Aldehyde, Ketone & Carboxylic Acids

By Sachin Sir
Jnana Sarita Jr. College,
Mulund (W).

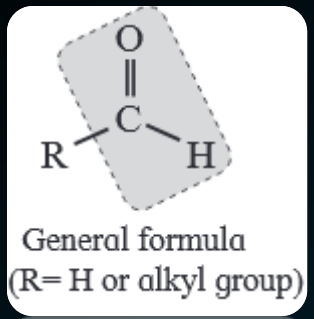
CHEM GURU

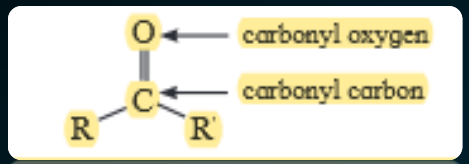
Like, Share and Subscribe.....

Introduction

Aldehydes & Ketones:

- Compounds containing carbonyl group.





Classification of aldehydes, ketones and carboxylic acids :

Aldehydes, ketones and carboxylic acids are classified as per the nature of carbon skeleton bonded to (>C=O).

Classification of aldehydes :

Aldehydes are classified as aliphatic and aromatic aldehydes.

a. Aliphatic aldehydes: The compounds in which the –CHO group (formyl group) is attached directly to sp^3 hybridized c-atom that is saturated c-atom are called aliphatic aldehydes.

(Exception: Formaldehyde, H-CHO is also classified as aliphatic aldehyde though –CHO group is not attached to any carbon).

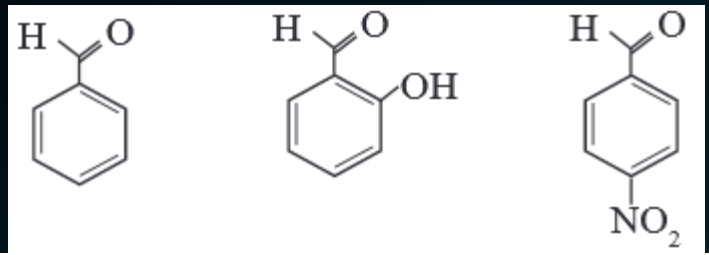
For example:

$CH_3 - CHO$	$CH_3 - CH_2 - CHO$
(Acetaldehyde)	(Propionaldehyde)

Classification of aldehydes :

b. Aromatic aldehydes: The compounds in which –CHO group is attached directly to an aromatic ring are called aromatic aldehydes.

For example:

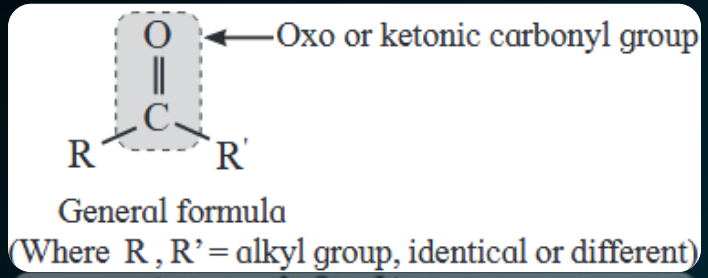


(Benzaldehyde) (Salicylaldehyde)(p-Nitrobenzaldehyde)

Classification of ketones :

Ketones are classified as aliphatic and aromatic ketones.

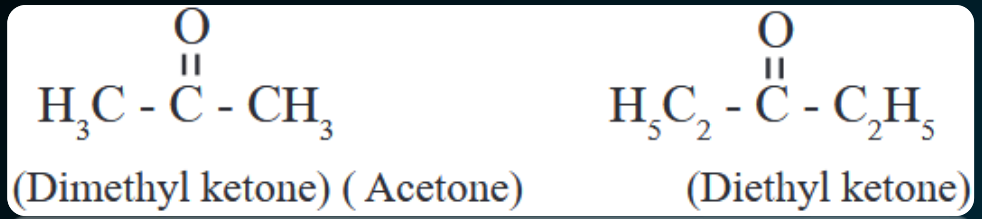
a. Aliphatic ketones : The compounds in which >C=O group is attached to two alkyl groups are called aliphatic ketones.



On the basis of types of alkyl groups bonded to carbonyl carbon, aliphatic ketones are further classified as simple and mixed ketones.

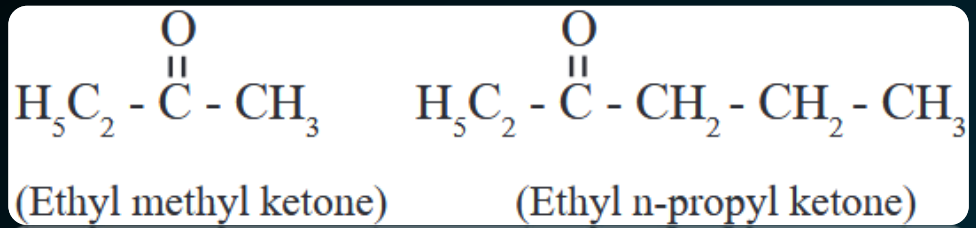
Classification of ketones :

i. Simple or symmetrical ketones : The ketones in which both the alkyl groups bonded to carbonyl carbon are identical, are called simple ketones or symmetrical ketones. For example :



Classification of ketones :

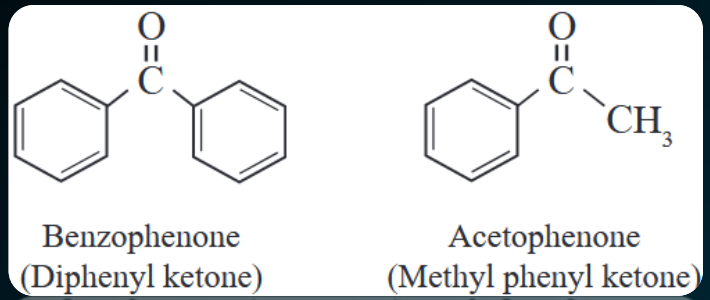
ii. Mixed or unsymmetrical ketones : The ketones in which two alkyl groups bonded to carbonyl carbon are different, are called mixed ketones or unsymmetrical ketones. For example :



Classification of ketones :

b. Aromatic ketones : The compounds in which a >C=O group is attached to either two aryl groups or one aryl and one alkyl group are called aromatic ketones.

For example :

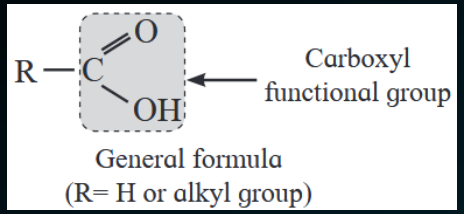


Benzophenone (Diphenyl ketone)

Acetophenone (Methyl phenyl ketone)

Classification of carboxylic acids

Carboxylic acids are classified as aliphatic and aromatic carboxylic acids.



a. Aliphatic carboxylic acids : carboxyl (-COOH) group is bonded to an alkyl group are called aliphatic carboxylic acids or fatty acids. (Exception : Formic acid, H-COOH is also classified as aliphatic carboxylic acid though –COOH group is not attached to any carbon).

For example :

H_3C - COOH

(Acetic acid)

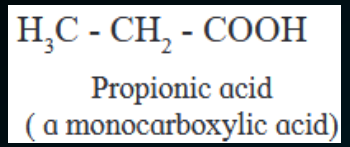
H_3C - CH_2 - COOH

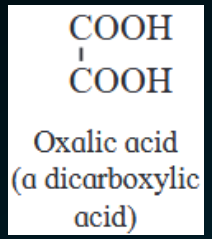
(Propionic acid)

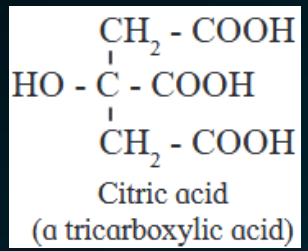
Classification of carboxylic acids

- Depending on the number of –COOH groups, mono, di, tri carboxylic acids and so on.

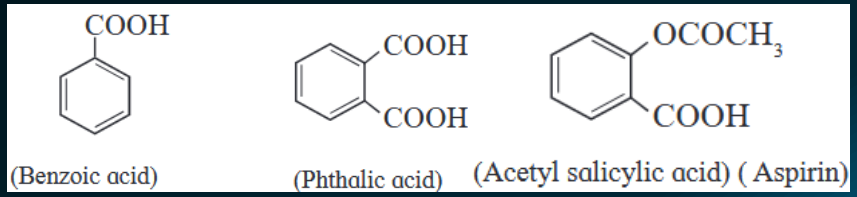
For example :







b. Aromatic carboxylic acids : one or more carboxyl groups (-COOH) are attached directly to the aromatic ring. For example :



sources of carboxylic acids

- Carboxylic acids are found in both the plants and animals.
- L-lactic acid is present in curd,
- Citric acid is found in citrus fruit (Lemons).
- Acetic acid is the key ingredient of vinegar.

Nomenclature

a. Trivial names of aldehydes and carboxylic acids :

- Names of aliphatic aldehydes are derived carboxylic acids.
- Ending ‘ic acid’ of carboxylic acid is replaced by the ending ‘aldehyde’.
- In case of carboxylic acids and aldehydes the position of substituent is indicated by labeling the carbon serially as α, β, γ and so on.
- The carbon atom adjacent to carbonyl carbon is labeled as α and next one is β and so on.

Nomenclature

b. IUPAC names of aldehydes and carboxylic acids :

- The name of an aliphatic aldehyde is by replacing ending ‘e’ of alkane with ‘al ’.
- Aldehyde is named as alkanal.
- The IUPAC name of carboxylic acid is derived from the name of the corresponding alkane by replacing ending ‘e’ of alkane with ‘oic acid ’.
- Alkane ----Alkanal
- Alkane----- Alkanoic acid

Nomenclature

b. IUPAC names of aldehydes and carboxylic acids:

- The longest chain including –CHO or –COOH group is identified as the parent chain.
- Numbering of the chain is done by giving number 1 to the –CHO or –COOH carbon.
- The name of substituent is included along with its locant.
- Aldehyde (-CHO) grp and carboxyl (-COOH) grp are always terminal.
- When two –CHO grps are present ending ‘e’ of alkane is retained and the suffix ‘dial’ is added parent aldehyde.
- In case of dicarboxylic acids, ‘dioic acid’ is added to the name of the parent alkane.

Nomenclature

b. IUPAC names of aldehydes and carboxylic acids:

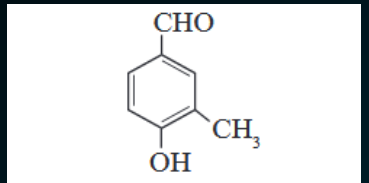
- In IUPAC nomenclature an alicyclic compound in which –CHO group is attached directly to the ring is named as a carb-aldehyde.
- The suffix ‘carb-aldehyde’ is added after the full name of parent cycloalkane structure.
- Similarly an alicyclic compound having a carboxyl group directly attached to alicyclic ring is named as cycloalkane carboxylic acid

Substituted aromatic aldehydes and carboxylic acids

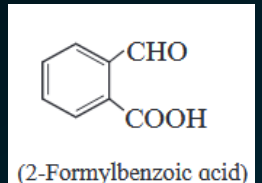
- When two or more different functional groups are attached to a ring, the higher priority grp is given lower number.

NOTE:- The principal functional group is decided on the basis of the following order of priority.-COOH > -SO_3H > -COOR > -COCl > -$CONH_2$ > -CN> -CHO>C = O > -OH > -NH_2 > C = C > -C ≡ C-

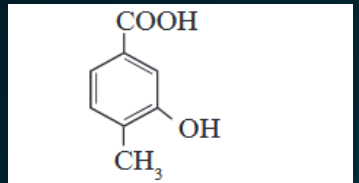
- When –CHO group, appears as substituent prefix ‘formyl’ is used in the IUPAC name.



(4-Hydroxy-3-methylbenzaldehyde)

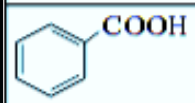
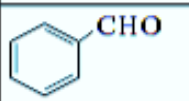
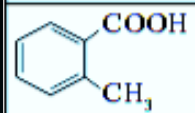
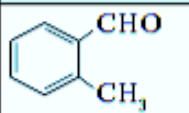
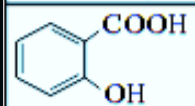
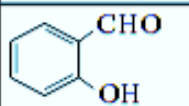
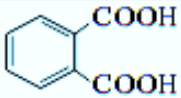
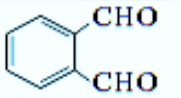
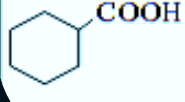
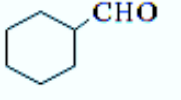


(2-Formylbenzoic acid)



(3-Hydroxy-4-methylbenzoic acid)

Table 12.1 Trivial and IUPAC names of carboxylic acids and aldehydes

Carboxylic acids			Aldehydes		
Structure	Trivial name	IUPAC name	Structure	Trivial name	IUPAC name
H - COOH	Formic acid	Methanoic acid	H-CHO	Formaldehyde	Methanal
CH_3 - COOH	Acetic acid	Ethanoic acid	CH_3-CHO	Acetaldehyde	Ethanal
CH_3 - CH_2 - COOH	Propionic acid	Propanoic acid	CH_3-CH_2-CHO	Propionaldehyde	Propanal
CH_3 - CH_2 - CH_2 - COOH	n-Butyric acid	Butanoic acid	CH_3-CH_2-CH_2-CHO	Butyraldehyde	Butanal
$(CH_3)_2CH$ - COOH	Isobutyric acid (α - methylpropionic acid)	2-Methylpropanoic acid	$(CH_3)_2CH$-CHO	Isobutyrlaldehyde (α - methylpropionaldehyde)	2 - Methylpropanal
CH_2 = CH - COOH	Acrylic acid	Prop-2-enoic acid	CH_2=CH-CHO	Acrolein	Prop-2-enal
HOOC - COOH	Oxalic acid	Ethanedioic acid	CHO-CHO	Oxaldehyde (Glyoxal)	Ethanedial
	Benzoic acid (Benzenecarboxylic acid)	Benzoic acid		Benzaldehyde	Benzaldehyde (Benzenecarbaldehyde)
	o-Toluic acid	2-Methylbenzoic acid		o-Tolualdehyde	2-Methylbenzaldehyde
	Salicyclic acid	2-Hydroxybenzoic acid		Salicylaldehyde	2-Hydroxybenzaldehyde
	Phthalic acid	Benzene-1,2-dicarboxylic acid		Phthalaldehyde	Benzene-1,2-dicarboaldehyde
	Cyclohexylcarboxylic acid	Cyclohexanecarboxylic acid		Cyclohexane aldehyde	Cyclohexanecarbaldehyde

Nomenclature

a. Trivial names of ketones:

- The trivial names of aliphatic ketones are based on the names of alkyl groups or aryl groups attached to carbonyl carbon.
- Names of alkyl or aryl groups are written in alphabetical order followed by the word ketone.
- In substituted aliphatic ketones the position of sub. is indicated by labeling the carbon serially as α, b, γ and so on.
- Names of aromatic ketones are based on a phenone.

Nomenclature

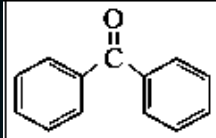
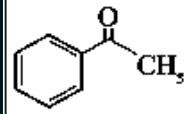
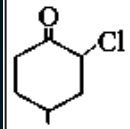
b. The IUPAC names of aliphatic ketones:

- Name of the alkanes by replacing ending ‘e’ of alkane with ‘one’.
- They are named as alkan-one. The longest chain of carbon atoms containing the ketonic carbonyl group is numbered from the end closer to the carbonyl carbon.

  Alkane_____Alkanone
- When two >C=O groups are present, then ending ‘e’ of alkane is retained and the suffix ‘dione’ is added to the name of parent ketone indicating the locants of ketonic carbonyl groups.
- In case of polyfunctional ketones, higher priority group is given lower number.
- When ketonic carbonyl is a lower priority group it is named as 'oxo', preceded by the locant.

Nomenclature

Compound	Trivial name	IUPAC name
CH_3-CO-CH_3	Dimethyl ketone (Acetone)	Propanone
CH_3-CO-CH_2-CH_3	Ethyl methyl ketone	Butanone
CH_3-CO-CH_2-CH_2-CH_3	Methyl n-propyl ketone	Pentan-2-one
CH_3-CH_2-CO-CH_2-CH_3	Diethyl ketone	Pentan-3-one
CH_3-CH(Br)-CO-CH_2-CH_2-CH_3	α-Bromoethyl-n-propyl ketone	2-Bromohexan-3-one

	Diphenyl ketone (Benzophenone)	Benzophenone
	Methyl phenyl ketone (Acetophenone)	Acetophenone
	----------	2-Chloro-4-methylcyclohexanone

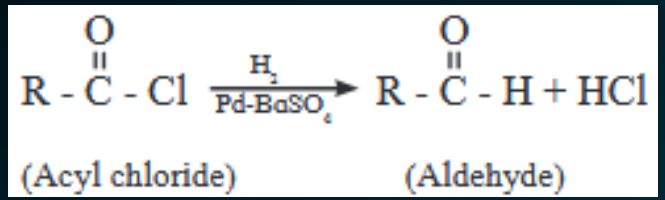
Preparation of aldehydes and ketones

a. From acyl chlorides (Acid chlorides) :

Aldehydes and ketones both can be obtained from acyl chloride, but the reactions involved are different.

- Preparation of aldehyde from acyl chloride:

Acyl chloride is reduced to corresponding aldehyde by hydrogen using a palladium catalyst poisoned with barium sulfate. This reaction is known as Rosenmund reduction.



Preparation of aldehydes and ketones

b. Preparation of ketone (aliphatic and aromatic) from acyl chloride:

i. Preparation of aliphatic ketones from acyl chloride:

ketones are obtained from acyl chloride by reaction with dialkyl cadmium which is prepared by the treatment of cadmium chloride with Grignard reagent.

$$2R\text{-}MgX + CdCl_2 \longrightarrow R_2Cd + 2Mg(X)Cl$$

$$2R'\text{-}COCl + R_2Cd \longrightarrow \underset{\text{(Ketone)}}{2\,R'\text{-}CO\text{-}R} + CdCl_2$$

(Acyl chloride)

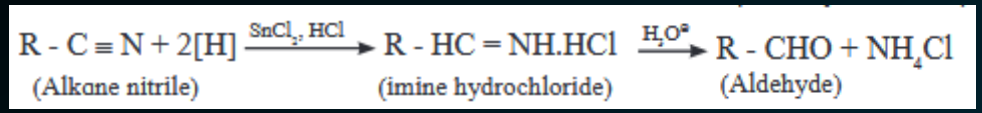
$$\underset{\text{(Ethanoyl chloride)}}{2CH_3\text{-}COCl} + \underset{\text{(Dimethyl cadmium)}}{(CH_3)_2Cd} \longrightarrow \underset{\text{Propanone (Acetone)}}{2CH_3\text{-}CO\text{-}CH_3} + CdCl_2$$

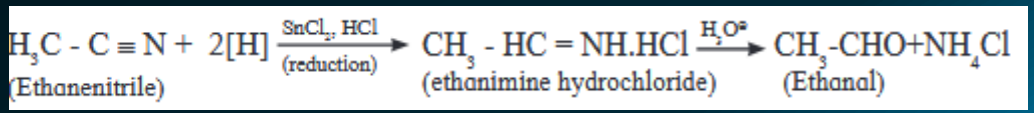
$$\underset{\text{(Benzoyl chloride)}}{2C_6H_5\text{-}COCl} + \underset{\text{(Dimethyl cadmium)}}{(CH_3)_2Cd} \longrightarrow \underset{\text{(Acetophenone)}}{C_6H_5\text{-}CO\text{-}CH_3} + CdCl_2$$

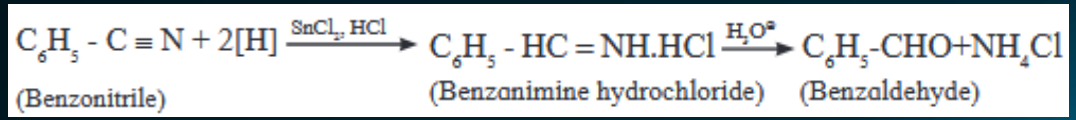
Preparation of aldehydes and ketones

c. From nitriles : Aldehydes and ketones both can be obtained from nitriles but by different reaction.

- Preparation of aldehydes from nitriles: Nitriles are reduced to imine hydrochloride by stannous chloride in presence of HCl which on acid hydrolysis give corresponding aldehydes. This reaction is called Stephen reaction.

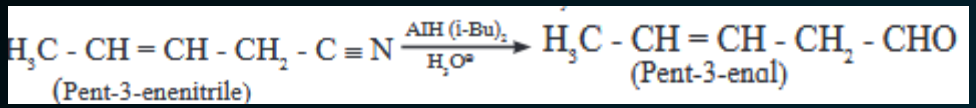




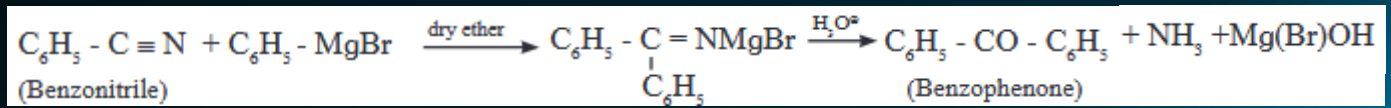


Preparation of aldehydes and ketones

Alternatively, nitriles are also reduced by diisobutylaluminium hydride (DIBAl-H) or $AlH(i\text{-}Bu)_2$ to imines followed by acid hydrolysis to aldehydes. An advantage of this method is that double or triple bond present in the same molecule is not reduced..



- Preparation of ketones from nitriles: Ketones are prepared by reacting nitriles with Grignard reagent in dry ether as solvent followed by acid hydrolysis.



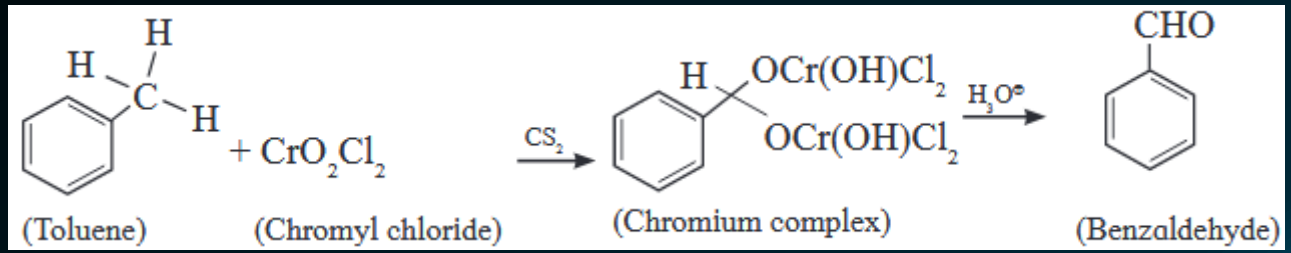
Preparation of aldehydes and ketones

d. From aromatic hydrocarbons : Aromatic aldehydes and ketones are both prepared from aromatic hydrocarbons but by different methods.

- Preparation of aromatic aldehydes from hydrocarbon Strong oxidizing agents transform -CH3 group bonded to aromatic ring into carboxyl group (-COOH). For obtaining aromatic aldehyde from methyl arene the following special methods are used.

Preparation of aldehydes and ketones

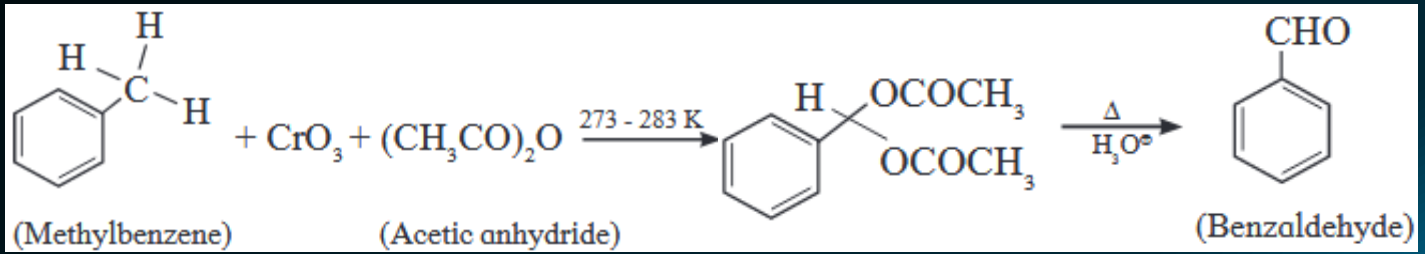
i. Etard reaction : Methyl group in methyl benzene (or methyl arene) is oxidized by chromyl chloride in carbon disulfide as solvent, to form a chromium complex, from which benzaldehyde is obtained on acid hydrolysis. This reaction is known as Etard reaction.



Preparation of aldehydes and ketones

ii. By oxidation of methyl arene using CrO3:

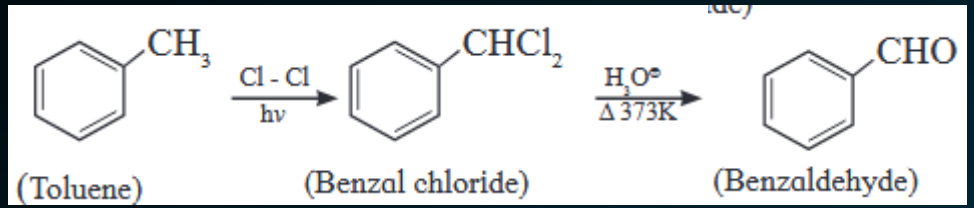
Methylarene is converted into a benzyllidene diacetate on treatment with chromium oxide in acetic anhydride at 273-278 K. The diacetate derivative on acid hydrolysis gives corresponding aldehyde.



Preparation of aldehydes and ketones

iii. By side chain chlorination of toluene:

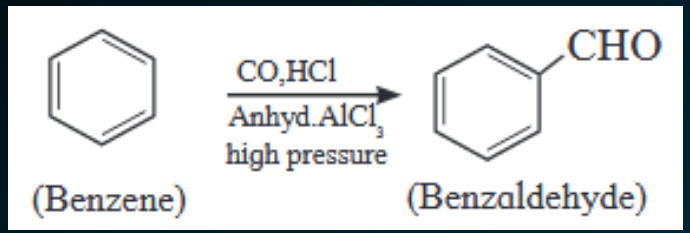
Side chain chlorination of toluene gives benzal-chloride which on acid hydrolysis at 373K gives benzaldehyde. Benzaldehyde, is manufactured commercially by this method.



Preparation of aldehydes and ketones

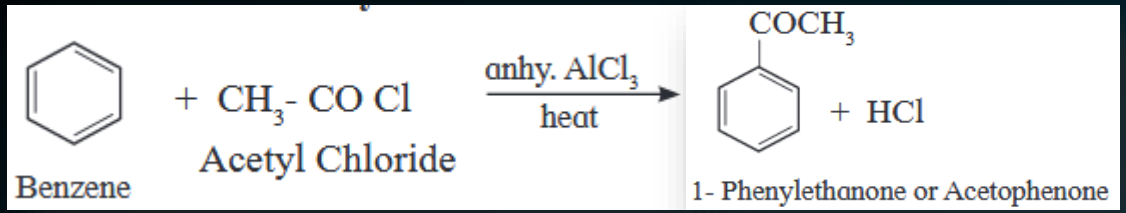
v. Gatterman–Koch formylation of arene:

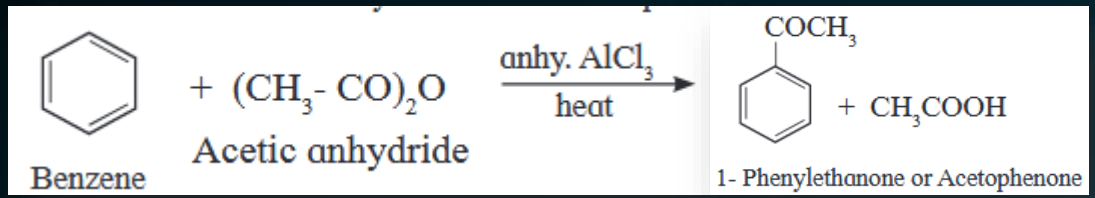
Benzene or substituted benzene is treated under high pressure with carbon monoxide and hydrogen chloride in presence of anhydrous aluminium chloride or cuprous chloride to give benzaldehyde or substituted benzaldehyde



Preparation of aldehydes and ketones

- Preparation of Aromatic ketones from hydrocarbons :
  By Friedel-crafts acylation of arene :

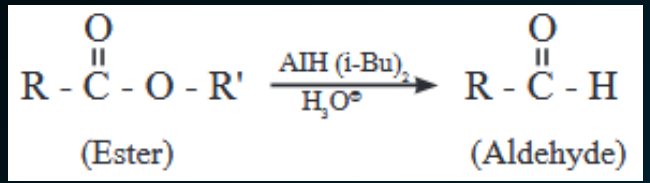




Preparation of aldehydes and ketones

- Preparation of aldehydes only from esters :

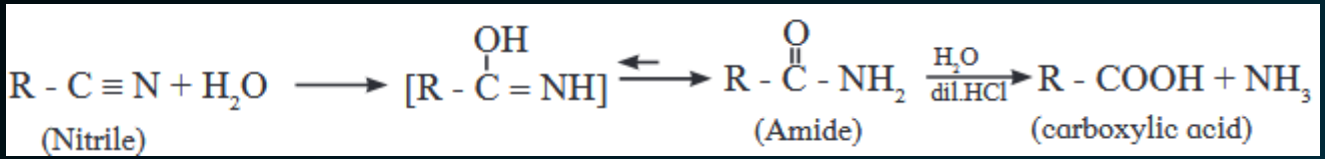
Aliphatic or aromatic esters are reduced to aldehydes by using diisobutylaluminium hydride DIBAl-H or $AlH(i\text{-}Bu)_2$. The reaction is usually carried out at 195K to prevent further reduction of the aldehyde produced.

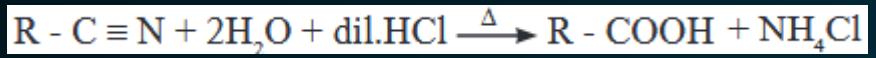


Preparation of carboxylic acids :

From nitriles and amides:

Alkyl nitriles or aryl nitriles on acid hydrolysis give amides . Amides on further acid hydrolysis give corresponding carboxylic acids. Hydrolysis is carried out by using dilute mineral acids like dilute sulfuric acid or dilute hydrochloric acid.

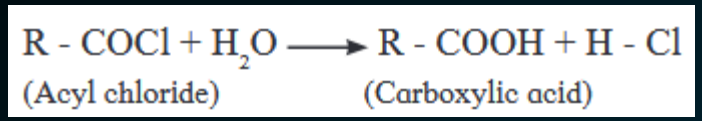




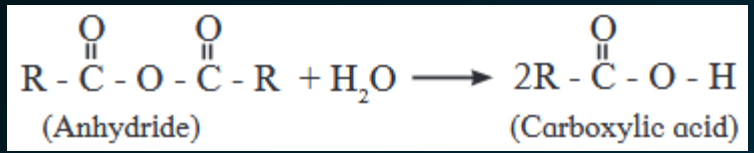
Preparation of carboxylic acids :

From acyl chloride and anhydrides:

a. Acyl chlorides on hydrolysis with water give carboxylic acids. This method is useful for preparation of aliphatic as well as aromatic acid.



b. Anhydrides on hydrolysis with water give carboxylic acids.

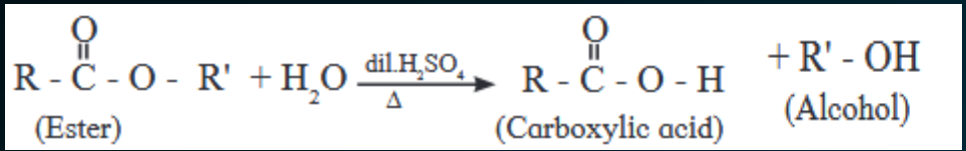


Preparation of carboxylic acids :

From esters :

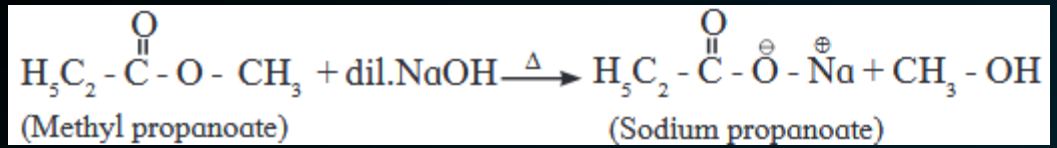
Carboxylic acids can be obtained from esters either by acid hydrolysis or alkaline hydrolysis.

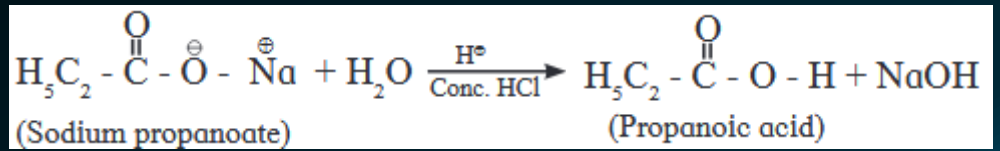
a. Acid hydrolysis of ester: Esters on hydrolysis with dilute mineral acid like dilute HCl or dilute H2SO4 give the corresponding carboxylic acid .



Preparation of carboxylic acids :

b. Alkaline hydrolysis of ester: using dilute alkali like dilute NaOH or dilute KOH form solution of water soluble sodium or potassium salt of the acid (carboxylate). On acidification with concentrated HCl, free acid is formed.

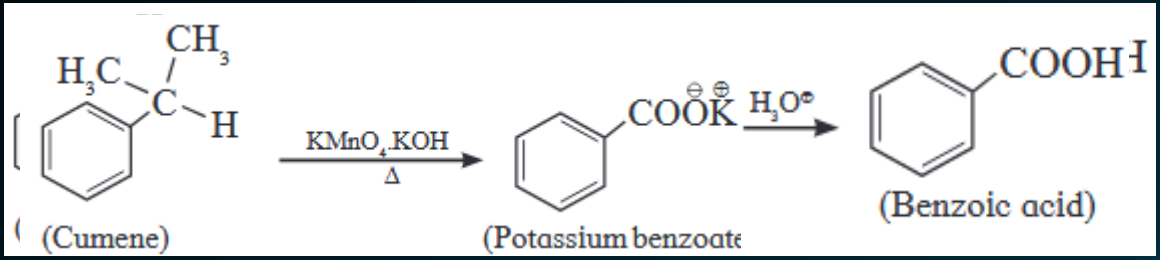




The sodium or potassium salts of higher fatty acids are known as soaps. Hence alkaline hydrolysis of esters is called <u>saponification.</u>

Preparation of carboxylic acids :

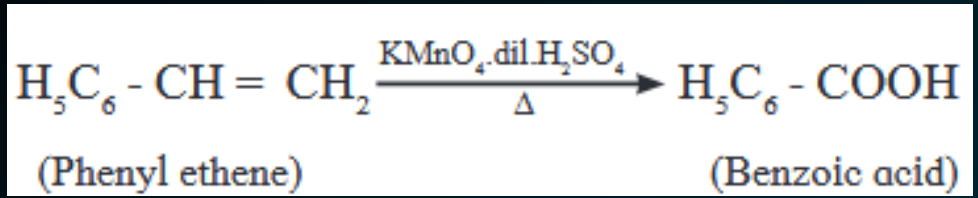
From alkyl benzene : Aromatic carboxylic acids can be prepared by oxidation of alkyl benzene with dilute HNO3 or alkaline /acidic KMnO4 or chromic acid. The entire alkyl chain, regardless of its length, is oxidized to a carboxyl group. (Tertiary alkyl substituent on benzene, however, is not oxidized).

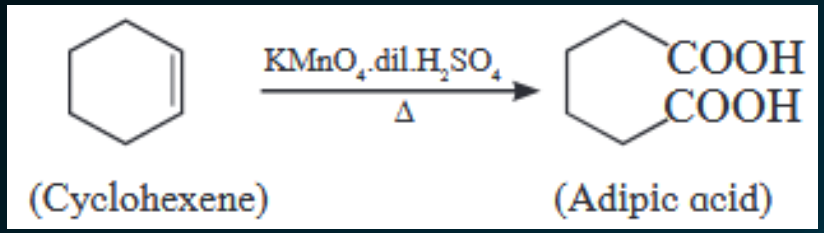


Preparation of carboxylic acids :

From alkenes:

Carboxylic acids can also be prepared by the oxidation of alkenes by KMnO4 in dilute H_2SO_4.

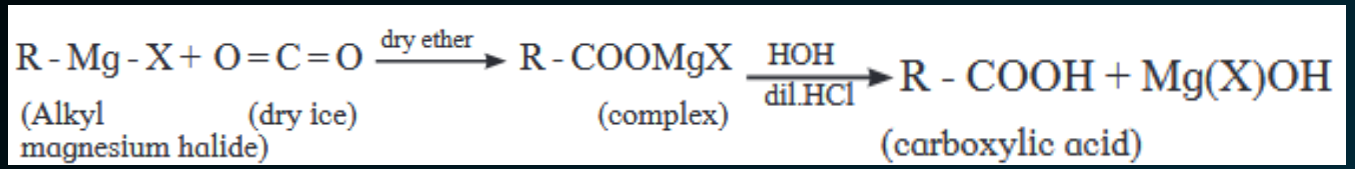




Preparation of carboxylic acids :

From Grignard reagent :

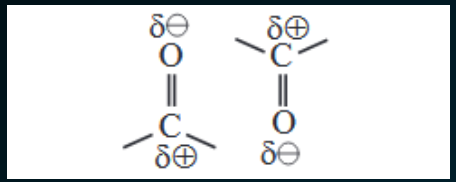
Grignard reagent in dry ether solvent is added to solid carbon dioxide (dry ice) to give a complex which on acid hydrolysis gives corresponding carboxylic acid.



Physical properties

1. Nature of intermolecular forces :

The carbonyl bond (C=O) in aldehydes and ketones is a polar covalent bond. As a result, these compounds contain dipole-dipole forces of attraction. The molecules orient in such a way as to have oppositely polarized atoms facing each other.



Carboxyl group of carboxylic acid contains O-H bond which is responsible for formation of hydrogen bonding. Thus, carboxylic acids have the strongest intermolecular forces of attraction.

Boiling points of aldehydes and ketones

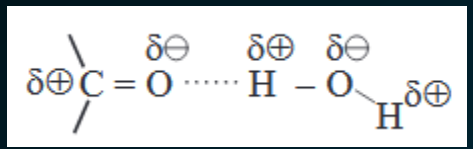
Number of carbon atoms	Aldehyde	Boiling point	Ketone	Boiling point
1	Methanal	252 K	-----	--------
2	Ethanal	294 K	-------	---------
3	Propanal	319 K	Propanone	329 K
4	Butanal	348 K	Butan -2-one	353 K
5	Pentanal	376 K	Pentan-2-one	375 K
6	Hexanal	392 K	Hexan-2-one	400 K

Physical state and boiling points

- Formaldehyde is a gas at room temperature and has irritating odour.
- Acetaldehyde is extremely volatile, colourless liquid.
- Higher aldehydes have pleasant odour.
- Acetone is a liquid at room temperature and has pleasant odour.
- Increasing boiling points in the homologous series of aldehydes and ketones.

Solubility of aldehydes and ketones

- The oxygen atom of (C=O) can involve in hydrogen bonding with water molecule. As a result of this, the lower aldehydes and ketones are water soluble (For example : acetaldehyde, acetone).
- As the molecular mass increases, the proportion of hydrocarbon part of the molecule increases which cannot form hydrogen bond; and the water solubility decreases.

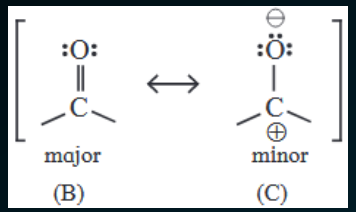


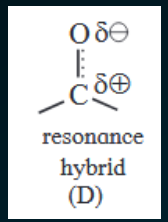
Physical state, boiling points and solubility's of carboxylic acids

- Lower aliphatic carboxylic acids upto nine carbon atoms are colourless liquids with irritating odours.
- The higher homologues are colourless, odourless wax like solids, have low volatility.
- Carboxylic acids have higher boiling points than those of alkanes, ethers, alcohols aldehydes and ketones of comparable mass.
- in liquid phase, carboxylic acids form dimer in which two molecules are held by two hydrogen bonds.

Polarity of carbonyl group

- The polarity of a carbonyl group originates from higher electronegativity of oxygen relative to carbon as well as resonance effects as shown





- The carbonyl carbon has positive polarity (see structures (A) and (D)). Therefore, it is electron deficient.
- As a result, this carbon atom is electrophilic (electron loving) and is susceptible to attack by a nucleophile (Nu:).

Reactivity of aldehydes and ketones

- Reactivity of aldehydes and ketones is due to the polarity of carbonyl group which results in electrophilicity of carbon.
- Aldehydes are more reactive than ketones toward nucleophilic attack.

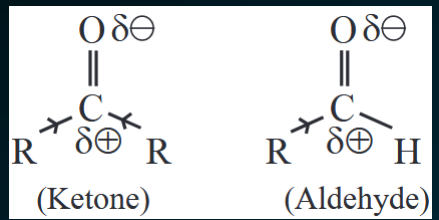
1. Influence of electronic effects :

- Alkyl groups have +I effect.
- A ketone has two +I groups, decreasing c=o`s elecropositivity.
- In contrast, aldehydes have only one electron donating group, bonded to carbonyl carbon.
- Hence aldehydes more electrophilic than ketones.

Reactivity of aldehydes and ketones

2. Steric effects :

- Two bulky alkyl groups in ketone come in the way of incoming nucleophile. This is called steric hindrance to nucleophilic attack.
- On the other hand, nucleophile can easily attack the carbonyl carbon in aldehyde, because it has one alkyl group and is less crowded or sterically less hindered.
- Hence, aldehyde are more easily attacked by nucleophiles.



Laboratory tests for aldehydes and ketones

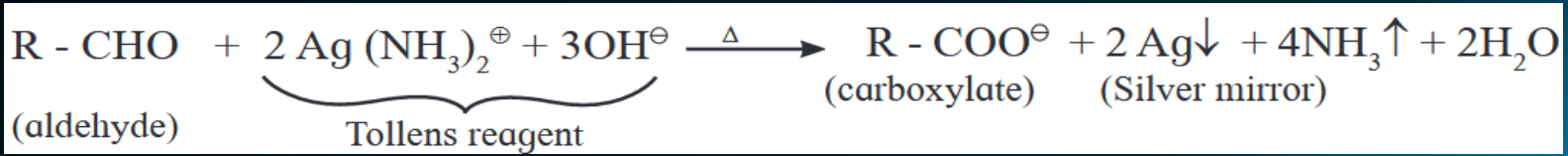
- Aldehydes are easily oxidized to carboxylic acids,
- therefore, act as reducing agents toward mild oxidizing agents.
- Ketones, do not have hydrogen atom directly attached to carbonyl carbon.
- Hence, they are not oxidized by mild oxidizing agents.

Laboratory tests for aldehydes and ketones

a. Tests given by only aldehydes :

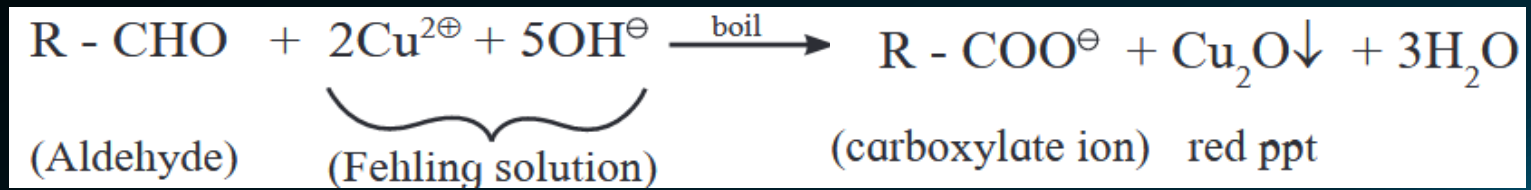
1. Schiff's test: When alcoholic solution of aldehyde is treated with few drops of Schiff 's reagent, pink or red or magenta colour appears. This confirms the presence of aldehydic (-CHO) group.

2. Tollens' test or silver mirror test: When an aldehyde is boiled with Tollens' reagent (ammonical silver nitrate), silver mirror is formed. The aldehyde is oxidized to carboxylate ion by Tollens' reagent and Ag^+ ion is reduced to Ag.



Laboratory tests for aldehydes and ketones

3. Fehling test: When a mixture of an aldehyde and Fehling solution is boiled in hot water, a red precipitate of cuprous oxide is formed. An aldehyde is oxidized to carboxylate ion by Fehling solution and $Cu_2^{\oplus}$ ion is reduced to $Cu^{\oplus}$ ion. It may be noted that α-hydroxy ketone also gives this test positive.



Chemical reactions of ald. and ket. with nucleophile

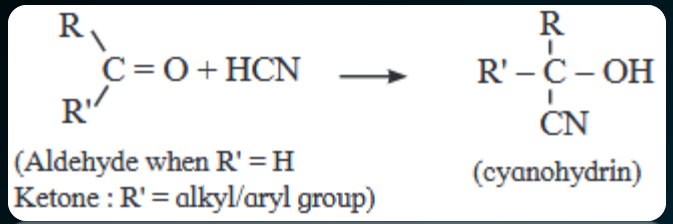
In all these reactions the nucleophilic reagent attacks on positively polarized electrophilic carbonyl carbon in aldehydes and ketones.

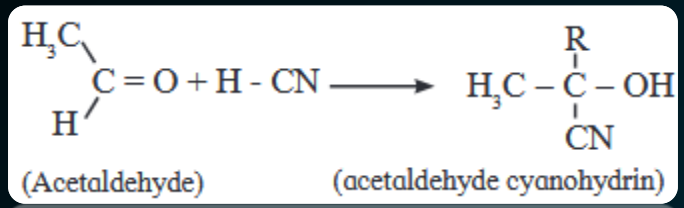
a. Addition of hydrogen cyanide (H-CN):

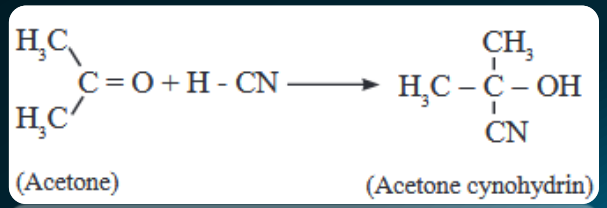
- Hydrogen cyanide (weak acid) adds across the carbon-oxygen double bond in aldehydes and ketones to produce compounds called cyanohydrins.

Chemical reactions of ald. and ket. with nucleophile

- The negative part of the reagent (CN) attacks the electrophilic carbon of carbonyl group. The reaction requires either acid or base as catalyst.



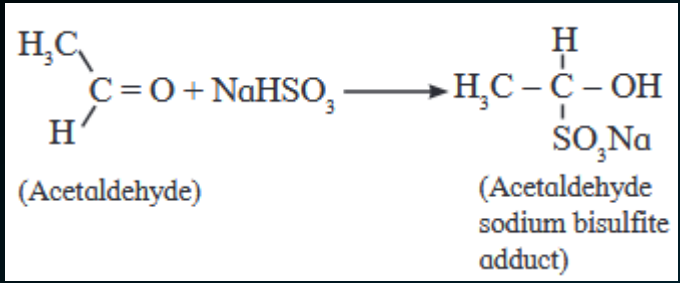


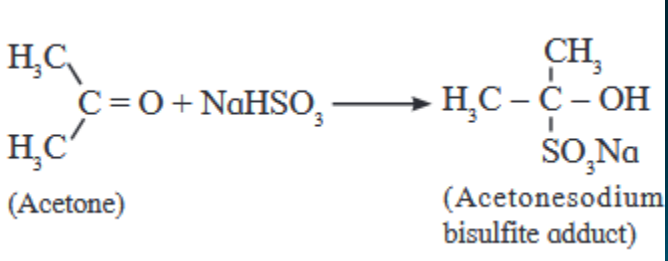


Chemical reactions of ald. and ket. with nucleophile

b. Addition of $NaHSO_3$ (Sodium bisulphite) :

- Aldehydes and ketones react with saturated aqueous solution of sodium bisulfite to give crystalline precipitate of sodium bisulfite adduct (addition compound). For example,

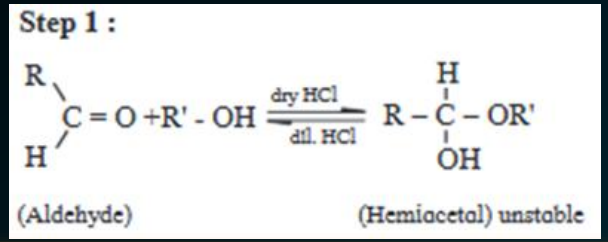




Chemical reactions of ald. and ket. with nucleophile

c. Addition of alcohols :

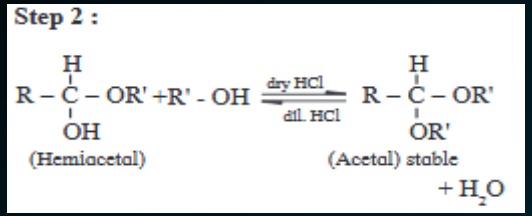
- Aldehyde reacts with one molecule of anhydrous monohydric alcohol in presence of dry hydrogen chloride to give alkoxyalcohol known as hemiacetal,

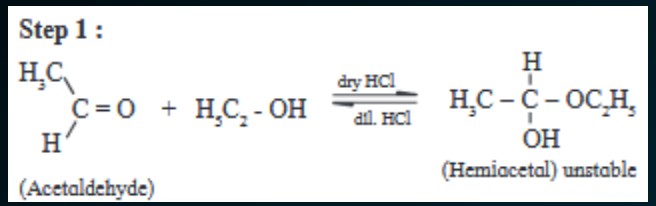


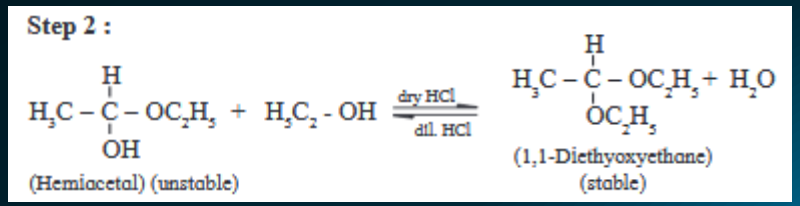
1. **Why is benzaldehyde NOT oxidized by Fehling solution?**
2. **Sodium bisulfite is sodium salt of sulfurous acid, write down its detailed bond structure.**

Chemical reactions of ald. and ket. with nucleophile

- which further reacts with one more molecule of anhydrous monohydric alcohol to give a geminaldialkoxy compound known as acetalas shown in the reaction.

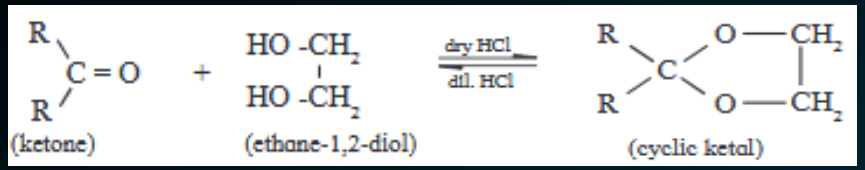






Chemical reactions of ald. and ket. with nucleophile

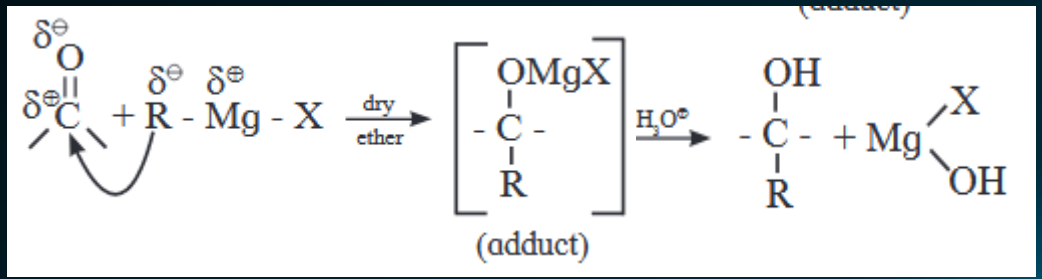
- Similarly, Ketones react with alcohol in presence of acid catalyst to form hemiketal and ketal.
- Ketones react with 1,2- or 1,3- diols in presence of dry hydrogen chloride to give five- or six -membered cyclic ketals .



- The reaction can be reversed by treating the cyclic ketal with aqueous HCl to regenerate the ketone.
- Acetals and ketals are hydrolysed with aqueous mineral acids to give corresponding aldehydes and ketones respectively.

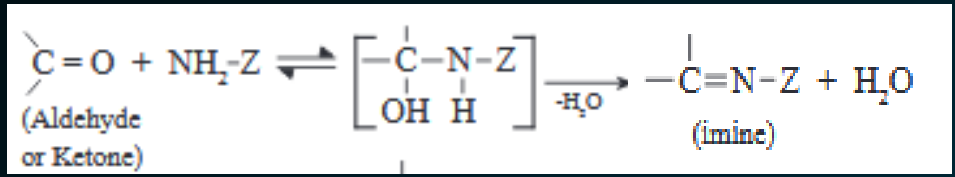
Chemical reactions of ald. and ket. with nucleophile

- d. Addition of Grignard reagent: Aldehydes and ketones on reaction with alkyl magnesium halide followed by acid hydrolysis give alcohols.(Refer to Chapter 11, sec. 11.4.1 d.)
- By addition of Grignard reagent to aldeheydes and ketones : Grignard reagent reacts with aldehyde or ketone to form an adduct which on hydrolysis with dilute acid gives the corresponding alcohols.



Chemical reactions of ald. and ket. with nucleophile

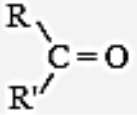
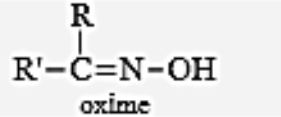
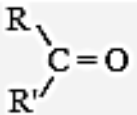
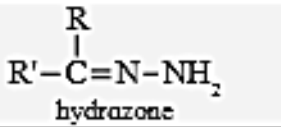
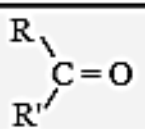
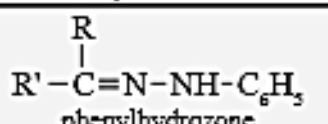
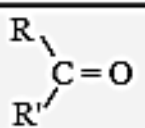
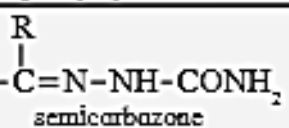
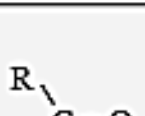
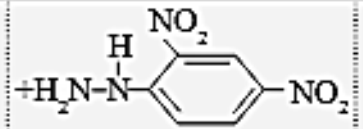
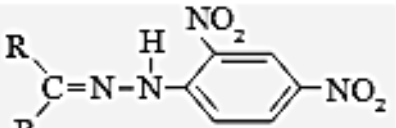
- e. Nucleophilic addition –elimination of aldehydes and ketones with ammonia derivatives: Aldehydes and ketones undergo addition elimination with some ammonia derivatives (NH2-Z) to give product containing C = N bonds (imines). The reaction is reversible and takes place in weakly acidic medium. The substituted imine is called a Schiff 's base.



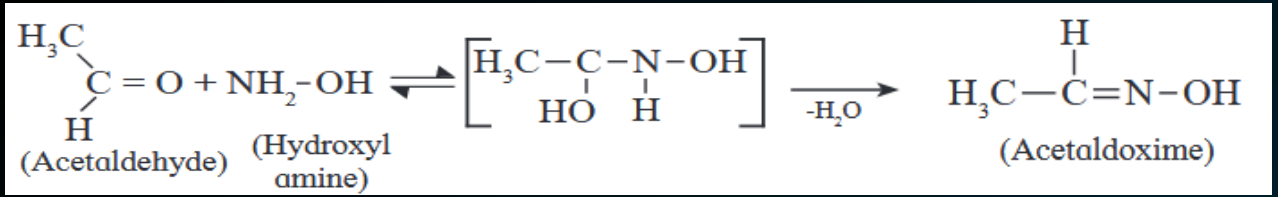
- Where Z = -R, -Ar, $-NH_2$, $-NHC_6H_5$, $-NHCONH_2$, $-NHC_6H_3(NO_2)_2$

Chemical reactions of ald. and ket. with nucleophile

- Nuc… …and keto…

Sr. No.	Aldehyde(R'=H)/ Ketone(R'≠H)	+ NH_2 - Z		imine (a crystalline derivative)
1.		+ NH_2-OH Hydroxyl amine	$\xrightarrow{-H_2O}$	 oxime
2.		+ NH_2-NH_2 Hydrazine	$\xrightarrow{-H_2O}$	 hydrazone
3.		+ NH_2-NH-C_6H_5 Phenyl hydrazine	$\xrightarrow{-H_2O}$	 phenylhydrazone
4.		+ NH_2-NH-$CONH_2$ Semicarbazide	$\xrightarrow{-H_2O}$	 semicarbazone
5.		 2, 4 - Dinitrophenyl hydrazine	$\xrightarrow{-H_2O}$	 2, 4 - Dinitrophenylhydrazone

Chemical reactions of ald. and ket. with nucleophile



- All aldehydes and ketones give similar reactions. The resulting products have high molecular mass and are crystalline solids.
- These reactions are, therefore, useful for characterization of the original aldehydes and ketones.

Draw the structures of

i. **The semicarbazone of cyclohexanone**
ii. **The imine formed in the reaction between**

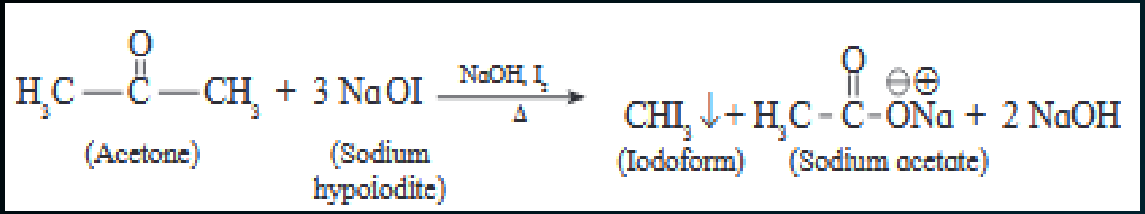
Chemical reactions of ald. and ket. with nucleophile

f. Haloform reaction :

- This reaction is given by acetaldehyde, all methyl ketones (CH_3-CO-R) and all alcohols containing CH_3-(CHOH)- group.
- When an alcohol or methyl ketone is warmed with sodium hydroxide and iodine, a yellow precipitate is formed.
- Here the reagent sodium hypoiodite is produced in situ.
- During the reaction, sodium salt of carboxylic acid is formed which contains one carbon atom less than the substrate.
- The methyl group is converted in to haloform.

Chemical reactions of ald. and ket. with nucleophile

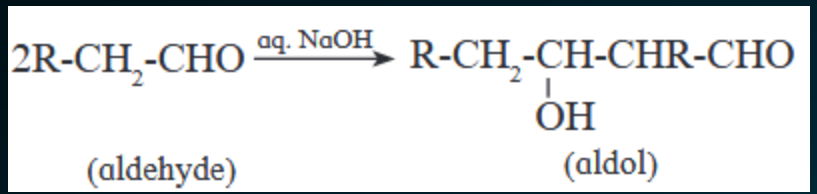
- For example : Acetone is oxidized by sodium hypoiodite to give sodium salt of acetic acid and yellow precipitate of iodoform.



Chemical reactions of ald. and ket. with nucleophile

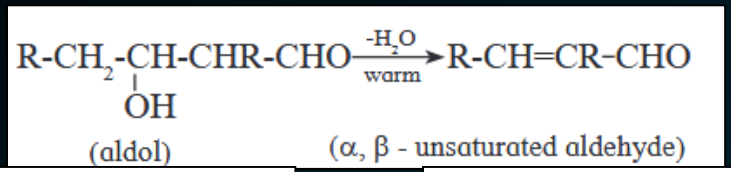
g. Aldol condensation :

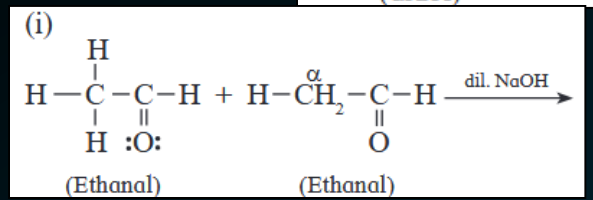
- Aldehydes containing at <u>least one α –hydrogen atom</u> undergo a reaction in presence of dilute alkali (dilute NaOH, KOH or Na_2CO_3) as catalyst to form b-hydroxy aldehydes (aldol). This reaction is known as aldol reaction.

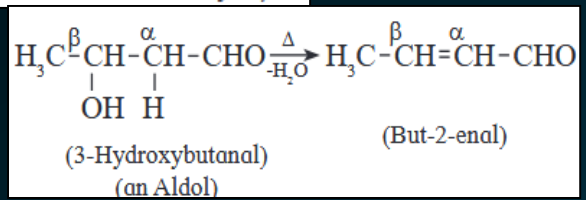


Chemical reactions of ald. and ket. with nucleophile

- Formation of aldol is an addition reaction. Aldol formed from aldehyde having α-hydrogens undergoes subsequent elimination of water molecule on warming, giving rise to α, b - unsaturated aldehyde.





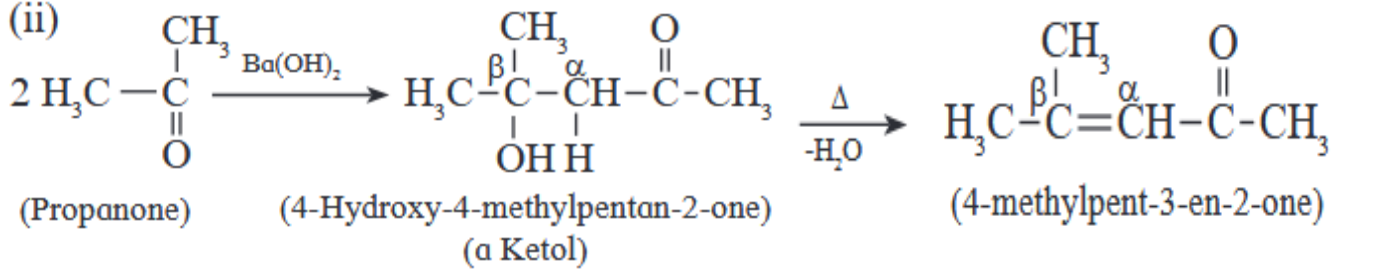


- The overall reaction is called aldol condensation. It is a nuclephilic addition-elimination reaction.

Chemical reactions of ald. and ket. with nucleophile

- Ketones containing at least two α- hydrogens, also undergo aldol condensation reaction and give an α, b - unsaturated ketone.

For example:

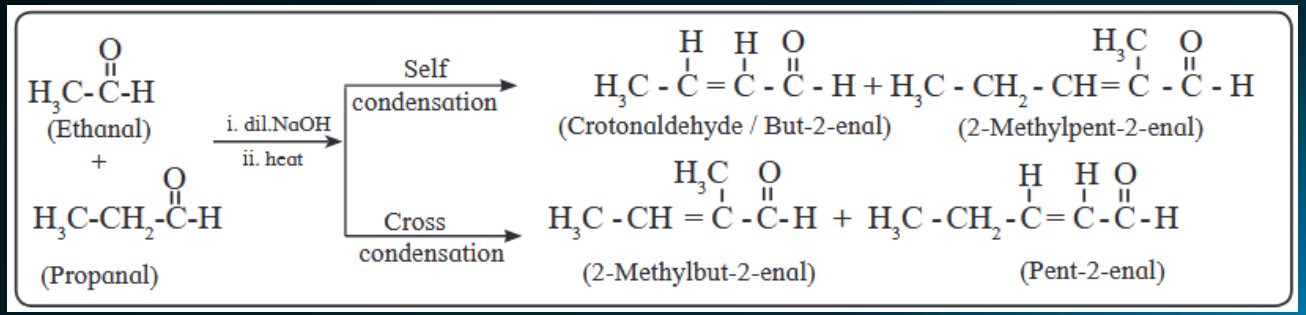


Chemical reactions of ald. and ket. with nucleophile

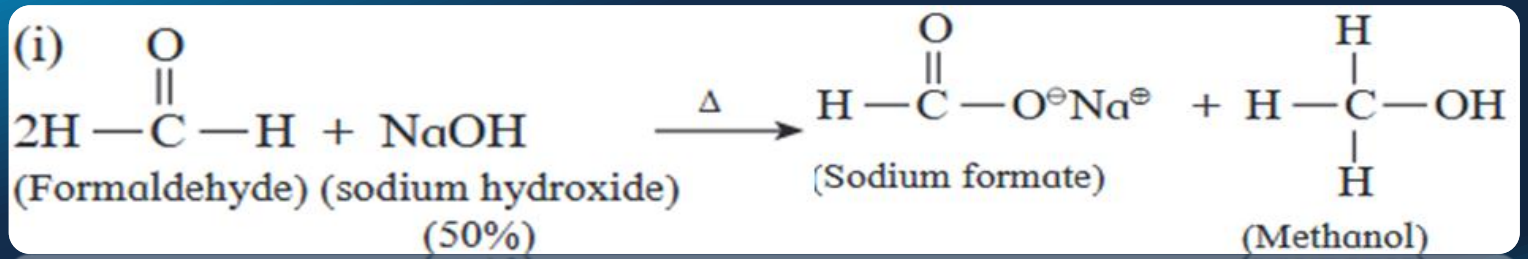
g'. Cross aldol condensation :

- Cross aldol condensation refers to the aldol condensation that takes place in between two different aldehydes or ketones .
- If both aldehydes or ketones contain two α-hydrogen atoms each, then a mixture of four products, is formed.

For example: a mixture of ethanal and propanal on reaction with dilute alkali followed by heating gives a mixture of four products



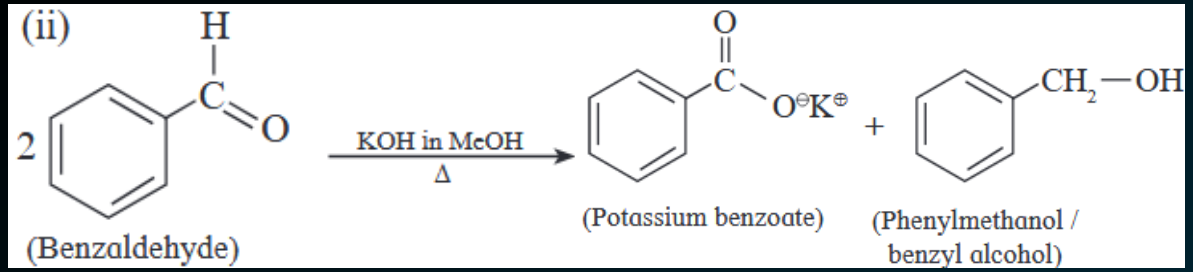
Chemical reactions of ald. and ket. with nucleophile



- In cannizzaro reaction one molecule of an aldehyde is reduced to alcohol and at the same time second molecule is oxidized to carboxylic acid salt.

Chemical reactions of ald. and ket. with nucleophile

- For example, Formaldehyde and benzaldehyde

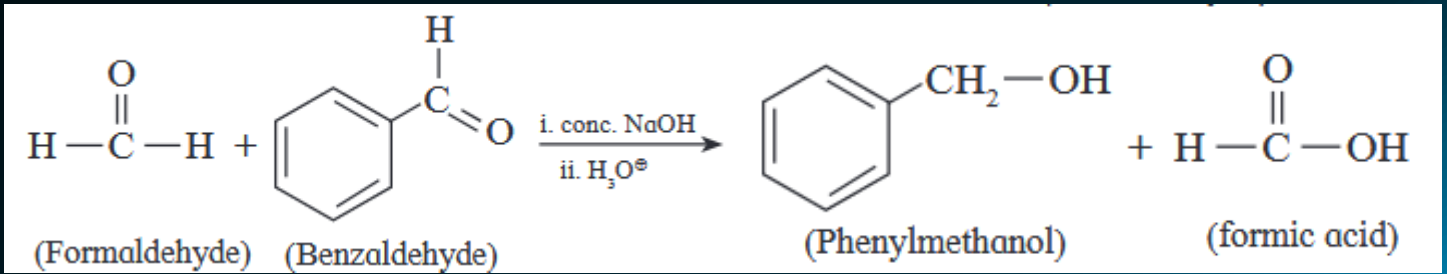


➢ **Can isobutyraldehyde undergo Cannizzaro reaction ? Explain.**

Chemical reactions of ald. and ket. with nucleophile

h`. Cross Cannizzaro reaction: When a mixture of formaldehyde and non-enolisable aldehyde (aldehyde with no α-hydrogen) is treated with a strong base, formaldehyde is oxidized to formic acid while the other non-enolisable is reduced to alcohol. Formic acid forms sodium formate with NaOH. On acidification sodium formate is converted into formic acid.

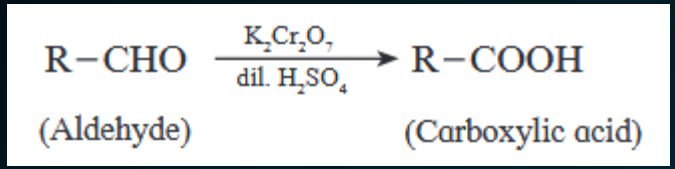
For example :



Oxidation and reduction reactions of aldehydes and ketones ;

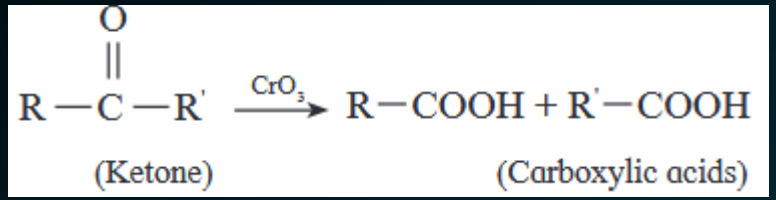
a. Oxidation of aldehydes and ketones by dilute HNO3, KMnO4 and K2Cr2O7:

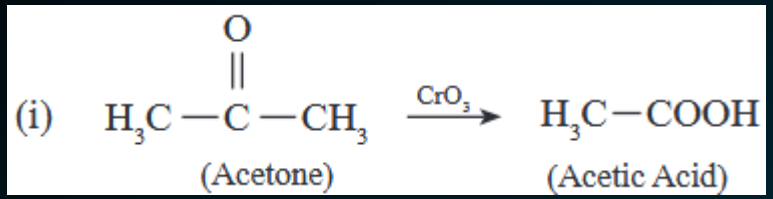
Aldehydes are oxidized to the corresponding carboxylic acids by oxidant such as dilute nitric acid, potassium permanganate and sodium or potassium dichromate in acidic medium.

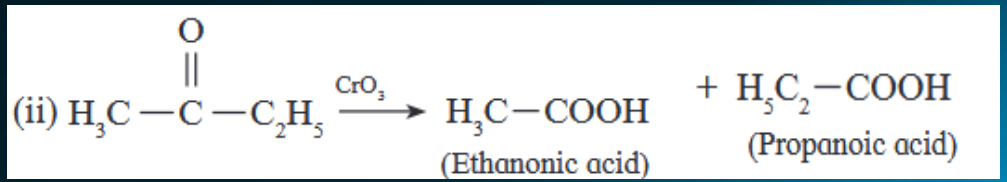


Oxidation and reduction reactions of aldehydes and ketones ;

- Ketones resist oxidation due to strong CO-C bond ,but they are oxidized by strong oxidizing agents such as CrO_3, alkaline KMnO4 or hot concentrated HNO_3 to a mixture of carboxylic acids having less number of carbon atoms than the starting ketone. Thus, Oxidation of ketones is accompanied by breaking C - C bond.







Oxidation and reduction reactions of aldehydes and ketones ;

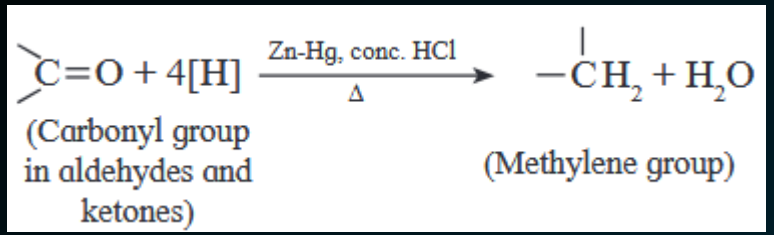
b. Clemmensen and Wolf-Kishner reduction:

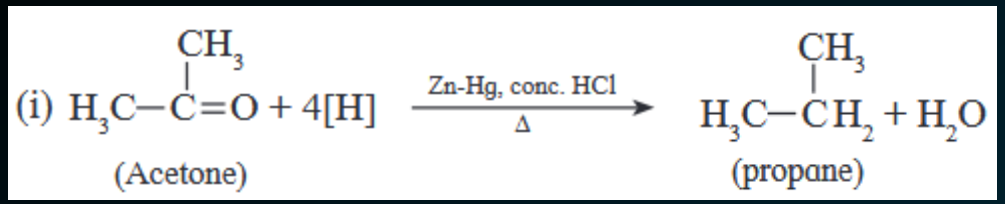
The carbonyl group of aldehydes and ketones is reduced to methylene group (-CH2-) on treatment with zinc –amalgam and concentrated hydrochloric acid (Clemmensen reduction) or hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent like ethylene glycol (Wolf-Kishner reduction).

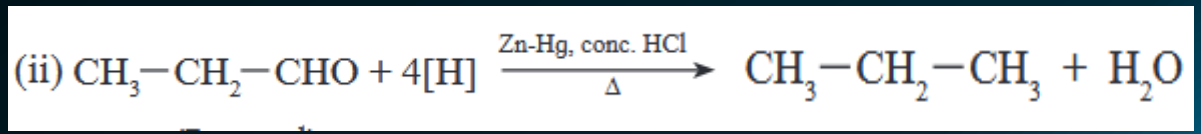
In both the reactions, oxygen is replaced by two hydrogen atoms.

Oxidation and reduction reactions of aldehydes and ketones ;

- Clemmensen reduction :

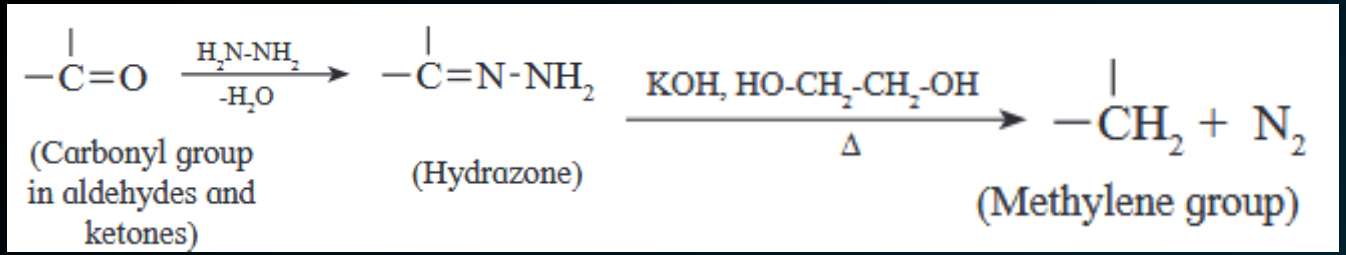


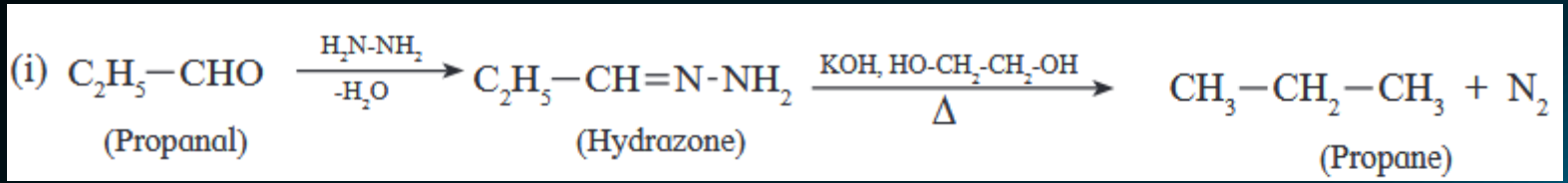




Oxidation and reduction reactions of aldehydes and ketones ;

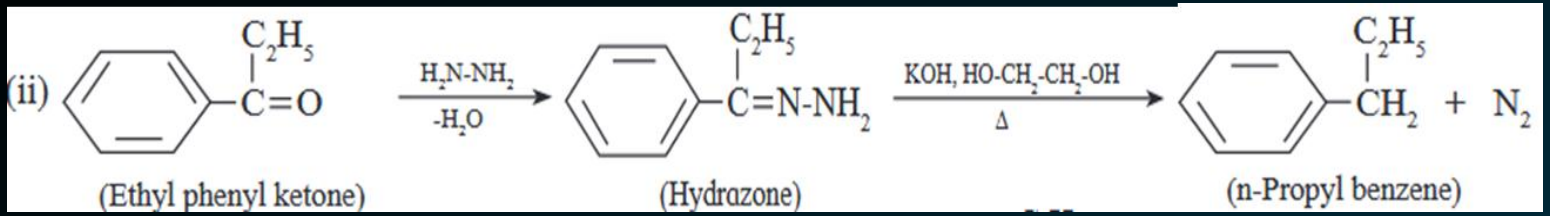
- Wolf-Kishner reduction :





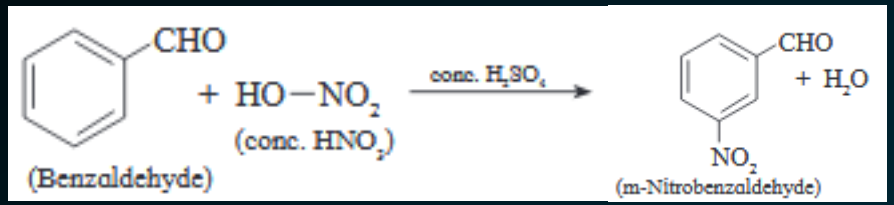
Oxidation and reduction reactions of aldehydes and ketones ;

- Wolf-Kishner reduction is used to synthesize straight chain alkyl substituted benzenes which is not possible by Friedel-Crafts alkylation reaction.



Electrophilic substitution reactions:

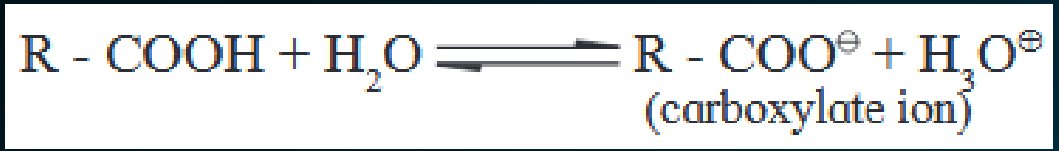
- Aromatic aldehydes and ketones undergo electrophilic substitution reactions such as nitration, Sulfonation and halogenation. The aldehydic (-CHO) and ketonic (>C=O) groups are electron-withdrawing by inductive as well as resonance effects. They deactivate the benzene ring at ortho- and para- positions. This results in the formation of meta-product.
- For example ,



Chemical properties of carboxylic acids :

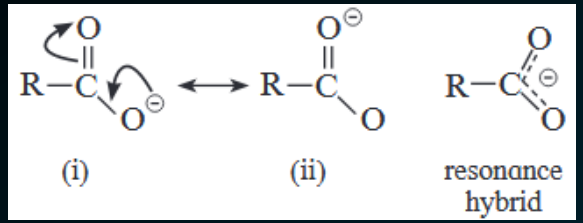
Acidic character of carboxylic acids:

- The carboxyl group (- COOH) imparts acidic character to carboxylic acids. A carboxyl group is made of -OH group bonded to a carbonyl group. In aqueous solution the H atom in OH of carboxyl group dissociates as proton and carboxylate ion is formed as the conjugate base,



Chemical properties of carboxylic acids :

- Carboxylate ion is resonance stabilized by two equivalent resonance structures as shown below.



- Carboxylate ion has two resonance structures (i) and (ii) and both of them are equivalent to each other.
- This gives good resonance stabilization to carboxylate ion, which in turn gives acidic character to carboxylic acids.

Chemical properties of carboxylic acids :

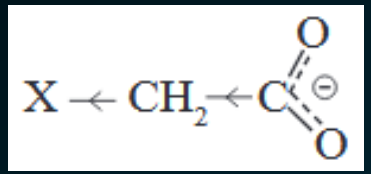
Influence of electronic effects on acidity of carboxylic acids:

- All the carboxylic acids do not have the same pKa value. The structure of 'R' in R-COOH has influence on the acid strength of carboxylic acids. Various halo-acetic acids illustrate this point very well (Tables 12.8 and 12.9).

Acid	pK_a	Acid strength
$F\text{-}CH_2\text{-}COOH$	2.56	decreases ↓
$Cl\text{-}CH_2\text{-}COOH$	2.86	
$Br\text{-}CH_2\text{-}COOH$	2.90	
$I\text{-}CH_2\text{-}COOH$	3.18	
$CH_3\text{-}COOH$	4.76	

Chemical properties of carboxylic acids :

- Halogens are electronegative atoms and exert electron withdrawing inductive effect (-I effect). The negatively charged carboxylate ion in the conjugate base of halo-acetic acid gets stabilized by the -I effect of halogen. Which is responsible to diffuse the native charge.



- Higher the electronegativity of halogen greater is the stabilization of the conjugate base, stronger is the acid and smaller is the pKa value.

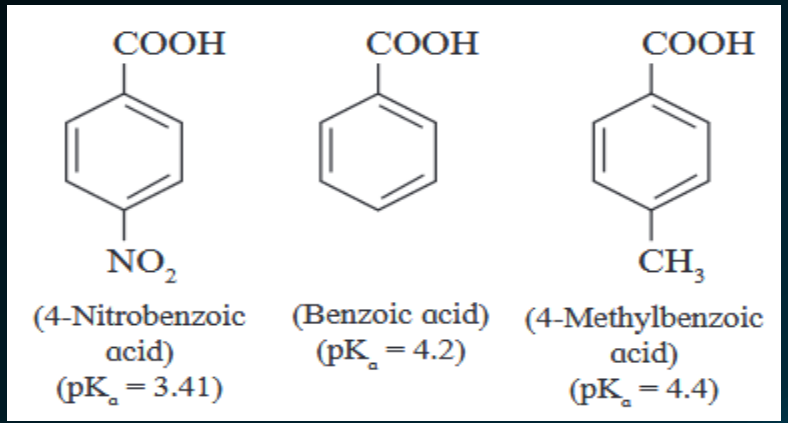
Chemical properties of carboxylic acids :

- Acidity of aromatic carboxylic acids :

Benzoic acid is the simplest aromatic acid. From the pKa value of benzoic acid (4.2) we understand that it is stronger than acetic acid (pKa 4.76). The sp2 hybrid carbon of aromatic ring exerts electron withdrawing inductive effect (-I effect) which stabilizes the conjugate base and increases the acid strength of aromatic acids. ***More the number of electron withdrawing substituents higher is the acid strength.***

Chemical properties of carboxylic acids :

- Electron–withdrawing groups like -Cl, -CN, and -NO2 increase the acidity of substituted benzoic acids while electron–donating group like $–CH_3$, - OH , - OCH_3 and -NH_2 decrease the acidity of substituted benzoic acids .



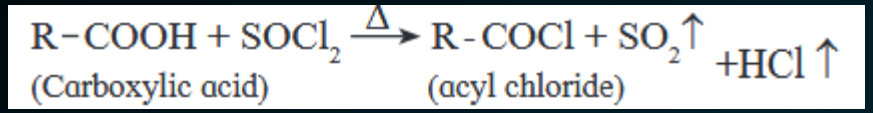
(4-Nitrobenzoic acid) ($pK_a = 3.41$)

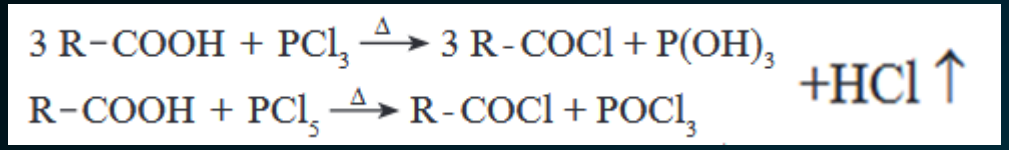
(Benzoic acid) ($pK_a = 4.2$)

(4-Methylbenzoic acid) ($pK_a = 4.4$)

Chemical properties of carboxylic acids :

- Formation of acyl chloride Reaction with PCl_3, PCl_5, $SOCl_2$: Carboxylic acids on heating with PCl_3, PCl_5, $SOCl_2$ give the corresponding acyl chlorides. Thionyl chloride ($SOCl_2$) is preferred because the byproducts formed are in gaseous state so they can easily escape from the reaction mixture. In this reaction –OH group of –COOH is replaced by –Cl.

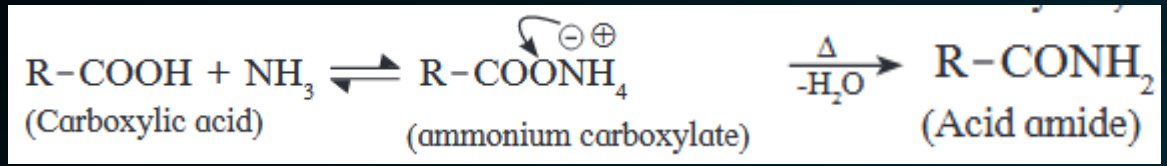




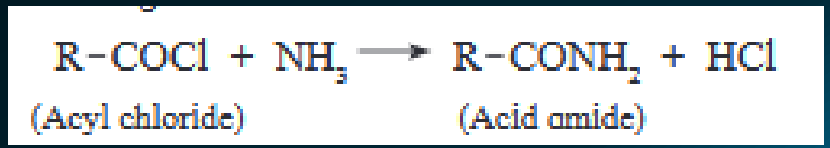
Chemical properties of carboxylic acids :

- Reaction with ammonia :
- Formation of amide :

Carboxylic acids react with ammonia to from ammonium carboxylate salt which on further strong heating at high temperature decomposes to give acid amide.

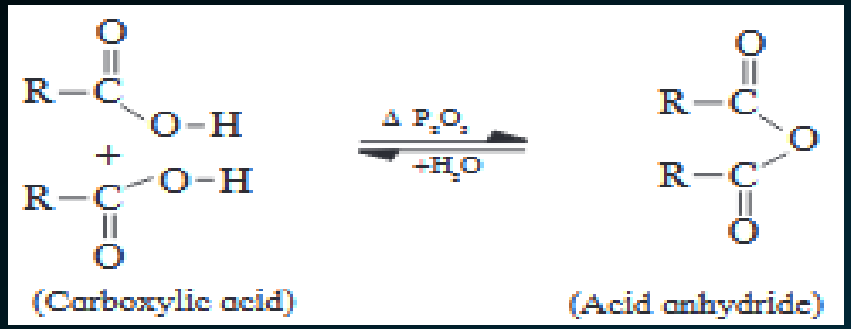


b. Acid amides can also be prepared by reacting acid chloride with ammonia.



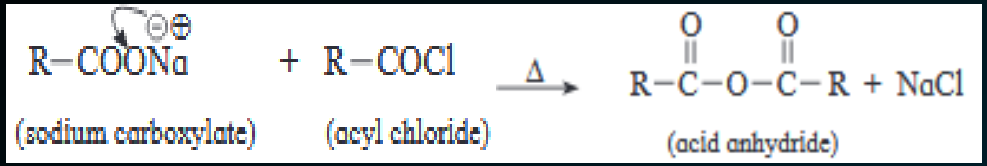
Chemical properties of carboxylic acids :

- Formation of acid anhydride :
- Mono carboxylic acids on heating with strong dehydrating agent like P2O5 concentrated H2SO4 give acid anhydrides. The reaction is reversible. Anhydrides are readily hydrolyzed back to acids on reaction with water.



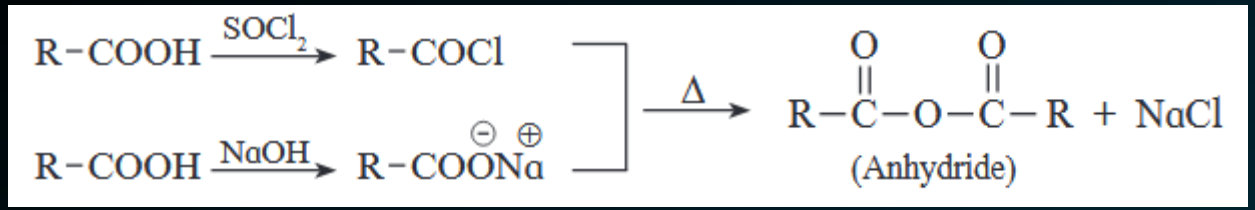
Chemical properties of carboxylic acids :

Better yield of acid anhydride is obtained by heating sodium carboxylate with acyl chloride.



Chemical properties of carboxylic acids :

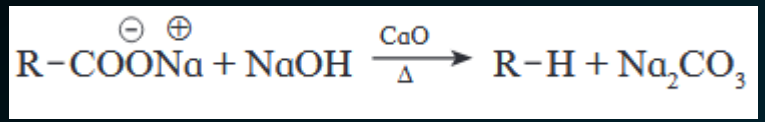
- Acyl chloride and sodium salt of acid are prepared by reacting carboxylic acid separately with thionyl chloride and sodium hydroxide respectively

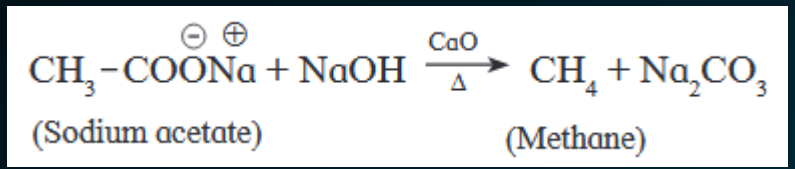


Chemical properties of carboxylic acids :

- Decarboxylation of carboxylic acids:

Sodium salts of carboxylic acids on heating with soda lime give hydrocarbons which contain one carbon atom less than the carboxylic acid. For example,

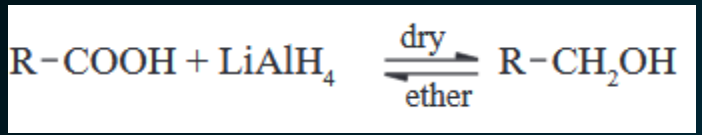




Chemical properties of carboxylic acids :

- Reduction of carboxylic acids :

Carboxylic acids are reduced to primary alcohols by powerful reducing agent like lithium aluminium hydride. Carboxylic acid can also be reduced by diborane
(diborane does not reduce –COOR , -NO_2 , -X).
(Note : Sodium borohydride ($NaBH_4$)does not reduce-COOH group).



Aldehyde, Ketones & Carboxylic Acids.

Thank You

Chemical properties of carboxylic acids :

Chemical properties of carboxylic acids :