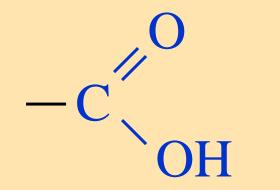


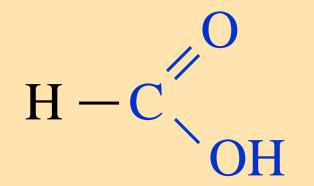
### The Carboxyl Group



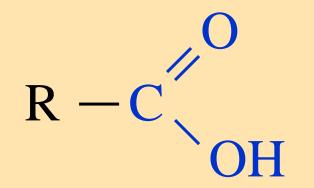
or



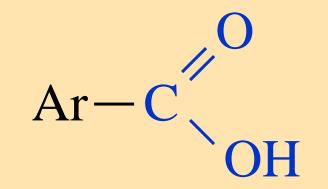
### Attachment to Hydrogen



#### Attachment to an Alkyl Group



#### Attachment to an Aryl Group



- Common Names
  - Named for their sources
  - Known for a long time
  - well ingrained
  - Branched chains are named and their position indicated by Greek letters
  - Aromatic acids are named as derivatives of the parent acid (benzoic acid)

 $\begin{array}{ccc} \delta & \gamma & \beta & \alpha \\ \text{C-C-C-C-COOH} \end{array}$ 

<ul> <li>Common Names</li> </ul>	# carbon atoms
Formic	1
Acetic	2
Propionic	3
Butyric	4
Valeric	5
Isovaleric	5

•	Common Names
	Caproic
	Caprylic
	Capric

# carbon atoms

CH<sub>3</sub>CH<sub>2</sub>CHCOOH | CH<sub>3</sub> α-Methylbutyric

CH<sub>3</sub>CH<sub>2</sub>CH—CHCOOH | |CH<sub>3</sub> CH<sub>3</sub>  $\alpha,\beta$ -Dimethylvaleric



γ-Phenylbutyric



#### IUPAC

- Name the longest chain
- replace -e with -oic acid
- Position of substituent groups is indicated by number with the carboxyl carbon as C-1

5 4 3 2 1 C-C-C-C-COOH

#### CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOH

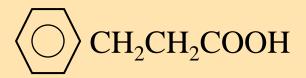
Pentanoic

 $CH_{3}$ 

3-(*p*-Chlorophenyl)butanoic

CH<sub>3</sub>CH=CHCOOH

2-Butenoic



3-Phenylpropanoic

- Salts
  - Name the cation
  - name the acid replacing -ic with -ate

## **Preparation of Organic Acids**

#### PREPARATION OF CARBOXYLIC ACIDS.

1. Oxidation of primary alcohols. Discussed in Sec. 6.15.

 $R-CH_2OH \xrightarrow{KMnO_4} R-COOH$ 

**Examples:** 

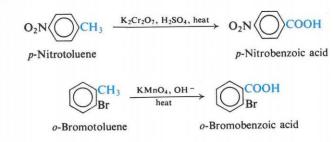
 $\begin{array}{c} CH_{3} & CH_{3} \\ CH_{3}CH_{2}CHCH_{2}OH \xrightarrow{KMnO_{4}} CH_{3}CH_{2}CHCOOH \\ 2-Methyl-1-butanol & 2-Methylbutanoic acid \end{array}$ 

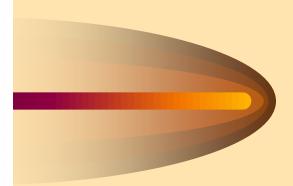
 $\begin{array}{c} CH_3 & CH_3 \\ \downarrow \\ CH_3CHCH_2OH & \xrightarrow{KMnO_4} & CH_3CHCOOH \\ Isobutyl alcohol & Isobutyric acid \end{array}$ 

2. Oxidation of alkylbenzenes. Discussed in Sec. 16.11.

Ar-R 
$$\xrightarrow{\text{KMnO}_4 \text{ or } K_2 \text{Cr}_2 \text{O}_7}$$
 Ar-COOH

Examples:

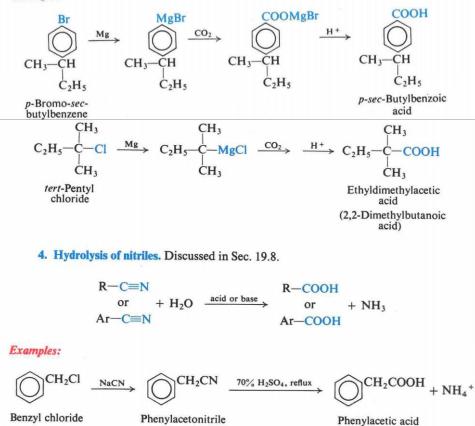


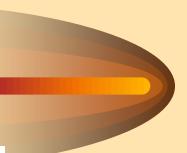


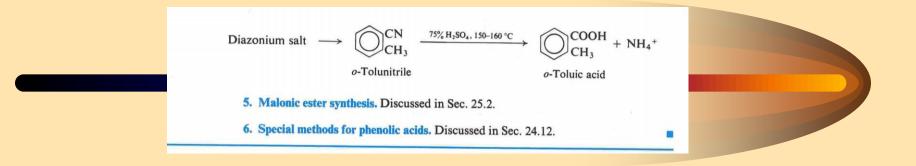
3. Carbonation of Grignard reagents. Discussed in Sec. 19.7.

$$\begin{array}{cccc} R \longrightarrow & R$$

#### Examples:



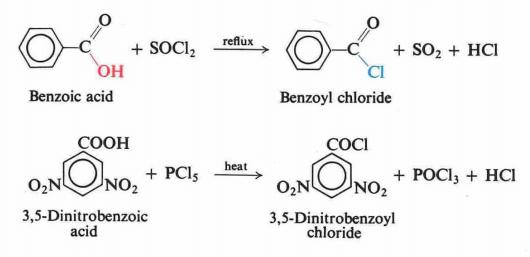




#### **Conversion into acid chlorides**

A carboxylic acid is perhaps more often converted into the acid chloride than into any other of its functional derivatives. From the highly reactive acid chloride there can then be obtained many other kinds of compounds, including esters and amides (Sec. 20.8).

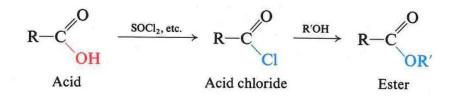
An acid chloride is prepared by substitution of -Cl for the -OH of a carboxylic acid. Three reagents are commonly used for this purpose: *thionyl chloride*,  $SOCl_2$ ; *phosphorus trichloride*,  $PCl_3$ ; and *phosphorus pentachloride*,  $PCl_5$ . (Of what inorganic acids might we consider these reagents to be the acid chlorides?) For example:

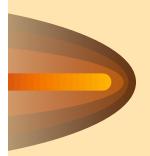


Thionyl chloride is particularly convenient, since the products formed besides the acid chloride are gases and thus easily separated from the acid chloride; any excess of the low-boiling thionyl chloride (79 °C) is easily removed by distillation.

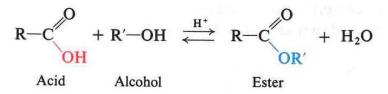
#### **Conversion into esters**

Acids are frequently converted into their esters via the acid chlorides:





A carboxylic acid is converted directly into an ester when heated with an alcohol in the presence of a little mineral acid, usually concentrated sulfuric acid or dry hydrogen chloride. This reaction is reversible, and generally reaches equilibrium when there are appreciable quantities of both reactants and products present.



For example, when we allow one mole of acetic acid and one mole of ethyl alcohol to react in the presence of a little sulfuric acid until equilibrium is reached (after several hours), we obtain a mixture of about two-thirds mole each of ester and water, and one-third mole each of acid and alcohol. We obtain this same equilibrium

### Reactions of Carboxylic Acids

- Determined by their functional group,
   -COOH (carboxyl group)
- Composed of the carbonyl group (-C=O) and a hydroxyl group (-OH)
- It is the –OH that actually undergoes nearly every reaction –loss of H<sup>+</sup>, or replacement by another group

### **Reactions of Organic Acids**

#### **REACTIONS OF CARBOXYLIC ACIDS** \_

1. Acidity. Salt formation. Discussed in Secs. 19.4, 19.10-19.14.

RCOOH  $\implies$  RCOO<sup>-</sup> + H<sup>+</sup>

Examples:

 $\begin{array}{rcl} 2CH_{3}COOH + Zn & \longrightarrow & (CH_{3}COO^{-})_{2}Zn^{2+} + H_{2} \\ Acetic \ acid & Zinc \ acetate \end{array}$ 

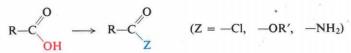
 $\begin{array}{rcl} CH_3(CH_2)_{10}COOH + NaOH &\longrightarrow & CH_3(CH_2)_{10}COO^-Na^+ + H_2O\\ Lauric acid & & Sodium \ laurate \end{array}$ 

$$\bigcirc^{\text{COOH}} + \text{NaHCO}_3 \longrightarrow \bigcirc^{\text{COO}^-\text{Na}^+} + \text{CO}_2 + \text{H}_2\text{O}$$

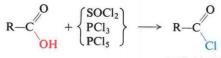
Benzoic acid

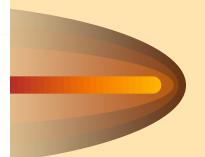
Sodium benzoate

2. Conversion into functional derivatives

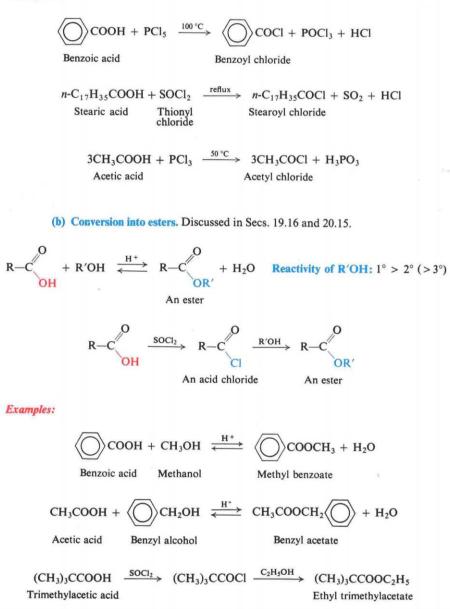


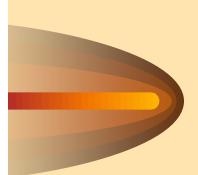
(a) Conversion into acid chlorides. Discussed in Sec. 19.15.



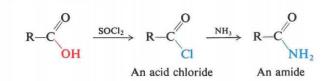








(c) Conversion into amides. Discussed in Sec. 19.17.



#### Example:

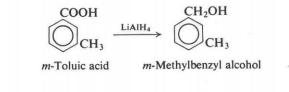
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> COOH	$\xrightarrow{\text{SOCI}_2}  C_6H_5CH_2COCI  \xrightarrow{\text{NH}_3} \rightarrow$	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CONH <sub>2</sub>
Phenylacetic acid	Phenylacetyl chloride	Phenylacetamide

3. Reduction. Discussed in Sec. 19.18.

$$R-COOH \xrightarrow{\text{LiAlH}_4} R-CH_2OH \qquad Also reduced via esters (Sec. 20.22)$$
1° alcohol

#### Examples:

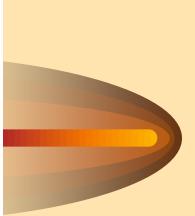
4(CH <sub>3</sub> ) <sub>3</sub> CCOOH + 3LiAlH <sub>4</sub>	$\xrightarrow{\text{ether}}$ [(CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> O] <sub>4</sub> AlLi	$\xrightarrow{\mathrm{H}^+}$ (CH <sub>3</sub> ) <sub>3</sub> CCH <sub>2</sub> OH
Trimethylacetic acid	$+ 2LiAlO_2 + 4H_2$	Neopentyl alcohol (2,2-Dimethyl- 1-propanol)

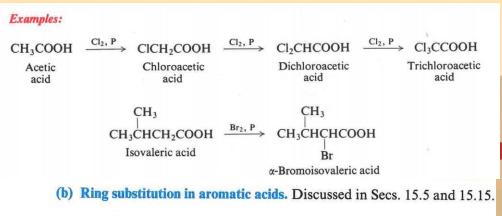


#### 4. Substitution in alkyl or aryl group

(a) Alpha-halogenation of aliphatic acids. Hell-Volhard-Zelinsky reaction. Discussed in Sec. 19.19.

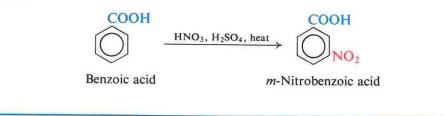
$$\begin{array}{ccc} \text{RCH}_2\text{COOH} + X_2 & \xrightarrow{P} & \text{RCHCOOH} + \text{HX} & X_2 = \text{Cl}_2, \text{Br}_2 \\ & & \\ & X \\ & & \\ & \\ & & \\$$





-COOH: deactivates, and directs meta in electrophilic substitution.





### Nomenclature of Diacids

#### HOOC-R-COOH

### Nomenclature of Diacids

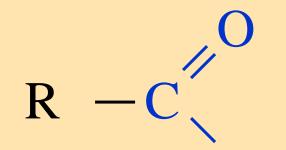
<ul> <li>Common Names</li> </ul>	# carbon atoms
Oxalic	2
Malonic	3
Succinic	4
Glutaric	5
Adipic	6
Pimelic	7

### Nomenclature of Diacids

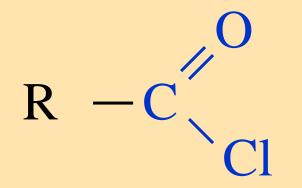
Common Names	# carbon atoms
Suberic	8
Azelaic	9
Sebacic	10

25

Oh	Oxalic
My	Malonic
Such	Succinic
Good	Glutaric
Apple	Adipic
Pie	Pimelic
Sweet	Suberic
As	Azelaic
Sugar	Sebacic







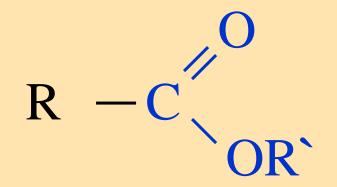
Acid chloride

R - C R - C

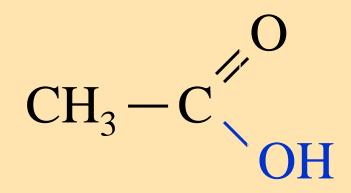
Anhydride



Amide

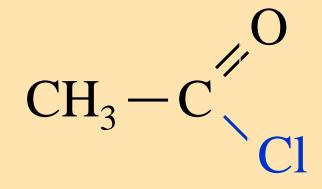


Ester



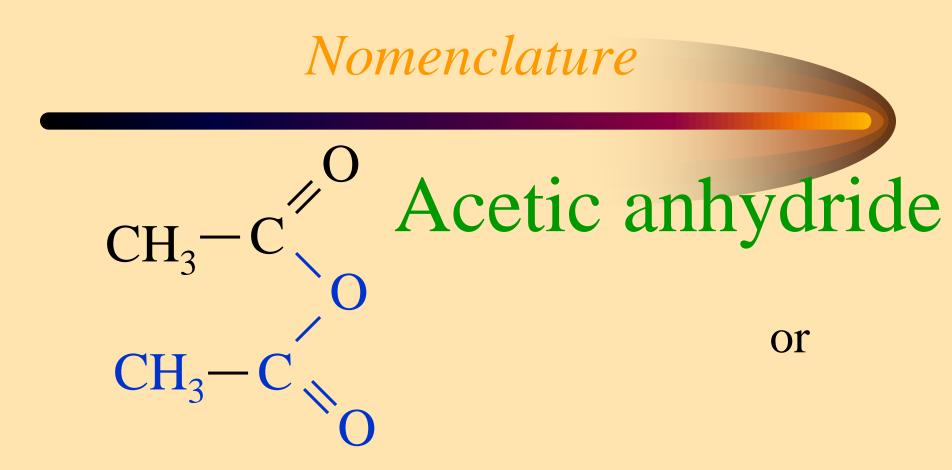
# Acetic Acid

## or Ethanoic Acid



# Acetyl chloride

# or Ethanoyl chloride

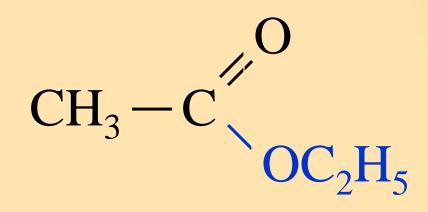


# Ethanoic anhydride

 $CH_3 - C$ 

# Acetamide

or Ethanamide



# Ethyl acetate

# or Ethyl ethanoate

http://web.ukonline.co.uk/stinsv/