Chapter 5
Carboxylic Acids and Esters

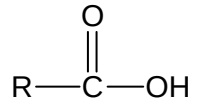
Chapter Objectives:

- 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.

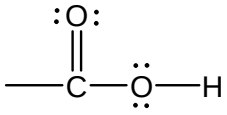
Mr. Kevin A. Boudreaux
Angelo State University
CHEM 2353 Fundamentals of Organic Chemistry
Organic and Biochemistry for Today (Seager & Slabaugh)
www.angelo.edu/faculty/kboudrea

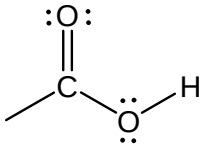
Carboxylic Acids

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



a **carboxylic acid**





the **carboxyl** group

RCOOH RCO_2H

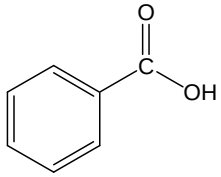
condensed ways of writing the carboxyl group

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

Nomenclature of Carboxylic Acids

Nomenclature of Carboxylic Acids

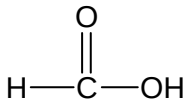
- Select the longest carbon chain containing the carboxyl group. The **-e** ending of the parent alkane name is replaced by the suffix **-oic acid**.
- The carboxyl carbon is always numbered "1" but the number is not included in the name.
- Name the substituents attached to the chain in the usual way.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

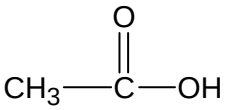


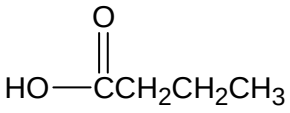
Benzoic acid

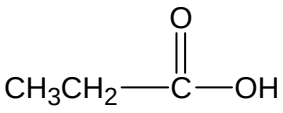
Examples: Naming Carboxylic Acids

- Name the following compounds:









Examples: Naming Carboxylic Acids

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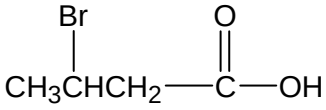
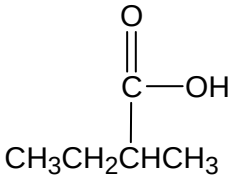
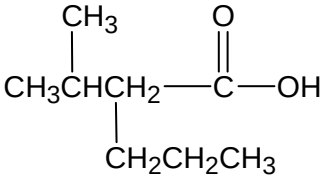
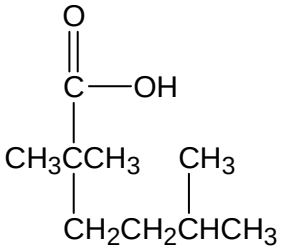


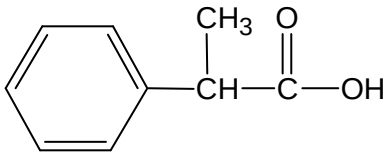




Examples: Naming Carboxylic Acids

- Name the following compounds:





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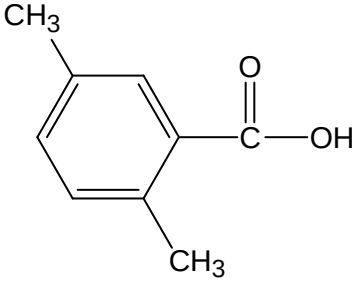
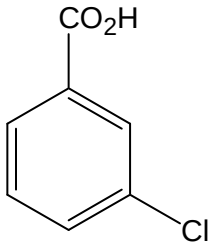
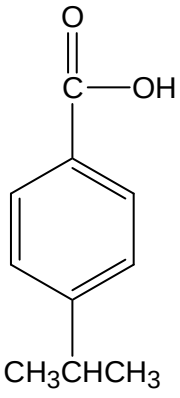
Examples: Naming Carboxylic Acids

- Name the following compounds:







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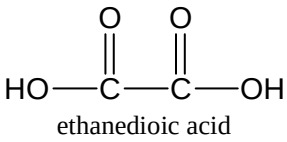
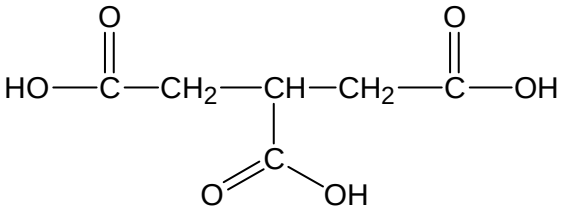
More Complicated Acids

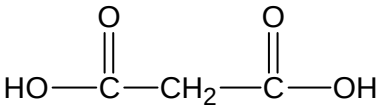
- For molecules with two carboxylic acid groups the carbon chain in between the two carboxyl groups (including the carboxyl carbons) is used as the longest chain; the suffix **-dioic acid** is used.
- For molecules with more than two carboxylic acid groups, the carboxyl groups are named as *carboxylic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



ethanedioic acid



propane-1,2,3-tricarboxylic acid



propanedioic acid

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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

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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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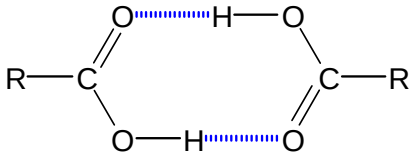
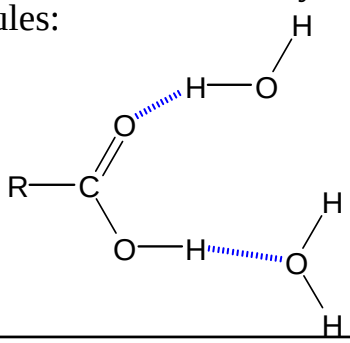
Physical Properties of Carboxylic Acids

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

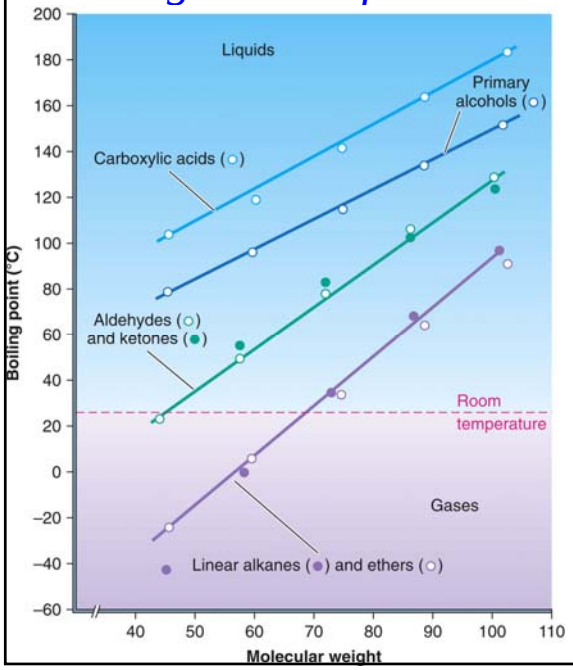

Figure 5.4
The boiling points of carboxylic acids compared to 1° alcohols, aldehydes and ketones, ethers and alkanes.

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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

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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

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Some Important Carboxylic Acids

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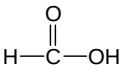
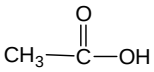
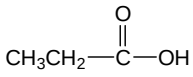
Important Carboxylic Acids



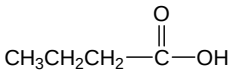
Methanoic acid
(Formic acid)
(from Latin *formica,* ant)
A component of the venom of ants and caterpillars; produced in the body when methanol is consumed



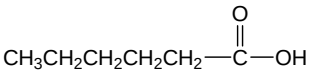
Ethanoic acid
(Acetic acid)
(from Latin *acetum*, vinegar)
Vinegar is a 5% solution of acetic acid dissolved in water; acetic acid is also responsible for the taste of sour wine (from the oxidation of ethanol) and sourdough bread



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



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



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

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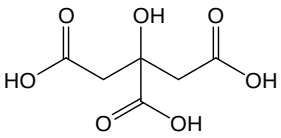
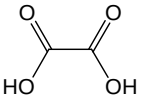
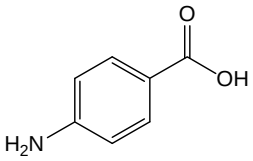


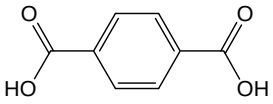
2-hydroxy-1,2,3-propanetricarboxylic acid (Citric acid)
Found in citrus fruits (lemons, grapefruit, oranges, etc.); commonly used in buffering solutions with sodium citrate



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



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



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

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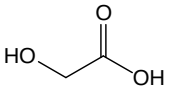
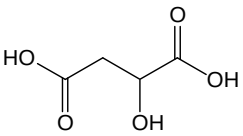
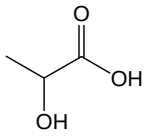


Glycolic acid
An **alpha-hydroxy acid** used in cosmetics and skin creams; alpha-hydroxy acids are thought to loosen the cells of the epidermis and accelerate the flaking off of dead skin; however these compounds can increase the skin's sensitivity to UV light



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

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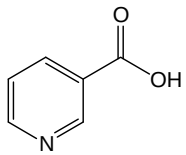
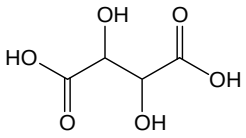
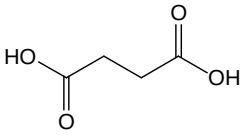


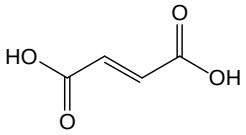
Niacin
A water-soluble, B-Complex vitamin obtained from fish, green vegetables, lean meat, poultry, whole-grain and enriched bread and cereal; produced in the body from tryptophan; essential for growth, healthy tissues, the production of energy from carbohydrates, and the production of fats



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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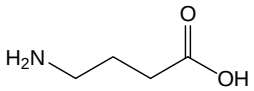
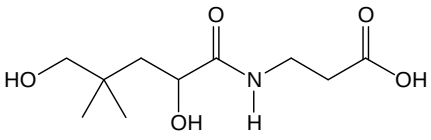
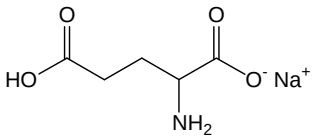


Gamma-aminobutanoic acid (GABA)
A *inhibitory neurotransmitter*; ethanol binds to the same protein as GABA at a neighboring location, distorting the protein so that GABA binds more easily, further inhibiting the cell from firing; benzodiazepines such as Valium also bind to the same protein but at a different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

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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**:

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

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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

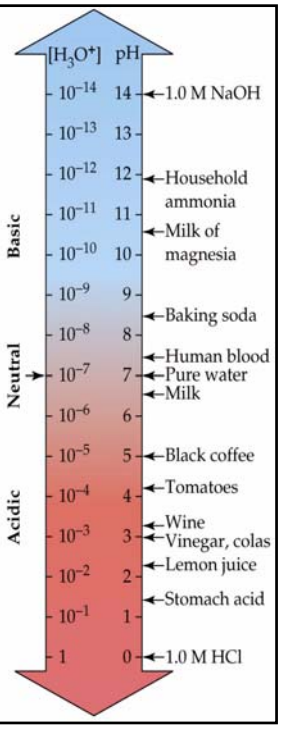
- The acidity of a solution is measured using the **pH scale**. The pH of a solution is defined as

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

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

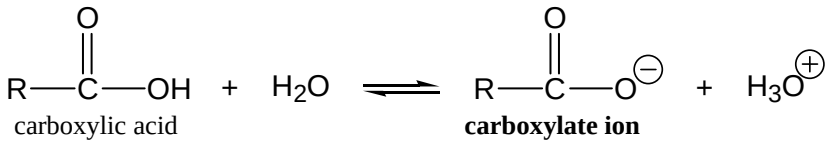
Basic: **pH > 7.00** $[H_3O^+] < [OH^-]$

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



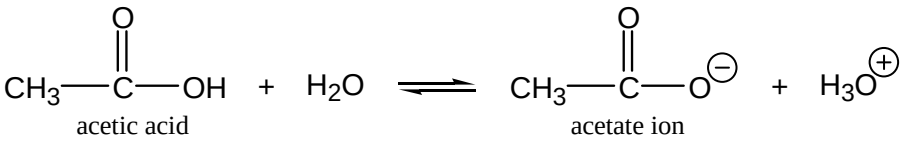
The Acidity of Carboxylic Acids

- 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

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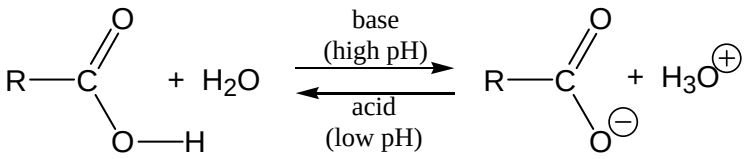
The Acidity of Carboxylic Acids

- 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.

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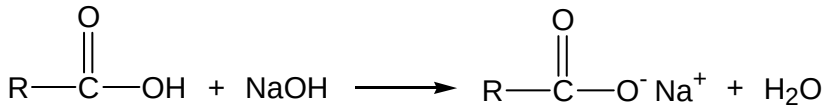
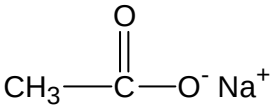
Carboxylate Salts

Carboxylate Salts

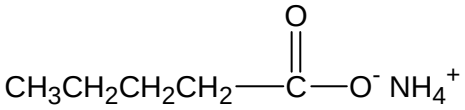
- Carboxylic acids react with strong bases such as sodium hydroxide (NaOH) and potassium hydroxide (KOH) to produce **carboxylate salts**.
- Carboxylate salts are named by naming the metal first, and changing the **-ic acid** ending of the carboxylic acid name to **-ate**.



carboxylic acid base metal carboxylate

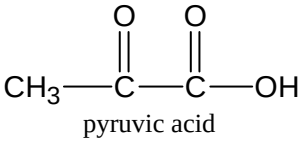


sodium ethanoate
(sodium acetate)



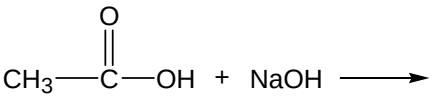
Examples: Carboxylate Salts

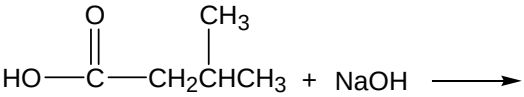
- Draw the structure of pyruvate, the form of pyruvic acid which is found as an intermediate in energy conversion reactions in living organisms.



pyruvic acid

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





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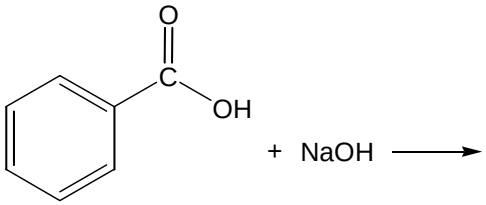
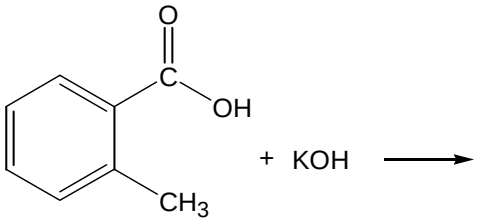
Examples: Carboxylate Salts

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





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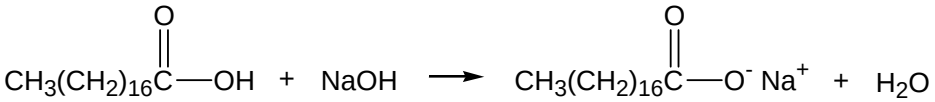
Physical Properties of Carboxylate Salts

- 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).



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

Sodium stearate
(sodium octadecanoate)
soluble in water

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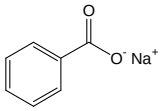
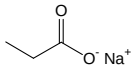
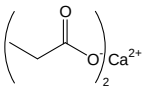
Important Carboxylate Salts



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

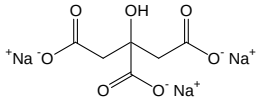


Sodium propanoate

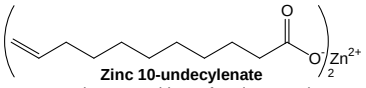


Calcium propanoate

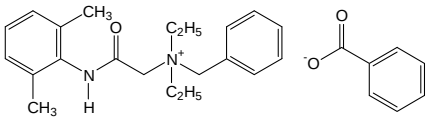
Commonly used preservatives; found in bread, cakes, and cheeses



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



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



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.

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Esters

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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:

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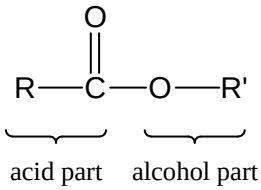
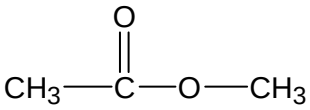
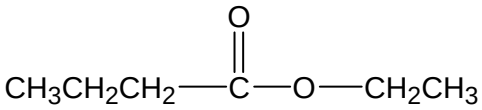
Nomenclature of Esters



- 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**.





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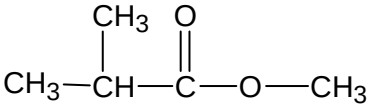
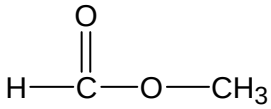
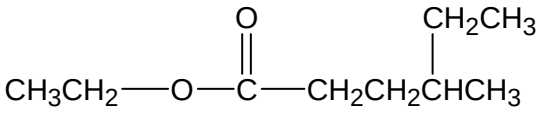
Examples: Ester Nomenclature

- Name the following compounds:







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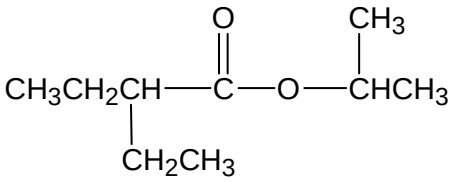
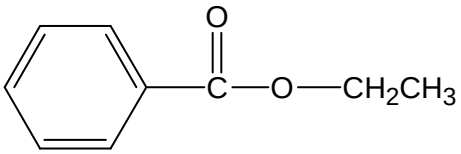
Examples: Ester Nomenclature

- Name the following compounds:





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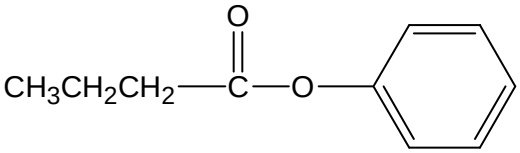
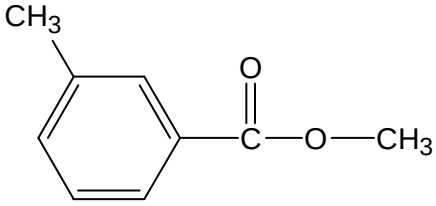
Examples: Ester Nomenclature

- 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

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Examples: Drawing Esters

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

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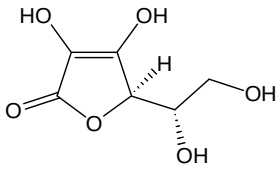
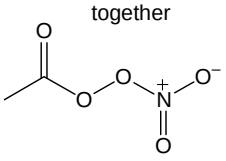
Some Important Esters

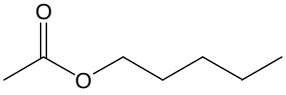
Important Esters



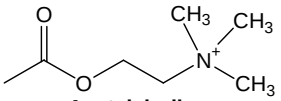
Vitamin C (ascorbic acid)
A water-soluble vitamin found in citrus fruits; prevents scurvy; essential for healthy blood vessels, bones, and teeth; helps form collagen, a protein that holds tissues together



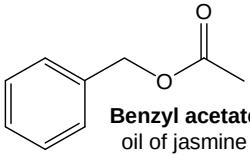
Peroxyacetyl nitrate (PAN)
Produced by the action of sunlight on fragments of unburnt hydrocarbon fuel, oxygen, and nitrogen dioxide; one of the irritants (lachrymator) found in photochemical smog



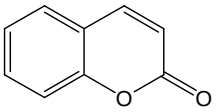
Amyl acetate
Also known as banana oil and pear oil; the commercially available compound is a mixture of amyl (pentyl) isomers



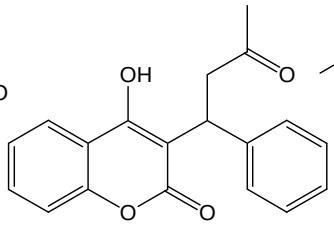
Acetylcholine
an important neurotransmitter



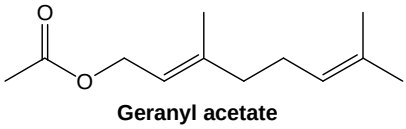
Benzyl acetate
oil of jasmine



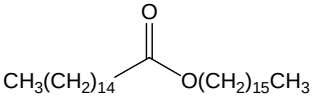
Coumarin
Found in lavender oil, sweet clover and tonka beans



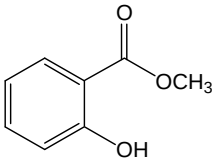
Warfarin
A potent rodenticide



Geranyl acetate
geranium oil



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.



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

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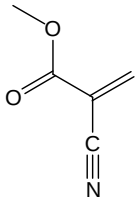
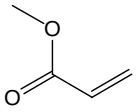
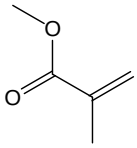
Polymers with Ester Groups



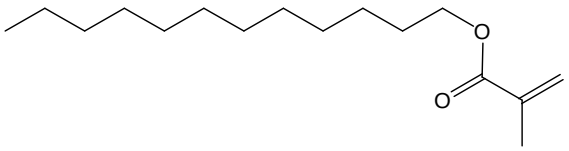
Methyl cyanoacrylate
Polymerizes on contact with surfaces containing trace amounts of water and alcohols to form Superglue; superglue is also used in surgery in place of sutures, and by morticians to seal the eyes and lips of their clients



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

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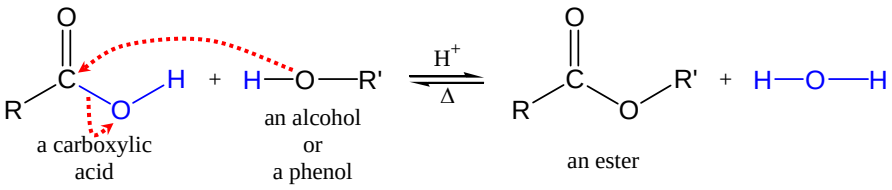
Reactions of Esters

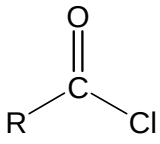
Synthesis of Esters: Esterification Reactions

- 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*).

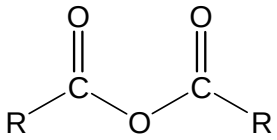


Synthesis of Esters: Esterification Reactions

- 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.



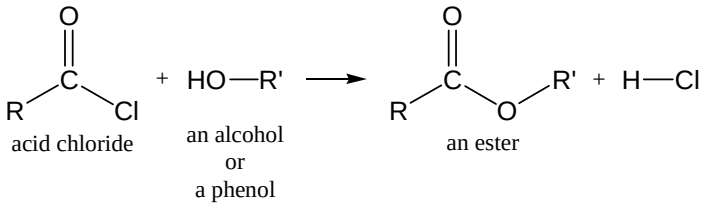
acid chloride



acid anhydride

53

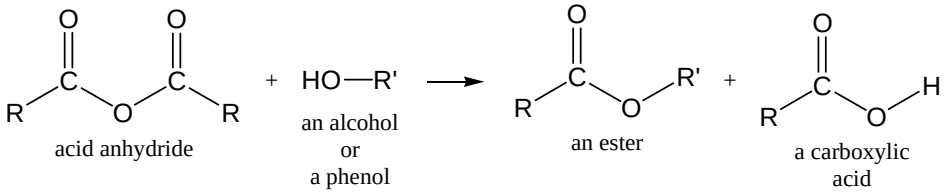
Synthesis of Esters: Esterification Reactions



acid chloride

an alcohol or a phenol

an ester



acid anhydride

an alcohol or a phenol

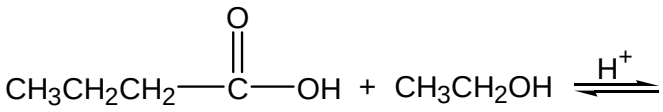
an ester

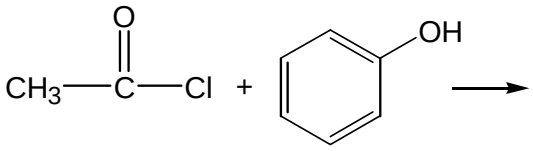
a carboxylic acid

54

Examples: Esterification Reactions

- Write both products of the following reactions:

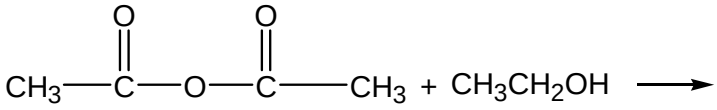




55

Examples: Esterification Reactions

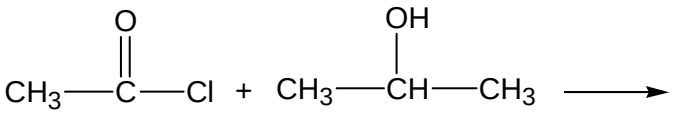
- Write both products of the following reactions:



56

Examples: Esterification Reactions

- Write both products of the following reactions:



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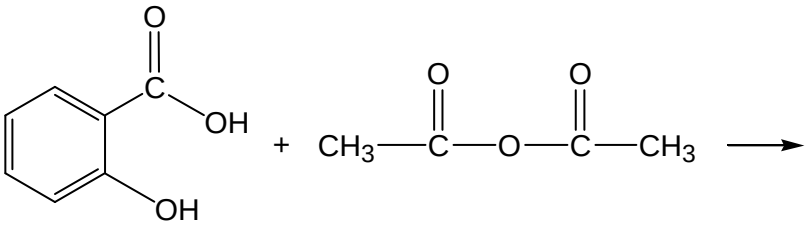
Examples: Esterification Reactions

- Write both products of the following reactions:



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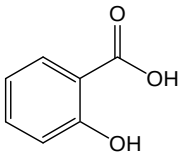
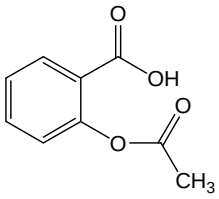
Pain, Pain, Go Away



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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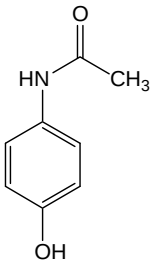
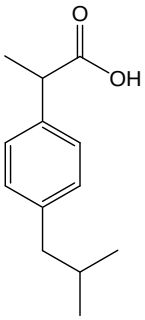
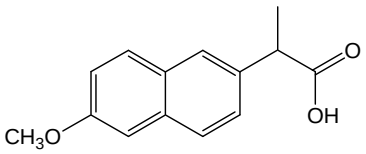
More Pain Relievers



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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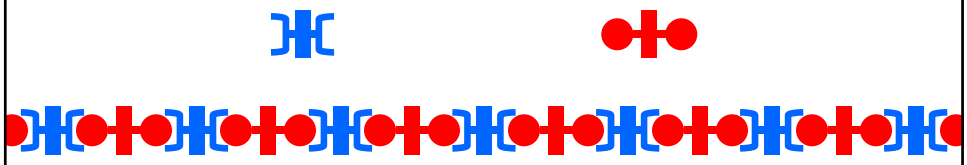
Condensation Polymers: Polyesters

- **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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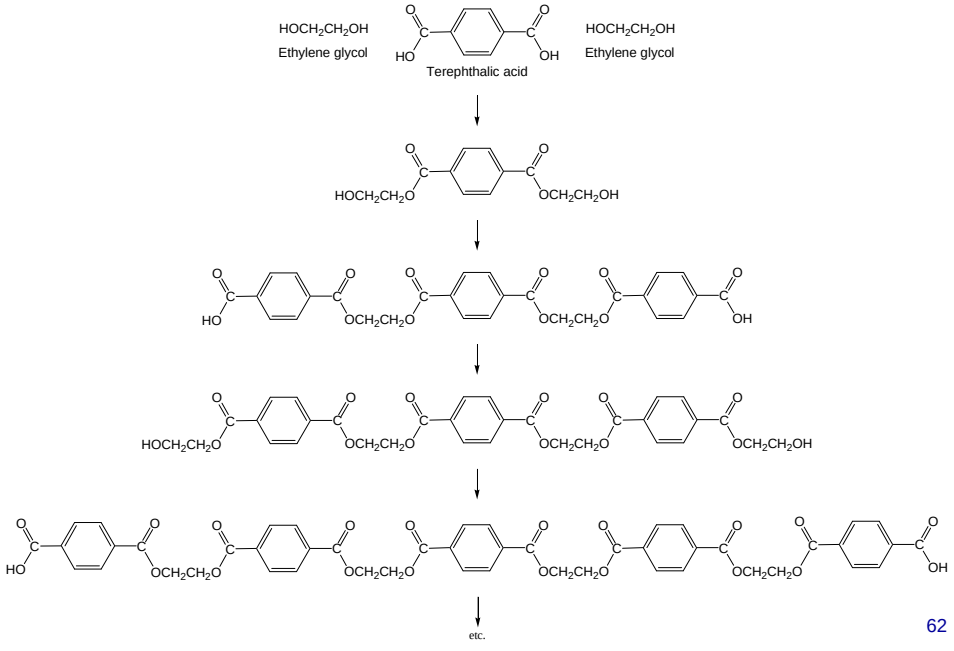
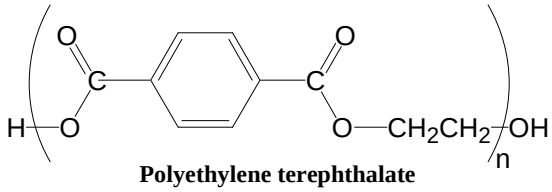
Condensation Polymers: Polyesters



62

Condensation Polymers: Polyesters



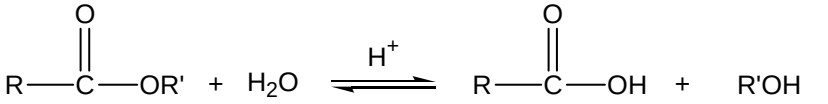
PETE

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.

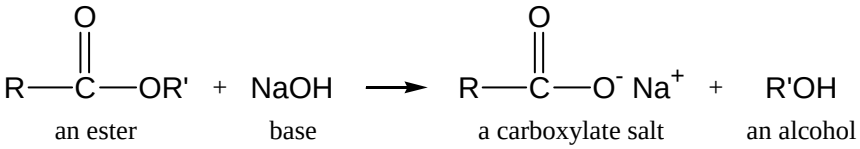


an ester — a carboxylic acid — an alcohol

- 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**.

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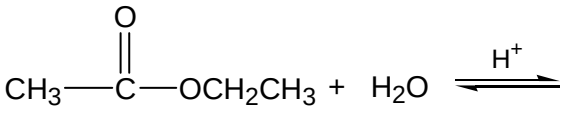
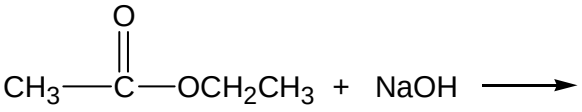
Examples: Splitting Esters

(Because Breaking Up Is Hard To Do)

- Complete the following reactions:





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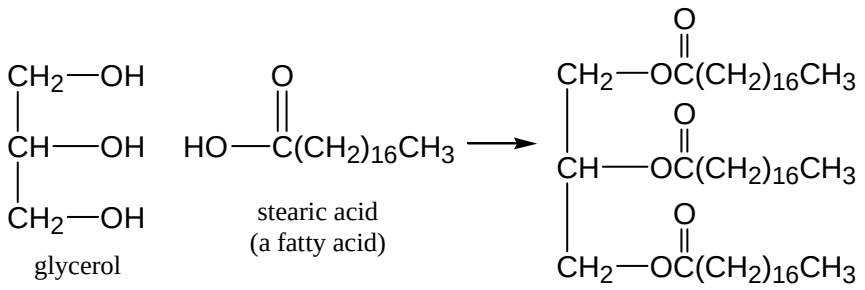
Triglycerides and Soaps

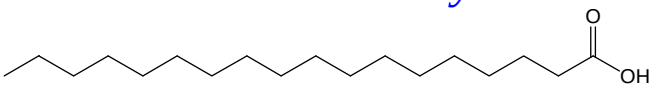
Triglycerides

- 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**).

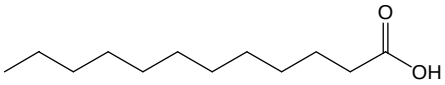


glyceryl tristearate (tristearin)
a **triglyceride**

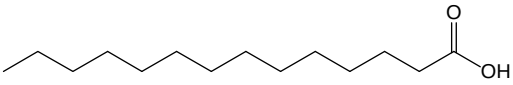
Some Saturated Fatty Acids



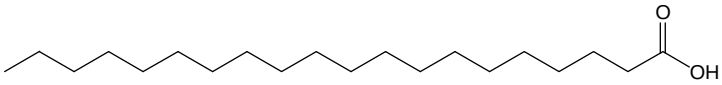
Stearic acid
A saturated fatty acid found in lard, beef fat, butterfat, cottonseed oil; the sodium salt, produced by heating lard with sodium hydroxide, can be used as a soap



Lauric acid
Found in coconut oil; commonly used in soaps

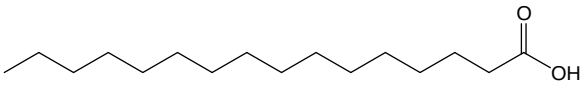


Myristic acid
A fatty acid found in butterfat, coconut oil, and nutmeg oil



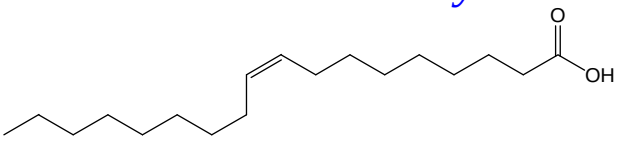
Arachidic acid
A fatty acid found in peanut oil

Some Saturated Fatty Acids

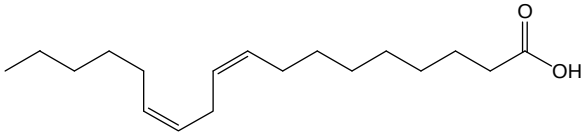


Palmitic acid
A fatty acid, found in lard, beef fat, butterfat, and cottonseed oil; the triglycerides in cocoa butter have oleic acid attached to the central oxygen, with stearic acid or palmitic acid on the other oxygens; this more regular composition gives cocoa butter a much sharper melting point 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

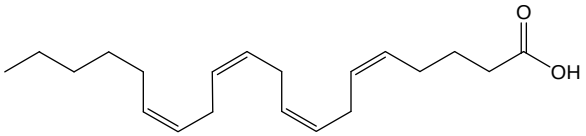
Some Unsaturated Fatty Acids



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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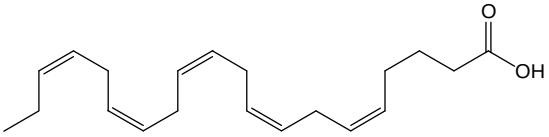
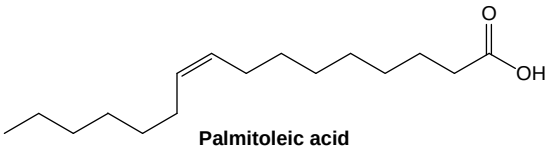
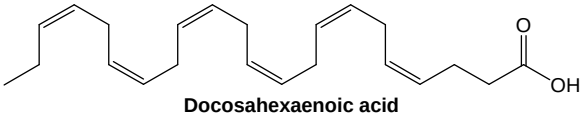
Some Unsaturated Fatty Acids



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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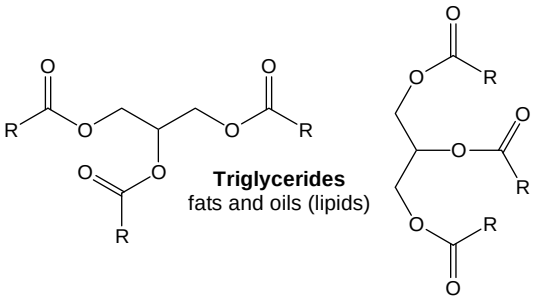
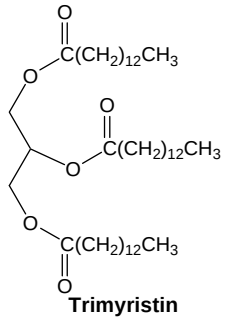
Triglycerides (Fats and Oils)

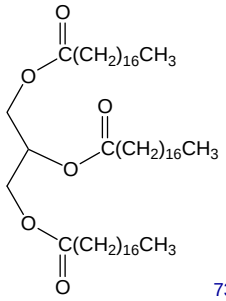


Triglycerides
fats and oils (lipids)



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.



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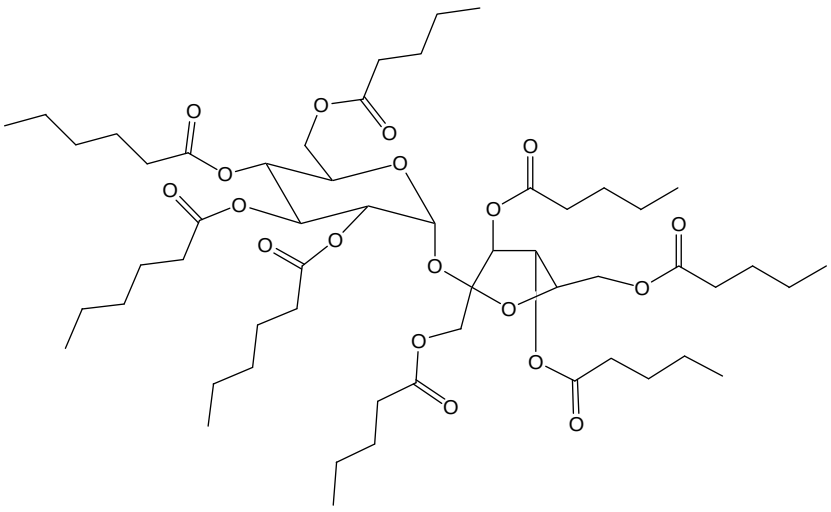

Olestra
A substitute for dietary fats developed by Procter & Gamble after 30 years and $200 million dollars worth of research; it is a combination of sucrose and fatty acids obtained from soybean oil and cottonseed oil; it is too hindered for digestive enzymes to react with; can carry small amounts of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

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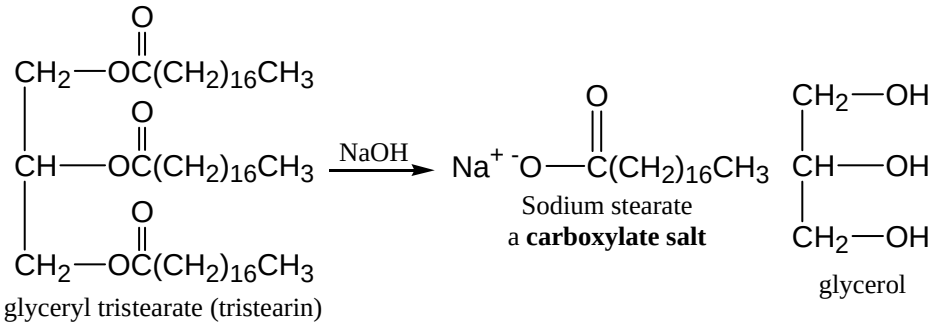
Saponification of Triglycerides

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



glyceryl tristearate (tristearin)
a **triglyceride**

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

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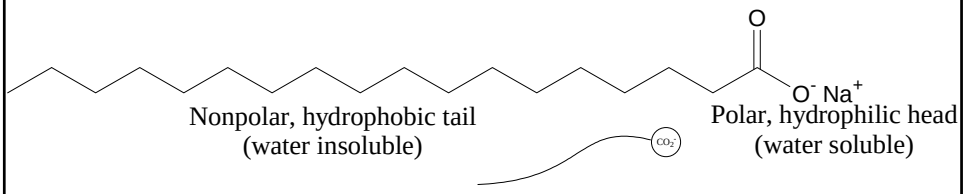
Fatty Acid Salts

- 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**.

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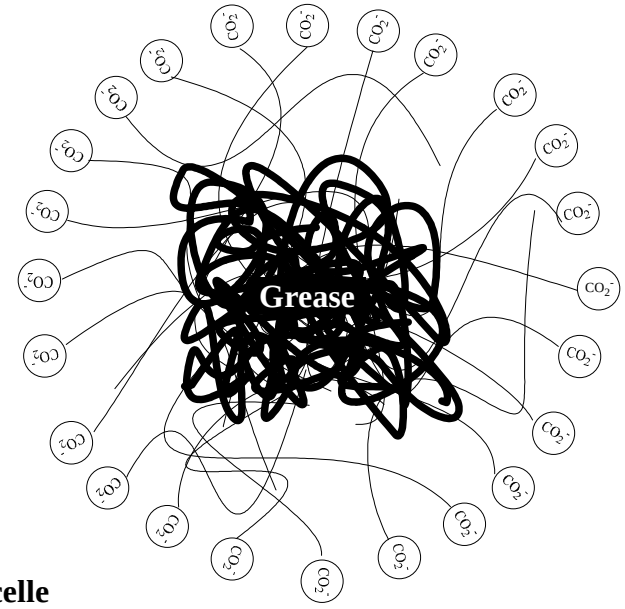
Soap



a **soap micelle**

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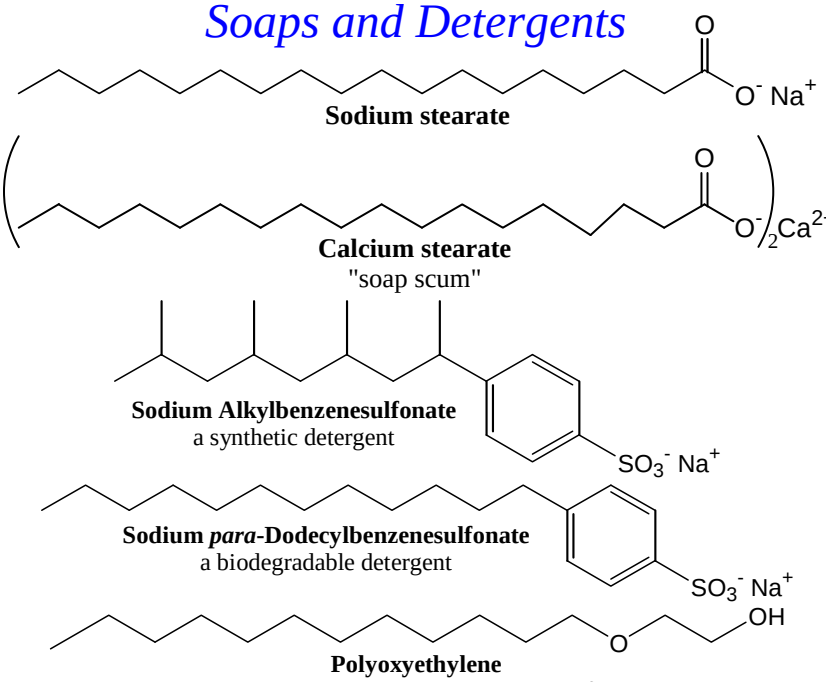
Soaps and Detergents



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

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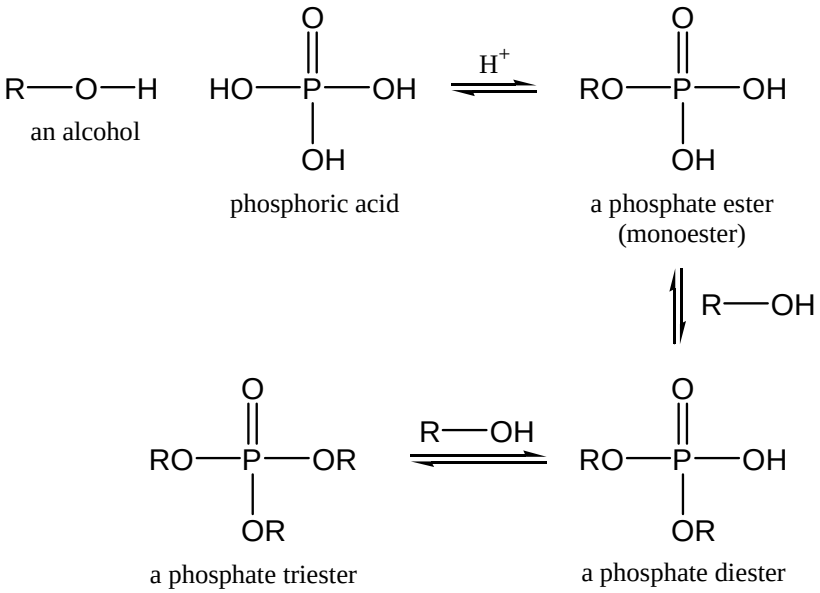
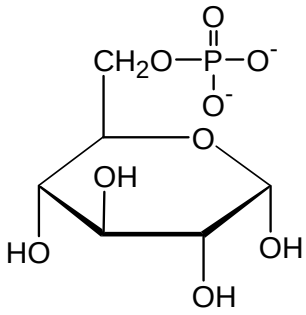
Esters of Inorganic Acids

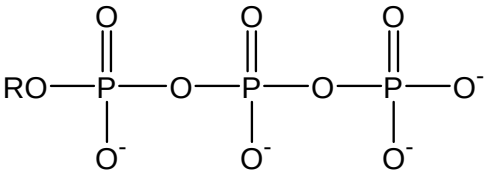


80

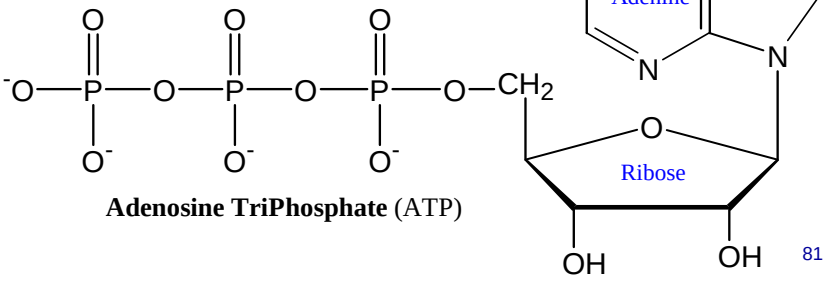
Some Important Phosphate Esters



glucose-6-phosphate

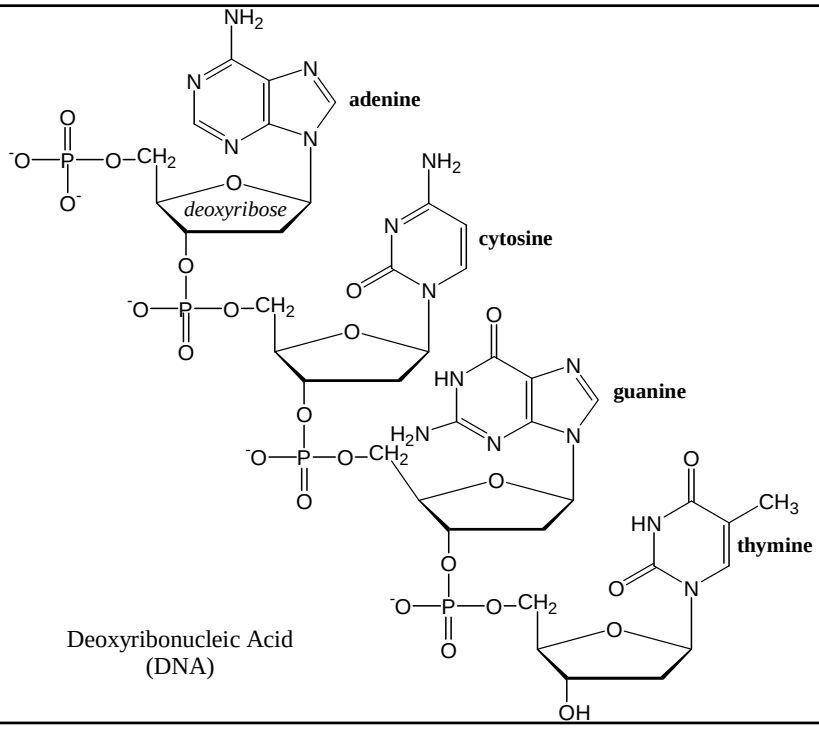


a phosphate triester



Adenosine TriPhosphate (ATP)

81



Deoxyribonucleic Acid
(DNA)

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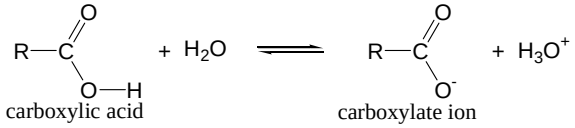
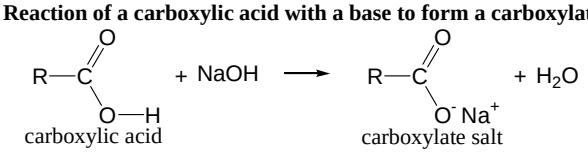
Reactions of Carboxylic Acids

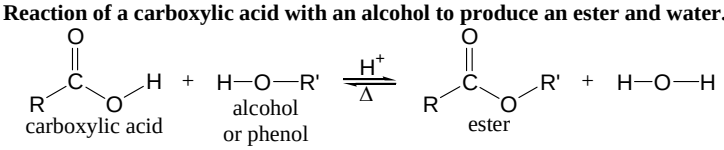
1. Reaction of a carboxylic acid with water to form a carboxylate ion.



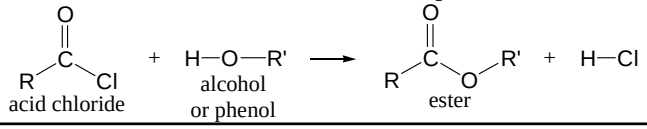
2. Reaction of a carboxylic acid with a base to form a carboxylate salt and water.



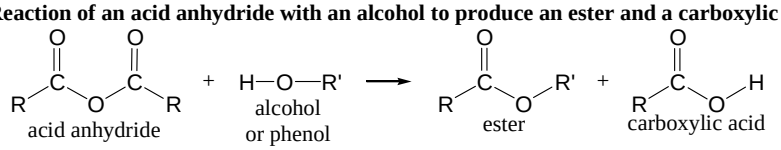
3. Reaction of a carboxylic acid with an alcohol to produce an ester and water.



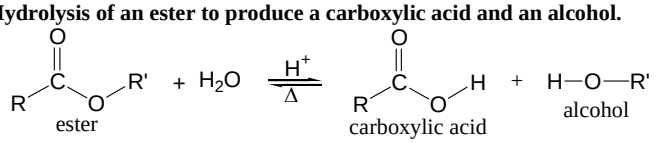
4. Reaction of an acid chloride with an alcohol to produce an ester and HCl.



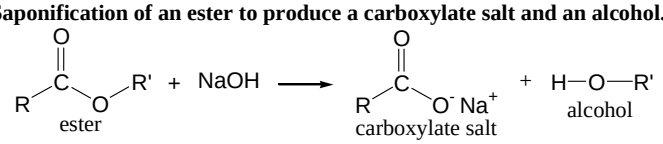
5. Reaction of an acid anhydride with an alcohol to produce an ester and a carboxylic acid.



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.