Carboxylic Acides And Their Derivative

Chapter 10

1432-2011

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Chapter outlines:

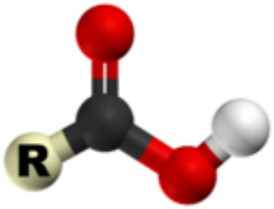
Part I: Carboxylic acids

- ✓Definition of carboxylic acids.
- ✓Nomenclature of carboxylic acids.
  - Common Names.
  - IUPAC Nomenclature.
- ✓Physical properties of carboxylic acids.
- ✓Acidity and acid strength.
- ✓General methods for carboxylic acids.
- ✓Reactions for carboxylic acids.

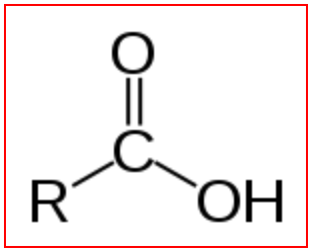
Part II: Derivatives of Carboxylic acids

1. Acid Chloride : *short nomenclature; reactions*.
2. Esters: *short nomenclature; reactions*.
3. Amides: *short nomenclature; reactions*.
4. Acid Anhydride: *short nomenclature; reactions*.

Carboxylic Acids



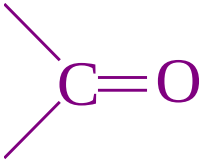
Definition



- A carboxylic acid contains a carboxy (carboxyl) group; which can be expressed by either –COOH, $–CO_2H$,or

- A carboxylic acid has one oxygen atom **doubly bonded** to the carbon atom and a hydroxy (OH) group **singly bonded** to the carbon atom.

- The name is a combination of two the components of the group

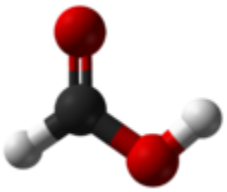
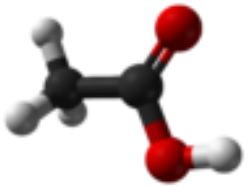
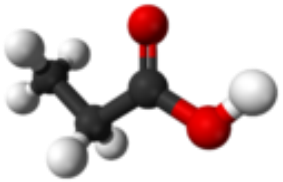
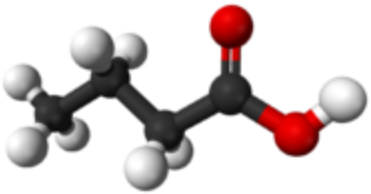
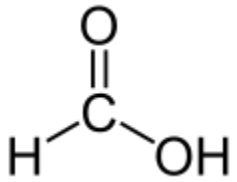
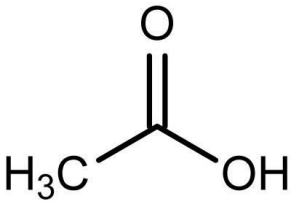
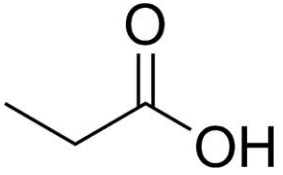
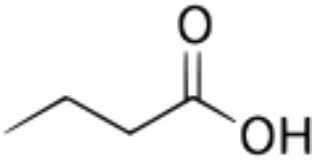


, carbonyl, and hydroxyl —OH

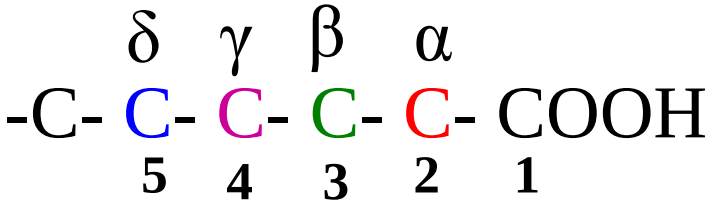
- Carboxylic acids are classified as aliphatic or aromatic depending on whether R or an Ar is attached to the carboxylic group R-COOH or Ar-COOH.

Common Names

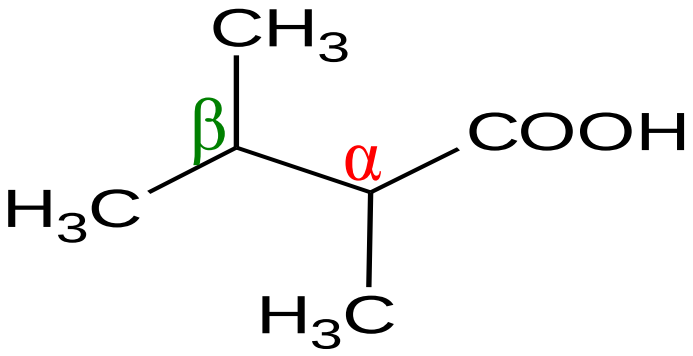
- Carboxylic acids are example of a situation where the compounds were known and named long before anyone thought of the IUPAC method of naming compounds.

				
				
Common	Formic acid	Acetic Acid	Propionic acid	Butyric acid
IUPAC	Methanoic acid	Ethanoic acid	Propanoic acid	Butanoic acid

- the position of the carbons present on the acid chain, are located by the Greek letters α indicating the carbon atom next to COOH group (C2), β (C3), γ (C4), δ (C5), etc



Examples

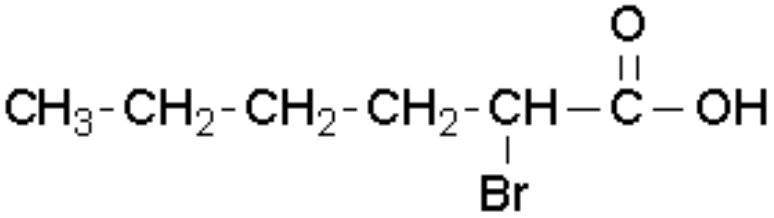


α-β- Dimethyl butyric acid

IUPAC Nomenclature

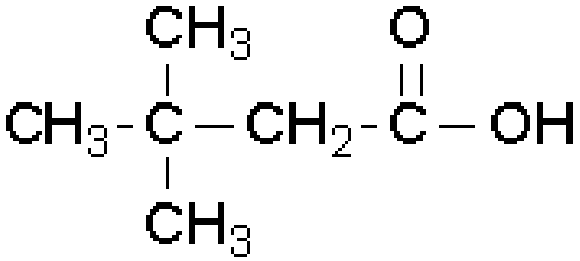
- Carboxylic acids are named by dropping the -e ending of the parent name and adding -oic acid
- The carboxylic carbon is numbered 1.
- The substituent name for a -COOH group is carboxy.
- If there are substituents identify their names, positions and list them as prefixes in alphabetical order.

Examples:



IUPAC: 2, bromohexanoic acid

Common: α, bromohexanoic acid

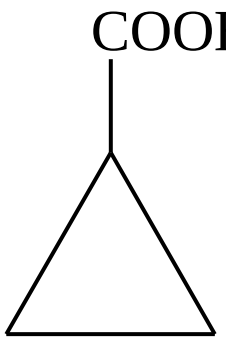


IUPAC: 3,3-dimethylbutanoic acid

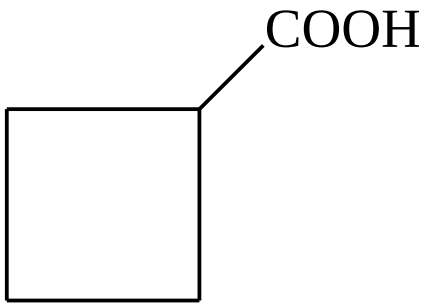
Common: β,β-dimethylbutyric acid

Naming cyclic carboxylic acids

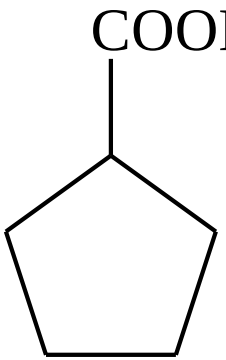
➢Cyclic compounds containing one or more COOH groups attached to the ring are **named by** identifying the name of the ring followed by the word carboxylic acid or dicarboxylic acids etc.



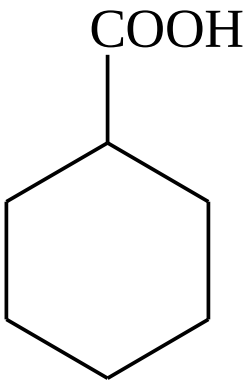
Cyclopropane carboxylic acid



Cyclobutanecarboxylic acid



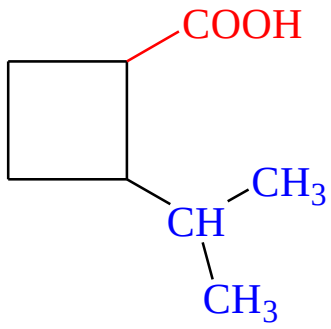
Cyclopentanecarboxylic acid



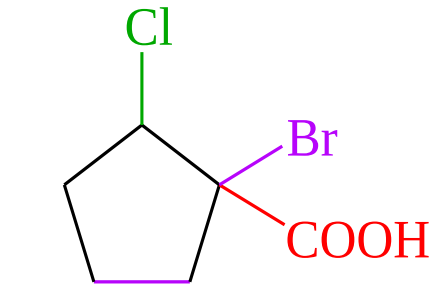
Cyclohexanecarboxylic acid

Examples

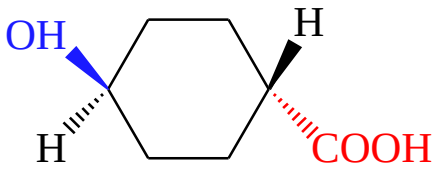
➢ The carbon atom bearing the carboxylic group is numbered 1 and the substituents are numbered relative to it.



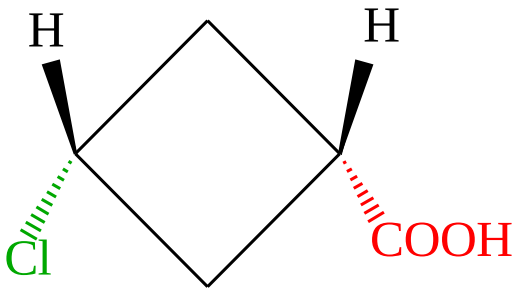
2-Isopropylcyclobutane carboxylic acids



1-Bromo-2-chlorocyclopentane carboxylic acids



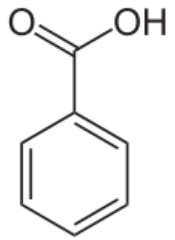
Trans-4-hydroxycyclohexane carboxylic acids



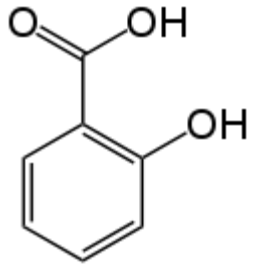
Cis-3-chlorocyclobutane carboxylic acid

Naming Aromatic carboxylic acids

- The simplest aromatic carboxylic acid is benzoic acid.
- Substituted benzoic acids are named with benzoic acid as the parent name.
- Derivatives are named using numbers to show the location of substituents relative to the carboxyl group.
- The ring carbon attached to the carboxyl group is the #1 position.

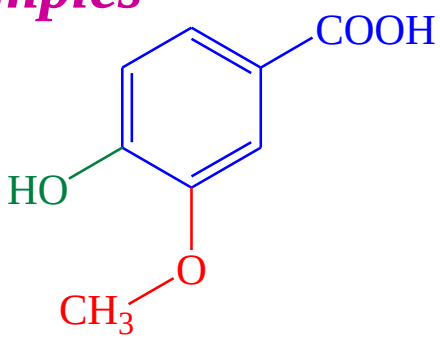


Benzoic acid
Benzene carboxylic acid

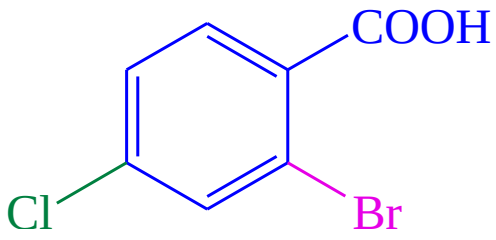


Salicylic acid
2-Hydroxybenzoic acid

Examples



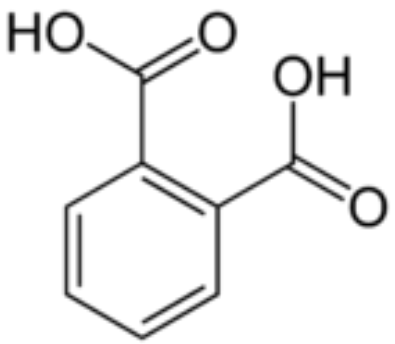
4-hydroxy-5-methoxy benzoic acid



2-Bromo-4-chloro benzoic acid

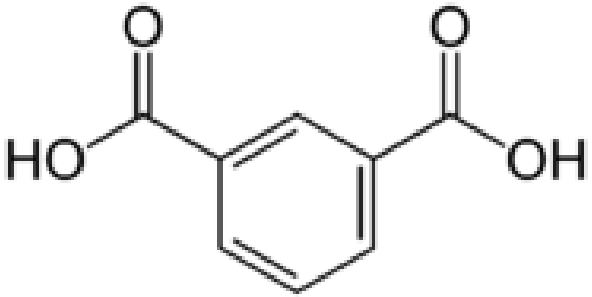
• Phthalic acid is one of three isomers (1,2-dicarboxylic acid) benzene with the composition benzenedicarboxylic acid, the others being isophthalic and terephthalic acid.

• Sometimes the term "phthalic acids" is used to ***refer to*** this family of isomers, but in the singular, "phthalic acid", refers exclusively to the *ortho*- isomer



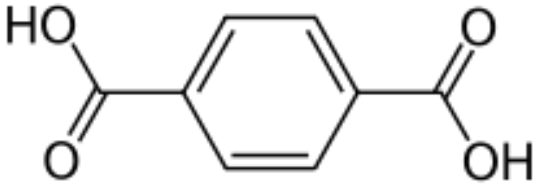
Phthalic acid

Benzene-1,2-dicarboxylic acid



Isophthalic acid

Benzene-1,3-dicarboxylic acid



Terephthalic acid

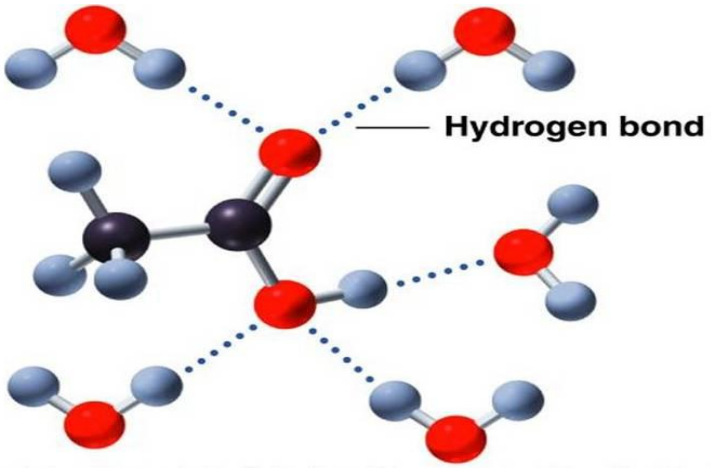
Benzene-1,4-dicarboxylic acid

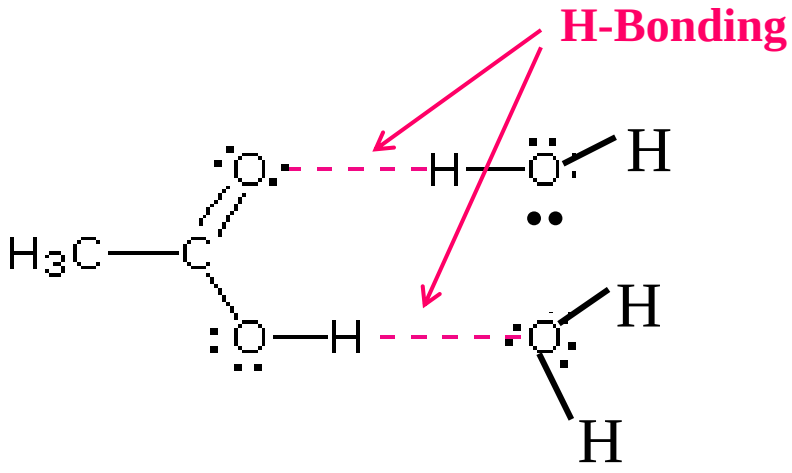
Physical Properties of Carboxylic Acids

1. Solubility

- The carboxylic acid are highly polar organic compounds.

- This polarity results from the presence of a strongly polarized carbonyl (C=O) group and hydroxyl (O-H) group.

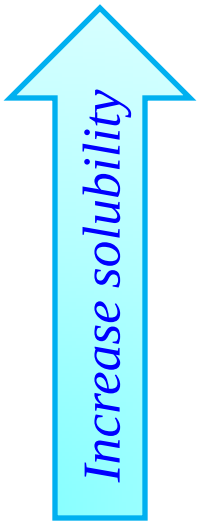




- They form hydrogen bonds with water molecules **through both** the C=O and OH groups

•The lower members of carboxylic acids are miscible with water , the solubility of the bigger acids decreases very rapidly with size.

– Carbons 1-4 = water soluble
– Carbons 5-8 = slightly water soluble
– Carbons 8 and above = virtually insoluble in water.



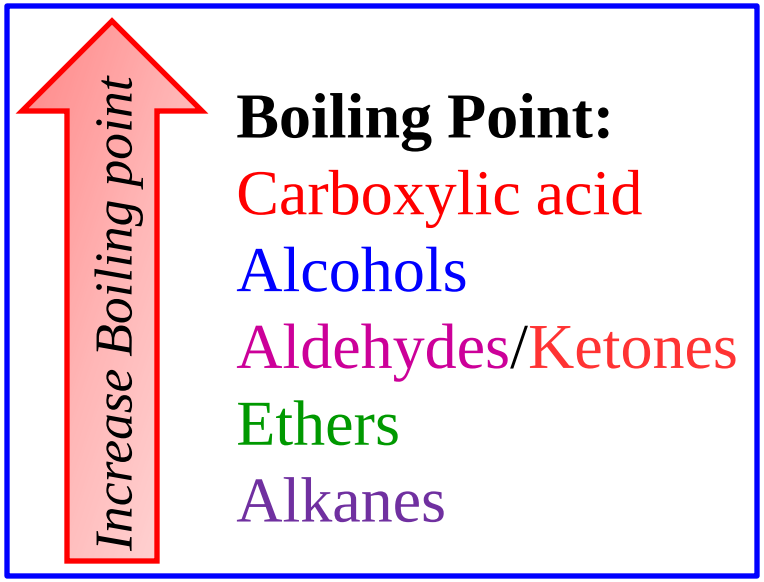
Water Solubility:
Carboxylic acid
Alcohols
Aldehydes/Ketones
Ethers
Alkanes

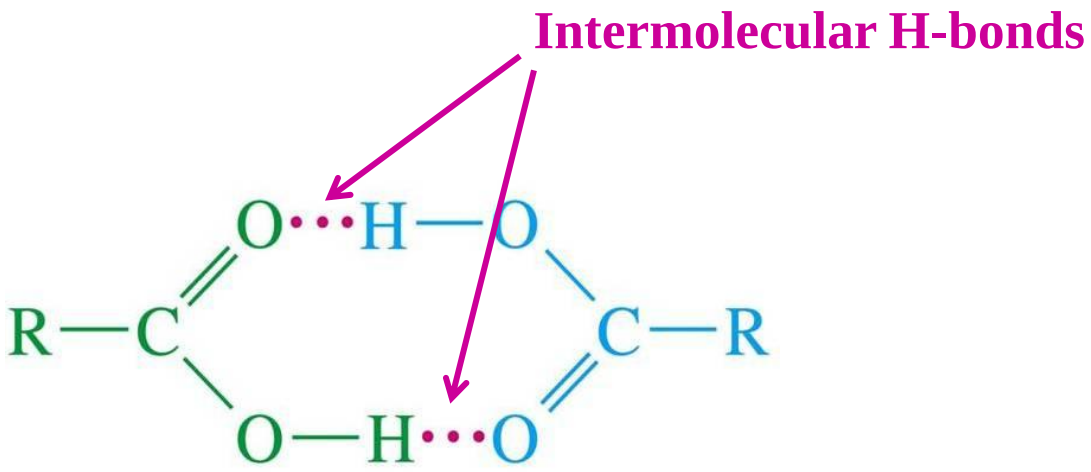
• Carboxylic acids are more soluble in water than alcohols, ethers, aldehydes, and ketones of comparable molecular weight.

•Aromatic carboxylic acids are **insoluble** in water.

2. Boiling Point

- Carboxylic acids are polar compounds and form very strong intermolecular hydrogen bonds.



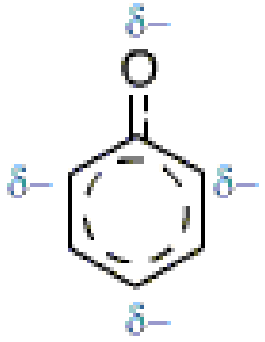


- Carboxylic acids have significantly higher boiling points than other types of organic compounds of comparable molecular weight.

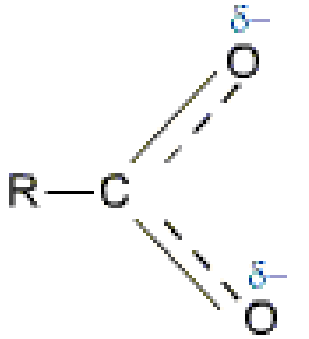
Compound	Structure	Chem. formula	Mol wt	Bp (°C)
Acetic acid	CH_3COOH	$C_2H_4O_2$	60.05	118
n- Propylalcohol	$CH_3CH_2CH_2OH$	C_3H_8O	60.01	97

Acidity and Acid Strength

- The most important chemical property of carboxylic acids chemistry is their acidic nature.
- The mineral acids (HCl, HBr, HI, H_2SO_4, H_3PO_4) are defined as "strong acids" because they undergo complete dissociation.
- Carboxylic acids are weak acids, they are much more acidic than alcohols.
- Carboxylic acids are stronger acids than phenols.



Phenoxide ion
(Less stable)



Carboxylate ion
(More stable)

"Because in carboxylate ion, the negative charge is equally distributed over two electronegative atoms (oxygen atoms) while in phenoxide ion, it is present only on one oxygen".

Effect of substituents on the acidity of carboxylic acids

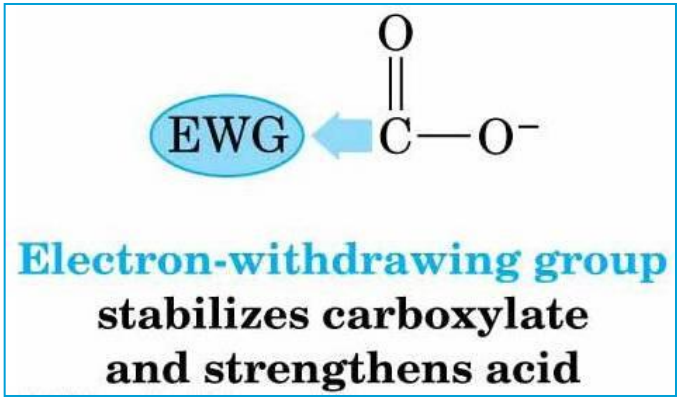
1. Effect of Substituent **Type**:

If we compare the acid strength of an unsubstituted carboxylic acid with one that bears an EWG or EDG substituted on the R or the Ar of the molecule.

We find that:

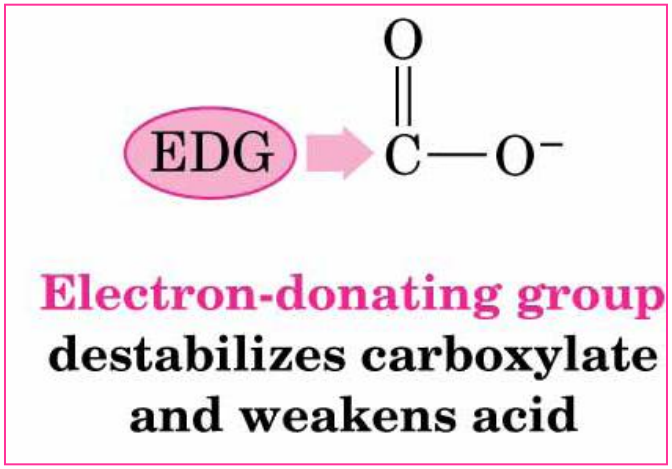
✓An electronegative group will drive the ionization equilibrium toward dissociation, increasing acidity.

Examples: F, Cl, Br, NO_2, CN, SO_3H, COOH



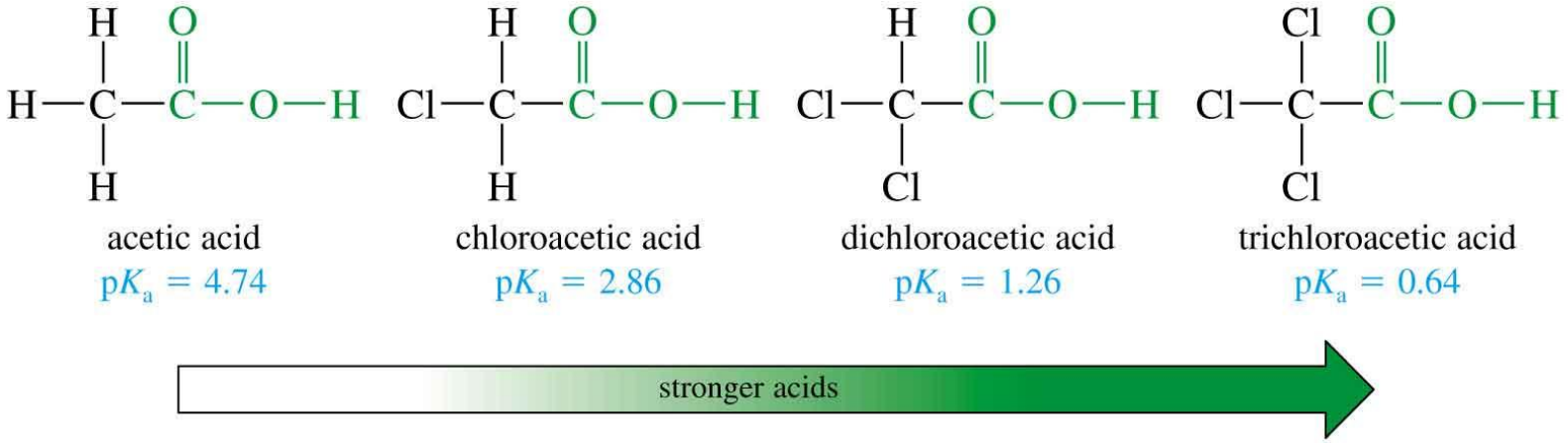
✓An electron-donating group destabilizes the carboxylate anion and decreases acidity.

Examples: CH_3, C_2H_5, C_3H_7,… etc



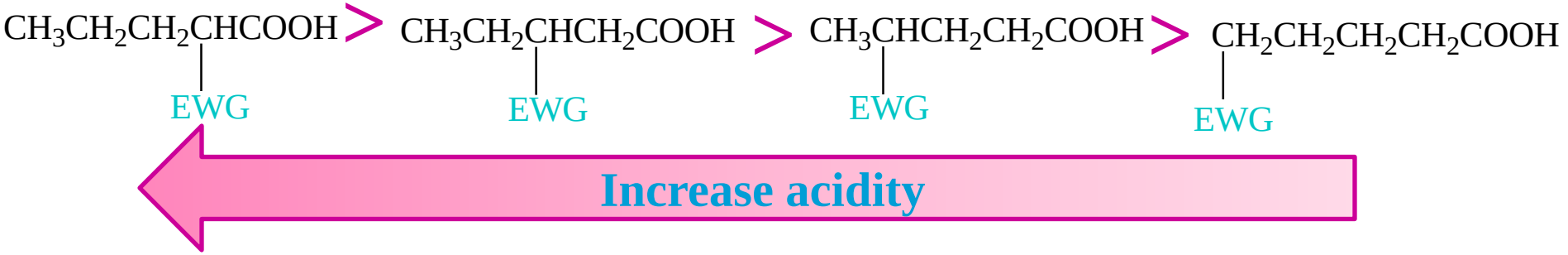
2. Effect of **number** of electron withdrawing groups:

As the number of electron withdrawing groups increases, the acid strength increasing.



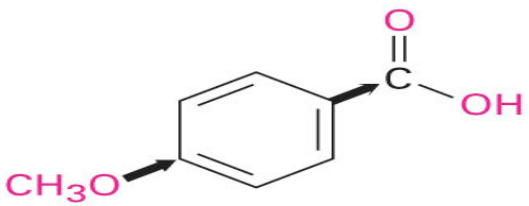
3. Effect of **position** of electron withdrawing group:

As the distance between electron withdrawing group and carboxylic group increases, electron withdrawing influence decreases.

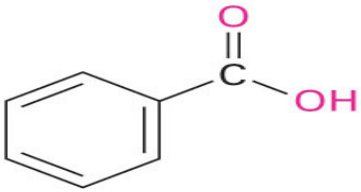


Aromatic Substituent Effects

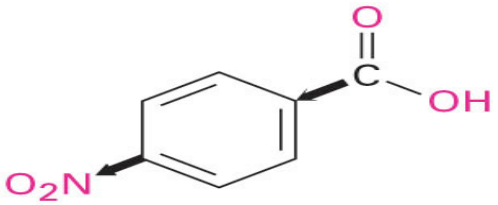
- An electron-withdrawing group (-NO_2) increases acidity by stabilizing the carboxylate anion.
- An electron donating (activating) group (OCH_3) decreases acidity by destabilizing the carboxylate anion.



p-Methoxybenzoic acid
($pK_a = 4.46$)



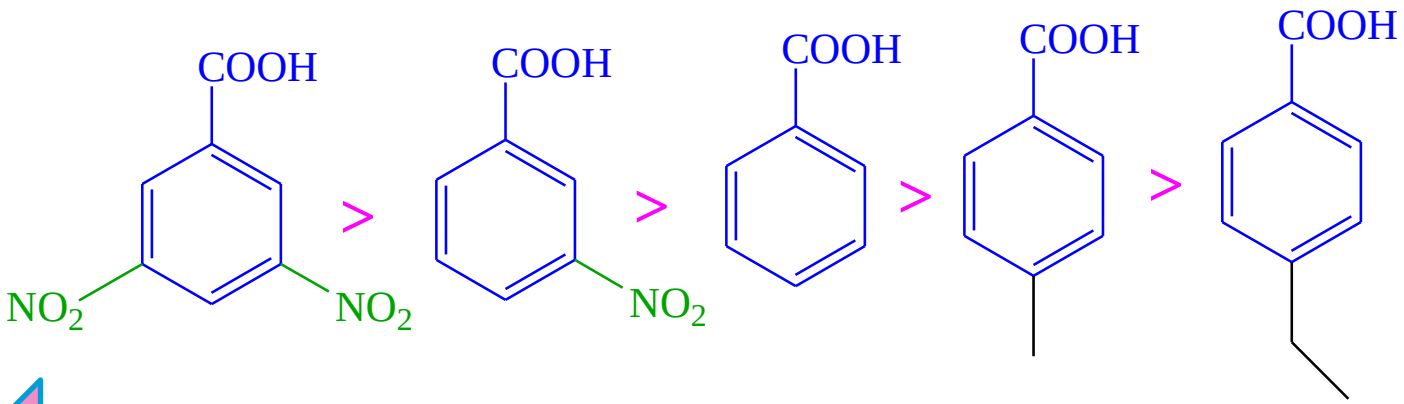
Benzoic acid
($pK_a = 4.19$)



p-Nitrobenzoic acid
($pK_a = 3.41$)

Acidity

Example



Increase acidity

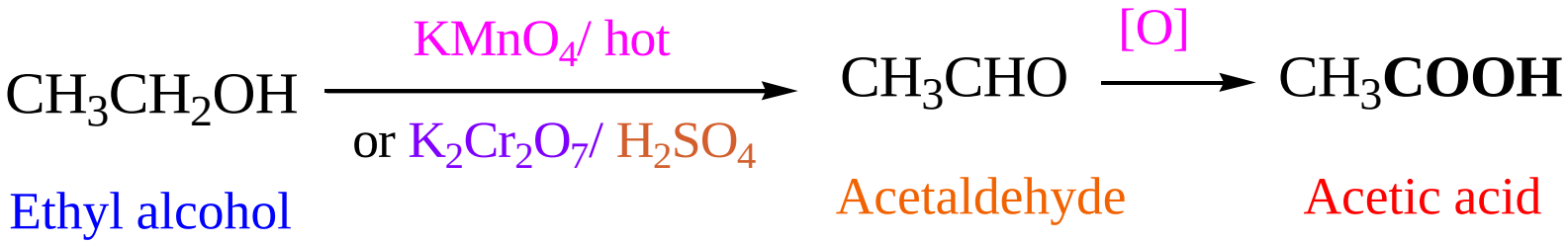
General methods for preparing Carboxylic acids:

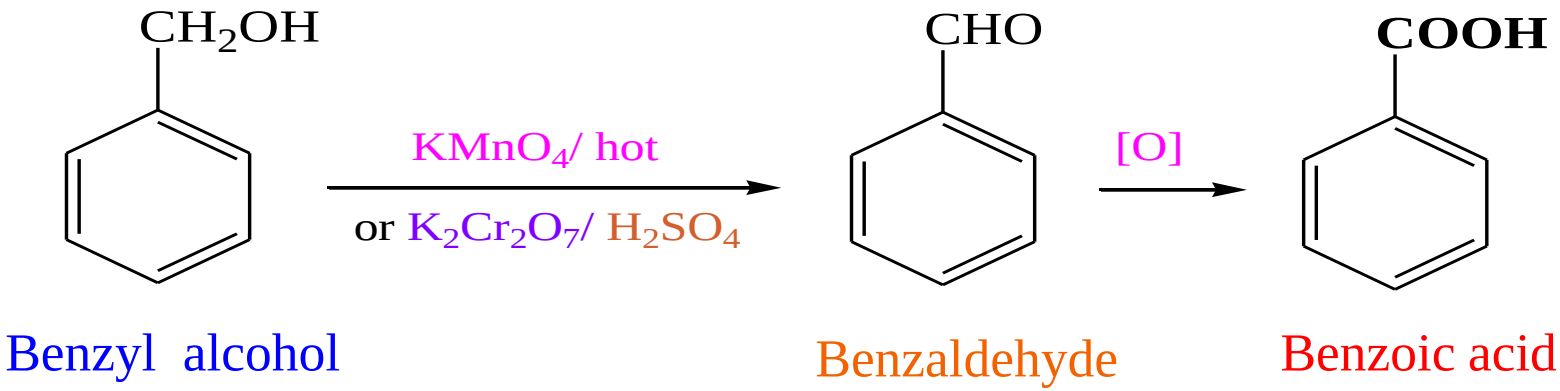
There are three general methods for preparing carboxylic acids.

1. Oxidation:

a. Oxidation of primary alcohols and aldehydes

Primary alcohols are oxidized quickly to carboxylic acids by potassium permanganate, $KMNO_4$, or by a mixture of potassium dichromate; $K_2C_{r2}O_7$, and sulfuric acid.

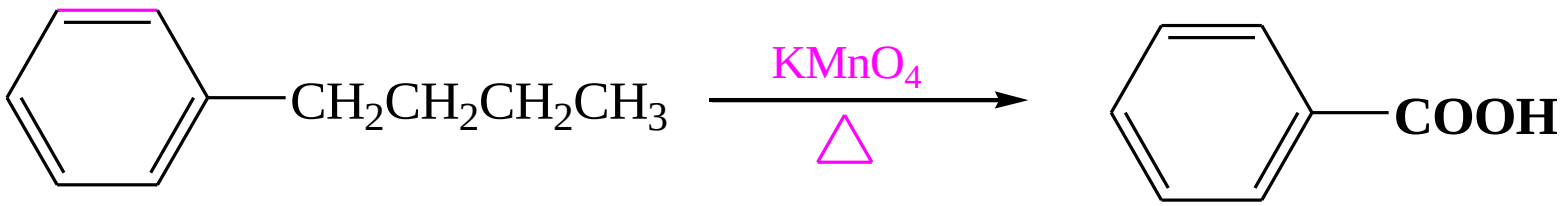




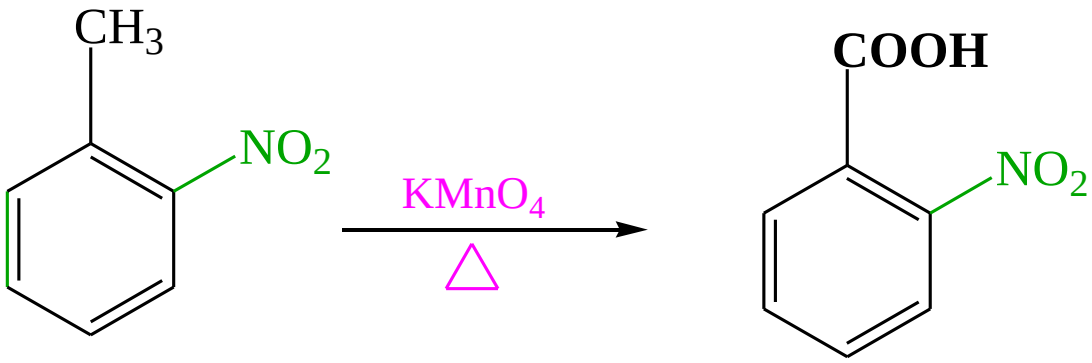
b. Oxidation of Alkylbenzene

If the carbon directly attached to the aromatic ring has > 1 hydrogen attached to it, it can be oxidized to the corresponding carboxylic acid with hot aqueous potassium permanganate ($KMnO_4$) as shown below.

Examples



n-butyl benzene — Benzoic acid

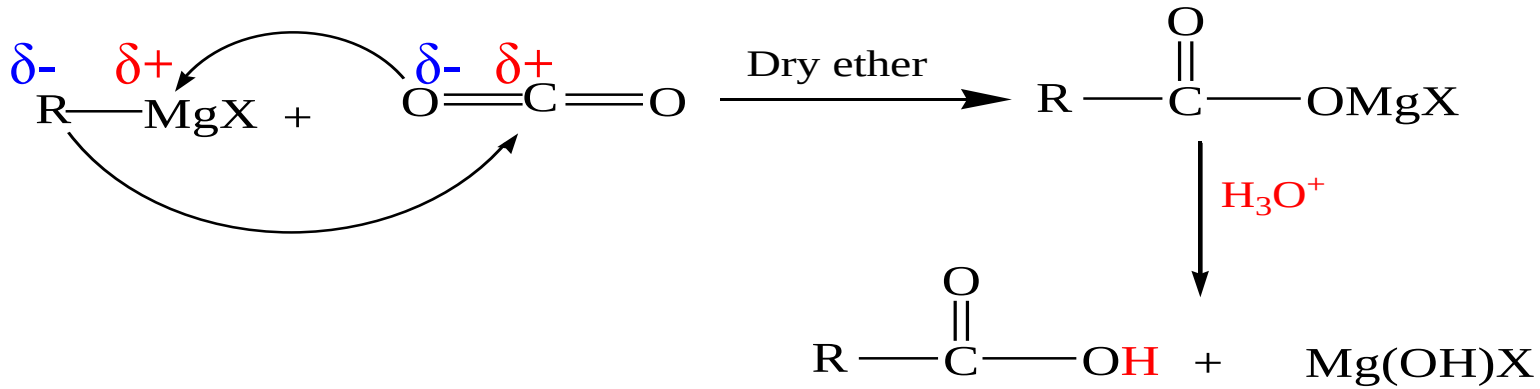


o- Nitro toluene — *o*- Nitro benzoic acid

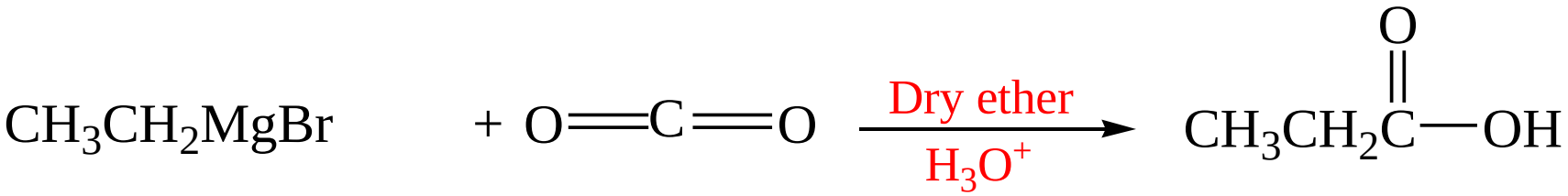
2. Carbonation of Grignard Reagents:

The addition of Grignard reagents to CO_2 in form of dry ice **gives** an acid with one more carbon more than the original Grignard reagent.

General Equation



Example:



3. Hydrolysis of Nitriles:

Nitriles are compounds with general formula: $RC{\equiv}N$ or $ArC{\equiv}N$

They are prepared by reacting a 1° or 2° alkyl halide with cyanide salt.

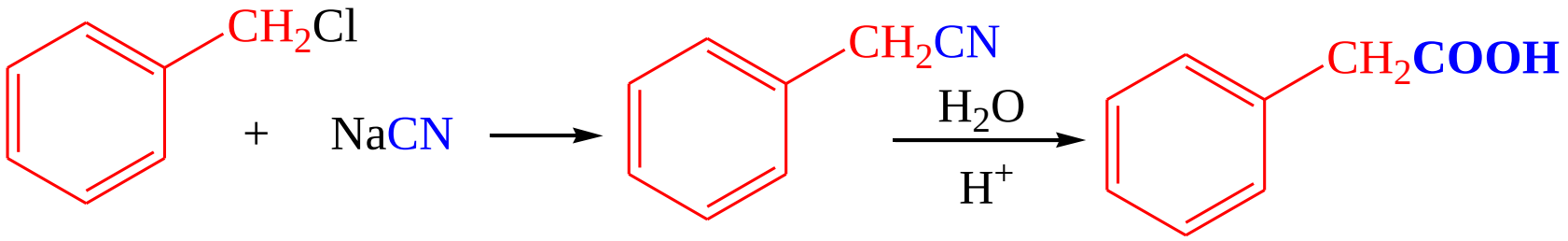
Acid hydrolysis of a nitriles yields a carboxylic acids.

General Equation

$$RX + NaC{\equiv}N \longrightarrow RC{\equiv}N \xrightarrow[H^+]{H_2O} \mathbf{RCOOH}$$

Example:

$$CH_3CH_2Cl + NaCN \longrightarrow CH_3CH_2CN \longrightarrow \mathbf{CH_3CH_2COOH}$$

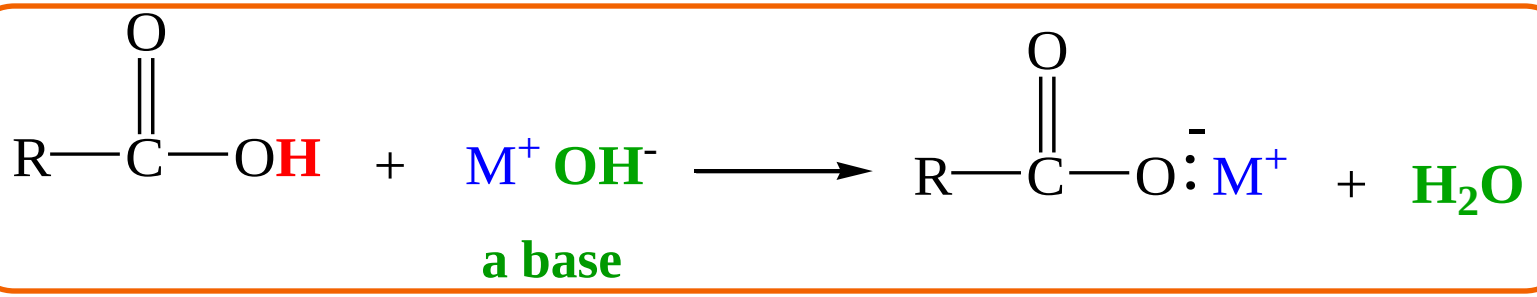


Reactions with Carboxylic acids:

The reactions of acids are basically of two types:

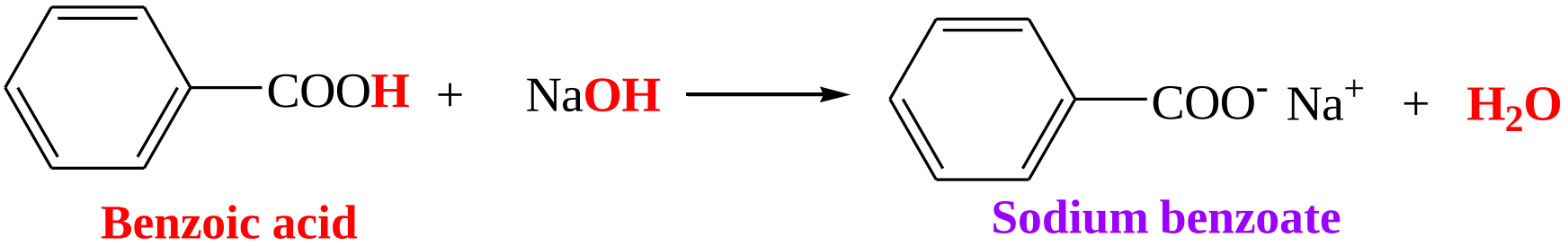
1. Reaction with bases to form salts:

General Equation



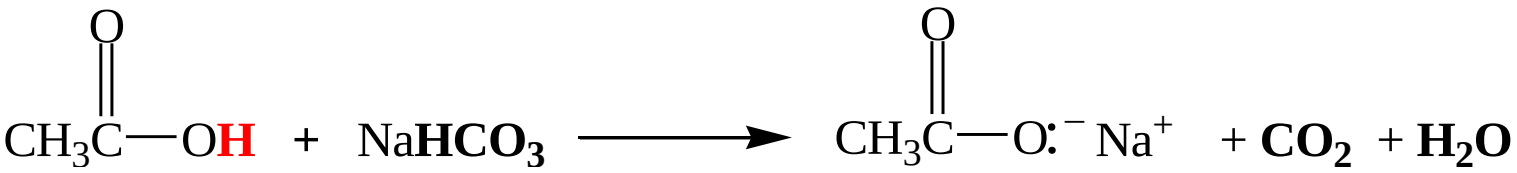
The carboxyl hydrogen is replaced by metal ion, M^+.

Case "1" with stroge base

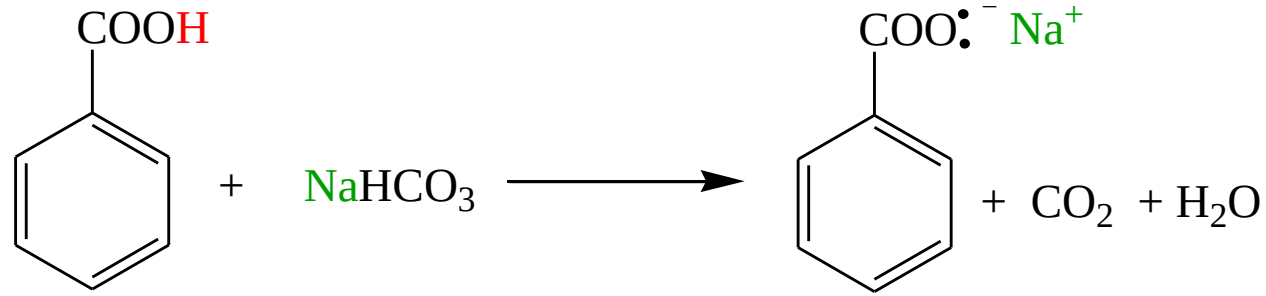


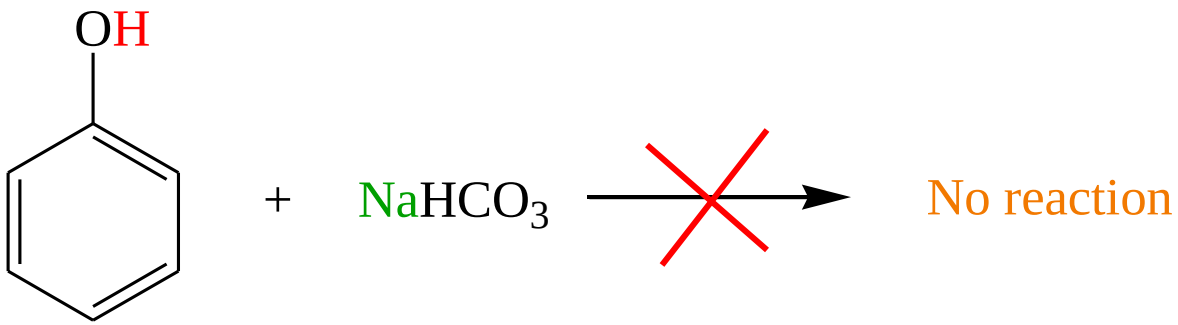
Case "2" with weak base

Carboxylic acids will also react with a weak base such as sodium bicarbonate, To form water soluble salt.



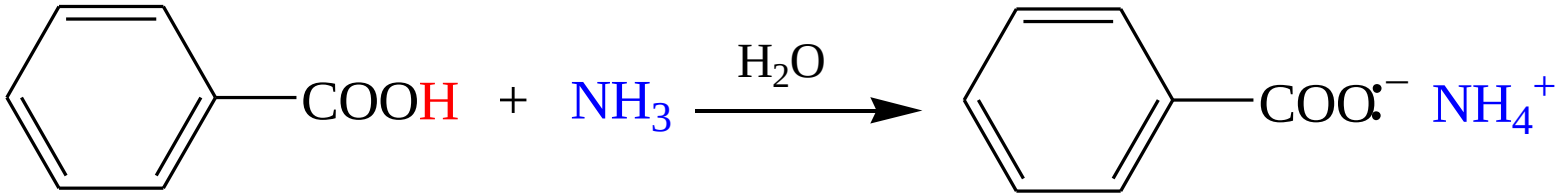
Weaker acids like phenols react only with strong bases like (NaOH or KOH) and will not react with $NaHCO_3$





Case "3" with basic amines

Carboxylic acids also form water-soluble salts with ammonia; NH_3 and amines.

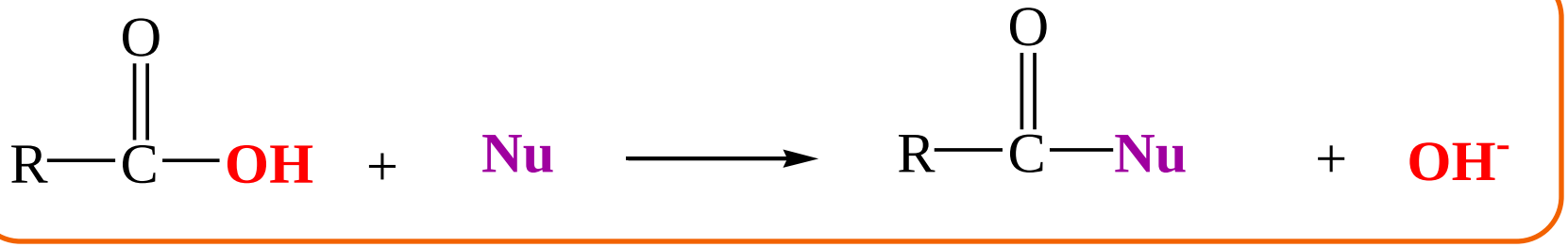


Benzoic acids **Ammonium benzoate**

2. Reaction with nucleophiles to form acid derivatives:

The OH of the carboxyl group is replaced by a nucleophile, a process known as nucleopilic substitution.

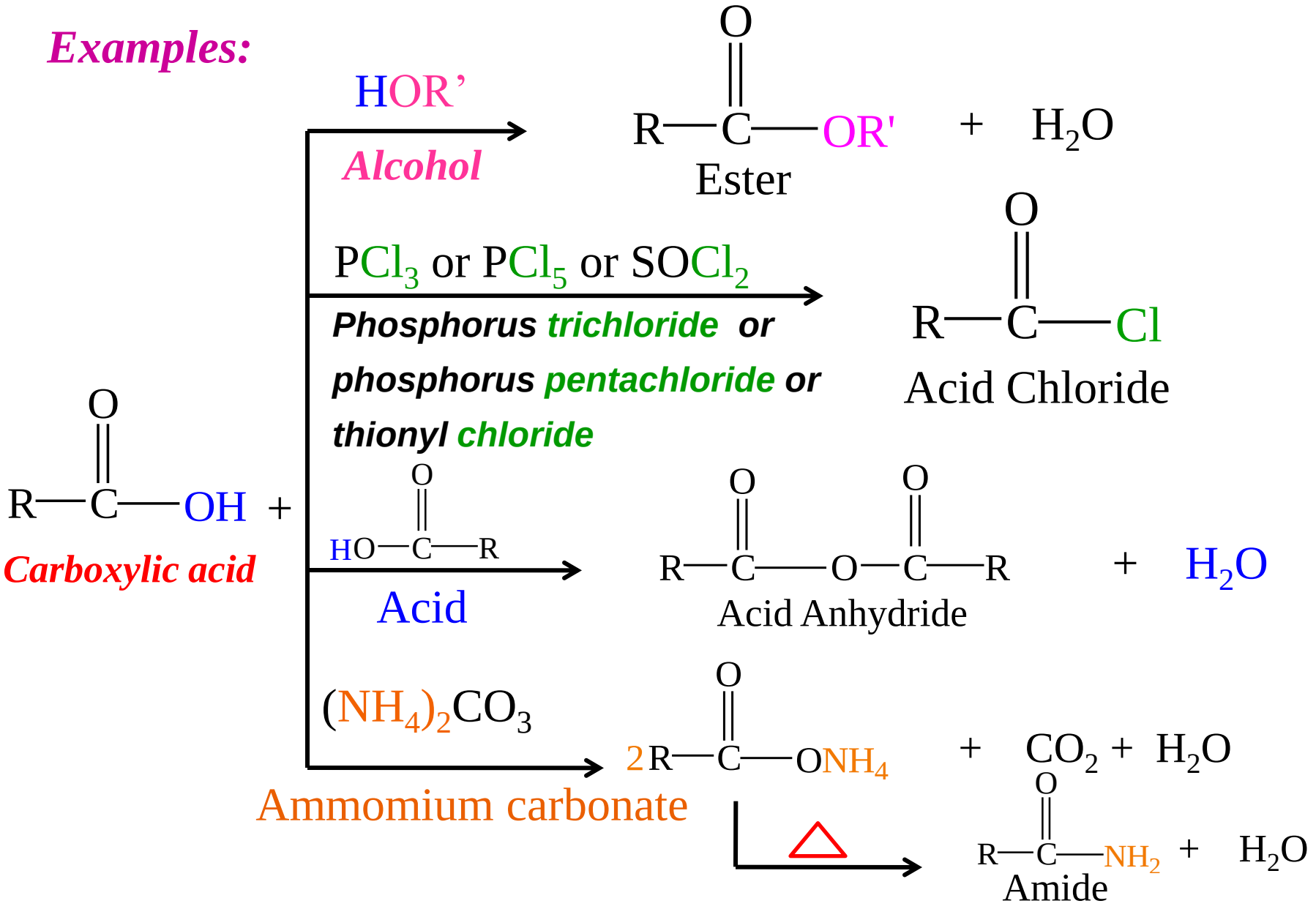
General Equation



a nucleophile

When the OH of a carboxylic acid is replaced by a nucleophile, :Nu, a **carboxylic acid derivative** is produced.

Examples:



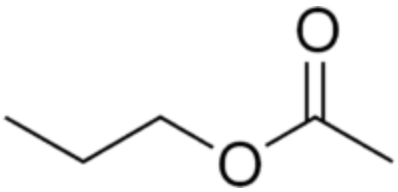
Part II: Derivatives of Carboxylic acids

1. Esters

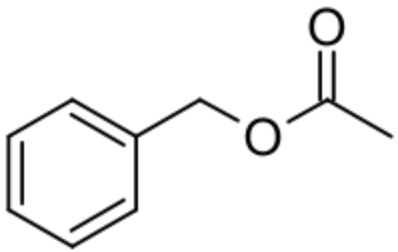
- -OH of acid is replaced with -OR group.
- Name R group like a side chain (with a space).

- Then name acid portion with -oate ending.

Examples:

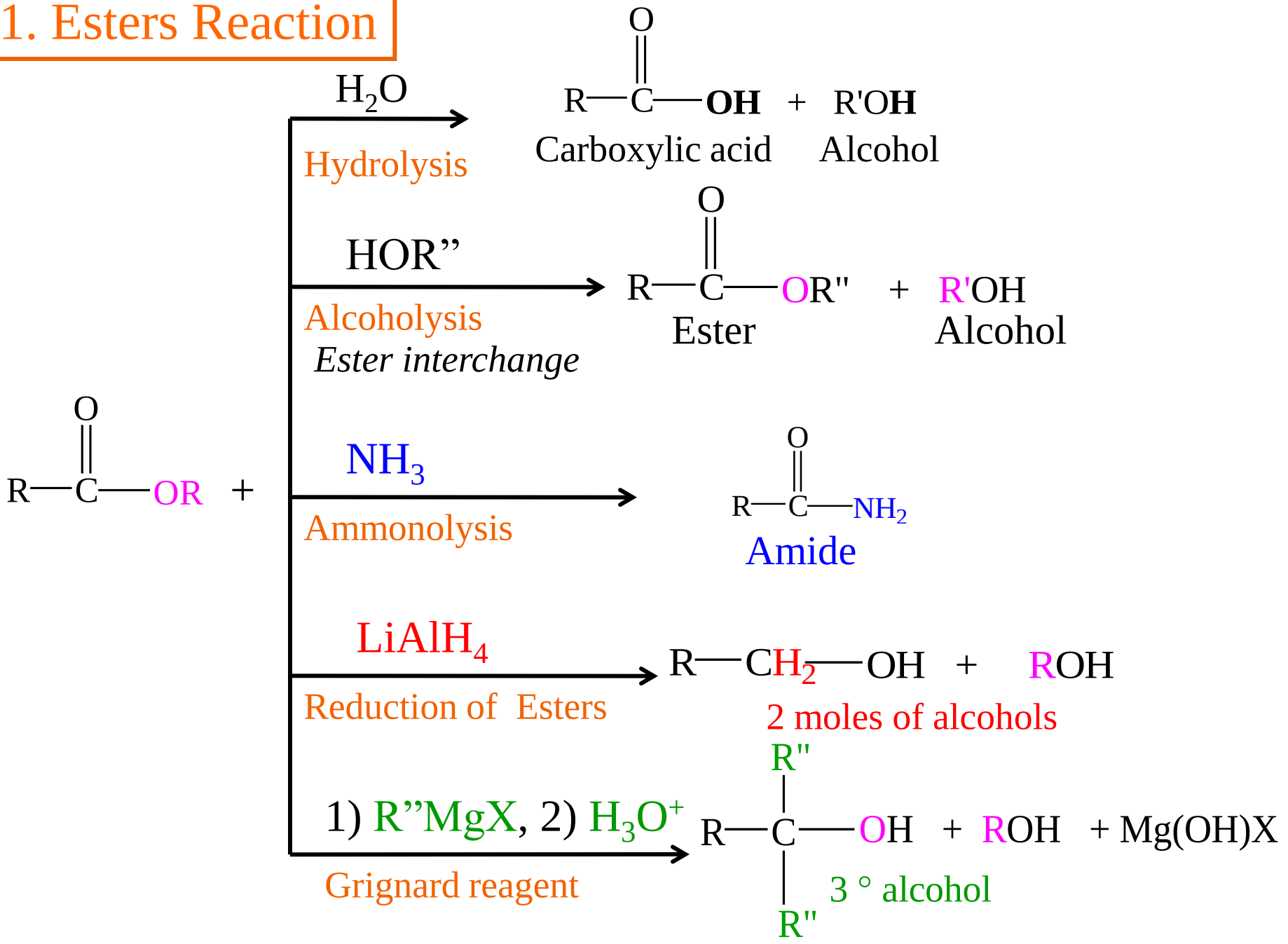


Propyl ethanoate



Benzyl ethanoate

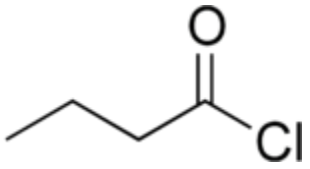
1. Esters Reaction



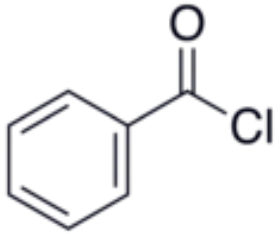
2. Acid Halide

-OH of acid is replaced with a F, Cl, Br or I.
Name like with acid but use -oyl halide.

Examples:

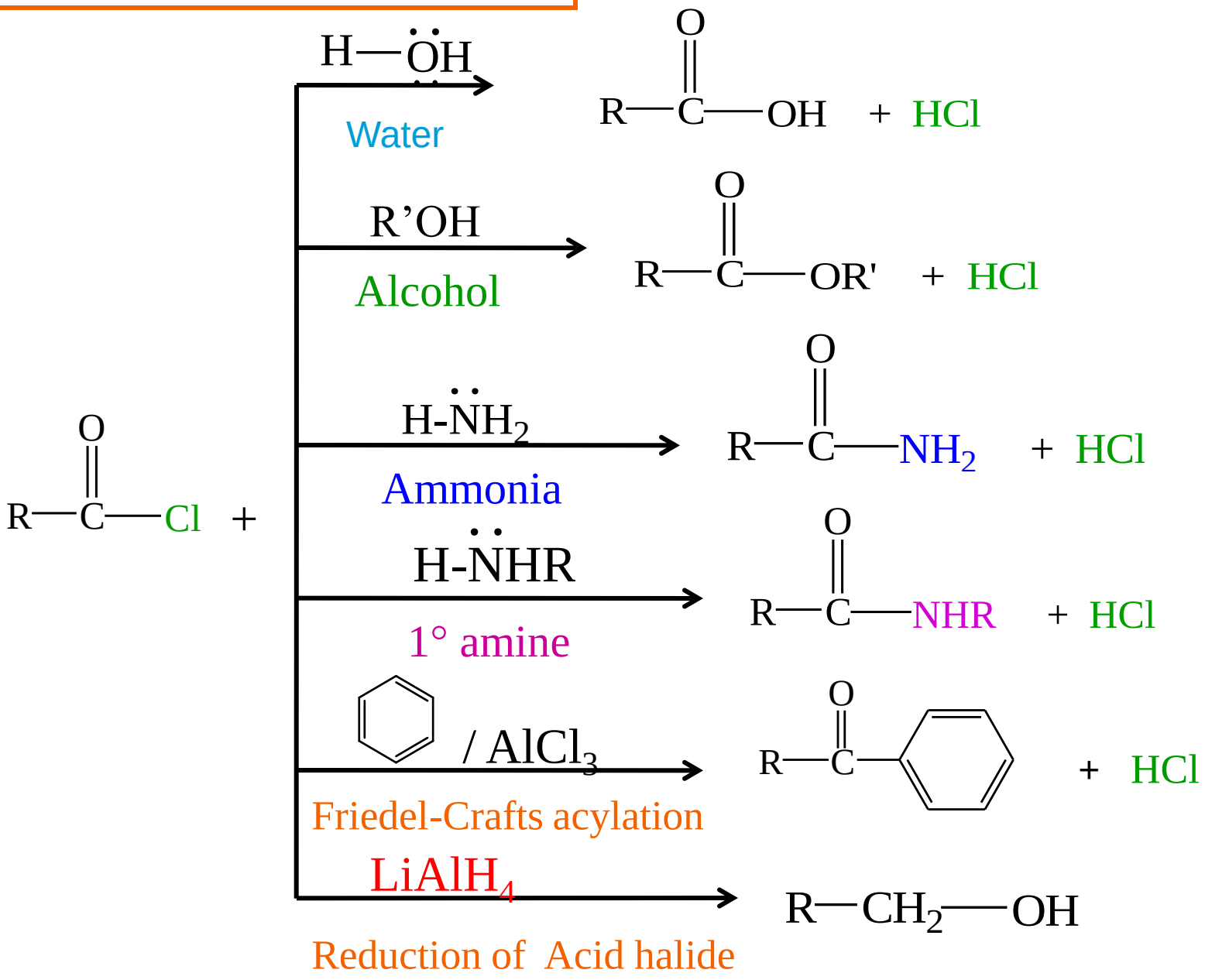


Butanoyl chloride



Benzoyl chloride

2. Acid Halide Reactions



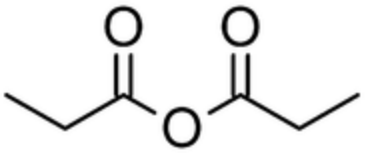
3. Acid Anhydride

Formed from the combination of two acids and the loss of water.

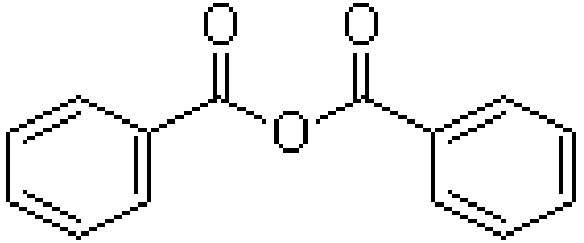
Name by changing acid ending to anhydride.

Examples:

both halves are from the same acid.

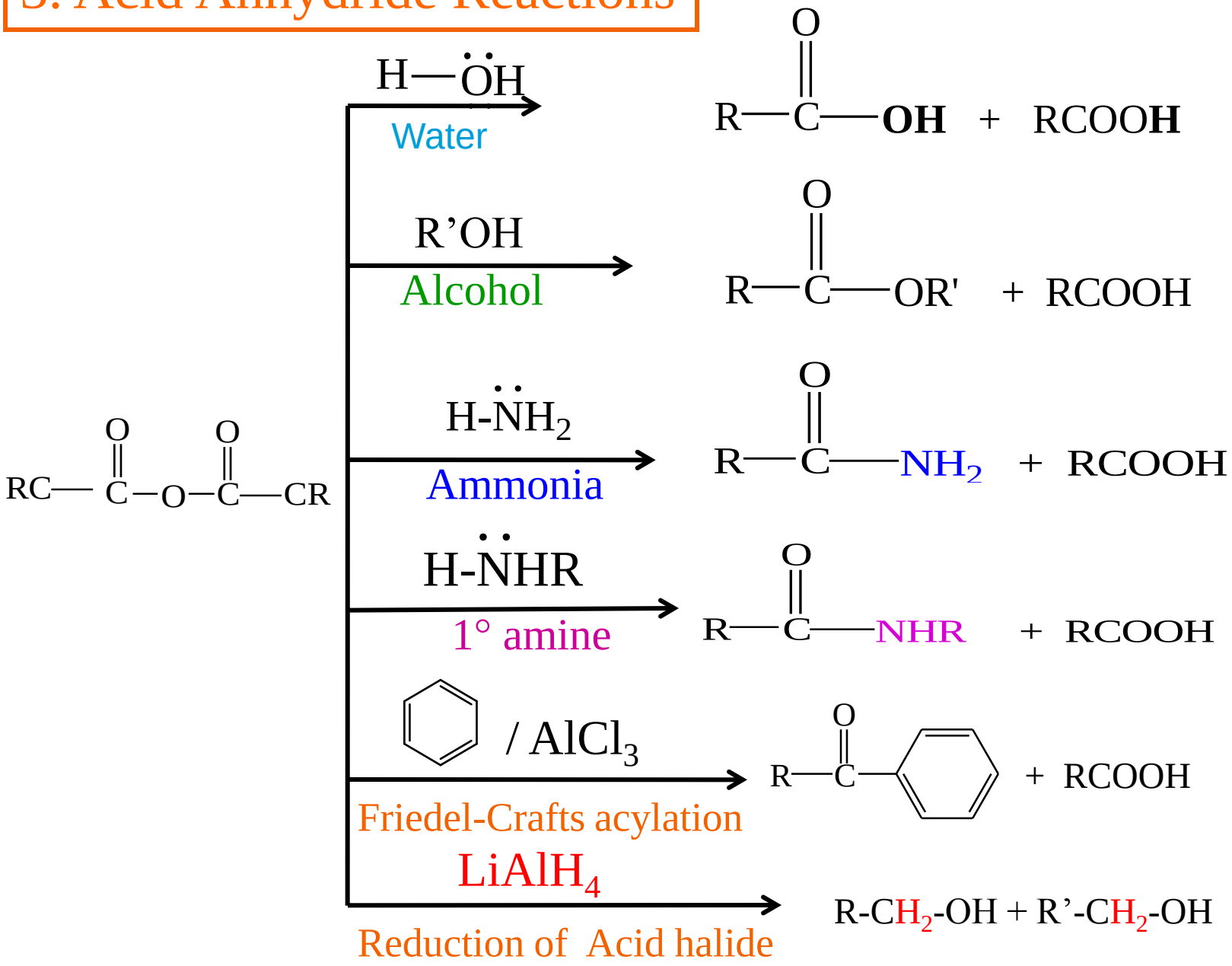


Propanoic anhydride



Benzoic anhydride

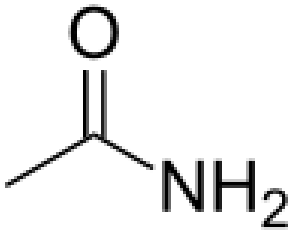
3. Acid Anhydride Reactions

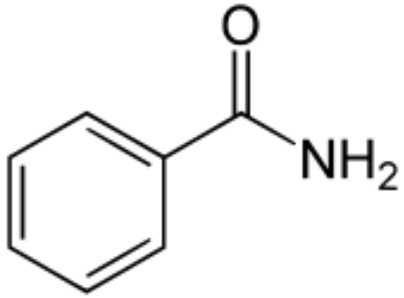


4. Amides

Primary amides are named by changing the name of the acid by dropping the -oic acid or -ic acid endings and adding –amide.

Examples:





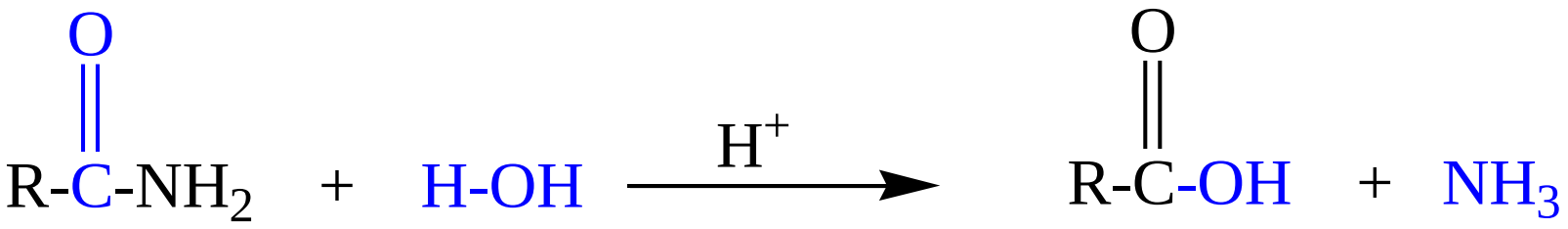
Common: Acetamide

IUPAC: Ethanamide

Benzamide

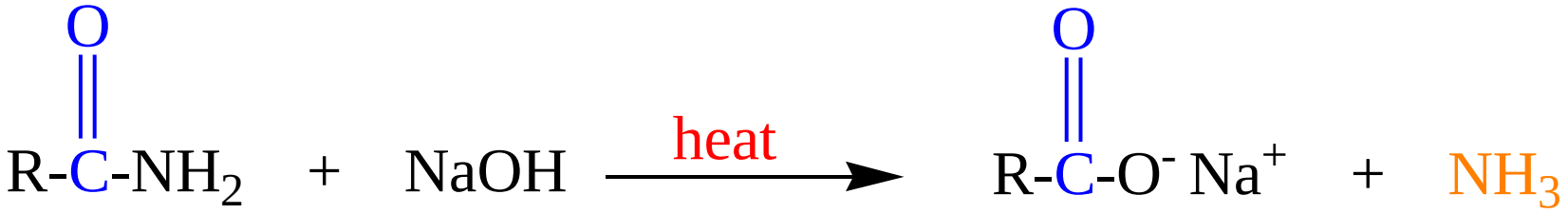
4. Amides Reactions

1- Hydrolysis with water:

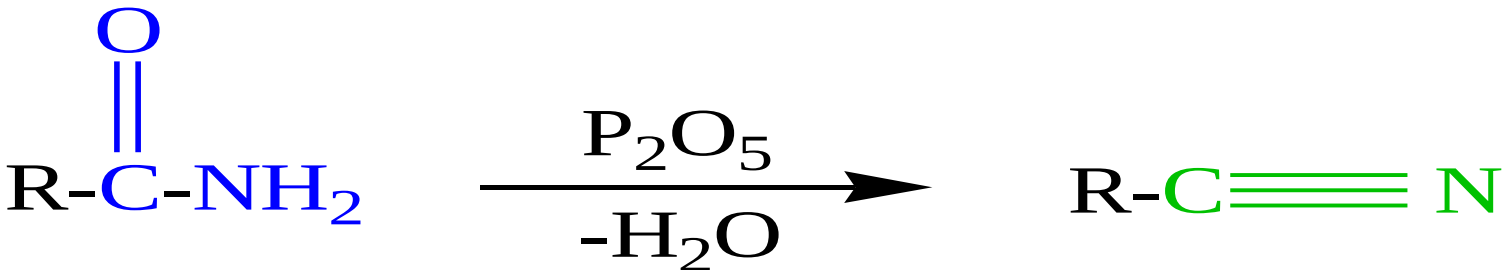


2- Base catalyzed hydrolysis:

Produces a carboxylate salt and free ammonia



3- The conversion of amide to nitrile:

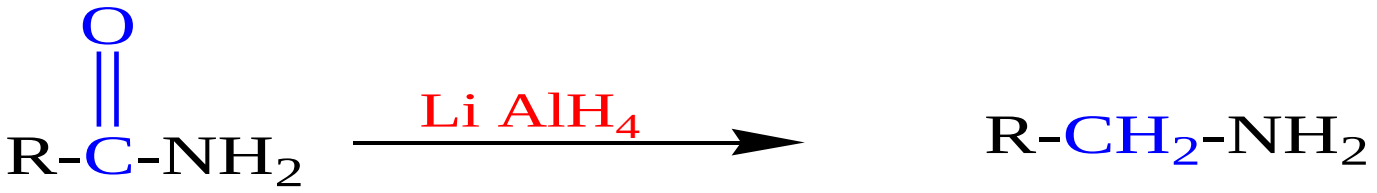


4- Reaction of amides with alkaline hypohalite solution:

Simple amides can be reduced to amines *containing one less carbon atom* by reaction with alkaline hypohalite solution.

An amine with one less carbon

5- Reduction of amides with lithium aluminium hydride to amines:



H.W(11)

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