

Dr.D.k.Awasthi

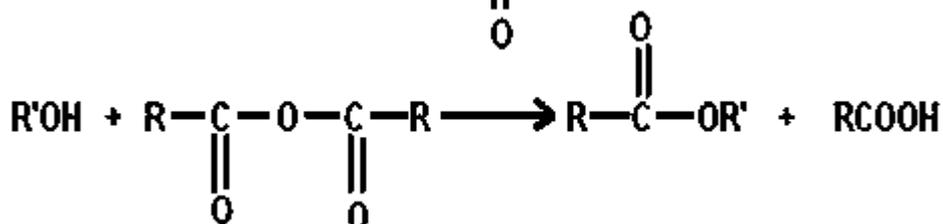
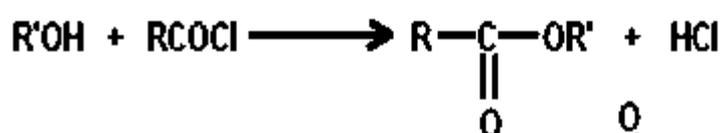
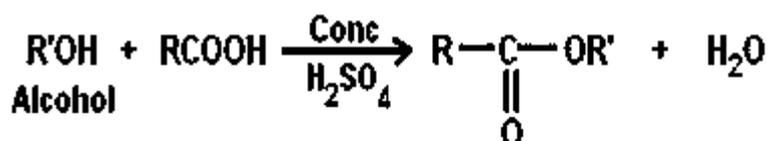
B.Sc.4<sup>th</sup> semester

Department of chemistry

Sri.JNMGCollege Lucknow

## Ester

Ester preparation

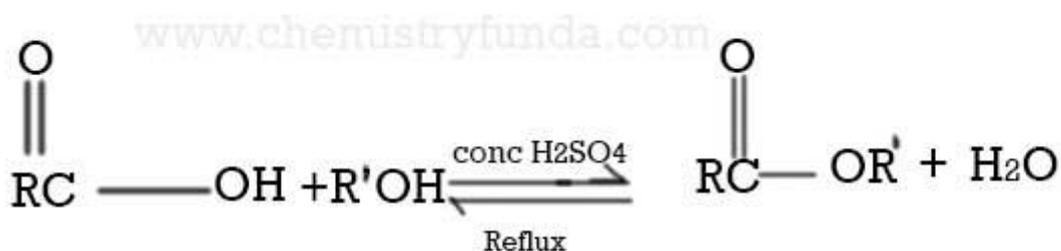


## Preparation of Esters

Ester is usually prepared by their reaction with alcohols (or phenols) from carboxylic acids or their functional derivatives. Some of the common methods for the preparation of esters are given below.

### 1. Preparation of ester by Direct esterification:

Esters are usually prepared by refluxing a mixture of a carboxylic acid and an alcohol in the presence of a little mineral acid, usually conc. H<sub>2</sub>SO<sub>4</sub> or dry HCl that acts as a catalyst. This reaction which is known as esterification, is reversible, and at equilibrium, appreciable quantities of both the reactants and the products are present.

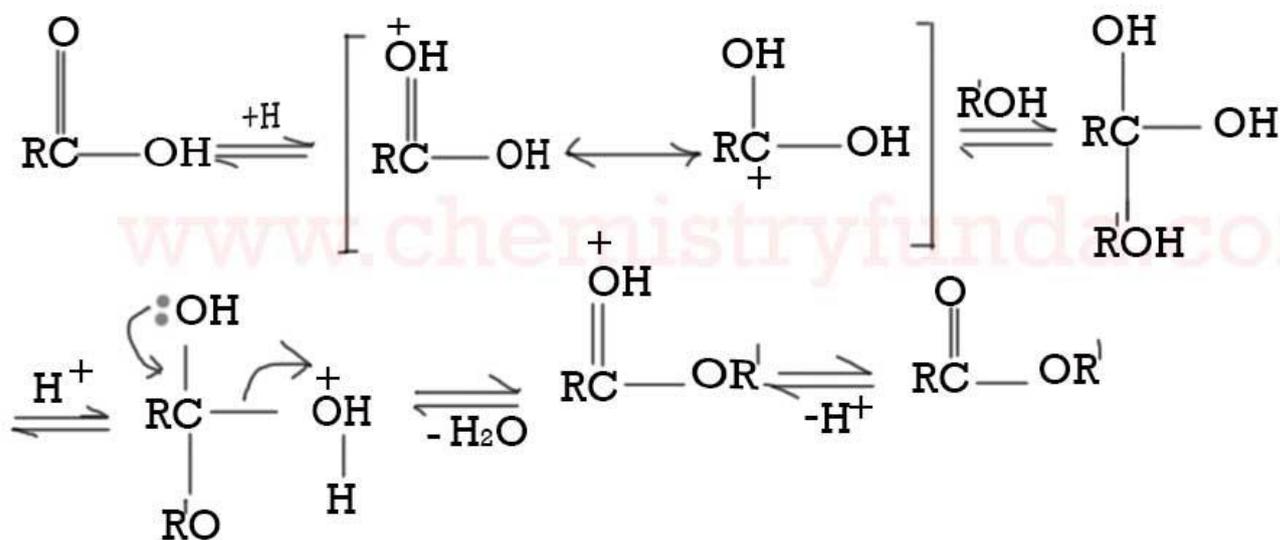


A carboxylic acid    An alcohol

An ester    Water

However, the equilibrium can be shifted to the right side by, remove water from the mixture of the reaction as it is formed, thereby increasing the yield of the ester.

The mechanism of the esterification reaction is that of a typical acid catalyzed nucleophilic substitution reaction at an acyl carbon atom, **as shown below:**

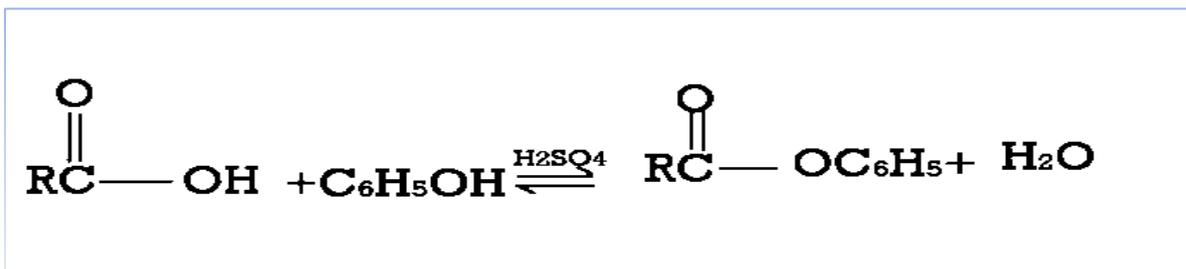


If we follow this pathway backward, it will provide the mechanism for the acid catalyzed hydrolysis of an ester. Whether we push the reaction forward (esterification) or backward (hydrolysis of ester) depends on the conditions we choose **For esterification**, we use acid or alcohol (whichever is cheaper) in excess, and, if

possible, remove the water as it is formed ; for ester hydrolysis, we use a large excess of water, i.e we **reflux** the ester with dilute aqueous **HCl** .

### **Steric hindrance:**

The presence of large groups near the reaction site, whether in alcohol or in acid, slows down both the forward (esterification) and the reverse (ester hydrolysis) reactions. due to **steric hindrance**, Tertiary alcohols, for **example**, react so slowly in esterification that instead they usually undergo elimination.



If both a carboxyl and a hydroxyl groups are present in the same molecule and are suitably situated with respect to each other (1, 4 or 1,5-positions) the molecule undergoes intramolecular esterification to form a cyclic ester, commonly known as a lactone. Thus, **Gymma** -and sigma-hydroxy carboxylic acids on heating yield **7** and **5** **lactones**, respectively, under the usual **esterification conditions**. The most common lactones are those with five- or **six membered rings**.

Lactones are hydrolysed by an aqueous base to yield open-chain salts of hydroxy carboxylic acids.

## **2. Preparation of Esters by the use of diazomethane:.**

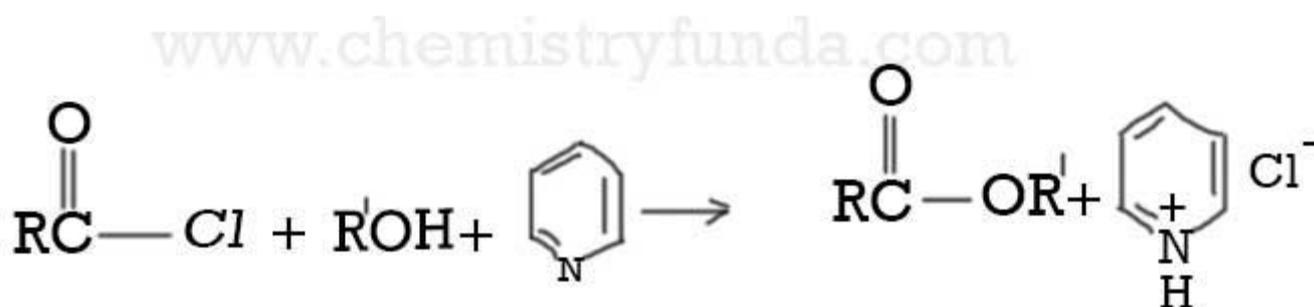
Methyl esters can be prepared by the reaction of carboxylic acids with diazomethane in ethereal solution.



The reaction occurs almost instantaneously, but is limited by the high price and the hazardous nature of diazomethane.

### 3. Preparation of Esters from acid chlorides:.

Esters can also be prepared by the reaction of acid chlorides with alcohols. Since acid chlorides are much more reactive than **carboxylic acids** toward nucleophilic substitution. This reaction occurs rapidly and does not require a catalyst. **However**, pyridine is usually used to react with HCl that is formed in reaction.

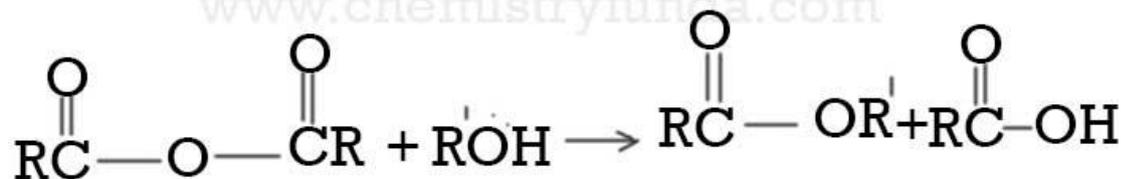


Thus, the problems encountered in the **direct esterification** of carboxylic acids, i.e. reversibility of the reaction and difficulty with the sterically hindered reactants, can't easily avoided if the acid is first converted to acid chloride which is then allowed to react with an ester forming alcohol (or phenol). All classes of alcohols can be used when esters are prepared by this method.

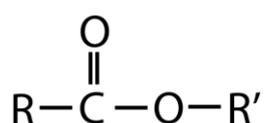
This reaction is not reversible because the ester is much more stable than the acid chloride, and also because one of the products, i.e., **HCl** is a gas that can be easily removed from the reaction mixture, thus preventing the reverse reaction from taking place.

### 4. Preparation of Esters from acid Anhydrides.

Esters can also be prepared from acid anhydrides by their reaction with alcohols. In this case also no catalyst is required.



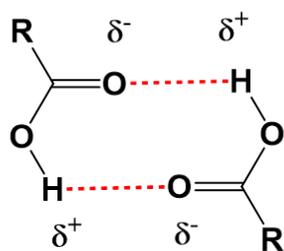
An **ester** is an organic compound that is a derivative of a carboxylic acid in which the hydrogen atom of the hydroxyl group has been replaced with an alkyl group. The structure is the product of a carboxylic acid (the R-portion) and an alcohol (the R'-portion). The general formula for an ester is shown below.



The R group can either be a hydrogen or a carbon chain. The R' group must be a carbon chain since a hydrogen atom would make the molecule a carboxylic acid. The steps for naming esters along with two examples are shown below.

#### Boiling Points, Melting Points and Solubility

Carboxylic acids can form hydrogen bond dimers which increases their boiling points above that of alcohols of similar size



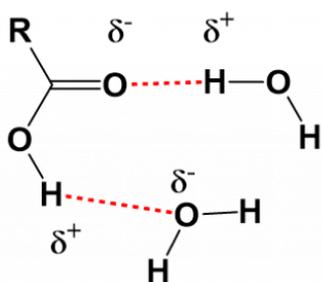
Carboxylic Acid

Hydrogen Bond Dimer

## Table Comparison of Boiling Points for Compounds of Similar Size

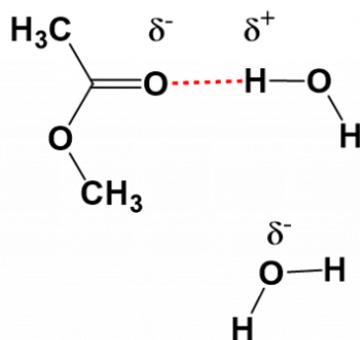
Small esters have boiling points which are lower than those of aldehydes and ketones with similar mass. Esters, like aldehydes and ketones, are polar molecules. However, their dipole-dipole interactions are weaker than that of aldehydes and ketones and they are unable to form hydrogen bonds. Thus, their boiling points are higher than ethers and lower than aldehydes and ketones of similar size.

Low molecular weight carboxylic acids tend to be liquids at room temperature, whereas larger molecules form waxy solids. Carboxylic acids that range in carbon chain length from 12 -20 carbons are typically called fatty acids, as they are commonly found in fats and oils. Comparable to other oxygen containing molecules, the short-chain carboxylic acids tend to be soluble in water, due to their ability to form hydrogen bonds. As the carbon chain length increases, the solubility of the carboxylic acid in water goes down. Esters can also hydrogen bond with water, although not as efficiently as carboxylic acids, and thus they are slightly less soluble in water than carboxylic acids of similar size.



Carboxylic Acid

Hydrogen Bonding with Water



Ester

Hydrogen Bonding with Water

## Physical Properties

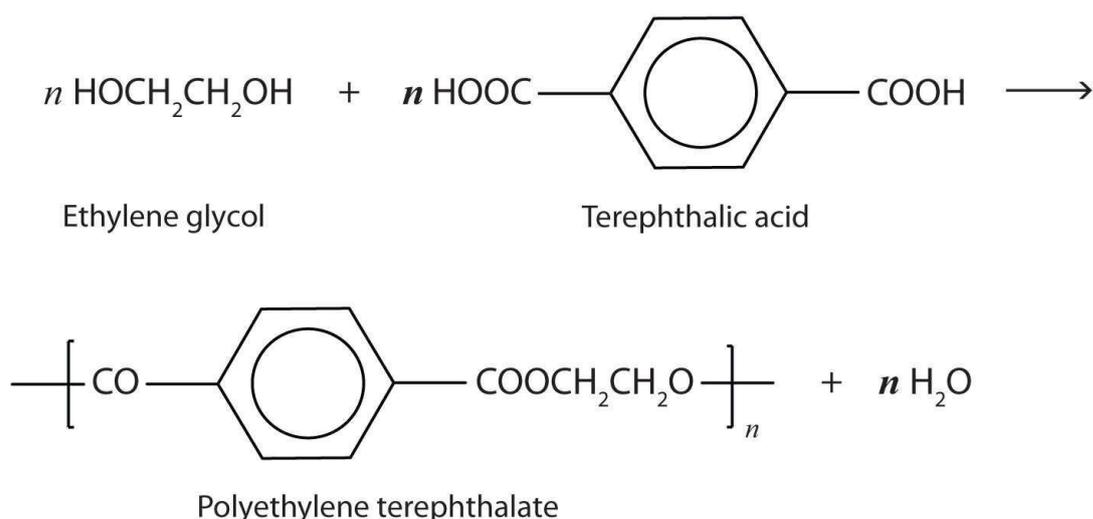
- No hydrogen atom attached to oxygen atoms, therefore they don't form H-bonding among other molecules of itself
- Therefore have lower BP than those of alcohols and acids
- Lower molecular weight esters are soluble in water because they can form H-bonding with water molecules
- Esters with 5 or more carbon atoms are sparingly soluble in water
- Esters have pleasant odor

## Condensation Polymers

A commercially important esterification reaction is condensation polymerization, in which a reaction occurs between a

dicarboxylic acid and a dihydric alcohol (diol), with the elimination of water. Such a reaction yields an ester that contains a free (unreacted) carboxyl group at one end and a free alcohol group at the other end. Further condensation reactions then occur, producing polyester polymers.

The most important polyester, polyethylene terephthalate (PET), is made from terephthalic acid and ethylene glycol monomers:

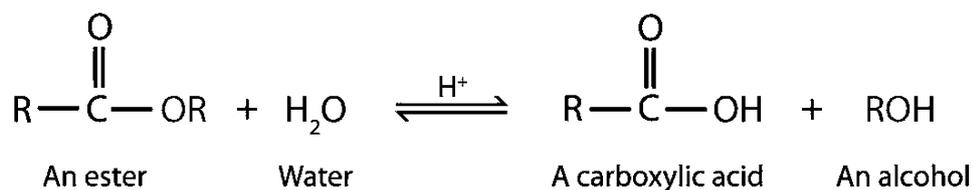


Polyester molecules make excellent fibers and are used in many fabrics. A knitted polyester tube, which is biologically inert, can be used in surgery to repair or replace diseased sections of blood vessels. PET is used to make bottles for soda pop and other beverages. It is also formed into films called Mylar. When magnetically coated, Mylar tape is used in audio- and videocassettes. Synthetic arteries can be made from PET, polytetrafluoroethylene, and other polymers.

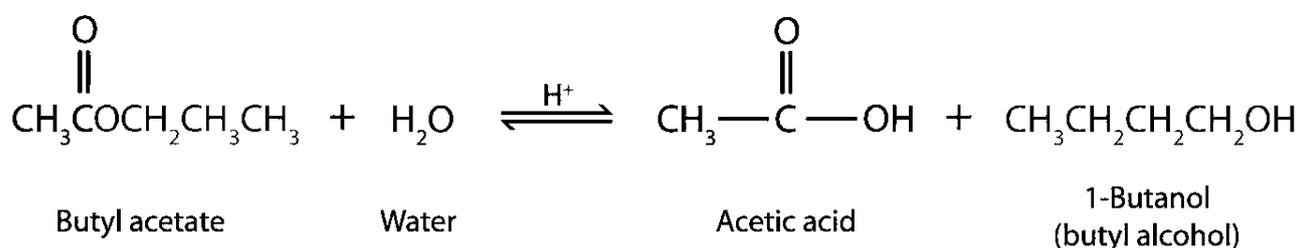
### Hydrolysis of Esters

The reverse reaction of ester formation can be used to breakdown esters into a carboxylic acid and an alcohol. This reaction requires the incorporation of water into the ester linkage, and is thus called a **hydrolysis reaction**.

The ester is heated with a large excess of water containing a strong-acid catalyst. Like esterification, the reaction is reversible and does not go to completion.

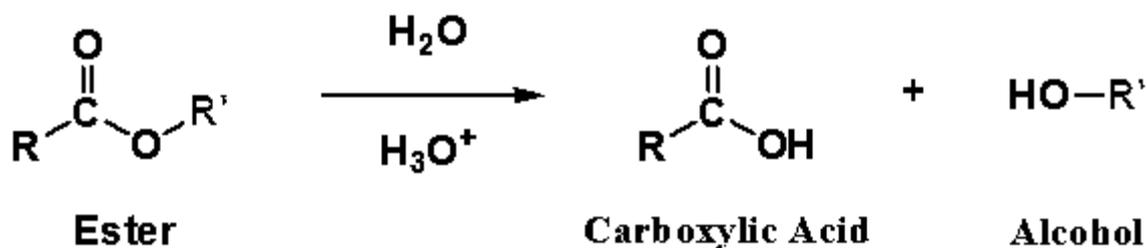


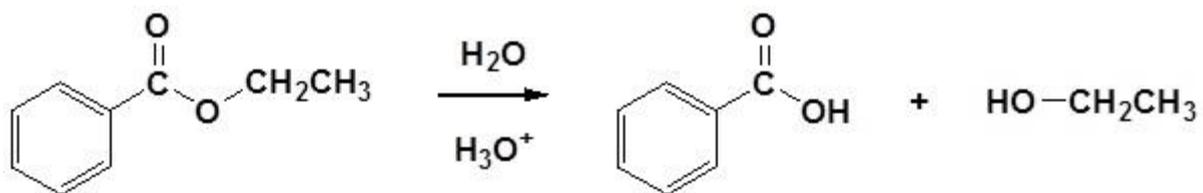
As a specific example, butyl acetate and water react to form acetic acid and 1-butanol. The reaction is reversible and does not go to completion.



Esters can be cleaved back into a carboxylic acid and an alcohol by reaction with water and a catalytic amount of acid.

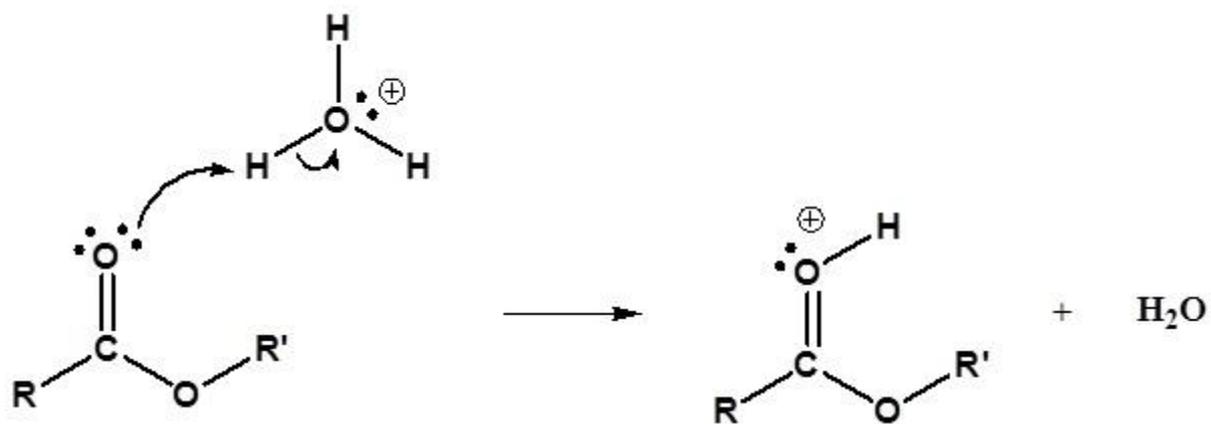
General Reaction



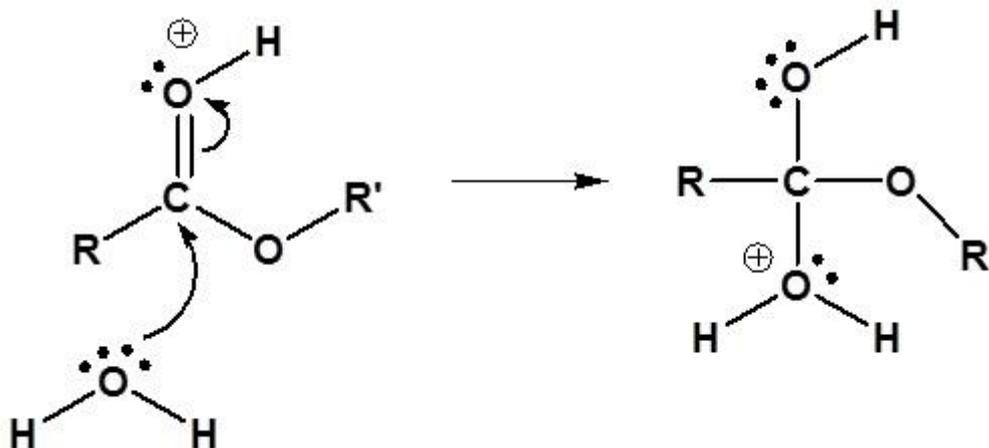


## Mechanism

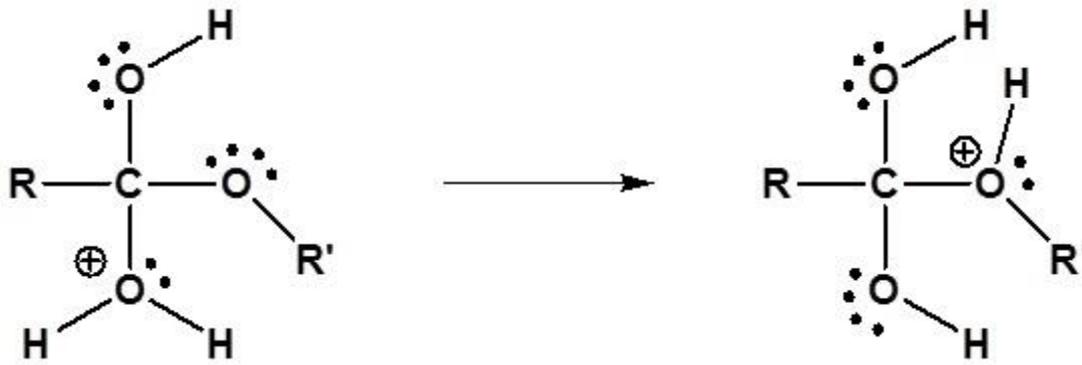
### 1) Protonation of the Carbonyl



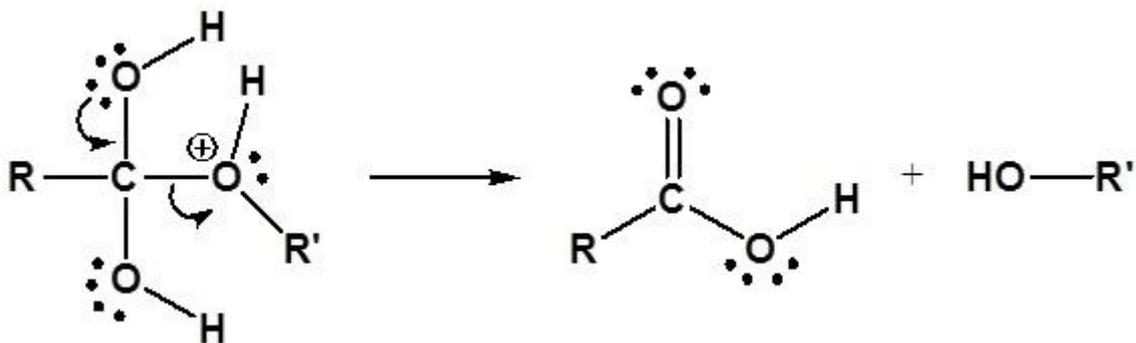
### 2) Nucleophilic attack by water



### 3) Proton transfer



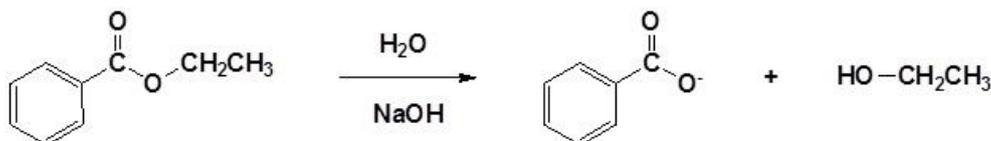
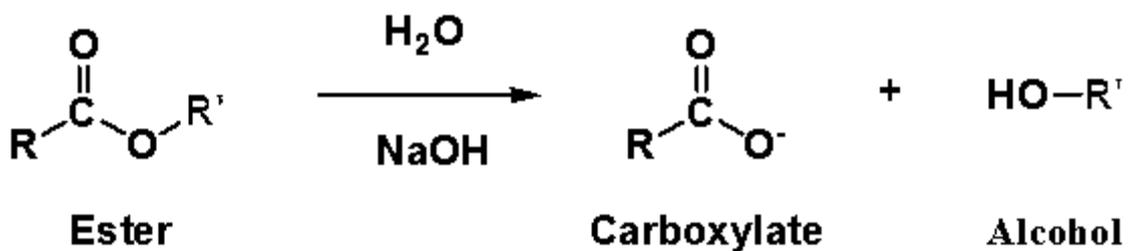
4) Leaving group removal



Esters can be cleaved back into a carboxylic acid and an alcohol by reaction with water and a base

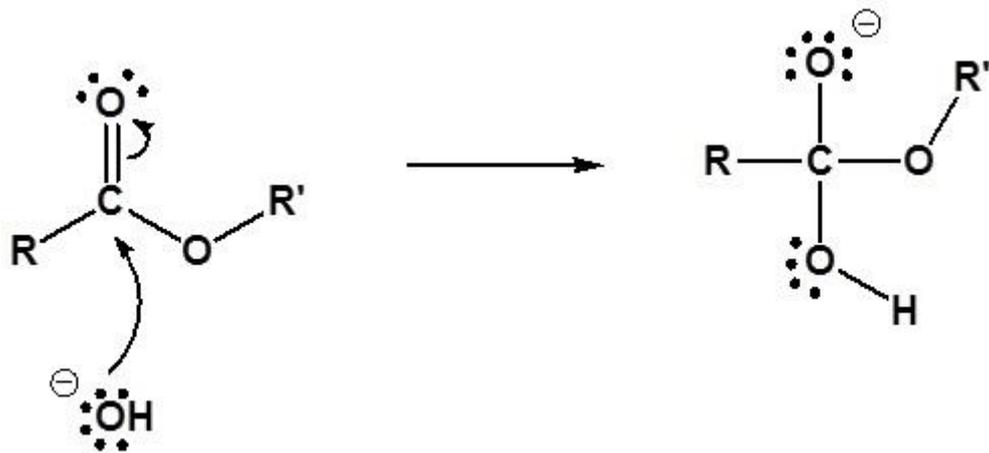
The reaction is called a saponification from the Latin *sapo* which means soap. The name comes from the fact that soap used to be made by the ester hydrolysis of fats. Due to the basic conditions a carboxylate ion is made rather than a carboxylic acid.

General reaction

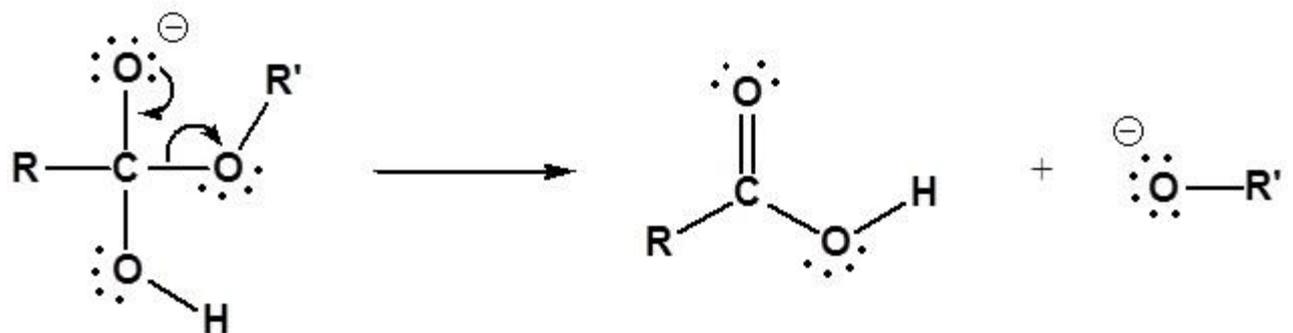


## Mechanism

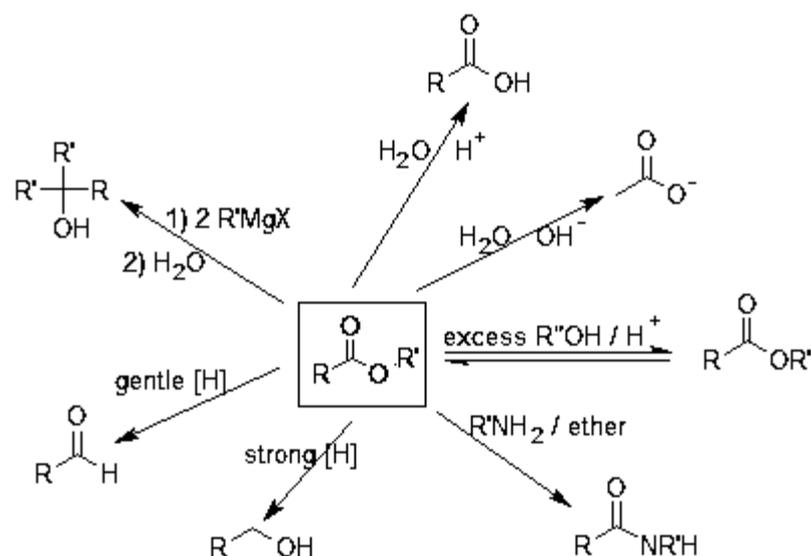
### 1) Nucleophilic attack by hydroxide



### 2) Leaving group removal

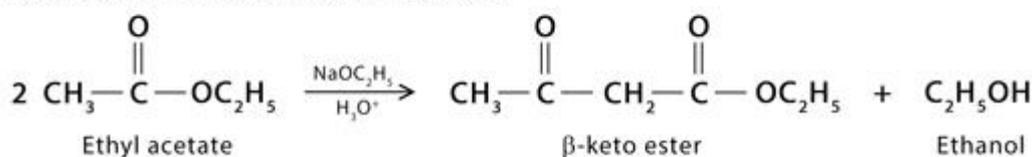


### 3) Deprotonation

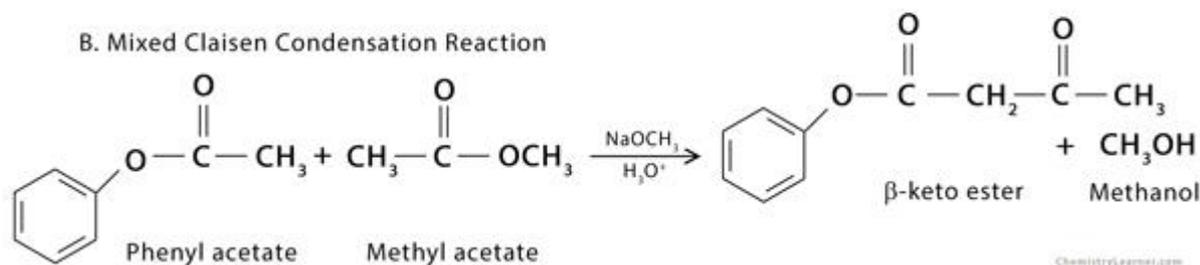


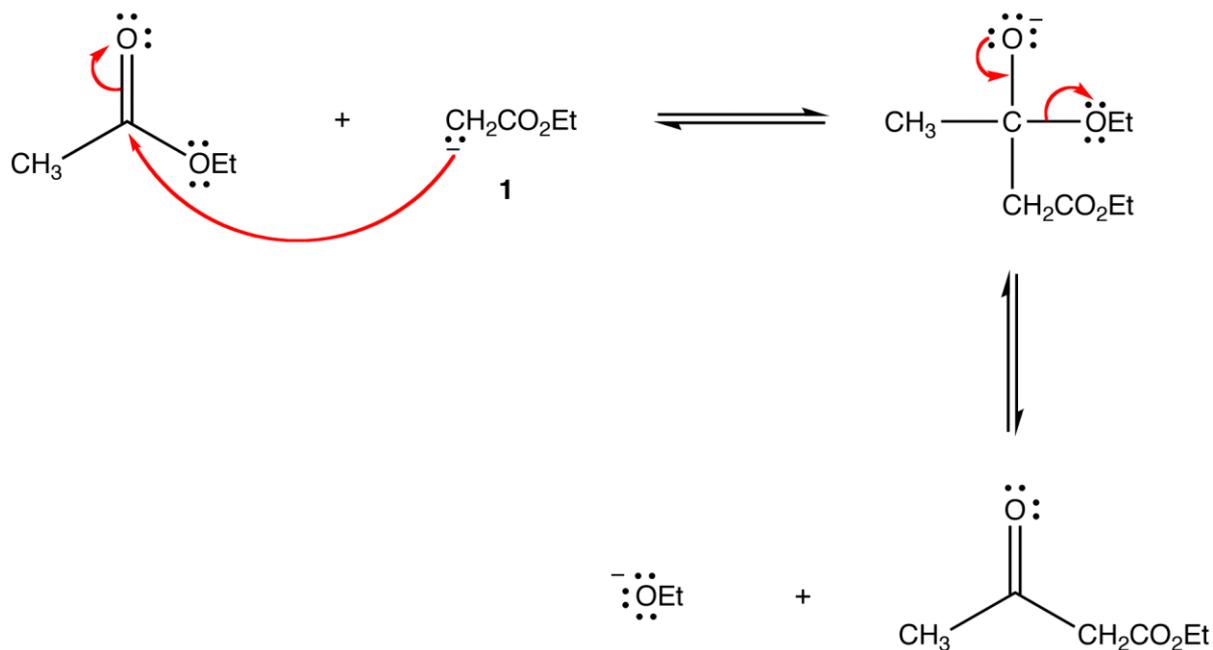
## Examples of Claisen Condensation Reaction

### A. General Claisen Condensation Reaction



### B. Mixed Claisen Condensation Reaction

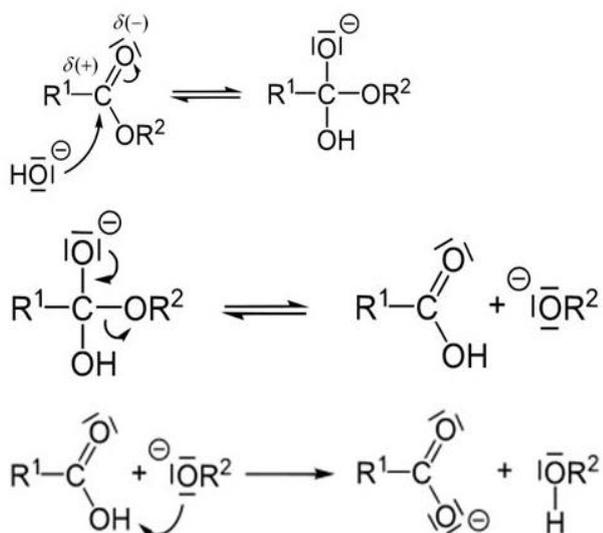




## Saponification

1. Hydroxyl anion attacks carbonyl group of the ester to form an orthoester.
2. Orthoester splits into a carboxylic acid and alkoxide.
3. Alkoxide is more basic than the conjugate base of carboxylic acid, so a proton is exchanged to form an alcohol.

Note: Recall that a carboxylic acid can associate with the alkali metal from the catalyst and make soap.



# Importance of Esters

- 1) **Flavorings and fragrances**

Common esters used for flavors and fragrances

Ester	Smells like	Prepared from	
		Alcohol	Acid
isoamyl acetate	Banana	Isoamyl alcohol	Acetic acid
ethyl butyrate	Pineapple	Ethanol	Butanoic acid
benzyl acetate	Peaches	Benzyl alcohol	Acetic acid
n-propyl acetate	Pears	n-propyl alcohol	Acetic acid
benzyl butyrate	Flowers	Benzyl alcohol	Butanoic acid
methyl butyrate	Apples	Methanol	Butanoic acid
isobutyl propionate	Rum	Isobutyl alcohol	Propionic acid
octyl acetate	Oranges	Octanol	Acetic acid
methyl anthranilate	Grapes	methanol	2-aminobenzoic