Introduction to Organic Chemistry

CHEM 108

Credit hrs.: (3+1)

King Saud University

College of Science, Chemistry Department

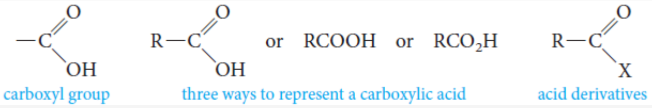
CHAPTER 8: Carboxylic Acids

Structure of Carboxylic Acids

- The functional group common to all carboxylic acids is the carboxyl group.

  The name is a contraction of the parts: the carbonyl and hydroxyl groups.

- The general formula for a carboxylic acid can be written in expanded or abbreviated forms.



$-C(=O)OH$ carboxyl group

$R-C(=O)OH$ or $RCOOH$ or RCO_2H three ways to represent a carboxylic acid

$R-C(=O)X$ acid derivatives

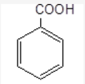
- Depending on whether an R or an Ar. residue is attached to the carboxyl group; Carboxylic acids are classified as;
  - Aliphatic Carboxylic Acids.

    $R-COOH$ (R = H or alkyl)
    Aliphatic acid

    CH_3-COOH
    Acetic acid

  - Aromatic Carboxylic Acids.

    $Ar-COOH$ ($R = C_6H_5$-)
    Aromatic acid



Benzoic acid

Nomenclature of Carboxylic Acids

Common Names

- The common names of carboxylic acids all end in *-ic acid*.
- These names usually come from some Latin or Greek word that indicates the original source of the acid.
- Common name, substituents are located with Greek letters, beginning with the α–carbon atom.

IUPAC System

- We replace the final *e* in the name of the corresponding alkane with the suffix *-oic* and add the word *acid*.

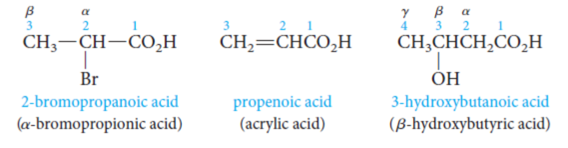
Alkane- e + *oic acid = Alkanoic acid*

- IUPAC system, the chain is numbered beginning with the carboxyl carbon atom, and substituents are located in the usual way.

Nomenclature of Carboxylic Acids

Carbon atoms	Formula	Source	Common name	IUPAC name
1	HCOOH	ants (Latin, *formica*)	formic acid	methanoic acid
2	CH_3COOH	vinegar (Latin, *acetum*)	acetic acid	ethanoic acid
3	CH_3CH_2COOH	milk (Greek, *protos pion*, first fat)	propionic acid	propanoic acid
4	$CH_3(CH_2)_2COOH$	butter (Latin, *butyrum*)	butyric acid	butanoic acid
5	$CH_3(CH_2)_3COOH$	valerian root (Latin, *valere*, to be strong)	valeric acid	pentanoic acid
6	$CH_3(CH_2)_4COOH$	goats (Latin, *caper*)	caproic acid	hexanoic acid
7	$CH_3(CH_2)_5COOH$	vine blossom (Greek, *oenanthe*)	enanthic acid	heptanoic acid
8	$CH_3(CH_2)_6COOH$	goats (Latin, *caper*)	caprylic acid	octanoic acid
9	$CH_3(CH_2)_7COOH$	pelargonium (an herb with stork-shaped seed capsules; Greek, *pelargos*, stork)	pelargonic acid	nonanoic acid
10	$CH_3(CH_2)_8COOH$	goats (Latin, *caper*)	capric acid	decanoic acid

Nomenclature of Carboxylic Acids

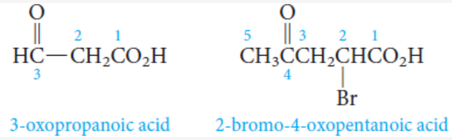


$\overset{\beta}{\overset{3}{CH_3}}-\underset{\text{Br}}{\overset{\alpha}{\overset{2}{CH}}}-\overset{1}{CO_2H}$ 2-bromopropanoic acid (α-bromopropionic acid)

$\overset{3}{CH_2}=\overset{2}{CH}\overset{1}{CO_2H}$ propenoic acid (acrylic acid)

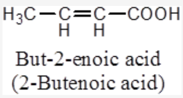
$\overset{\gamma}{\overset{4}{CH_3}}\underset{\text{OH}}{\overset{\beta}{\overset{3}{CH}}}\overset{\alpha}{\overset{2}{CH_2}}\overset{1}{CO_2H}$ 3-hydroxybutanoic acid (β-hydroxybutyric acid)

- The carboxyl group has priority over alcohol, aldehyde, or ketone functionality in naming.
- The prefix *oxo-* is used to locate the carbonyl group of the aldehyde or ketone.



$\underset{3}{\overset{\text{O}}{\overset{\|}{HC}}}-\overset{2}{CH_2}\overset{1}{CO_2H}$ 3-oxopropanoic acid

$\overset{5}{CH_3}\underset{4}{\overset{\text{O}}{\overset{\|}{C}}}\overset{3}{CH_2}\underset{\text{Br}}{\overset{2}{CH}}\overset{1}{CO_2H}$ 2-bromo-4-oxopentanoic acid



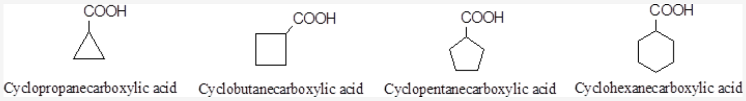
$H_3C-\underset{\text{H}}{C}=\underset{\text{H}}{C}-COOH$

But-2-enoic acid
(2-Butenoic acid)

Nomenclature of Carboxylic Acids

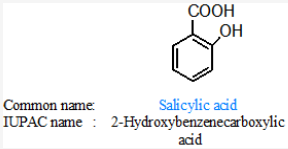
- **Cycloalkane carboxylic acid**

  When the carboxyl group is attached to a ring, the ending -carboxylic acid is added to the name of the parent cycloalkane. (i.e. Cycloalkanecarboxylic acid)

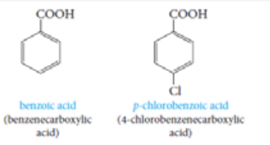


Cyclopropanecarboxylic acid Cyclobutanecarboxylic acid Cyclopentanecarboxylic acid Cyclohexanecarboxylic acid

- Aromatic acids are named by attaching the suffix *-oic acid* or *-ic acid* to an appropriate prefix derived from the aromatic hydrocarbon.



Common name: Salicylic acid
IUPAC name : 2-Hydroxybenzenecarboxylic acid

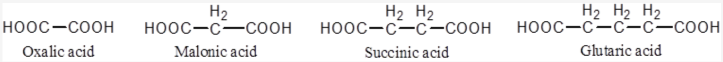


benzoic acid (benzenecarboxylic acid) *p*-chlorobenzoic acid (4-chlorobenzenecarboxylic acid)

Nomenclature of Carboxylic Acids

- **Dicarboxylic acids** (*acids that contain two carboxyl groups*)
  - **Common names**.

    They are known almost exclusively by their common names.

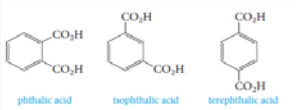


$HOOC-COOH$ Oxalic acid

$HOOC-\overset{H_2}{C}-COOH$ Malonic acid

$HOOC-\overset{H_2}{C}-\overset{H_2}{C}-COOH$ Succinic acid

$HOOC-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-COOH$ Glutaric acid

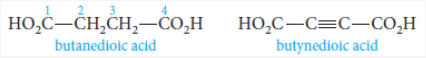


Common name: phthalic acid, isophthalic acid, terephthalic acid

IUPAC name: Benzene-1,2-dicarboxylic acid, Benzene-1,3-dicarboxylic acid, Benzene-1,4-dicarboxylic acid

  - IUPAC system

    They are given the suffix *-dioic acid* in the IUPAC system.

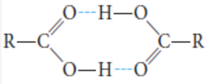


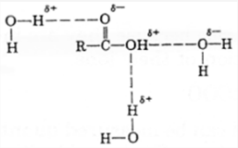
$\overset{1}{HO_2C}-\overset{2}{C}H_2\overset{3}{C}H_2-\overset{4}{C}O_2H$ butanedioic acid

$HO_2C-C\equiv C-CO_2H$ butynedioic acid

Physical Properties of Acids

- Carboxylic acids are polar and they form hydrogen bonds with themselves or with other molecules.
- Carboxylic acids form dimer, with the individual units held together by two hydrogen bonds between the electron-rich oxygens and the electron-poor hydrogens.





Boiling Points

Therefore, they have high boiling points for their molecular weights-higher even those of comparable alcohols.

Solubility in water

Hydrogen bonding also explains the water solubility of the lower molecular weight carboxylic acids.

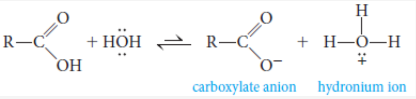
- The first four aliphatic acids (formic through butyric) are completely miscible in water.
- Aromatic acids are insoluble in water.

Physical Properties of Acids

Structure	Name	Mol. Wt.	b.p. °C	Solubility in H_2O at 25°C
HCOOH CH_3CH_2OH	Formic acid Ethyl alcohol	46 46	100 78	Very soluble Very soluble
CH_3COOH $CH_3CH_2CH_2OH$	Acetic acid *n*-Propyl alcohol	60 60	118 97	Very soluble Very soluble
$CH_3(CH_2)_3COOH$ $CH_3(CH_2)_4CH2OH$	Valeric acid *n*-Hexyl alcohol	102 102	187 156	4.0 g/100 g H_2O 0.6 g/100 g H_2O
Ph-COOH Ph-CH_2CH_2OH	Benzoic acid 3-Phenylethanol	122 122	250 250	Insoluble Insoluble

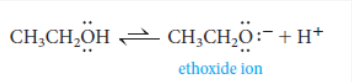
Acid Strength and Structure

- Carboxylic acids (RCOOH) dissociate in water, yielding a carboxylate anion ($RCOO^-$) and hydronium ion.

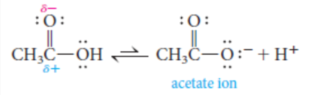


Why carboxylic acids are more acidic than alcohols?

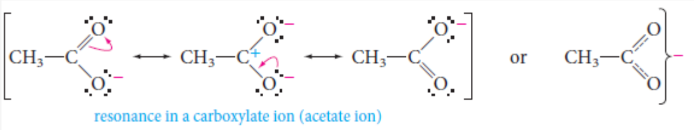
- In ethoxide ion, the negative charge is localized on a single oxygen atom.
- In acetate ion, on the other hand, the negative charge can be delocalized through resonance.


$CH_3CH_2\ddot{O}H \rightleftharpoons CH_3CH_2\ddot{O}:^- + H^+$

ethoxide ion



acetate ion



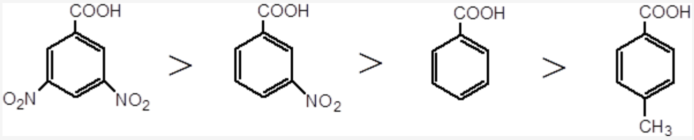
resonance in a carboxylate ion (acetate ion)

Acid Strength and Structure

Effect of Structure on Acidity; the Inductive Effect

- Acidities can vary depending on what other groups are attached to the molecule.
- Recall that *electron-withdrawing groups (-I) enhance acidity*, *and* *electron-releasing groups (+I) reduce acidity*.

  This effect relays charge through bonds, by displacing bonding electrons toward electronegative atoms, or away from electropositive atoms.



Acid Strength and Structure

Effect of Structure on Acidity; the Inductive Effect

- Formic acid is a substantially stronger acid than acetic acid.

  This suggests that the methyl group is more electron-releasing (hence anion-destabilizing and acidity-reducing) than hydrogen.

$$HCOOH > CH_3COOH > CH_3CH_2COOH > CH_3CH_2CH_2COOH$$

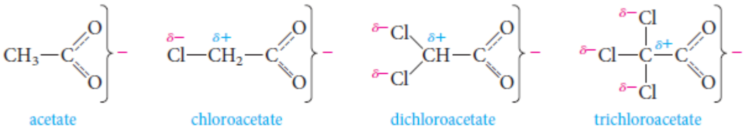
- Example: acetic acid with those of mono-, di-, and trichloroacetic acids.

  Comparison of acid strengths of acetic Acid and chlorinated acetic acids

$$Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$$

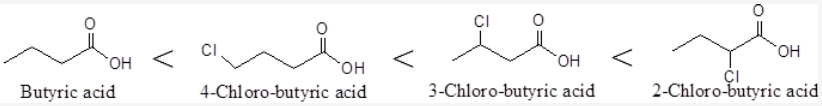
Acid Strength and Structure

Effect of Structure on Acidity; the Inductive Effect



The more chlorines, the greater the effect and the greater the strength of the acid.

- Comparison of acid strengths of butyric acid and the monochlorinated acids.



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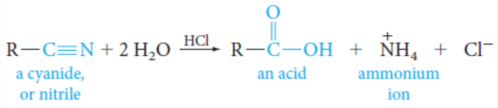
1) Hydrolysis of Cyanides (Nitriles)

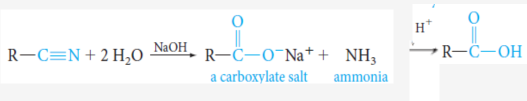
Preparation of Acids

- The reaction requires either acid or base.
  - In acid, the nitrogen atom of the cyanide is converted to an ammonium ion.



$$R{-}C{\equiv}N + 2\,H_2O \xrightarrow{HCl} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH + \overset{+}{N}H_4 + Cl^-$$

  - In base, the nitrogen atom is converted to ammonia and the organic product is the carboxylate salt, which must be neutralized in a separate step to give the acid.



$$R{-}C{\equiv}N + 2\,H_2O \xrightarrow{NaOH} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^-Na^+ + NH_3 \xrightarrow{H^+} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH$$

- Alkyl cyanides are generally made from the corresponding alkyl halide.

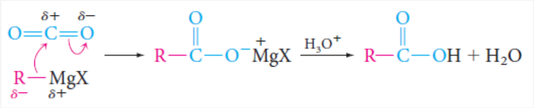
$$CH_3CH_2CH_2Br \xrightarrow{NaCN} CH_3CH_2CH_2CN \xrightarrow[H^+]{H_2O} CH_3CH_2CH_2CO_2H + NH_4^+$$

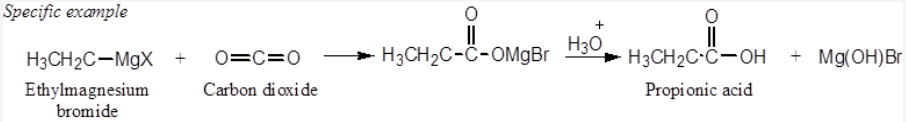
propyl bromide (1-bromopropane) — butyronitrile (butanenitrile) — butyric acid (butanoic acid)

Preparation of Acids

2) Reaction of Grignard Reagents with Carbon Dioxide
(Carbonation of Grignard Reagent)

- Grignard reagents add to the carbonyl group of carbon dioxide to give acids, after protonation of the intermediate carboxylate salt with a mineral acid like aqueous HCl.
- The acid obtained has one more carbon atom (*the reaction provides a way to increase the length of a carbon chain*).

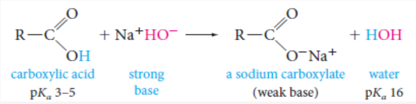


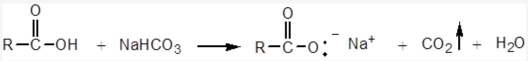


Reactions of Acids

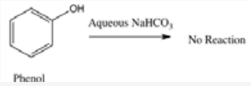
1) Reactions with Bases: Salt Formation

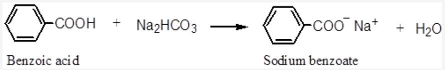
- Carboxylic acids, when treated with a strong base, form carboxylate salts.





- Examples.

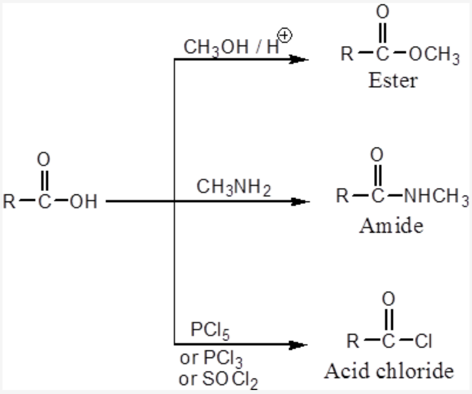




2) Nucleophilic Substitution Reactions

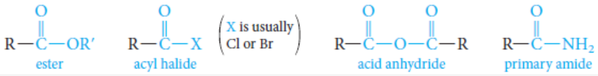
Reactions of Acids

$$R-\overset{\overset{O}{\|}}{C}-OH + :Nu \longrightarrow R-\overset{\overset{O}{\|}}{C}-Nu + OH^{\ominus}$$

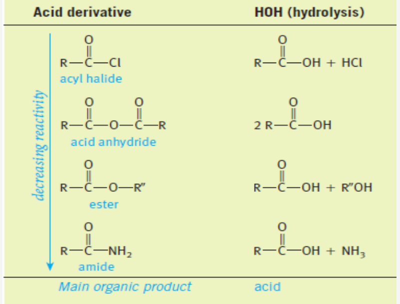


Carboxylic Acid Derivatives

- Carboxylic acid derivatives are compounds in which the hydroxyl part of the carboxyl group is replaced by various other groups.



- All acid derivatives can be hydrolyzed to the corresponding carboxylic acid.



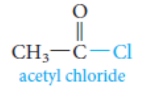
Acid derivative	HOH (hydrolysis)
$R-\overset{\overset{O}{\|}}{C}-Cl$ acyl halide	$R-\overset{\overset{O}{\|}}{C}-OH + HCl$
$R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R$ acid anhydride	$2\ R-\overset{\overset{O}{\|}}{C}-OH$
$R-\overset{\overset{O}{\|}}{C}-O-R''$ ester	$R-\overset{\overset{O}{\|}}{C}-OH + R''OH$
$R-\overset{\overset{O}{\|}}{C}-NH_2$ amide	$R-\overset{\overset{O}{\|}}{C}-OH + NH_3$
Main organic product	acid

Acid Chloride

Carboxylic Acid Derivatives

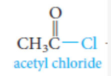
- Acyl chlorides have the general formula RCOCl.
- Acyl chlorides are more common and less expensive than bromides or iodides.
- **Nomenclature:**

  Acyl chlorides, or acid chlorides, are named by replacing the -ic acid ending of the parent acid by -yl chloride.



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

acetyl chloride

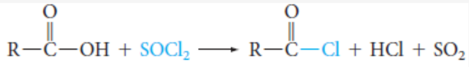


$CH_3\overset{O}{\overset{\|}{C}}-Cl$

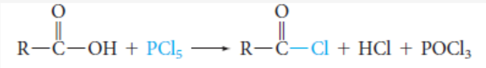
acetyl chloride

- **Preparation:**

  They can be prepared from acids by reaction with thionyl chloride or phosphorous pentachloride.



$$R-\overset{O}{\overset{\|}{C}}-OH + SOCl_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl + HCl + SO_2$$

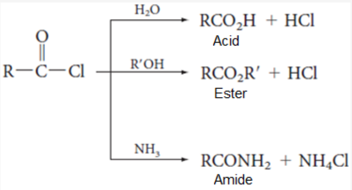


$$R-\overset{O}{\overset{\|}{C}}-OH + PCl_5 \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl + HCl + POCl_3$$

Acid Chloride

Carboxylic Acid Derivatives

- **Reactions:** *They can react rapidly with most nucleophile.*



$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{H_2O} RCO_2H + HCl$$

Acid

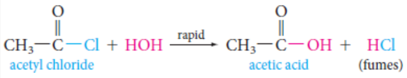
$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{R'OH} RCO_2R' + HCl$$

Ester

$$R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{NH_3} RCONH_2 + NH_4Cl$$

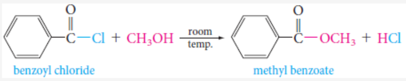
Amide

- **Examples:**

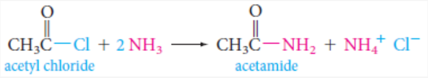


$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + HOH \xrightarrow{rapid} CH_3-\overset{O}{\overset{\|}{C}}-OH + HCl$$

acetyl chloride — acetic acid — (fumes)



benzoyl chloride — methyl benzoate



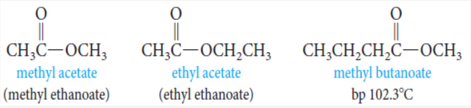
$$CH_3\overset{O}{\overset{\|}{C}}-Cl + 2\,NH_3 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}-NH_2 + NH_4^+\ Cl^-$$

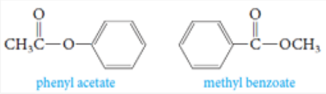
acetyl chloride — acetamide

Carboxylic Acid Derivatives

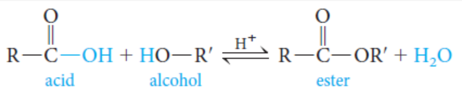
Esters

- Esters are derived from acids by replacing the –OH group by an –OR group and have the general formula R/COOR.
- **Nomenclature:**
  - They are named in a manner analogous to carboxylic acid salts.
  - The R part of the –OR group is name first, followed by the name of the acid, with the *–ic acid* ending changed to *–ate*.





- **Preparation:**
  When a carboxylic acid and an alcohol are heated in the presence of an acid catalyst (HCl or H_2SO_4), an equilibrium is established with the ester and water.

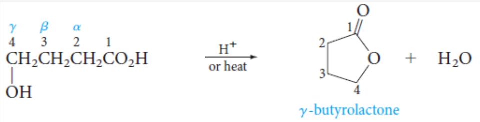


$$R-\overset{O}{\overset{\|}{C}}-OH + HO-R' \xrightleftharpoons{H^+} R-\overset{O}{\overset{\|}{C}}-OR' + H_2O$$

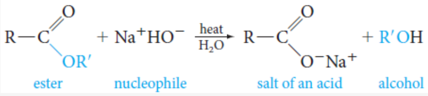
Carboxylic Acid Derivatives

Esters

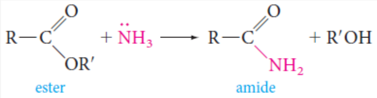
- **Reactions**
  - Cyclic esters (lactones) can be prepared from hydroxy acids if these groups can come in contact through bending of the chain.



  - Saponification; esters are commonly hydrolyzed with base.



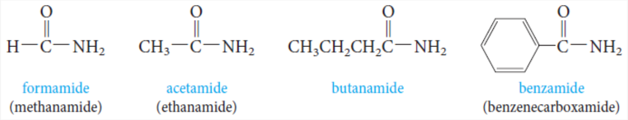
  - Ammonia converts esters to amides.

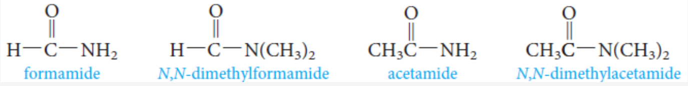


Amides

Carboxylic Acid Derivatives

- Amides are the least reactive of the common carboxylic acid derivatives.
- Primary amides have general formula $RCONH_2$.
- **Nomenclature:**
  Amides are named by replacing the *–ic or –oic acid* ending of the acid name, either the common or the IUPAC name, with the *–amide* ending.





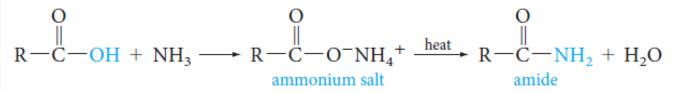
$$H-\overset{\overset{\large O}{\|}}{C}-NH_2 \qquad H-\overset{\overset{\large O}{\|}}{C}-N(CH_3)_2 \qquad CH_3\overset{\overset{\large O}{\|}}{C}-NH_2 \qquad CH_3\overset{\overset{\large O}{\|}}{C}-N(CH_3)_2$$

formamide, *N,N*-dimethylformamide, acetamide, *N,N*-dimethylacetamide

Amides

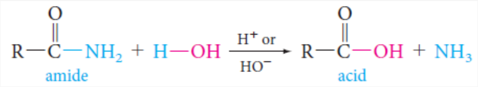
Carboxylic Acid Derivatives

- **Preparation:**
  - They can be prepared by the reaction of ammonia with esters, with acyl halides, or with acid anhydrides.
  - Amides can also prepared by heating the ammonium salts of acids.



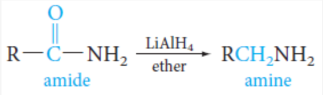
$$R-\overset{\overset{\large O}{\|}}{C}-OH + NH_3 \longrightarrow \underset{\text{ammonium salt}}{R-\overset{\overset{\large O}{\|}}{C}-O^-NH_4^+} \xrightarrow{\text{heat}} \underset{\text{amide}}{R-\overset{\overset{\large O}{\|}}{C}-NH_2} + H_2O$$

- **Reactions**
  - Amides react with nucleophiles and they can be hydrolyzed by water.



$$\underset{\text{amide}}{R-\overset{\overset{\large O}{\|}}{C}-NH_2} + H-OH \xrightarrow[HO^-]{H^+ \text{ or}} \underset{\text{acid}}{R-\overset{\overset{\large O}{\|}}{C}-OH} + NH_3$$

  - Amides can be reduced by lithium aluminums hydride to give amines.



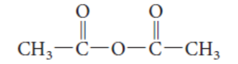
$$\underset{\text{amide}}{R-\overset{\overset{\large O}{\|}}{C}-NH_2} \xrightarrow[\text{ether}]{LiAlH_4} \underset{\text{amine}}{RCH_2NH_2}$$

Acid Anhydrides

Carboxylic Acid Derivatives

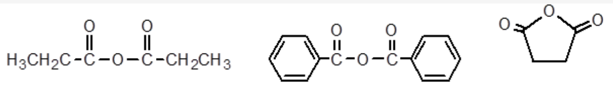
- Acid anhydrides have general formula RCOOCOR.
- **Nomenclature:**

The name of an anhydrides is obtained by naming the acid from which is derived and replacing the word acid with anhydride.



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

ethanoic anhydride or acetic anhydride



IUPAC name: Propanoic anhydride
Common name: Propionic anhydride

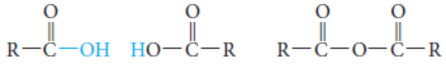
Benzoic anhydride

Succinic anhydride

Acid Anhydrides

Carboxylic Acid Derivatives

- **Preparation**
  - Acid anhydrides are derived from acids by removing water from two carboxyl groups and connecting the fragments.



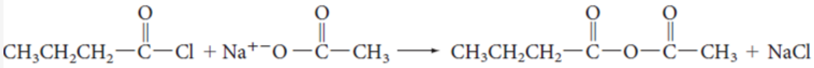
$$R-\overset{O}{\overset{\|}{C}}-OH \quad HO-\overset{O}{\overset{\|}{C}}-R \qquad R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$$

two acid molecules

an acid anhydride

  - Anhydrides can also be prepared from acid chlorides and carboxylate salts.

This method is used for preparing anhydrides derived from two different carboxylic acids (mixed anhydrides).



$$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-Cl + Na^{+-}O-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + NaCl$$

butanoic ethanoic anhydride

Acid Anhydrides

Carboxylic Acid Derivatives

- **Reactions**
  - Anhydrides undergo nucleophilic acyl substitution reactions (*They are more reactive than esters, but less reactive than acyl halides*).