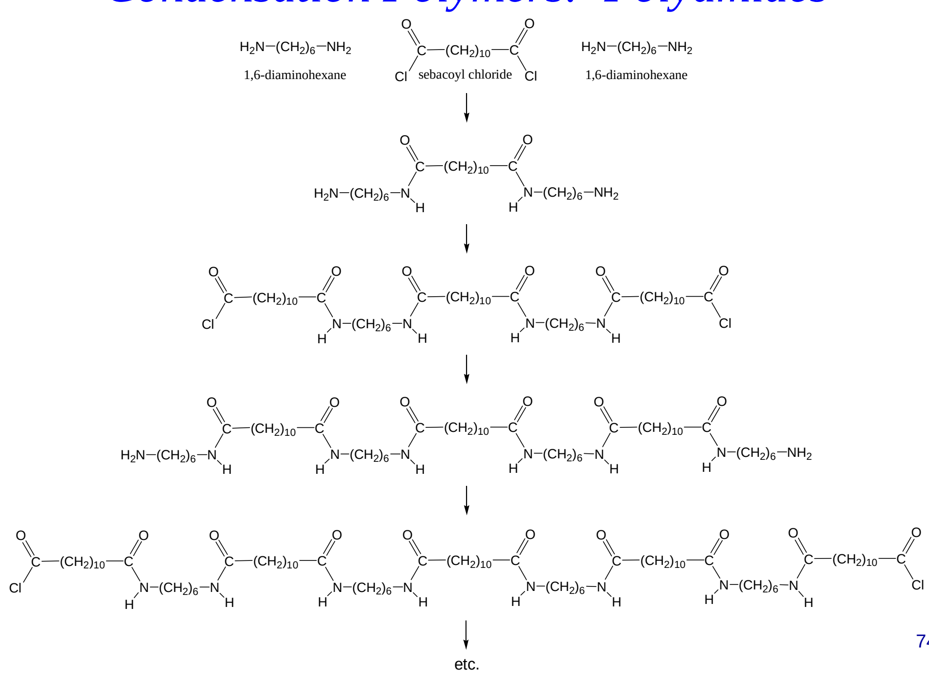
- Complete the following reactions:



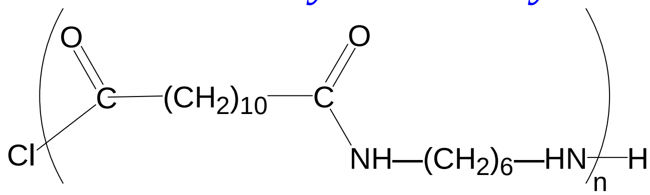


Condensation Polymers: Polyamides

Condensation Polymers: Polyamides

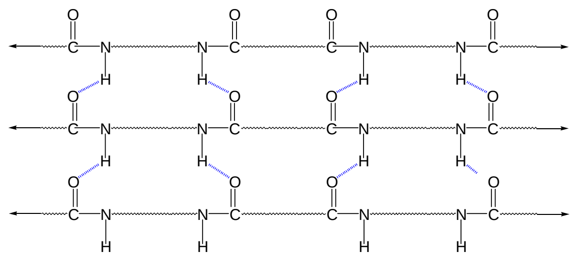


Condensation Polymers: Polyamides

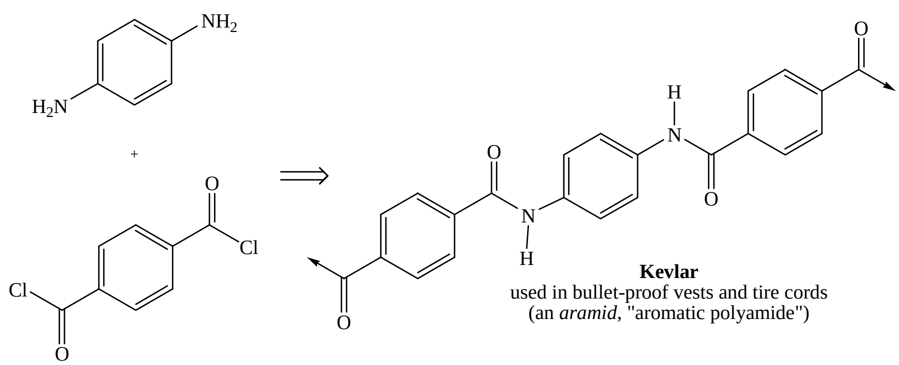


Nylon-6,12
a **polyamide**

Discovered by Wallace Carrothers at DuPont in 1934; polymers average about 10,000 g/mol; 3 billion pound of Nylon made per year; 60% used for nylon fiber in home furnishings (carpet); also used in textile fibers, tire cord, rope, parachutes, paint brushes, Velcro, electrical parts, medical applications (sutures, etc.)

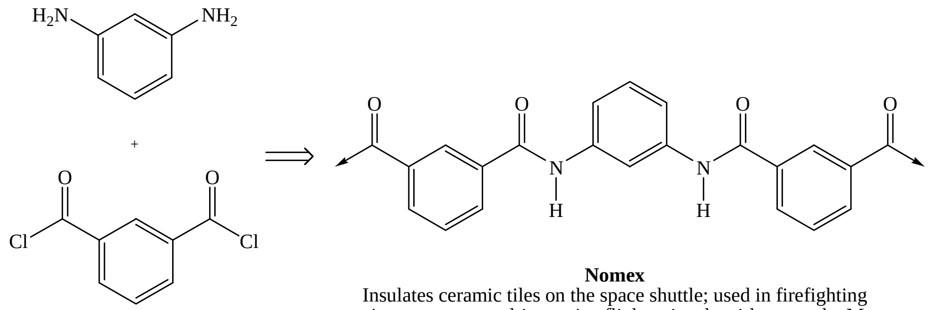


Polyamides



Kevlar
used in bullet-proof vests and tire cords
(an *aramid*, "aromatic polyamide")

Polyamides



Nomex
Insulates ceramic tiles on the space shuttle; used in firefighting equipment, race car driver suits, flight suits, the airbags on the Mars Pathfinder, Spirit, and Opportunity rovers (less strong than Kevlar, but has excellent thermal, chemical, and radiation resistance)

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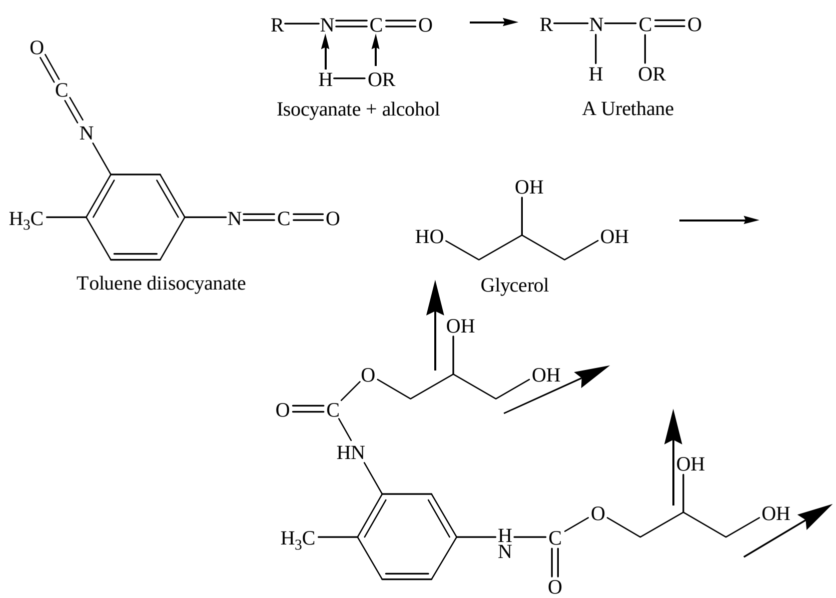
Polyurethanes



Isocyanate + alcohol

A Urethane

Toluene diisocyanate

Glycerol

A **Polyurethane**

78

Neurotransmitters

Neurotransmitters

- **Neurotransmitters** are small molecules that carry nerve impulses from one neuron to the next.
- Neurons consist of the main cell body (the **soma**), long stemlike projections (the **axons**), and short fibers connected to the soma (the **dendrites**).
- Neurons are not connected directly to each other, but are separated by a small gap called a **synapse**.
- When an electrical current originating in a neuron reaches the **synaptic terminals** at the end of the axon, the terminals release neurotransmitter molecules into the synapse; these molecules diffuse across the synapse and bind to receptors on the dendrites of the next neuron, stimulating an electrical current, which travels along that neuron until it reaches the next synapse, and so on until the nerve impulse reaches the brain.

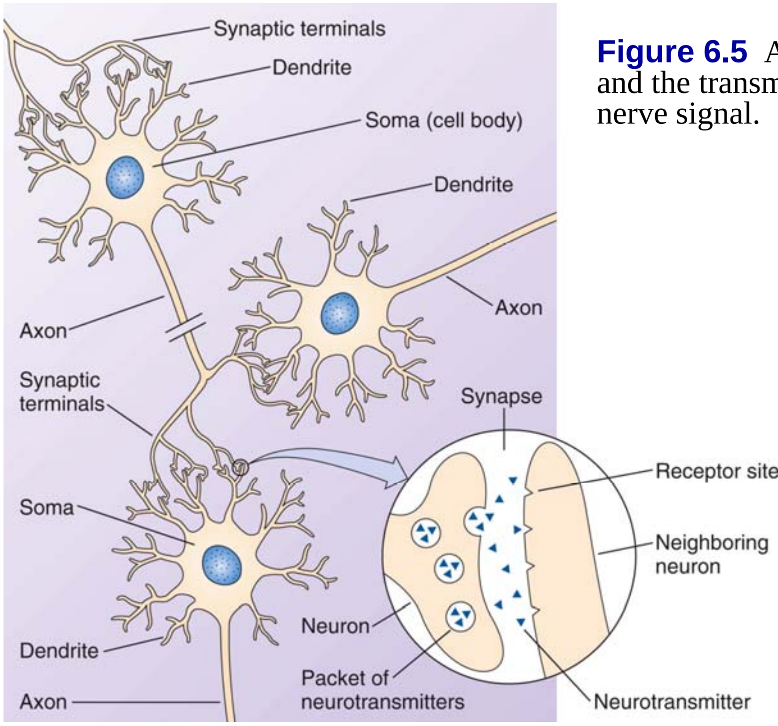


Figure 6.5 A nerve cell and the transmission of a nerve signal.

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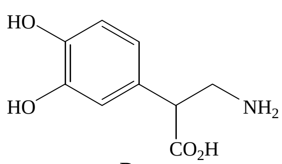
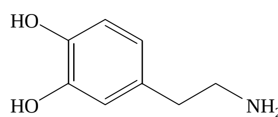
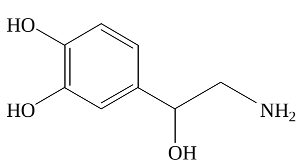


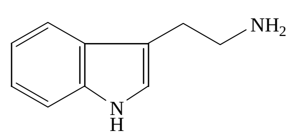
Dopa
Synthesized from the amino acid tyrosine; used as a treatment for Parkinson's disease, which is caused by a breakdown of dopamine-based neurons that control the brain's motor system (dopamine cannot be administered directly because it does not cross the blood-brain barrier; however, the L-form of dopa does)



Dopamine
Synthesized from dopa; used as a treatment for low blood pressure



Norepinephrine (NE)
Synthesized from dopamine; an excess of NE in the brain is related to feelings of elation or manic states; low NE levels are linked to depression; the stimulant action of epinephrine and NE in some cells can be reduced by *beta blockers*, which are used to treat cardiac arrhythmias, angina, and hypertension



Serotonin
Synthesized from the amino acid tryptophan; influences sleeping, body temperature, and sensory perception; drugs that mimic serotonin are used to treat depression, anxiety, and obsessive-compulsive disorder; serotonin blockers are used to treat migraine headaches and nausea resulting from chemotherapy

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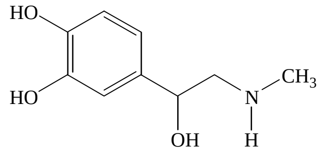
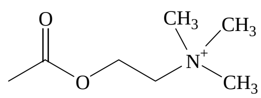
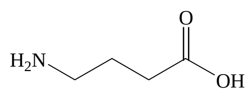


Epinephrine (Adrenalin)
More important as a hormone than a neurotransmitter; synthesized in the adrenal glad; release of adrenalin into the bloodstream in response to pain, anger, or fear increases blood glucose levels, and provides a sudden burst of energy (fight-or-flight response); increases force of heart contractions (raising blood pressure); also a vasoconstrictor; used in local anesthetics to keep the anesthetic from being washed away

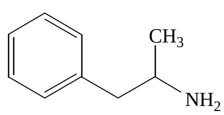


Acetylcholine

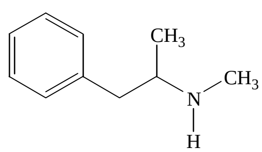


Gamma-aminobutanoic acid (GABA)
A *inhibitory neurotransmitter*

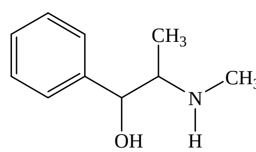
Pheynlephrines and Amphetamines



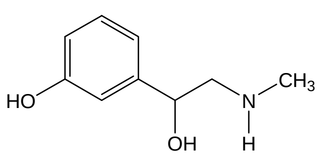
Amphetamine (Benzedrine)
a powerful nervous stimulant; raises blood glucose levels, increases heart rate and blood pressure



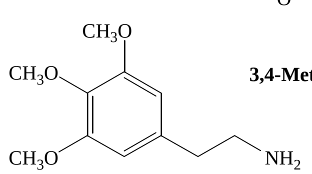
***N*-Methylamphetamine (Methedrine, "speed")**
Also a powerful nervous stimulant



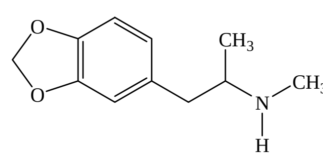
Ephedrine / Pseudoephedrine
found in the Chinese ma-huang plant; a decongestant used in many cold remedies



Phenylephrine
Common decongestant



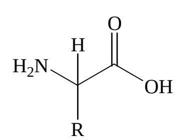
Mescaline
Hallucinogen from peyote cactus



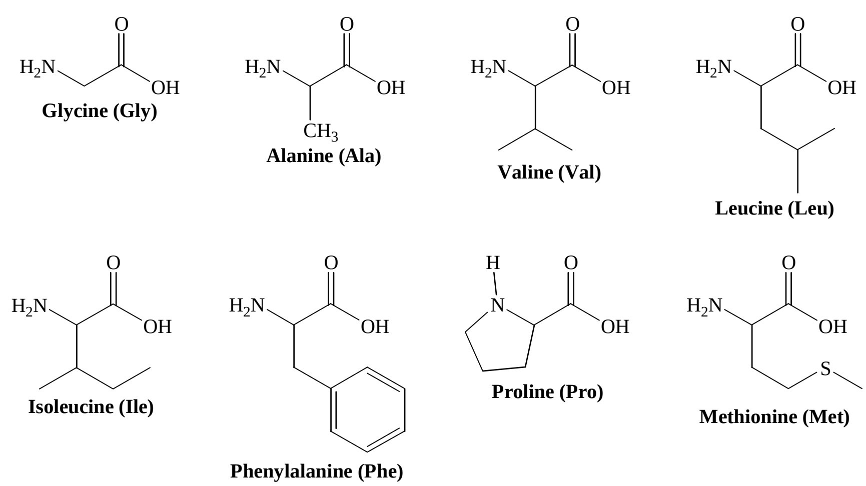
3,4-Methylenedioxymethamphetamine (MDMA), "Ectasy"

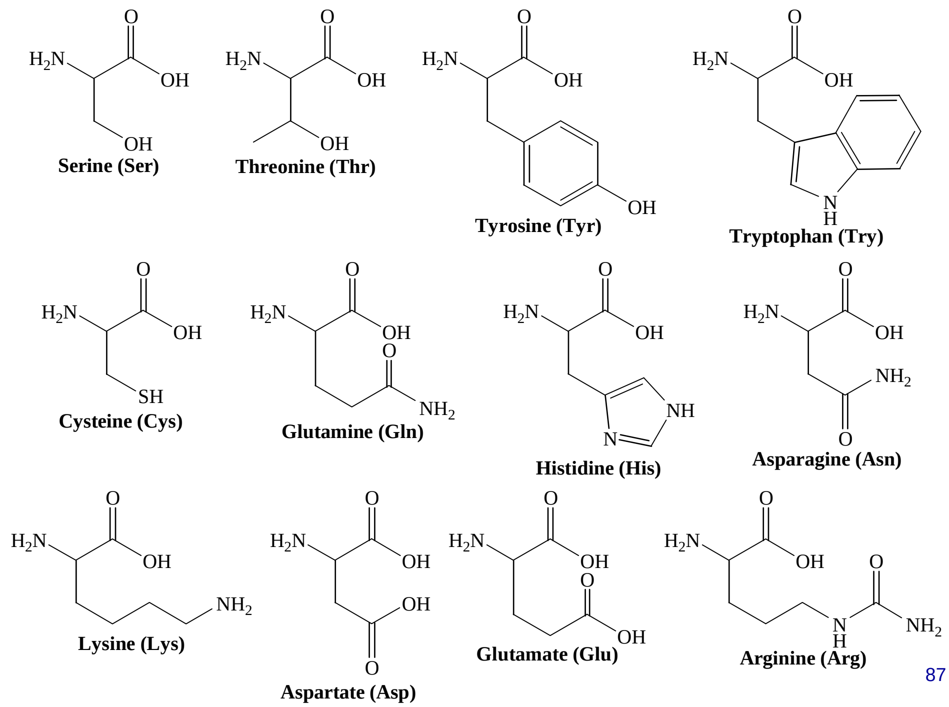
Amino Acids and Proteins

Amino Acids



Amino Acids




Serine (Ser)
Threonine (Thr)
Tyrosine (Tyr)
Tryptophan (Try)
Cysteine (Cys)
Glutamine (Gln)
Histidine (His)
Asparagine (Asn)
Lysine (Lys)
Aspartate (Asp)
Glutamate (Glu)
Arginine (Arg)

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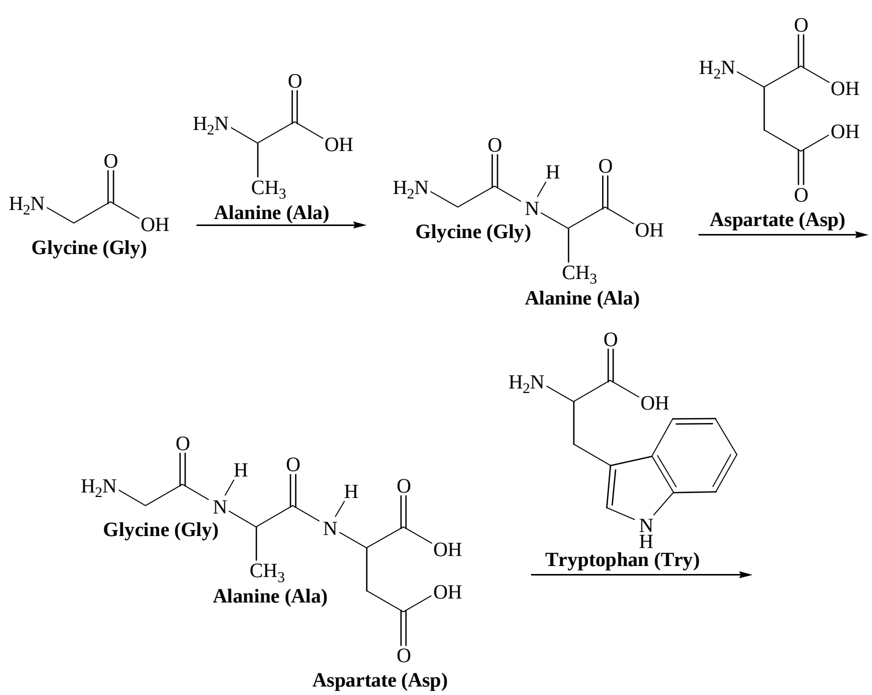
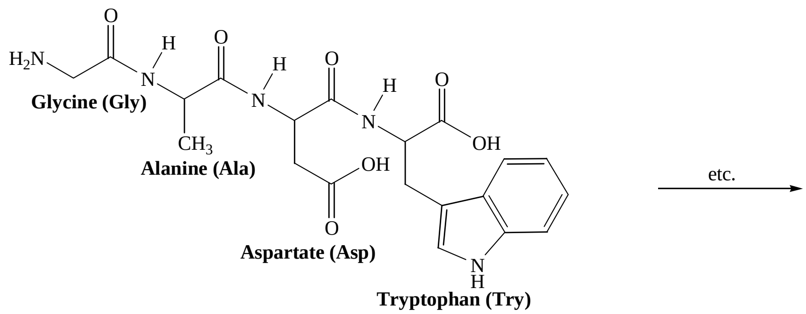
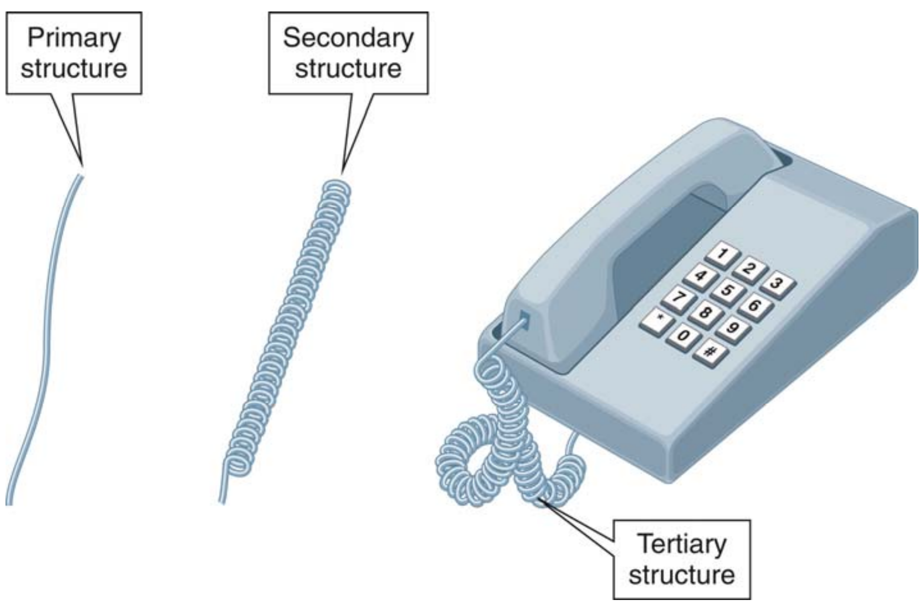

Glycine (Gly)
Alanine (Ala)
Glycine (Gly)
Alanine (Ala)
Aspartate (Asp)
Glycine (Gly)
Alanine (Ala)
Aspartate (Asp)
Tryptophan (Try)

88

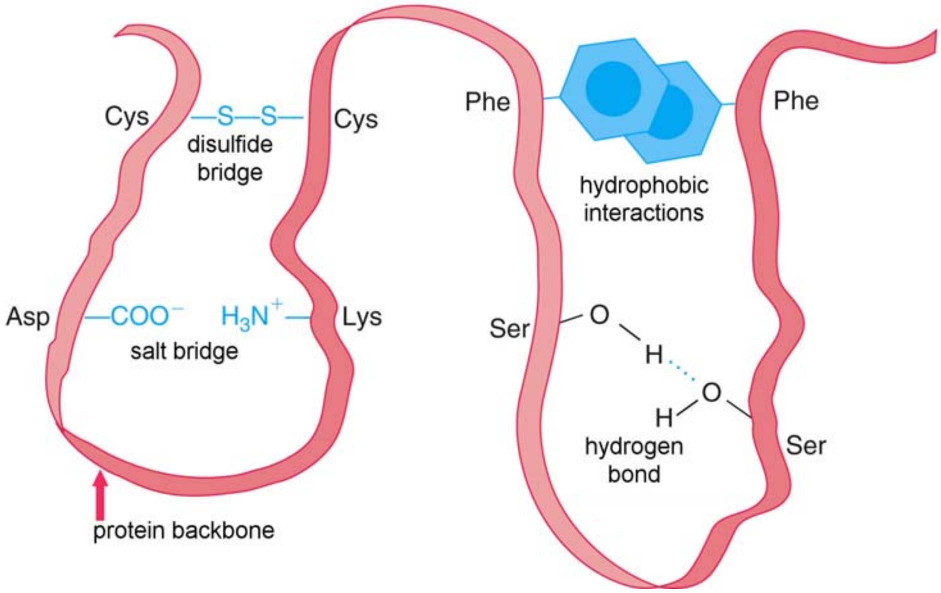


Gly—Ala—Asp—Try

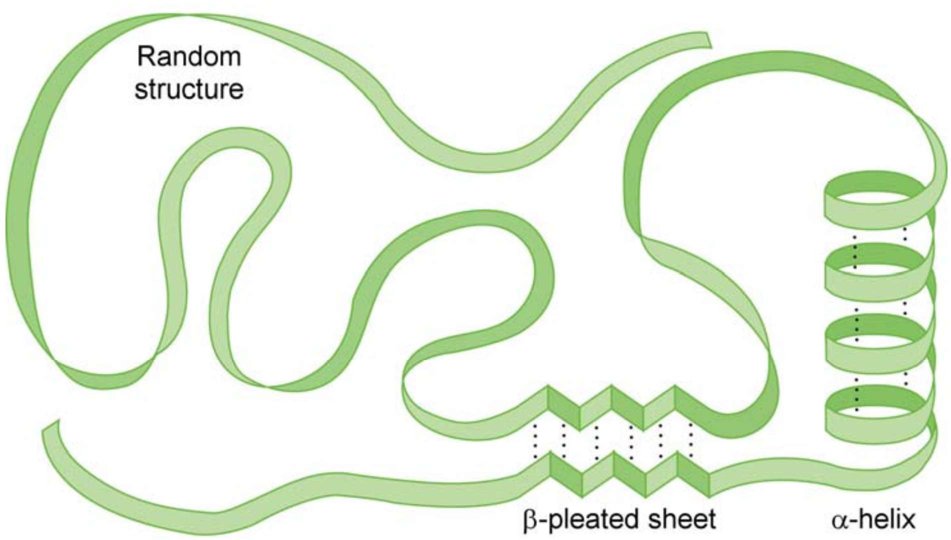
a **protein**
(a polyamide)
Instructions for making proteins
are encoded in DNA.



Three levels of structure in a telephone cord

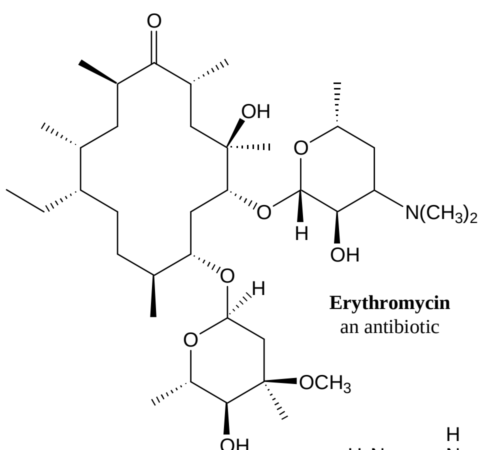


R-group interactions leading to a protein tertiary structure 91

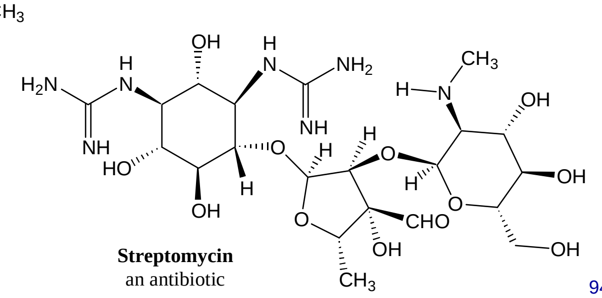


Segment of a protein showing α-helix, β-pleated sheet,
and random coil structures 92

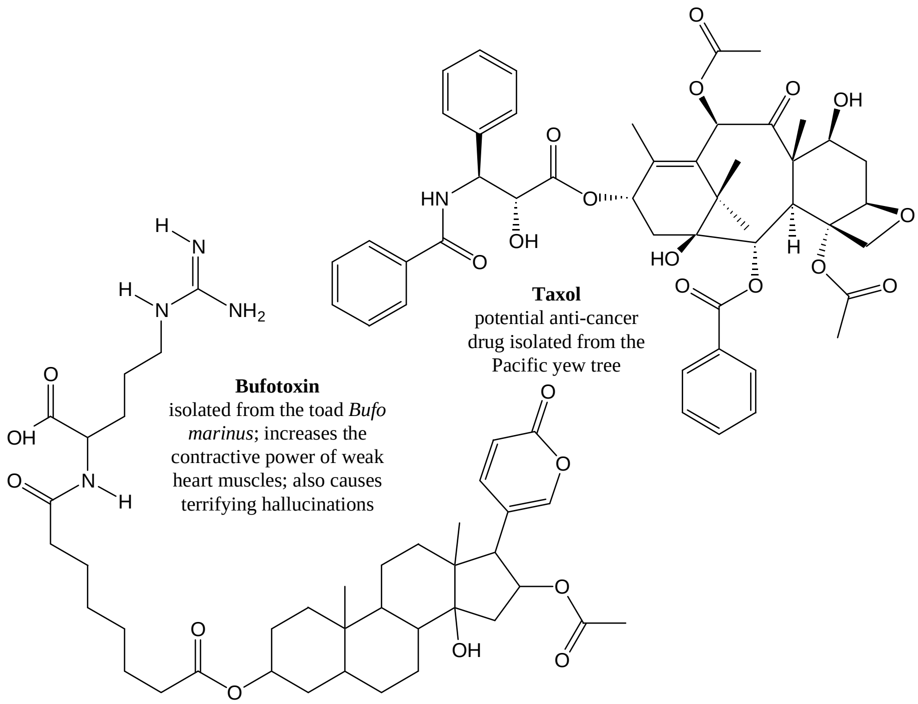
Some Hideously Complex Molecules



Erythromycin
an antibiotic



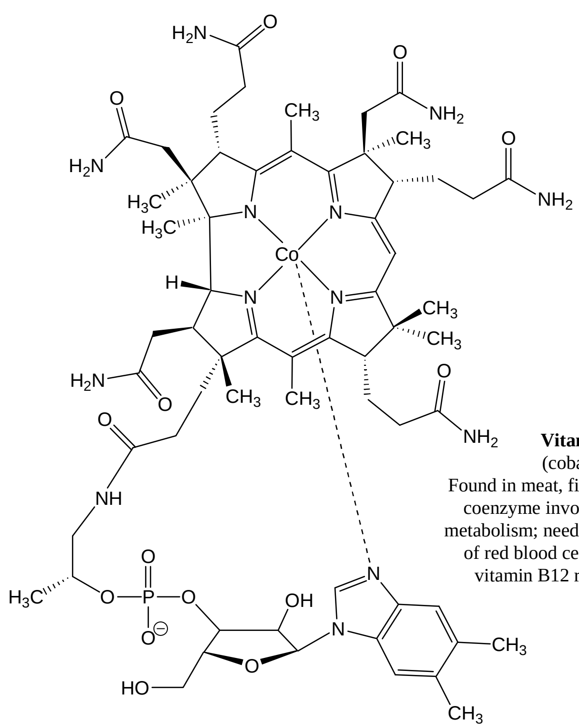
Streptomycin
an antibiotic



Taxol
potential anti-cancer drug isolated from the Pacific yew tree

Bufotoxin
isolated from the toad *Bufo marinus*; increases the contractive power of weak heart muscles; also causes terrifying hallucinations

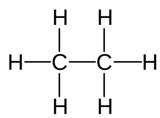
95



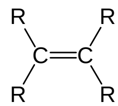
Vitamin B12
(cobalamine)
Found in meat, fish, eggs, and milk; a coenzyme involved in amino acid metabolism; needed for the production of red blood cells (a deficiency in vitamin B12 results in anemia)

96

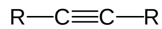
Functional Groups



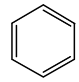
alkane
(-ane)



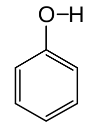
alkene
(-ene)



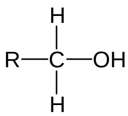
alkyne
(-yne)



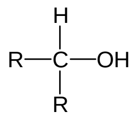
aromatic ring
(phenyl-, -benzene)



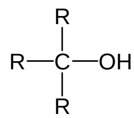
phenol
(-phenol)



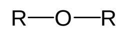
primary (1°) alcohol
(-ol)



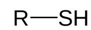
secondary (2°) alcohol
(-ol)



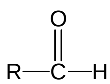
tertiary (3°) alcohol
(-ol)



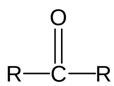
ether
(alkoxy-, -ether)



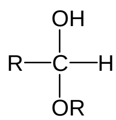
thiol



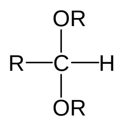
aldehyde
(-al)



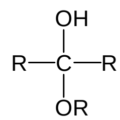
ketone
(-one)



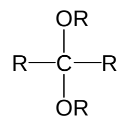
hemiacetal



acetal

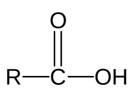


hemiketal

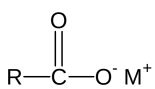


ketal

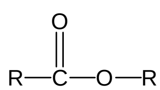
97



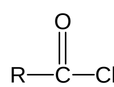
carboxylic acid
(-oic acid)



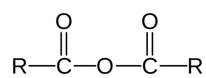
carboxylate salt
(metal + -oate)



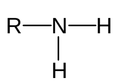
ester
(alkyl + -oate)



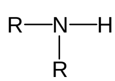
acid chloride



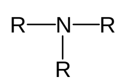
acid anhydride



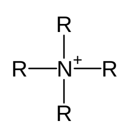
primary (1°) amine
(amino-, -amine)



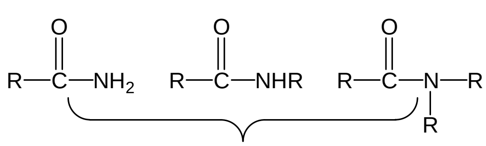
secondary (2°) amine
(-amine)



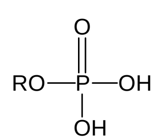
tertiary (3°) amine
(-amine)



quaternary ammonium salt
(alkyl ammonium + anion)



amide
(*N*-alkyl + -amide)



phosphate ester

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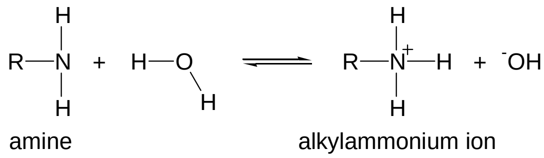
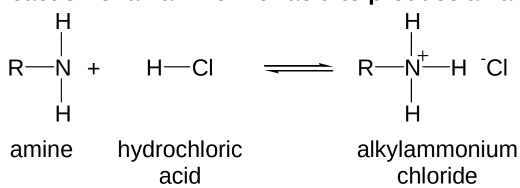
Reactions of Amines and Amides

1. Reaction of an amine with water to produce an alkylammonium ion.



2. Reaction of an amine with acid to produce an alkylammonium salt.

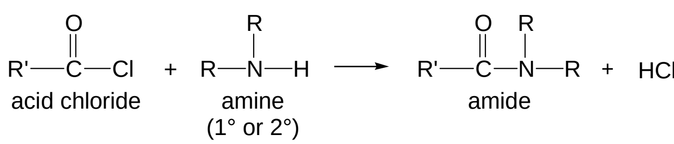


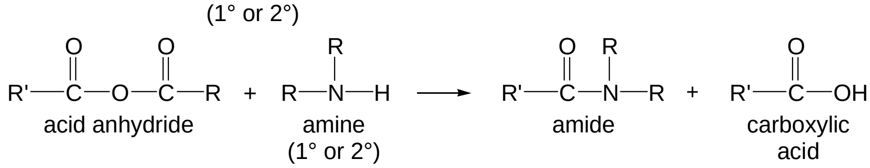
3. Conversion of an alkylammonium salt back to an amine.

$$R—NH_3^+\ Cl^- \ + \ NaOH \longrightarrow R—NH_2 \ + \ H_2O \ + \ NaCl$$

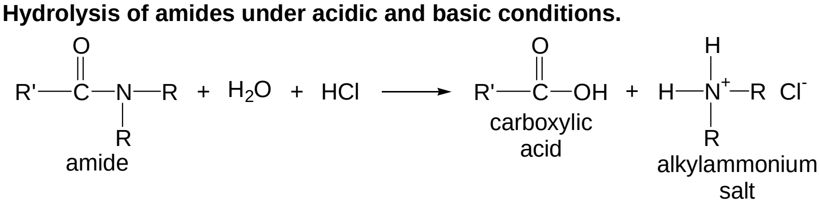
99

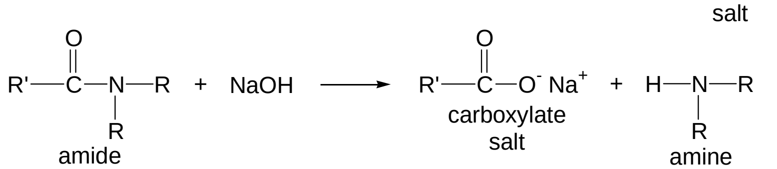
4. Formation of an amide. (NR with tertiary amines.)





5. Hydrolysis of amides under acidic and basic conditions.





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