VIII Functional Groups 2

8.1 Carboxylic Acids

**Carboxylic Acid**: Functional group in which OH is attached to carbon-oxygen double bond

Representations of Carboxylic Acids:

Functional Groups in Carboxylic Acids:

*Examples:*
8.1.1 Nomenclature

a) Common Names:

B) IUPAC Names:
The suffix for carboxylic acids is -oic
Priority:
carboxylic acid ⇒ aldehyde ⇒ ketone

Examples:
General Procedure for Naming Organic Compounds:

1) Name the longest carbon chain containing the highest priority functional group
2) Name the chain based on its single, double, or triple bonds
3) Name the highest priority group with its suffix and other groups with prefixes
4) Number the carbon chain
5) Name and number all other functional groups

8.1.2 Physical Properties

• Carboxylic acids can build hydrogen bonds:

• They can build very stable dimers:

**Dimers:** Two structural units
• Carboxylic acids have relatively high boiling points
• Low molecular weight carboxylic acids are water-soluble
8.1.3 Acidity

Like phenols, carboxylic acids are neutralized by NaOH:

- The pKₐ’s of carboxylic acids are around 5 (lower than phenols and alcohols)

*Example:*

- Reason for high stability is a very polar bond and a very stable anion:

**Structural Effects:**
- Electron donating group intensifies the negative charge ⇒ less acidic
- Electron withdrawing groups remove negative charge ⇒ more acidic

*Strength or EWG:*
Number of EWG:

Proximity of EWG:

- Aromatic carboxylic acids
- EWG enhance acidity (most potent in ortho and para)

Examples:

Nomenclature of the Salts of Carboxylic Acids:

**Salt**: Ionic compound composed of cation from a base and anion from neutralized acid

- In inorganic acids the suffix *-ic acid* is changed to ate and prefixing the name with the name of the cation that replaces the acidic hydrogen

Examples:
• Salts of carboxylic acids are named the same way

Examples:

8.1.4 Synthesis of Carboxylic Acids

A) Oxidations of Alkylbenzenes:

B) Oxidations of Primary Alcohols:

C) Hydrolysis of Nitriles:
D) Carbonation of Grignard Reagents:

8.2 Derivatives of Carboxylic Acid

General Formula:

**Acyl Group:**

**Carboxylic Acid:** Functional group in which OH, hydroxy, is attached to an acyl group

**Ester:** Functional group in which OR, alkoxy, is attached to an acyl group

**Amide:** Functional group in which NH₂, NHR, or NR₂, is attached to an acyl group

**Acid Chloride:** Functional group in which Cl, chloride, is attached to an acyl group

**Acid Anhydride:** Functional group in which RCO₂ of one acid molecule is bonded to the acyl group of another
Examples:

8.2.1 Nomenclature of Carboxylic Acid Derivatives

- Named by changing the suffix

A) Acid Chlorides:

B) Acid Anhydrides:
C) Esters:

D) Amides:

8.2.2 Nucleophilic Acyl Substitution Reactions

**Nucleophilic Acyl Substitution:** Nucleophilic substitution in which an atom or group attached to an acyl group, RC=O, is replaced

*Examples:*

Order of Reactivity:
Reaction Mechanism:
A) Nucleophilic Acyl Substitution Reactions of Acid Chlorides:

• Synthesis of acid chlorides:

• Reactions:

Examples:
• Mechanism:

B) Nucleophilic Acyl Substitution Reactions of Acid Anhydrides:
• Synthesis:

• Reactions:
C) Nucleophilic Acyl Substitution Reactions of Carboxylic Acids:

• Mechanism:
D) Nucleophilic Acyl Substitution Reactions of Esters:

**Hydrolysis:** Cleavage of a bond by water

**Transesterification:** Conversion of one ester into another by replacing the OR group

- Reactions of esters:

- Mechanism:
• Synthesis of Esters by Nucleophilic Acyl Substitution:

E) Nucleophilic Acyl Substitution Reactions of Amides:

*Where are these reactions used?*

**Polyamide:** Polymer in which the structural repeating units are connected by amide linkages

**Polyester:** Polymer in which the structural repeating units are connected by ester linkages

*Examples:*
8.2.3 Addition Reactions

- Reductions with LiAlH$_4$:

Examples:

- Reactions with Grignard Reagents
8.2.4 Reactions Involving Carbanions

A) Malonic Ester Synthesis

**Malonic Ester Synthesis**: A method of preparing disubstituted acetic acids
B) Claisen Condensation:

**Claisen Condensation**: A method for making β keto esters from esters with α hydrogens

**Mechanism:**
Examples from Biology:
8.3 Amines

Amine: Derivative of ammonia in which one or more hydrogens are replaced by organic groups

Examples:

Structure:

| Ammonia | Primary Amine | Secondary Amine | Tertiary Amine |

Arylamine: Derivative of ammonia in which one or more hydrogens are replaced by aromatic rings

Example:
8.3.1 Nomenclature

General: alkyl-amine

Examples:

If you have a ring as substituent:

If you have an unsaturated amine:
8.3.2 Physical Properties

- Can undergo hydrogen bonding

Decrease in hydrogen bonding

Basicity of amines

- Amines are LEWIS BASES, they have a lone pair
- The lone pair can be shared to form salts:

- Amines are weak bases
  
  if dissolved in water you get an equilibrium:

  
  with an equilibrium constant

$pK_b$: The negative logarithm of the basicity constant

Weak base           Increasing basicity           Strong base
• Relationship of structure and basicity in amines:
  - electron-releasing (donating) groups increase basicity
  - electron-withdrawing groups decrease basicity
  - aromatic amines are less basic than alkyl amines (resonance)
  - electron-donating groups on aromatic rings increase basicity

8.3.3 Synthesis of Amines

A) Reduction:

**Reduction**: Introduction of hydrogen into a molecule, often resulting in the loss of oxygen or conversion of double bonds to single bonds
• Reduction of aromatic nitro compounds

Examples:

• Reduction of nitriles

Examples:

• Reduction of amides

Examples:
8.3.4 Amines as Nucleophiles

- Amines are effective nucleophiles than can react with alkylhalides

Examples:

- The salt formed is called **Quaternary Ammonium Salt**

Consecutive alkylation:

8.3.5 Aromatic Diazonium Salts

**Diazonium salt:** Compound in which a molecule of nitrogen is bonded to an aromatic ring

- Preparation:
• Resonance form:

• Replacement reactions (Sandmeyer Reaction)
• Coupling reactions:
• Diazonium salts can couple to HIGHLY activated aromatic rings

General Reaction:

Examples:

8.3.6 Heterocyclic Amines

Heterocycle: Cyclic compound where at least one ring atom is NOT carbon

Piperidine Pyridine Pyrrolidine Pyrrole

Alkaloids: Plant-produced nitrogenous bases that have physiological effects on humans
Examples:
Summary of Chapter 6:

⇒ **Carboxylic Acids**
  → Nomenclature
  → Physical Properties
  → Acidity
  → Preparation

⇒ **Derivatives of Carboxylic Acids**
  → Esters
  → Amides
  → Anhydrides
  → Acid Chlorides
  → Nomenclature
  → Nucleophilic Acyl Substitution
  → Preparation of Derivatives
  → Reactivity of Derivatives
  → Addition Reactions
  → Reactions Containing Carbanion

⇒ **Amines**
  → Nomenclature
  → Physical Properties
  → Preparation
  → Reactivity
  → Sandmeyer Reaction
  → Heterocycles
  → Alkaloids