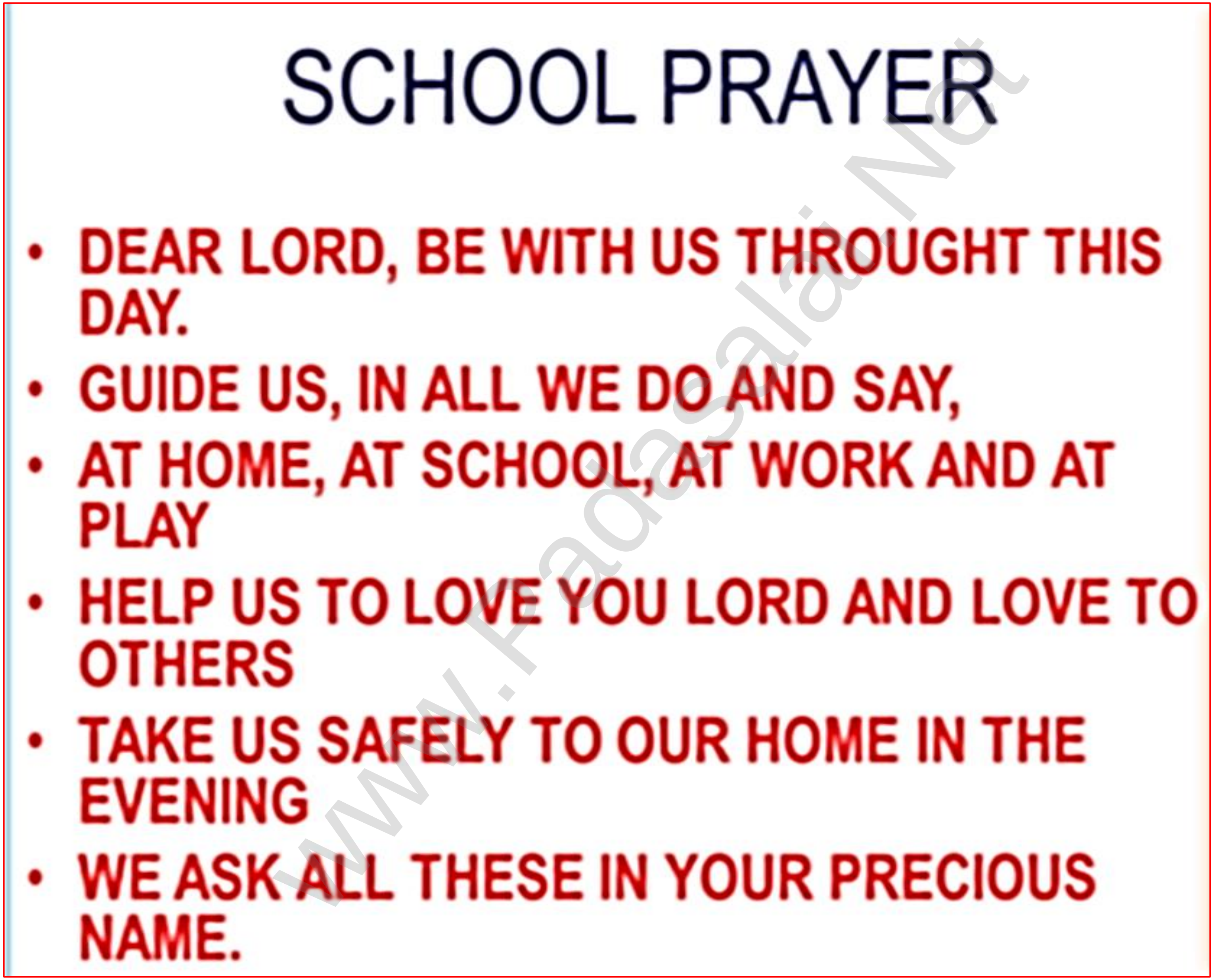
Velammal
Matric. Hr. Sec. School
Surapet

Department of Chemistry

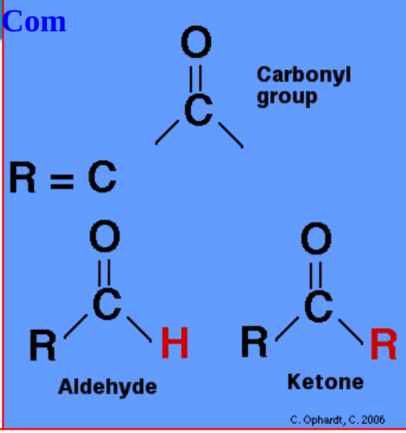
UNIT 12
CARBONYL COMPOUNDS AND CARBOXYLIC ACIDS



SCHOOL PRAYER

- DEAR LORD, BE WITH US THROUGHT THIS DAY.
- GUIDE US, IN ALL WE DO AND SAY,
- AT HOME, AT SCHOOL, AT WORK AND AT PLAY
- HELP US TO LOVE YOU LORD AND LOVE TO OTHERS
- TAKE US SAFELY TO OUR HOME IN THE EVENING
- WE ASK ALL THESE IN YOUR PRECIOUS NAME.

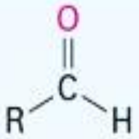
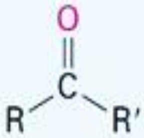
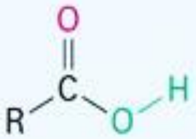
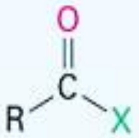
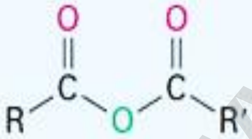
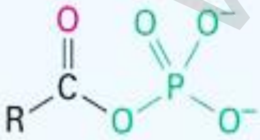
Introduction

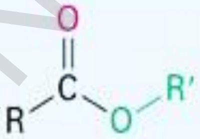
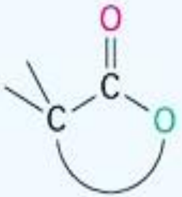
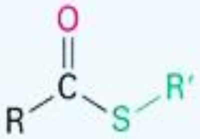
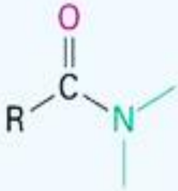
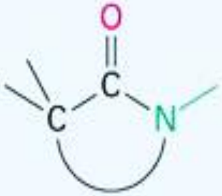


- We come across many organic compounds containing a -C=O group in our everyday Life.
- Biomolecules such as protein, carbohydrate etc… that makeup all plants and animals contains carbonyl group.
- They play an important role in the metabolic process. For example, pyridoxal, an aldehyde derived from vitamin B, function as a co – enzyme.
- Carbonyl compounds are important constituents of fabrics, plastis and drugs. For example, Formaldehyde is used for the manufacture of Bakelite and paracetamol, (p– acetylated aminophenol) a drug used to reduce fever, contains a carbonyl group.
- In this unit, we will learn the preparation, properties and uses of aldhydes, ketones and carboxylic acids.

Types of carbonyl compounds

Table 1 Some Types of Carbonyl Compounds

Name	General formula	Name ending
Aldehyde		*-al*
Ketone		*-one*
Carboxylic acid		*-oic acid*
Acid halide		*-yl or -oyl halide*
Acid anhydride		*-oic anhydride*
Acyl phosphate		*-yl phosphate*

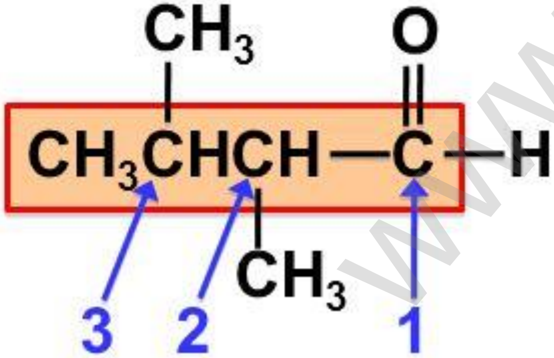
Name	General formula	Name ending
Ester		*-oate*
Lactone (cyclic ester)		None
Thioester		*-thioate*
Amide		*-amide*
Lactam (cyclic amide)		None

Nomenclature

Naming Aldehydes

To name an aldehyde using the IUPAC system:

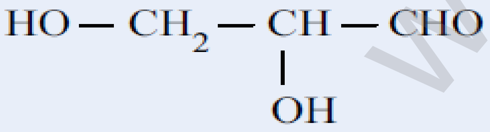
- Find the longest chain containing the CHO group.
- Change the "-e" ending of the parent alkane to "-al."
- Number the chain to put the CHO group at C1, but omit "1" from the name.
- Apply all other nomenclature rules.



$CH_3CH(CH_3)CH(CH_3)CHO$

butane → butanal

Answer:
2,3-dimethylbutanal

Compound (common name, Structural formula, IUPAC Name)	IUPAC Name			
	Prefix with position number	Root used	Primary suffix	Secondary Suffix
Formaldehyde $H-CHO$ methanal	–	meth	an~~e~~	al
Acetaldehyde CH_3-CHO ethanal	–	eth	an~~e~~	al
Acrolein $CH_2=CH-CHO$ prop – 2- enal	–	prop	2-en~~e~~	al
Crotonaldehyde $CH_3-CH=CH-CHO$ but – 2 – enal	–	but	2-en~~e~~	al
Glyceraldehyde  $HO-CH_2-\underset{\displaystyle OH}{\underset{\mid}{CH}}-CHO$ 2, 3 – dihydroxy propanal	2, 3 dihydroxy	prop	an~~e~~	al

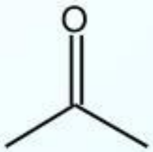
Naming Ketones

- Parent name ends in -one
- Find longest chain containing the carbonyl group
- Number C's starting at end nearest carbonyl group
- Locate and number substituents and give full name

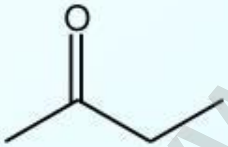
  - use a number to indicate position of carbonyl group

  - cyclic ketones have cyclo- before the parent name; numbering begins at the carbonyl group, going in direction that gives substituents lowest possible numbers

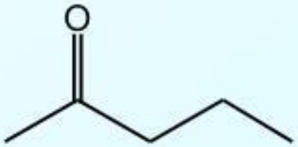
  - use a prefix (di-, tri-) to indicate multiple carbonyl groups in a compound



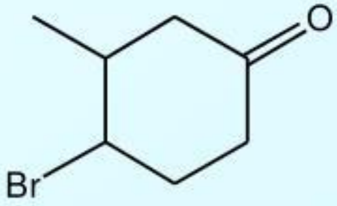
propanone
(acetone)



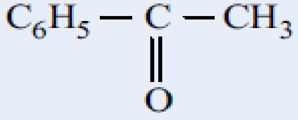
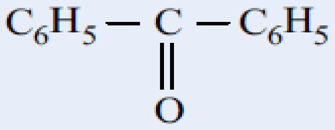
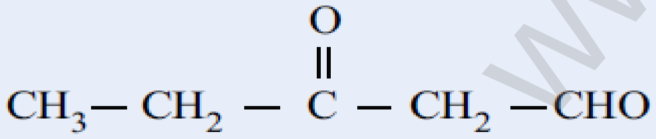
butanone



2-pentanone

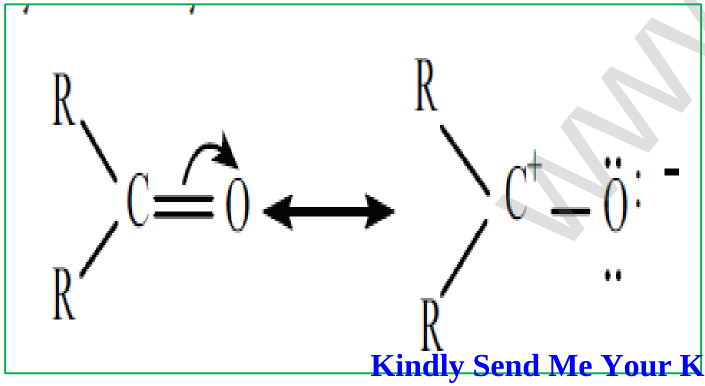


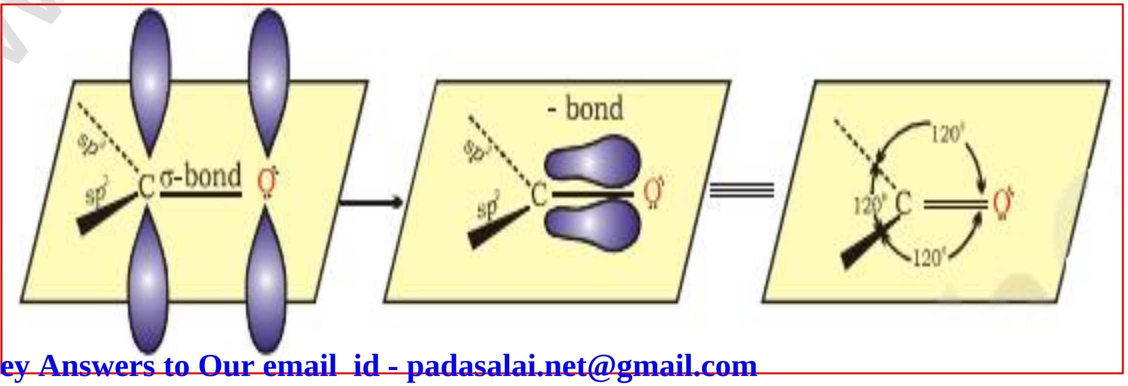
4-bromo-3-methylcyclohexanone

Acetone / Dimethyl ketone $CH_3 - CO - CH_3$ propanone	–	prop	an~~e~~	one
Mesityl oxide $(CH_3)_2C = CHCOCH_3$ 4 – methylpent-3-en-2-one	4 – methyl	pent	3-en~~e~~	2-one
Methyl Phenyl ketone  $C_6H_5 - \underset{\underset{O}{\Vert}}{C} - CH_3$ Acetophenone (PIN)* 1-phenylethan-1-one	1-phenyl	eth	an~~e~~	1-one
Diphenyl ketone  $C_6H_5 - \underset{\underset{O}{\Vert}}{C} - C_6H_5$ Benzophenone (PIN)* Diphenylmethanone	Diphenyl	meth	an~~e~~	one
 $CH_3 - CH_2 - \overset{\overset{O}{\Vert}}{C} - CH_2 - CHO$ 3 - oxopentanal	3 - oxo	pent	an~~e~~	al

Structure of carbonyl group

- The carbonyl carbon[– C=O] is sp^2 hybridised and the carbon – oxygen bond is similar to carbon – carbon double bond in alkenes.
- The carbonyl carbon forms three σ bonds using their three sp^2 hybridised orbital.
- One of the sigma bond is formed with oxygen and the other two with hydrogen and carbon (in aldehydes) or with two carbons (in ketones).
- All the three ' σ ' bonded atoms are lying on the same plane .
- The fourth valence electron of carbon remains in its unhybridised ‘2p’ orbital which lies perpendicular to the plane and it overlaps with 2p orbital of oxygen to form a carbon – oxygen π bond.
- The oxygen atom has two nonbonding pairs of electrons, which occupy its remaining two p-orbitals.
- Oxygen, the second most electro negative atom attracts the shaired pair of electron between the carbon and oxygen towards itself and hence the bond is polar. This polarization contributes to the reactivity of aldehydes and ketones.





General methods of preparation of aldehydes and ketones

A. Preparation of aldehydes and ketones

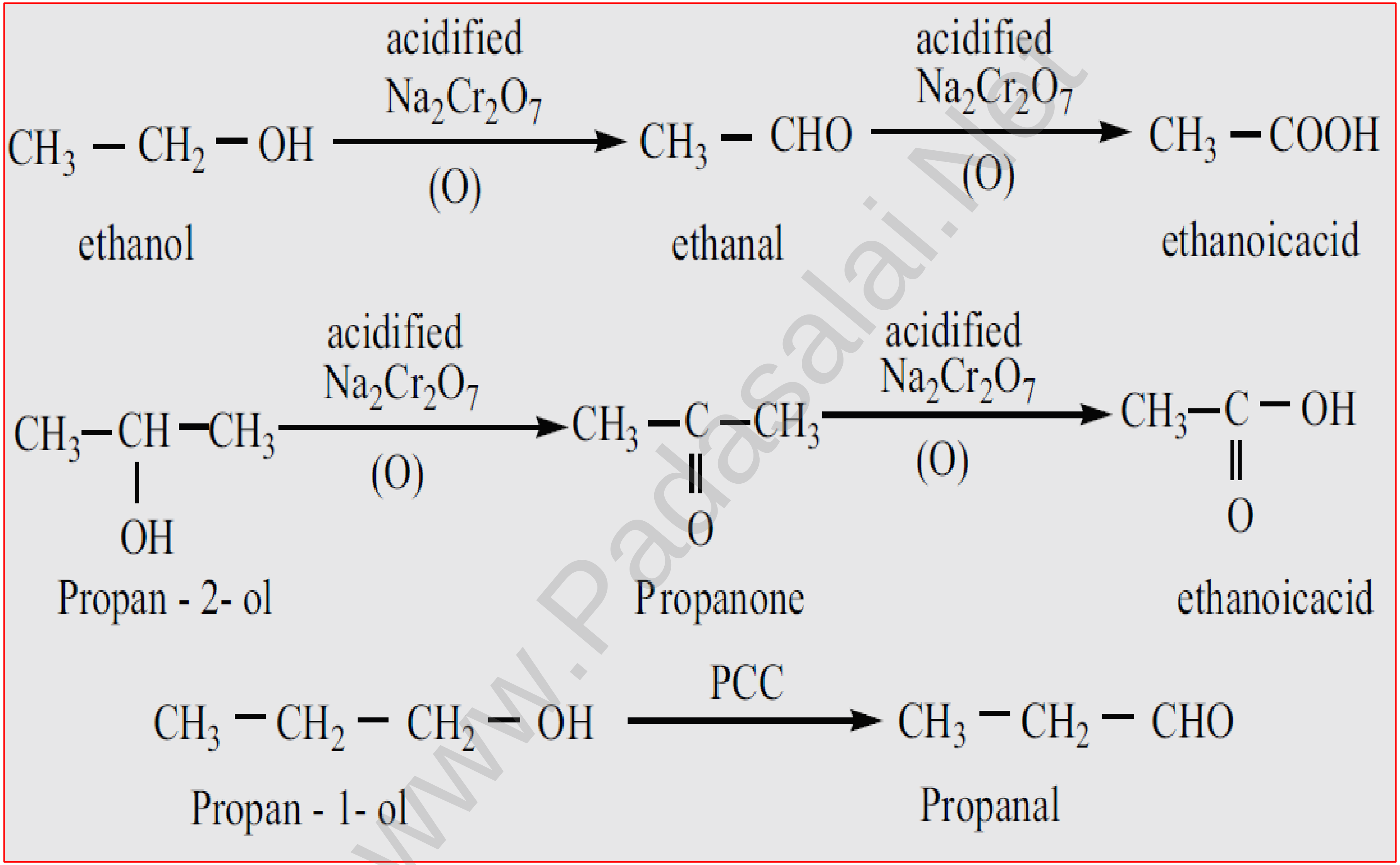
1.) Oxidation and catalytic dehydrogenation of alcohols

- We have already learnt that the oxidation of primary alcohol gives aldehydes and secondary alcohol gives a ketone.

- Oxidising agents such as acidified $Na_2Cr_2O_7$ $KMnO_4$ PCC , are used for oxidation.

- Oxidation using PCC yield aldehydes .

- Other oxidising agents further oxidise the aldhydes / ketones in to carboxylic acids.
-
- When vapours of alcohols are passed over heavy metal catalyst such as Cu, Ag, alcohols give aldehydes and ketons.



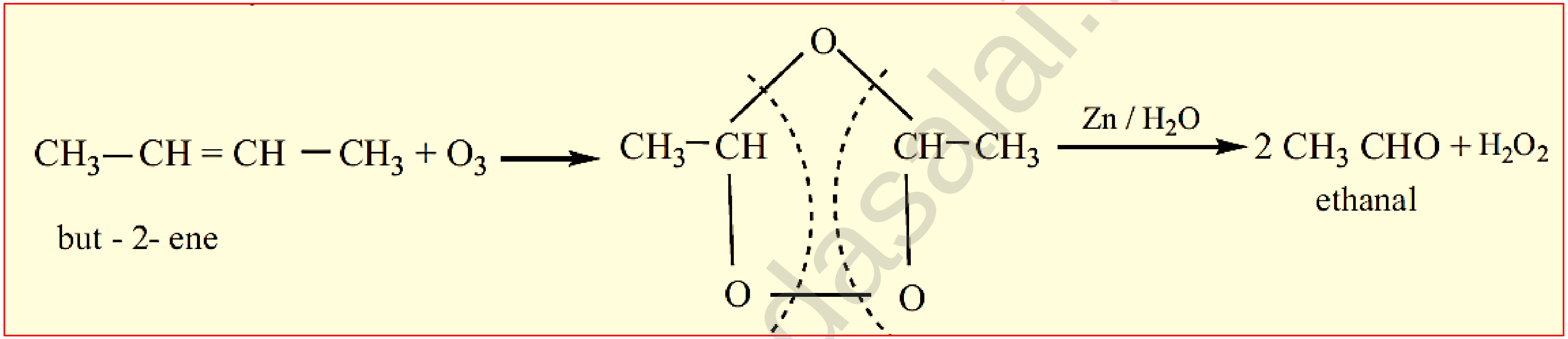
$$\underset{\text{ethanol}}{CH_3-CH_2-OH}\xrightarrow[\text{(O)}]{\text{acidified } Na_2Cr_2O_7}\underset{\text{ethanal}}{CH_3-CHO}\xrightarrow[\text{(O)}]{\text{acidified } Na_2Cr_2O_7}\underset{\text{ethanoicacid}}{CH_3-COOH}$$

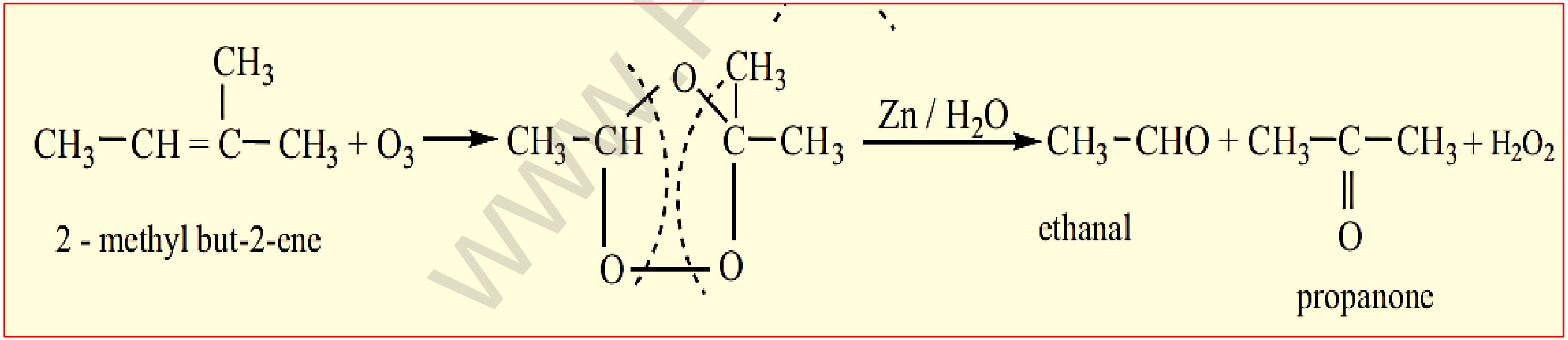
$$\underset{\text{Propan - 2- ol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3}\xrightarrow[\text{(O)}]{\text{acidified } Na_2Cr_2O_7}\underset{\text{Propanone}}{CH_3-\underset{\underset{O}{\|}}{C}-CH_3}\xrightarrow[\text{(O)}]{\text{acidified } Na_2Cr_2O_7}\underset{\text{ethanoicacid}}{CH_3-\underset{\underset{O}{\|}}{C}-OH}$$

$$\underset{\text{Propan - 1- ol}}{CH_3-CH_2-CH_2-OH}\xrightarrow{\text{PCC}}\underset{\text{Propanal}}{CH_3-CH_2-CHO}$$

2.) Ozonolysis of alkenes

Alkenes react with ozone to form ozonide which on subsequent cleavage with zinc and water gives aldehydes and ketones.
Zinc dust removes H_2O_2 formed, which otherwise can oxidise aldehydes / ketones.

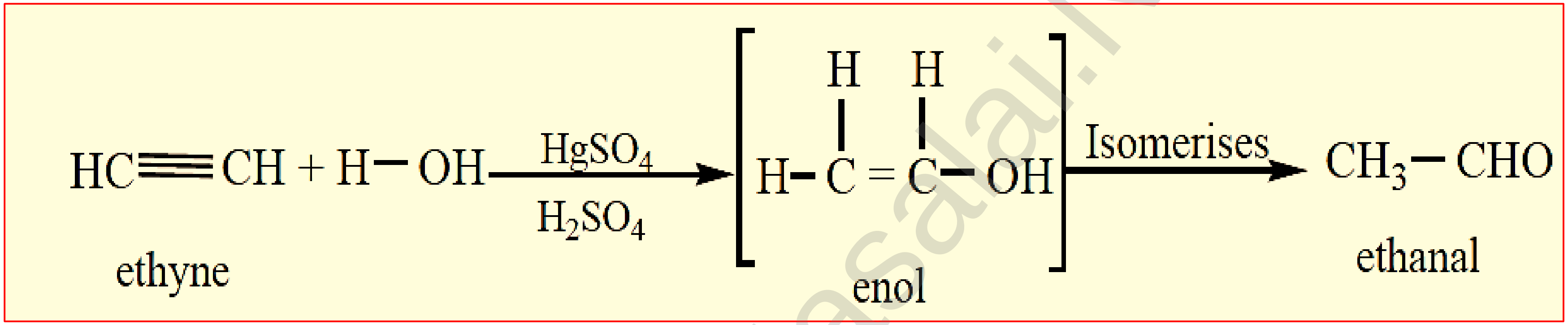




3. Hydration of alkynes

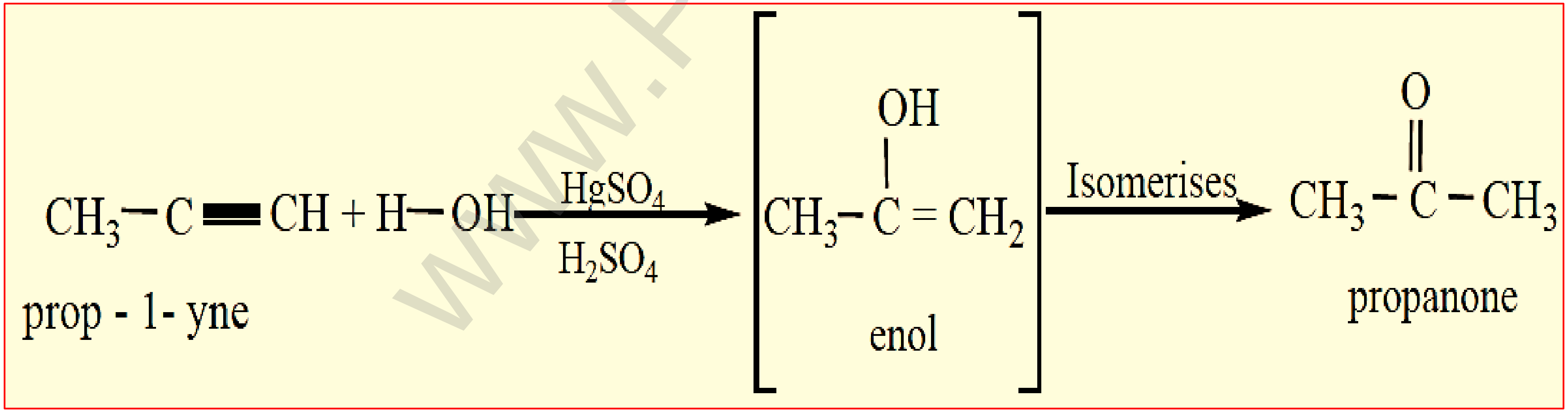
- The hydration of alkynes in presence of 40% dilute sulpuric acid and 1% $HgSO_4$ to give the corresponding aldehydes / ketones.

a) Hydration of acetylene yields acetaldehyde



$$HC \equiv CH + H-OH \xrightarrow[H_2SO_4]{HgSO_4} \left[H-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-OH \right] \xrightarrow{\text{Isomerises}} CH_3-CHO$$

b) Hydration of alkynes, other than acetylene gives ketones

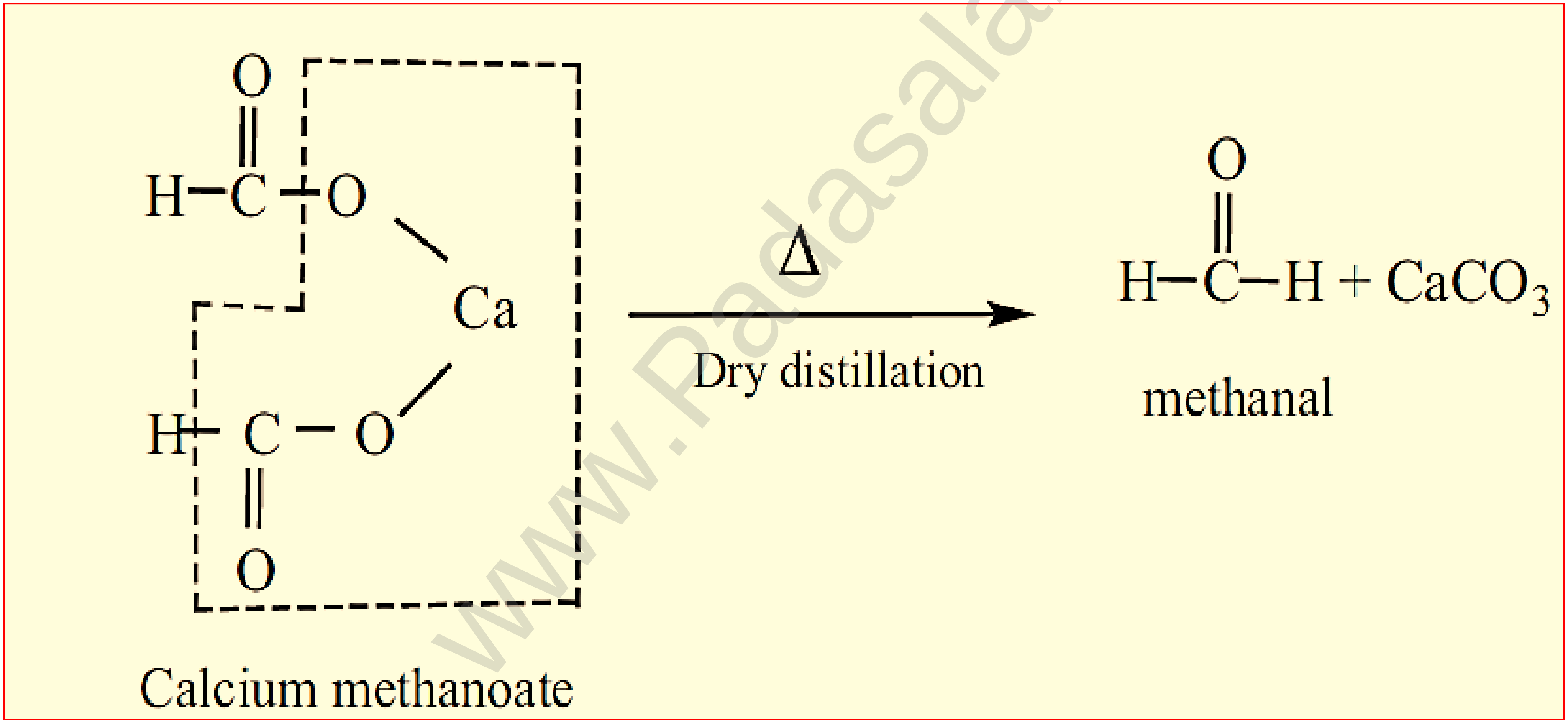


$$CH_3-C \equiv CH + H-OH \xrightarrow[H_2SO_4]{HgSO_4} \left[CH_3-\overset{OH}{\overset{|}{C}}=CH_2 \right] \xrightarrow{\text{Isomerises}} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

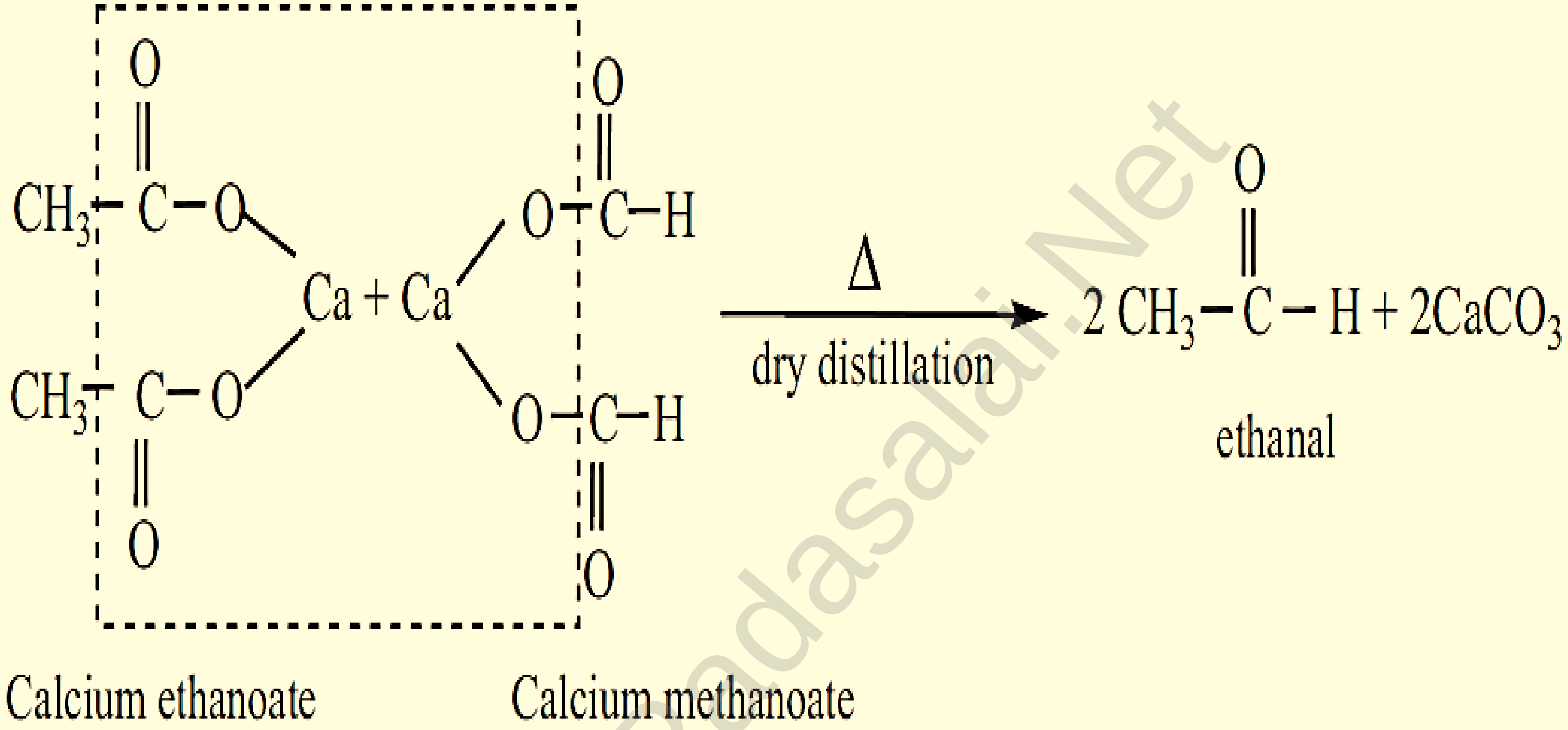
4. From calcium salts of carboxylic acids

- Aldehydes and ketones may be prepared by the **dry distillation** of calcium salts of carboxylic acids.

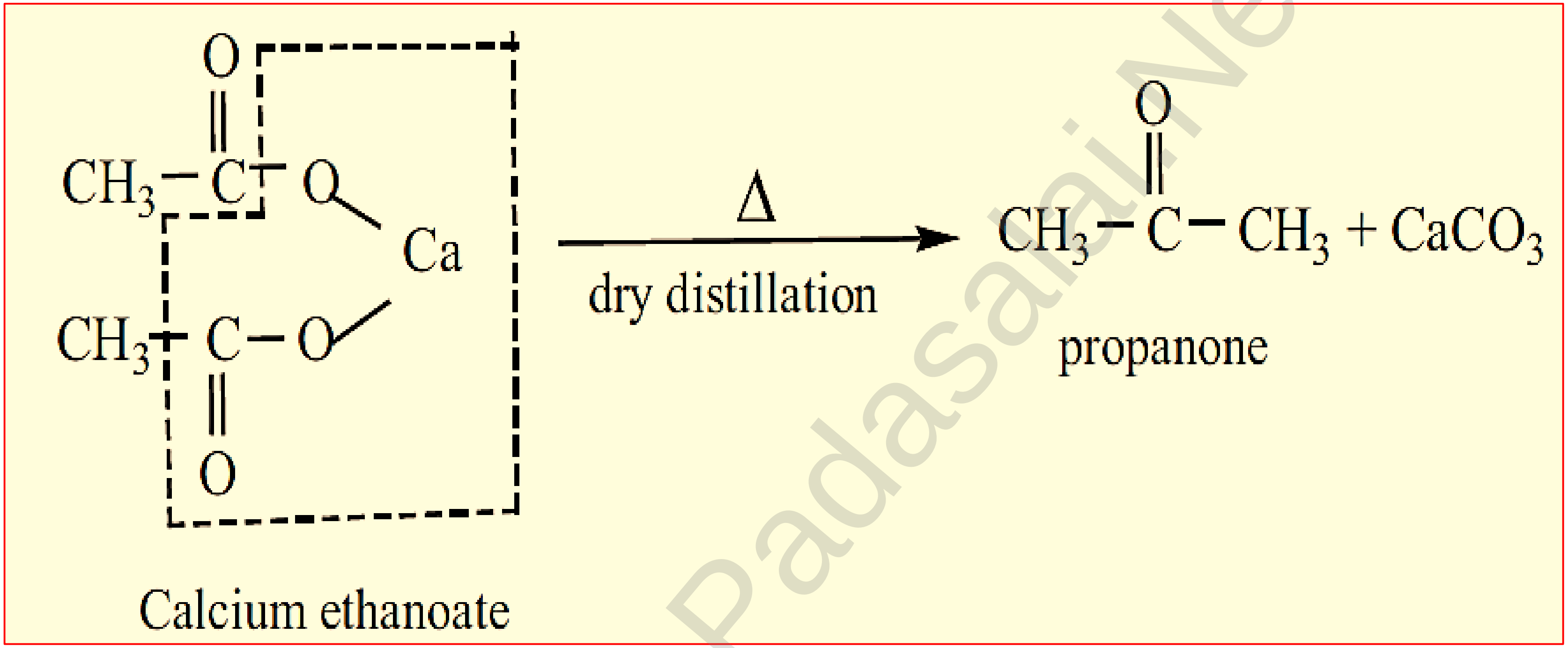
a) **Aldehydes** are obtained when the mixture of calcium salt of carboxylic acid and calcium formate is subjected to dry distillation.



Calcium methanoate


Calcium ethanoate
Calcium methanoate
Δ
dry distillation
2 CH3–C–H + 2CaCO3
ethanal

b) Symmetrical ketones can be obtained by dry distillation of the calcium salt of carboxylic acid (except formic acid)

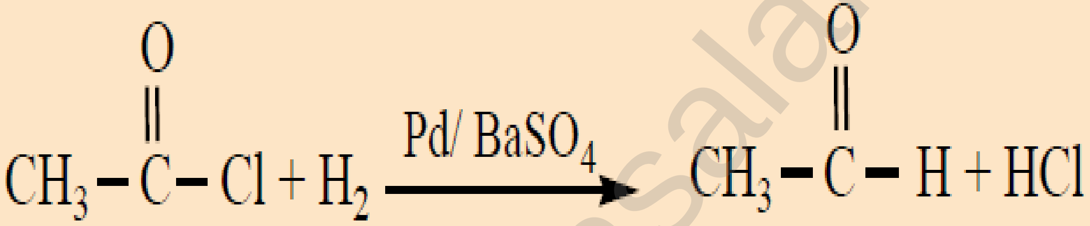


$$(CH_3COO)_2Ca \xrightarrow[\text{dry distillation}]{\Delta} CH_3COCH_3 + CaCO_3$$

B. Preparation of aldehydes

1) Rosenmund reduction

a) Aldehydes can be prepared by the hydrogenation of acid chloride, in the presence of **palladium supported by barium sulphate.** This reaction is called Rosenmund reduction.



$$CH_3-\overset{\overset{O}{\|}}{C}-Cl+H_2\xrightarrow{Pd/\,BaSO_4}CH_3-\overset{\overset{O}{\|}}{C}-H+HCl$$

Acetyl chloride Acetaldehyde

In this reaction, barium sulphate act as a catalytic poison to palladium catalyst, so that aldehyde cannot be further reduced to alcohol.

Formaldehyde and ketones cannot be prepared by this method.

2. Stephen's reaction

- When alkylcyanides are reduced using $SnCl_2$ / HCl, imines are formed, which on hydrolysis gives corresponding aldehyde.

$$CH_3-C\equiv N \xrightarrow[(H)]{SnCl_2/HCl} CH_3-CH=NH \xrightarrow{H_3O^+} CH_3-CHO + NH_3$$

3. Selective reduction of cyanides

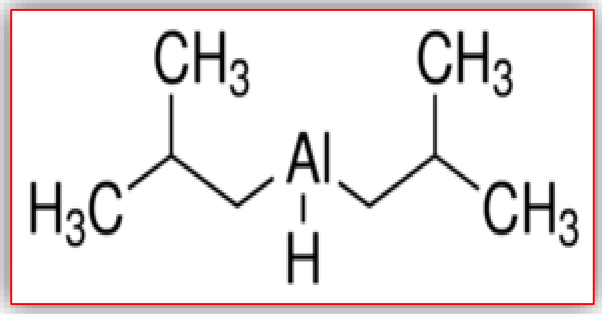
- Di isobutyl aluminium hydride (DIBAL –H) selectively reduces the alkyl cyanides to form imines which on hydrolysis gives aldehydes.

$$CH_3-CH=CH-CH_2-CH_2-CN \xrightarrow[ii)\ H_2O]{i)\ AlH(iso\text{-}butyl)_2} CH_3-CH=CH-CH_2-CH_2-CHO$$

hex - 4- ennitrile

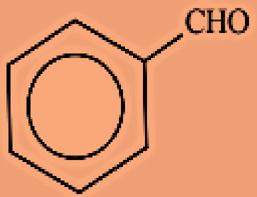
hex - 4- enal

DIBAL-H



Benzaldehyde

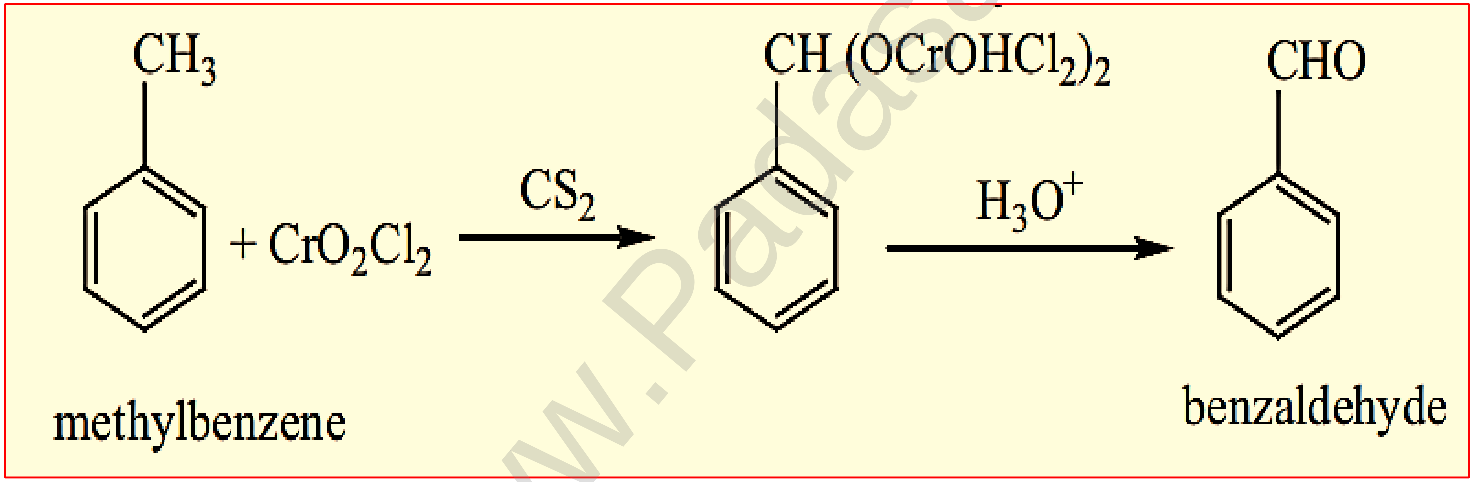
C_6H_5CHO

Benzaldehyde  phenyl methanal	phenyl	meth	an~~e~~	al

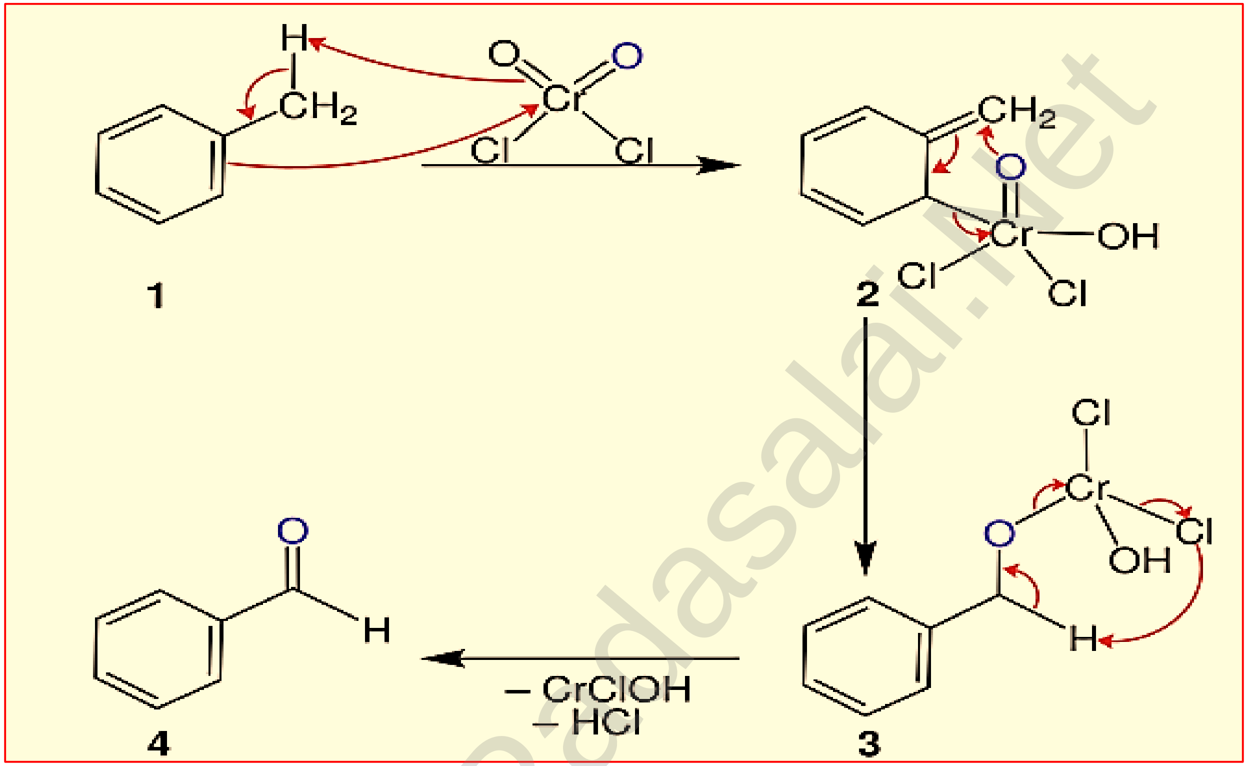
C) Preparation of benzaldehyde

1. Side chain oxidation of toluene and its derivatives

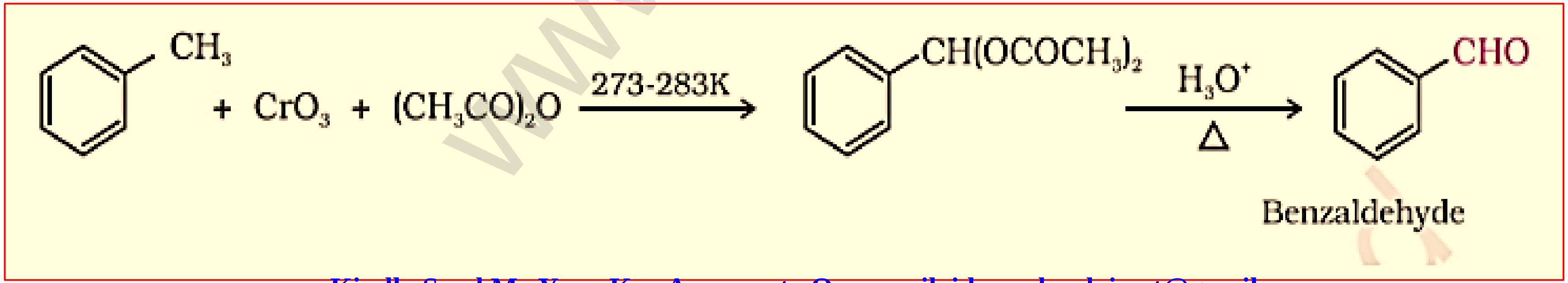
- By strong oxidising agents such as **$KMnO_4$** gives benzoic acid.
- When chromyl chloride is used as an oxidising agent, toluene gives benzaldehyde.
- This reaction is called Etard reaction.
- Acetic anhydride and CrO_3 can also be used for this reaction.



Etard reaction mechanism

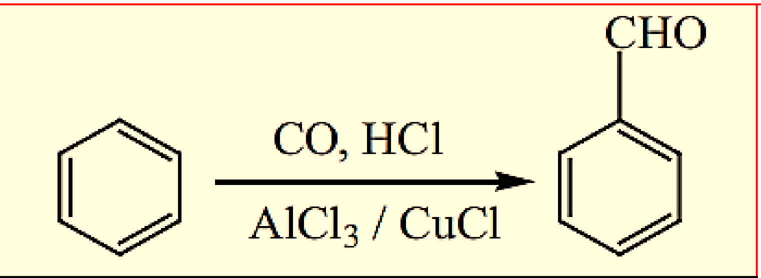


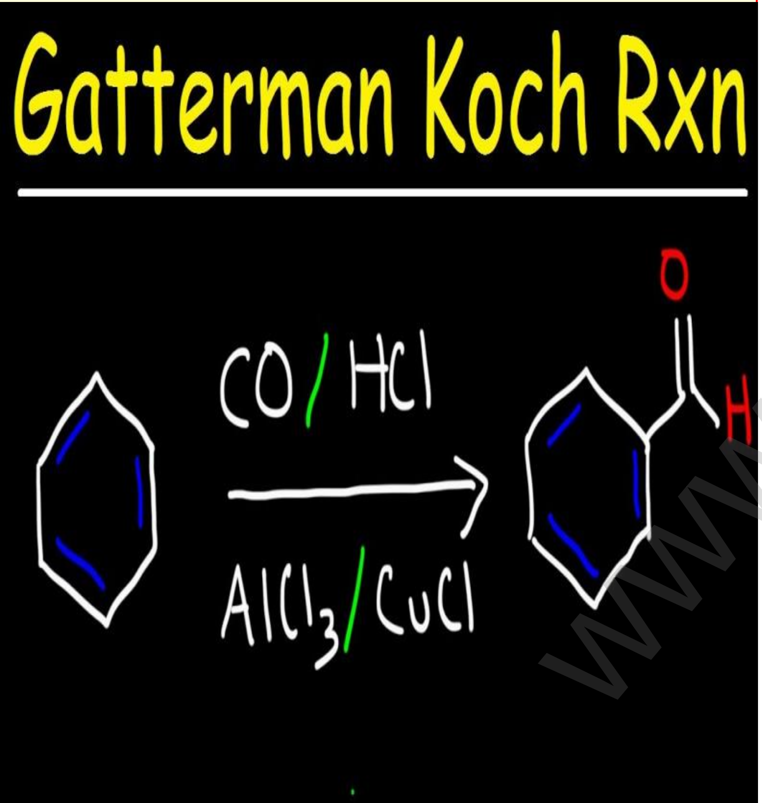
- Oxidation of toluene by chromic oxide gives benzylidine diacetate which on hydrolysis gives benzaldehyde.

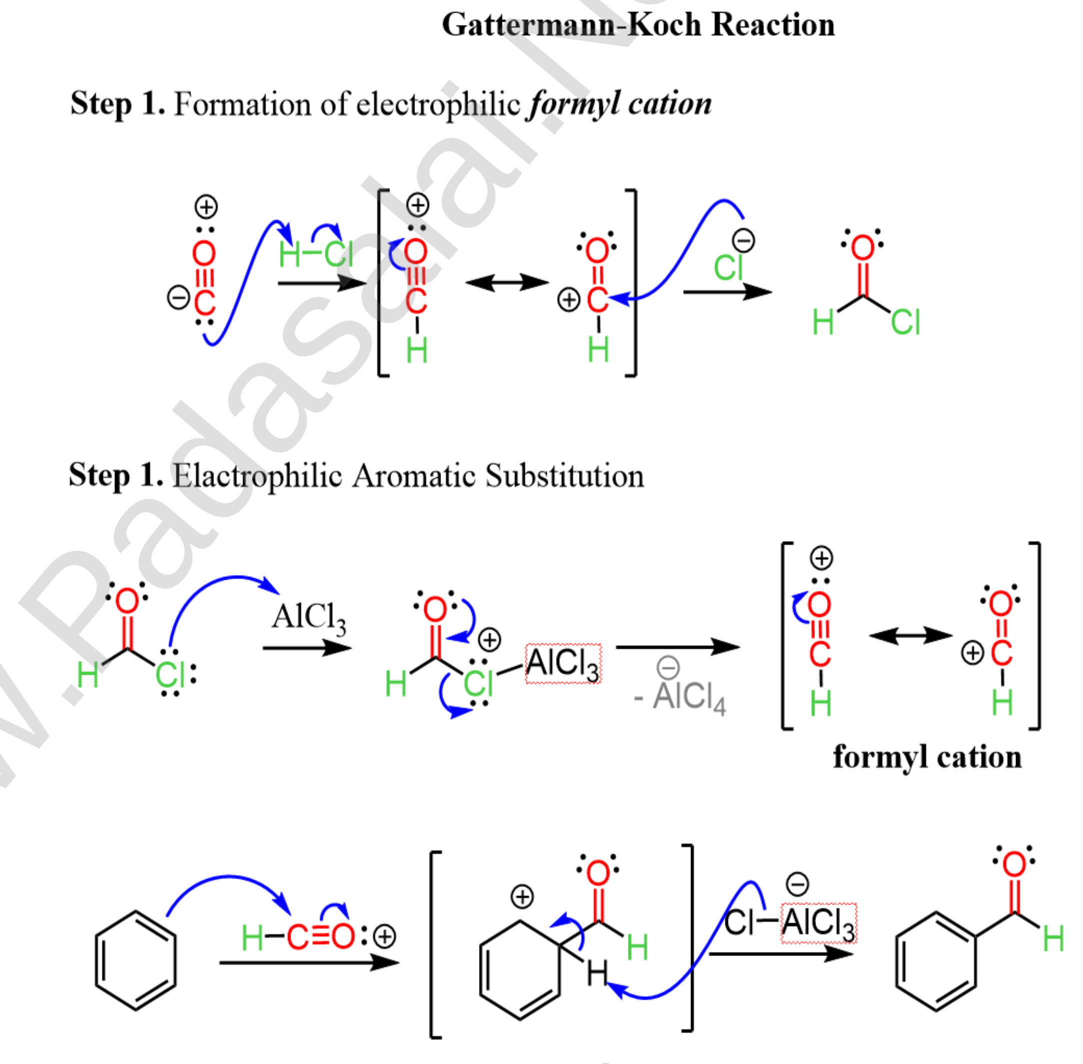


2) Gattermann – Koch reaction

- This reaction is a variant of Friedel – Crafts acylation reaction.
- In this method, reaction of carbon monoxide and HCl generate an intermediate which reacts like formyl chloride.

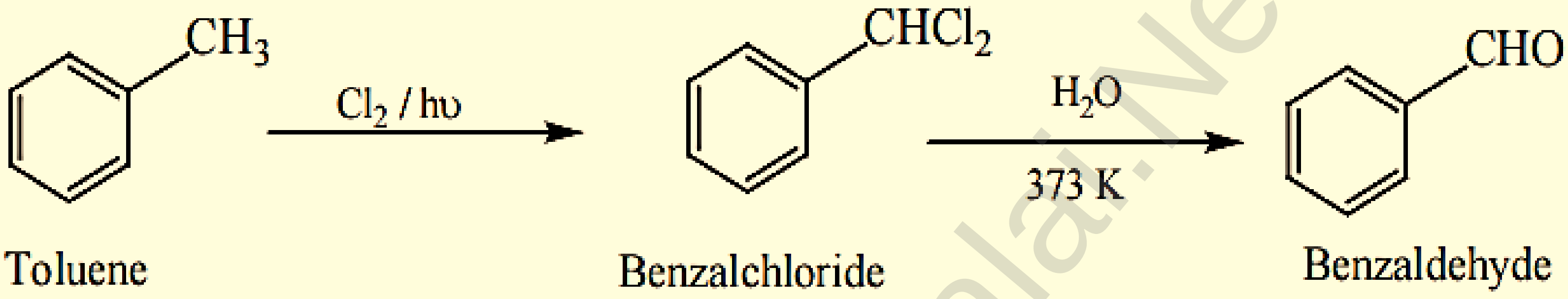






3) Manufacture of benzaldehyde from toluene

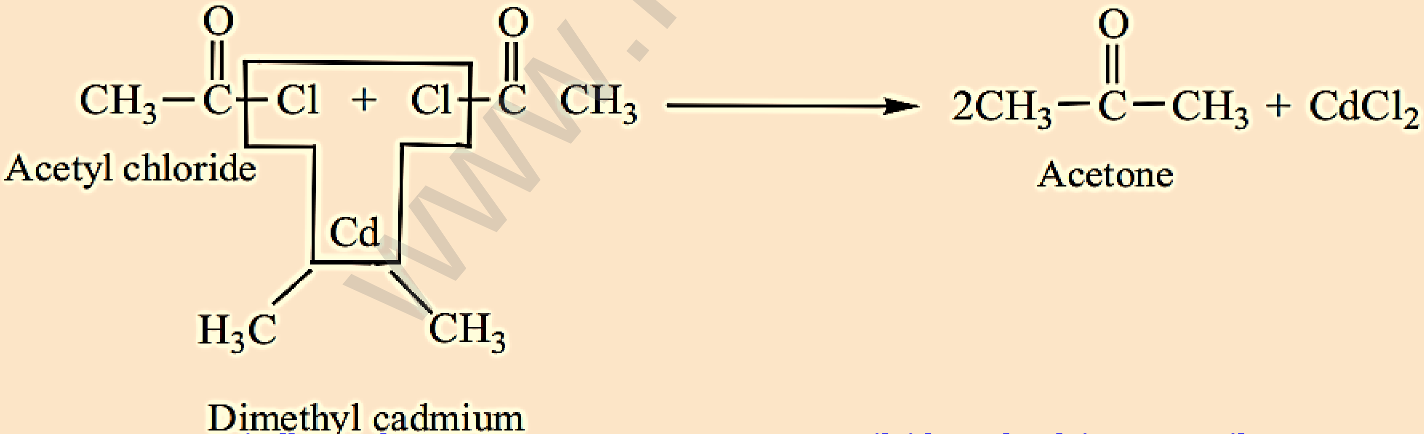
- Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde.



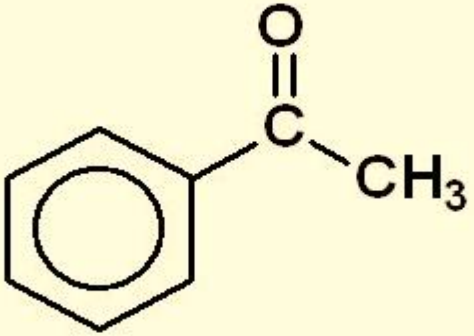
This is the commercial method for the manufacture of benzaldehye.

D) Preparation of ketones

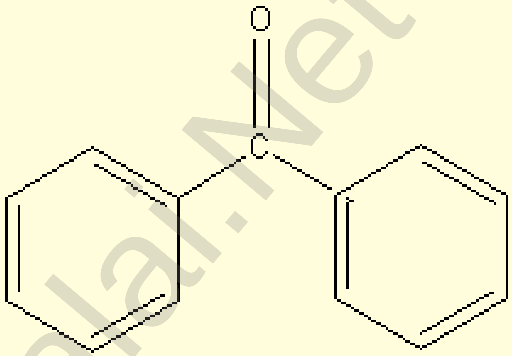
1) Ketones can be prepared by the action of acid chloride with dialkyl cadmium.



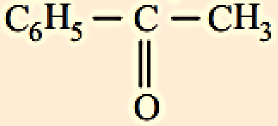
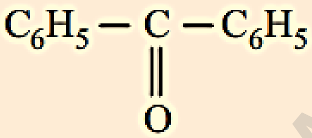
phenyl ketones



acetophenone



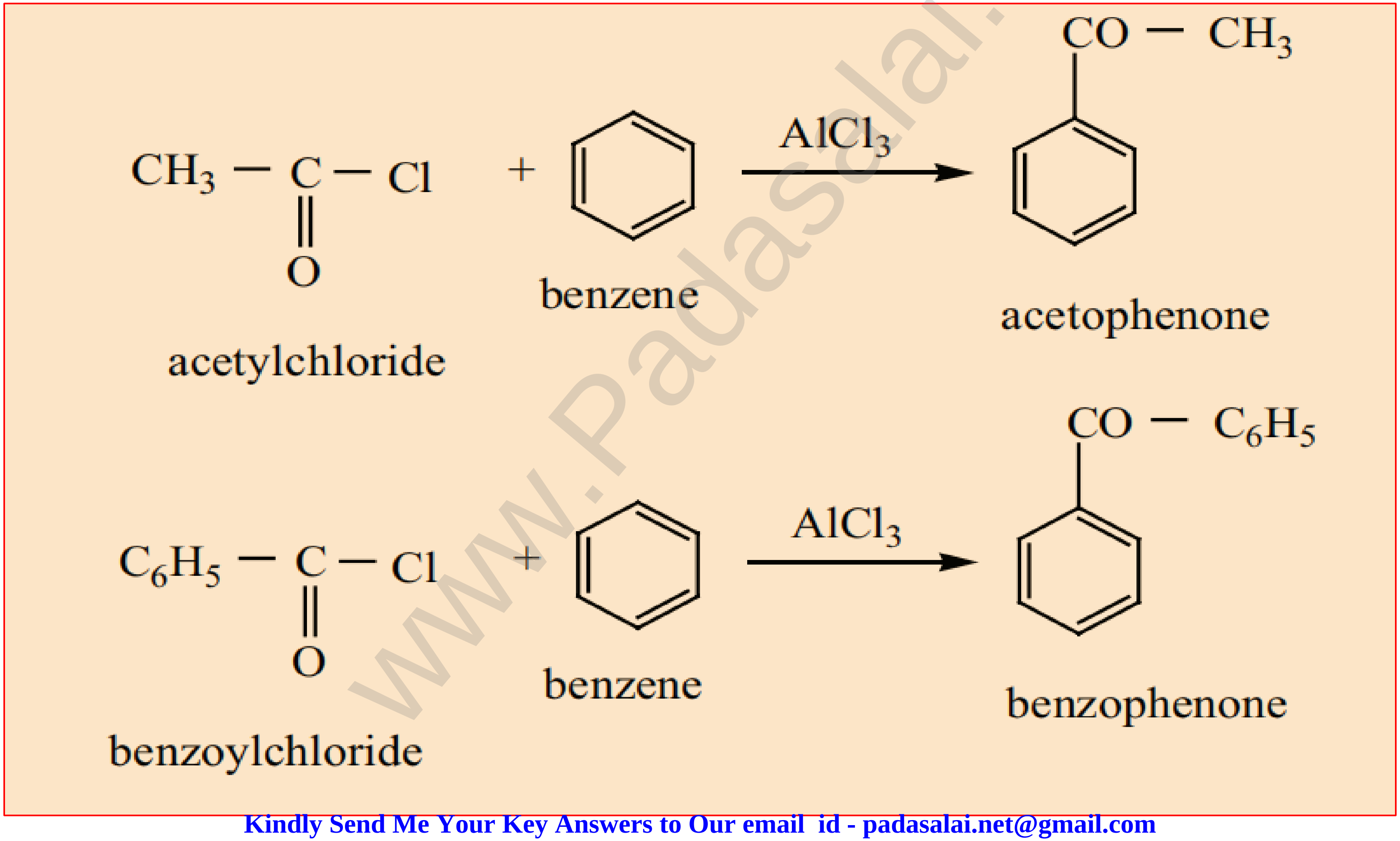
benzophenone

Methyl Phenyl ketone  $C_6H_5-\underset{\underset{O}{\parallel}}{C}-CH_3$ Acetophenone (PIN)* 1-phenylethan-1-one	1-phenyl	eth	an~~e~~	1-one
Diphenyl ketone  $C_6H_5-\underset{\underset{O}{\parallel}}{C}-C_6H_5$ Benzophenone (PIN)* Diphenylmethanone	Diphenyl	meth	an~~e~~	one

2) Preparation of phenyl ketones

Friedel – Crafts acylation

- **It is the best method for preparing alkyl aryl ketones or diaryl ketones. This reaction succeeds only with benzene and activated benzene derivatives.**

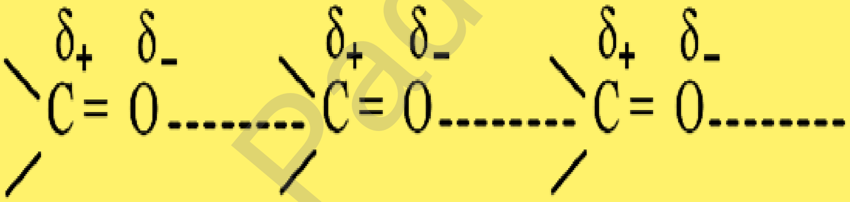


Physical properties of aldehydes and ketones

1. **Physical State:** Formaldehyde is a gas at room temperature and acetaldehyde is a volatile liquid. All other aldehydes and ketones upto to C_{11} are colourless liquids while the higher ones are solids.

2. **Boiling points**

Aldehydes and ketones have relatively high boiling point as compared to hydrocarbons and ethers of comparable molecular mass. It is due to the weak molecular association in aldehydes and ketones arising out of the dipole-dipole interactions.



These dipole-dipole interactions are weaker than intermolecular H-bonding. The boiling points of aldehydes and ketones are much lower than those of corresponding alcohols and carboxylic acids which possess inter molecular hydrogen bonding.

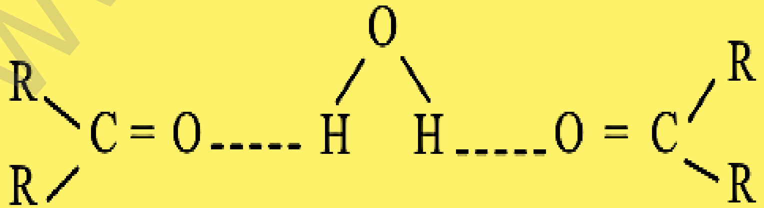
Compound	Molar mass	Boiling point (K)
$CH_3(CH_2)_3CH_3$ Pentane	72	309
$CH_3(CH_2)_2CHO$ butanal	72	349
$CH_3(CH_2)_3OH$ butanol	74	391

Compound	Molar mass	Boiling point (K)
$CH_3CH_2COCH_3$ butan - 2- one	72	353
CH_3CH_2COOH Propanoicacid	74	414

3. Solubility

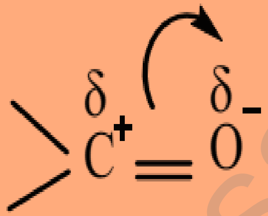
Lower members of aldehydes and ketones like formaldehyde, acetaldehyde and acetone are miscible with water in all proportions because they form hydrogen bond with water.

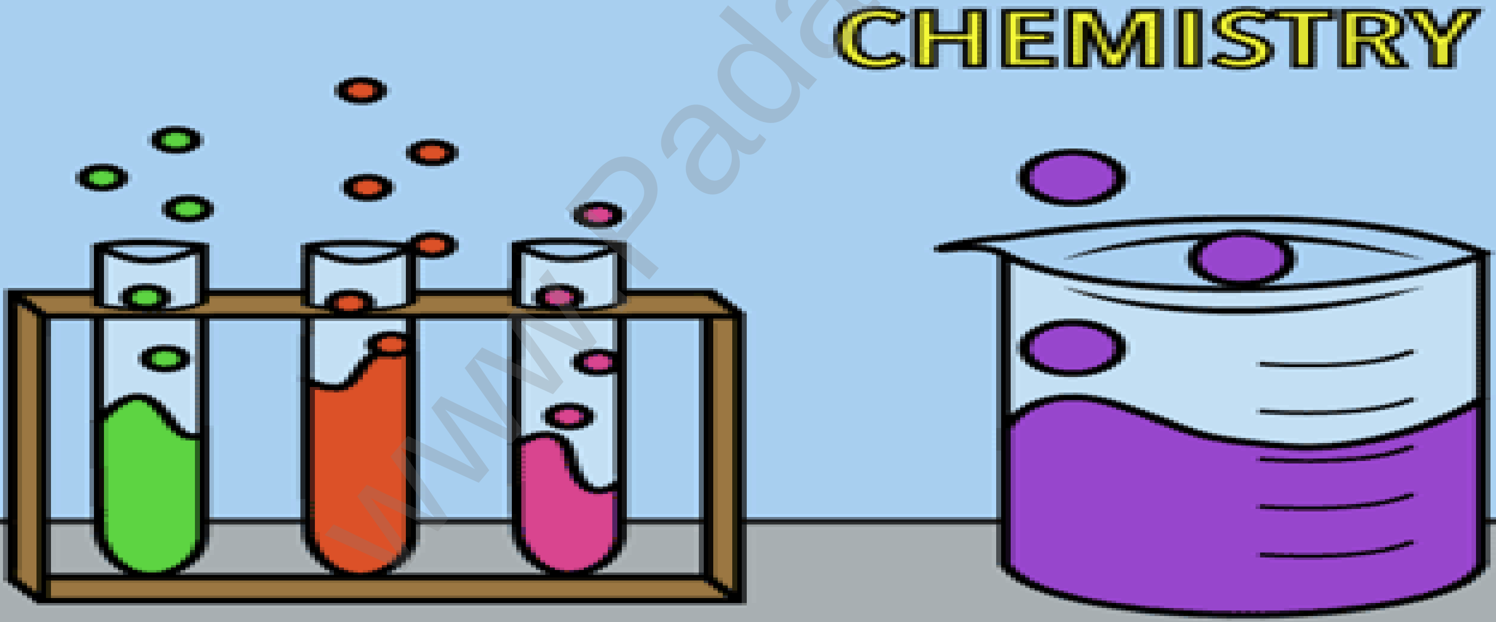
Solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain.



4. Dipolemoment:

The carbonyl group of aldehydes and ketones contains a double bond between carbon and oxygen. Oxygen is more electronegative than carbon and it attracts the shared pair of electron which makes the carbonyl group as polar and hence aldehydes and ketones have high dipole moments.

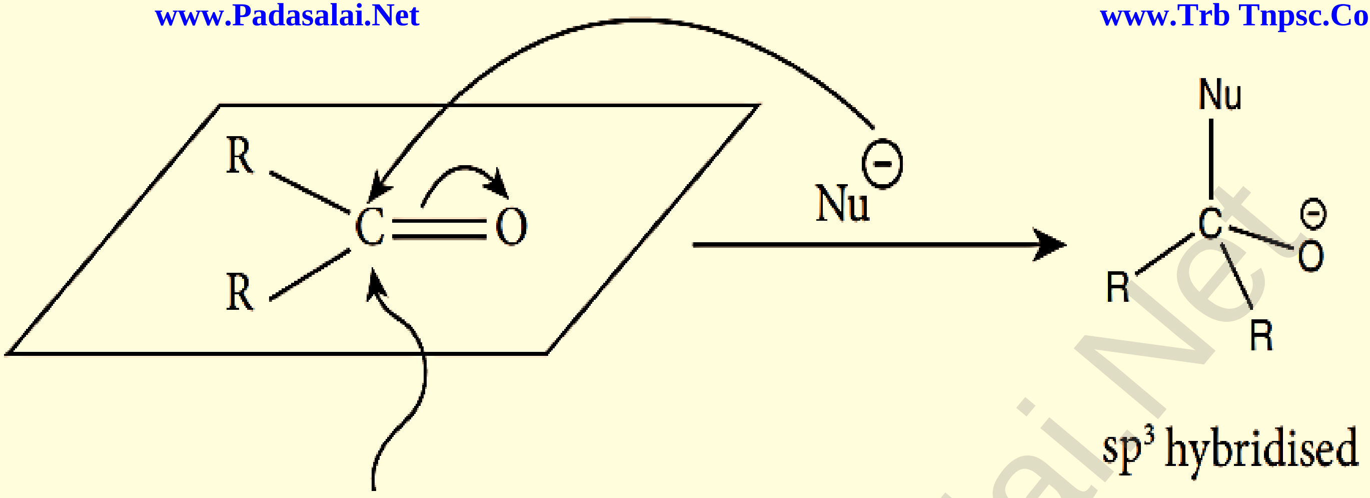




Chemical properties of aldehydes and ketones

A) Nucleophilic addition reactions

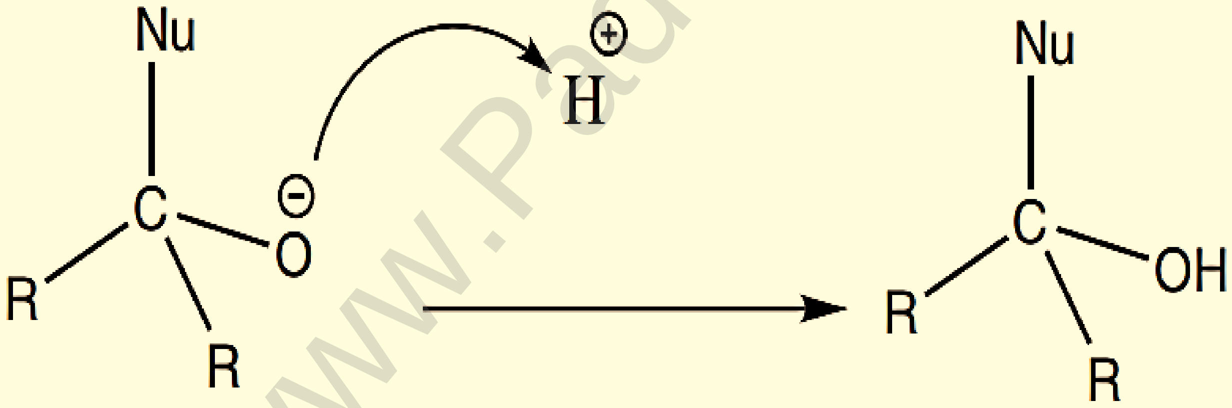
- This reaction is the most common reactions of aldehydes and ketones.
- The carbonyl carbon carries a small degree of positive charge.
- Nucleophile such as CN^- can attack the carbonyl carbon and uses its lone pair to form a new carbon – nucleophile 'σ' bond, at the same time two electrons from the carbon – oxygen double bond move to the most electronegative oxygen atom.
- This results in the formation of an alkoxide ion. In this process, the hybridisation of carbon changes from sp^2 to sp^3.



sp^{2}hybridised carbon

sp^3 hybridised carbon
tetrahedral alkoxide ion

The tetrahedral intermediate can be protonated by water or an acid to form an alcohol.

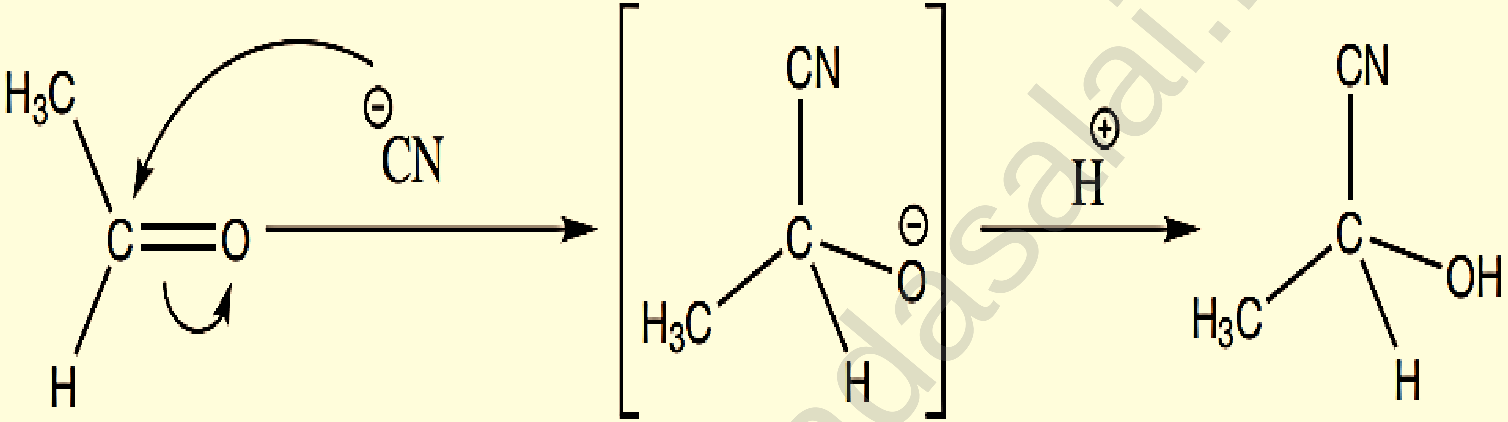


In general, aldehydes are more reactive than ketones towards nucleophilic addition reactions due to +I and steric effect of alkyl groups.

Examples for Nucleophilic substitution reaction:

1) Addition of HCN

Attack of CN^- on carbonyl carbon followed by protonation gives cyanohydrins.



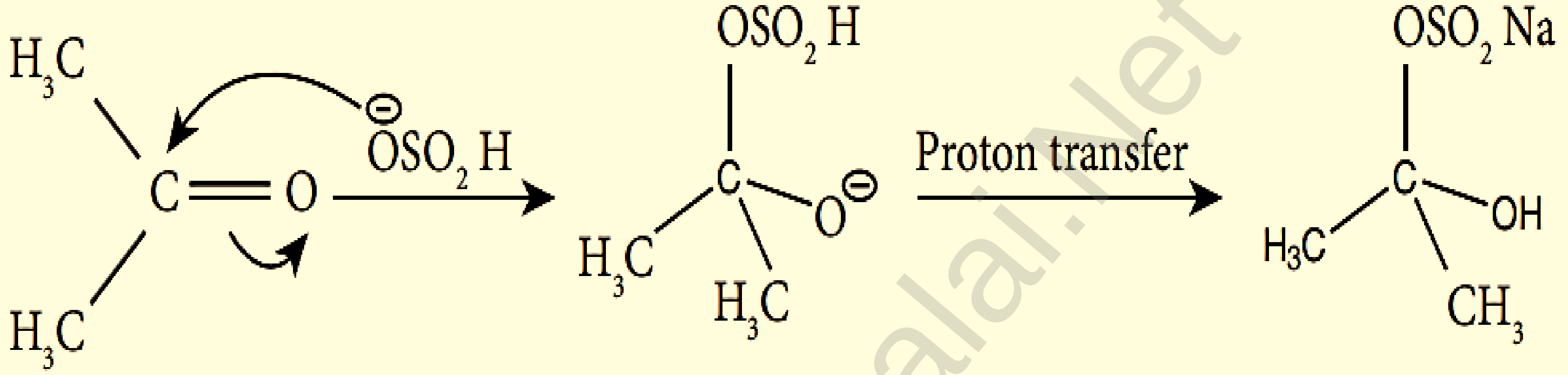
ethanal
(acetaldehyde)

tetrahedral
intermediate

2-hydroxy propanenitrile
(acetaldehyde cyano hydrin)

The cyanohydrins can be converted into hydroxy acid by acid hydrolysis. Reduction of cyanohydrins gives hydroxy amines

2) Addition of $NaHSO_3$



acetone (propanone)

bisulphite addition compound

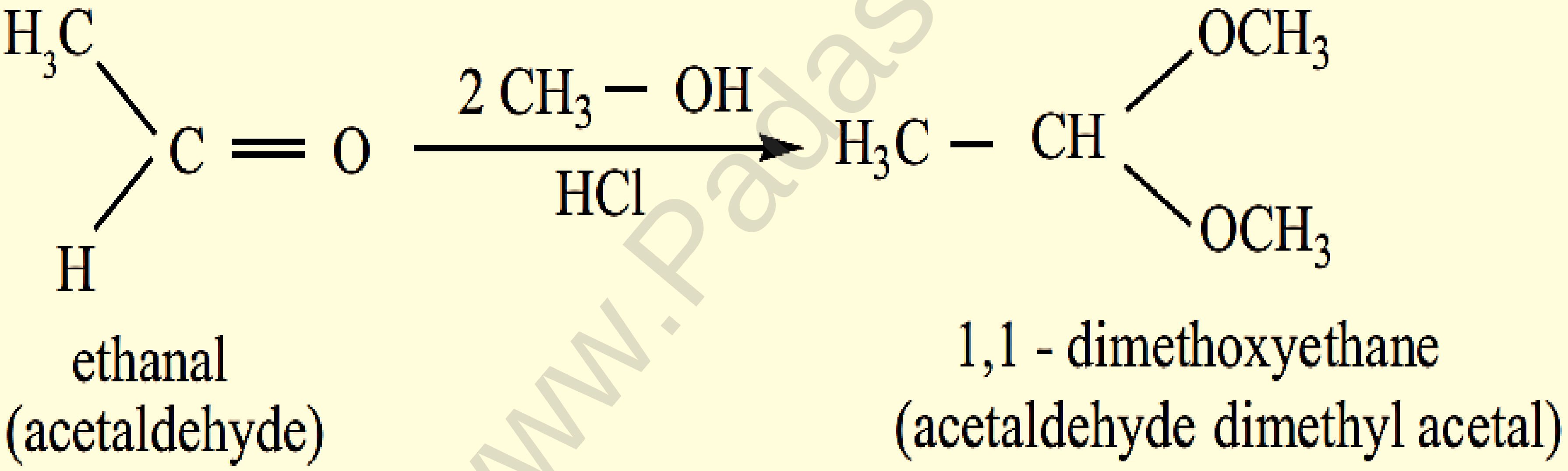
- This reaction finds application in the separation and purification of carbonyl compound.
- The bisulphate addition compound is water soluble and the solution is treated with mineral acid to regenerate the carbonyl compounds.

3) Addition of alcohol

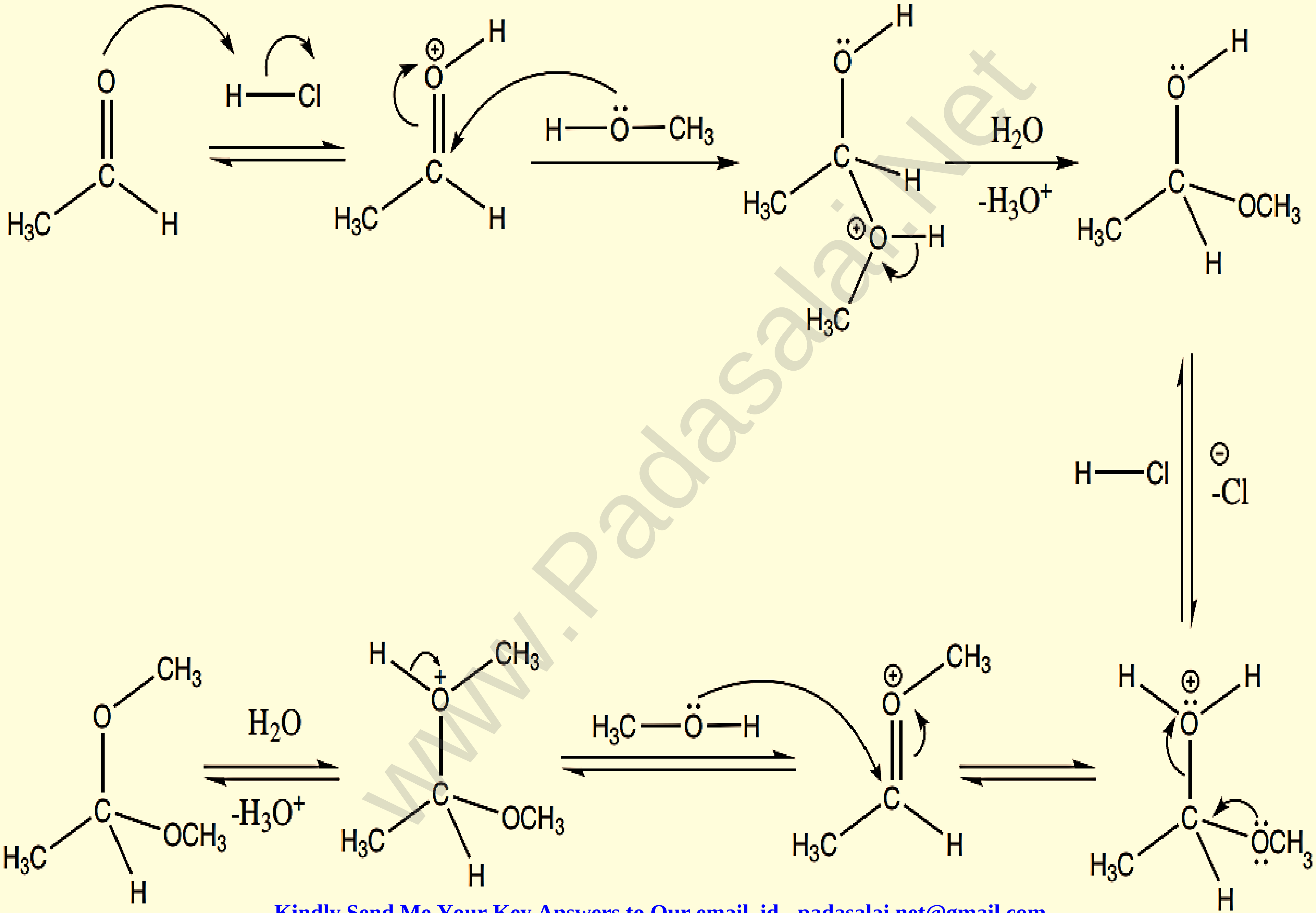
- When aldehydes / ketones is treated with 2 equivalents of an alcohol in the presence of an acid catalyst to form acetals.

Example:

When acetaldehyde is treated with 2 equivalent of methanol in presence of HCl, 1,1, - dimethoxy ethane is obtained.



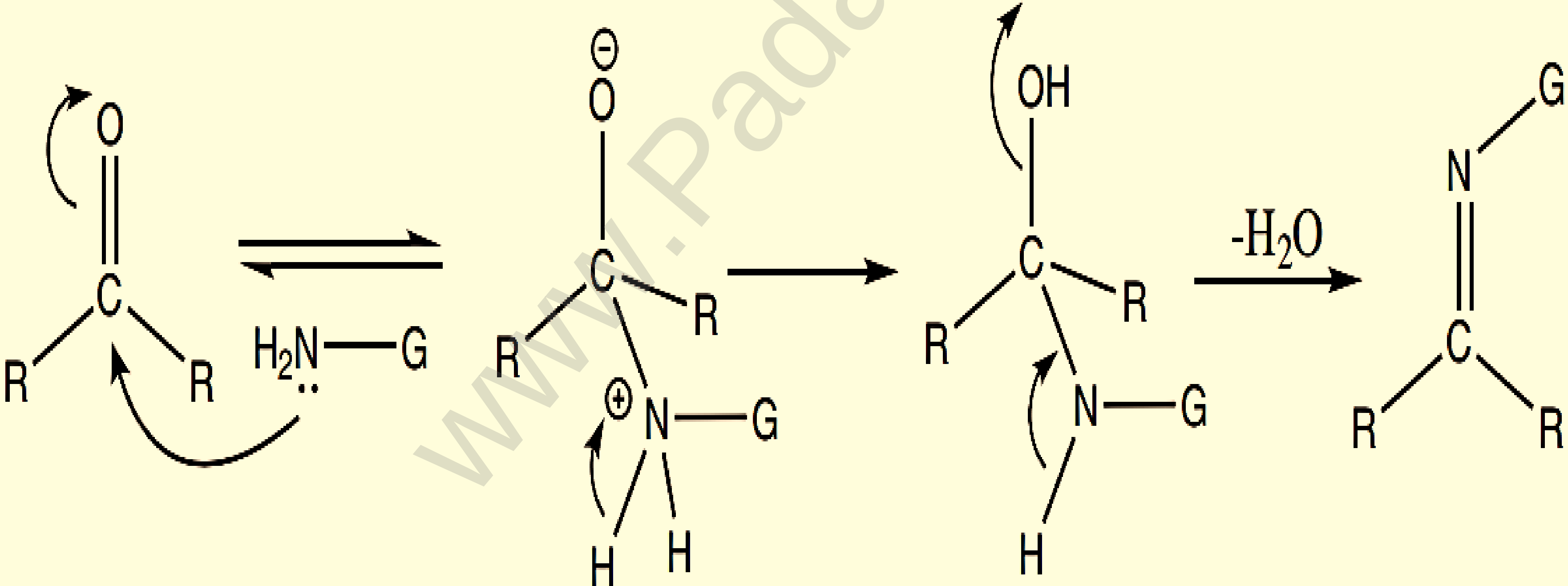
Mechanisum

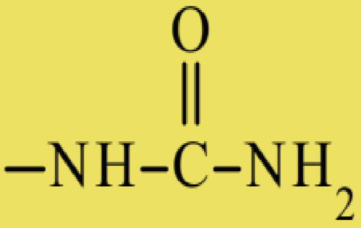
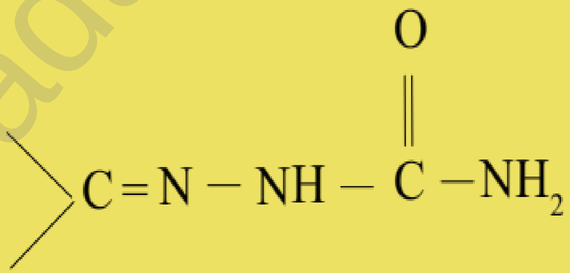
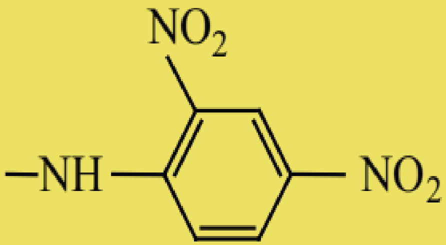
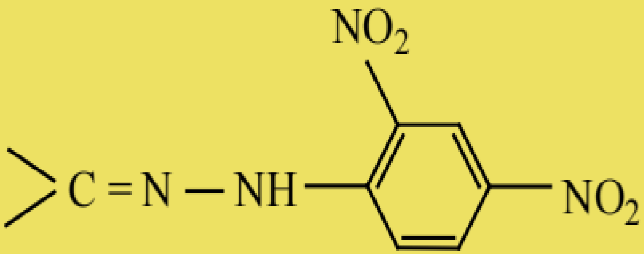


4) Addition of ammonia and its derivatives

When the nucleophiles, such as ammonia and its derivative $H_2\ddot{N}$-G is treated with carbonyl compound, nuceophilic addition takes place, the carbonyl oxygen atom is protonated and then elimination takes place to form carbon – nitrogen double bond $\left(>C=N-G \right)$

When G – alkyl, aryl, OH, NH_2, C_6H_5NH, $NHCONH_2$ etc...

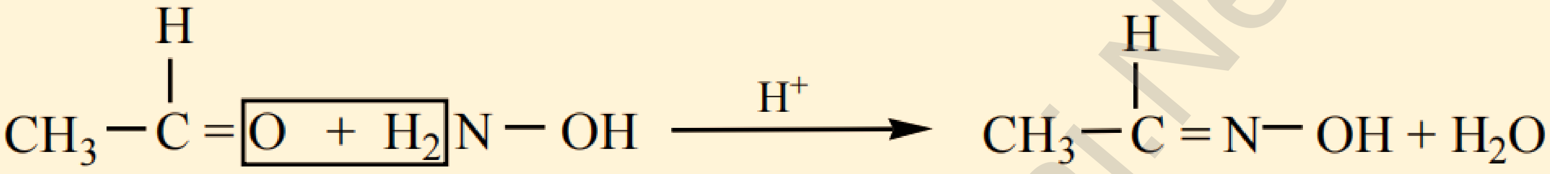


G	Ammonia derivatives	Carbonyl derivatives	Product name
$-OH$	Hydroxyl amine	$>C=N-OH$	Oxime
$-NH_2$	Hydrazine	$>C=N-NH_2$	Hydrazone
$-HN-C_6H_5$	Phenyl hydrazine	$>C=N-NH-C_6H_5$	Phenyl hydrazone
 $-NH-\overset{O}{\overset{\Vert}{C}}-NH_2$	Semi carbabazide	 $>C=N-NH-\overset{O}{\overset{\Vert}{C}}-NH_2$	Semi carbazone
	2,4 – dinitrophenyl hydrazine		2,4 – dinitrophenyl hydrazone

i) Reaction with hydroxyl amine

Aldehyde and ketones react with hydroxylamine to form **oxime.**

Example:



$$CH_3-\overset{\overset{H}{|}}{C}=\boxed{O\ +\ H_2}N-OH \xrightarrow{H^+} CH_3-\overset{\overset{H}{|}}{C}=N-OH+H_2O$$

Acetaldehyde (ethanal)

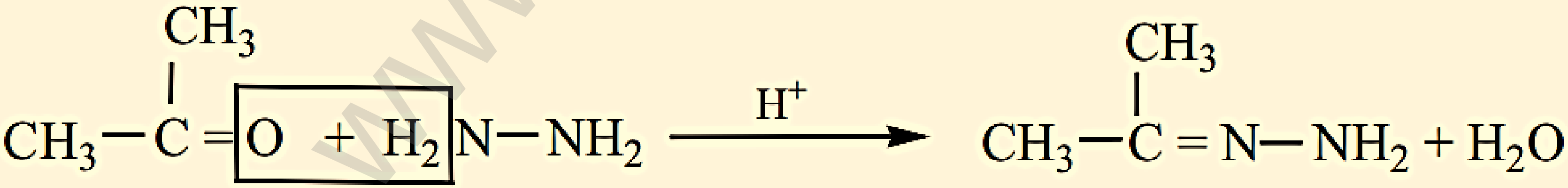
Hydroxylamine

Acetaldoxime (N - ethylidene hydroxylamine)

ii) Reaction with hydrazine

Aldehydes and ketones react with hydrazine to form **hydrazone.**

Example:



$$CH_3-\overset{\overset{CH_3}{|}}{C}=\boxed{O\ +\ H_2}N-NH_2 \xrightarrow{H^+} CH_3-\overset{\overset{CH_3}{|}}{C}=N-NH_2+H_2O$$

Acetone

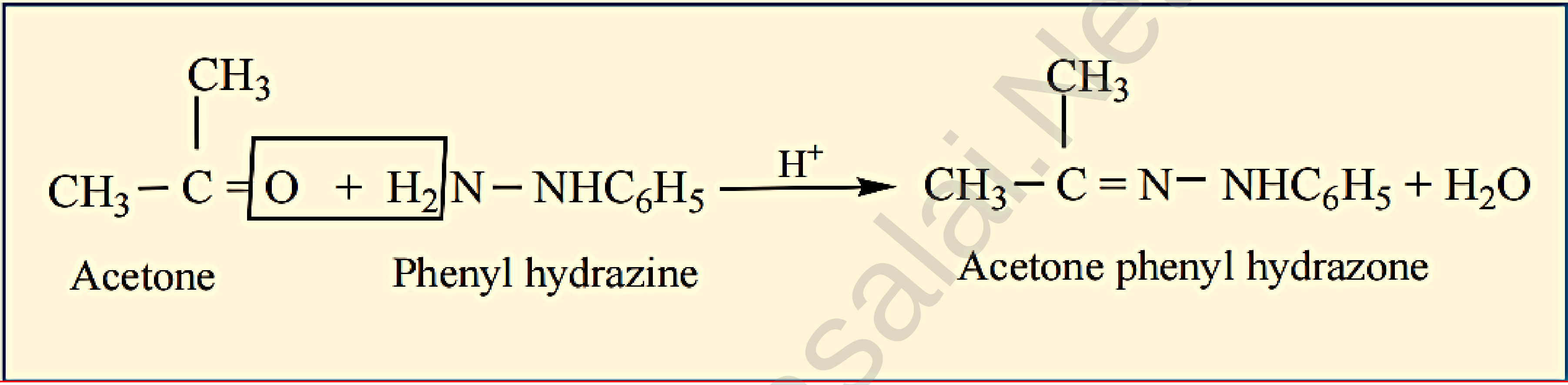
Hydrazine

Acetone hydrazone

iii) Reaction with phenyl hydrazine

Aldehydes and ketones react with phenyl hydrazine to form **phenyl hydrazone.**

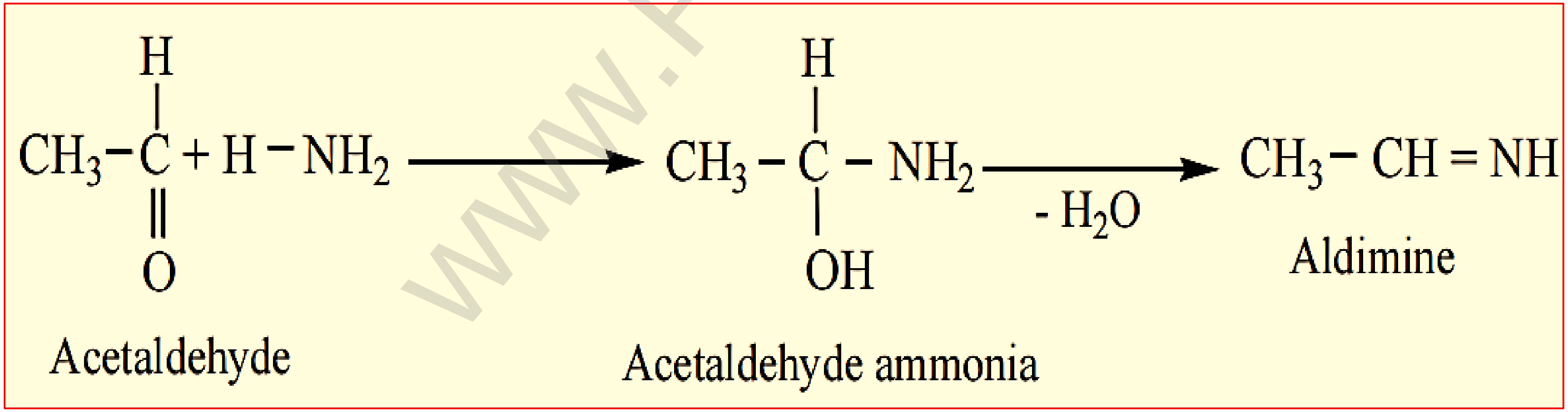
Example:



$$CH_3-\overset{\overset{CH_3}{|}}{C}=\boxed{O\;+\;H_2}N-NHC_6H_5 \xrightarrow{H^+} CH_3-\overset{\overset{CH_3}{|}}{C}=N-NHC_6H_5+H_2O$$

5) Reaction with NH_3

i) **Aliphatic aldehydes** (**except formaldehyde**) react with an ethereal solution of ammonia to form aldimines.

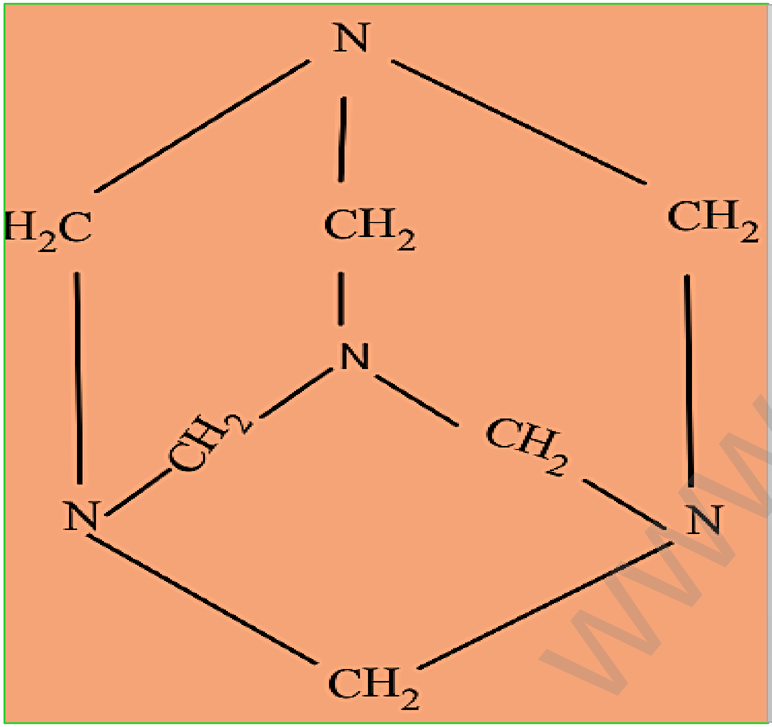


$$CH_3-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{C}}+H-NH_2 \longrightarrow CH_3-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-NH_2 \xrightarrow[-H_2O]{} CH_3-CH=NH$$

ii) Formaldehyde reacts with ammonia to form hexa methylene tetramine, which is also known as Urotropine.

$$\underset{\text{Formaldehyde}}{6HCHO} + 4\,NH_3 \longrightarrow \underset{\text{Hexamethylene tetramine}}{(CH_2)_6N_4} + 6\,H_2O$$

Structure



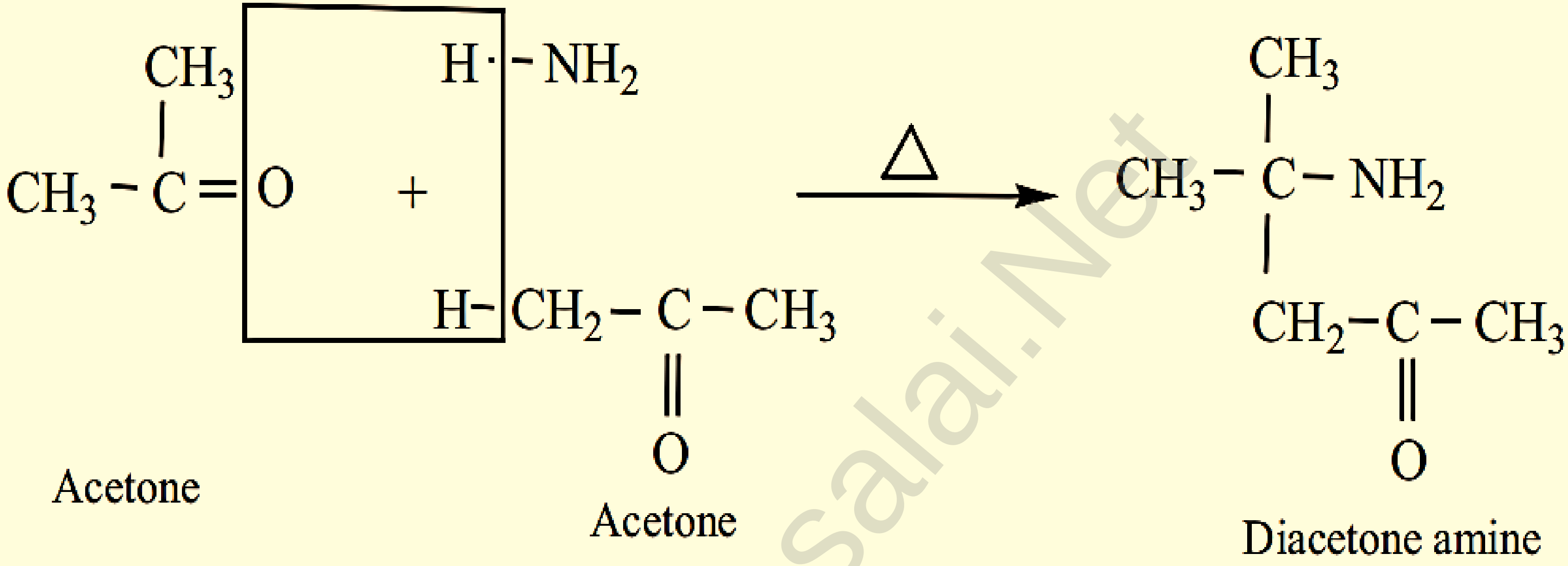
Uses

(i) Urotropine is used as a medicine to treat urinary infection.

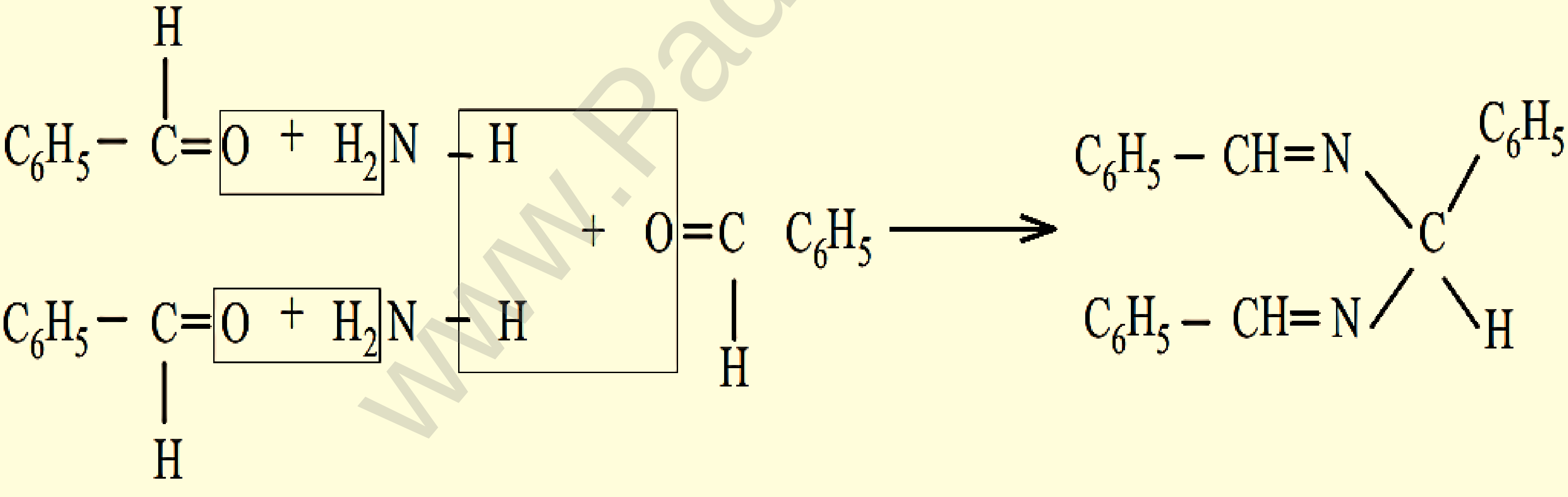
(ii) Nitration of Urotropine under controlled condition gives an explosive RDX (Research and development explosive).

It is also called cyclonite or cyclotri methylene trinitramine.

iii) Acetone reacts with ammonia to form diacetone amine.



iv) Benzaldehyde form a complex condensation product with ammonia.



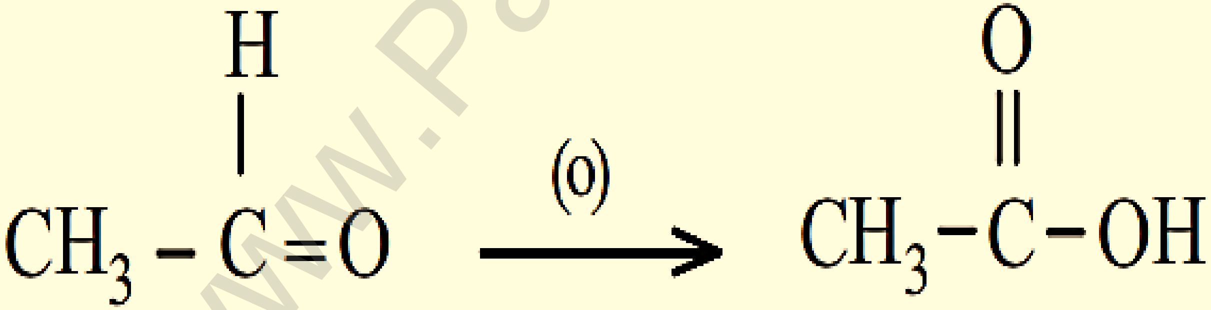
B) Oxidation of aldehydes and ketones

a) Oxidation of aldehydes

- Aldehydes are easily oxidised to carboxylic acid containing the same number of carbon atom, as in parent aldehyde.

- The common oxidising agents are acidified $K_2Cr_2O_7$, acidic or alkaline $KMnO_4$ or chromic oxide.

Example

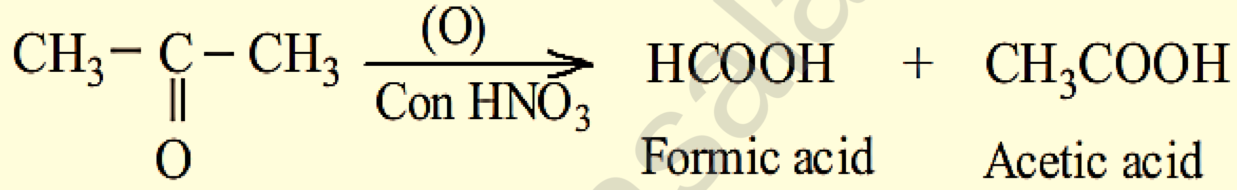


$$CH_3-\overset{\overset{\displaystyle H}{|}}{C}=O \xrightarrow{(o)} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Acetaldehyde Aceticacid

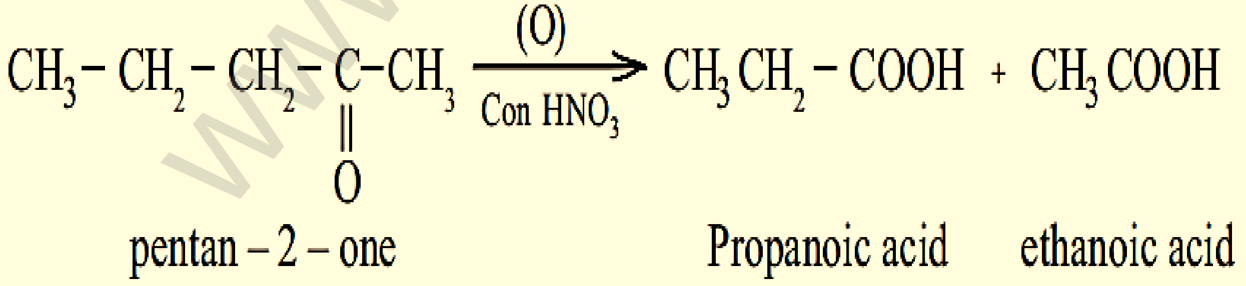
b) Oxidation of ketone

- Ketones are not easily oxidised. Under drastic condition or with powerful oxidising agent like Con.HNO_3, $H^+/KMnO_4$, $H^+/K_2Cr_2O_7$, cleavage of carbon-carbon bond takes place to give a mixture of carboxylic acids having less number of carbon atom than the parent ketone.



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[\text{Con } HNO_3]{(O)} \underset{\text{Formic acid}}{HCOOH} + \underset{\text{Acetic acid}}{CH_3COOH}$$

- The oxidation of unsymmetrical ketones is governed by **Popoff 's rule.** It states that during the oxidation of an unsymmetrical ketone, a (C–CO) bond is cleaved in such a way that the keto group stays with the smaller alkyl group.



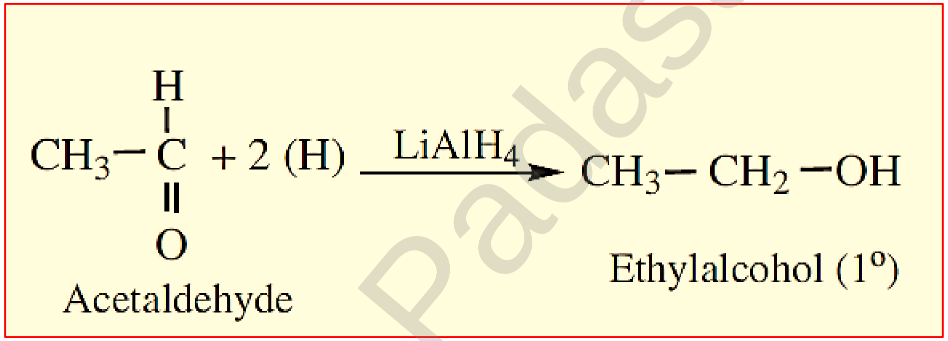
$$\underset{\text{pentan}-2-\text{one}}{CH_3-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-CH_3} \xrightarrow[\text{Con } HNO_3]{(O)} \underset{\text{Propanoic acid}}{CH_3CH_2-COOH} + \underset{\text{ethanoic acid}}{CH_3COOH}$$

C) Reduction reactions

(i) Reduction to alcohols

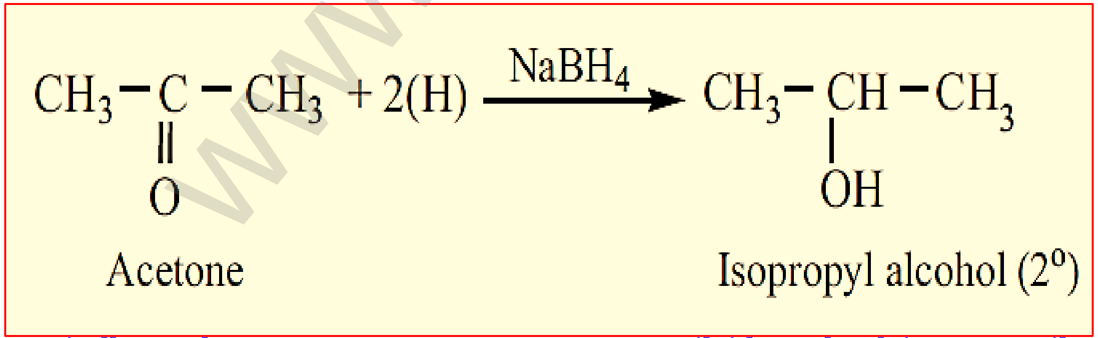
- We have already learnt that aldehydes and ketones can be easily reduced to primary and secondary alcohols respectively.
- The most commonly used reducing agents are Lithium Aluminium hydride ($LiAlH_4$), and Sodium borohydride ($NaBH_4$).

a) Aldehyde are reduced to primary alcohols.



$$CH_3-\overset{\overset{H}{|}}{\underset{\underset{O}{\|}}{C}} + 2\,(H) \xrightarrow{LiAlH_4} CH_3-CH_2-OH$$

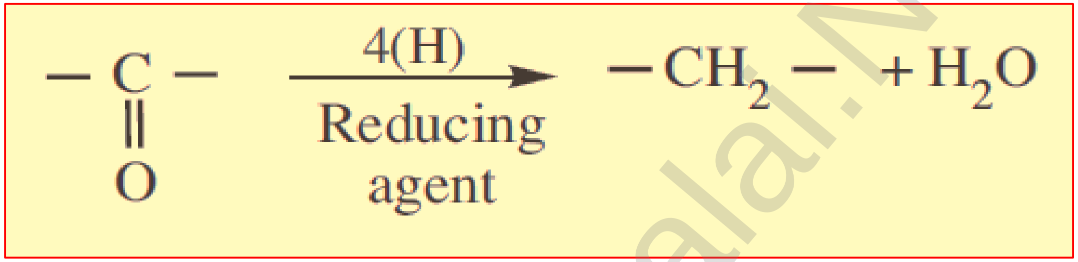
b) Ketone are reduced to Secondary alcohols.



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + 2(H) \xrightarrow{NaBH_4} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

ii) Reduction to hydrocarbon

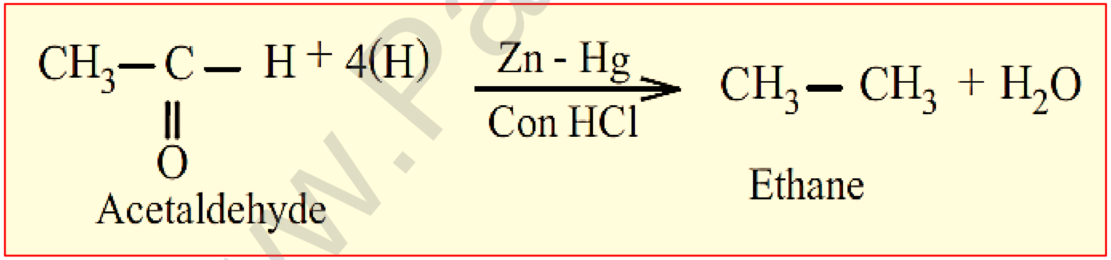
- **The carbonyl group of aldehydes and ketones can be reduced to methylene group using suitable reducing agents to give hydrocarbons.**



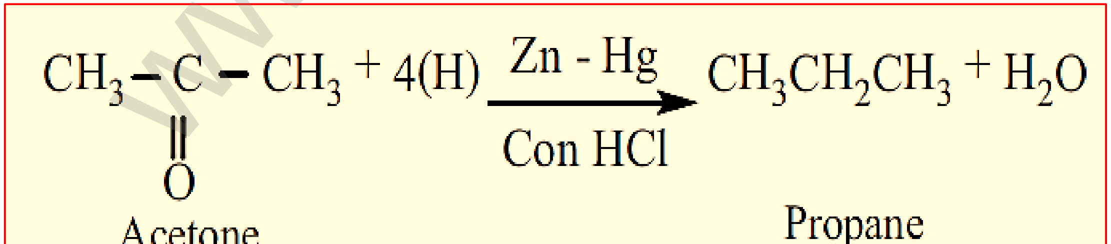
$$-\underset{\underset{O}{\|}}{C}- \xrightarrow[\text{Reducing agent}]{4(H)} -CH_2- + H_2O$$

a) Clemmensen reduction

- **Aldehydes and Ketones when heated with zinc amalgam and concentrated hydrochloric acid gives hydrocarbons.**



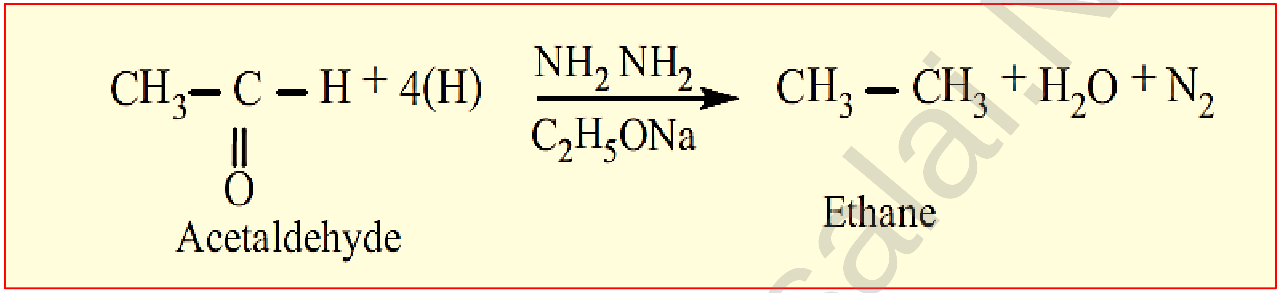
$$\underset{\text{Acetaldehyde}}{CH_3-\underset{\underset{O}{\|}}{C}-H} + 4(H) \xrightarrow[\text{Con HCl}]{\text{Zn - Hg}} \underset{\text{Ethane}}{CH_3-CH_3} + H_2O$$



$$\underset{\text{Acetone}}{CH_3-\underset{\underset{O}{\|}}{C}-CH_3} + 4(H) \xrightarrow[\text{Con HCl}]{\text{Zn - Hg}} \underset{\text{Propane}}{CH_3CH_2CH_3} + H_2O$$

b) Wolf Kishner reduction

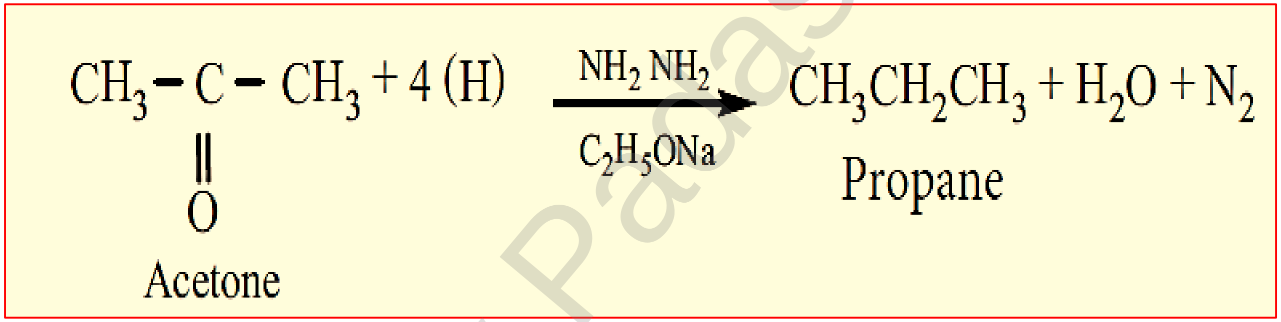
- **Aldehydes and Ketones when heated with hydrazine (NH_2NH_2) and sodium ethoxide, hydrocarbons are formed Hydrazine acts as a reducing agent and sodium ethoxide as a catalyst.**



$$CH_3-\underset{\overset{\|}{O}}{C}-H + 4(H) \xrightarrow[C_2H_5ONa]{NH_2NH_2} CH_3-CH_3 + H_2O + N_2$$

Acetaldehyde

Ethane



$$CH_3-\underset{\overset{\|}{O}}{C}-CH_3 + 4(H) \xrightarrow[C_2H_5ONa]{NH_2NH_2} CH_3CH_2CH_3 + H_2O + N_2$$

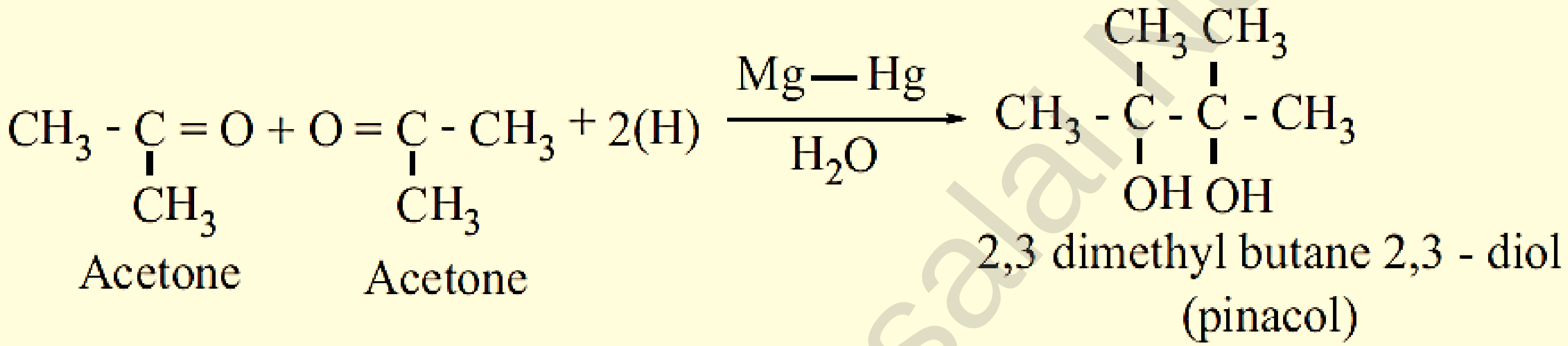
Acetone

Propane

- **Aldehyde (or) ketones is first converted to its hydrazone which on heating with strong base gives hydrocarbons.**

(iii) Reduction to pinacols:

- **Ketones, on reduction with magnesium amalgam and water, are reduced to symmetrical diols known as pinacol.**



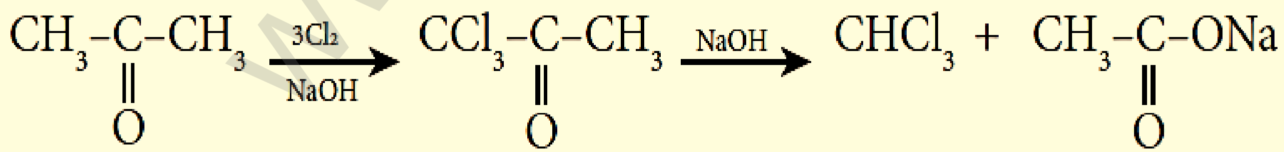
$$CH_3-\underset{\underset{CH_3}{|}}{C}=O + O=\underset{\underset{CH_3}{|}}{C}-CH_3 + 2(H) \xrightarrow[H_2O]{Mg-Hg} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$$

Acetone Acetone

2,3 dimethyl butane 2,3 - diol (pinacol)

D) Haloform reaction

Acetaldehyde and methyl ketones, containing $CH_3-\underset{\underset{O}{\|}}{C}-$ group, when treated with halogen and alkali give the corresponding haloform. This is known as Haloform reaction.



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[NaOH]{3Cl_2} CCl_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{NaOH} CHCl_3 + CH_3-\underset{\underset{O}{\|}}{C}-ONa$$

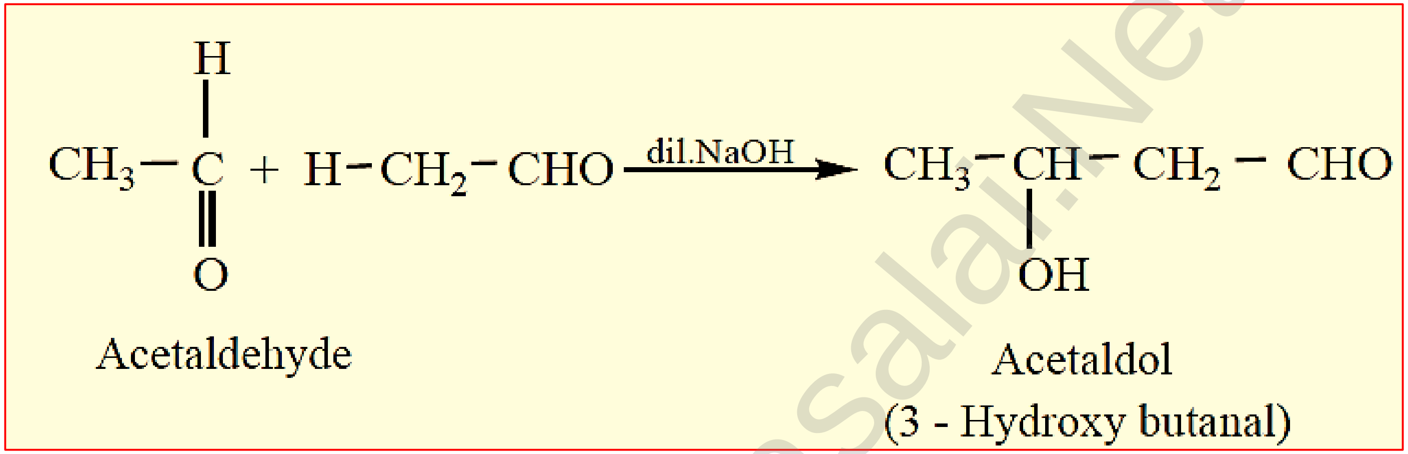
E) Reaction involving alkyl group

Aldol condensation

- **The carbon attached to carbonyl carbon is called α - carbon and the hydrogen atom attached to α - carbon is called α - hydrogen.**
- **In presence of dilute base NaOH, or KOH, two molecules of an aldehyde or ketone having α - hydrogen add together to give β- hydroxyl aldehyde (aldol) or β - hydroxyl ketone (ketol).**
- **The reaction is called aldol condensation reaction.**
- **The aldol or ketol readily loses water to give α,β – unsaturated compounds which are aldol condensation products.**

a) Simple Aldol condensation

- Acetaldehyde when warmed with dil NaOH gives β - hydroxyl butyraldehyde (acetaldol)



$$CH_3-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{C}} + H-CH_2-CHO \xrightarrow{dil.NaOH} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO$$

Acetaldehyde

Acetaldol

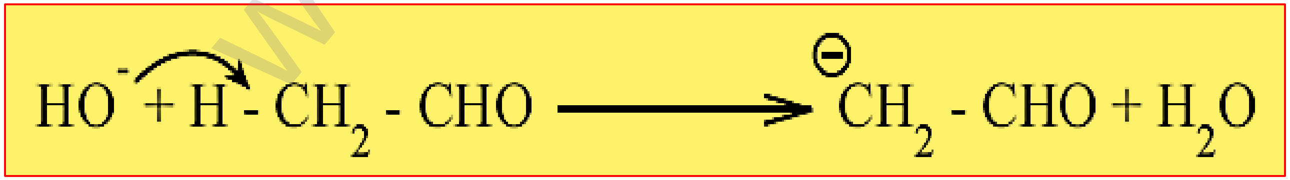
(3 - Hydroxy butanal)

Mechanism

- The mechanism of aldol condensation of acetaldehyde takes place in three steps.

Step 1 :

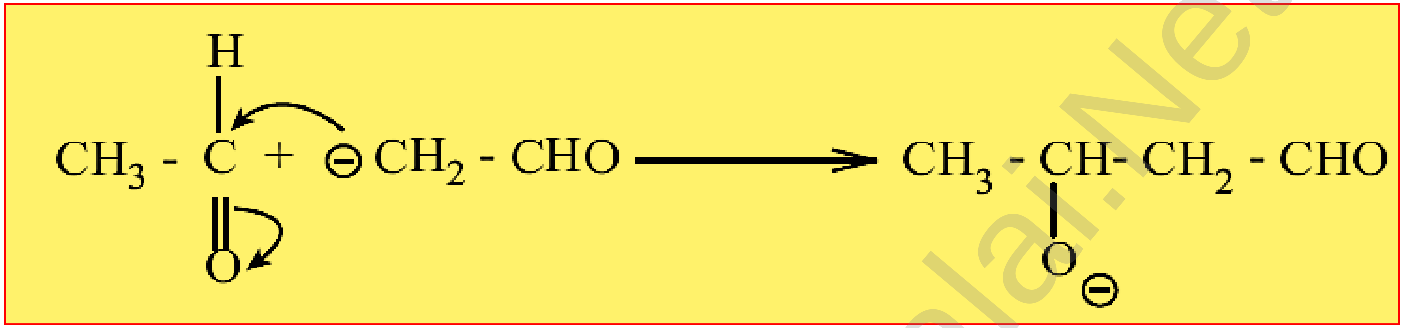
The carbanion is formed as the α **- hydrogen atom** is removed as a proton by the base.



$$HO^- + H-CH_2-CHO \longrightarrow \overset{\ominus}{C}H_2-CHO + H_2O$$

Step 2 :

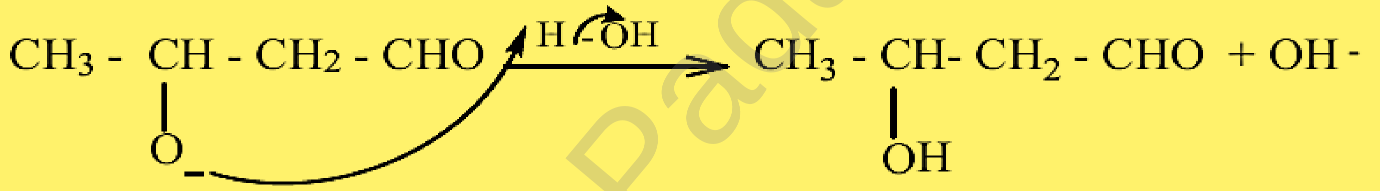
The carbanion attacks the carbonyl carbon of another unionized aldehyde to form an alkoxide ion.



$$CH_3-\underset{\underset{O}{\|}}{\overset{\overset{H}{|}}{C}} + {}^{\ominus}CH_2-CHO \longrightarrow CH_3-\underset{\underset{O^{\ominus}}{|}}{CH}-CH_2-CHO$$

Step 3 :

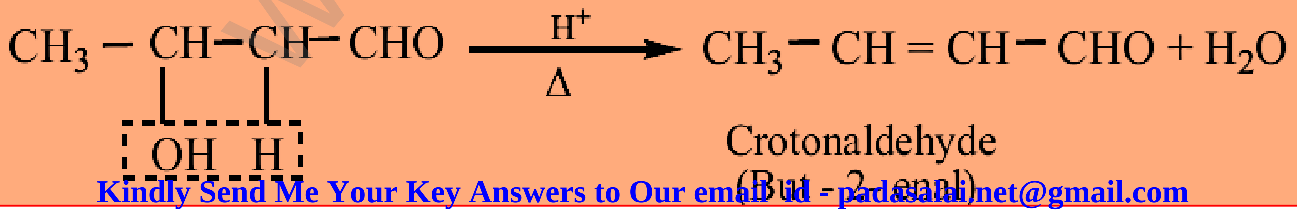
The alkoxide ion formed is protonated by water to form aldol.



$$CH_3-\underset{\underset{O^{-}}{|}}{CH}-CH_2-CHO \xrightarrow{H-OH} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CHO + OH^{-}$$

3-Hydroxy butanal

The aldol rapidly undergoes dehydration on heating with acid to form α - β unsaturated aldehyde.



$$CH_3-\underset{\underset{OH}{|}}{CH}-\underset{\underset{H}{|}}{CH}-CHO \xrightarrow[\Delta]{H^+} CH_3-CH=CH-CHO+H_2O$$

Crotonaldehyde

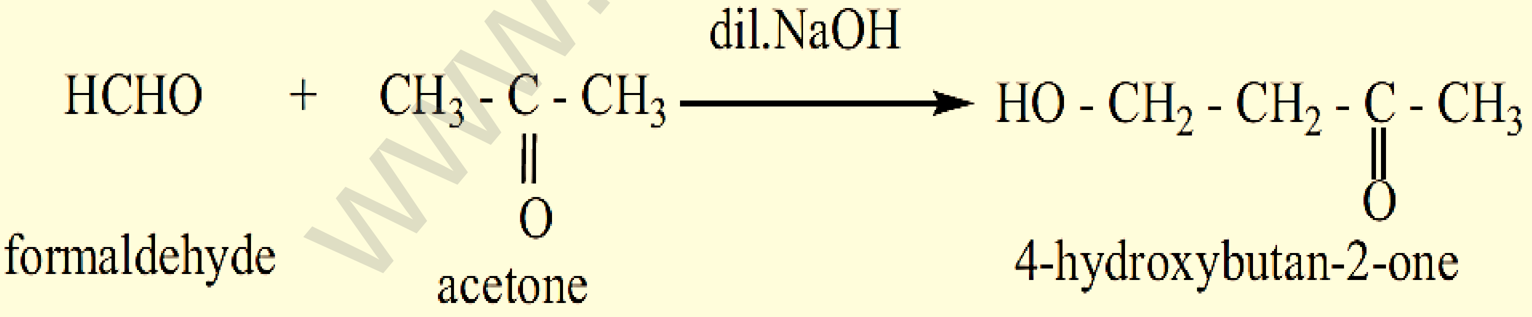
(But - 2 - enal)

b) Crossed aldol condensation

- Aldol condensation can also take place between two different aldehydes or ketones or between one aldehyde and one ketone such an aldol condensation is called **crossed or mixed aldol condensation.**
- This reaction is not very useful as the product is usually a mixture of all possible condensation products and cannot be separated easily.

Example :

$$\underset{\text{formaldehyde}}{HCHO} + \underset{\text{acetaldehyde}}{CH_3CHO} \xrightarrow{\text{dil.NaOH}} \underset{\text{3-hydroxypropanal}}{HO - CH_2 - CH_2 - CHO}$$



$$\underset{\text{formaldehyde}}{HCHO} + \underset{\text{acetone}}{CH_3 - \underset{\underset{O}{\|}}{C} - CH_3} \xrightarrow{\text{dil.NaOH}} \underset{\text{4-hydroxybutan-2-one}}{HO - CH_2 - CH_2 - \underset{\underset{O}{\|}}{C} - CH_3}$$

F) Some important reactions of benzaldehyde

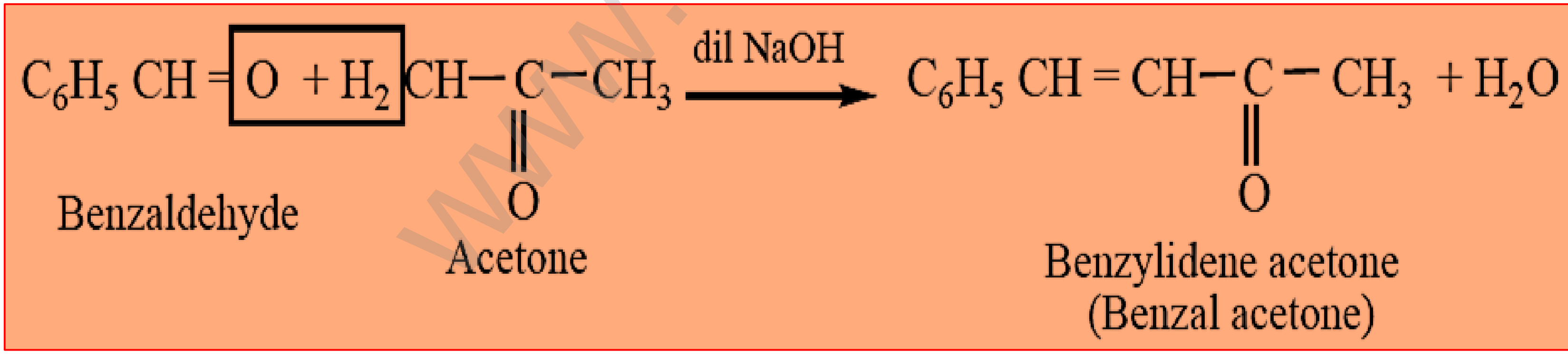
i) Claisen – Schmidt Condensation

- Benzaldehye condenses with aliphatic aldehyde or methyl ketone in the presence of dil. alkali at room temperature to form unsaturated aldehyde or ketone.

- This type of reaction is called **Claisen – Schmidt condensation.**

$$C_6H_5CH=\boxed{O+H_2}CH-CHO \xrightarrow{\text{dil NaOH}} C_6H_5CH=CH-CHO+H_2O$$

Benzaldehyde Acetaldehyde Cinnamaldehyde



$$C_6H_5\,CH=\boxed{O+H_2}CH-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{\text{dil NaOH}} C_6H_5\,CH=CH-\underset{\underset{O}{\|}}{C}-CH_3+H_2O$$

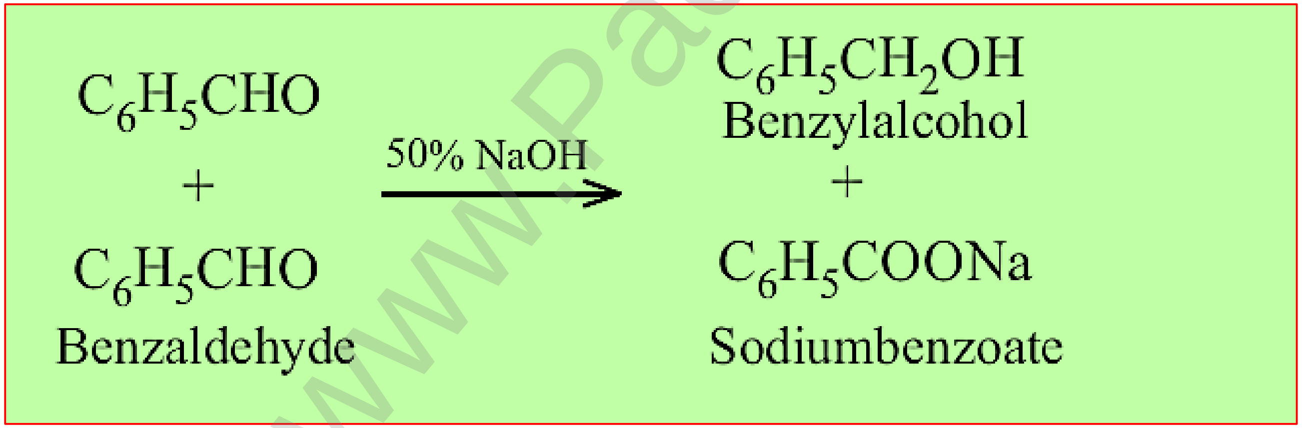
Benzaldehyde Acetone Benzylidene acetone (Benzal acetone)

ii) Cannizaro reaction

- In the presence of concentrated aqueous or alcoholic alkali, aldehydes which do not have **α - hydrogen** atom undergo self oxidation and reduction (disproportionation) to give a mixture of alcohol and a salt of carboxylic acid.

- This reaction is called **Cannizaro reaction**.

- Benzaldehyde on treatment with concentrated NaOH (50%) gives benzyl alcohol and sodium benzoate.



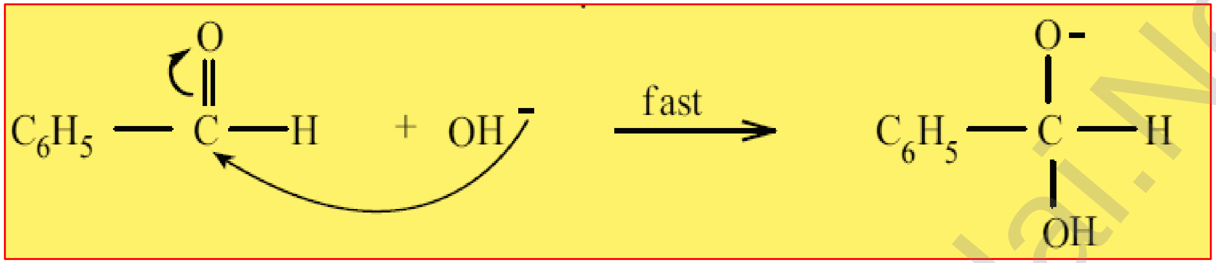
$$\underset{\text{Benzaldehyde}}{C_6H_5CHO + C_6H_5CHO} \xrightarrow{50\%\ NaOH} \underset{\text{Benzylalcohol}}{C_6H_5CH_2OH} + \underset{\text{Sodiumbenzoate}}{C_6H_5COONa}$$

- **This reaction is an example disproportionation reaction**

Mechanism of Cannizaro reaction

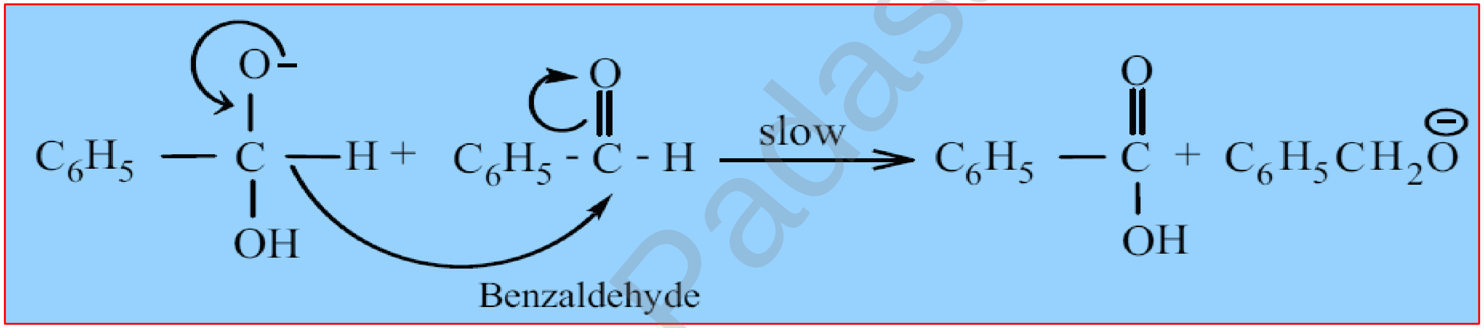
Cannizaro reaction involves three steps.

Step 1 : Attack of OH$^-$ on the carbonyl carbon



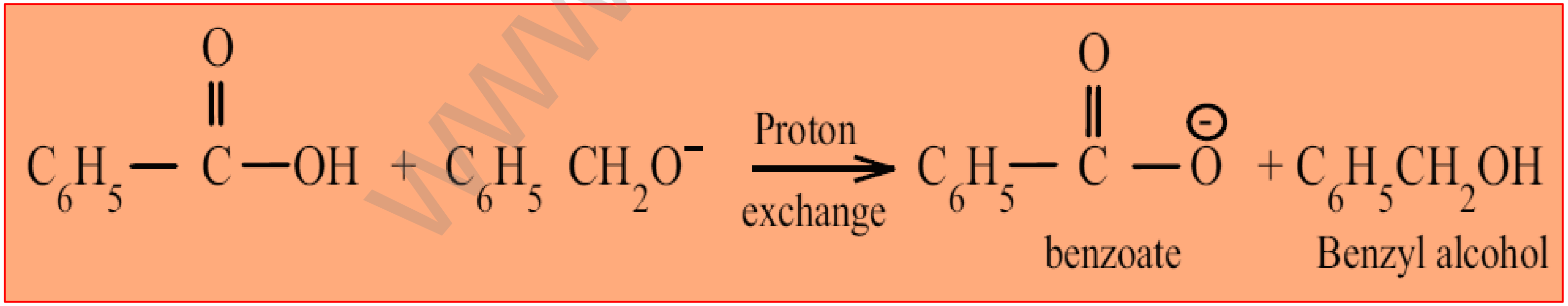
$$C_6H_5-\overset{\overset{O}{\|}}{C}-H + OH^- \xrightarrow{fast} C_6H_5-\underset{\underset{OH}{|}}{\overset{\overset{O^-}{|}}{C}}-H$$

Step 2 : Hydride ion transfer



$$C_6H_5-\underset{\underset{OH}{|}}{\overset{\overset{O^-}{|}}{C}}-H + C_6H_5-\overset{\overset{O}{\|}}{C}-H \xrightarrow{slow} C_6H_5-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{C}} + C_6H_5CH_2O^{\ominus}$$

Step 3 : Acid – base reaction.



$$C_6H_5-\overset{\overset{O}{\|}}{C}-OH + C_6H_5\,CH_2O^- \xrightarrow[\text{exchange}]{\text{Proton}} C_6H_5-\overset{\overset{O}{\|}}{C}-O^{\ominus} + C_6H_5CH_2OH$$

Cannizaro reaction is a characteristic of aldehyde having no α – hydrogen.

Crossed Cannizaro reaction

- When Cannizaro reaction takes place between two different aldehydes (neither containing an α hydrogen atom), the reaction is called as crossed cannizaro reaction.

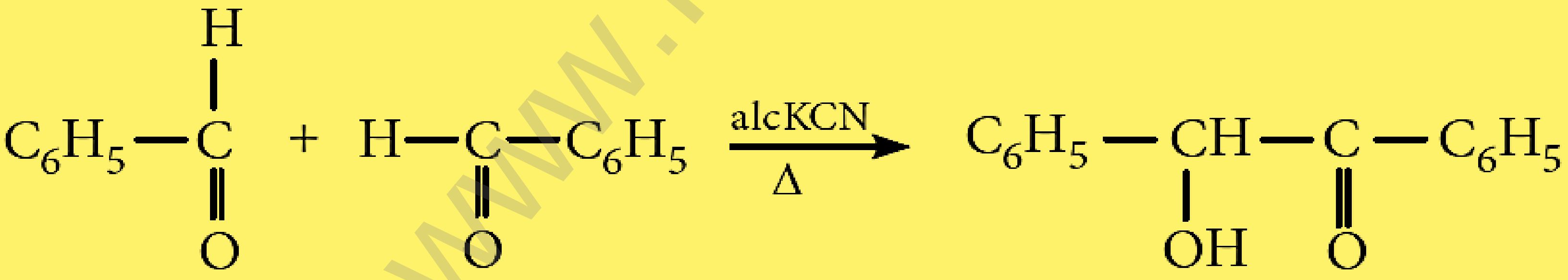
$$C_6H_5CHO + HCHO \xrightarrow{NaOH} C_6H_5CH_2OH + HCOONa$$

Benzaldehyde	Formaldehyde	Benzyl alcohol	sodium formate

- **In crossed cannizaro reaction more reactive aldehyde is oxidized and less reactive aldehyde is reduced.**

3) Benzoin condensation

- The Benzoin condensation involves the treatment of an aromatic aldehyde with aqueous alcoholic KCN. The products are α hydroxy ketone.



$$C_6H_5-\overset{\overset{H}{|}}{\underset{\underset{O}{\|}}{C}} + H-\underset{\underset{O}{\|}}{C}-C_6H_5 \xrightarrow[\Delta]{alcKCN} C_6H_5-\underset{\underset{OH}{|}}{CH}-\underset{\underset{O}{\|}}{C}-C_6H_5$$

Benzaldehyde

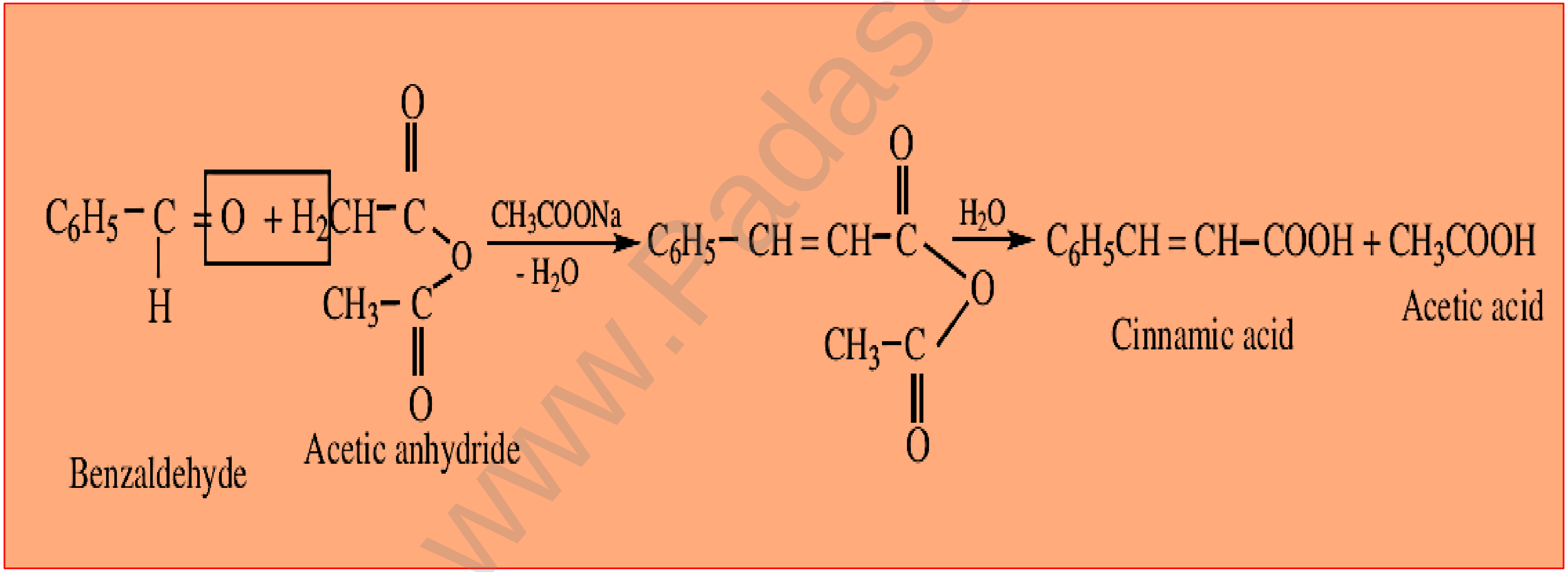
Benzoin

2-hydroxy – 1, 2 – diphenyl ethanone

4) Perkins' reaction

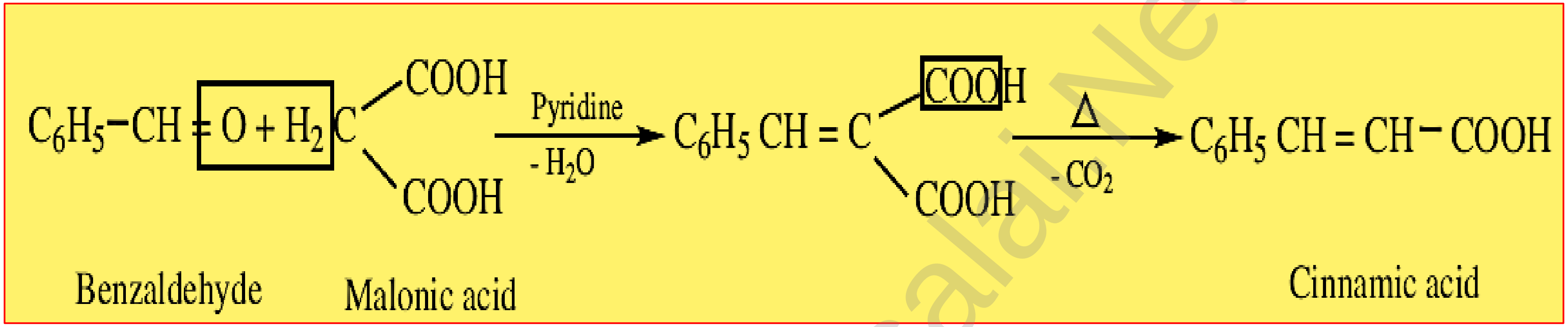
- When an aromatic aldehyde is heated with an aliphatic acid anhydride in the presence of the sodium salt of the acid corresponding to the anhydride, condensation takes place and an α, β unsaturated acid is obtained.

- This reaction is known as **Perkin's reaction**.



5) Knoevenagal reaction

- Benzaldehyde condenses with malonic acid in presence of pyridine forming cinnamic acid, Pyridine act as the basic catalyst.



6) Reaction with amine

- Aromatic aldehydes react with primary amines (aliphatic or aromatic) in the presence of an acid to form **schiff's base**.

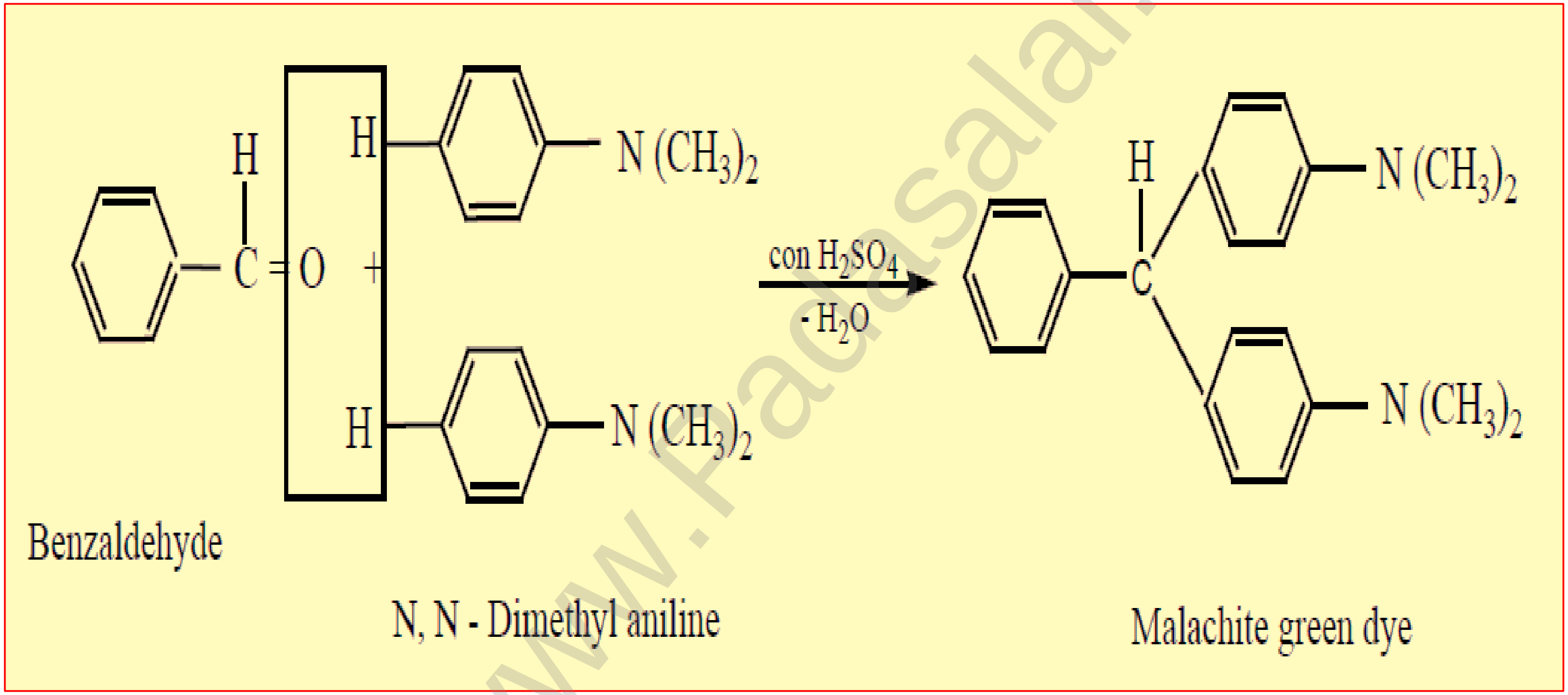
$$C_6H_5-CH\boxed{=O+H_2}N-C_6H_5 \xrightarrow[\Delta]{H^+} C_6H_5-CH=N-C_6H_5 + H_2O$$

Benzaldehyde Aniline

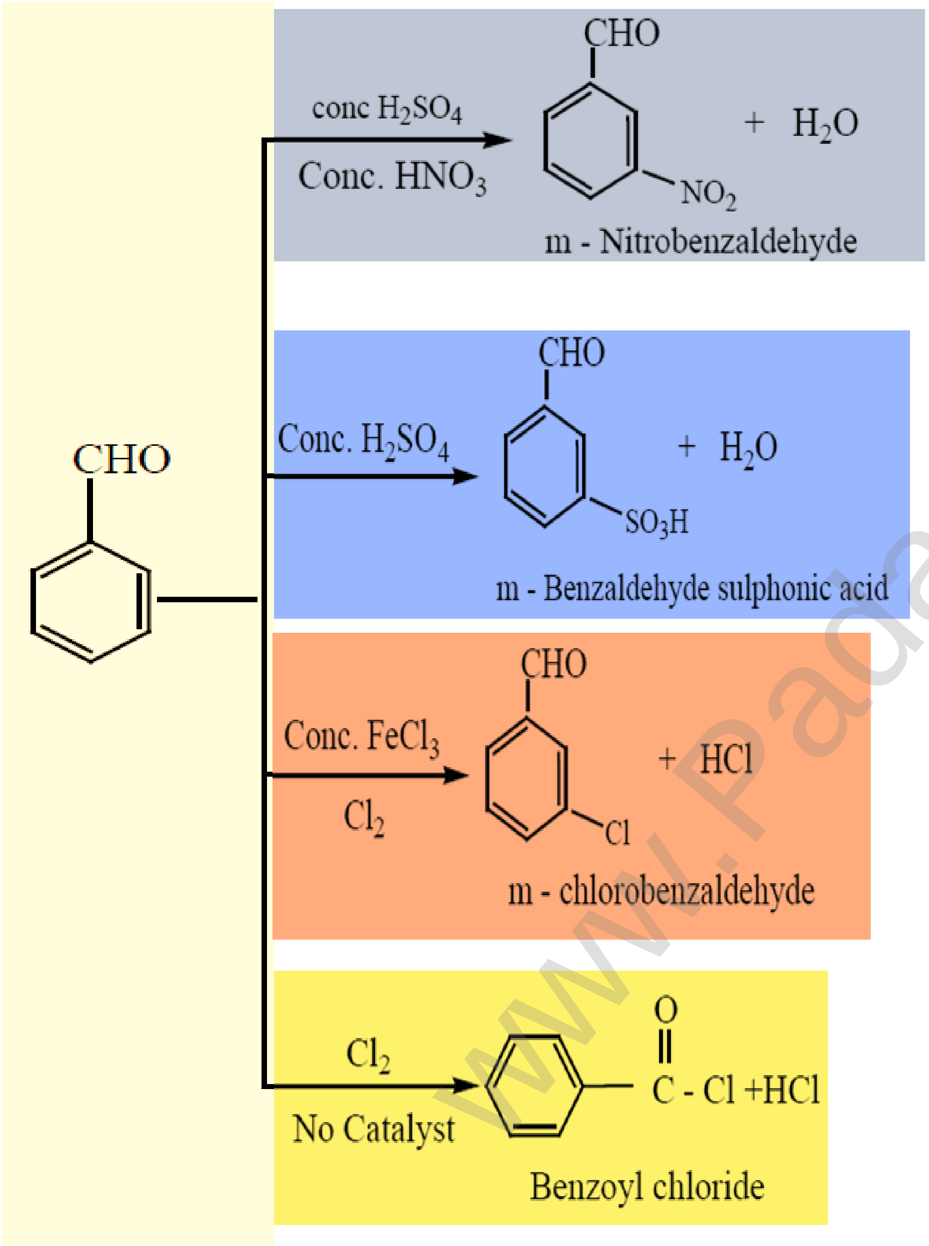
Benzal aniline
(Schiff's base)

7) Condensation with tertiary aromatic amines

- Benzaldehyde condenses with tertiary aromatic amines like N, N – dimethyl aniline in the presence of strong acids to form triphenyl methane dye.

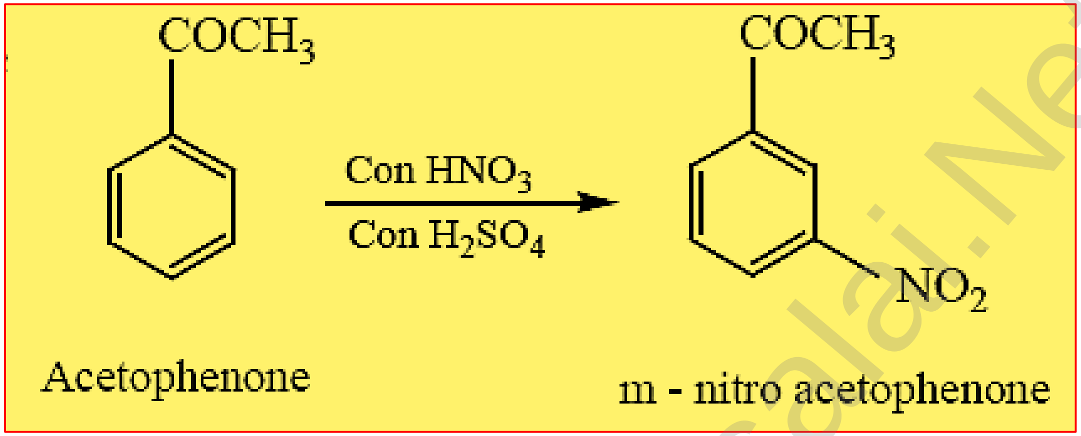


8) Electrophilic substitution reactions of benzaldehyde



Electrophilic substitution reaction of acetophenone

Acetophenone reacts with Nitrating mixture to form m –nitroacetophenone.



Test for Aldehydes

i) Tollens Reagent Test

Acetophenone m - nitro acetophenone

Tollens reagent is an ammonical silver nitrate solution. When an aldehyde is warmed with Tollens reagent a bright silver mirror is produced due to the formation of silver metal. This reaction is also called **silver mirror test** for aldehydes.

$$CH_3\,CHO + 2\,[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow CH_3COO^- + 4NH_3 + 2Ag + 2H_2O$$

Silver

ii) Fehlings solution Test

Fehlings solution is prepared by mixing equal volumes of Fehlings solution ‘A’ containing aqueous copper sulphate and Fehlings solution ‘B’ containing alkaline solution of sodium potassium tartarate (Rochelle salt)

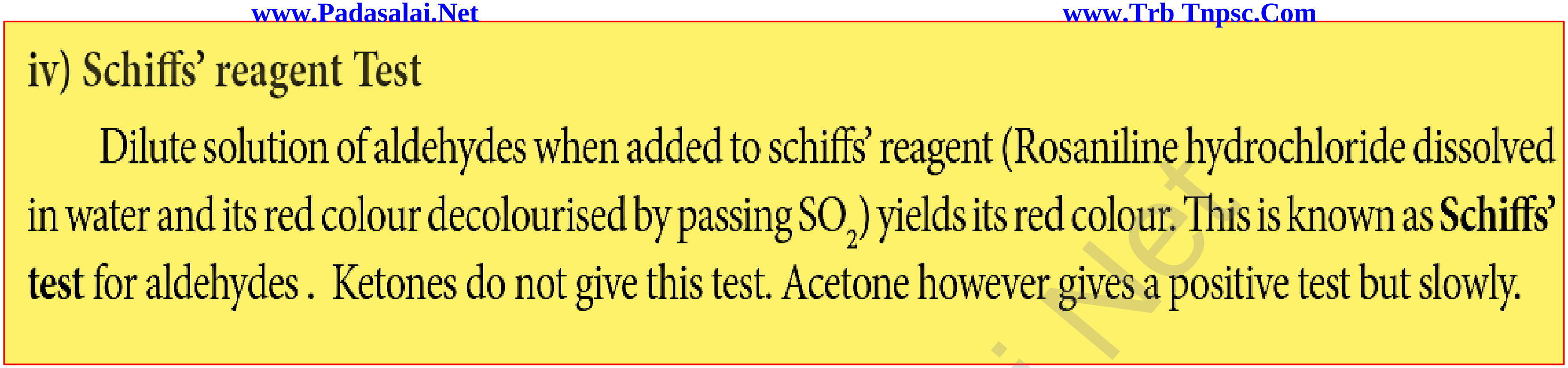
When aldehyde is warmed with Fehlings solution deep blue colour solution is changed to red precipitate of cuprous oxide.

$$CH_3\,CHO + \underset{\text{(blue)}}{2Cu^{2+}} + 5OH^- \longrightarrow CH_3COO^- + \underset{\text{(red)}}{Cu_2O} \downarrow + 3H_2O$$

iii) Benedict's solution Test:

Benedicts solution is a mixture of $CuSO_4$ + sodium citrate + NaOH. Cu^{2+} is reduced by aldehyde to give red precipitate of cuprous oxide.

$$CH_3\,CHO + \underset{\text{(blue)}}{2Cu^{2+}} + 5OH^- \longrightarrow CH_3COO^- + \underset{\text{(red)}}{Cu_2O} \downarrow + 3H_2O$$



iv) Schiffs' reagent Test

Dilute solution of aldehydes when added to schiffs' reagent (Rosaniline hydrochloride dissolved in water and its red colour decolourised by passing SO_2) yields its red colour. This is known as **Schiffs' test** for aldehydes . Ketones do not give this test. Acetone however gives a positive test but slowly.

Uses of Aldehydes and Ketones

Formaldehyde

(i) 40% aqueous solution of formaldehyde is called **formalin**. It is used for preserving biological specimens.

(ii) Formalin has hardening effect, hence it is used for tanning.

(iii) Formalin is used in the production of thermo setting plastic known as bakelite, which is obtained by heating phenol with formalin.

Acetaldehye

(i) Acetaldehyde is used for silvering of mirrors

(ii) Paraldehyde is used in medicine as a hypnotic.

(iii) Acetaldehyde is used in the commercial preparation of number of organic compounds like acetic acid, ethyl acetate etc.,

Acetone

(i) Acetone is used as a solvent, in the manufacture of smokeless gun powder (cordite)

(ii) It is used as a nail polish remover.

(iii) It is used in the preparation of sulphonal, a hypnotic.

(iv) It is used in the manufacture of thermosoftening plastic **Perspex.**

Benzaldehyde is used

(i) as a flavoring agent

(ii) in perfumes

(iii) in dye intermediates

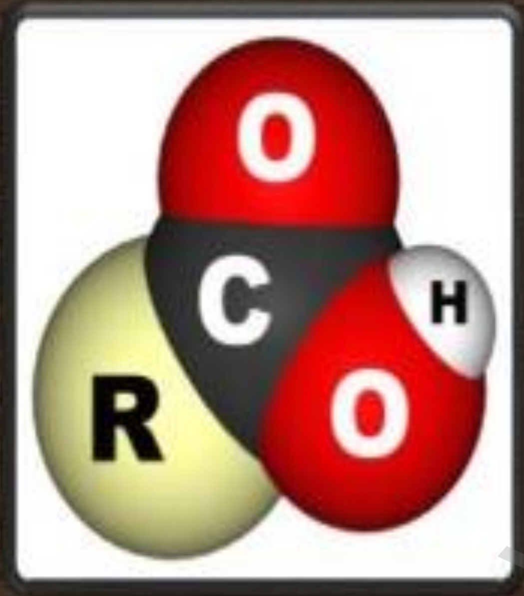
(iv) as starting material for the synthesis of several other organic compounds like cinnamaldehyde, cinnamic acid, benzoyl chloride etc.

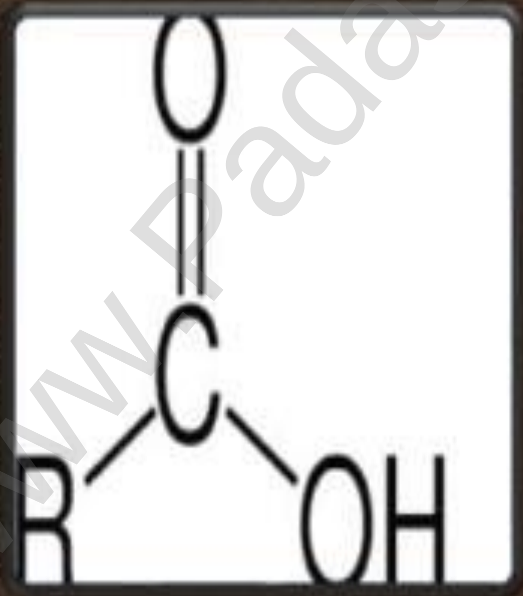
Aromatic Ketones

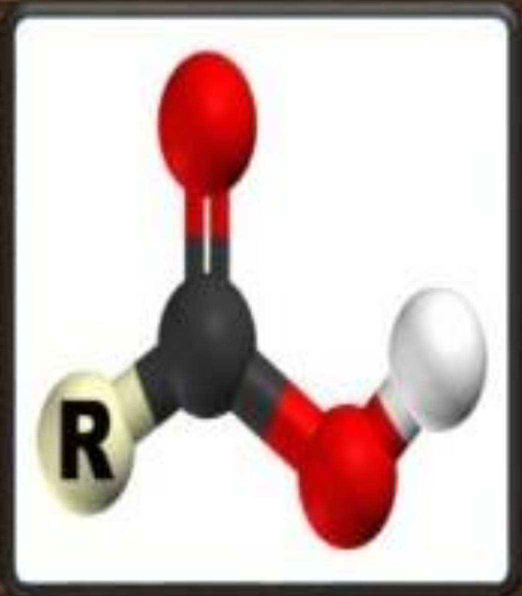
(i) Acetophenone has been used in perfumery and as a hypnotic under the name **hypnone.**

(ii) Benzophenone is used in perfumery and in the preparation of **benzhydrol eye drop.**

“CARBOXYLIC ACID”

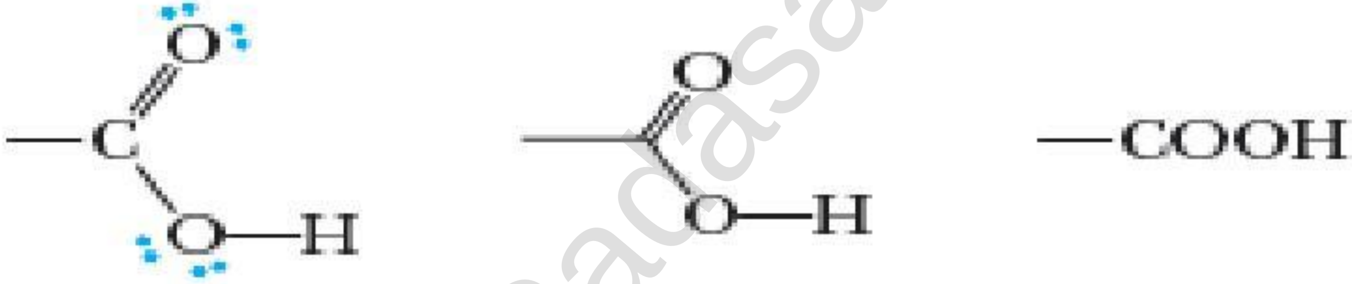






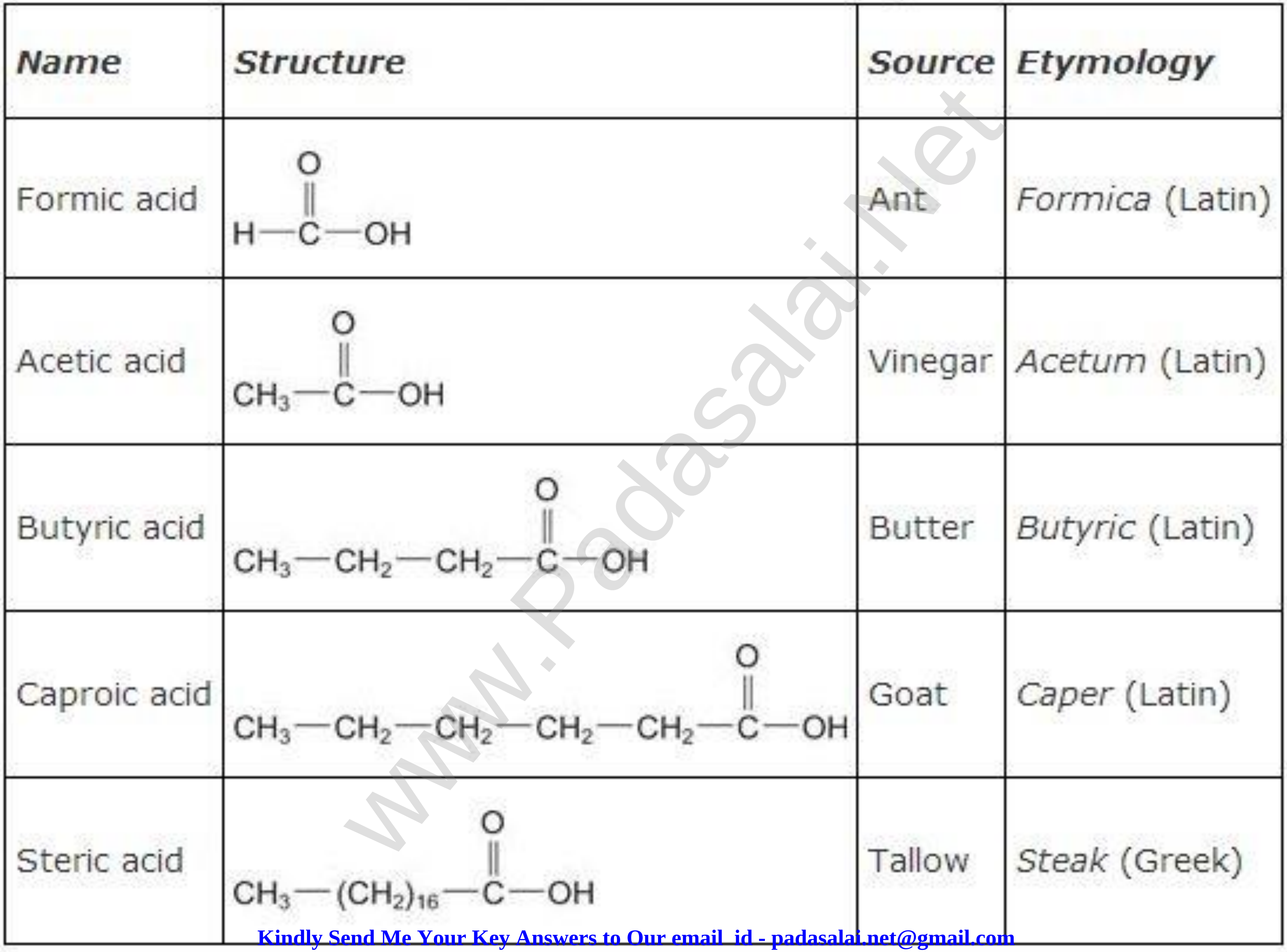
Introduction

- The functional group of a carboxylic acid is the **carboxyl group** so named because it is made up of a *carb*onyl group and a hydr*oxyl* group



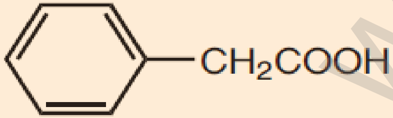
- The general formula for an aliphatic carboxylic acid is RCOOH

TABLE 1 Common Names of Carboxylic Acids



Name	Structure	Source	Etymology
Formic acid	$\mathrm{H-\overset{O}{\overset{\|}{C}}-OH}$	Ant	*Formica* (Latin)
Acetic acid	$\mathrm{CH_3-\overset{O}{\overset{\|}{C}}-OH}$	Vinegar	*Acetum* (Latin)
Butyric acid	$\mathrm{CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH}$	Butter	*Butyric* (Latin)
Caproic acid	$\mathrm{CH_3-CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OH}$	Goat	*Caper* (Latin)
Steric acid	$\mathrm{CH_3-(CH_2)_{16}-\overset{O}{\overset{\|}{C}}-OH}$	Tallow	*Steak* (Greek)

IUPAC nomenclature of Carboxylic acids

Compound (common name, Structural formula, IUPAC Name)	IUPAC Name			
	Prefix with position number	Root used	Primary suffix	Secondary Suffix
Formic acid HCOOH methanoicacid	–	meth	an~~e~~	oicacid
Acetic acid CH_3COOH Ethanoic acid	–	eth	an~~e~~	oicacid
Isobutyric acid $(CH_3)_2CHCOOH$ 2 – methylpropanoic acid	2 – methyl	prop	an~~e~~	oicacid
Phenyl acetic acid  2-phenyl ethanoic acid	2-phenyl	eth	an~~e~~	oicacid

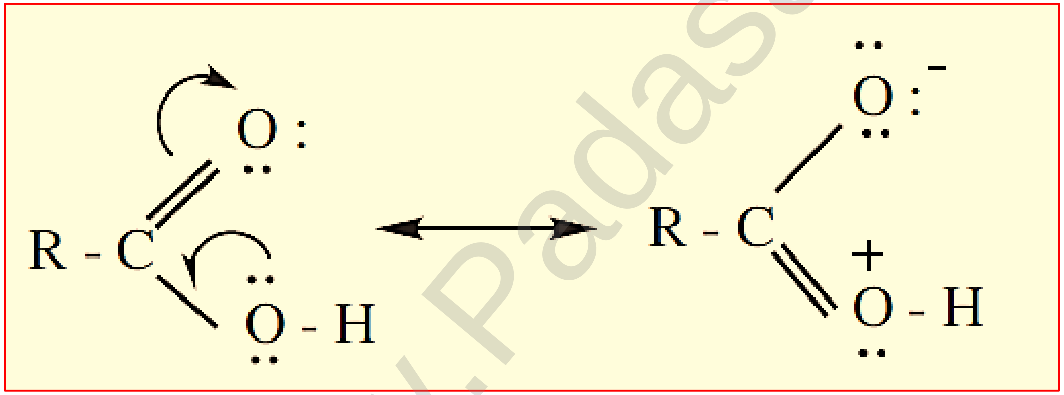
Oxalic acid HOOC - COOH ethane–1, 2 – dioicacid	–	eth	ane	1, 2 – dioicacid
Malonic acid $HOOC-CH_2-COOH$ Propanedioic acid	–	prop	ane	1, 3 – dioicacid
Succinic acid $HOOC-(CH_2)_2-COOH$ Butanedioic acid	–	but	ane	1, 4 – dioicacid
Glutaric acid $HOOC-(CH_2)_3-COOH$ Pentanedioic acid	–	pent	ane	1,5 – dioicacid
Adipic acid $HOOC-(CH_2)_4-COOH$ Hexanedioic acid	–	hex	ane	1,6 – dioicacid

Structure of carboxyl group:

- The carboxyl group represent a planar arrangement of atoms.
- In – COOH group, the centre carbon atom and both the oxygen atoms are in sp^2 hybridisation.
- The three sp^2 hybrid orbitals of the carbon atom overlap.
- The two sp^2 – hybridised orbitals of the carboxyl carbon overlap with one sp^2 hybridized orbital of each oxygen atom while the third sp^2 hybridised orbital of carbon overlaps with either a s -orbital of H – atom or a sp^2 – hybridised orbital of C –atom of the alkyl group to form three s- bonds.
- Each of the two oxygen atoms and the carbon atom are left with one unhybridised p – orbital which is perpendicular to the s-bonding skeleton.

- All these three p – orbitals being parallel overlap to form a π- bond which is partly delocalized between carbon and oxygen atom on one side, and carbon and oxygen of the OH group on the other side.

- In other words, RCOOH may be represented as a resonance hybrid of the following two canonical structures.



- The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure. i.e., delocalisation of lone pair electrons from the oxygen in hydroxyl group.

Methods of Preparation of carboxylic acids

1. From Primary alcohols and aldehydes

- Primary alcohols and aldehydes can easily be oxidised to the corresponding carboxylic acids with oxidising agents such as **potassium permanganate (in acidic or alkaline medium), potassium dichromate (in acidic medium)**

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[(O)]{H^+/\,K_2Cr_2O_7} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[(O)]{} \underset{\text{Acetic acid}}{CH_3COOH}$$

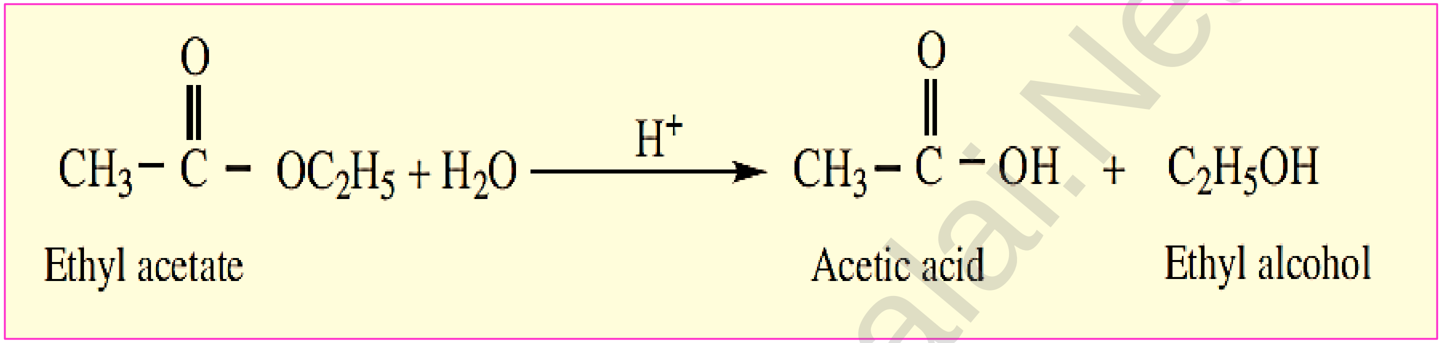
2. Hydrolysis of Nitriles

- Nitriles yield carboxylic acids when subjected to hydrolysis with an acid or alkali.

$$\underset{\text{Methyl cyanide}}{CH_3-C\equiv N} + 2H_2O \xrightarrow{H^+} \underset{\text{Acetic acid}}{CH_3COOH} + NH_3$$

3. Acidic hydrolysis of esters

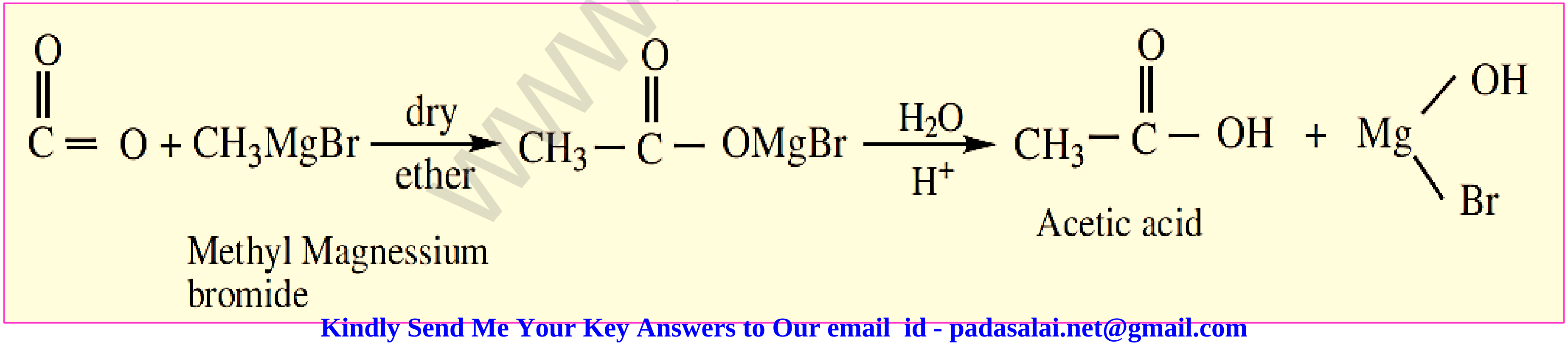
- Esters on hydrolysis with dilute mineral acids yield corresponding carboxylic acid



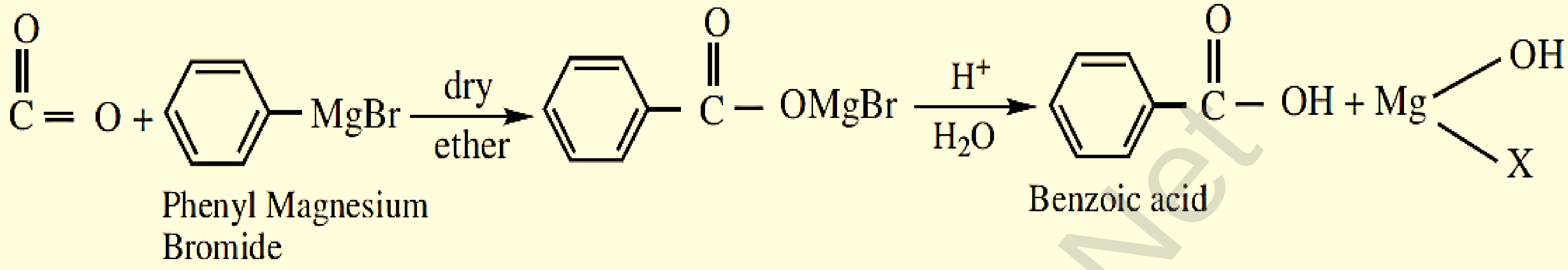
$$CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + H_2O \xrightarrow{H^+} CH_3-\overset{\overset{O}{\|}}{C}-OH + C_2H_5OH$$

4. From Grignard reagent

- Grignard reagent reacts with carbon di oxide (dry ice) to form salts of carboxylic acid which in turn give corresponding carboxylic acid after acidification with mineral acid.



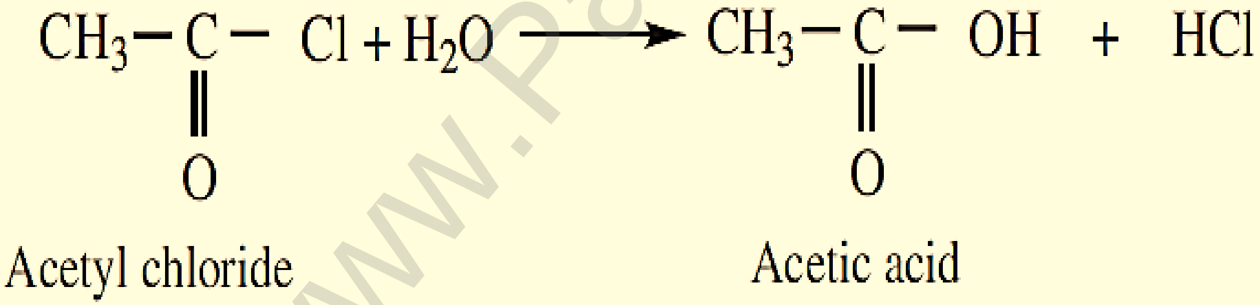
$$\overset{\overset{O}{\|}}{C}=O + CH_3MgBr \xrightarrow[ether]{dry} CH_3-\overset{\overset{O}{\|}}{C}-OMgBr \xrightarrow[H^+]{H_2O} CH_3-\overset{\overset{O}{\|}}{C}-OH + Mg\begin{matrix}/OH\\ \backslash Br\end{matrix}$$



- ***Formic acid cannot be prepared by Grignard reagent*** since the acid contains only one carbon atom

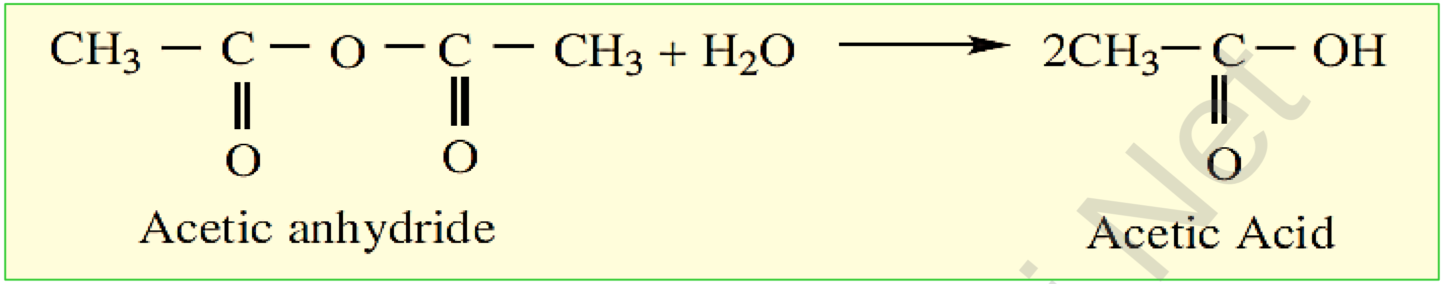
5. Hydrolysis of acyl halides and anhydrides

a) Acid chlorides when hydrolysed with water give Carboxylic acids.



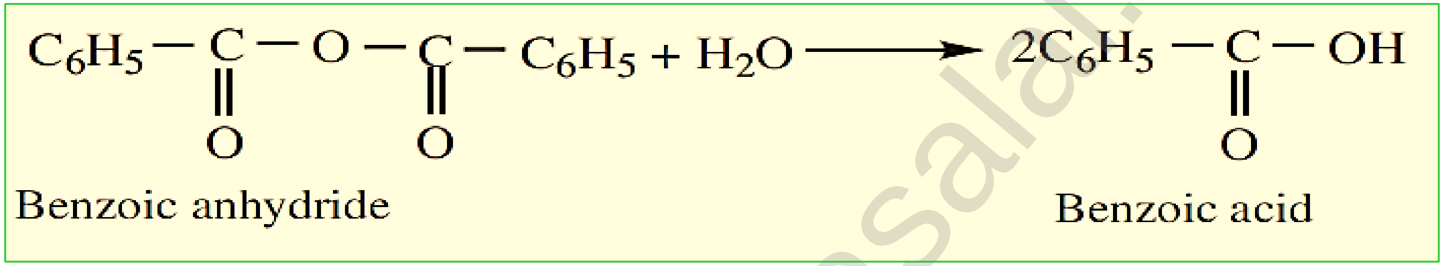
$$CH_3-\underset{\underset{O}{\|}}{C}-Cl + H_2O \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-OH + HCl$$

b) Acid anhydride when hydrolysed with water give corresponding carboxylic acids.



$$CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_3 + H_2O \longrightarrow 2CH_3-\underset{\underset{O}{\|}}{C}-OH$$

Acetic anhydride Acetic Acid

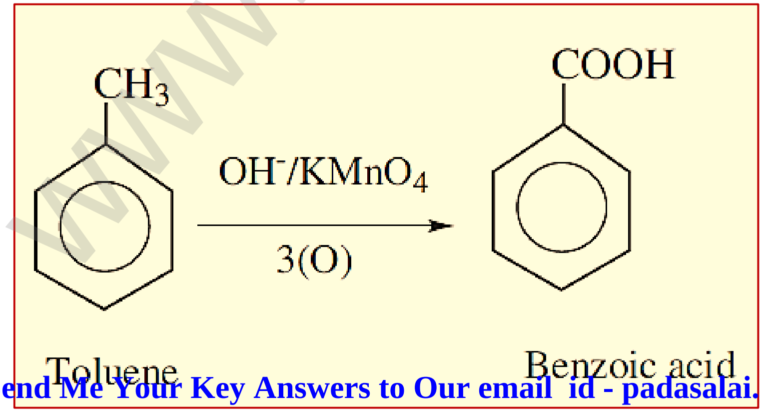


$$C_6H_5-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-C_6H_5 + H_2O \longrightarrow 2C_6H_5-\underset{\underset{O}{\|}}{C}-OH$$

Benzoic anhydride Benzoic acid

6)Oxidation of alkyl benzenes

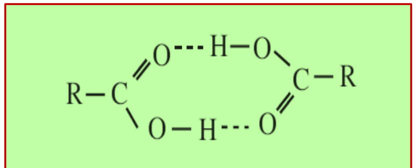
Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzene with chromic acid or acidic or alkaline potassium permanganate. The entire side chain is oxidized to –COOH group irrespective of the length of the side chain.



Physical Properties of carboxylic acids.

i) Aliphatic carboxylic acid upto nine carbon atoms are colour less liquids with pungent odour. The higher members are odourless wax like solids.

ii) Carboxylic acids have higher boiling point than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more association of carboxylic acid molecules through intermolecular hydrogen bonding.



Inter molecular hydrogen bonding

In fact, most of the carboxylic acids exist as dimer in its vapour phase.

iii) Lower aliphatic carboxylic acids (up to four carbon) are miscible with water due to the formation of hydrogen bonds with water. Higher carboxylic acid are insoluble in water due to increased hydrophobic interaction of hydrocarbon part. The simplest aromatic carboxylic acid, benzoic acid is insoluble in water.

iv) Vinegar is 6 to 8% solution of acetic acid in water. Pure acetic acid is called **glacial acetic acid.** Because it forms ice like crystal when cooled. When aqueous acetic acid is cooled at 289.5 K, acetic acid solidifies and forms ice like crystals, where as water remains in liquid state and removed by filtration. This process is repeated to obtain glacial acetic acid.

Chemical properties of carboxylic acids.

Carboxylic acid do not give the characteristic reaction of carbonyl group [- C = O] as given by the aldehydes and ketones. as the carbonyl group of carboxylic acid is involved in resonance:

The reactions of carboxylic acids can be classified as follows:

A)Reactions involving cleavage of O – H bond.

B)Reactions involving cleavage of C – OH bond.

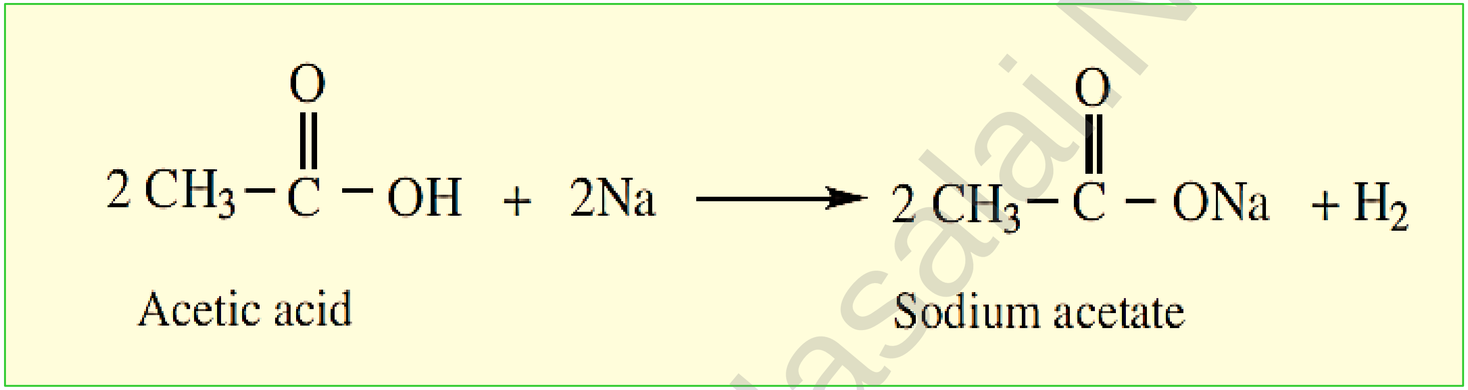
C)Reactions involving – COOH group.

D)Substitution reactions involving hydrocarbon part

A) Reactions involving cleavage of O – H bond.

1) Reactions with metals

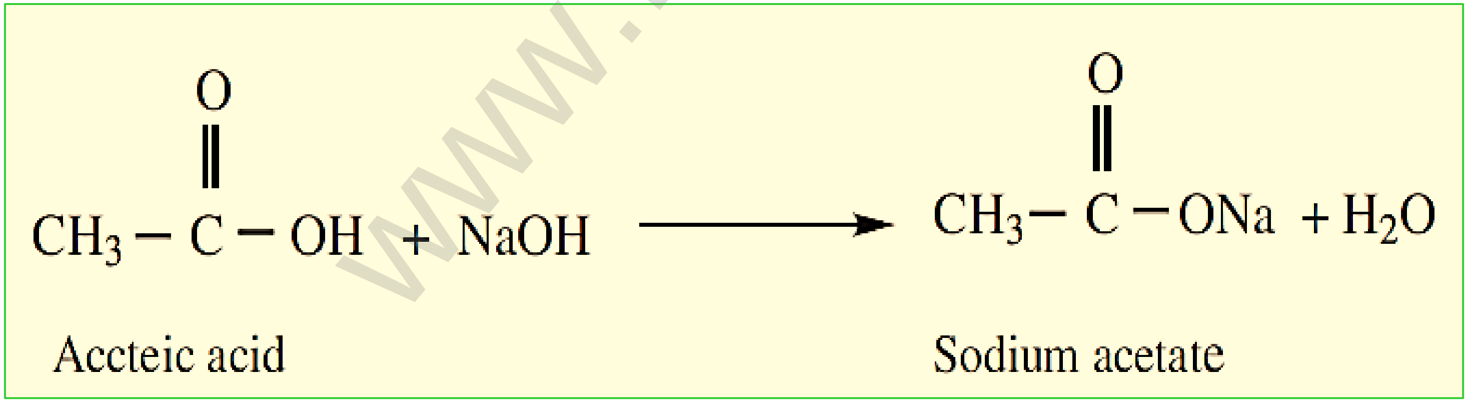
- Carboxylic acid react with active metals like Na, Mg, Zn etc to form corresponding salts with the liberation of hydrogen.



$$2\,CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + 2Na \longrightarrow 2\,CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-ONa + H_2$$

2) Reaction with alkalies

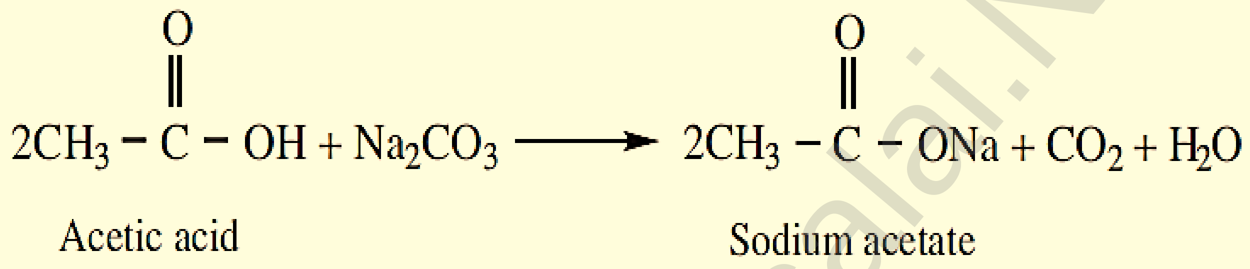
- Carboxylic acid reacts with alkalies to neutralise them and form salts.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + NaOH \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-ONa + H_2O$$

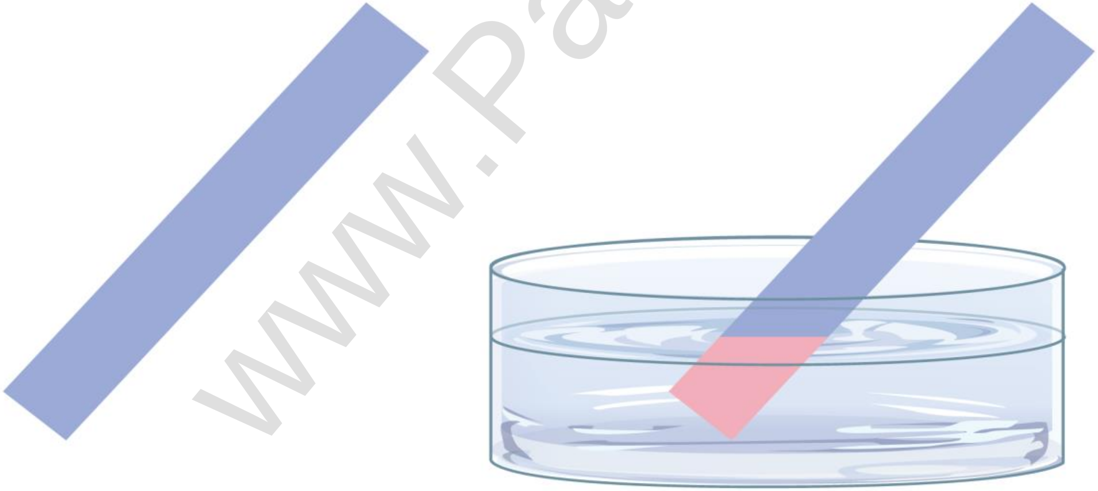
3) Reaction with carbonates and bicarbonates (Test for carboxylic acid group)

- Carboxylic acids decompose carbonates and bicarbonates evolving carbondioxide gas with effervescence.



$$2CH_3-\overset{\overset{O}{\|}}{C}-OH+Na_2CO_3 \longrightarrow 2CH_3-\overset{\overset{O}{\|}}{C}-ONa+CO_2+H_2O$$

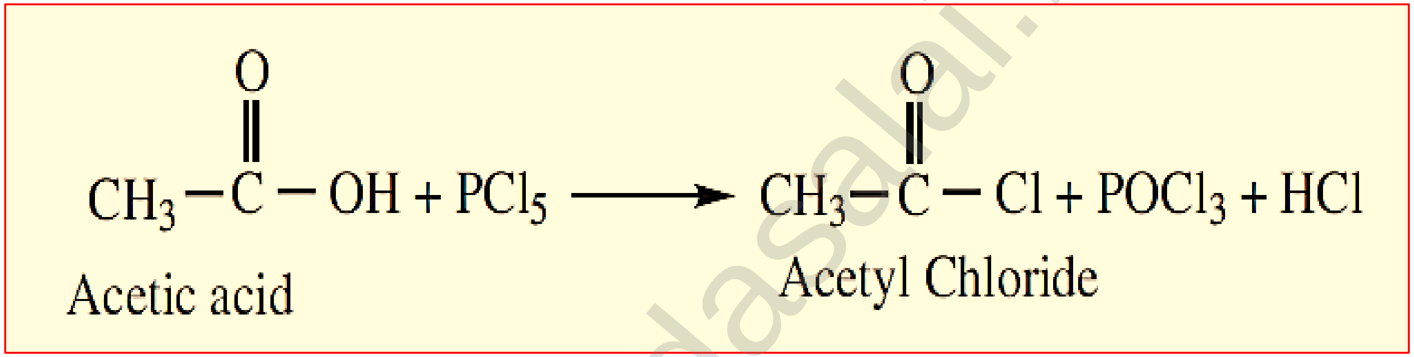
4) All Carboxylic acids turn blue litmus red



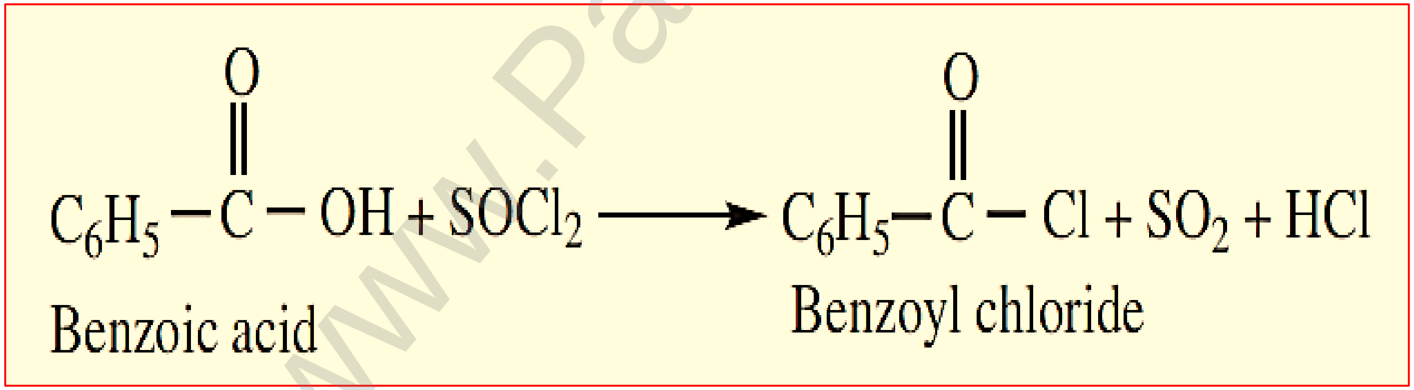
B) Reactions involving cleavage of C-OH bond

1) Reactions with PCl_5 , PCl_3 and $SOCl_2$

- The hydroxyl group of carboxylic acids behaves like that of an alcoholic group and is easily replaced by chlorine atom on treating with PCl_5, PCl_3 or $SOCl_2$.



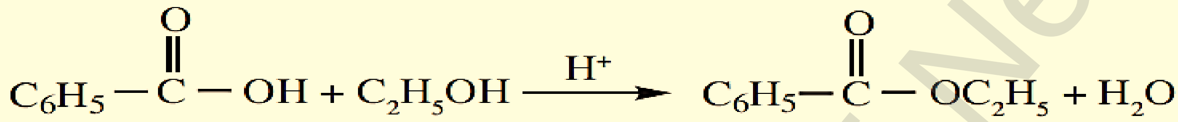
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + PCl_5 \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + POCl_3 + HCl$$



$$C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-OH + SOCl_2 \longrightarrow C_6H_5-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + SO_2 + HCl$$

2) Reactions with alcohols (Esterification)

- When carboxylic acids are heated with alcohols in the presence of conc. H_2SO_4 or dry HCl gas, esters are formed. The reaction is reversible and is called esterification.

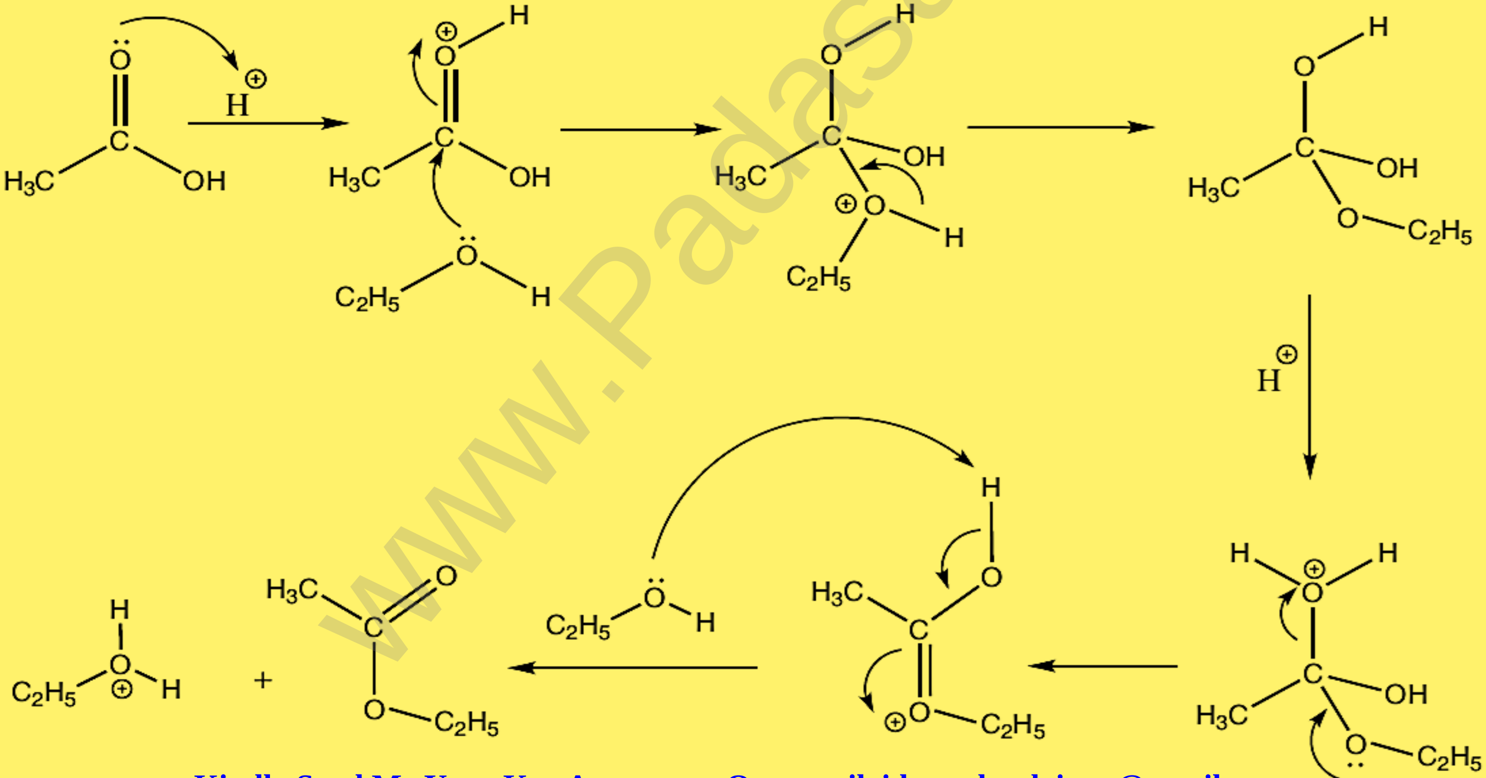


$$C_6H_5-\overset{\overset{O}{\|}}{C}-OH + C_2H_5OH \xrightarrow{H^+} C_6H_5-\overset{\overset{O}{\|}}{C}-OC_2H_5 + H_2O$$

Benzoic acid ethyl benzoate

Mechanism of esterification:

The Mechanism of esterification involves the following steps.

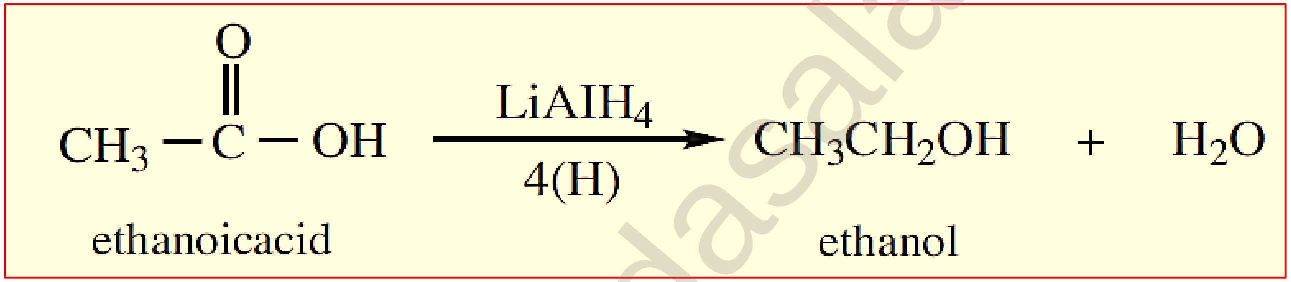


C) Reactions involving – COOH group

1) Reduction

i) Partial reduction to alcohols

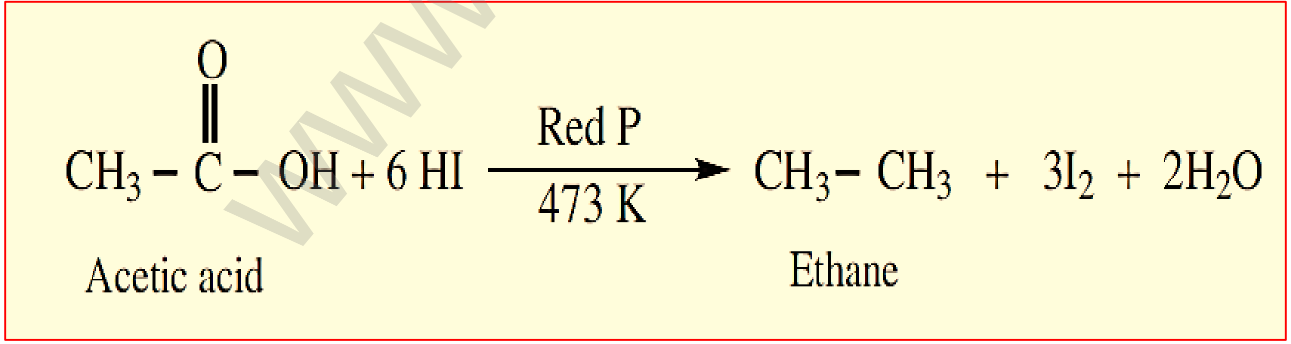
- Carboxylic acids are reduced to primary alcohols by $LiAlH_4$ or with hydrogen in the presence of copper chromite as catalyst. Sodium borohydride does not reduce the – COOH group.



$$\underset{\text{ethanoicacid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} \xrightarrow[4(H)]{LiAlH_4} \underset{\text{ethanol}}{CH_3CH_2OH} + H_2O$$

ii) Complete reduction to alkanes

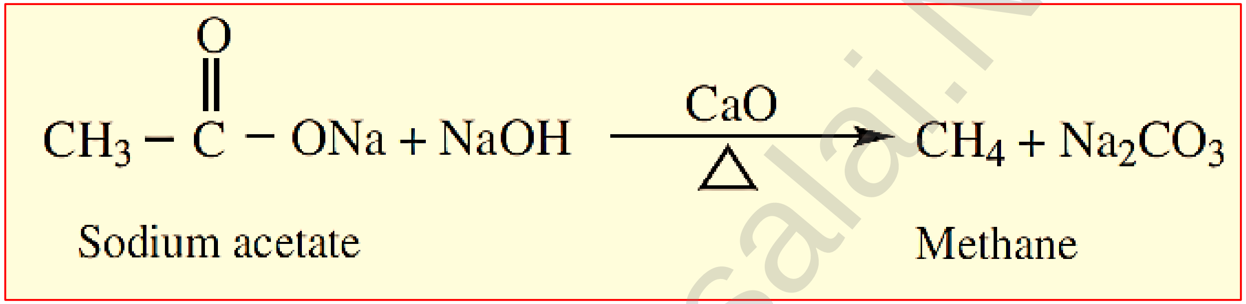
- When treated with HI and red phosphorous, carboxylic acid undergoes complete reduction to yield alkanes containing the same number of carbon atoms.



$$\underset{\text{Acetic acid}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH} + 6\,HI \xrightarrow[473\ K]{Red\ P} \underset{\text{Ethane}}{CH_3-CH_3} + 3I_2 + 2H_2O$$

2) Decarboxylation

- Removal of CO_2 from carboxyl group is called as **decarboxylation.** Carboxylic acids lose carbon di oxide to form hydrocarbon when their sodium salts are heated with soda lime (NaOH and CaO in the ratio 3: 1)

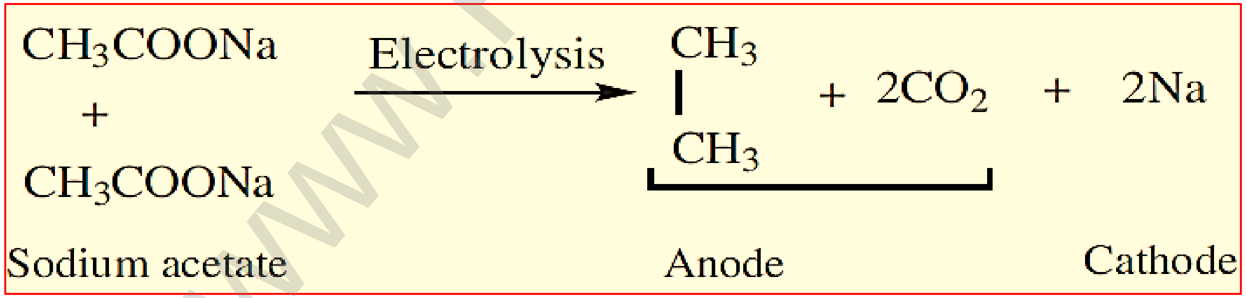


$$\mathrm{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-ONa+NaOH\xrightarrow[\Delta]{CaO}CH_4+Na_2CO_3}$$

Sodium acetate Methane

3) Kolbe’s electrolytic decarboxylation

- The aqueous solutions of sodium or potassium salts of carboxylic acid on electrolysis gives alkanes at anode. This reaction is called Kolbe’s electrolysis.



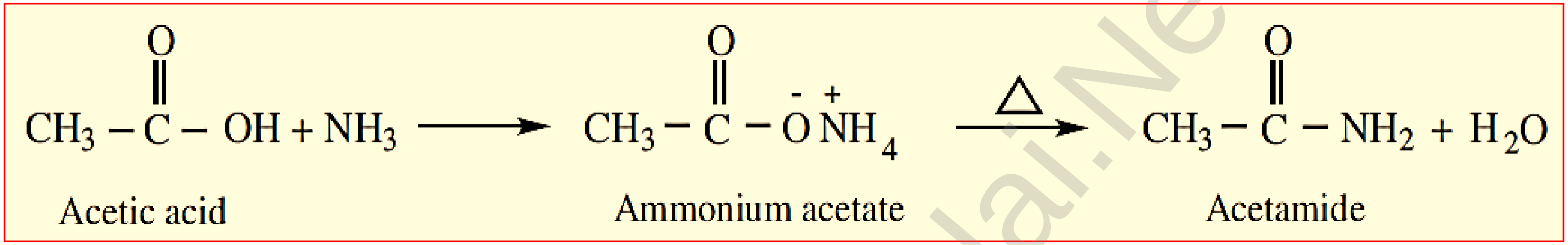
$$\begin{matrix}\mathrm{CH_3COONa}\\+\\\mathrm{CH_3COONa}\end{matrix}\xrightarrow{\text{Electrolysis}}\underbrace{\begin{matrix}\mathrm{CH_3}\\|\\\mathrm{CH_3}\end{matrix}+2\mathrm{CO_2}}+2\mathrm{Na}$$

Sodium acetate Anode Cathode

- Sodium formate solution on electrolysis gives hydrogen

4) Reactions with ammonia

- Carboxylic acids react with ammonia to form ammonium salt which on further heating at high temperature gives amides.

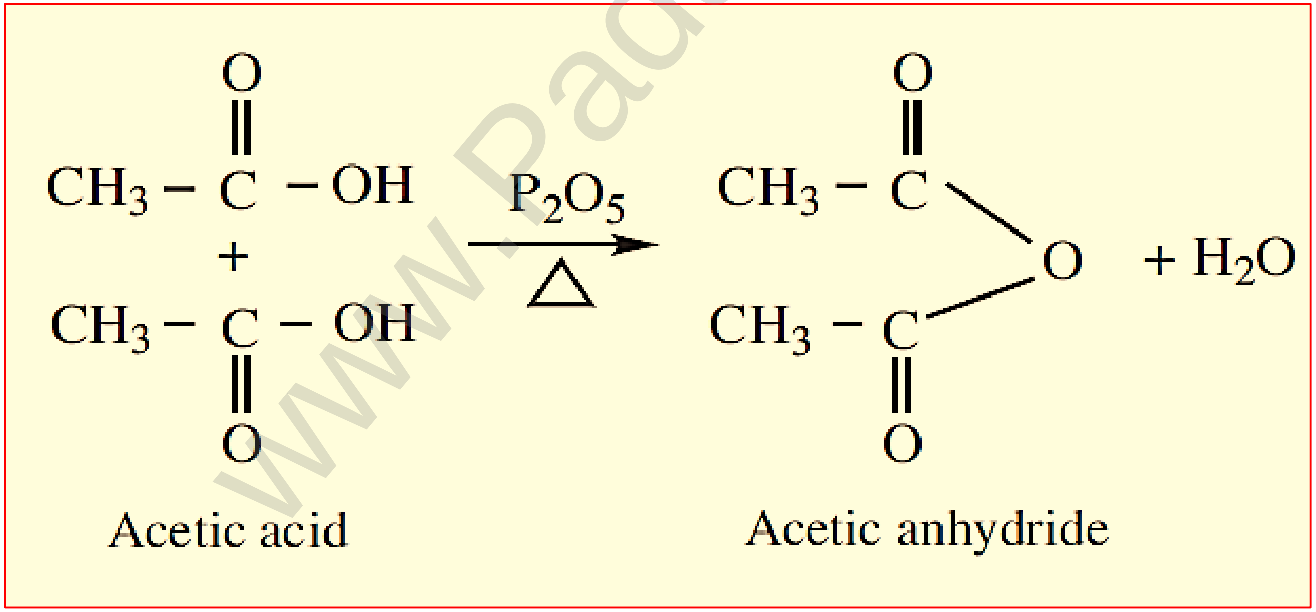


$$CH_3-\overset{O}{\overset{\|}{C}}-OH+NH_3\longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\,\overset{+}{N}H_4\xrightarrow{\Delta}CH_3-\overset{O}{\overset{\|}{C}}-NH_2+H_2O$$

Acetic acid Ammonium acetate Acetamide

5) Action of heat in the presence of P_2O_5

- Carboxylic acid on heating in the presence of a strong dehydrating agent such as P_2O_5 forms acid anhydride.

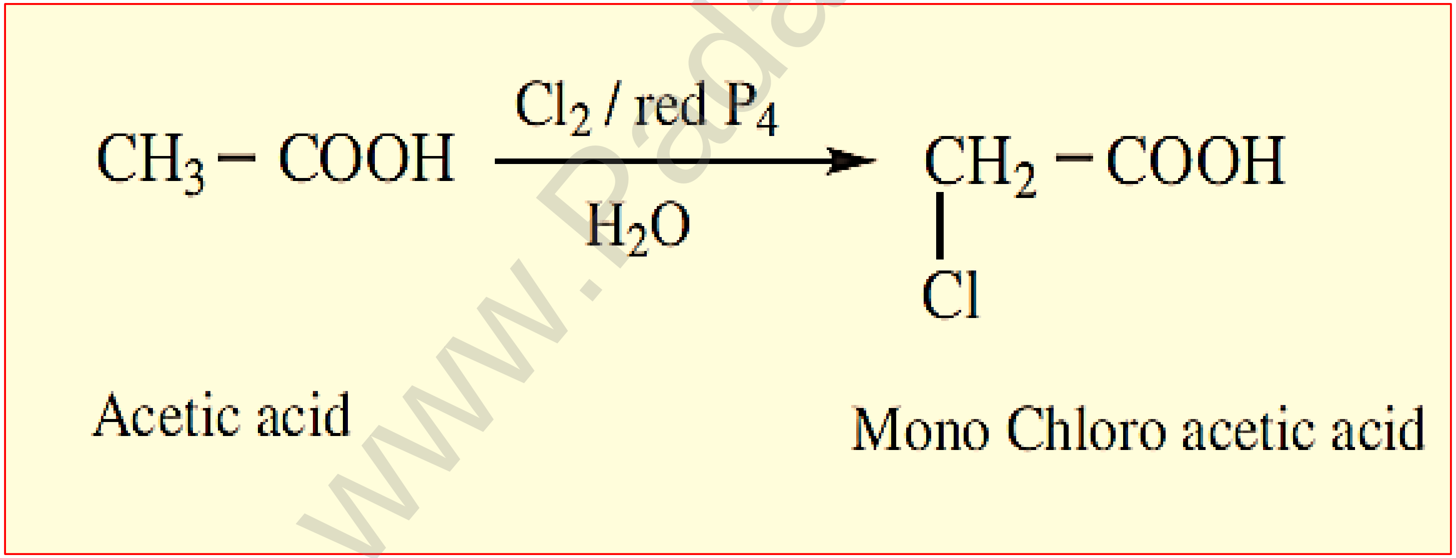


D) Substitution reactions in the hydrocarbon part

1) α - Halogenation

- Carboxylic acids having an ɑ - hydrogen are halogenated at the ɑ - position on treatment with chlorine or bromine in the presence of small amount of red posphorus to form ɑ halo carboxylic acids.

- This reaction is known as **Hell – Volhard – Zelinsky reaction (HVZ reaction)** The ɑ - Halogenated acids are convenient starting materials for preparing ɑ - substituted acids.

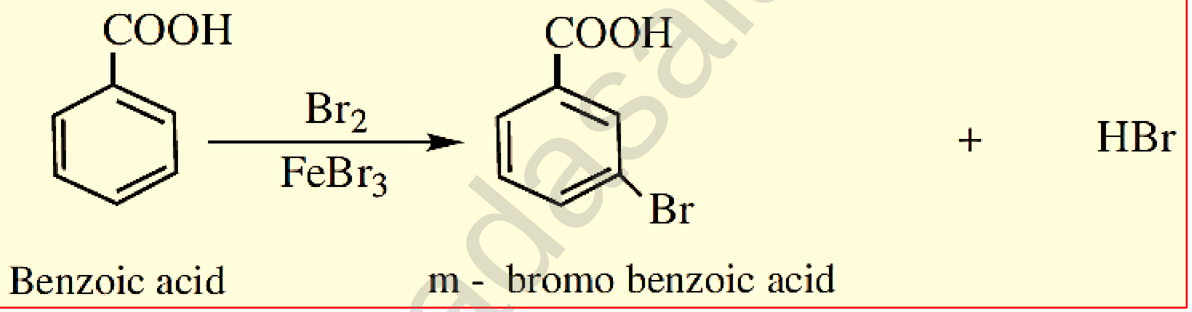


$$\underset{\text{Acetic acid}}{CH_3-COOH} \xrightarrow[H_2O]{Cl_2 / \text{red } P_4} \underset{\text{Mono Chloro acetic acid}}{\underset{\displaystyle Cl}{\underset{|}{CH_2}}-COOH}$$

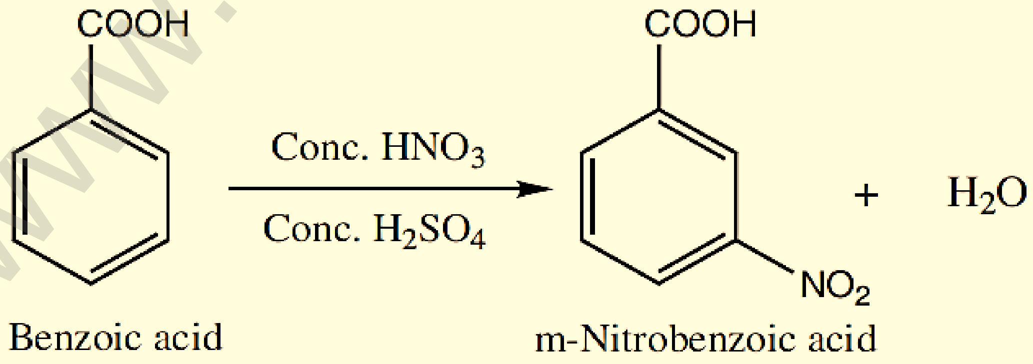
2) Electrophilic substitution in aromatic carboxylic acids

- Aromatic carboxylic acid undergoes electrophilic substitution reactions.
- The carboxyl group is a deactivating and meta directing group.
- Some common electrophilic substitution reactions of benzoic acid are given below

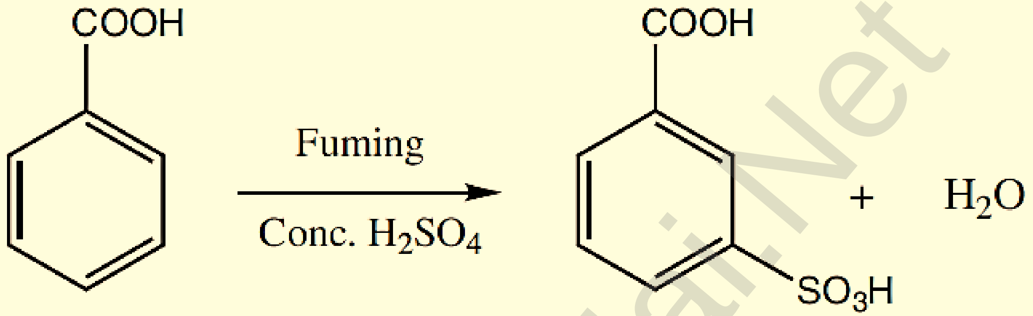
i) Halogenation



ii) Nitration



iii) Sulphonation



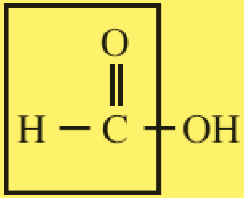
Benzoic acid m-Sulphobenzoic acid

iv) Benzoic acid does not undergo friedal craft's reaction.

This is due to the strong deactivating nature of the carboxyl group.

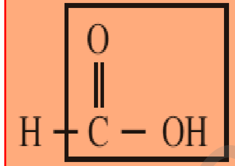
E) Reducing action of Formic acid

- Formic acid contains both an aldehyde as well as an acid group.
- Hence, like other aldehydes, formic acid can easily be oxidised and therefore acts as a strong reducing agent



$H-\overset{\overset{O}{\|}}{C}-OH$

Aldehyde group



$H-\overset{\overset{O}{\|}}{C}-OH$

Carboxylic acid group

i) Formic acid reduces Tollens reagent (ammonical silver nitrate solution) to metallic silver.

$$HCOO^- + 2Ag^+ + 3OH^- \longrightarrow 2\,Ag + CO_3^{2-} + 2H_2O$$

(Tollens reagent) Silver mirror

ii) Formic acid reduces Fehlings solution. It reduces blue coloured cupric ions to red coloured cuprous ions.

$$HCOO^- + 2Cu^{2+} + 5\,OH^- \longrightarrow Cu_2O + CO_3^{2-} + 3\,H_2O$$

(Fehlings solution) red precipitate

Tests for carboxylic acid group

i) In aqueous solution carboxylic acid turn blue litmus red.

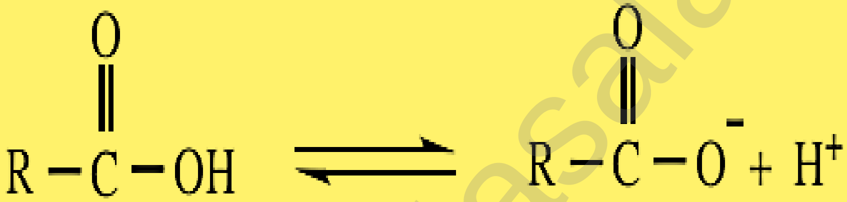
ii) Carboxylic acids give brisk effervescence with sodium bicarbonate due to the evolution of carbon-di -oxide.

iii) When carboxylic acid is warmed with alcohol and Con H_2SO_4 it forms an ester, which is detected by its fruity odour.

Acidity of Carboxylic acids

- Carboxylic acids undergo ionisation to produce H^+ and carboxylate ions $[COO^-]$ in aqueous solution.

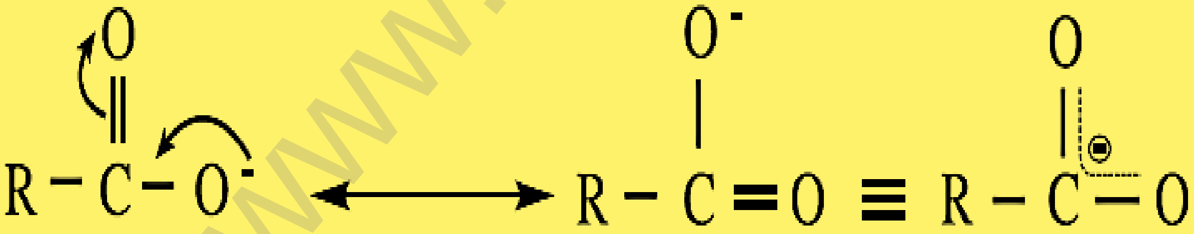
- The carboxylate anion is stabilised by resonance which make the Carboxylic acid to donate the proton easily.



$$R-\overset{O}{\overset{\|}{C}}-OH \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-O^- + H^+$$

Carboxylic acid Carboxylate ion

The resonance structure of carboxylate ion are given below.



$$R-\overset{O}{\overset{\|}{C}}-O^- \longleftrightarrow R-\overset{O^-}{\overset{|}{C}}=O \equiv R-\overset{O}{\overset{|}{C}}-O$$

The strength of carboxylic acid can be expressed in terms of the dissociation constant(Ka):

$$R-COOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

$$Ka = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

The dissociation constant is generally called acidity constant because it measures the relative strength of an acid. The stronger the acid, the higher will be its Ka value.

The dissociation constant of an acid can also be expressed in terms of pKa value.

$$pKa = -\log Ka$$

A stronger acid will have higher Ka value but smaller pKa value.

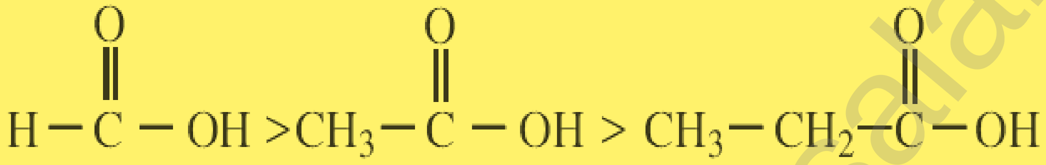
Ka and pKa values of some Carboxylic acids of 298 K

Carboxylic acid		pKa Value
Name of acid	**Molecular formula**	
Trichloroacetic acid	Cl_3CCOOH	0.64
Dichloroacetic acid	$Cl_2CHCOOH$	1.26
Fluoroacetic acid	FCH_2COOH	2.59
Chloroacetic acid	$ClCH_2COOH$	2.87
Bromoacetic acid	$BrCH_2COOH$	2.90
Iodoacetic acid	ICH_2COOH	3.17
Formic acid	$HCOOH$	3.75
Benzoic acid	C_6H_5COOH	4.20
Acetic acid	CH_3COOH	4.76
Propionic acid	CH_3CH_2COOH	4.88
o – nitrobenzoic acid	$o\text{-}NO_2C_6H_4COOH$	2.17
m-nitrobenzoic acid	$m\text{-}NO_2C_6H_4COOH$	3.49
p- nitrobenzoic acid	$p\text{-}NO_2C_6H_4COOH$	3.44

Effect of substituents on the acidity of carboxylic acid.

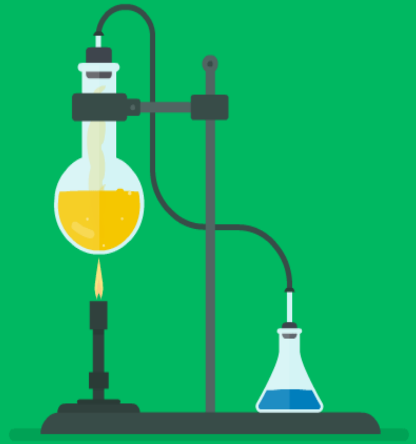
i) Electron releasing alkyl group decreases the acidity

The electron releasing groups (+I groups) increase the negative charge on the carboxylate ion and destabilise it and hence the loss of proton becomes difficult. For example, formic acid is more stronger than acetic acid.



$$H-\overset{\overset{O}{\|}}{C}-OH > CH_3-\overset{\overset{O}{\|}}{C}-OH > CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH$$

Formic acid Acetic acid Propionic acid



ii) Electron withdrawing substituents increases the acidity

The electron – withdrawing substituents decrease the negative charge on the carboxylate ion and stabilize it. In such cases, the loss of proton becomes relatively easy.

Acidity increases with increasing electronegativity of the substituents. For example, the acidity of various halo acetic acids follows the order

$$F-CH_2-COOH > Cl-CH_2-COOH > Br-CH_2-COOH > I-CH_2-COOH$$

Acidity increases with increasing number of electron – withdrawing substituents on the α - carbon. For example

$$Cl_3C-COOH > Cl_2CH-COOH > ClCH_2COOH > CH_3COOH$$

The effect of various, electron withdrawing groups on the acidity of a carboxylic acid follows the order,

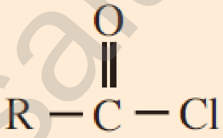
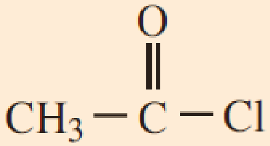
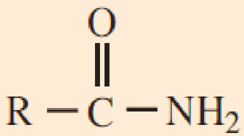
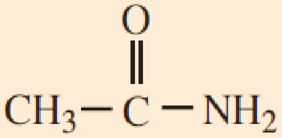
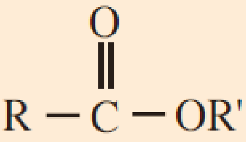
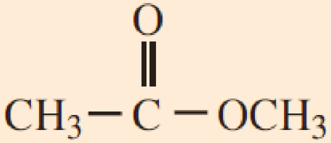
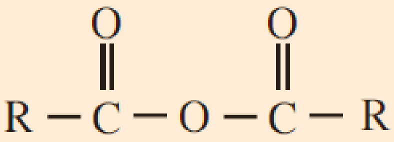
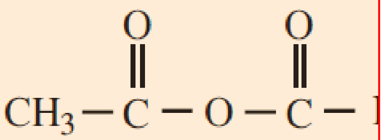
$$-NO_2 > -CN > -F > -Cl > -Br > -I > Ph$$

The relative acidities of various organic compounds are

$$RCOOH > ArOH > H_2O > ROH > RC\equiv CH$$

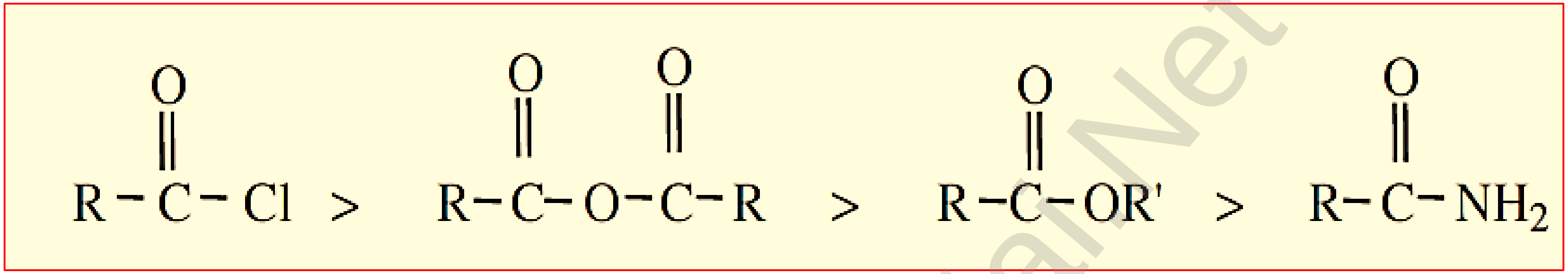
Functional derivatives of carboxylic acids

- Compounds such as acid chlorides, amides, esters etc., are called carboxylic acid derivatives because they differ from a carboxylic acid only in the nature of the group or atom that has replaced the -OH group of carboxylic acid.

Group replacing - OH	Name	Structure	Example
–Cl	Acid chloride	 $R-\overset{\overset{\displaystyle O}{\parallel}}{C}-Cl$	 $CH_3-\overset{\overset{\displaystyle O}{\parallel}}{C}-Cl$ Acetyl chloride
$-NH_2$	Acid amide	 $R-\overset{\overset{\displaystyle O}{\parallel}}{C}-NH_2$	 $CH_3-\overset{\overset{\displaystyle O}{\parallel}}{C}-NH_2$ Acetamide
–OR'	ester	 $R-\overset{\overset{\displaystyle O}{\parallel}}{C}-OR'$	 $CH_3-\overset{\overset{\displaystyle O}{\parallel}}{C}-OCH_3$ Methyl acetate
–OOCR	Acid anhydride	 $R-\overset{\overset{\displaystyle O}{\parallel}}{C}-O-\overset{\overset{\displaystyle O}{\parallel}}{C}-R$	 $CH_3-\overset{\overset{\displaystyle O}{\parallel}}{C}-O-\overset{\overset{\displaystyle O}{\parallel}}{C}-$ Acetic anhydride

Relative reactivity of Acid derivatives

- The reactivity of the acid derivatives follows the order



$$R-\overset{\overset{O}{\|}}{C}-Cl > R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R > R-\overset{\overset{O}{\|}}{C}-OR' > R-\overset{\overset{O}{\|}}{C}-NH_2$$

- The above order of reactivity can be explained in terms of
  - i) Basicity of the leaving group
  - ii) Resonance effect

Basicity of the leaving group

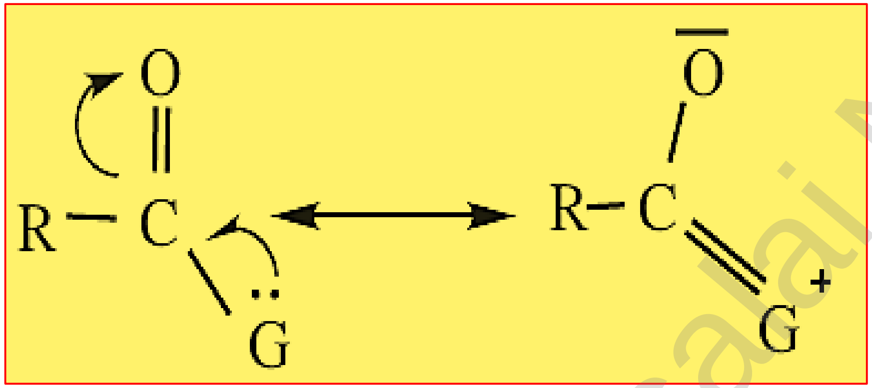
- Weaker bases are good leaving groups. Hence acyl derivatives with weaker bases as leaving groups (L) can easily rupture the bond and are more reactive. The correct order of the basicity of the leaving group is

$$H_2\bar{N}: > :\bar{O}R > RCO\bar{O}: > :\bar{Cl}$$

- Hence the reverse is the order of reactivity.

(ii) Resonance effect

- Lesser the electronegativity of the group, greater would be the resonance stabilization as shown below.



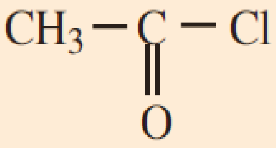
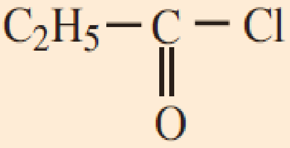
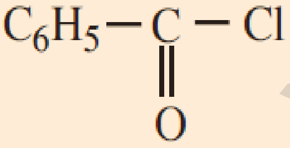
- This effect makes the molecule more stable and reduces the reactivity of the acyl compound.
- The order of electronegativity of the leaving groups follows the order

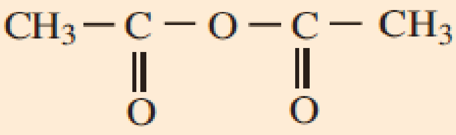
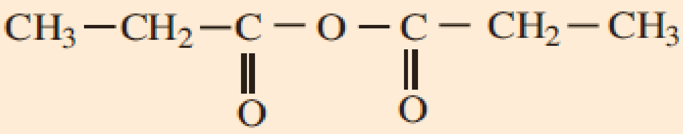
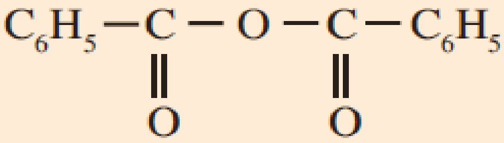
$$-Cl > -OCOR > -OR > -NH_2$$

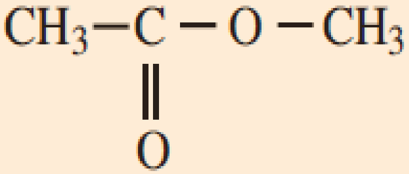
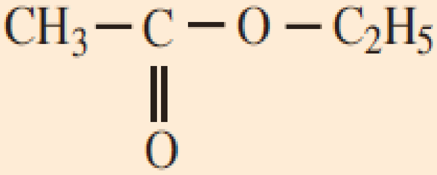
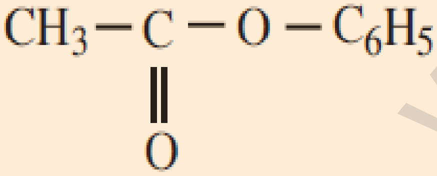
- Hence the order of reactivity of the acid derivatives with nucleophilic reagent follows the order

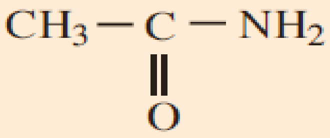
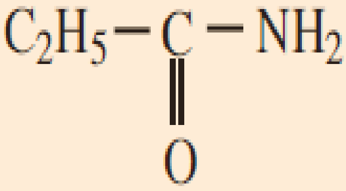
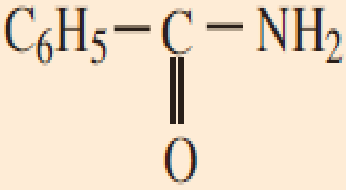
acid halide > acid anhydride > esters > acid amides

Nomenclature

Compound (common name, Structural formula, IUPAC Name)	IUPAC Name			
	Prefix with position number	Root used	Primary suffix	Secondary Suffix
Acetyl chloride  $CH_3-\underset{\underset{O}{\|}}{C}-Cl$ Ethanoylchloride	–	eth	an~~e~~	oyl chloride
Propionyl chloride  $C_2H_5-\underset{\underset{O}{\|}}{C}-Cl$ Propanoylchloride	–	prop	an~~e~~	oyl chloride
Benzoyl chloride  $C_6H_5-\underset{\underset{O}{\|}}{C}-Cl$ Benzoylchloride	–	Benz	an~~e~~	oyl chloride

Acetic anhydride  $CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_3$ Ethanoic anhydride	–	eth	an~~e~~	oic anhydride
Propionic anhydride  $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_2-CH_3$ Propanoic anhydride	–	prop	an~~e~~	oic anhydride
Benzoic anhydride  $C_6H_5-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-C_6H_5$ Benzoic anhydride	–	Benz		oic anhydride

Esters				
Methyl acetate  $CH_3-\underset{\underset{O}{\Vert}}{C}-O-CH_3$ Methyl ethanoate	Methyl	meth	an~~e~~	oate
Ethyl acetate  $CH_3-\underset{\underset{O}{\Vert}}{C}-O-C_2H_5$ Ethyl ethanoate	Ethyl	eth	an~~e~~	oate
Phenyl acetate  $CH_3-\underset{\underset{O}{\Vert}}{C}-O-C_6H_5$ Phenyl ethanoate	Phenyl	eth	an~~e~~	oate

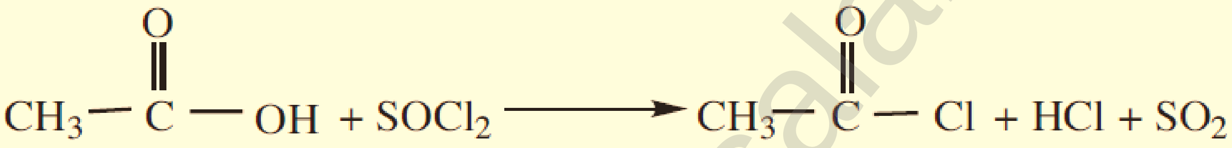
Acid Amides				
Acetamide  $CH_3-\underset{\underset{O}{\Vert}}{C}-NH_2$ Ethanamide	–	eth	an~~e~~	amide
Propionamide  $C_2H_5-\underset{\underset{O}{\Vert}}{C}-NH_2$ Propanamide	–	prop	an~~e~~	amide
Benzamide  $C_6H_5-\underset{\underset{O}{\Vert}}{C}-NH_2$ Benzamide	–	benz	_	amide

Acid Halides:

Methods of Preparation of acid chloride:

Acid chlorides are prepared from carboxylic acid by treating it with anyone of the chlorinating agent such as $SOCl_2$, PCl_5, or PCl_3

1) By reaction with thionyl Chloride ($SOCl_2$)



$$CH_3-\overset{O}{\overset{\|}{C}}-OH + SOCl_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + HCl + SO_2$$

Acetic acid Acetyl chloride

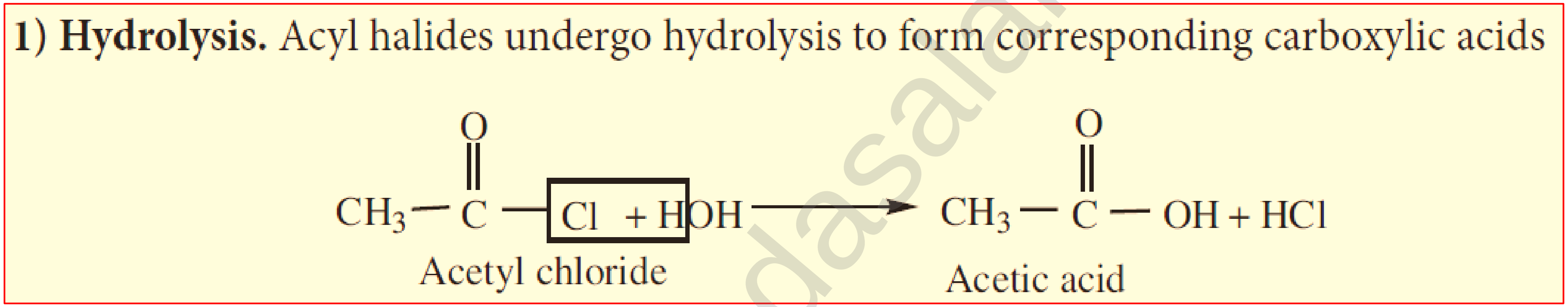
This method is superior to others as the by products being gases escape leaving the acid chloride in the pure state.

Physical properties:

- They emit pale fumes of hydrogen chloride when exposed to air on account of their reaction with water vapour.
- They are insoluble in water but slowly begins to dissolve due to hydrolysis.

Chemical properties:

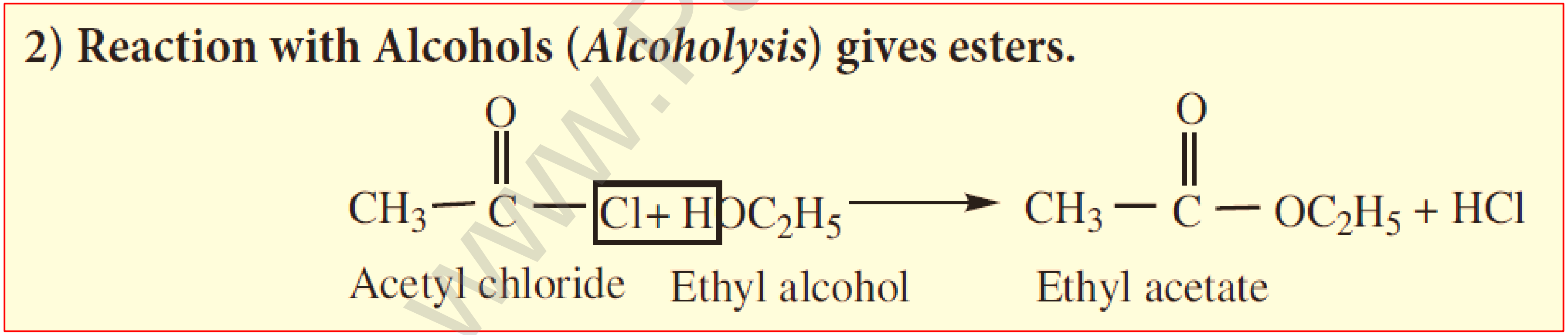
- They react with weak nucleophiles such as water, alcohols, ammonia and amines to produce the corresponding acid, ester, amide or substituted amides.



1) Hydrolysis. Acyl halides undergo hydrolysis to form corresponding carboxylic acids

$$CH_3-\overset{\overset{O}{\|}}{C}-\boxed{Cl\ +H}OH \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OH + HCl$$

Acetyl chloride Acetic acid

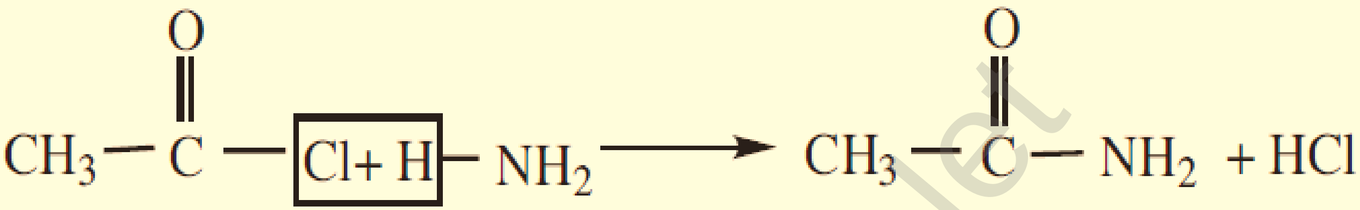


2) Reaction with Alcohols (*Alcoholysis*) gives esters.

$$CH_3-\overset{\overset{O}{\|}}{C}-\boxed{Cl+H}OC_2H_5 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + HCl$$

Acetyl chloride Ethyl alcohol Ethyl acetate

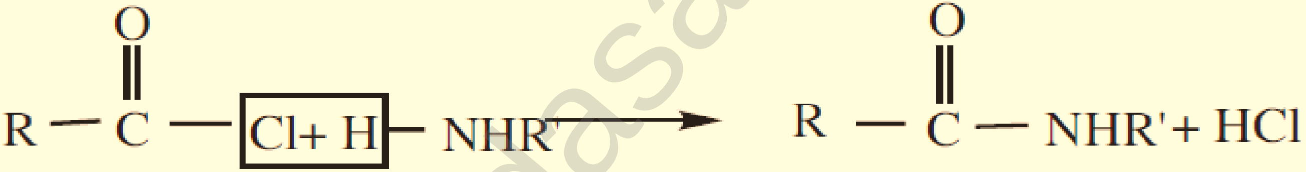
3) Reaction with Ammonia (*Ammonolysis*) gives acid amides.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\boxed{Cl+H}-NH_2 \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2 + HCl$$

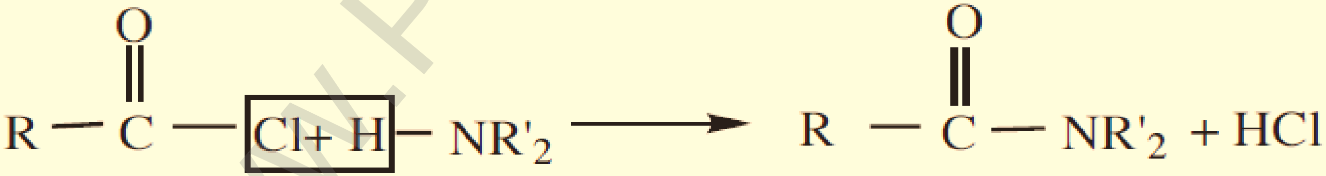
Acetyl chloride Ammonia Acetamide

4) Reaction with 1° and 2° Amines gives N-alkyl amides.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\boxed{Cl+H}-NHR' \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-NHR' + HCl$$

1° amine N-alkylamide

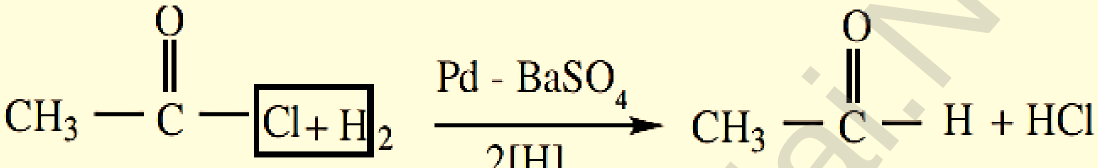


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-\boxed{Cl+H}-NR'_2 \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-NR'_2 + HCl$$

2° amine N,N-dialkylamide

(5) Reduction.

(a) When reduced with hydrogen in the presence of 'poisoned' palladium catalyst, they form aldehydes. This reaction is called Rosenmund reduction. We have already learnt this reaction under the preparation of aldehydes



$$CH_3-\overset{\overset{O}{\|}}{C}-\boxed{Cl + H}_2 \xrightarrow[2[H]]{Pd - BaSO_4} CH_3-\overset{\overset{O}{\|}}{C}-H + HCl$$

Acetyl chloride Acetaldehyde

(b) When reduced with $LiAlH_4$ gives primary alcohols.

$$CH_3-\overset{\overset{O}{\|}}{C}-Cl + 4(H) \xrightarrow{LiAlH_4} CH_3-CH_2-OH + HCl$$

Ethyl alcohol

Acid anhydride

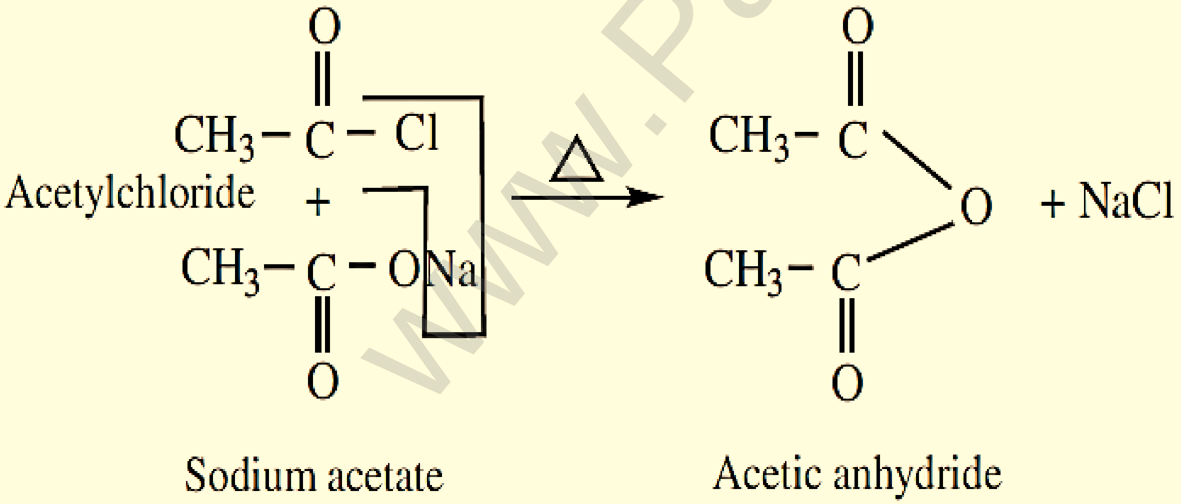
Methods of preparation

1. Heating carboxylic acid with P_2O_5

We have already learnt that when carboxylic acids are heated with P_2O_5 dehydration takes place to form acid anhydride.

2. By reaction of acid halide with a salt of carboxylic acids.

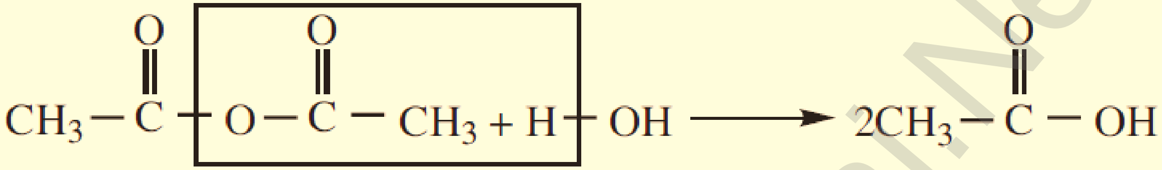
Acid chlorides on heating with sodium salt of carboxylic acids gives corresponding anhydride.



Chemical properties

1. Hydrolysis

Acid anhydride are slowly hydrolysed, by water to form corresponding carboxylic acids.

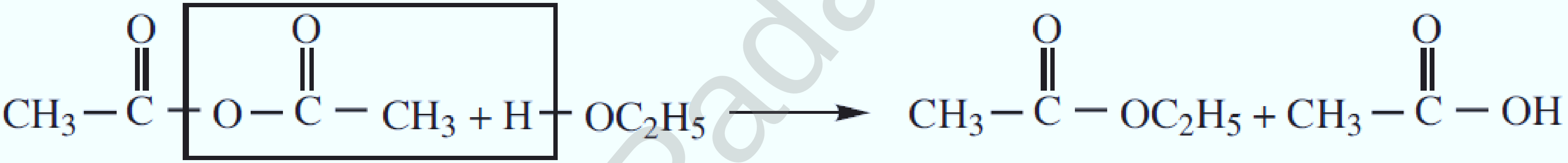


$$CH_3-\overset{O}{\overset{\|}{C}}\boxed{-O-\overset{O}{\overset{\|}{C}}-CH_3+H}-OH \longrightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Acetic anhydride Acetic acid

2. Reaction with alcohol

Acid anhydride reacts with alcohols to form esters.

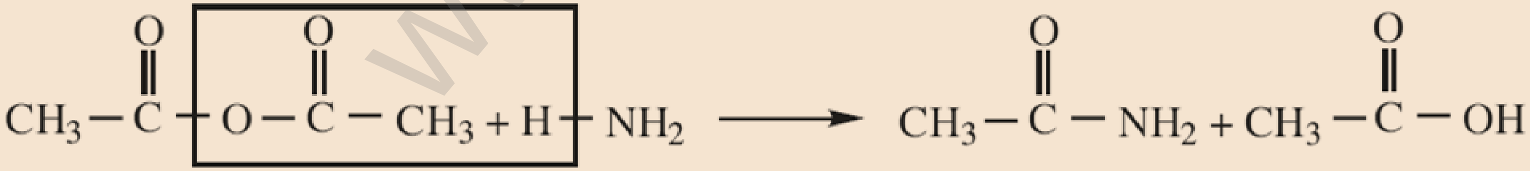


$$CH_3-\overset{O}{\overset{\|}{C}}\boxed{-O-\overset{O}{\overset{\|}{C}}-CH_3+H}-OC_2H_5 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5+CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Acetic anhydride Ethylalcohol Ethyl acetate Acetic acid

3. Reaction with ammonia

Acid anhydride reacts with ammonia to form amides.

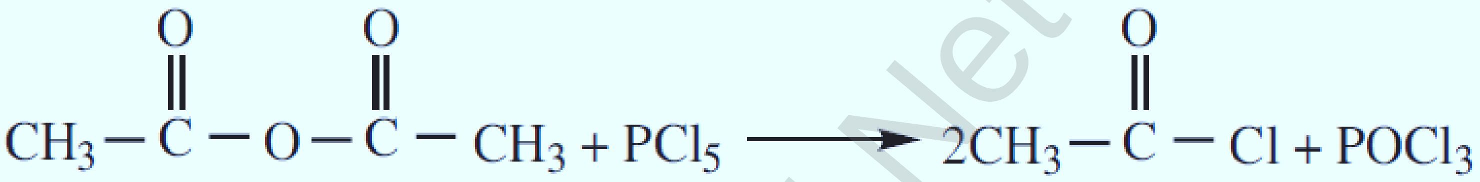


$$CH_3-\overset{O}{\overset{\|}{C}}\boxed{-O-\overset{O}{\overset{\|}{C}}-CH_3+H}-NH_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2+CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Acetic anhydride Ammonia Acetamide Acetic acid

4. Reaction with PCl_5

Acid anhydride reacts with PCl_5 to form acyl chlorides.



$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + PCl_5 \longrightarrow 2CH_3-\overset{O}{\overset{\|}{C}}-Cl + POCl_3$$

Acetic anhydride

Acetyl chloride

Esters

Methods of preparation

1. Esterification

- We have already learnt that treatment of alcohols with carboxylic acids in presence of mineral acid gives esters. The reaction is carried to completion by using an excess of reactant or by removing the water from the reaction mixture.

2. Alcoholysis of Acid chloride or Acid anhydrides

- Treatment of acid chloride or acid anhydride with alcohol also gives esters

Physical Properties

- Esters are colourless liquids or solids with characteristic fruity smell.
- Flavours of some of the esters are given below.

S.No	Ester	Flavour
1	Amyl acetate	Banana
2	Ethyl butyrate	Pineapple
3	Octyl acetate	Orange
4	Isobutyl formate	Raspberry
5	Amyl butyrate	Apricot

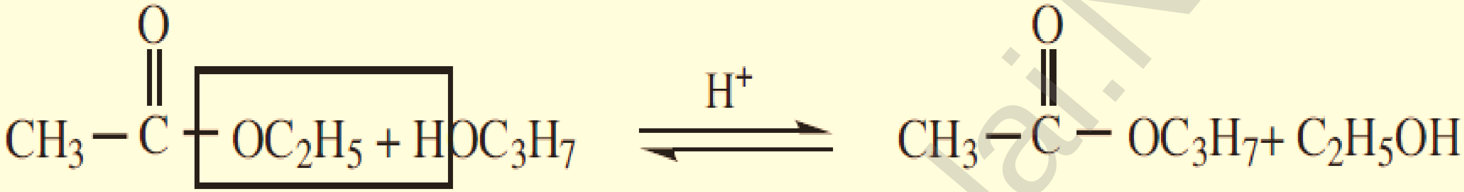
Chemical Properties

1. Hydrolysis

➢ We have already learnt that hydrolysis of esters gives alcohol and carboxylic acid.

2. Reaction with alcohol (Transesterification)

Esters of an alcohol can react with another alcohol in the presence of a mineral acid to give the ester of second alcohol. The interchange of alcohol portions of the esters is termed **transesterification**



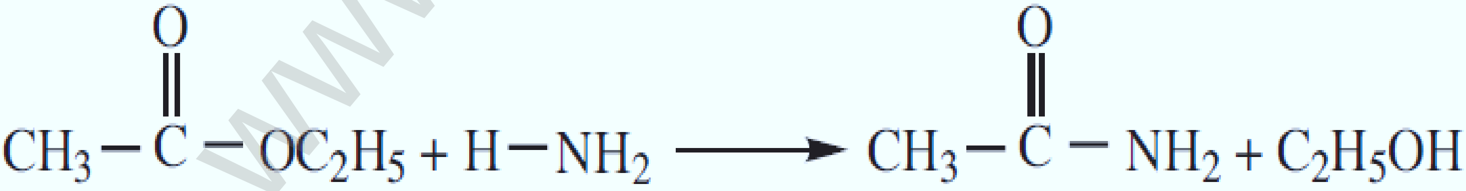
$$CH_3-\overset{\overset{O}{\|}}{C}\boxed{-OC_2H_5+H}OC_3H_7 \xrightleftharpoons{H^+} CH_3-\overset{\overset{O}{\|}}{C}-OC_3H_7+C_2H_5OH$$

Ethyl acetate　Propyl alcohol　Propyl acetate　Ethyl alcohol

The reaction is generally used for the preparation of the esters of a higher alcohol from that of a lower alcohol.

3. Reaction with ammonia (Ammonolysis)

Esters react slowly with ammonia to form amides and alcohol.

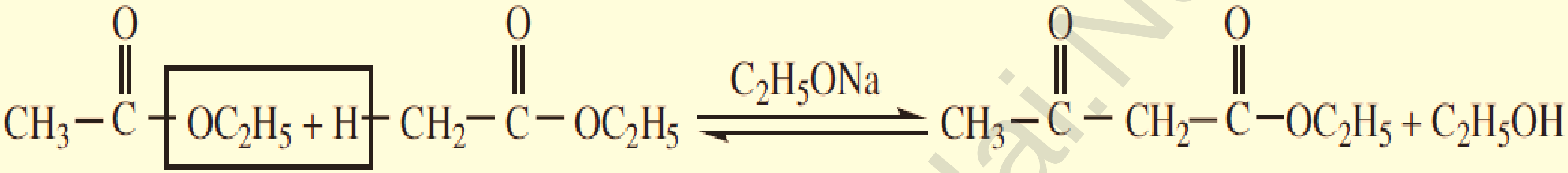


$$CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5+H-NH_2 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-NH_2+C_2H_5OH$$

Ethyl acetate　Acetamide　Ethyl alcohol

4. Claisen Condensation

Esters containing at least one ∝- hydrogen atom undergo self condensation in the presence of a strong base such as sodium ethoxide to form **β- keto ester.**

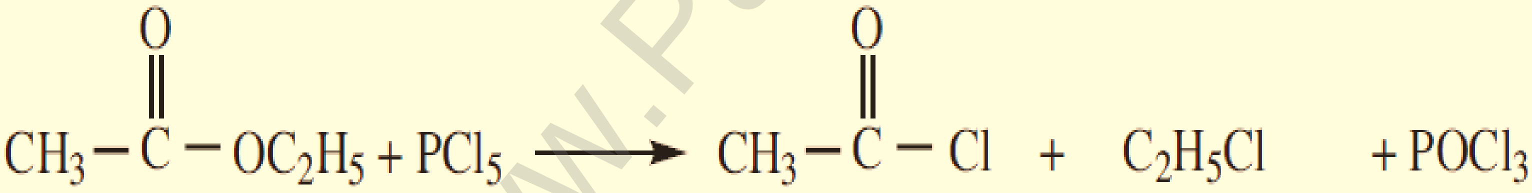


$$CH_3-\overset{\overset{O}{\|}}{C}-\boxed{OC_2H_5 + H}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5 \xrightleftharpoons{C_2H_5ONa} CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5 + C_2H_5OH$$

Ethyl acetate Ethyl acetate Ethyl aceto acetate Ethyl alcohol

5. Reaction with PCl_5

Esters react with PCl_5 to give a mixture of acyl and alkyl chloride

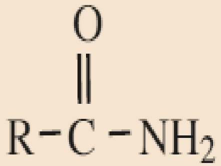


$$CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + PCl_5 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-Cl + C_2H_5Cl + POCl_3$$

Ethyl acetate Acetyl chloride Ethyl chloride

Acid Amides

Acid amides are derivatives of carboxylic acid in which the – OH part of carboxyl group has been replaced by – NH_2 group. The general formula of amides are given as follows.



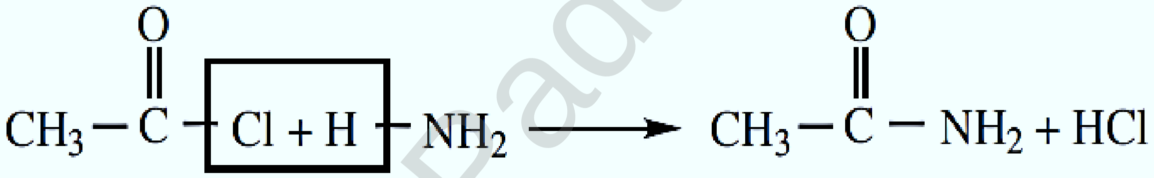
$R-\overset{O}{\overset{\|}{C}}-NH_2$

Now, we shall focus our attention mainly on the study of chemistry of acetamide.

Methods of Preparation

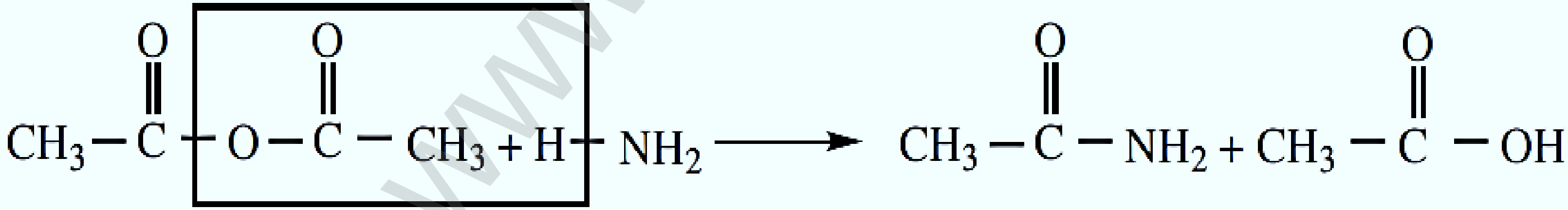
1. Ammonolysis of acid derivatives

Acid amides are prepared by the action of ammonia with acid chlorides or acid anhydrides.



$$CH_3-\overset{O}{\overset{\|}{C}}-\boxed{Cl+H}-NH_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2+HCl$$

Acetyl chloride Acetamide

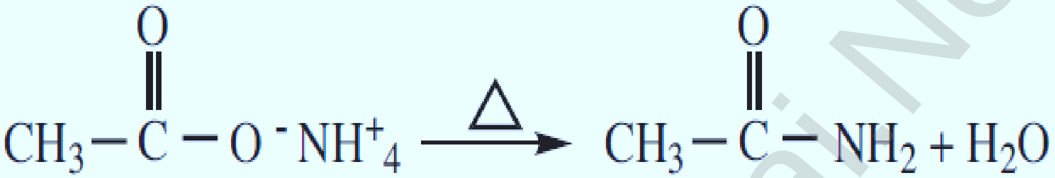


$$CH_3-\overset{O}{\overset{\|}{C}}-\boxed{O-\overset{O}{\overset{\|}{C}}-CH_3+H}-NH_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-NH_2+CH_3-\overset{O}{\overset{\|}{C}}-OH$$

Acetic anhydride Acetamide

2) Heating ammonium carboxylates

Ammonium salts of carboxylic acids (ammonium carboxylates) on heating, lose a molecule of water to form amides.

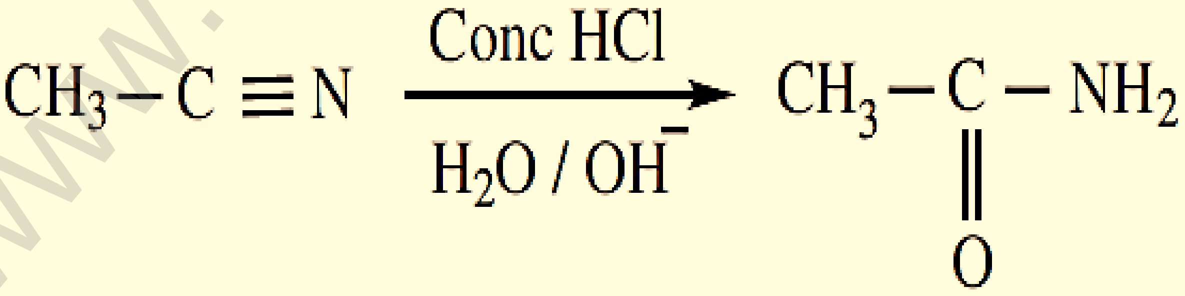


$$CH_3-\overset{\overset{O}{\|}}{C}-O^{-}NH^{+}_4 \xrightarrow{\Delta} CH_3-\overset{\overset{O}{\|}}{C}-NH_2+H_2O$$

Ammonium acetate Acetamide

3) Partial hydrolysis of alkyl cyanides (Nitriles)

Partial hydrolysis of alkyl cyanides with cold con HCl gives amides



$$CH_3-C\equiv N \xrightarrow[H_2O\,/\,OH^{-}]{\text{Conc HCl}} CH_3-\underset{\underset{O}{\|}}{C}-NH_2$$

Methyl cyanide Acetamide

Chemical Properties

1. Amphoteric character

Amides behave both as weak acid as well as weak base and thus show amphoteric character. This can be proved by the following reactions.

Acetamide (as base) reacts with hydrochloric acid to form salt

$$CH_3-\overset{\overset{O}{\parallel}}{C}-NH_2 + HCl \longrightarrow CH_3-\overset{\overset{O}{\parallel}}{C}-\overset{+}{N}H_3\,Cl^-$$

Acetamide Acetamide hydrochloride

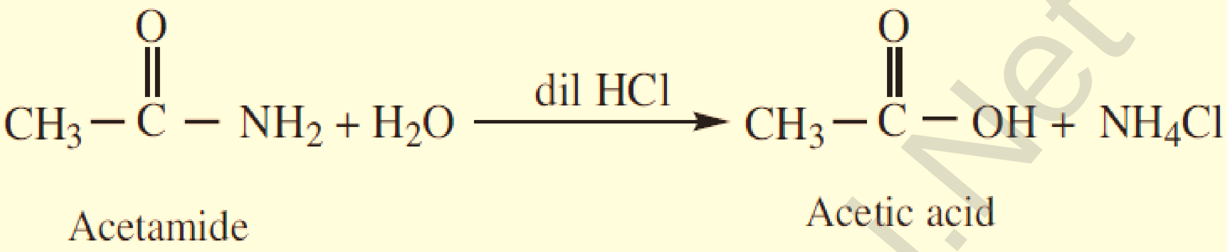
Acetamide (as acid) reacts with sodium to form sodium salt and hydrogen gas is liberated.

$$2CH_3-\overset{\overset{O}{\parallel}}{C}-NH_2 + 2Na \longrightarrow 2CH_3-\overset{\overset{O}{\parallel}}{C}-NHNa + H_2$$

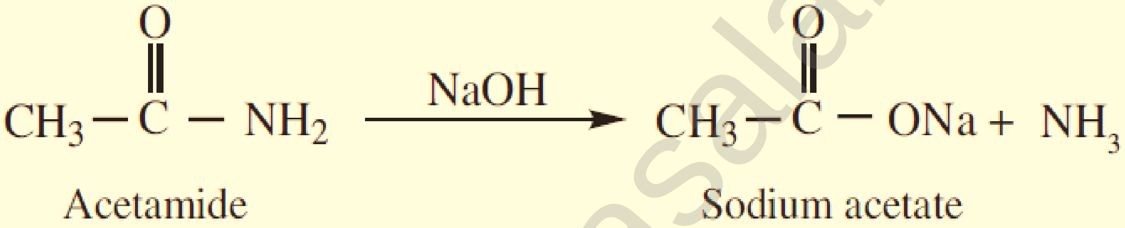
Acetamide Sodium acetamide

2) Hydrolysis

Amides can be hydrolysed in acid or in alkaline solution on prolonged heating



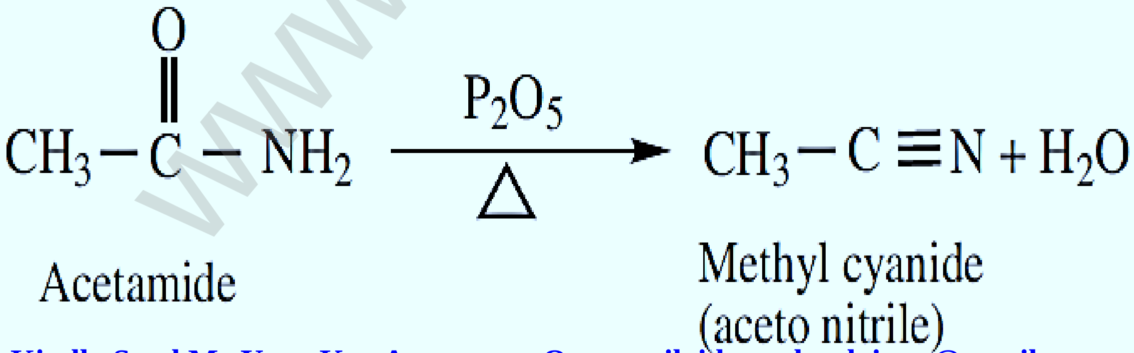
$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2 + H_2O \xrightarrow{\text{dil HCl}} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-OH + NH_4Cl$$



$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2 \xrightarrow{\text{NaOH}} CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-ONa + NH_3$$

3) Dehydration

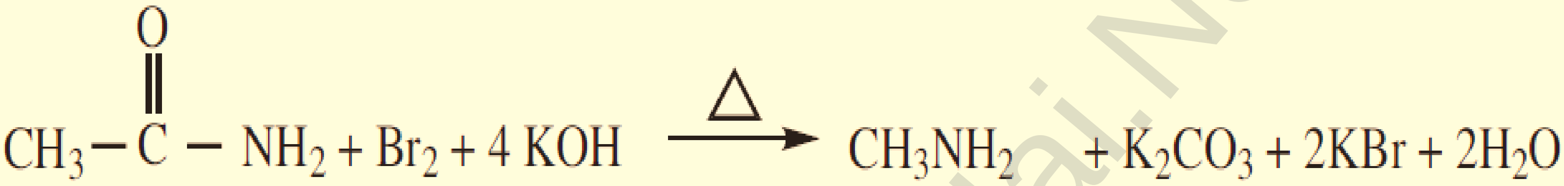
Amides on heating with strong dehydrating agents like P_2O_5 get dehydrated to form cyanides.



$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-NH_2 \xrightarrow[\Delta]{P_2O_5} CH_3-C\equiv N + H_2O$$

4) Hoff mann's degradation

Amides reacts with bromine in the presence of caustic alkali to form a primary amine carrying one carbon less than the parent amide.



$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + Br_2 + 4\,KOH \xrightarrow{\Delta} CH_3NH_2 + K_2CO_3 + 2KBr + 2H_2O$$

Acetamide Methyl amine

5) Reduction

Amides on reduction with $LiAlH_4$ or Sodium and ethyl alcohol to form corresponding amines.

$$CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + 4\,(H) \xrightarrow{LiAlH_4} CH_3-CH_2-NH_2 + H_2O$$

Acetamide Ethyl amine

Uses of carboxylic acids and its derivatives

Formic acid

It is used

i) for the dehydration of hides.

ii) as a coagulating agent for rubber latex

iii) in medicine for treatment of gout

iv) as an antiseptic in the preservation of fruit juice.

Acetic acid

It is used

i) as table vinegar

ii) for coagulating rubber latex

iii) for manufacture of cellulose acetate and poly vinylacetate

Benzoic acid

It is used

i) as food preservative either in the pure form or in the form of sodium benzoate

ii) in medicine as an urinary antiseptic

iii) for manufacture of dyes

Acetyl Chloride

It is used

i) as acetylating agent in organic synthesis

ii) in detection and estimation of – OH, - NH_2 groups in organic compounds

Acetic anhydride

It is used

i) acetylating agent

ii) in the preparation of medicine like asprin and phenacetin

iii) for the manufacture plastics like cellulose acetate and poly vinyl acetate.

Ethyl acetate is used

i) in the preparation of artificial fruit essences.

ii) as a solvent for lacquers.

iii) in the preparation of organic synthetic reagent like ethyl acetoacetate.

UTHRAKUMAR B

PGT CHEMISTRY

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