Al-Rasheed University College
Department of Dentistry
1st Stage

MEDICAL CHEMISTRY

lecture 9
Aldehyde, Ketone and Carboxylic Acids

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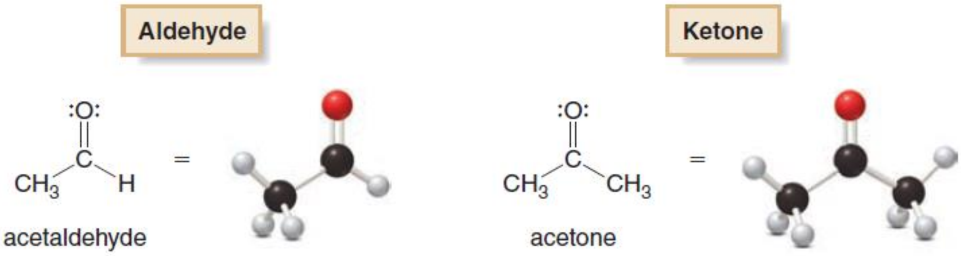
Aldehydes and Ketones

- Aldehydes (RCHO) and ketones (RCOR) contain a carbonyl group (C=O) with the carbonyl carbon bonded to carbon or hydrogen atoms.
- ***An aldehyde*** has at least one H atom bonded to the carbonyl carbon.
- ***A ketone*** has two alkyl groups bonded to the carbonyl carbon.



The double bond of a carbonyl group is usually omitted in shorthand structures. *Acetaldehyde*, for example, is written as CH_3CHO. Remember that the H atom is bonded to the carbon atom, not the oxygen. Likewise, acetone is written as CH_3COCH_3 or $(CH_3)_2CO$. Remember that each compound contains a C=O.

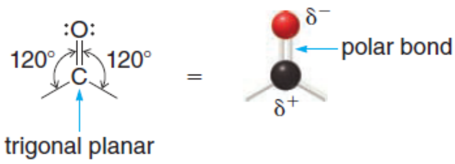
Problem: Draw out each compound to clearly show what groups are bonded to the carbonyl carbon. Label each compound as a ketone or aldehyde.

a. CH_3CH_2CHO b. $CH_3CH_2COCH_3$

c. $(CH_3)_3CCOCH_3$ d. $(CH_3CH_2)_2CHCHO$

Structure of Aldehydes and Ketones

- ✓ Aldehydes (RCHO) and ketones (RCOR or R_2CO) are two families of compounds that contain a carbonyl group. Two structural features dominate the properties and chemistry of the carbonyl group.
- ✓ The carbonyl carbon atom is trigonal planar, and all bond angles are 120°.
- ✓ Since oxygen is more electronegative than carbon, a carbonyl group is polar. The carbonyl carbon is electron poor (δ^+) and the oxygen is electron rich (δ^-).



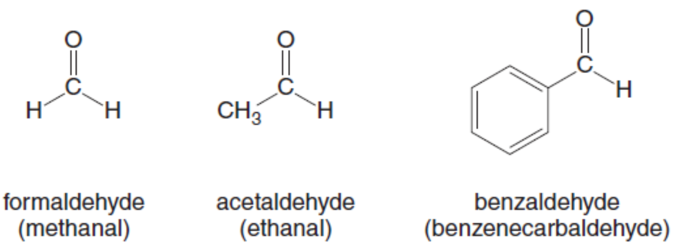
Naming Aldehydes

- In IUPAC nomenclature, aldehydes are identified by the suffix ***-al***.

To name an aldehyde using the IUPAC system:

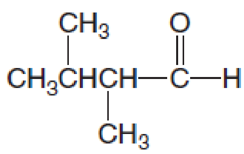
- Find the longest chain containing the CHO group, and change the **-e** ending of the parent alkane to the suffix ***-al***.
- Number the chain or ring to put the CHO group at C_1, but omit this number from the name. Apply all of the other usual rules of nomenclature.

Simple aldehydes have common names that are virtually always used instead of their IUPAC names. Common names all contain the suffix -aldehyde.



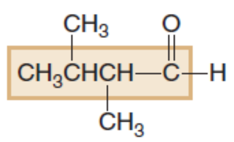
(IUPAC names are in parentheses.)

Example: Give the IUPAC name for the following aldehyde.

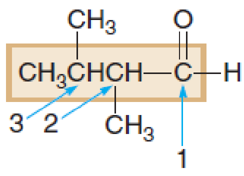


Solution

[1] Find and name the longest chain containing the CHO.



[2] Number and name substituents, making sure the CHO group is at C_1.



Answer: 2,3-dimethylbutanal

Naming Ketones

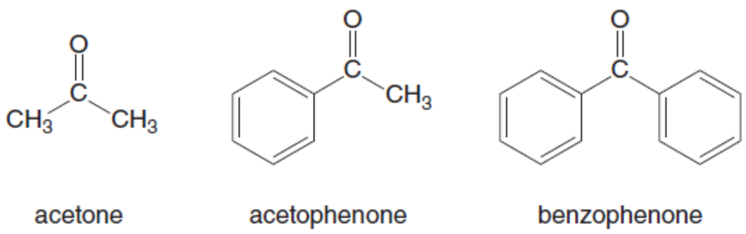
- In the IUPAC system, ketones are identified by the suffix ***-one***.

To name an acyclic ketone using IUPAC rules:

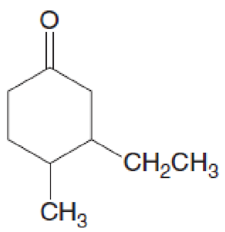
- Find the longest chain containing the carbonyl group, and change the **-e** ending of the parent alkane to the suffix ***-one***.
- Number the carbon chain to give the carbonyl carbon the lower number. Apply all of the other usual rules of nomenclature.

With cyclic ketones, numbering always begins at the carbonyl carbon, but the "1" is usually omitted from the name. The ring is then numbered clockwise or counterclockwise to give the first substituent the lower number.

- Three simple ketones have widely used common names.

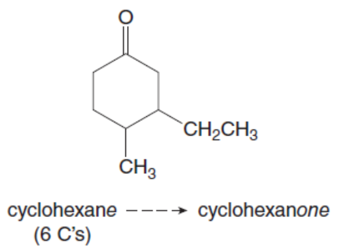


Example: Give the IUPAC name for the following ketone.

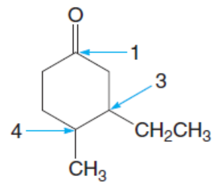


Solution:

[1] Name the ring.



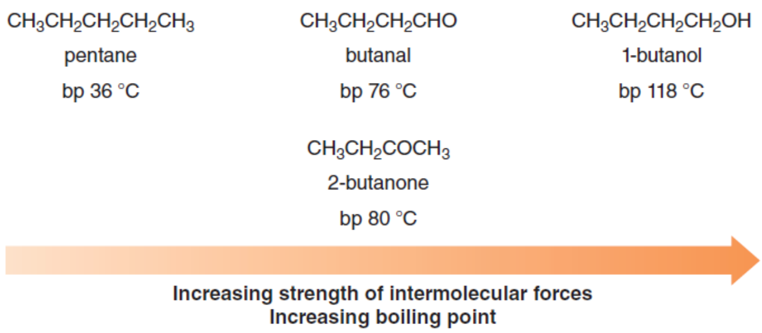
[2] Number and name substituents, making sure the carbonyl carbon is at C1.



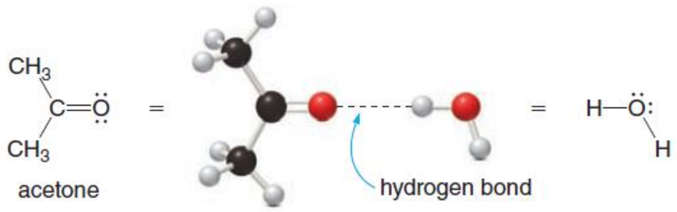
Answer: 3-ethyl-4-methylcyclohexanone

Physical Properties of Aldehydes and ketones

1. They are polar molecules with stronger intermolecular forces than the hydrocarbon, because aldehydes and ketones have a polar carbonyl group.
2. Since they have no O-H bond, two molecules of RCHO or RCOR are incapable of intermolecular hydrogen bonding, giving them weaker intermolecular forces than alcohols.
3. Aldehydes and ketones have higher boiling points than hydrocarbons of comparable size.
4. Aldehydes and ketones have lower boiling points than alcohols of comparable size.



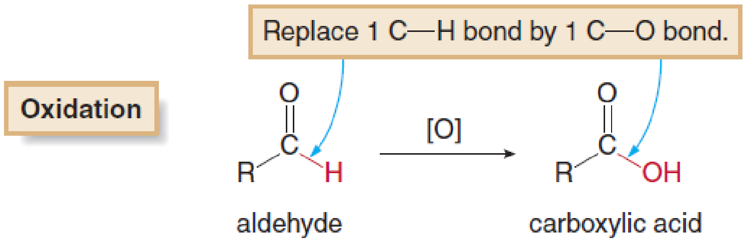
5. Aldehydes and ketones are soluble in organic solvents, based on the general rule governing solubility (i.e., "*like dissolves like*").
6. They can intermolecularly hydrogen bond to water, because aldehydes and ketones contain an oxygen atom with an available lone pair.



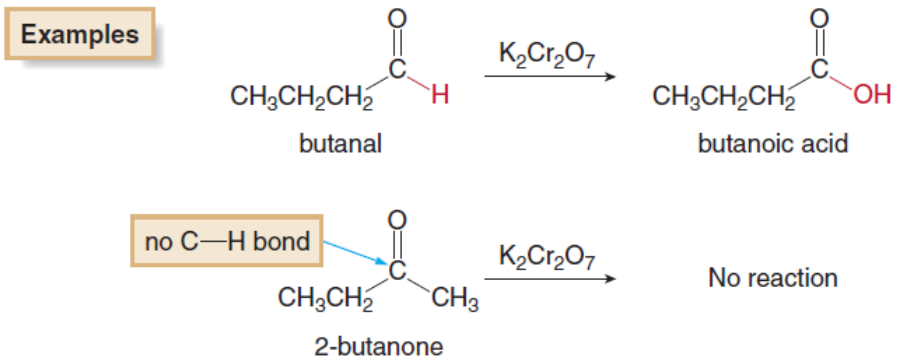
7. Low molecular weight aldehydes and ketones (*those having less than six carbons*) are soluble in both organic solvents and water.
8. Higher molecular weight aldehydes and ketones (*those having six carbons or more*) are soluble in organic solvents, but insoluble in water.

Oxidation of Aldehydes

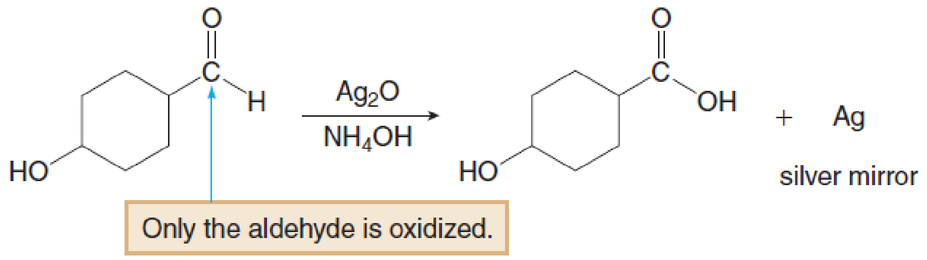
- Since aldehydes contain a hydrogen atom bonded directly to the carbonyl carbon, they can be oxidized to carboxylic acids; that is, the aldehyde C-H bond can be converted to a C-OH bond.
- Since ketones have no hydrogen atom bonded to the carbonyl group, they are not oxidized under similar reaction conditions.



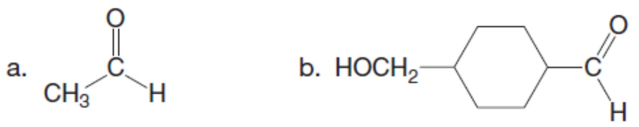
☒ A common reagent for this oxidation is potassium dichromate, $K_2Cr_2O_7$, a red-orange solid that is converted to a green Cr^{3+} product during oxidation.



- ✓ As we learned in previous lecture (Lec.8), $K_2Cr_2O_7$ oxidizes 1° and 2° alcohols as well. Aldehydes can be oxidized selectively in the presence of other functional groups using silver(I) oxide (Ag_2O) in aqueous ammonium hydroxide (NH_4OH). This is ***called Tollens reagent***.
- ✓ *Only aldehydes react with Tollens reagent; all other functional groups are inert.*
- ✓ Oxidation with Tollens reagent provides a distinct color change because the Ag^+ reagent is converted to silver metal (Ag), which precipitates out of the reaction mixture as a silver mirror.

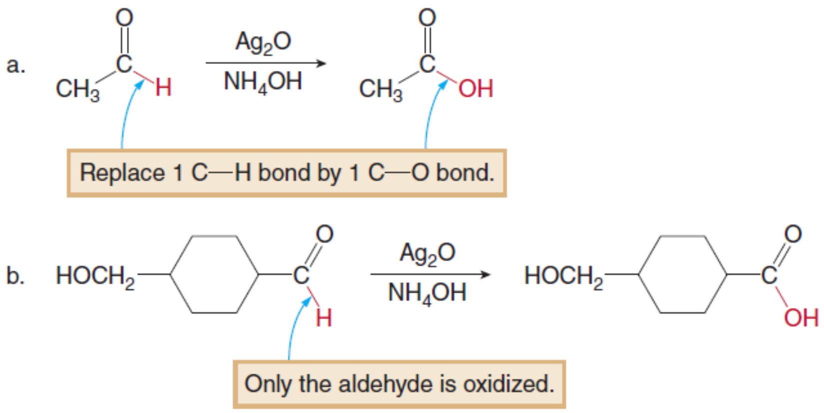


Example: What product is formed when each compound is treated with Tollens reagent (Ag_2O, NH_4OH)?

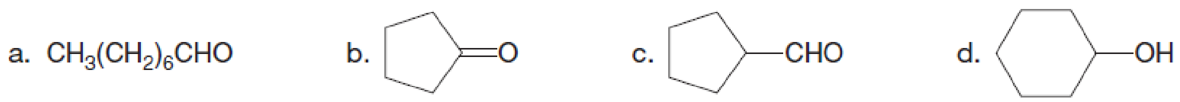


Solution: Only aldehydes (RCHO) react with Tollens reagent. Ketones and alcohols are inert to oxidation.

The aldehyde in both compounds is oxidized to RCO_2H, but the 1° alcohol in part (b) does not react with Tollens reagent.



Problem: What product is formed when each compound is treated with Tollens reagent (Ag_2O, NH_4OH)? In some cases, no reaction occurs.

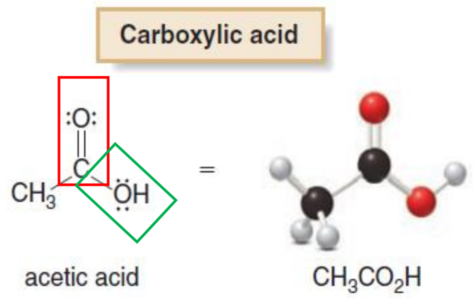


Carboxylic acids

Carboxylic acids of organic molecules that contain a carbonyl group (C=O) singly bonded to an oxygen atom.

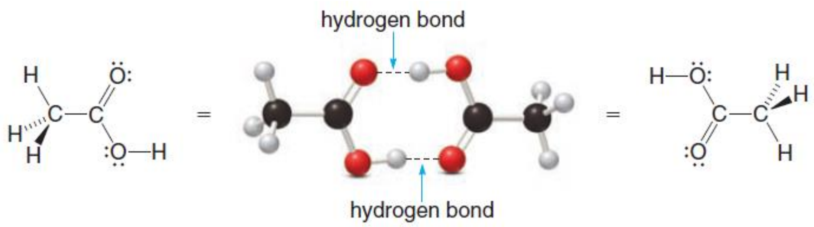
The structure of a carboxylic acid is often abbreviated as RCOOH or RCO_2H. *Keep in mind that the central carbon in both functional groups has a double bond to one oxygen and a single bond to another*.

- ✓ A carboxylic acid contains a carboxyl group (COOH).



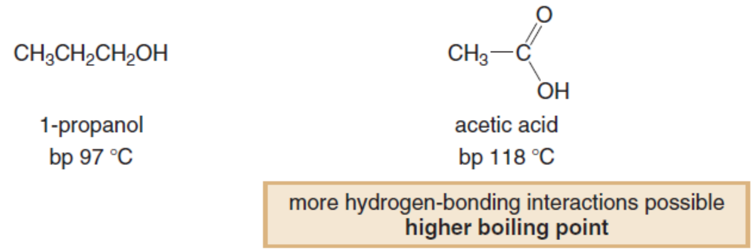
Physical Properties of Carboxylic Acid

1. Carboxylic acids are polar compounds because they possess a polar carbonyl group.
2. Carboxylic acids also exhibit intermolecular hydrogen bonding.



3. Carboxylic acids have stronger intermolecular forces than alcohols, giving them higher boiling points and melting points, when comparing compounds of similar size.

- ✓ *Carboxylic acids have higher boiling points and melting points than alcohols of comparable size.*



4. Like other oxygen-containing compounds, carboxylic acids having **fewer than six carbons are soluble in water**. **Higher molecular weight compounds are insoluble in water** because the nonpolar part of the molecule, the C-C and C-H bonds, gets larger than the polar carbonyl group.

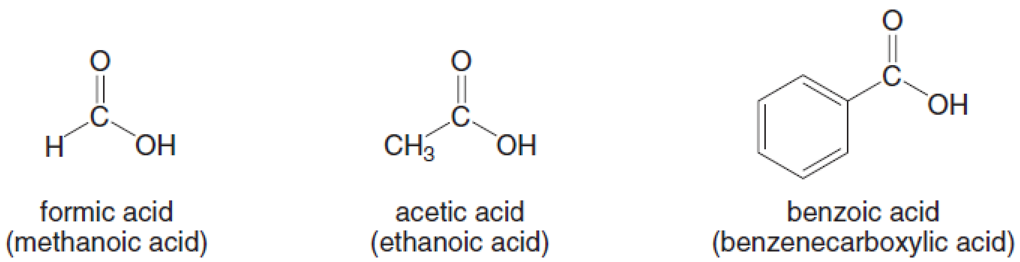
Nomenclature of Carboxylic Acids

- ❑ In the IUPAC system, carboxylic acids are identified by the suffix ***-oic acid***.

- ➢ To name a carboxylic acid using the IUPAC system:

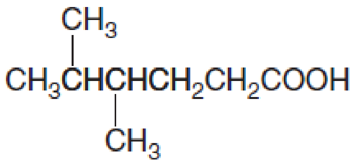
1. Find the longest chain containing the COOH group, and change the -e ending of the parent alkane to the suffix ***-oic acid***.
2. Number the carbon chain to put the COOH group at C_1, but omit this number from the name. Apply all of the other usual rules of nomenclature.

✓ Many simple carboxylic acids are often referred to by their common names. A common name uses the suffix ***-ic*** acid. Three common names are virtually always used.



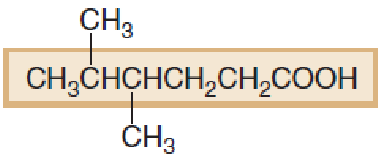
[IUPAC names are given in parentheses, and are rarely used.]

Example: Give the IUPAC name of the following carboxylic acid.



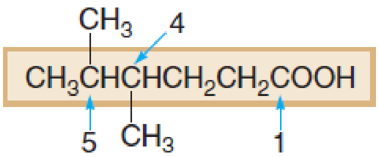
Solution:

1. Find and name the longest chain containing COOH.



Hexane (6 C's) ………….. hexanoic acid , The COOH contributes one C to the longest chain.

2. Number and name the substituents, making sure the COOH group is at C1.



two methyl substituents on C4 and C5

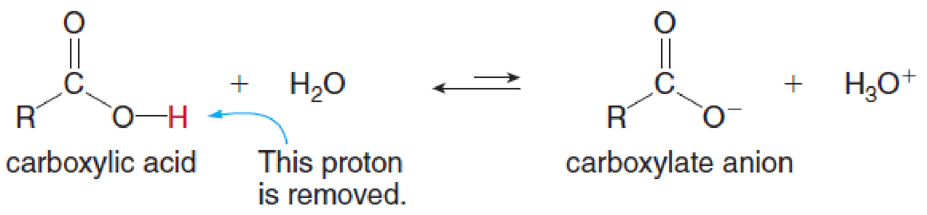
Answer: 4,5-dimethylhexanoic acid

Reactions of Carboxylic Acids

1. Reaction with water

Carboxylic acids are acids; that is, they are proton donors.

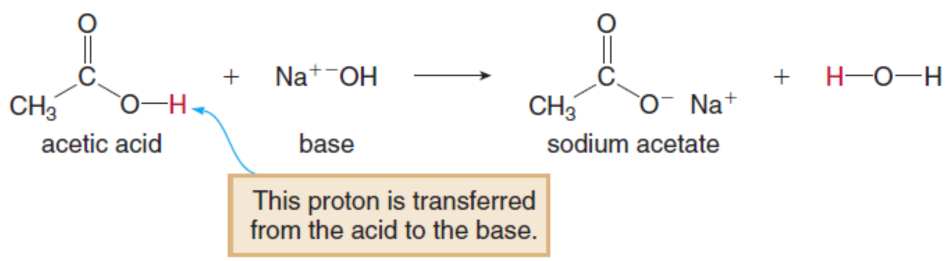
When a carboxylic acid is dissolved in water, **an acid–base reaction occurs**: the carboxylic acid donates a proton to H_2O, forming its **conjugate base**, a carboxylate anion, and water gains a proton, forming its conjugate acid, H_3O^+.



- While carboxylic acids are more acidic than other families of organic compounds, they are weak acids compared to inorganic acids like HCl or H_2SO_4.

2. Reaction with Bases

Carboxylic acids react with bases such as NaOH to form **water-soluble salts**. In this reaction, essentially all of the carboxylic acid is converted to its carboxylate anion.



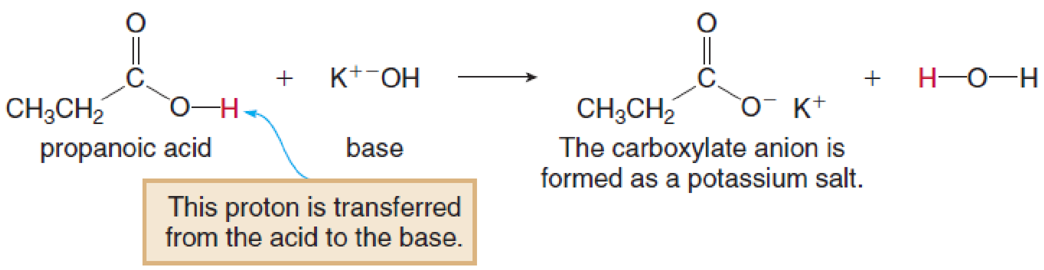
- ✓ A proton is removed from acetic acid (CH_3COOH) to form its conjugate base, the acetate anion (CH_3COO^-), which is present in solution as its sodium salt, sodium acetate (CH_3COONa) .
- ✓ Hydroxide (^-OH) gains a proton to form neutral H_2O.
- ➢ Similar *acid–base reactions* occur with other hydroxide bases (KOH), sodium bicarbonate ($NaHCO_3$), and sodium carbonate (Na_2CO_3). In each reaction, a proton is transferred from the acid (RCOOH) to the base.

Example: What products are formed when propanoic acid (CH_3CH_2COOH) reacts with potassium hydroxide (KOH)?

Solution:

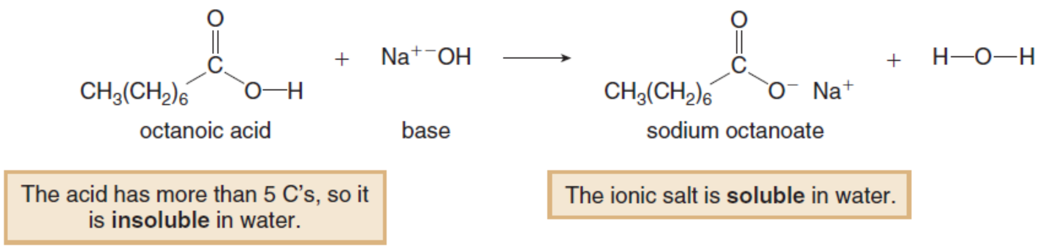
In any acid–base reaction with a carboxylic acid:

- Remove a proton from the carboxyl group (COOH) and form the carboxylate anion ($RCOO^-$).
- Add a proton to the base.
- Balance the charge of the carboxylate anion by drawing it as a salt with a metal cation.



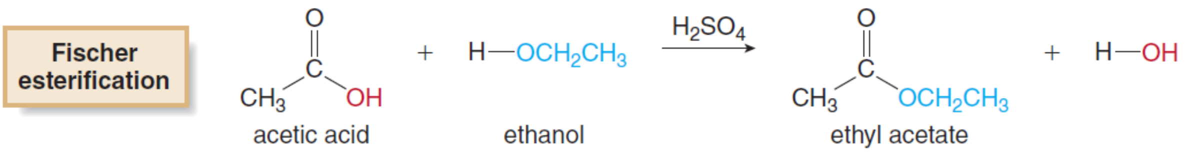
➢ Thus, CH_3CH_2COOH loses a proton to form CH_3CH_2COO–, which is present in solution as its potassium salt, $CH_3CH_2COO^- K^+$. Hydroxide (^-OH) gains a proton to form H_2O.

The salts of carboxylic acids that are formed by acid–base reactions are water-soluble ionic solids. Thus, a water-insoluble *carboxylic acid* like octanoic acid can be converted to its *water-soluble sodium salt* by reaction with NaOH.



3. Reaction with Alcohols

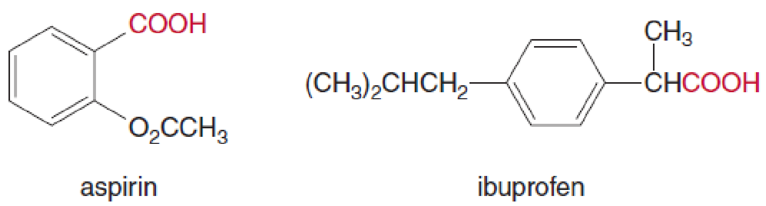
- Treatment of a **carboxylic acid (RCOOH)** with an **alcohol (R'OH)** in the presence of an acid catalyst forms an **ester (RCOOR')**. This reaction is called a **Fischer esterification**. Esterification is a substitution because the **OR' group** of an alcohol replaces the **OH group** of the starting carboxylic acid.



Focus on Health & Medicine

1. *Aspirin and Anti-Inflammatory Agents*

Aspirin and *ibuprofen* are common pain relievers and anti-inflammatory agents that contain a carboxyl group.

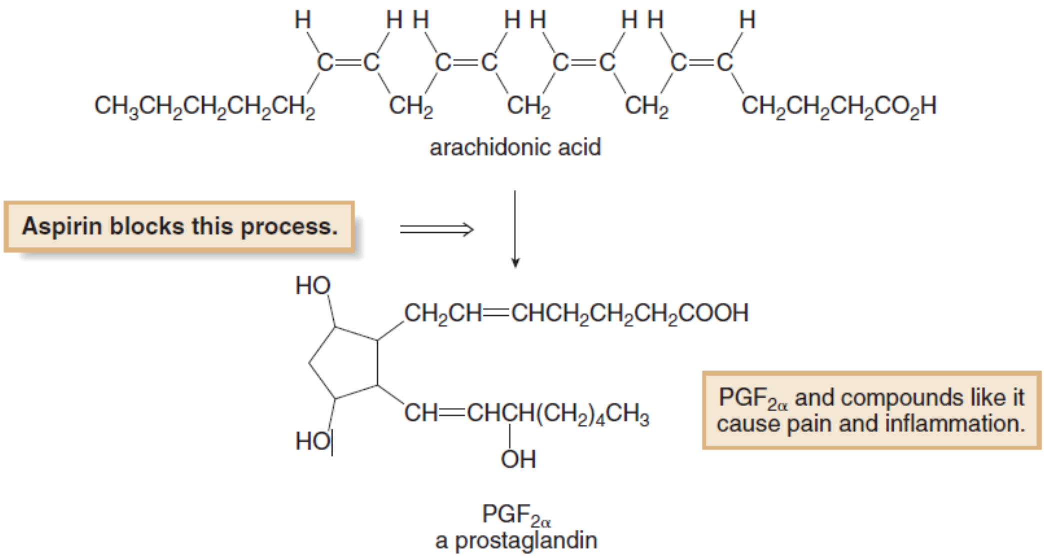


How does *aspirin* relieve pain and reduce inflammation? In the 1970s, it was shown that aspirin blocks the synthesis of prostaglandins, carboxylic acids containing 20 carbons that are responsible for mediating pain, inflammation, and a wide variety of other biological functions.

Prostaglandins are not stored in cells. Rather, they are synthesized on an as-needed basis from arachidonic acid, an unsaturated fatty acid with four cis double bonds.

Aspirin relieves pain and decreases inflammation because it prevents the synthesis of prostaglandins, the compounds responsible for both of these physiological responses, from arachidonic acid.

- ***Aspirin*** was first used in medicine for its analgesic (pain-relieving), antipyretic (fever-reducing), and anti-inflammatory properties. Today it is also commonly used to prevent blood clots from forming in arteries.



2. *Carboxylic salt as preservatives*

Salts of carboxylic acids are commonly used as preservatives.

Sodium benzoate, which inhibits the growth of fungus, is a preservative used in soft drinks, and potassium sorbate is an additive that prolongs the shelf-life of baked goods and other foods.

These salts do not kill bacteria or fungus. They increase the pH of the product, thus preventing further growth of microorganisms.