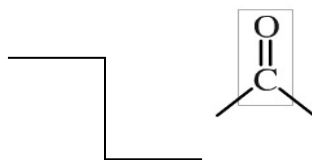## ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

1.Carbonyl group-structure and properties

Carbonyl functional group

usually subdivided into two families :

• aldehydes and ketones • both R groups are C or H	• carboxylic acid & its derivatives • X is some electronegative element (halogen, O, N, S, others)

The Carbonyl Group - Structure and Properties

The carbonyl carbon is sp² hybridized and thus has three sp² hybrid orbitals and one unhybridized p-orbital.	• polar C=O double bond
	• O is nucleophilic
	  reacts with acids & electrophiles
	• C is electrophilic
	  reacts with Lewis bases and nucleophiles
	• alpha-C-H position is acidic (pKa ~ 20)
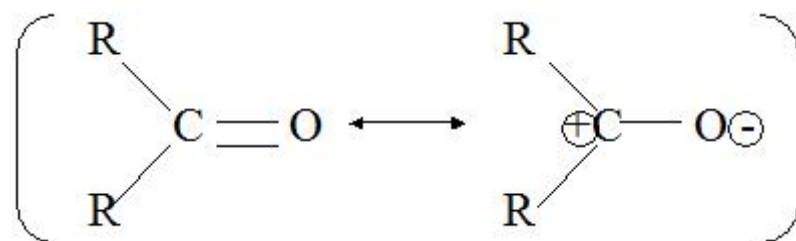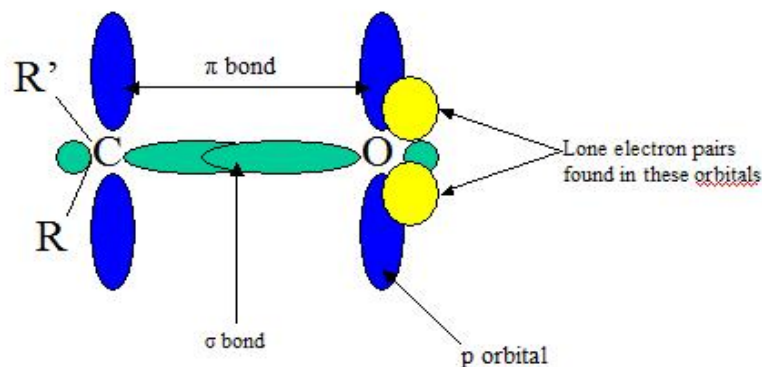
Sigma-pi bond representation of carbonyl group
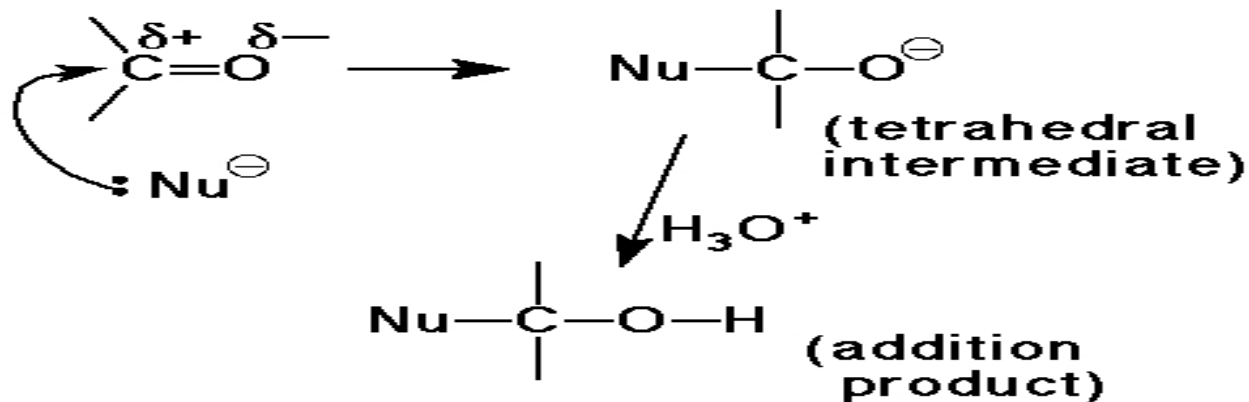
Some Carbonyl Compounds

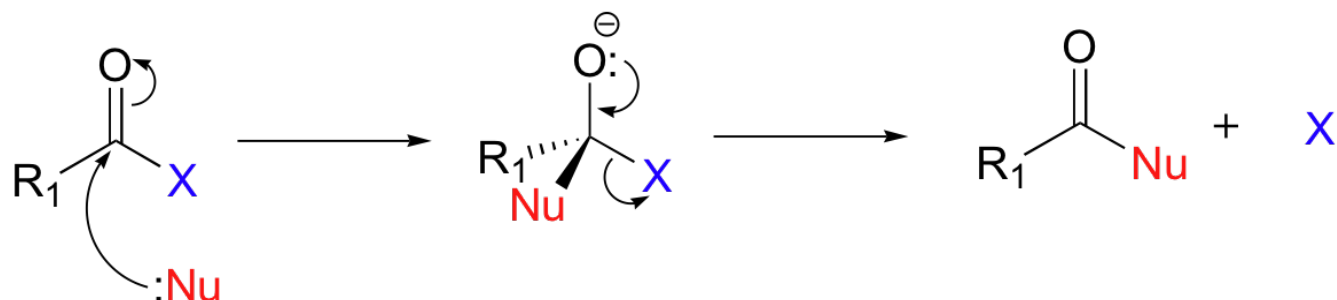| Compound	Aldehyde	Ketone	Formaldehyde	Carboxylic Acid	Ester	Amide	Enone	Acyl Halide	Acid Anhydride
Structure									
General Formula	RCHO	RCOR'	CH2O	RCOOH	RCOOR'	RCONR'R''	RC(O)C(R')CR''R'''	RCOX	(RCO)2O

Nucleophile reactions of Carbonyl Group

| Nucleophilic addition	Nucleophilic substitution
Given by aldehyde & ketones	Given by carboxylic acid & its derivatives

1.Nucleophilic Addition of Carbonyl compounds :

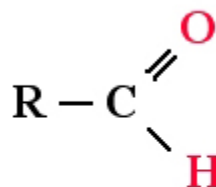**Nucleophilic substitution of Carbonyl group :**

Note : The term carbonyl compounds is used for aldehyde & ketones. And rest of the compounds which have carbonyl functional group are termed as *acid & acid derivatives.*

Aldehyde & ketones
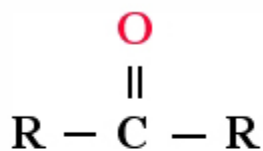
It is also important to know here that aldehydes are more reactive than ketones towards nucleophilic reactions. This is because of the folowing two reasons :

(i) Aldehydes have only one alkyl group whereas ketones have two. Since the alkyl groups are electron donating in nature, the carbonyl carbon in ketones which is bonded to two alkyl groups, is less positve (electrophilc) as compared to the aldehydic carbonyl carbon. Hence, it is less susceptible to atack by nucleophiles.

(ii) The two alkyl groups in ketones also make the carbonyl carbon more crowded as compared to carbonyl carbon in aldehydes. This factor also makes the aldehydic carbonyl carbon more acesible for atack by the nucleophiles as compared to carbonyl carbon of the ketone.

General Trends:

- aldehydes more reactive than ketones
  (due to steric hindrance with ketones)
- aromatic carbonyls less reactive than aliphatic
  (due to conjugation effects)
- a large variety of nucleophiles can undergo addition reactions

C nucleophiles: CN-, RLi, RMgX

O nucleophiles: OH-, H_2O, ROH

S nucleophiles: RSH

N nucleophiles: NH_3, RNH_2 , NH_2OH, $RNHNH_2$

H nucleophiles: $LiAlH_4$, $NaBH_4$

IUPAC Nomenclature of Aldehydes:

1. Number the longest chain starting from carbon of aldehyde group.
2. Name the compound by changing -e to -al (e.g. ethane to ethanal)

4-bromo-3-methylheptanal

ethanal
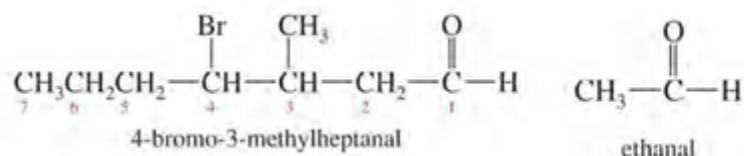
Note : If the -CHO group is attached to a ring, then the compound is called as carbaldehyde.

2-hydroxycyclopentane-1-carbaldehyde

4-Nitrobenzenecarbaldehyde
or
4-Nitrobenzaldehyde
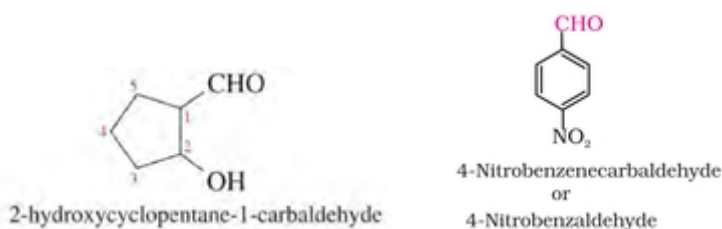
IUPAC Nomenclature of ketones:

1. Number the longest chain from the end nearest to the carbonyl group.
2. Name the compound by changing -e to -one (e.g. ethane to ethanone)

2-cyclohexenone
cyclohex-2-en-1-one

2,4-dimethyl-3-pentanone
2,4-dimethylpentan-3-one

1-phenyl-1-propanone
1-phenylpropan-1-one
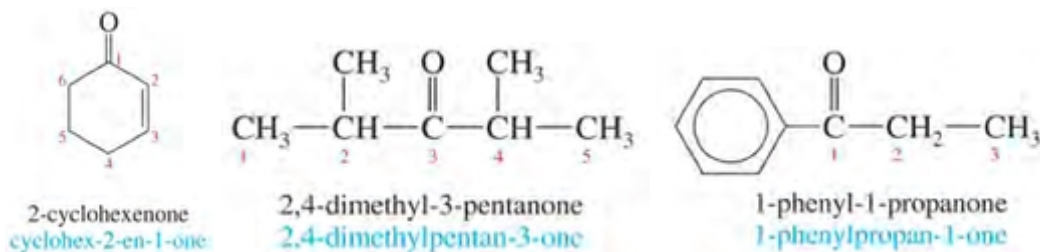
2.Preparation of aldehyde and ketones
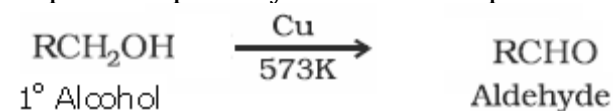## 1.Preparation of Aldehydes:

1.By oxidation of alcohols:

Oxidation of primary alcohols in the presence of an oxidising agent such as , $K_2Cr_2O_7$ /H_2SO_4 $KMnO_4$,CrO_3 gives aldehydes.

$$RCH_2OH \xrightarrow{\text{Oxidation}} R-\overset{\overset{\displaystyle H}{|}}{C}=O$$

1° Alcohol

Aldehyde

2.By dehydrogenation of alcohols:

Vapours of primary alcohol when passed over heated copper at 573 K form aldehyde.

$$RCH_2OH \xrightarrow[573K]{Cu} RCHO$$

1° Alcohol

Aldehyde

3.By hydration of alkynes:

Ethyne on hydration with $HgSO_4$ / dil H_2SO4 at 333 K forms acetaldehyde

$$HC\equiv CH + H-OH \xrightarrow[333K]{Hg^{2+}/H^+} CH_2=\underset{\underset{\displaystyle OH}{|}}{C}-H$$

Ethyne

$$\downarrow \text{Isomerisation}$$

$$CH_3 - \underset{\underset{\displaystyle O}{\|}}{C} - H$$

Ethanal
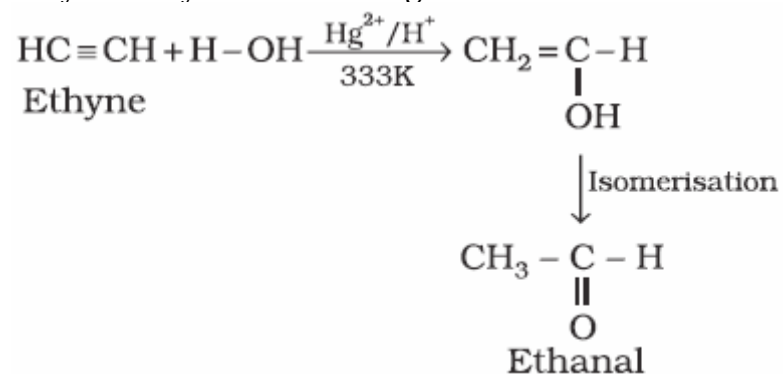
4. From acyl chloride (Rosenmund reduction) :

Benzoyl chloride → Benzaldehyde

H_2 / Pd – $BaSO_4$
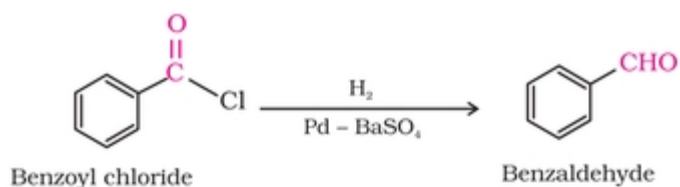
5. From nitriles:

(I) Stephen reaction :

$$RCN + SnCl_2 + HCl \longrightarrow RCH = NH \xrightarrow{H_3\overset{+}{O}} RCHO$$

(II) reduction of nitrile by diisobutylaluminium hydride (AlH(i-Bu)2) and (DIBAL-H) to imine followed by hydrolysis:

$$CH_3 - CH{=}CH\text{-}CH_2CH_2\text{-}CN \xrightarrow[\text{2. } H_2O]{\text{1. AlH(i-Bu)}_2} CH_3 - CH{=}CH\text{-}CH_2CH_2\text{-}CHO$$

$$CH_3(CH_2)_9 - \overset{O}{\overset{\|}{C}} - OC_2H_5 \xrightarrow[\text{2. } H_2O]{\text{1. DIBAL-H}} CH_3(CH_2)_9 - \overset{O}{\overset{\|}{C}} - H$$
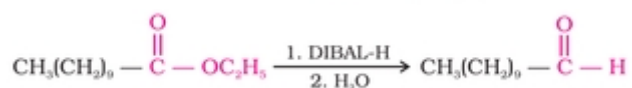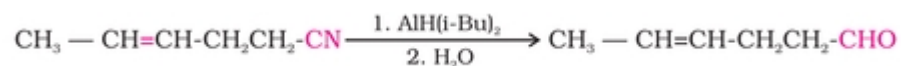
6. From aromatic hydrocarbons to aromatic aldehydes:
(I) By oxidation of methylbenzene:

(a) Using chromyl chloride (CrO2Cl2) (Etard reaction):

Toluene + CrO_2Cl_2 $\xrightarrow{CS_2}$ Chromium complex $CH(OCrOHCl_2)_2$ $\xrightarrow{H_3O^+}$ Benzaldehyde CHO

(b) Using chromic oxide (CrO3):

Toluene + CrO_3 + $(CH_3CO)_2O$ $\xrightarrow{\text{273-283K}}$ $CH(OCOCH_3)_2$ $\xrightarrow[\Delta]{H_3O^+}$ Benzaldehyde CHO

(II) Chlorination followed by hydrolysis:

Toluene $\xrightarrow{Cl_2/h\upsilon}$ Benzal chloride $CHCl_2$ $\xrightarrow[\text{373 K}]{H_2O}$ Benzaldehyde CHO
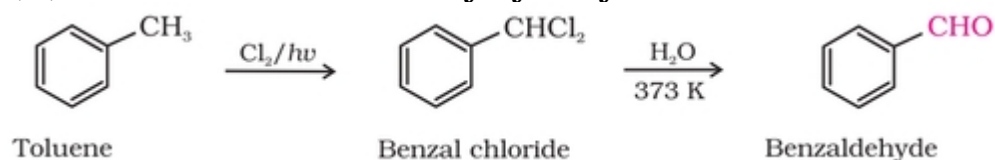
(III) by Gatterman - Koch reaction:

Benzene → Benzaldehyde

$$\text{Benzene} \xrightarrow[\text{Anhyd. AlCl}_3/\text{CuCl}]{\text{CO, HCl}} \text{Benzaldehyde (CHO)}$$
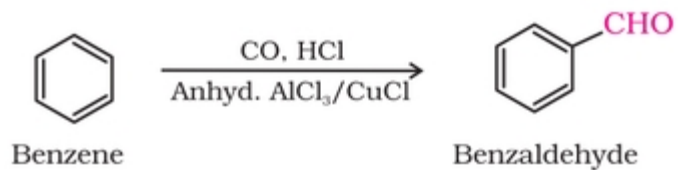
2.Preparation of Ketones:

1.By oxidation of alcohols

Oxidation of secondary alcohols in the presence of an oxidising agents gives ketones.

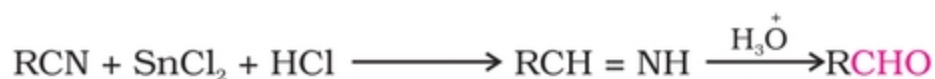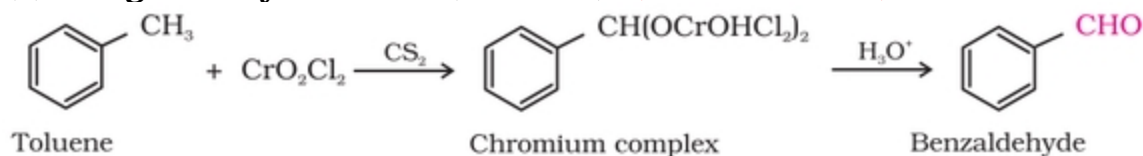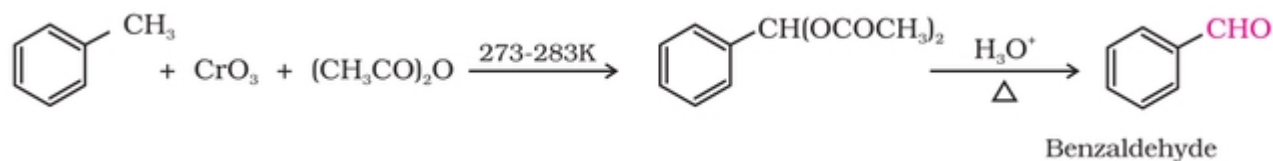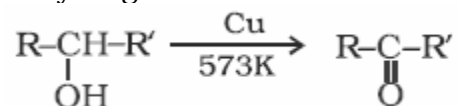$$\underset{\text{2° Alcohol}}{\overset{R'}{\underset{|}{R-C-OH}}} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{\text{Oxidation}} \underset{\text{Ketone}}{\overset{R'}{\underset{|}{R-C=O}}}$$
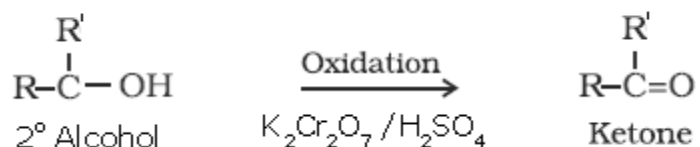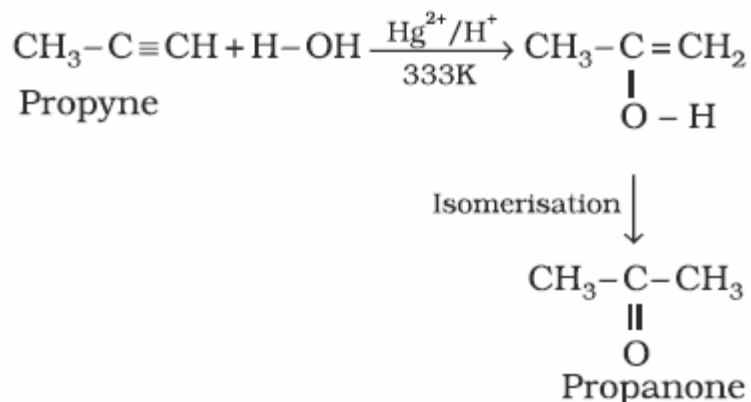
2.By dehydrogenation of alcohols

When the vapours of a secondary alcohol are passed over heated copper at 573 K, dehydrogenation occurs and a ketone is formed.
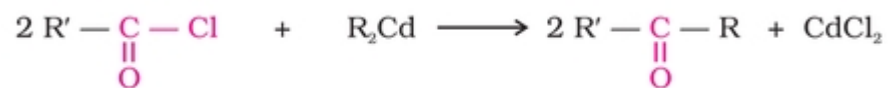
$$\underset{\overset{|}{OH}}{R-CH-R'} \xrightarrow[573K]{Cu} \underset{\overset{\|}{O}}{R-C-R'}$$

3.By hydration of alkynes

Hydration of alkynes other than acetylene yields ketone. Example: Propyne on hydration with $HgSO_4$ / dil H_2 SO4 at 333 K forms propanone.

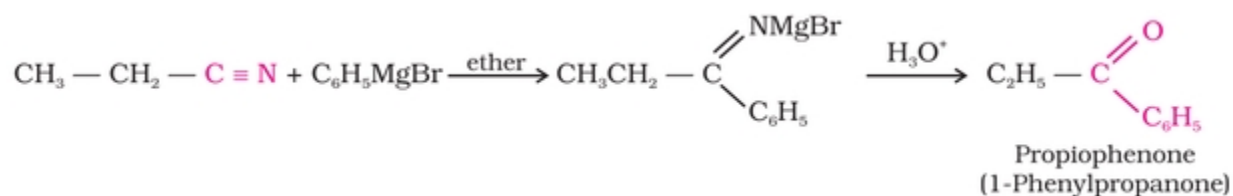$$\underset{\text{Propyne}}{CH_3-C\equiv CH} + H-OH \xrightarrow[333K]{Hg^{2+}/H^+} \underset{\overset{|}{O-H}}{CH_3-C=CH_2}$$

$$\text{Isomerisation} \downarrow$$

$$\underset{\underset{\text{Propanone}}{O}}{\overset{\|}{CH_3-C-CH_3}}$$

4.From acyl chlorides:

$$2 \text{ R}' - \underset{\underset{O}{\|}}{C} - Cl \quad + \quad R_2Cd \longrightarrow 2 \text{ R}' - \underset{\underset{O}{\|}}{C} - R \ + \ CdCl_2$$

5. From nitriles:

Nitriles on treatment with Grignard reagent followed by hydrolysis give ketones.

$$CH_3 - CH_2 - C \equiv N + C_6H_5MgBr \xrightarrow{\text{ether}} CH_3CH_2 - C\overset{NMgBr}{\underset{C_6H_5}{\diagdown}} \xrightarrow{H_3O^+} C_2H_5 - C\overset{O}{\underset{C_6H_5}{\diagdown}}$$
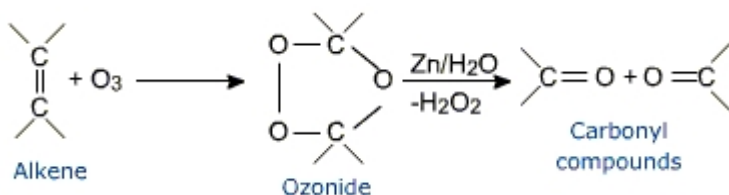
**Propiophenone
(1-Phenylpropanone)**

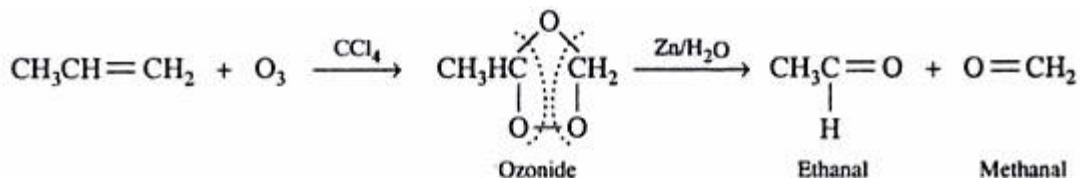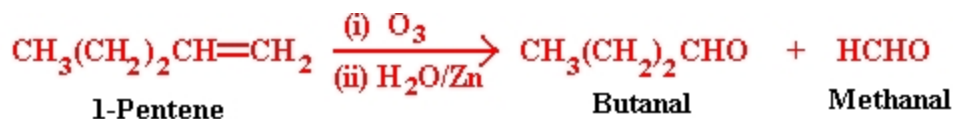## 6. From Friedel-Crafts acylation reaction:
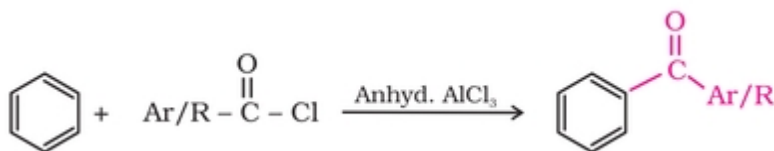
Ozonolysis

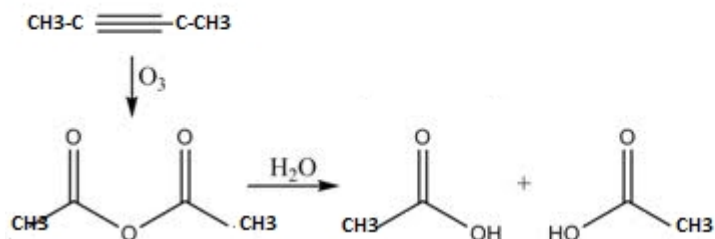Ozonolysis of alkene and alkyne produces aldehyde/ ketones.

- In first step alkene is oxidized to ozonide by ozone.
- In the second step ozonide is converted to carbonyl compound.
- The whole reaction is reversible in nature.
- Ozonide is very less stable.

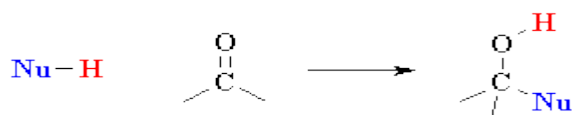$$CH_3(CH_2)_2CH=CH_2 \xrightarrow[\text{(ii) } H_2O/Zn]{\text{(i) } O_3} CH_3(CH_2)_2CHO + HCHO$$

1-Pentene   Butanal   Methanal

$$CH_3CH=CH_2 + O_3 \xrightarrow{CCl_4} CH_3HC \overset{O}{\underset{O \cdots O}{\diagup\diagdown}} CH_2 \xrightarrow{Zn/H_2O} CH_3C=O + O=CH_2$$

Ozonide   Ethanal   Methanal

Ozonolysis of alkyne

CH3-C≡C-CH3

↓ O_3

H₂O →

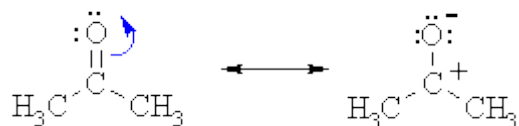## Example 3: Oxidative cleavage of alkynes

1. O_3
2. H_2O

3.Reactions of aldehydes and ketones:

1.Nucleophilic addition reactions

Nu−H

Aldehydes and ketones are attacked by **nucleophiles** due to the **electrophilic character of the carbonyl C**.
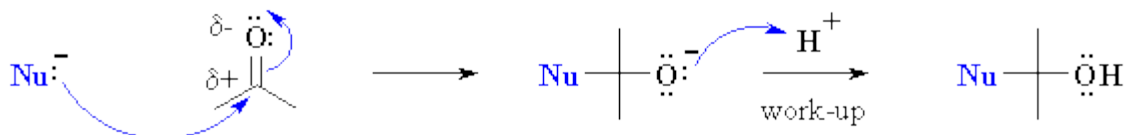

*A nucleophile, **Nu⁻**, is an electron rich species that reacts with an electron deficient species.*

Mechanism :

Depending on the reactivity of the nucleophile, there are two possible general scenarios:

- **Strong nucleophiles** (anionic) add directly to the **C=O** to form the intermediate alkoxide. The alkoxideis then protonated on work-up with dilute acid.
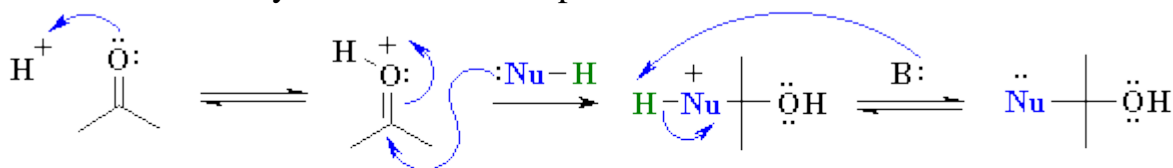
Nucleophilic Addition under **BASIC** conditions with stronger nucleophiles

Examples of such nucleophilic systems are : **RMgX**, **RLi**, **LiAlH₄**, **NaBH₄**

- **Weaker nucleophiles** (neutral) require that the **C=O** be activated prior to attack of the **Nu**.

This can be done using a acid catalyst which protonates on the Lewis basic O and makes the system more electrophilic.
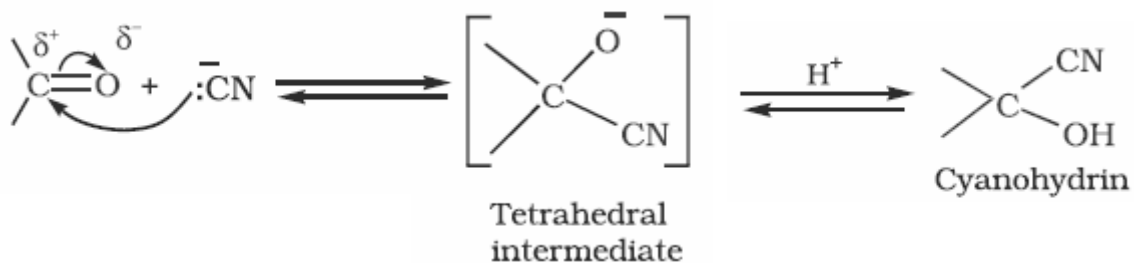
Nucleophilic Addition under **ACIDIC** condition with weaker nucleophiles
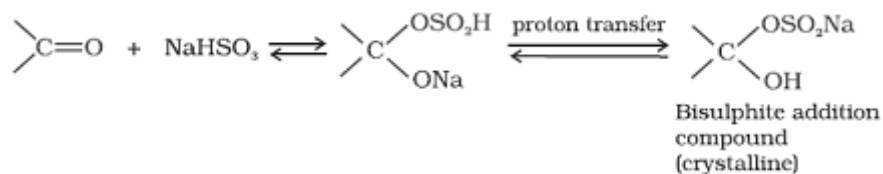
Examples of such nucleophilic systems are : **H₂O**, **ROH**, **R-NH₂**
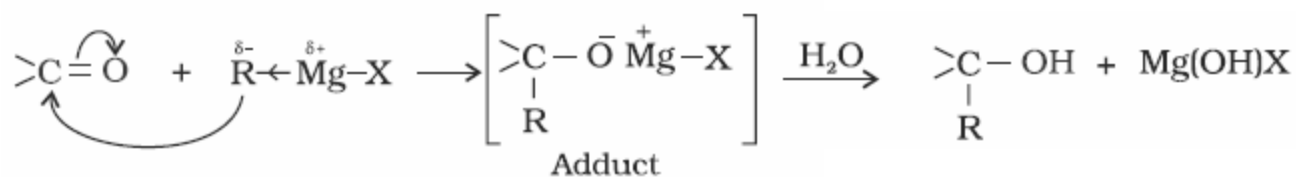
Examples of nucleophilic addition reactions
a. Addition of hydrogen cyanide (HCN) to form cyanohydrins

Tetrahedral
intermediate

Cyanohydrin

b. Addition of sodium hydrogen sulphite (NaHSO3) to form bisulphate addition compound:

c. Addition of Grignard reagent (RMgX) to form alcohol:

- Grignard + formaldehyde → 1° alcohol
- Grignard + aldehyde → 2° alcohol
- Grignard + ketone → 3° alcohol

d. Addition of alcohol:

i. On addition of monohydric alcohol in the presence of dry HCl, aldehydes form hemiacetal and acetal.
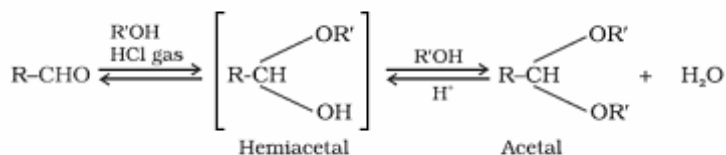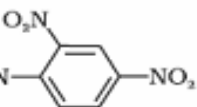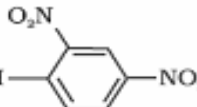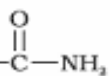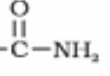
ii. Ketones do not react with monohydric alcohols. Ketones react with ethylene glycol under similar conditions to form cyclic products known as ethylene glycol ketals.

Ethylene glycol ketal

e. Addition of ammonia and its derivatives

Z = Alkyl, aryl, OH, NH_2, C_6H_5NH, $NHCONH_2$, etc.

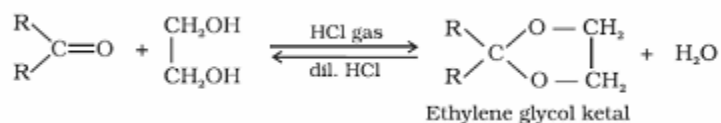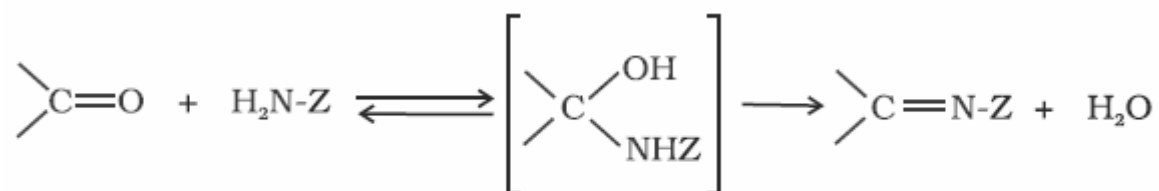| Z	Reagent name	Carbonyl derivative	Product name
-H	Ammonia	$>C=NH$	Imine
-R	Amine	$>C=NR$	Substituted imine (Schiff's base)
—OH	Hydroxylamine	$>C=N-OH$	Oxime
—NH_2	Hydrazine	$>C=N-NH_2$	Hydrazone
—HN—⬡	Phenylhydrazine	$>C=N-NH$—⬡	Phenylhydrazone
—HN—⬡(O₂N)(NO₂)	2,4-Dinitrophenyl-hydrazine	$>C=N-NH$—⬡(O₂N)(NO₂)	2,4 Dinitrophenyl-hydrazone
—NH—C(=O)—NH₂	Semicarbazide	$>C=N-NH-C(=O)-NH_2$	Semicarbazone

2. Reduction:

 (i) Reduction of aldehydes and ketones to primary or secondary alcohol using sodium borohydride or lithium aluminum hydride.

$$\text{C=O} \xrightarrow[\substack{\text{or} \quad \text{LiAlH}_4 \\ \text{or} \quad \text{NaBH}_4}]{\text{H}_2/\text{Ni,Pt or Pd}} \text{CH}\text{—OH}$$
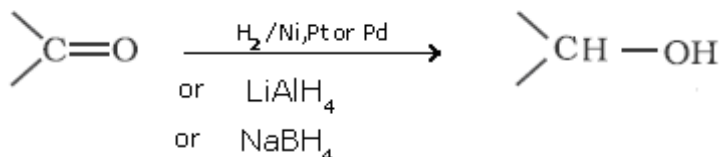
(ii) Reduction of aldehydes or ketones to hydrocarbons using **Clemmensor reduction** or **Wolff-Kishner** reduction

$$\text{C=O} \xrightarrow[\text{HCl}]{\text{Zn-Hg}} \text{CH}_2 + \text{H}_2\text{O}$$

$$\text{C=O} \xrightarrow[-\text{H}_2\text{O}]{\text{NH}_2\text{NH}_2} \text{C=NNH}_2 \xrightarrow[\text{heat}]{\text{KOH/ethylene glycol}} \text{CH}_2 + \text{N}_2$$
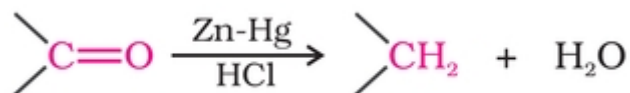
3. Oxidation:

Aldehydes can be easily oxidized to carboxylic acids using nitric acid, potassium permanganate, potassium dichromate, etc. Even mild oxidizing agents, mainly Tollens' reagent and Fehlings' reagent also oxidize aldehydes.

Oxidation of ketones, however, require more stronger oxidizing agent in more vigorous conditions.

(i) Tollen's test (used to distinguish aldehydes from ketones, aldehydes give positive test by producing a bright silver mirror)

$$\text{RCHO} + 2[\text{Ag(NH}_3)_2]^+ + 3\,\bar{\text{O}}\text{H} \longrightarrow \text{RCO}\bar{\text{O}} + 2\text{Ag} + 2\text{H}_2\text{O} + 4\text{NH}_3$$

Ketones do not form a silver mirror.

(ii) Fehling's test (used to distinguish aldehydes from ketones, aldehydes give positive test by producing a red-brown ppt. of cuprous oxide except aromatic aldehydes):

$$\text{R-CHO} + 2\text{Cu}^{2+} + 5\bar{\text{O}}\text{H} \longrightarrow \underset{\text{Red-brown ppt}}{\text{RCO}\bar{\text{O}}} + \text{Cu}_2\text{O} + 3\text{H}_2\text{O}$$
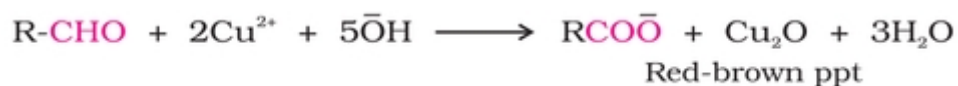
Ketones do not form a reddish-brown precipitate of cuprous oxide.

(iii) Oxidation of methyl ketones using haloform reaction: both aldehydes and ketones having at least one methyl group attached to the carbonyl carbon will react to give a product having one less carbon atom as shown in the reaction below:

$$R-\overset{\overset{\text{O}}{\|}}{C}-CH_3 \xrightarrow{\text{NaOX}} R-\overset{\overset{\text{O}}{\|}}{C}-ONa \ + \ CHX_3 \quad (X=Cl, Br, I)$$
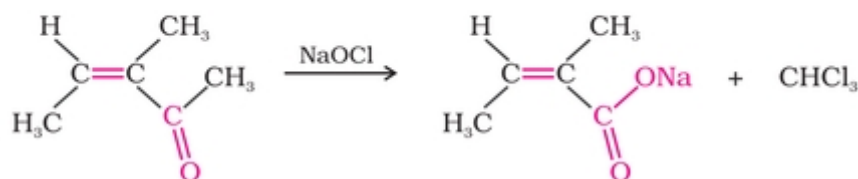
4. Reaction due to α-hydrogen:

Aldehydes and ketones also undergo reaction due to acidic nature of alpha hydrogen atom. The acidic nature of alpha hydrogen of aldehydes and ketones is due to strong electron withdrawing nature of carbonyl group and resonance stabilization of conjugate base as shown below:
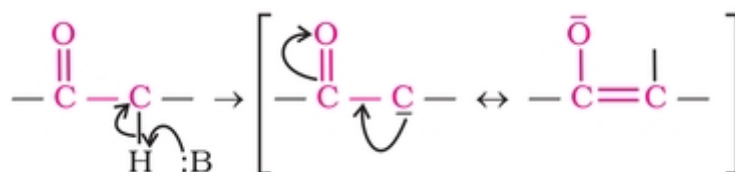
negative charge on alpha carbon is stabilized by the carbonyl group

(i) Aldol condensation: Aldehydes and ketones having at least one hydrogen α-hydrogen undergoes reaction in weakly basic condition to form β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol), respectively. β-hydroxy aldehydes (aldol) or β-hydroxy ketones (ketol) readily loses water to give α,β-unsaturated carbonyl compounds.

$$2CH_3\text{-}CO\text{-}CH_3 \underset{}{\overset{Ba(OH)_2}{\rightleftarrows}} \underset{\underset{OH}{|}}{CH_3\text{-}\overset{\overset{CH_3}{|}}{C}\text{-}CH_2CO\text{-}CH_3} \xrightarrow[-H_2O]{\Delta} CH_3\text{-}\overset{\overset{CH_3}{|}}{C}=CH\text{-}CO\text{-}CH_3$$

Propanone

(Ketol)
4-Hydroxy-4-methylpentan-2-one

4-Methylpent-3-en-2-one
(Aldol condensation product)
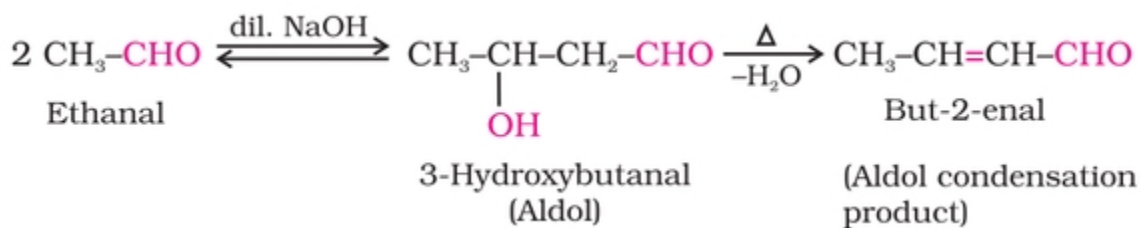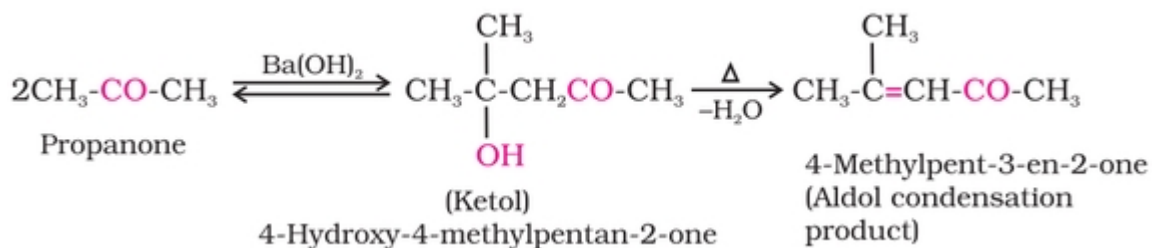
2. Cross aldol condensation: When aldol condensation is carried out between two different aldehydes or ketones or an aldehyde and a ketone having alpha-hydrogen, the reaction is called cross cross aldol condensation

$$\begin{matrix} CH_3CHO \\ + \\ CH_3CH_2CHO \end{matrix} \xrightarrow[2. \; \Delta]{1. \; NaOH} \begin{matrix} CH_3\text{-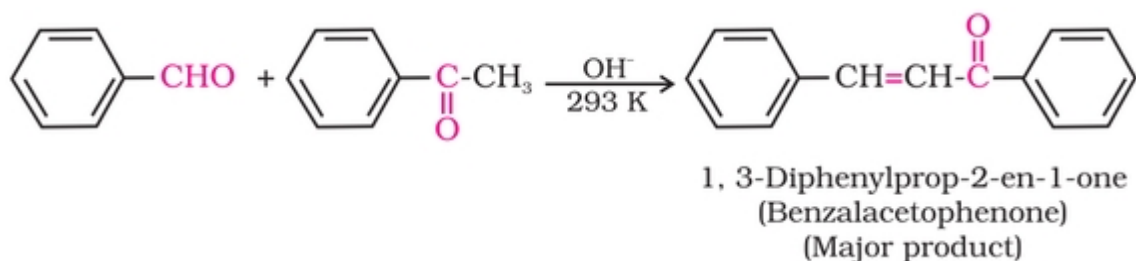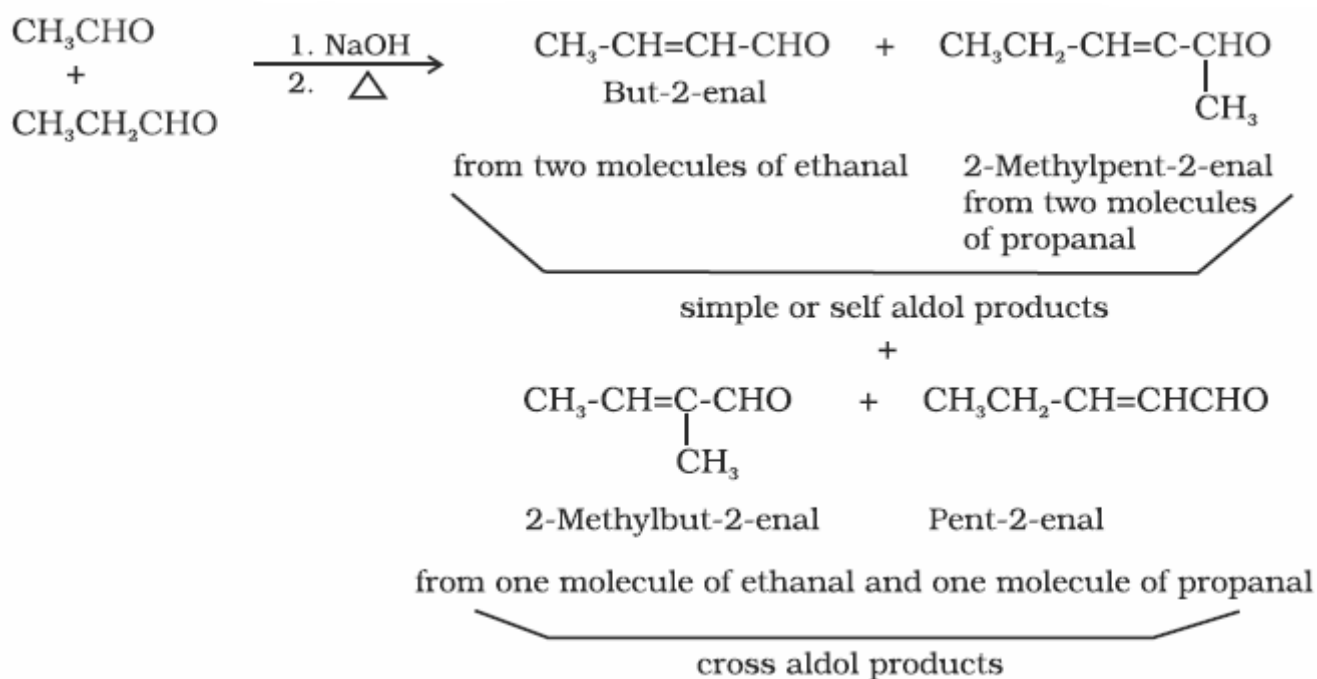}CH=CH\text{-}CHO \\ But\text{-}2\text{-}enal \end{matrix} + \begin{matrix} CH_3CH_2\text{-}CH=\overset{\overset{}{|}}{C}\text{-}CHO \\ \quad CH_3 \end{matrix}$$

from two molecules of ethanal

2-Methylpent-2-enal
from two molecules of propanal

simple or self aldol products
+

$$CH_3\text{-}CH=\underset{\underset{CH_3}{|}}{C}\text{-}CHO \quad + \quad CH_3CH_2\text{-}CH=CHCHO$$

2-Methylbut-2-enal   Pent-2-enal

from one molecule of ethanal and one molecule of propanal

cross aldol products

1, 3-Diphenylprop-2-en-1-one
(Benzalacetophenone)
(Major product)

(i) Cannizzaro reaction: Aldehydes with not alpha-hydrogen is self oxidized and reduced in the presence of conc. base to form alcohol and carboxylic acid salt respectively.

Formaldehyde   Methanol   Potassium formate

Benzaldehyde   Benzyl alcohol   Sodium benzoate
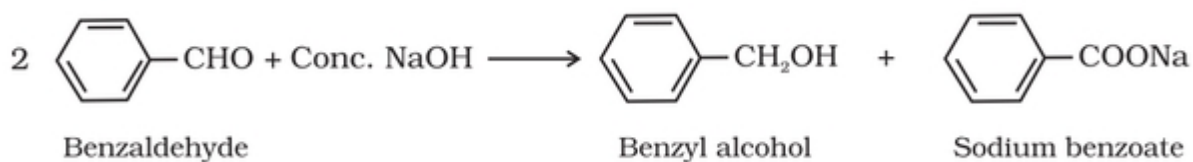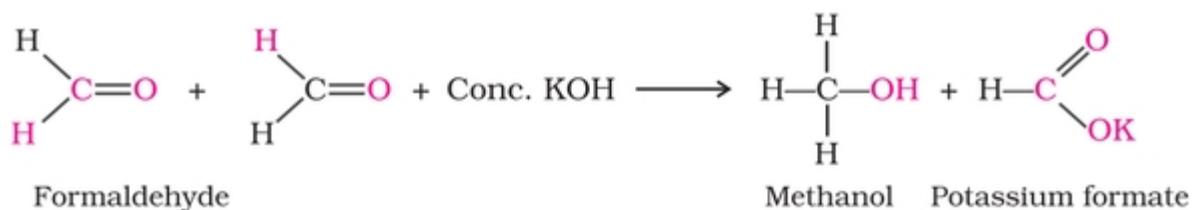
(ii) Electrophilic substitution reaction: Aromatic aldehydes and ketones act as moderately deactivating group and electrophiles are added to the meta position.

Benzaldehyde   *m*-Nitrobenzaldehyde
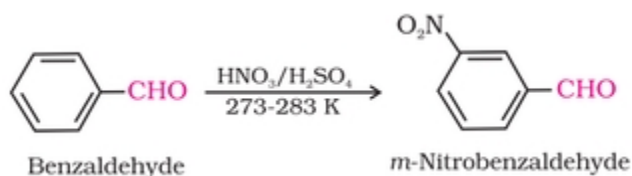
Carboxylic Acids

Carbon compounds containing a carboxyl functional group, –COOH are called carboxylic acids.

General Formula
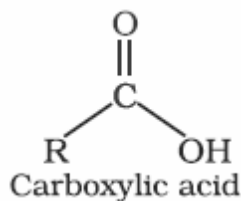
Carboxylic acid

Nomenclature:
Functional group suffix = *-oic acid*
If the acid is substituted onto a ring the suffix *-carboxylic acid* is used

Examples

IUPAC name: methanoic acid ethanoic acid propanedioic acid butanedioic acid
Trivial name: formic acid   acetic acid   malonic acid   succinic acid

Structure of Carboxyl Group

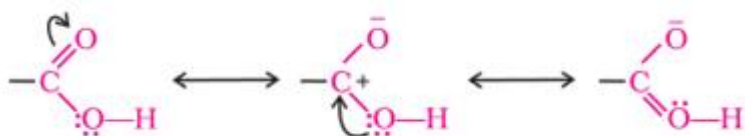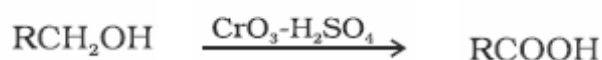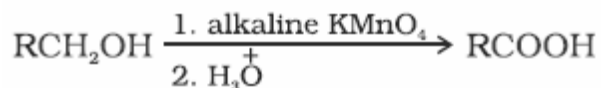- The **CO$_2$H** unit is planar and consistant with sp^2 hydridisation and a resonance interaction of the lone pairs of the hydroxyl oxygen with the π system of the carbonyl.

4.Preparation of carboxylic acid

i.From alcohols: Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate (KMnO4) in neutral, acidic or alkaline media or by potassium dichromate (K2Cr2O7) and chromium trioxide (CrO3) in acidic media.

$$RCH_2OH \xrightarrow[\text{2. } H_3\overset{+}{O}]{\text{1. alkaline KMnO}_4} RCOOH$$

$$RCH_2OH \xrightarrow{CrO_3\text{-}H_2SO_4} RCOOH$$

ii. From aldehydes: Oxidation of aldehydes in the presence of mild oxidising agents such as Tollen's reagent (ammoniacal solution of AgNO3) or Fehling reagent [Fehling solution A (aqueous solution of CuSO4) + Fehling solution B (aqueous solution of sodium potassium tartarate)] forms carboxylic acids.

$$RCHO + 2[Ag(NH_3)_2]^+ + 3\,\overline{O}H \longrightarrow RCO\overline{O} + 2Ag + 2H_2O + 4NH_3$$

$$R\text{-}CHO + 2Cu^{2+} + 5\overline{O}H \longrightarrow RCO\overline{O} + Cu_2O + 3H_2O$$
$$\text{Red-brown ppt}$$

iii. From alkylbenzenes:
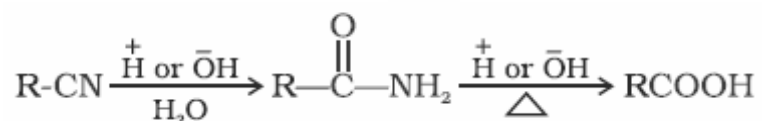Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate.

Benzoic acid
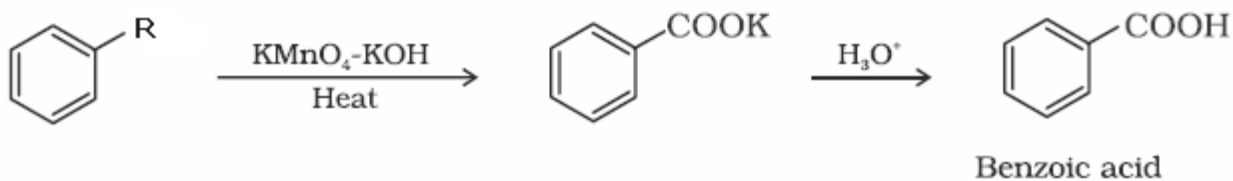
R is an alkyl group (primary or secondary)

iv. From nitriles:
Nitriles on hydrolysis in the presence of dilute acids or bases form amide, which on further hydrolysis gives carboxylic acid

v. From Grignard reagent:
Grignard reagents react with carbon dioxide (dry ice) to form salts of carboxylic acids, which on hydrolysis form carboxylic acids.
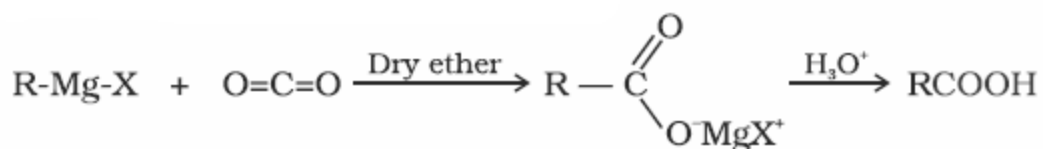
vi. From acyl halides and anhydrides:
Acid chlorides when hydrolysed with water give carboxylic acids. On basic hydrolysis, carboxylate ions are formed which on further acidification form corresponding carboxylic acids. Anhydrides on hydrolysis form corresponding acid(s).
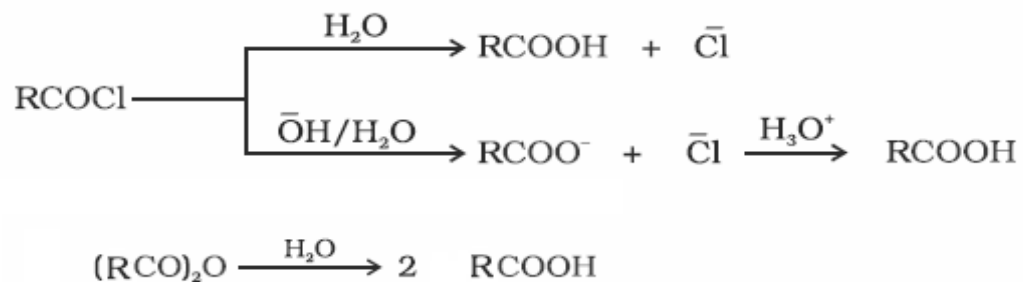
vii. From esters: Acidic hydrolysis of esters directly gives carboxylic acids, while basic hydrolysis gives carboxylates, which on acidification give corresponding carboxylic acids.

$$R - COO - R' \xrightleftharpoons{H_3O^+} R - COOH + R' - OH$$

$$R - COO - R' \xrightleftharpoons{NaOH} R - COO - Na + R' - OH$$

$$\downarrow H_3O^+$$

$$R - COOH$$
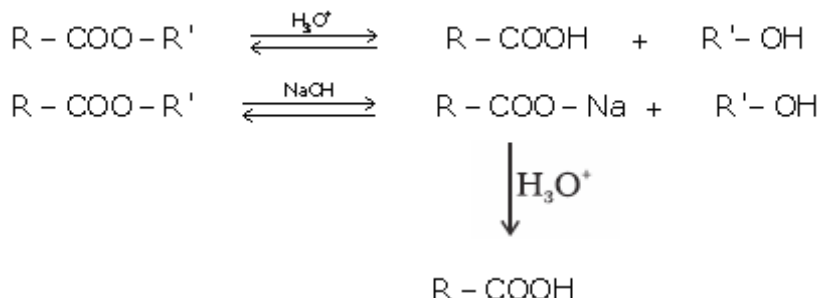
5.Physical and chemical properties
1.Physical Properties:

- Structure of carboxyl group is planner triangular

- The polar nature of both the **O-H** and **C=O** bonds (due to the electonegativity difference of the atoms) results in the formation of strong hydrogen bonds with other carboxylic acid molecules or other H-bonding systems (*e.g.* water). The implications are:
    - higher melting and boiling points compared to analogous alcohols
    - high solubility in aqueous media
    - hydrogen bonded dimers in gas phase and dimers or aggregates in pure liquid

$$R - C \begin{smallmatrix} O\text{--------}H - O \\ \\ O - H\text{-------}O \end{smallmatrix} C - R$$

dimer
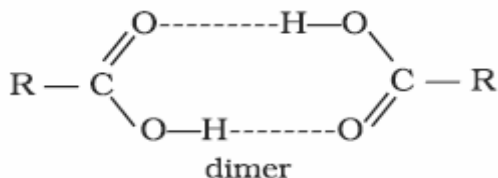
2.Chemical properties
Acidity:

- Carboxylic acids are the most acidic simple organic compounds ($pK_a \sim 5$).
- But they are only weak acids compared to acids like HCl or H_2SO_4. (Remember the lower the pK_a, the stronger the acid)

- Resonance stabilisation of the carboxylate ion allows the negative charge to be delocalised between the two electronegative oxygen atoms (compare with alcohols, $pK_a \sim 16$).
- Effect of electron-donating substituents on the acidity of carboxylic acids: Electron-donating substituent decreases the stability of carboxylate ion by intensifying the negative charge and hence decreases the acidity of carboxylic acids.

- Effect of electron-withdrawing substituent on the acidity of carboxylic acids: The electron-withdrawing group increases the stability of carboxylate ion by delocalising negative charge and hence increases acidity of carboxylic acid.

- The effect of the following groups in increasing acidity order is Ph < I < Br < Cl < F < CN < NO2 < CF3
- a. Effect of the number of electron-withdrawing groups: As the number of electron-withdrawing groups increases, the –I effect increases, increasing the acid strength.
- b. Effect of position of electron-withdrawing group: As the distance between electron-withdrawing group and carboxylic group increases, electron-withdrawing influence decreases.

Thus, the following acids are arranged in order of increasing acidity (based on pKa values):

CF3COOH > CCl3COOH > CHCl2COOH > NO2CH2COOH > NC-CH2COOH >FCH2COOH > ClCH2COOH > BrCH2COOH > HCOOH > ClCH2CH2COOH >C6H5COOH > C6H5CH2COOH > CH3COOH > CH3CH2COOH

6.Reactions of Carboxylic Acids

a.Reactions involving cleavage of C–OH bond

Carboxylic acids on heating with mineral acids such as H2SO4 or with P2O5 give corresponding anhydride

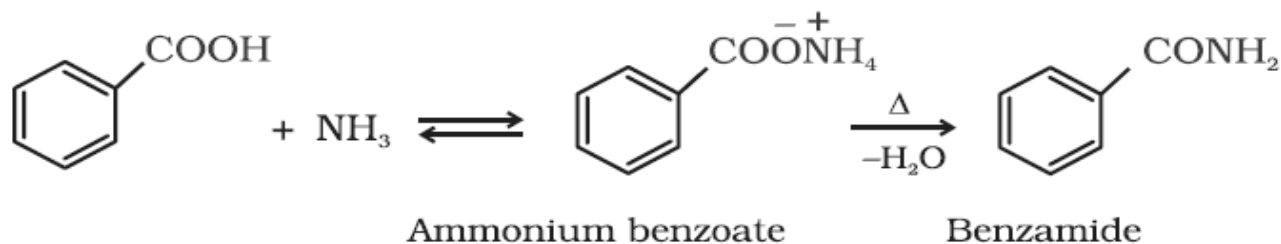### i. Anhydride formation:

Ethanoic acid → Ethanoic anhydride
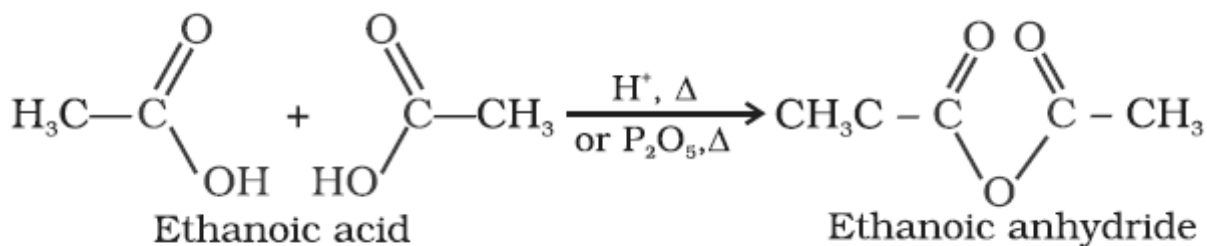
ii. Esterification: Carboxylic acids are esterified with alcohols in the presence of a mineral acid such as concentrated H2SO4 or HCl gas as a catalyst.

$$RCOOH \; + \; R'OH \underset{}{\overset{H^+}{\rightleftharpoons}} RCOOR' \; + \; H_2O$$
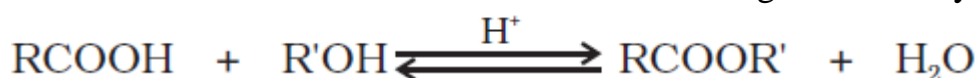
iii. Carboxylic acids react with PCl5, PCl3 and SOCl2 to form acyl chlorides.

$$RCOOH \; + \; PCl_5 \longrightarrow RCOCl \; + \; PCl_3 \; + \; HCl$$

$$3RCOOH \; + \; PCl_3 \longrightarrow 3RCOCl \; + \; H_3PO_3$$

$$RCOOH \; + \; SOCl_2 \longrightarrow RCOCl \; + \; SO_2 \; + \; HCl$$

iv. Reaction with ammonia (NH3): Carboxylic acids react with ammonia to give ammonium salt, which on further heating at high temperature gives amides.

$$CH_3COOH + NH_3 \rightleftharpoons \underset{\text{Ammonium acetate}}{CH_3C\overset{-}{O}\overset{+}{O}NH_4} \overset{\Delta}{\underset{-H_2O}{\longrightarrow}} \underset{\text{Acetamide}}{CH_3CONH_2}$$

Ammonium benzoate → Benzamide

b. Reactions involving COOH group:

i. Reduction: Carboxylic acids are reduced to alcohols in the presence of LiAlH4 or B2H6.

$$R\text{-}COOH \xrightarrow[\text{(ii) } H_3O^+]{\text{(i) } LiAlH_4/\text{ether} \quad \text{or } B_2H_6} R\text{-}CH_2OH$$
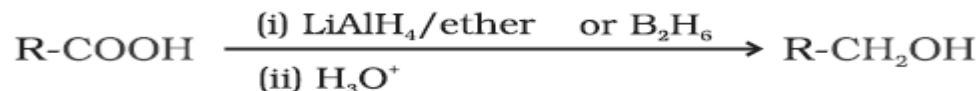
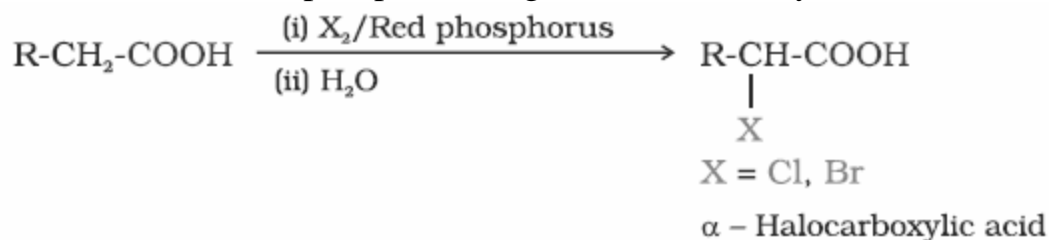**ii. Decarboxylation:** Sodium or potassium salts of carboxylic acids on heating with soda lime (NaOH + CaO in ratio of 3:1) give hydrocarbons which contain one carbon less than the parent acid.

$$R\text{-}COONa \xrightarrow[\text{Heat}]{\text{NaOH \& CaO}} R\text{-}H + Na_2CO_3$$
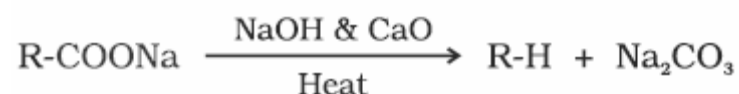
The reaction is known as **Kolbe electrolysis**

c. Reactions involving substitution reaction in hydrocarbon part:

i. Hell–Volhard–Zelinsky reaction: Carboxylic acids with an α -hydrogen are halogenated at the α -position on treatment with chlorine or bromine in the presence of a small amount of red phosphorus to give α-halocarboxylic acids).

$$R\text{-}CH_2\text{-}COOH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } X_2/\text{Red phosphorus}} R\text{-}CH\text{-}COOH$$
$$\underset{X}{|}$$

X = Cl, Br

α – Halocarboxylic acid

ii. Ring substitution in aromatic acids: Aromatic carboxylic acids undergo electrophilic substitution reactions. Carboxyl group in benzoic acid is electron-withdrawing group and is meta directing.

m-Nitrobenzoic acid

m-Bromobenzoic acid