

## Aldehyde and Ketones

$$\begin{array}{l} \text{RCH}_2\text{OH} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7} \text{R}-\overset{\text{H}}{\underset{\text{Aldehyde}}{\text{C}}}=\text{O} \quad (\text{By special distillation method}) \\ \text{1}^\circ \text{ alcohol} \\ \text{RCH}_2\text{OH} \xrightarrow[\text{CH}_2\text{Cl}]{\text{P.C.C.}} \text{R}-\text{CHO} \end{array}$$

$$\text{ArCH}_3 \xrightarrow[\text{CrO}_3, \text{ acetic anhydride}]{\text{Cl}_2, \text{ heat } h\nu} \text{ArCHCl}_2 \xrightarrow{\text{H}_2\text{O}} \text{ArCHO}$$

$$\text{ArCH} \left( \begin{array}{c} \text{OC} - \text{CH}_3 \\ \parallel \\ \text{O} \end{array} \right)_2 \xrightarrow{\text{H}_2\text{O}} \text{ArCHO}$$

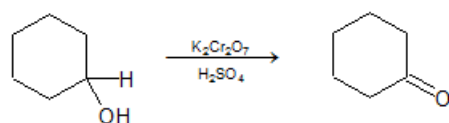
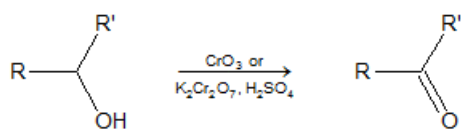
A gem-diacetate  
(Not oxidized)

Oc1ccccc1.ClC(Cl)Cl.[OH-]>>Oc1ccccc1C=O
$$\text{elimination. } \text{OH}^- + \text{HCCl}_3 \xrightarrow{-\text{HCl}} \text{:CCl}_2$$
$$\text{C}_6\text{H}_5\text{—COCl or RCOC l} \xrightarrow[\text{Pd-BaSO}_4]{\text{H}_2} \text{RCHO} + \text{HCl}$$

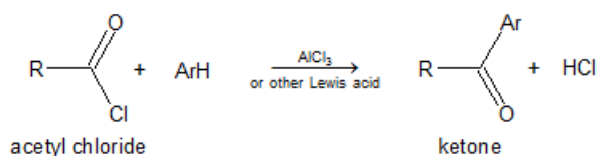
Poisoned with quinoline-S (trace)  
**Rosenmund's reaction**

$$\text{R}-\text{C}\equiv\text{N} \xrightarrow[\text{HCl, 2. H}_2\text{O}]{1. \text{SnCl}_2} \text{RCHO}$$

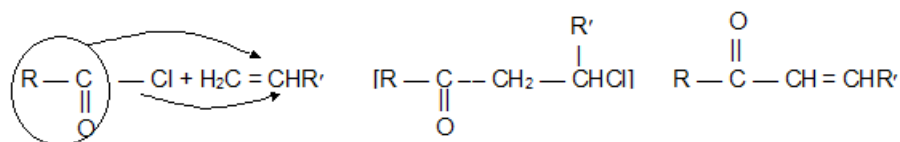
**a) Oxidation of Secondary alcohols:**



b) Friedel – Crafts acylation

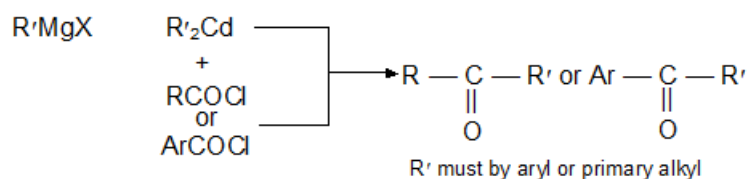


c) Acylation of Alkenes

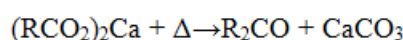


This is Markovnikov addition initiated by  $\text{R}-\overset{+}{\text{C}}=\ddot{\text{O}}:$ , an acylium cation.

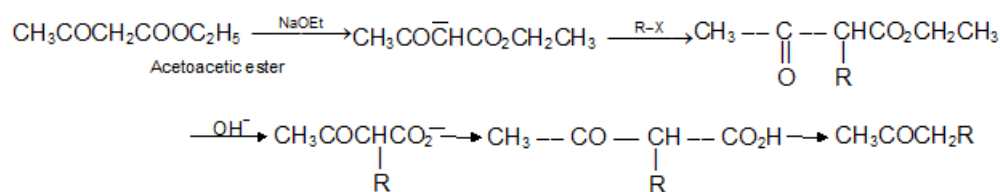
d) With Organometallics



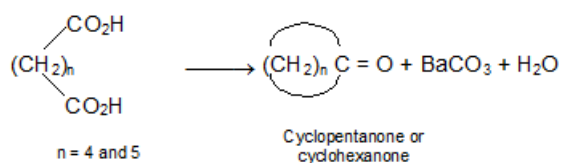
e) By heating the calcium salt of any monocarboxylic acid other than formic acid



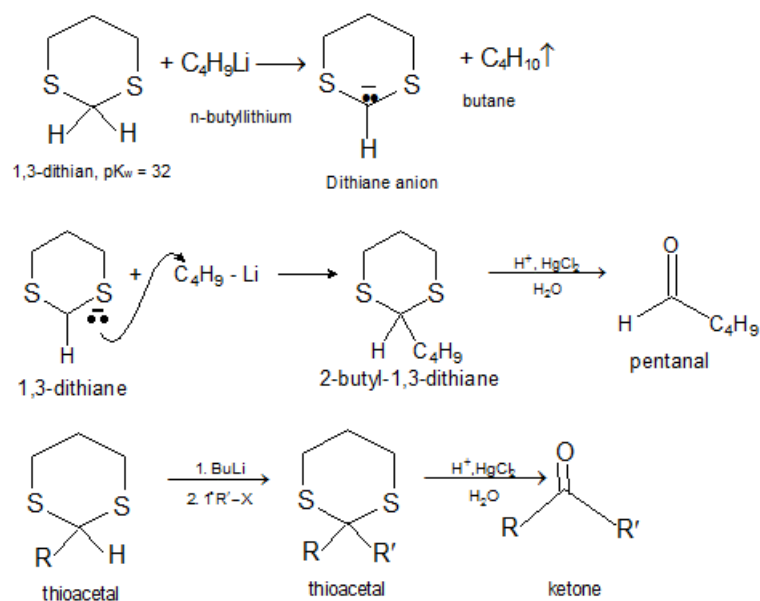
f) Acetoacetic ester synthesis of ketones



g) Ring Ketones from Dicarboxylic acids and their Derivatives:



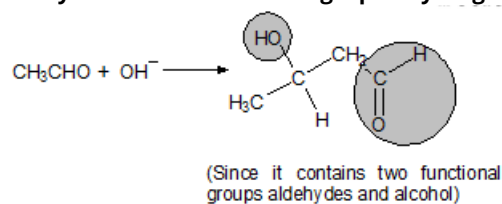
h) Synthesis of Ketones and Aldehydes Using 1,3-Dithianes:



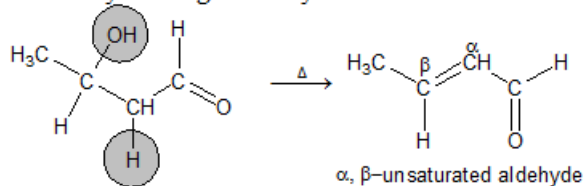
## Reactions of Aldehydes and Ketones:

### a) Aldol condensation

Aldehydes and ketones having alpha hydrogen atom:

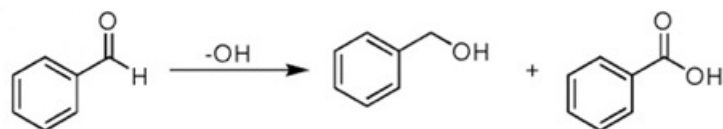


Aldol easily undergoes dehydration

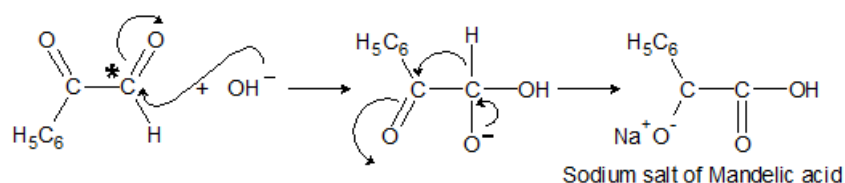


### b) Cannizzaro reaction:

Aldehydes and ketones having no alpha hydrogen atom:

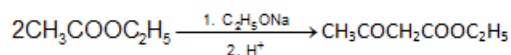


When two carbonyl groups are present within a molecule, think of intramolecular reaction.  $\text{OH}^-$  will attack more positively charged carbon. In this case, it is right  $>\text{C}=\text{O}$  group.



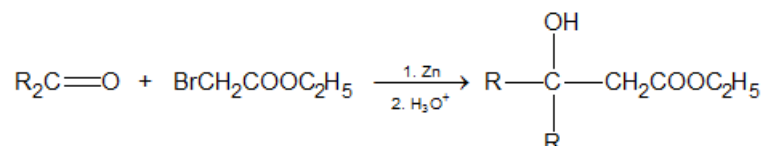
### c) Formation of Keto Esters

Esters having  $\alpha$ -hydrogen on treatment with a strong base e.g.  $\text{C}_2\text{H}_5\text{ONa}$ . Undergo self condensation to produce  $\beta$ -keto esters. This reaction is Claisen Condensation.



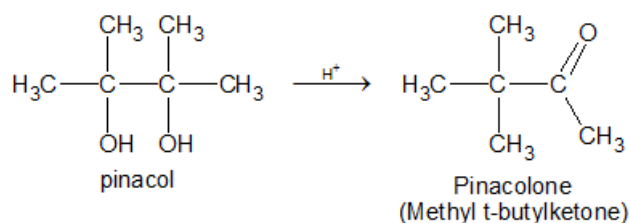
### d) Reformatsky Reaction

This is the reaction of  $\alpha$ -haloester, usually an  $\alpha$ -bromoester with an aldehyde or ketone in the presence of Zinc metal to produce  $\beta$ -hydroxyester.



### e) Pinacol-pinacolone Rearrangement

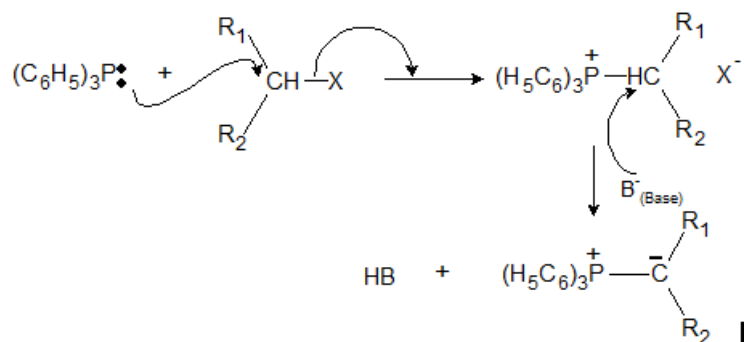
The acid catalysed rearrangement of 1,2 diols (Vicinal diols) to aldehydes or ketones with the elimination of water is known as pinacol pinacolone rearrangement.



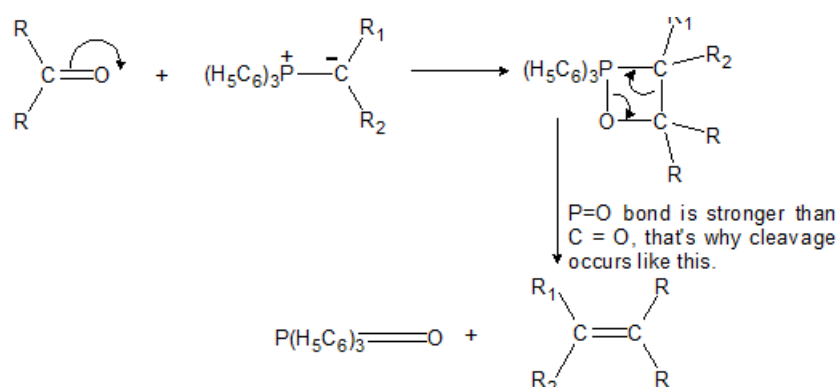
### a) Wittig-Ylide Reaction

Aldehydes and Ketones react with phosphorus Ylides to yield alkenes and triphenyl phosphine oxide. An Ylide is a neutral molecule having a negative carbon adjacent to a positive hetero atom. Phosphorus ylides are also called phosphoranes.

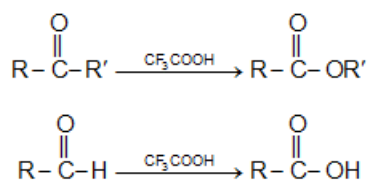
Preparation of Ylides



#### Reaction of Ylide with >C=O

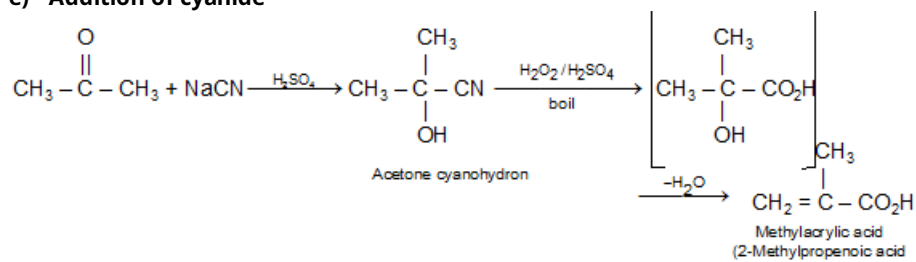


#### d) Baeyer-Villiger Oxidation

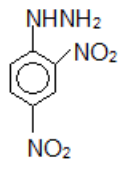
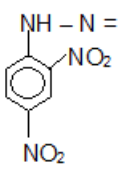


Above things happens in BVO (Bayer Villiger oxidation). Reagents are either per acetic acid or perbenzoic acid or pertrifluoroacetic acid or permonosulphuric acid.

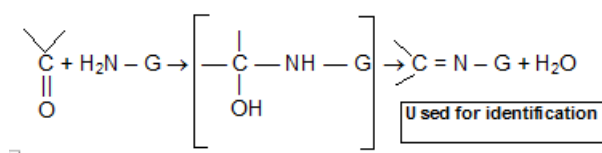
#### e) Addition of cyanide



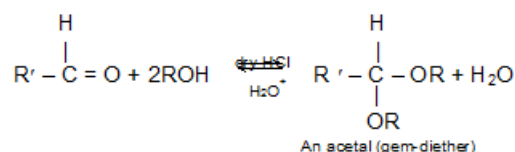
#### f) Addition of bisulfite:

	$\text{H}_2\text{N} - \text{G}$	Product	
$\text{H}_2\text{NOH}$	Hydroxylamine	$>\text{C} = \text{N} - \text{OH}$	Oxime
$\text{H}_2\text{N} - \text{NH}_2$	Hydrazine	$>\text{C} = \text{N} - \text{NH}_2$	Hydrazone
$\text{H}_2\text{N} - \text{NH} - \text{C}_6\text{H}_5$	Phenylhydrazine	$>\text{C} = \text{N} - \text{NHC}_6\text{H}_5$	Phenylhydrazone
$\text{H}_2\text{N} - \text{NH} - \text{CO} - \text{NH}_2$	Semicarbazide	$>\text{C} = \text{N} - \text{NHCONH}_2$	Semicarbazone
	2, 4-Dinitrophenyl hydrazine		2, 4-dinitrophenylhydrazo ne (bright orange or yellow precipitate used for identifying aldehydes and ketones)

#### g) Addition of derivative of ammonia

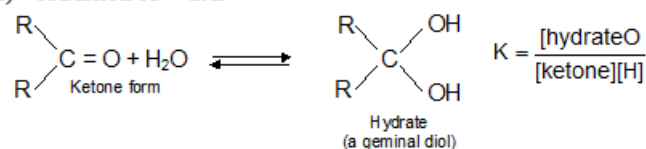


#### h) Addition of Alcohols; Acetal Formation

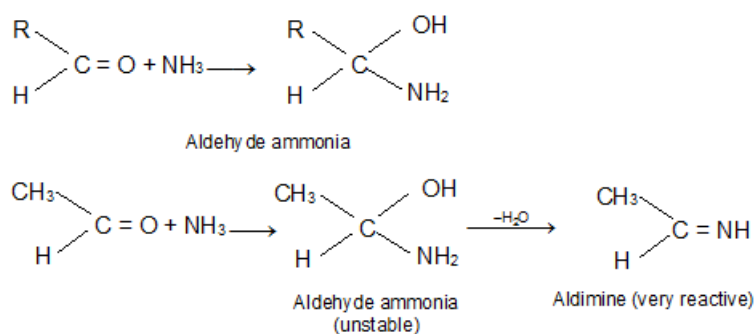


In  $\text{H}_3\text{O}^+$ ,  $\text{RCHO}$  is regenerated because acetals undergo acid catalyzed cleavage much more easily than do ethers. Since acetals are stable in neutral or basic media, they are used to protect the  $-\text{CH}=\text{O}$  group.

#### i) Addition of Water



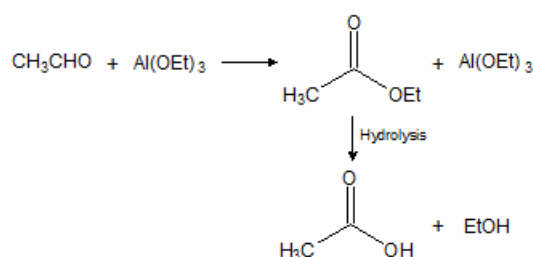
#### j) Addition of Ammonia:



#### k) Tischenko reaction:

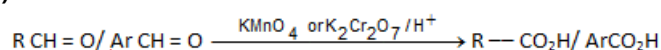
All aldehydes can be made to undergo the Cannizzaro reaction by treatment with *aluminium ethoxide*. Under these conditions the acids and alcohols are combined as the ester, and the reaction is then known as the

Tischenko reaction; eg, acetaldehyde gives ethyl acetate, and propionaldehyde gives propyl propionate.



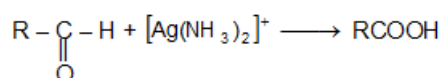
### Oxidation of Aldehydes and Ketones

a)



b) Tollen's Reagent

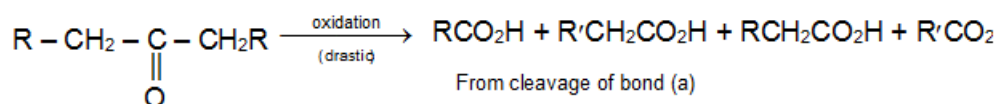
A specific oxidant for RCHO is  $[\text{Ag}(\text{NH}_3)_2]^+$



Tollen's test chiefly used for the detection of aldehydes.

Tollen's reagent doesnot attack carbon-carbon double bonds.

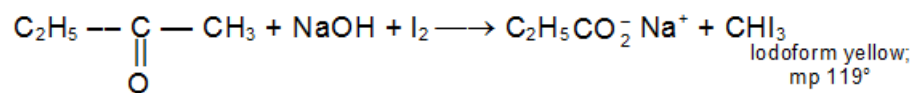
c) Strong Oxidants: Ketones resist mild oxidation, but with strong oxidants at high temperature they undergo cleavage of C - C bonds on either sides of the carbonyl group.



d) Haloform Reaction

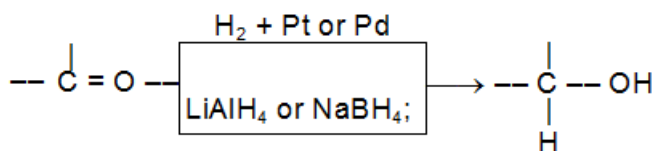
$\text{CH}_3\text{COR}$  are readily oxidised by NaOI ( $\text{NaOH} + \text{I}_2$ ) to iodoform,  $\text{CHI}_3$ , and  $\text{RCO}_2\text{Na}$

Example:



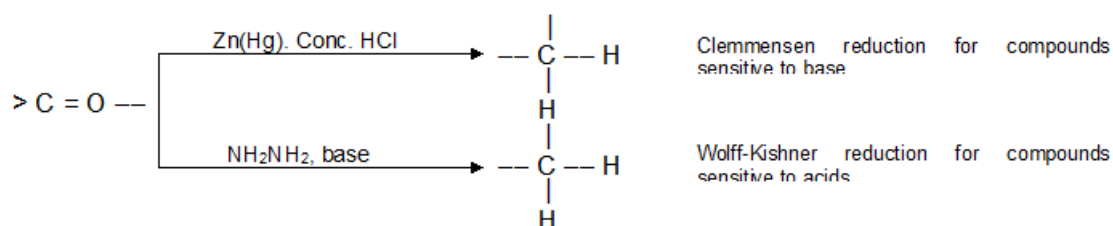
## • Reduction:

a) Reduction to alcohols



Aldehydes  $\rightarrow$  1° alcohols; Ketones  $\rightarrow$  2° alcohols

b) Reduction to hydrocarbons



## Carboxylic Acids:

Carboxylic Acids	Common Names
HCOOH	Formic acid
CH <sub>3</sub> COOH	Acetic acid
CH <sub>3</sub> -CH <sub>2</sub> -COOH	Propionic acid
CH <sub>3</sub> (CH <sub>2</sub> )COOH	Butyric acid
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOH	Valeric acid
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>14</sub> COOH	Palmitic acid
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>16</sub> COOH	Stearic Acid

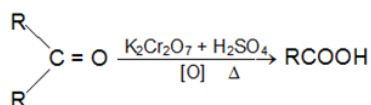
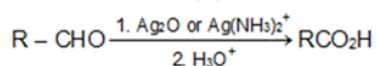
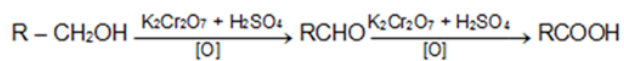
### Physical Properties of Carboxylic Acids

- The first three acids are colourless, pungent smelling liquids.
- First four members are miscible in water due to the intermolecular hydrogen bonding whereas higher members are miscible in non-polar solvents like ether.
- Benzene or ethanol but immiscible in water due to the increase in the size of lyophobic alkyl chain.
- The b.p. of carboxylic acids are higher than alcohols because carboxylic acids exist as dimers due to the presence of intermolecular H-bonding
- Increase in the number of Halogen atoms on  $\alpha$ -position increases the acidity, eg.  
 $\text{CCl}_3\text{COOH} > \text{CHCl}_2\text{COOH} > \text{ClCH}_2\text{COOH} > \text{CH}_3\text{COOH}$
- Increase in the distance of Halogen from COOH decreases the acidity e.g.  
 $\text{CH}_3 - \text{CH}_2 - \text{CH}(\text{Cl}) - \text{COOH} > \text{CH}_3 - \text{CH}(\text{Cl}) - \text{CH}_2 - \text{COOH} > \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{COOH}$
- Increase in the electro negativity of halogen increases the acidity.  
 $\text{FCH}_2\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ICH}_2\text{COOH}$

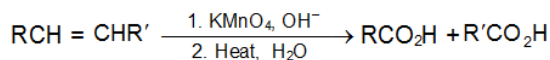
### Methods of Preparations of Carboxylic Acids

#### a. Oxidation of Aldehydes & Ketones

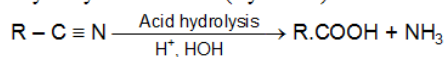




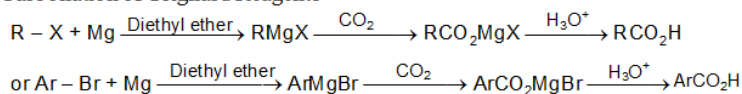
b. Oxidation of Alkanes:



c. Hydrolysis of Nitriles (Cyanides)

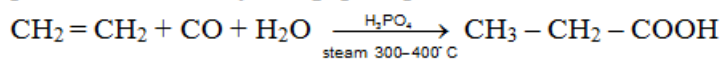


d. Carbonation of Grignard Reagents

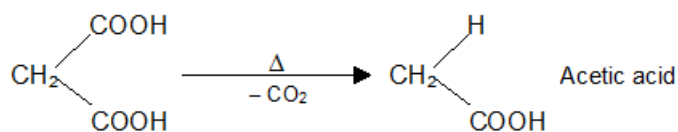


e. Koch Reaction:

An olefin is heated with carbon monoxide and steam under pressure at 300-400° in the presence of a catalyst, e.g. phosphoric acid.

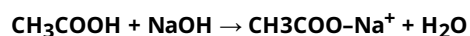
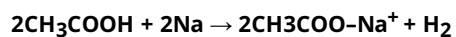


f. Heating Gem Dicarboxylic Acids:

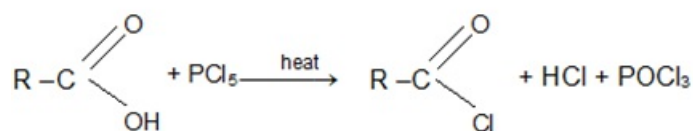
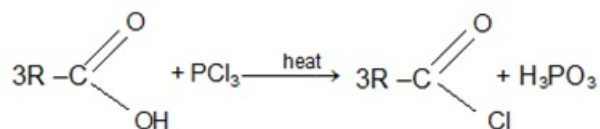
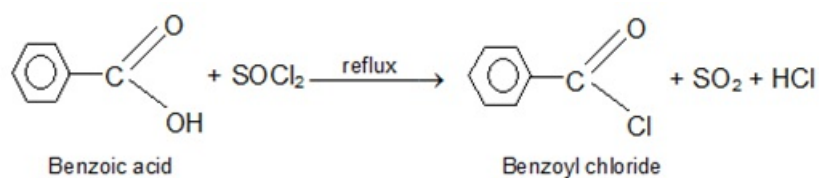


### Chemical Reactions of Carboxylic Acids

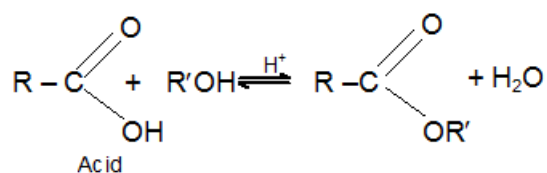
a. Salt formation:



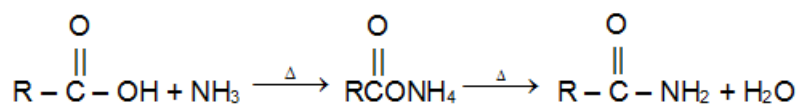
b. Conversion into Acid Chlorides:



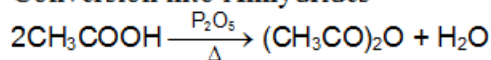
c. Conversion into Esters (Esterification)



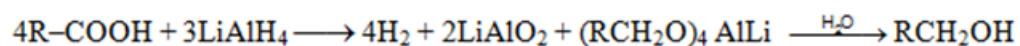
d. Conversion into Amides



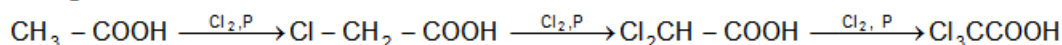
e. Conversion into Anhydrides



f. Reduction:

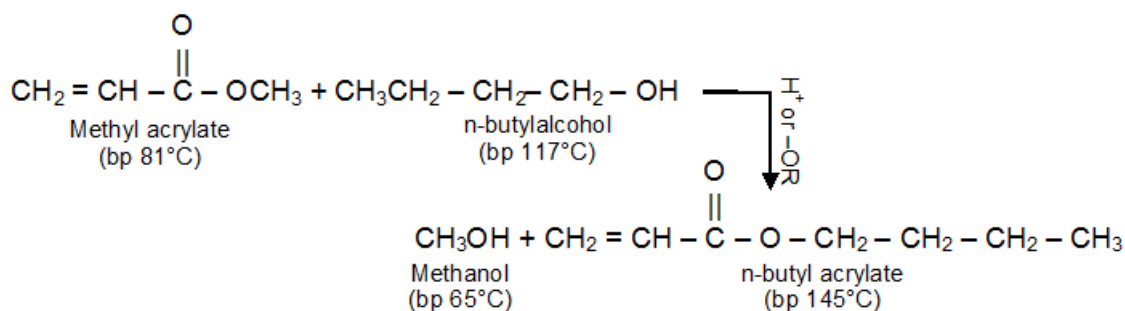


g. Halogenation:

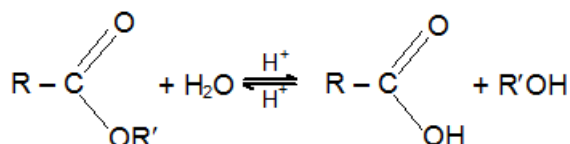


## Esters

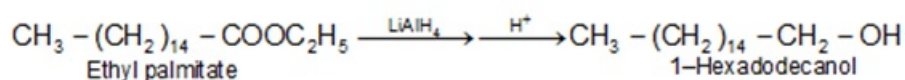
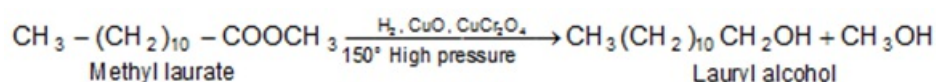
a) Transesterification :



**b) Hydrolysis:**

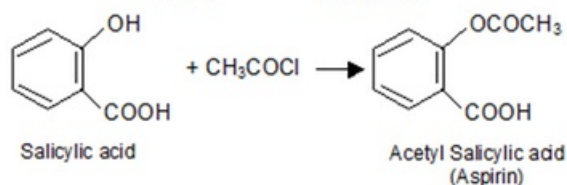
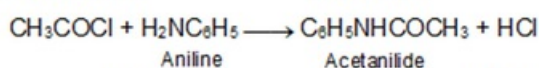
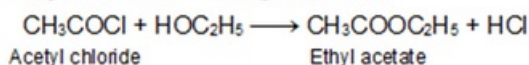


**c) Reduction:**

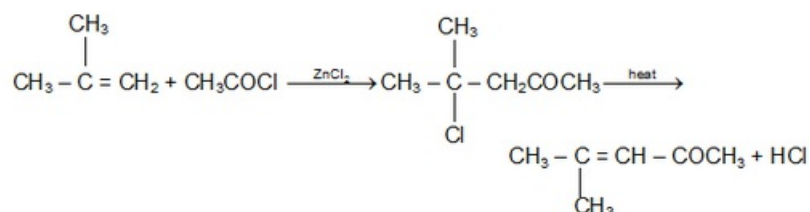


## Acid Chlorides:

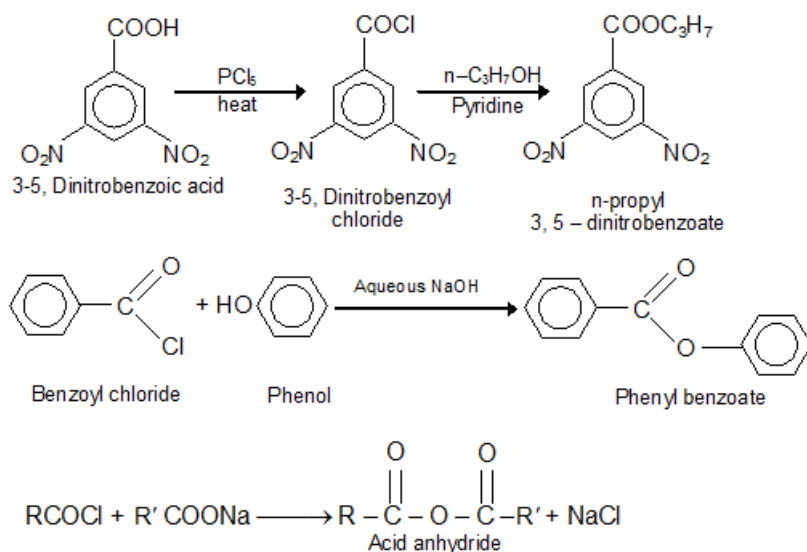
**a) Acetylation**



**b) Reaction with Olefins:**

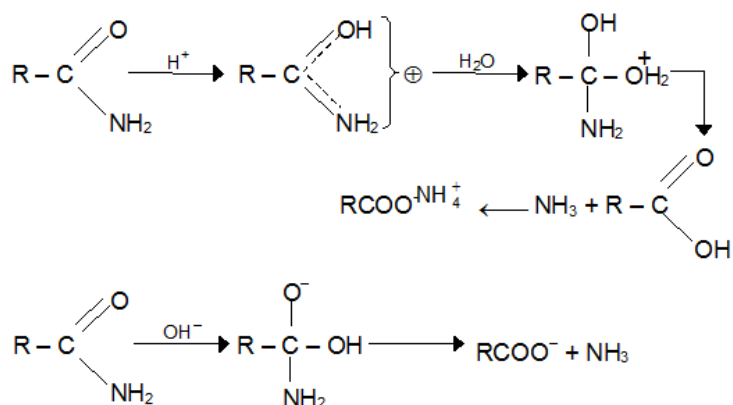


**c) Conversion of Acid Chlorides into Acid Derivatives:**

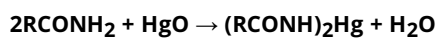


## Amides

### a. Hydrolysis:

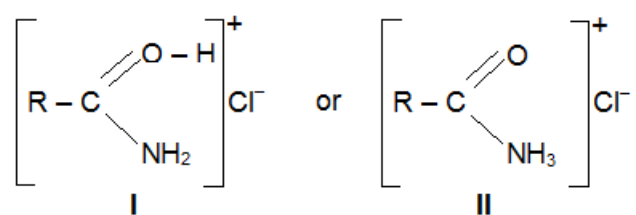


### b. Acidic Character of Amides:

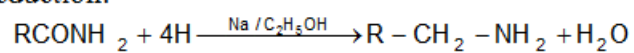


### c. Basic Character of Amides:

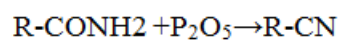
Amides are very feebly basic and form unstable salts with strong inorganic acids. e.g.  $\text{RCONH}_2\text{HCl}$ . The structure of these salts may be I or II



d. Reduction:



e. Reaction with Phosphorus Pentaoxide:



f. Reaction with Nitrous Acid:

