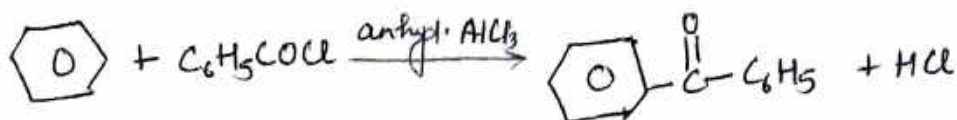
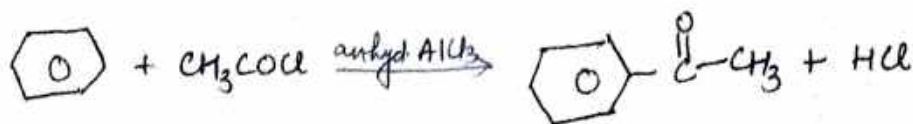


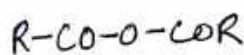
## Friedel-Craft acylation

Acy chlorides react with aromatic compounds in presence of a Lewis acid catalyst such as anhyd.  $AlCl_3$  to form aromatic ketones

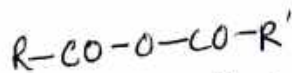


## Acid Anhydrides

They may be considered to be derived by the removal of a molecule of water either from two molecules of same acid or one molecule of the two different acids i.e.



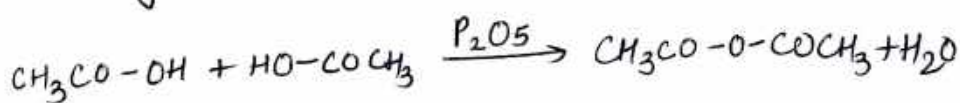
Simple  
anhydride



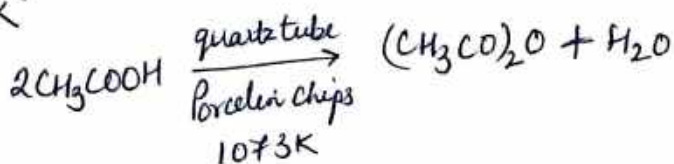
Mixed anhydride

## Preparation

1) From Carboxylic acids:- Simple acid anhydrides are obtained by heating Carboxylic acids with  $P_2O_5$ .



Acetic anhydride is prepared industrially by heating acetic acid to 1073K



## (8) From acid chlorides



## Physical Properties

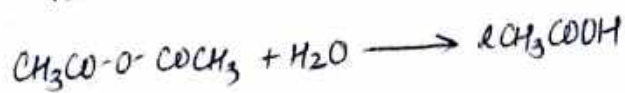
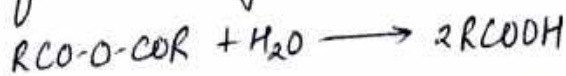
- ① Physical State, Colour, Smell: Lower aliphatic anhydrides are colourless liquids with sharp irritating smell while aromatic acid anhydrides are colourless solids.
- ② Boiling Point: The boiling points of acid anhydrides are higher than those of the acids from which they are derived. This is due to the reason that size of the acid anhydride molecule is much larger than the parent acid. As a result, they have stronger Van der Waals forces of attraction which account for their higher boiling points.
- ③ Solubility: They are generally soluble in common organic solvents such as ether, benzene etc.

## Chemical Properties:

Like acyl halide, acid anhydrides, undergo acyl nucleophilic substitution reactions. However they are much less reactive than the corresponding acyl halides.

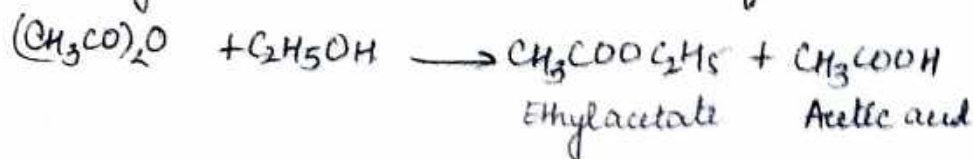
## Reactions

- 1) Hydrolysis: Acid anhydrides are slowly hydrolyzed by water to form carboxylic acids



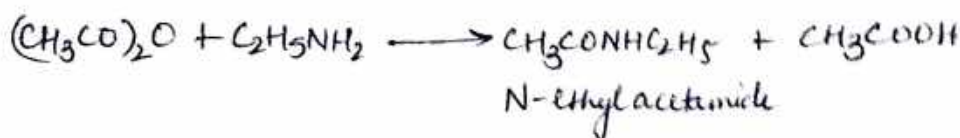
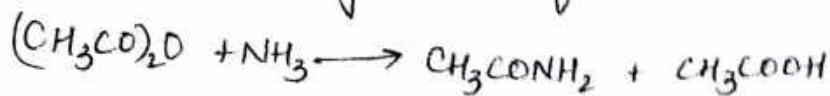
## 2) Alcoholysis

Acid anhydrides react with alcohols to form esters

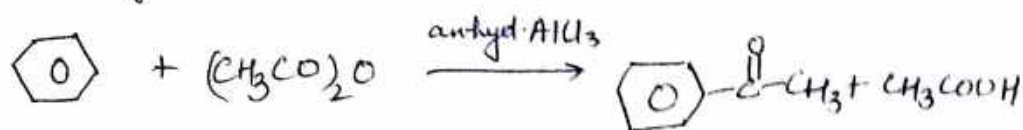


## 3) Ammonolysis

Ammonia and both primary amine and secondary amines react with acid anhydrides to form acid amides.

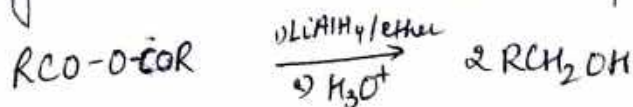


## 4) Friedel-Craft acylation

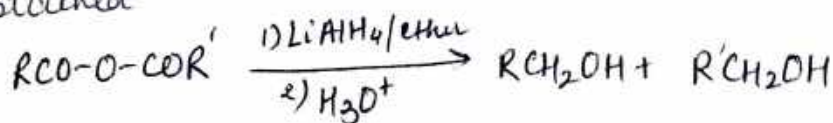


## 5) Reduction with LiAlH<sub>4</sub>

Anhydrides on reduction with LiAlH<sub>4</sub> gives primary alcohols

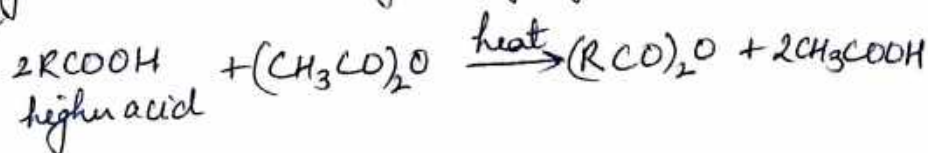


In case of mixed anhydrides, two different 1° alcohols are obtained



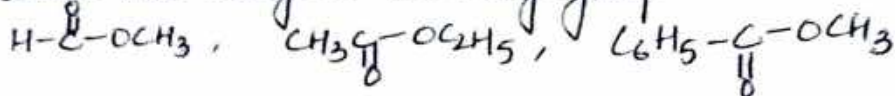
## 6) Dehydrating agent

Acetic anhydride act as a dehydrating agent. Higher acid anhydrides can be prepared by heating the acid with acetic anhydride or other dehydrating agents such as Phosphorous pentoxide



## Esters ( $R-\overset{\text{O}}{\parallel}{C}-OR'$ )

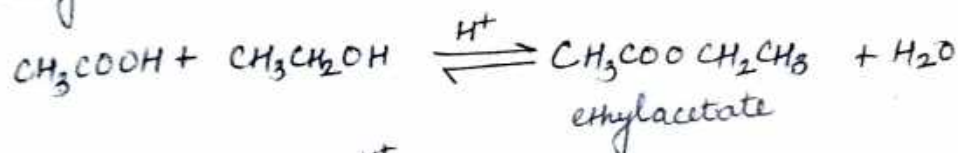
Esters may be considered to be derived from carboxylic acids by replacement of the OH part of  $-COOH$  group by  $(OR')$ . Therefore, the general formula of esters is  $RCOOR'$  where R may be H or any alkyl or aryl group while  $R'$  is always either an alkyl or an aryl group.



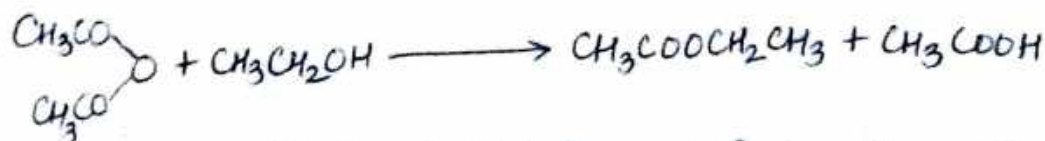
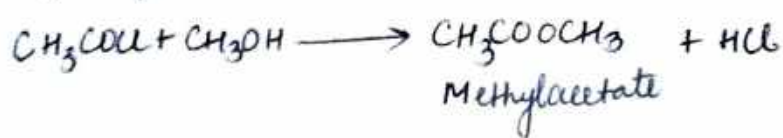
### Preparation

#### 1) By action of alcohols on carboxylic acids (Esterification)

Esters are generally prepared by heating carboxylic acids with alcohols in presence of a few drops of conc.  $H_2SO_4$  or dry HCl gas.



#### 2) Alcoholysis of acid chlorides or acid anhydrides



In contrast to direct esterification of carboxylic acids, alcoholysis of acid chlorides and anhydrides is an irreversible reaction and hence proceeds to completion to give esters in excellent yields.

## Physical Properties

### ① Physical State, Smell etc.:-

Esters of lower Carboxylic acids are Colourless, pleasant smelling liquids while those of higher acids are Colourless odourless Solids.

### ② Boiling Points:-

The boiling points of esters are lower than those of the corresponding acids since they cannot associate by intermolecular H-bonding.

### ③ Solubility

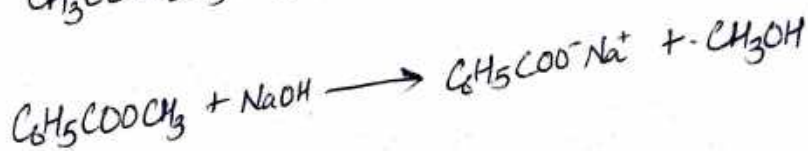
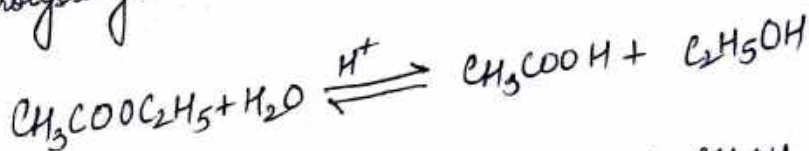
In general, esters are insoluble in water but are soluble in most of the common organic solvents such as alcohol, ether, benzene etc. They are themselves are excellent solvents

## Chemical Properties

Esters also undergo nucleophilic acyl substitution reactions. However, they are less reactive than both acid chlorides and anhydrides.

### ① Hydrolysis

Esters are hydrolyzed in acidic or alkaline medium. Acidic hydrolysis yield Carboxylic acid and an alcohol, the alkaline hydrolysis gives an alcohol and the salt of Carboxylic acid.



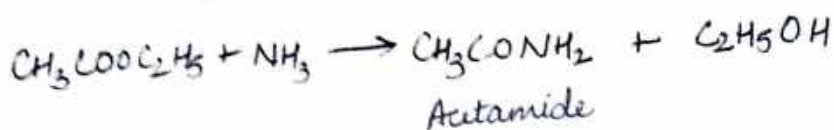
## 2) Alcoholysis or Trans-esterification

When an ester is treated with excess of another alcohol in presence of acid ( $H_2SO_4$  or  $HCl$ ) or base ( $KONa$ ) as Catalyst it gives another ester



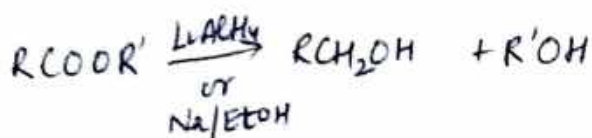
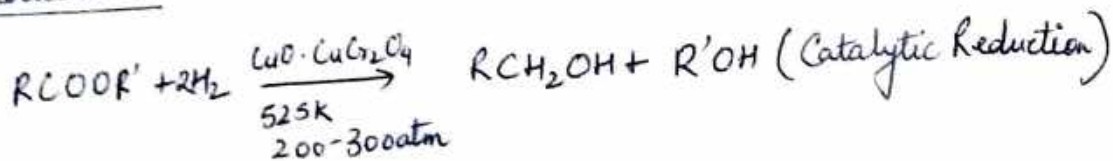
## 3) Ammonolysis

Esters react with ammonia, primary and secondary amines to form amides.



## Other reactions

### ① Reductions



Reduction of esters by  $(Na/EtOH)$  is called Bouveault-Blanco reduction.

### ② Grignard Reagent

