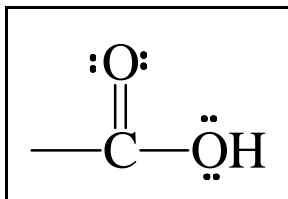


## CARBOXYLIC ACIDS

Carboxyl group:



*Nomenclature* —

### Structure

H-COOH

CH<sub>3</sub>-COOH

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

CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>-COOH

CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>-COOH

CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>-COOH

### Common Name

formic acid,

acetic acid,

propionic acid,

butyric acid,

valeric acid,

caproic acid,

### IUPAC

methanoic acid

ethanoic acid

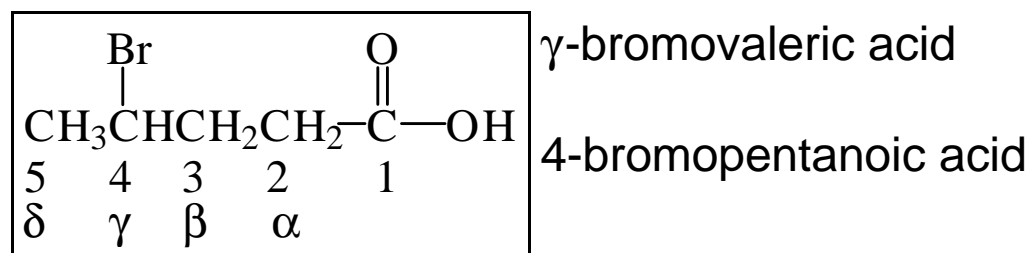
propanoic acid

butanoic acid

pentanoic acid

hexanoic acid

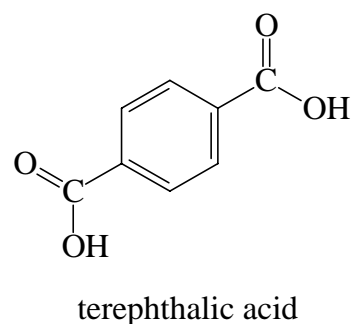
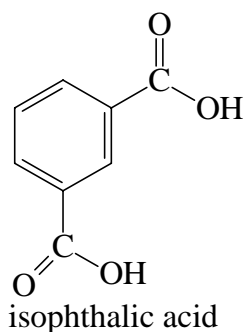
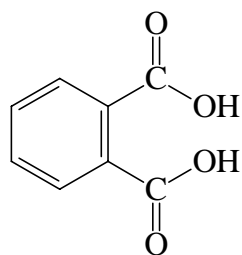
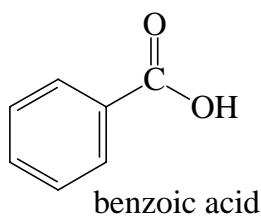
Positions along the chain are indicated by Greek letters (common names) or numbers (IUPAC).



## Dicarboxylic acids —

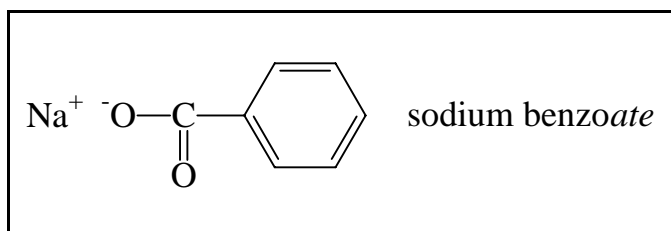
<u>Structure</u>	<u>Common Name</u>	<u>IUPAC</u>
HOOC-COOH	oxalic acid,	ethanedioic acid
HOOC-CH <sub>2</sub> -COOH	malonic acid,	propanedioic acid
HOOC-(CH <sub>2</sub> ) <sub>2</sub> -COOH	succinic acid,	butanedioic acid
HOOC-(CH <sub>2</sub> ) <sub>3</sub> -COOH	glutaric acid,	pentanedioic acid
HOOC-(CH <sub>2</sub> ) <sub>4</sub> -COOH	adipic acid,	hexanedioic acid

## Aromatic acids —



## Salts —

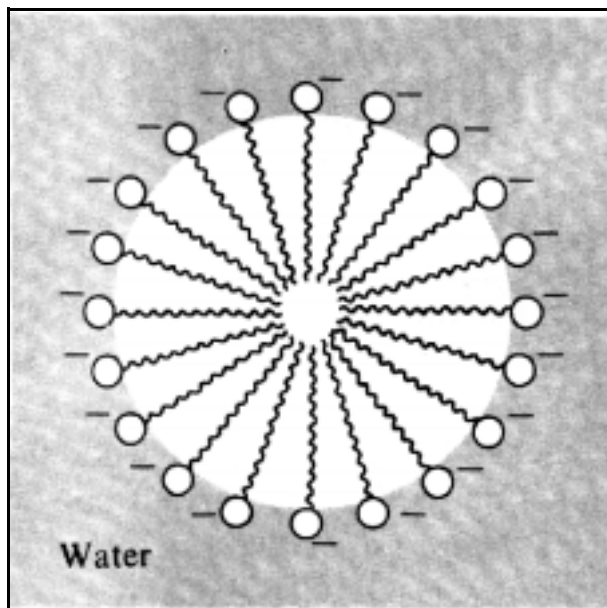
Name cation followed by acid name with -ic changed to -ate, *eg*



## Physical Properties —

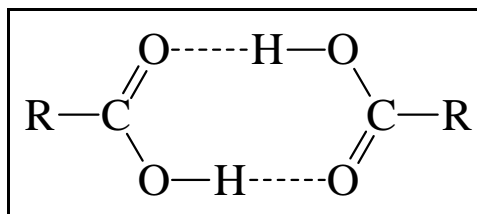
Lower molecular weight acids are soluble in  $\text{H}_2\text{O}$ : hydrogen bonding. Usually soluble in organic solvents.

Sodium and potassium salts of lower molecular weight acids are soluble in  $\text{H}_2\text{O}$  and not soluble in organic solvents of low polarity. The salts of long-chain carboxylic acids are *soaps*. Sodium and potassium soaps form micelles in water.



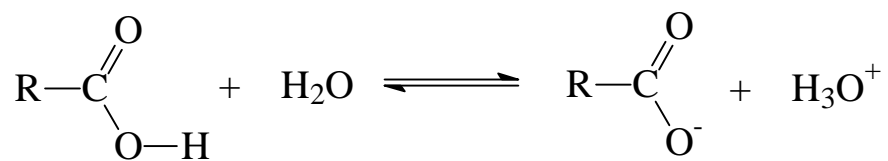
**A Micelle**

Carboxylic acids form *dimers* (pronounced die'-mers) in the liquid phase ---



These dimers also exist to some extent in the gas phase, consequently, carboxylic acids have high boiling points for a given molecular weight.

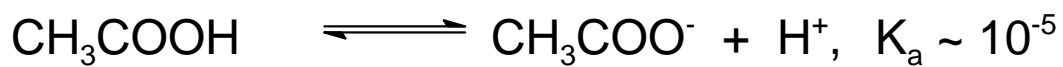
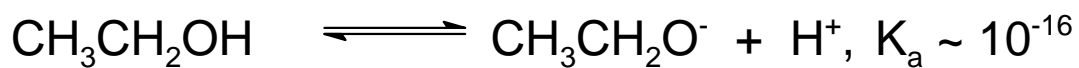
## Acidity —



$$K_{\text{eq}} = \frac{\left[ \text{R}-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{O}^- \end{array} \right] \left[ \text{H}_3\text{O}^+ \right]}{\left[ \text{R}-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{O}-\text{H} \end{array} \right] \left[ \text{H}_2\text{O} \right]} \quad K_{\text{a}} = \frac{\left[ \text{R}-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{O}^- \end{array} \right] \left[ \text{H}_3\text{O}^+ \right]}{\left[ \text{R}-\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{O}-\text{H} \end{array} \right]}$$

$$\text{p}K_{\text{a}} = -\log K_{\text{a}}$$

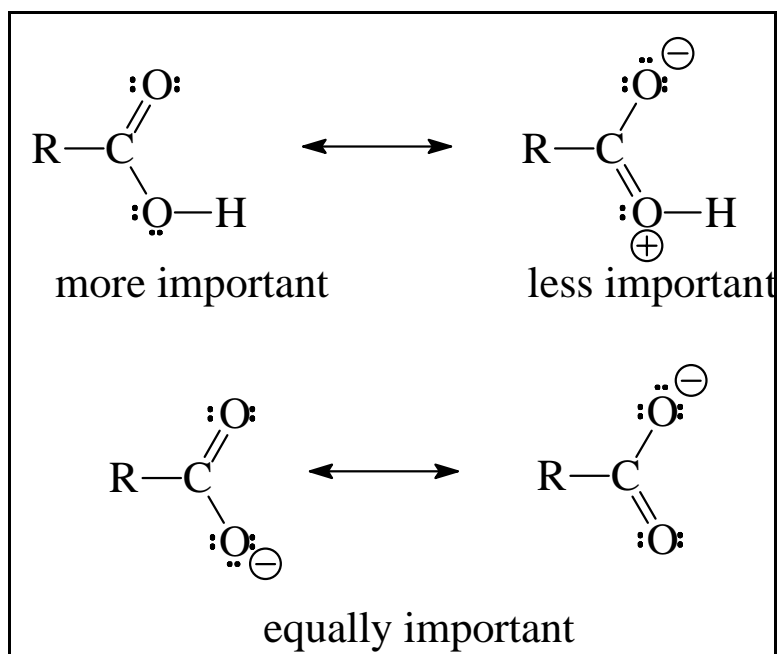
Compare acidity of carboxylic acids with alcohols:



Reason —

Carboxylate anion is more stable compared to carboxylic acid than alkoxide ion is compared to alcohol.

Neither alcohol nor alkoxide ion are stabilized by resonance, but the situation is different for a carboxylic acid and its anion; in this case the anion is stabilized more than the acid:

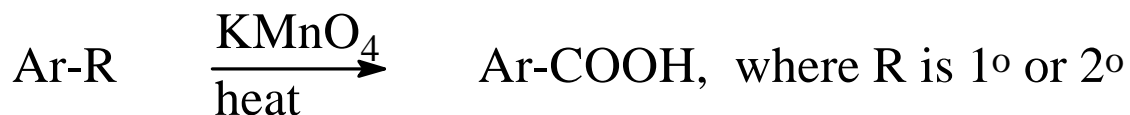


Substituent groups —

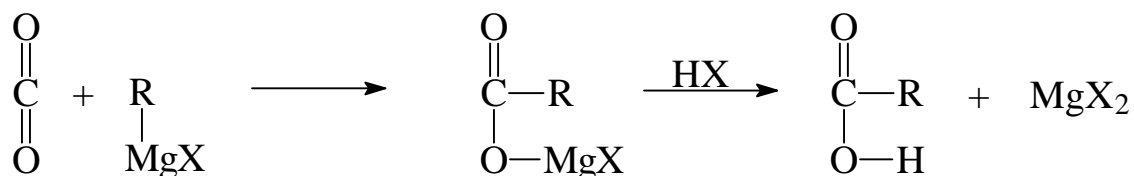
Those which stabilize the anion more than its conjugate acid (electron withdrawing) increase acid strength. Those which destabilize anion more than acid (electron donating) decrease acid strength.

## Synthesis of Carboxylic Acids —

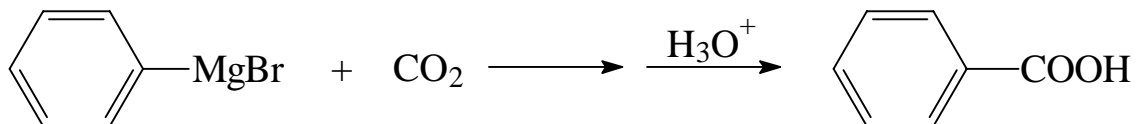
Oxidation of Primary Alcohols or Alkylbenzenes ---



Grignard Synthesis ---



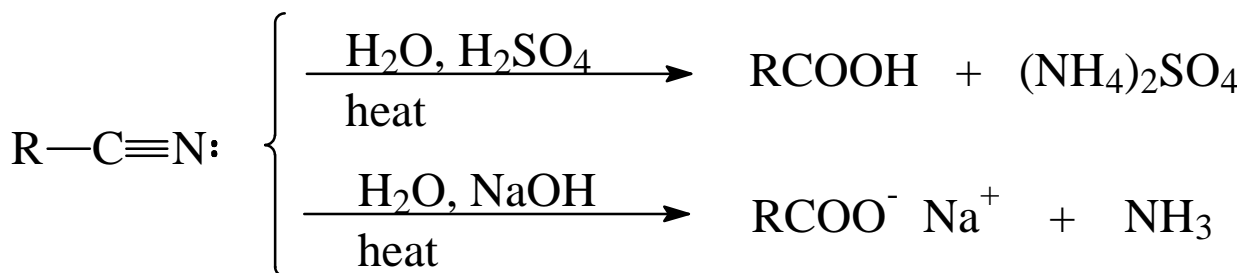
*eg*



This method results in a product which has one carbon more than the reactant.

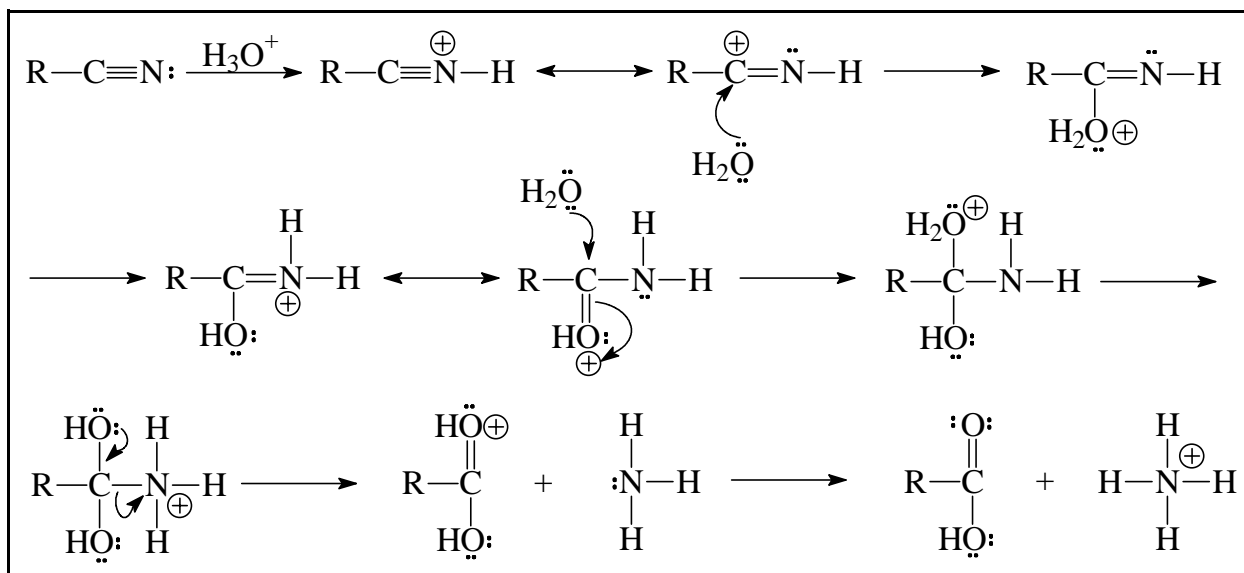
## Nitrile Hydrolysis —

May be carried out under acidic or basic conditions – conditions used may depend on other functional groups present.

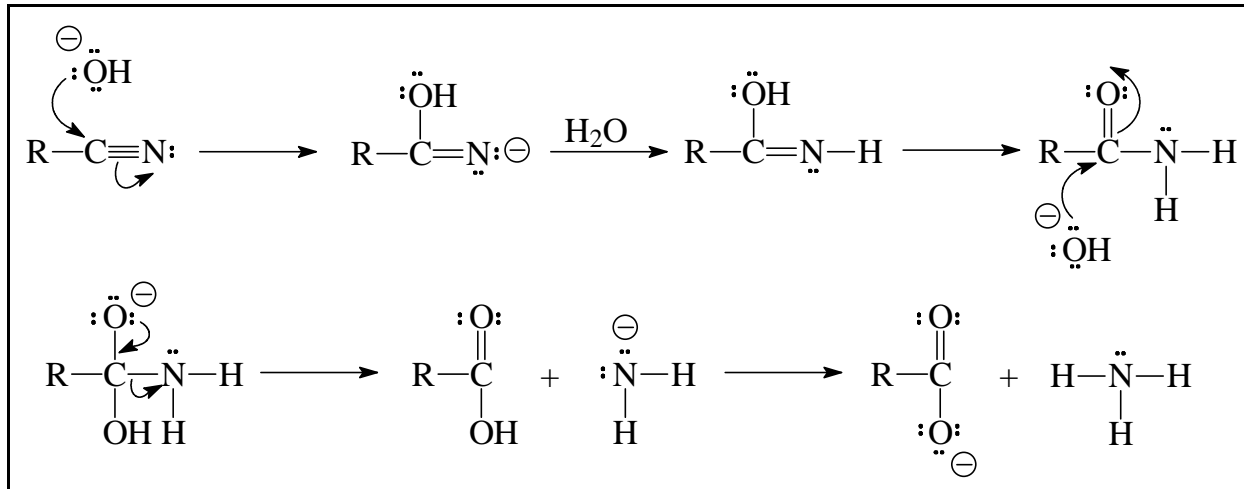


## Mechanism ---

Acidic Hydrolysis:



## Basic Hydrolysis:

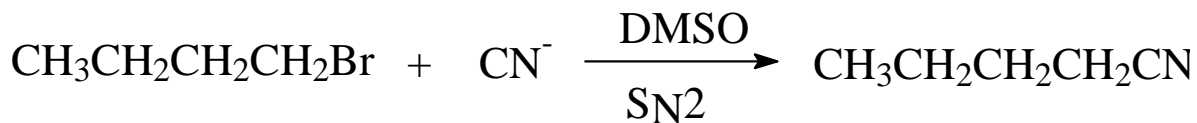


## \* Aliphatic Nitrile Synthesis —

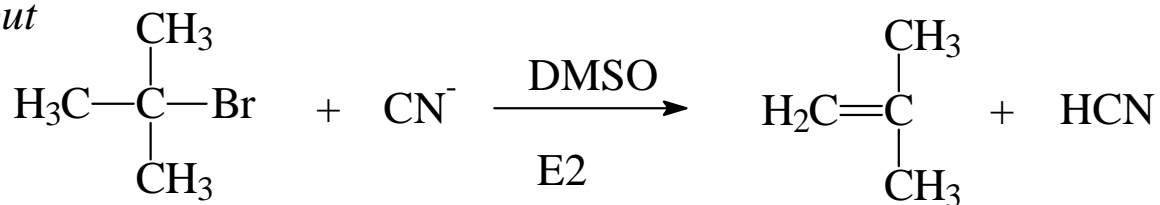


Best if R is primary, a disaster if it is tertiary.

*eg*

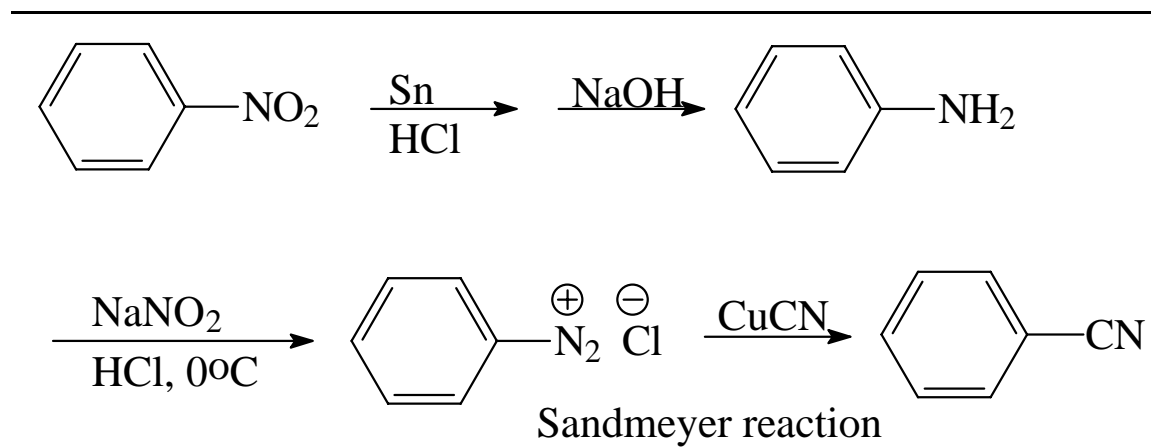


*but*



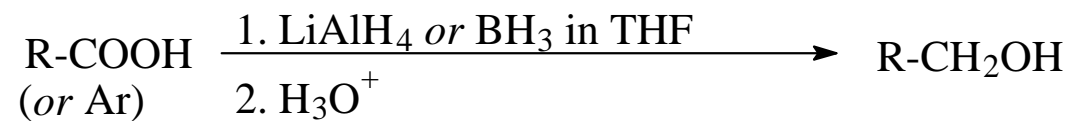


## \* Aromatic Nitrile Synthesis —



## Reactions of Carboxylic Acids —

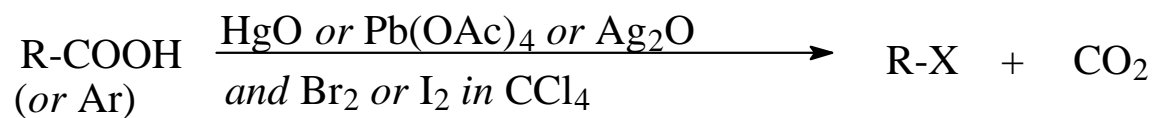
### Reduction to Primary Alcohols —



BH<sub>3</sub> has the advantage that most other groups will not be affected if an excess of the reagent is not used. LiAlH<sub>4</sub> will reduce nitro, nitrile, and various carbonyl groups, among others.

## Hunsdiecker Reaction —

In this reaction the carboxylic acid is decarboxylated to a bromide or iodide, having one less carbon.



## Mechanism —

