

## Carboxylic acid derivatives:-

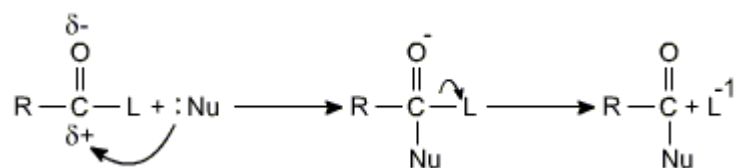
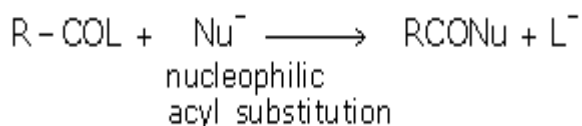
When other functional group combinations with the carbonyl group can be prepared from carboxylic acids, and are usually treated as related derivatives. Five common classes of these **carboxylic acid derivatives** are listed in the following table.

acyl halide	anhydride	ester	amide	nitrile
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\   \\ \text{X} \end{array}$ <p>X = F, Cl, Br or I</p>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\   \\ \text{O} \\   \\ \text{R}-\text{C} \\ \parallel \\ \text{O} \end{array}$	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\   \\ \text{O}-\text{R}' \end{array}$ <p>R' = H or alkyl</p>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\   \\ \text{NR}'_2 \end{array}$ <p>R' = H or alkyl</p>	$\text{R}-\text{C}\equiv\text{N}$
$\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_2\text{H}_5-\text{C} \\   \\ \text{Cl} \end{array}$ <p>propanoyl chloride</p>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{C} \\   \\ \text{O} \\   \\ \text{H}_3\text{C}-\text{C} \\ \parallel \\ \text{O} \end{array}$ <p>acetic anhydride</p>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}_3\text{C}-\text{C} \\   \\ \text{O}-\text{C}_2\text{H}_5 \end{array}$ <p>ethyl acetate</p>	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C} \\   \\ \text{NH}_2 \end{array}$ <p>formamide</p>	$\text{H}_3\text{C}-\text{C}\equiv\text{N}$ <p>acetonitrile</p>

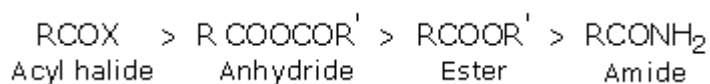
Although nitriles do not have a carbonyl group, they are included here because the functional carbon atoms all have the same oxidation state.

## Reactivity of Acid Derivatives

The reactions of carboxylic acids and their derivatives involve substitution of the group L with nucleophiles and are known as nucleophilic acyl substitution reaction.



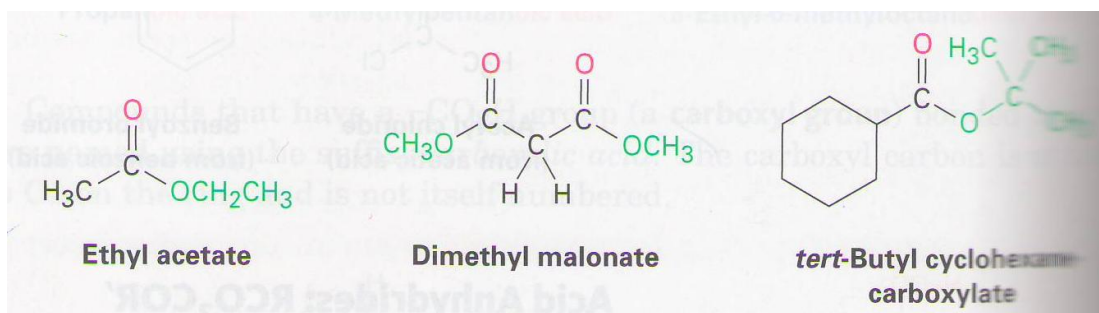
Order of reactivity of the acid derivatives is



Carboxylic acids and their derivatives can be interconverted by nucleophilic acyl substitution reactions.

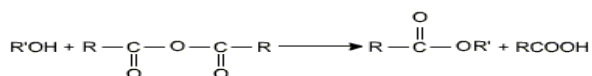
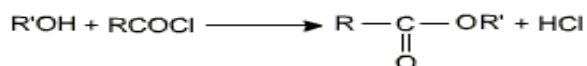
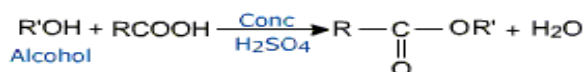
## Esters:-

Esters are named by first giving the named of the alkyl group attached to the oxygen and then identifying the carboxylic acid with –ic acid replaced by –ate



## Preparation of Esters

Esters are prepared by the acylation of alcohols or phenols.

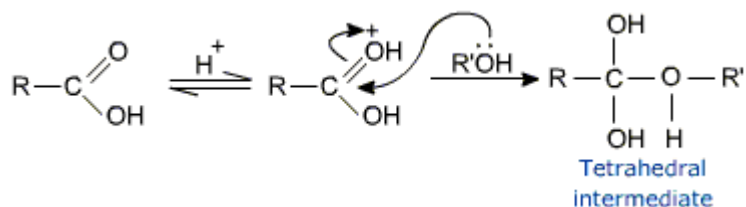


Esterification of carboxylic acids with alcohols requires a mineral acid such as concentrated H<sub>2</sub>SO<sub>4</sub> or HCl gas as a catalyst.

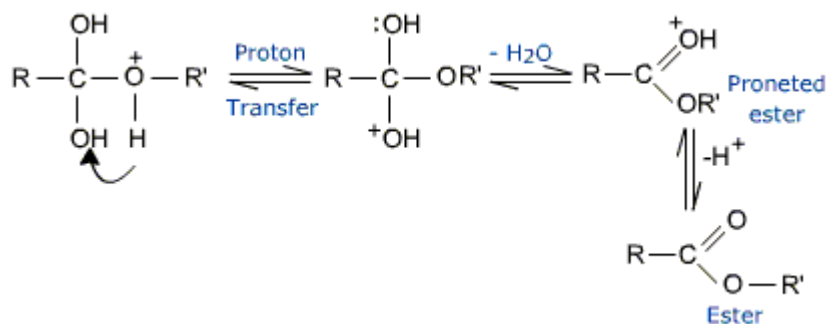
## Mechanism of Esterification of Carboxylic Acids

The esterification of carboxylic acids with alcohols is a kind of nucleophilic acyl substitution.

The first step is the protonation of the carbonyl oxygen, which activates the carbonyl group towards nucleophilic addition of the alcohol.



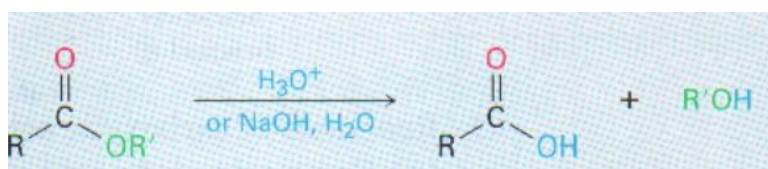
The tetrahedral intermediate, which is formed transfers a proton converting the hydroxyl group into  $-\overset{+}{\text{O}}\text{H}_2$  group. This species  $-\overset{+}{\text{O}}\text{H}_2$  is a better leaving group and is eliminated as a neutral water molecule.



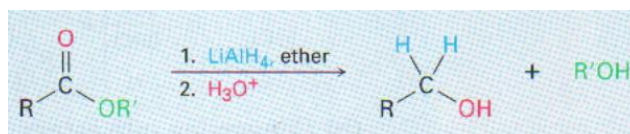
The protonated ester finally loses a proton to give the ester.

## Reaction of Esters

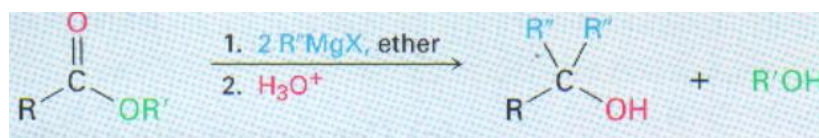
- 1- Conversion into acids



- 2- Conversion into primary alcohols by reduction



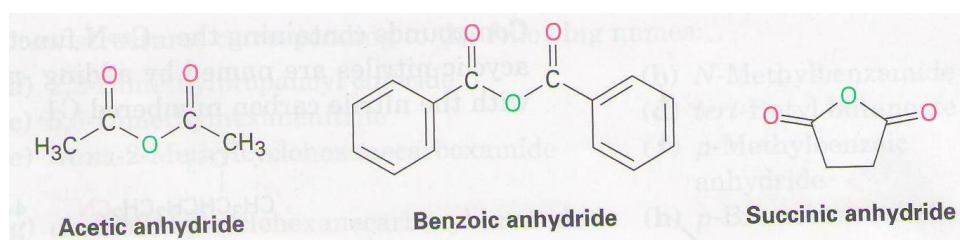
- 3- Conversion into tertiary alcohols by Grignard reaction



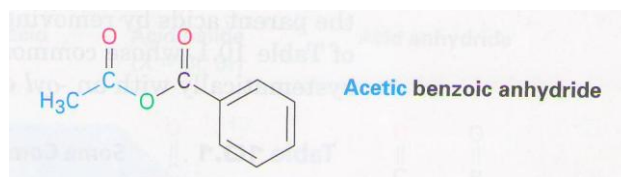
## Acid Anhydrides

Acid anhydrides are called symmetrical when the two acyl groups are identical when the two acyl groups are identical and if the two acyl groups are different it is said to be unsymmetrical

Symmetrical anhydrides of unsubstituted carboxylic acids are derived from the names of the carboxylic acids by replacing the word acid with anhydride.

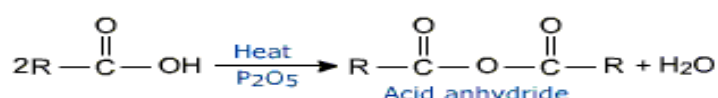


Unsymmetrical anhydrides are named by writing the names of the two acids alphabetically before the word anhydride.

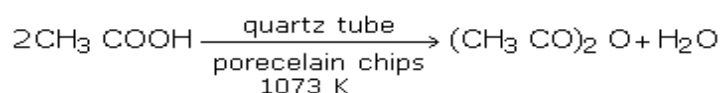


## Preparation of Acid Anhydrides

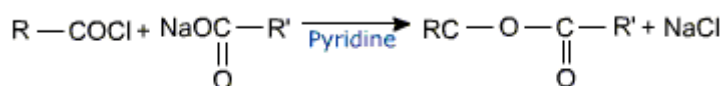
Acid anhydrides are considered to be derived from carboxylic acids by the removal of a molecule of water from two molecules of acid. So acid anhydrides can be prepared by heating carboxylic acid in the presence of  $P_2O_5$  in dehydrating agent.



Industrially, acetic anhydride is prepared by heating acetic acid to 1073 K.

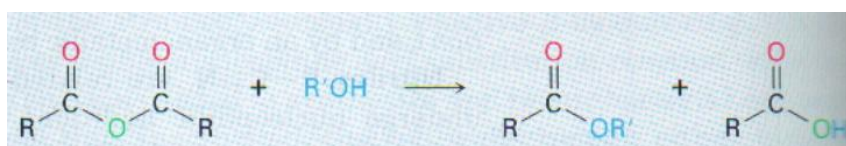


Asymmetrical and symmetrical anhydrides can be prepared by the reaction of acyl chlorides with sodium salts of carboxylic acids in the presence of pyridine.



## Reactions of Acid anhydrides.

### 1-Conversion into esters

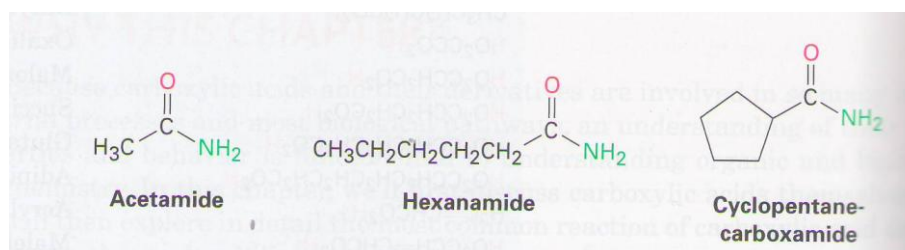


### 2-Conversion into Amides

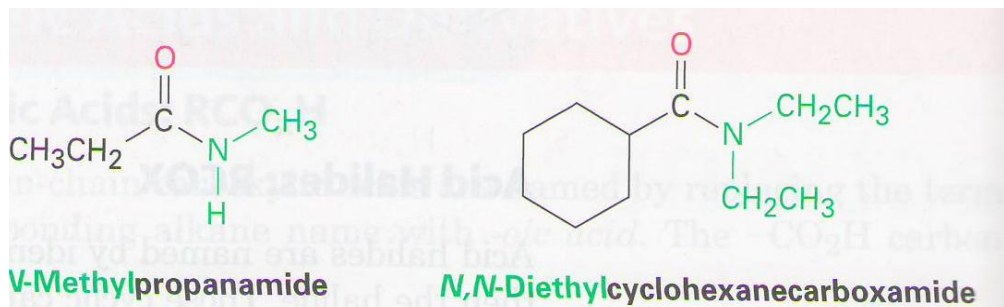


## Amides

Amides with an unsubstituted  $-NH_2$  group are named by *acid* or *-ic acid* ending with *-amide*, or by replacing the *-carboxylic acid* ending with *-carboxamide*.

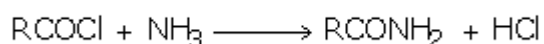


If the nitrogen atom is substituted, the amide is named by the substituent groups and then the parent amide. The substituents are prepared by the letter N to identify them as being directly attached to nitrogen.

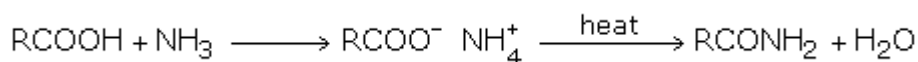


## Preparation of Amides

Amides are generally prepared by the reaction of acyl chlorides or anhydrides with ammonia or amines.

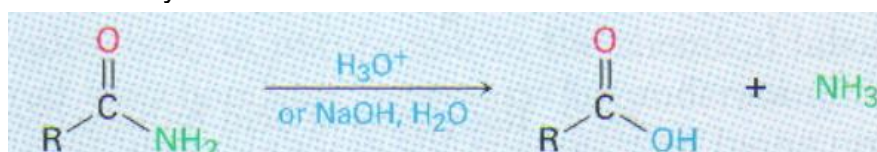


Carboxylic amines give ammonium carboxylates, which need to be heated to high temperatures to give amides. Thus this method is not useful for laboratory preparation of amides. It is however used in the industrial preparation of amides.

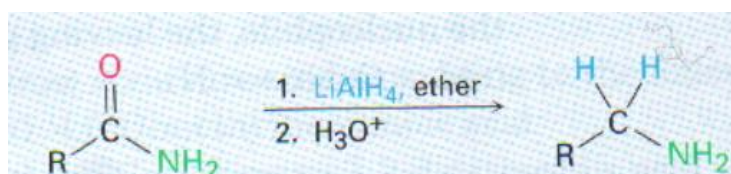


## Reactions of Acid Amides

### 1-Conversion into carboxylic acids

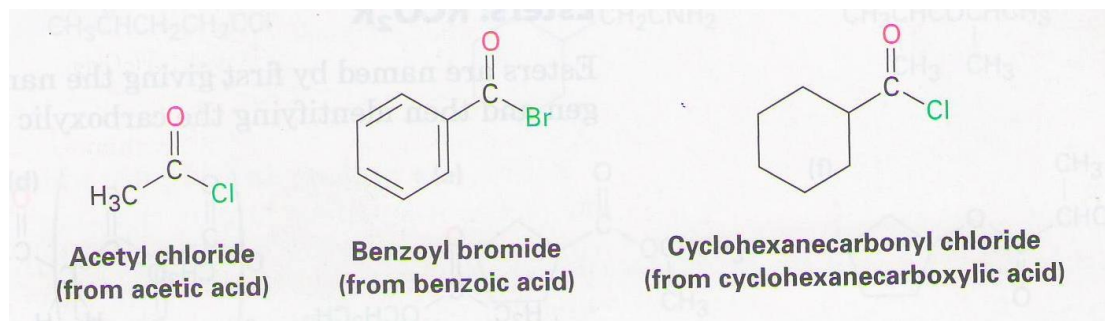


### 2-Conversion into amines by reduction



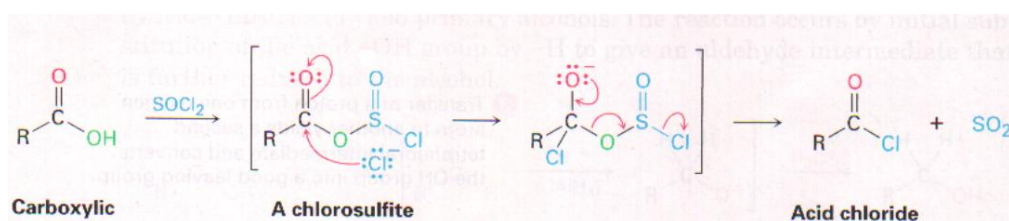
## Acid Halides

Acid halides are named by identifying first the acyl group and then the halide. Those cyclic carboxylic acids that take a *-carboxylic acid* ending use *-carbonyl* for the name ending of the corresponding acyl group. For example:



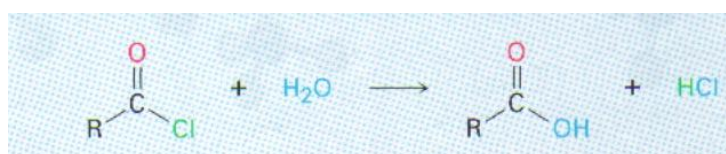
## Preparation of Halides

Acid chlorides are prepared from the corresponding acid with the thionyl chloride

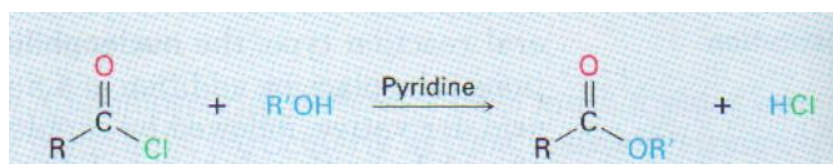


## Reaction of halides

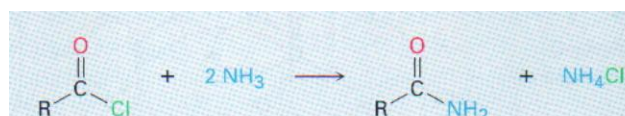
### 1-Conversion into carboxylic acids



### 2-Conversion into esters



### 3-Conversion into amides

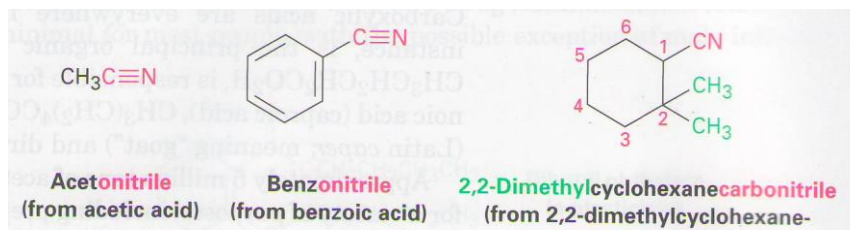


## Nitriles

Compounds containing the  $\text{-C}\equiv\text{N}$  functional group are called *nitriles*. Acyclic nitriles are named by adding *-nitrile* as a suffix to the alkane with the nitrile carbon numbered 1.

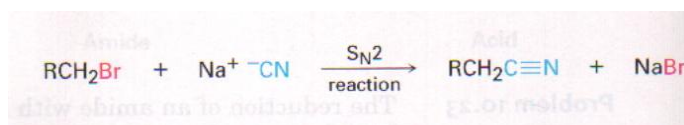


More complex nitriles are named as derivatives of carboxylic acids by replacing the *-ic acid* or *-oic acid* ending with *-onitrile*, or by replacing the *-carboxylic acid* ending with *-carbonitrile*. In this system, the nitrile carbon atom is attached to C1 but is not itself numbered.



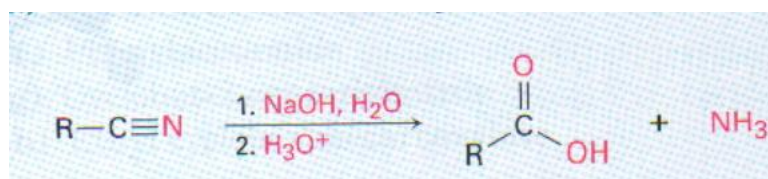
## Nitriles Preparation

The simplest method of preparing nitriles is by the  $\text{S}_{\text{N}}2$  reaction of a primary alkyl halide with a cyanide ion.

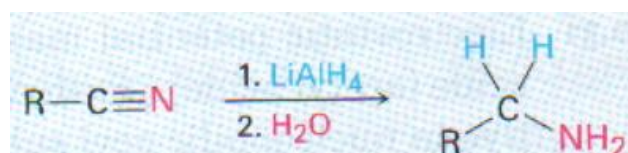


## Reactions of Nitriles

### 1-Conversion into carboxylic acids



### 2-Conversion into amines by reduction



### 3-Conversion into ketones by Grignard reaction

