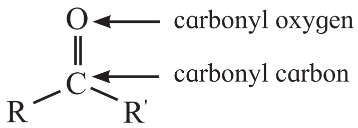
12. ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Can you recall ?

- Draw the structures of the following compounds and classify them on the basis of C-O single bond and C = O double bond present in them, Ethyl alcohol, acetaldehyde, o-nitrophenol, Diethyl ether, isopropyl alcohol, acetone.
- What are carbonyl compounds?

12.1 Introduction : In the previous chapter, you learnt about the organic compounds which contain carbon –oxygen single bond. In this chapter, we are going to study the organic compounds containing carbon - oxygen double bond (>C=O) called **carbonyl group**, which is one of the most important functional group in organic chemistry.



Both aldehydes and ketones contain a carbon –oxygen double bond $(-\underset{\underset{O}{\|}}{C}-)$ as their functional group. Therefore they are called carbonyl compounds. In aldehydes , carbonyl carbon is bonded to at least one hydrogen apart from an alkyl or aryl group. The functional group of aldehydes, therefore, is - CHO which is called **formyl group** or **aldehydic carbonyl group**. On the other hand in ketones, carbonyl carbon is bonded to two alkyl or aryl groups either identical (R = R) or different (R ≠ R'). It is called **ketonic carbonyl group**. The functional group of carboxylic acids is -COOH called **carboxyl group**. Due to the -OH group bonded to (>C=O) group, carboxylic acids are distinct from aldehydes and ketones.

12.2 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).

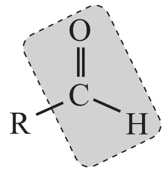
12.2.1 Classification of aldehydes :

(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 carbon atom that is saturated carbon 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 :

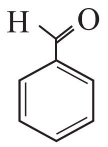
$CH_3 - CHO$ (Acetaldehyde)

$CH_3 - CH_2 - CHO$ (Propionaldehyde)

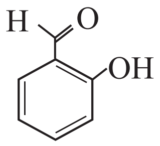


General formula
(R= H or alkyl group)

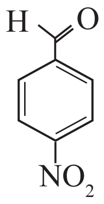
b. Aromatic aldehydes : The compounds in which –CHO group is attached directly to an aromatic ring are called aromatic aldehydes. For example :



(Benzaldehyde)



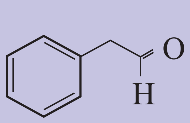
(Salicylaldehyde)

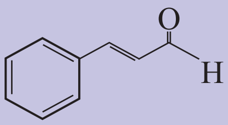


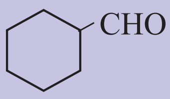
(p-Nitrobenzaldehyde)

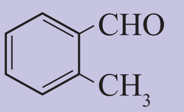
Use your brain power

Classify the following as aliphatic and aromatic aldehydes.





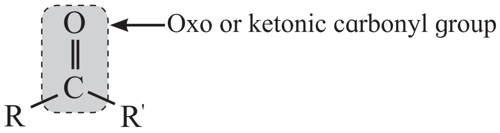




12.2.2 Classification of ketones :

Ketones are classified as aliphatic and aromatic ketones:

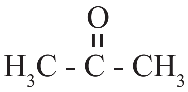
a. Aliphatic ketones : The compounds in which >C=O group is attached to two alkyl groups are called aliphatic ketones.



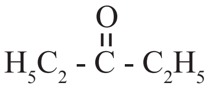
General formula
(Where R , R' = alkyl group, identical or different)

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

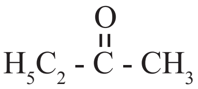

$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

(Dimethyl ketone) (Acetone)

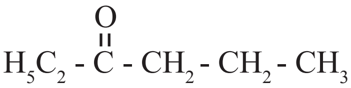

$H_5C_2-\overset{\overset{\displaystyle O}{\|}}{C}-C_2H_5$

(Diethyl ketone)

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 :

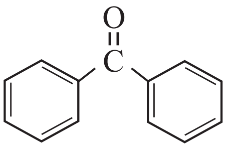

$H_5C_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

(Ethyl methyl ketone)

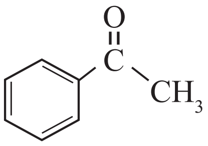

$H_5C_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_2-CH_3$

(Ethyl n-propyl ketone)

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)



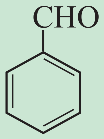
Acetophenone
(Methyl phenyl ketone)

Use your brain power

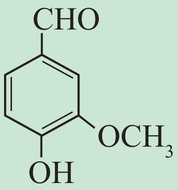
- Classify the followings as simple and mixed ketones.
- Benzophenone, acetone, butanone, acetophenone.

Do you know ?

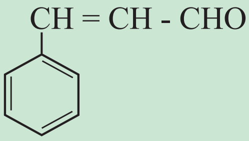
- Aldehydes and ketones are responsible for many flavours and odours that you will readily recognize :



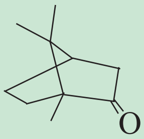
Benzaldehyde
(Bitter almond flavour)



Vanillin
(Vanilla flavour)



Cinnamaldehyde
(Cinnamon flavour)



Camphor
(Camphor fragance)

- Structures of many important biological compounds contain carbonyl moiety. For example progesterone and testosterone, the female and male sex hormones respectively.

Do you know ?

- Butyraldehyde is used in margarine and food for its buttery odour.
- Acetophenone has smell of pistachio and is used in ice-cream. Muscone has musky aroma and is used in perfumes. Popcorn has butter flavour which contains butane-2,3-dione.

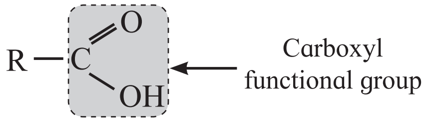
12.2.3 Classification of carboxylic acids :

Carboxylic acids are classified as aliphatic and aromatic carboxylic acids :

a. Aliphatic carboxylic acids : The organic compounds in which 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)



General formula
(R= H or alkyl group)

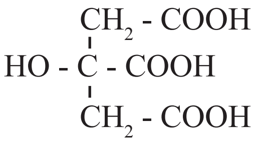
Depending on the number of –COOH groups present carboxylic acids are classified as mono, di, tri carboxylic acids and so on. For example :

$H_3C - CH_2 - COOH$

Propionic acid
(a monocarboxylic acid)

$$\begin{array}{c} COOH \\ | \\ COOH \end{array}$$

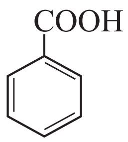
Oxalic acid
(a dicarboxylic acid)



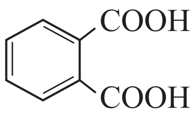
$$\begin{array}{rl} & CH_2 - COOH \\ & | \\ HO - & C - COOH \\ & | \\ & CH_2 - COOH \end{array}$$

Citric acid
(a tricarboxylic acid)

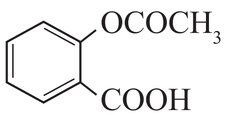
b. Aromatic carboxylic acids : These are the compounds in which one or more carboxyl groups (-COOH) are attached directly to the aromatic ring. For example :



(Benzoic acid)



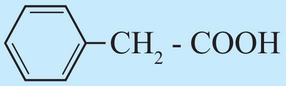
(Phthalic acid)



(Acetyl salicylic acid) (Aspirin)

Remember...

The aromatic compounds in which the –COOH group is not attached directly to the ring are called side-chain aromatic acids. For example :



(Phenyl acetic acid)

Carboxylic acids are widely distributed in nature; they 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.

12.3 Nomenclature of aldehydes, ketones and carboxylic acids :

12.3.1 Nomenclature of aldehydes and carboxylic acid :

The names of aldehydes and carboxylic acids are related to each other. There are two systems of naming aldehydes and carboxylic acids : trivial and IUPAC.

a. Trivial names of aldehydes and carboxylic acids : Trivial names of aliphatic aldehydes are derived from the corresponding trivial names of carboxylic acids. Here the ending 'ic acid' of carboxylic acid is replaced by the ending 'aldehyde'. In case of substituted aliphatic 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. (See Table 12.1).

Do you know ?

A series of straight chain dicarboxylic acids are commercially known by the following common names:

$COOH$ $COOH$	$COOH$ CH_2 $COOH$	$COOH$ $(CH_2)_2$ $COOH$	$COOH$ $(CH_2)_3$ $COOH$	$COOH$ $(CH_2)_4$ $COOH$
(oxalic acid)	(malonic acid)	(succinic acid)	(glutaric acid)	(adipic acid)

A series of lower fatty acids are commercially known by the following common names.

CH_3 $COOH$	CH_3 CH_2 $COOH$	CH_3 $(CH_2)_2$ $COOH$	CH_3 $(CH_2)_3$ $COOH$	CH_3 $(CH_2)_4$ $COOH$
(Acetic acid)	(n-propionic acid)	(n-butyric acid)	(n-valeric acid)	(n-caproic acid)

b. IUPAC names of aldehydes and carboxylic acids :

Can you recall ?

Which suffix do appear in the IUPAC names of aldehydes and carboxylic acids ?

According to IUPAC system, the name of an aliphatic aldehyde is derived from the name of the corresponding alkane by replacing ending 'e' of alkane with ' al '. Aldehyde is named as **alkanal** (Table 12.1). The IUPAC name of **aliphatic carboxylic acid** is derived from the name of the corresponding alkane by replacing ending ' e' of alkane with ' oic acid '. (Refer to Std. XI Chemistry Textbook sec. 14.4.7).

Alkane ⟶ Alkanal

Alkane ⟶ Alkanoic acid

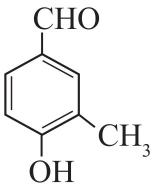
The longest chain including –CHO or –COOH group is identified as the parent chain. Numbering of the chain is done by giving number 1 to the –CHO or –COOH carbon. The name of substituent is included along with its locant.

$^4CH_3\text{-}^3CH_2\text{-}^2CH_2\text{-}^1CHO$; $^4CH_3\text{-}^3CH_2\text{-}^2CH_2\text{-}^1COOH$

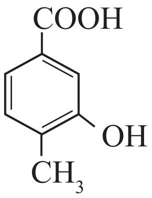
Aldehyde (-CHO) group and carboxyl (-COOH) group are always present at the end of the parent straight chain.

When two –CHO groups are present at the two ends of the chain the ending 'e'of alkane is retained and the suffix –'**dial**' is added to the name of parent aldehyde. In case of dicarboxylic acids, '**dioic acid**' is added to the name of the parent alkane. In IUPAC nomenclature an **alicyclic compound** in which –CHO group is attached directly to the ring is named as a **carbaldehyde**. The suffix 'carbaldehyde' 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**.

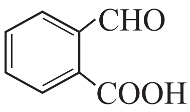
Substituted aromatic aldehydes and carboxylic acids : When two or more different functional groups are attached to a ring , the higher priority group (std. XI Chemistry Textbook, Chapter 14, sec.14.4.7) is given lower number. When –CHO group, appears as substituent prefix 'formyl' is used in the IUPAC name.



(4-Hydroxy-3-methylbenzaldehyde)



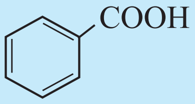
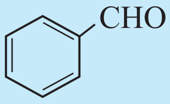
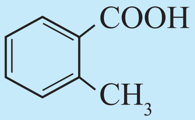
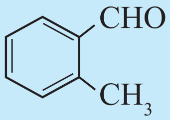
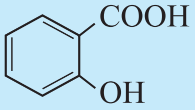
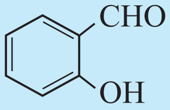
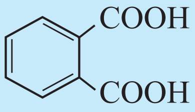
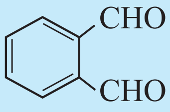
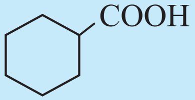
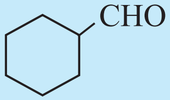
(3-Hydroxy-4-methylbenzoic acid)



(2-Formylbenzoic acid)

Trivial and IUPAC names of some aldehydes and carboxylic acids are given in Table 12.1.

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
$(CH_3)_2$CH - COOH	Isobutyric acid (α - methylpropionic acid)	2-Methylpropanoic acid	$(CH_3)_2$CH-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-dicarbaldehyde
	Cyclohexylcarboxylic acid	Cyclohexanecarboxylic acid		Cyclohexane aldehyde	Cyclohexanecarbaldehyde

Do you know ?

The trivial names of carboxylic acids are often derived from Latin names of their original natural source.

For example, Formic acid is obtained from red ants (Formica means ant), acetic acid is obtained from acetum (acetum means vinegar), propionic acid is from basic fat (propion means first fat), butyric acid is from butter (butyrum means butter).

12.3.2 Trivial and IUPAC names of ketones:

a. 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.

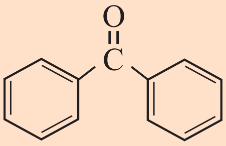
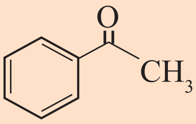
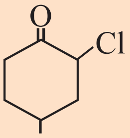
In case of substituted aliphatic ketones the position of substituent is indicated by labelling the carbon serially as α, β, γ and so on. The carbon atom adjacent to carbonyl carbon is labelled as α and next one is β and so on. Names of aromatic ketones are based on a phenone. (see Table 12.2)

b. The IUPAC names of aliphatic ketones are derived from the name of the corresponding alkanes by replacing ending 'e' of alkane with 'one'. They are named as **alkanone**. The longest chain of carbon atoms containing the ketonic carbonyl group is numbered from the end closer to the carbonyl carbon.

$$\textbf{Alkane} \longrightarrow \textbf{Alkanone}$$

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

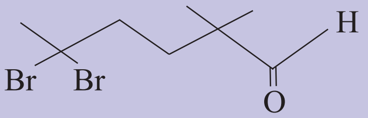
Table 12.2 Trivial and IUPAC names of some ketones

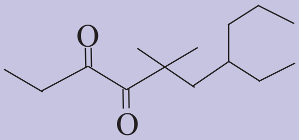
Sr.No.	Compound	Trivial name	IUPAC name
1	CH_3-CO-CH_3	Dimethyl ketone (Acetone)	Propanone
2	CH_3-CO-CH_2-CH_3	Ethyl methyl ketone	Butanone
3	CH_3-CO-CH_2-CH_2-CH_3	Methyl n-propyl ketone	Pentan-2-one
4	CH_3-CH_2-CO-CH_2-CH_3	Diethyl ketone	Pentan-3-one
5	CH_3-CHBr-CO-CH_2-CH_2-CH_3	α-Bromoethyln-propyl ketone	2-Bromohexan-3-one
6	$(CH_3)_2C$=CH-CO-CH_3	Mesityl oxide	4-Methylpent-3-en-2-one
7	CH_3-CO-CH_2-CO-CH_2-CH_3	---------------------	Hexane-2,4-dione
8	CH_3-CO-CH_2-CHO	---------------------	3-Oxobutanal
9		Diphenyl ketone (Benzophenone)	Benzophenone
10		Methyl phenyl ketone (Acetophenone)	Acetophenone
11		-----------------------	2-Chloro-4-methylcyclohexanone

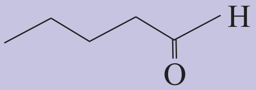
carbonyl groups. In case of polyfunctional ketones, higher priority group is given lower number. When ketonic carbonyl is a lower priority group it is named as 'oxo', preceded by the locant. In alicyclic ketones, carbonyl carbon is numbered as 1. (Refer Table 12.2).

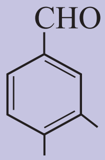
Use your brain power

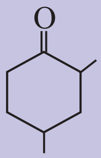
Write IUPAC names for the following compounds.

i.


ii.


iii.


iv.


v.


Try this...

Draw structures for the following

a. 2-Methylpentanal

b. Hexan-2-one

12.4 Preparation of aldehydes and ketones :

12.4.1 General methods of preparation of aldehydes and ketones :

a. By oxidation of alcohols : i. Aldehydes and ketones are prepared by the oxidation of primary and secondary alcohols respectively. (See Chapter 11)

Can you tell ?

What is the reagent which oxidizes primary alcohols to only aldehydes and does not oxidize aldehydes further into carboxylic acid ?

ii. By dehydrogenation of alcohols : This method has industrial application. Aldehydes and ketones are prepared by passing the vapours of primary and secondary alcohols respectively over hot copper powder. (See Chapter 11)

b. From hydrocarbons :

Can you recall ?

- What is ozonolysis ?
- What is the role of zinc dust in ozonolysis process?

i. By ozonolysis : Alkene reacts with ozone to give ozonide which on decomposition with zinc dust and water gives aldehyde and/or ketones. (See Std. XI Chemistry Textbook, Chapter 15)

ii. By hydration of alkynes : Alkynes react with water in presence of 40% sulfuric acid and 1% mercuric sulfate to give aldehydes or ketones. (See Std. XI Chemistry Textbook, Chapter 15)

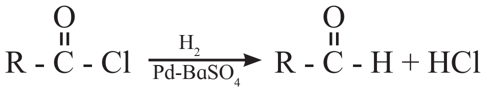
12.4.2 Other methods of preparation of aldehydes and ketones :

Some methods of preparation of aldehydes and ketones involve common starting functional groups but different types.

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**.



$$R-\overset{\overset{O}{\|}}{C}-Cl \xrightarrow[Pd\text{-}BaSO_4]{H_2} R-\overset{\overset{O}{\|}}{C}-H + HCl$$

(Acyl chloride) (Aldehyde)

Use your brain power

Write the structure of the product formed on Rosenmund reduction of ethanoyl chloride and benzoyl chloride.

Can you think ?

What is the alcohol formed when benzoyl chloride is reduced with pure palladium as the catalyst ?

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.

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

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

For example,

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

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

ii. Preparation of aromatic ketones from acyl chloride : Aromatic ketones are prepared by Friedel Craft's acylation reaction (Std. XI Chemistry Textbook, Chapter 15, sec. 15.4.6)

b. 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 hydrochloric acid which on acid hydrolysis give corresponding aldehydes. This reaction is called **Stephen reaction**.

$$\underset{\text{(Alkane nitrile)}}{R-C\equiv N} + 2[H] \xrightarrow{SnCl_2,\ HCl} \underset{\text{(imine hydrochloride)}}{R-HC=NH.HCl}$$

$$\xrightarrow{H_3O^{\oplus}} \underset{\text{(Aldehyde)}}{R-CHO + NH_4Cl}$$

For example,

$$\underset{\text{(Ethanenitrile)}}{H_3C-C\equiv N} + 2[H] \xrightarrow[\text{(reduction)}]{SnCl_2,\ HCl}$$

$$\underset{\text{(ethanimine hydrochloride)}}{CH_3-HC=NH.HCl} \xrightarrow{H_3O^{\oplus}} \underset{\text{(Ethanal)}}{CH_3\text{-}CHO} + NH_4Cl$$

$$\underset{\text{(Benzonitrile)}}{C_6H_5-C\equiv N} + 2[H] \xrightarrow{SnCl_2,\ HCl}$$

$$\underset{\text{(Benzanimine hydrochloride)}}{C_6H_5-HC=NH.HCl} \xrightarrow{H_3O^{\oplus}} \underset{\text{(Benzaldehyde)}}{C_6H_5\text{-}CHO} + NH_4Cl$$

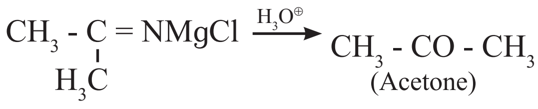
Alternatively, nitriles are also reduced by diisobutylaluminium hydride (DIBAl-H) or AlH (i-Bu)$_2$ to imines followed by acid hydrolysis to aldehydes. An advantage of this method is that double or triple bond present in the same molecule is not reduced..

$$\underset{\text{(Pent-3-enenitrile)}}{H_3C-CH=CH-CH_2-C\equiv N} \xrightarrow[H_3O^{\oplus}]{AlH\ (i\text{-}Bu)_2} \underset{\text{(Pent-3-enal)}}{H_3C-CH=CH-CH_2-CHO}$$

- **Preparation of ketones from nitriles :**

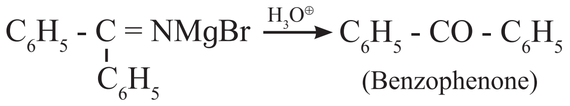
Ketones are prepared by reacting nitriles with Grignard reagent in dry ether as solvent followed by acid hydrolysis.

$$\underset{\text{(Ethanenitrile)}}{H_3C-C\equiv N} + H_3CMgCl \xrightarrow{\text{dry ether}}$$



$$\underset{\displaystyle H_3C}{CH_3-\underset{|}{C}=NMgCl} \xrightarrow{H_3O^{\oplus}} \underset{\text{(Acetone)}}{CH_3-CO-CH_3} + NH_3 + Mg(Cl)OH$$

$$\underset{\text{(Benzonitrile)}}{C_6H_5-C\equiv N} + C_6H_5-MgBr \xrightarrow{\text{dry ether}}$$



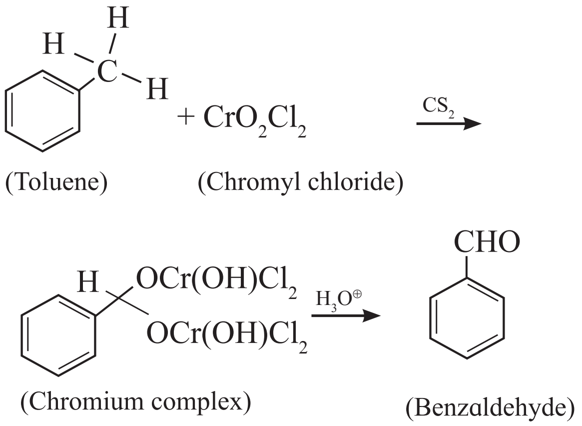
$$\underset{\displaystyle C_6H_5}{C_6H_5-\underset{|}{C}=NMgBr} \xrightarrow{H_3O^{\oplus}} \underset{\text{(Benzophenone)}}{C_6H_5-CO-C_6H_5} + NH_3 + Mg(Br)OH$$

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

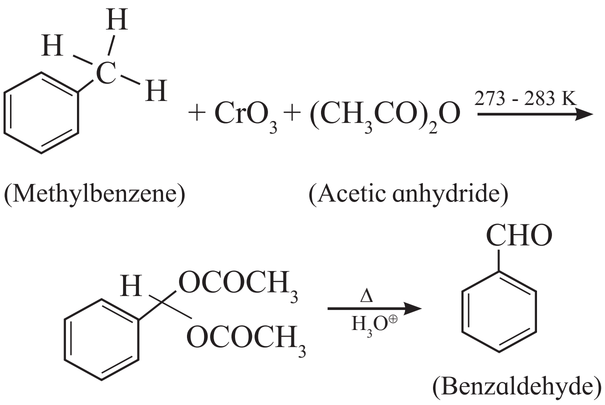
- **Preparation of aromatic aldehydes from hydrocarbon**

Strong oxidizing agents transform -CH_3 group bonded to aromatic ring into carboxyl group (-COOH). For obtaining aromatic aldehyde from methyl arene the following special methods are used.

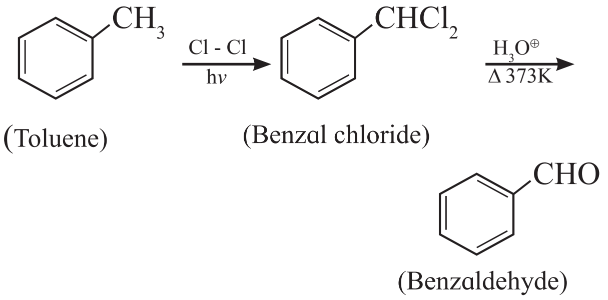
i. Etard reaction : Methyl group in methyl benzene (or methyl arene) is oxidized by oxidizing agent chromyl chloride in carbon disulfide as solvent, to form a chromium complex, from which the corresponding benzaldehyde is obtained on acid hydrolysis. This reaction is known as **Etard reaction**.



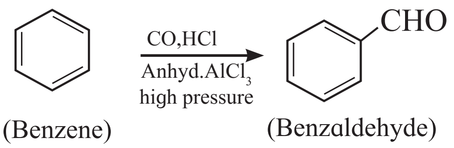
ii. By oxidation of methyl arene using CrO_3 : Methylarene is converted into a benzyllidene diacetate on treatment with chromium oxide in acetic anhydride at 273-278 K. The diacetate derivative on acid hydrolysis gives corresponding aldehyde.



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.



iv. 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 Aromatic ketones from hydrocarbons :**

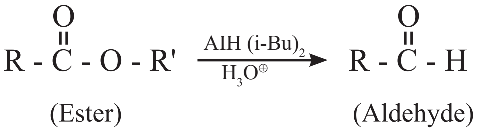
By Friedel-crafts acylation of arene : (Refer to sec. 12.4.2 (a) ii and Std. XI Chemistry Textbook, Chapter 15, sec. 15.4.6).

Use your brain power

Name the compounds which are used for the preparation of benzophenone by Friedel-Crafts acylation reaction. Draw their structures.

12.4.3 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 195 K to prevent further reduction of the aldehyde produced.



$$R-\overset{\overset{\large O}{\|}}{C}-O-R' \xrightarrow[H_3O^{\oplus}]{AlH\,(i\text{-}Bu)_2} R-\overset{\overset{\large O}{\|}}{C}-H$$

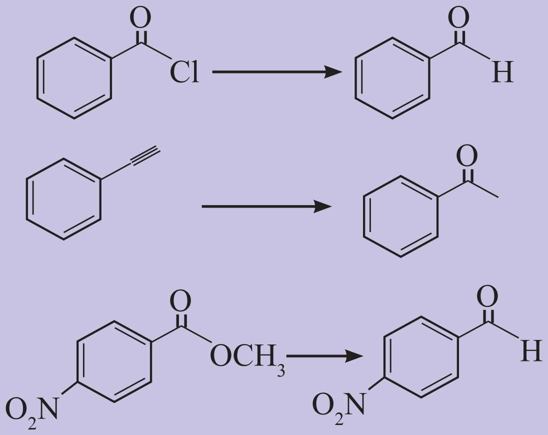
(Ester) (Aldehyde)

Try this...

Draw the structure of the product formed by the combination of carbon monoxide and HCl.

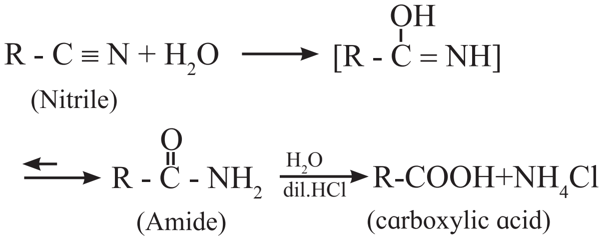
Use your brain power

Identify the reagents necessary to achieve each of the following transformation



12.5 Preparation of carboxylic acids :

12.5.1 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.



$$R-C\equiv N + H_2O \longrightarrow [R-\overset{OH}{\overset{|}{C}}=NH]$$

(Nitrile)

$$\rightleftarrows R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{dil.HCl}]{H_2O} R\text{-}COOH+NH_4Cl$$

(Amide) (carboxylic acid)

$$R-C\equiv N + 2H_2O + \text{dil.HCl} \xrightarrow{\Delta} R-COOH + NH_4Cl$$

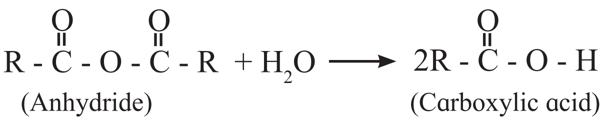
12.5.2 From acyl chloride and anhydrides :

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

$$R-COCl + H_2O \longrightarrow R-COOH + H-Cl$$

(Acyl chloride) (Carboxylic acid)

b. Anhydrides on hydrolysis with water give carboxylic acids.

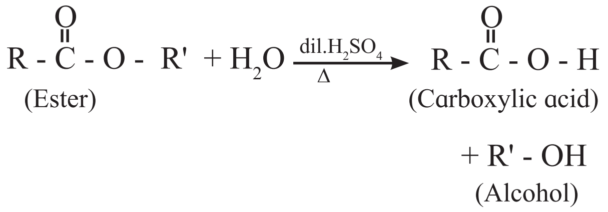


$$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + H_2O \longrightarrow 2R-\overset{O}{\overset{\|}{C}}-O-H$$

(Anhydride) (Carboxylic acid)

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

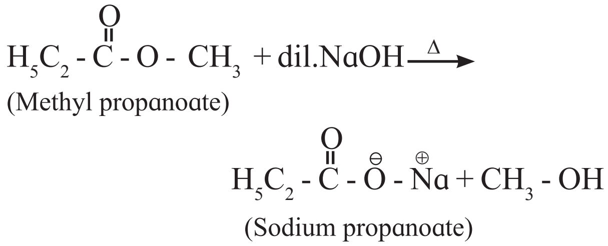
a. Acid hydrolysis of ester : Esters on hydrolysis with dilute mineral acid like dilute HCl or dilute H_2SO_4 give the corresponding carboxylic acid .



$$R-\overset{O}{\overset{\|}{C}}-O-R' + H_2O \xrightarrow[\Delta]{\text{dil.}H_2SO_4} R-\overset{O}{\overset{\|}{C}}-O-H + R'-OH$$

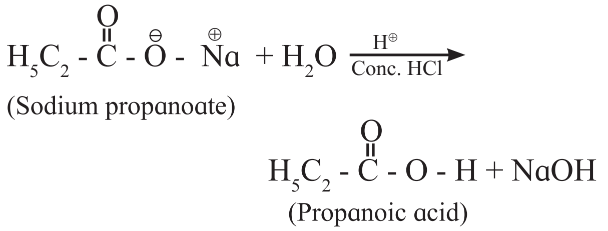
(Ester) (Carboxylic acid) (Alcohol)

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.



$$H_5C_2-\overset{O}{\overset{\|}{C}}-O-CH_3 + \text{dil.NaOH} \xrightarrow{\Delta} H_5C_2-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}-\overset{\oplus}{Na} + CH_3-OH$$

(Methyl propanoate) (Sodium propanoate)



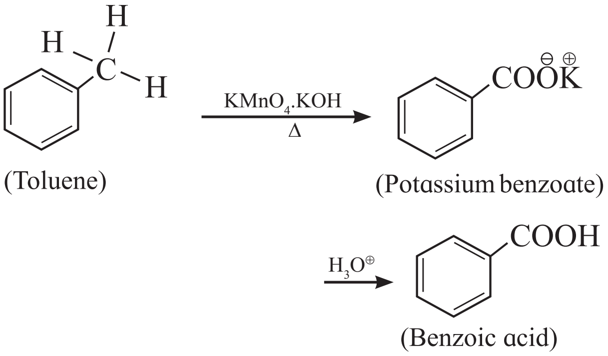
$$H_5C_2-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{O}-\overset{\oplus}{Na} + H_2O \xrightarrow[\text{Conc. HCl}]{H^{\oplus}} H_5C_2-\overset{O}{\overset{\|}{C}}-O-H + NaOH$$

(Sodium propanoate) (Propanoic acid)

The sodium or potassium salts of higher fatty acids are known as soaps. Hence alkaline hydrolysis of esters is called **saponification** (Std XI Chemistry Textbook, Chapter 16).

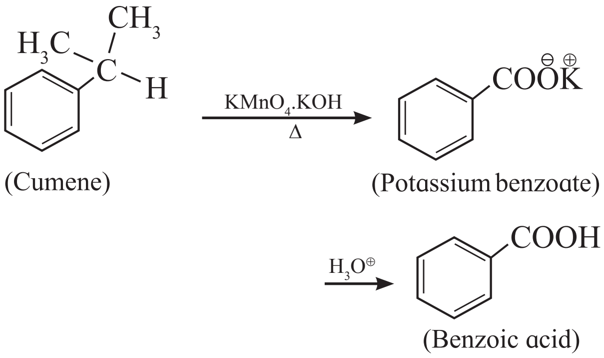
12.5.4 From alkyl benzene : Aromatic carboxylic acids can be prepared by oxidation of alkyl benzene with dilute HNO_3 or alkaline /acidic $KMnO_4$ or chromic acid. The entire alkyl chain, regardless of its length, is oxidized to a carboxyl group. (Tertiary alkyl substituent on benzene, however, is not oxidized).

For example,



(Toluene) (Potassium benzoate)

(Benzoic acid)



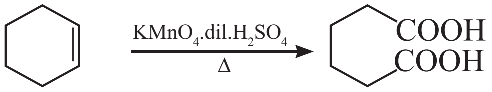
(Cumene) (Potassium benzoate)

(Benzoic acid)

12.5.5 From alkenes : Carboxylic acids can also be prepared by the oxidation of alkenes by $KMnO_4$ in dilute H_2SO_4.

$$H_5C_6 - CH = CH_2 \xrightarrow[\Delta]{KMnO_4.\text{dil.}H_2SO_4} H_5C_6 - COOH$$

(Phenyl ethene) (Benzoic acid)



(Cyclohexene) (Adipic acid)

12.5.6 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.

$$R - Mg - X + O = C = O \xrightarrow{\text{dry ether}} R - COOMgX$$

(Alkyl magnesium halide) (dry ice) (complex)

$$\xrightarrow[\text{dil.HCl}]{\text{HOH}} R - COOH + Mg(X)OH$$

(carboxylic acid)

Internet my friend

Collect information of dry ice and ice from internet. Draw chemical structures of dry ice and regular ice. Prepare a chart of uses of dry ice.

Use your brain power

Predict the products (name and structure) in the following reactions.

$CH_3CH_2CN \xrightarrow[\text{dil. HCl}]{\Delta} ?$

$CH_3\text{-}CONH_2 \xrightarrow[\text{dil. HCl}]{\Delta} ?$

$C_6H_5\text{-}CH_2\text{-}CH_3 \xrightarrow[\Delta]{\text{alk.}KMnO_4} ?$

$C_6H_5\text{-}COO\text{-}C_2H_5 \xrightarrow[\text{dil. }H_2SO_4]{\Delta} ?$

$CH_3MgBr \xrightarrow[\text{(ii) dil. HCl}]{\text{(i) dry ice/dry ether}} ?$

12.6 Physical properties :

12.6.1 Nature of intermolecular forces :

The carbonyl bond ($\gt C{=}O$) in aldehydes and ketones is a polar covalent bond. As a result, these compounds contain dipole-dipole forces of attraction. (Fig. 12.1) The molecules orient in such a way as to have oppositely polarized atoms facing each other.

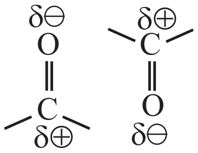


Fig. 12.1 Dipole-dipole attraction in carbonyl compounds

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. (Fig.12.3 in section 12.6.4).

Table 12.4 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

12.6.2 Physical state and boiling points of aldehydes and ketones :

Formaldehyde is a gas at room temperature and has irritating odour. **Acetaldehdye** is extremely volatile, colourless liquid. Higher aldehydes have pleasant odour. **Acetone** is a liquid at room temperature and has pleasant odour but most of the higher ketones have bland odours.

Increasing boiling points in the homologous series of aldehydes and ketones are listed in Table 12.4.

12.6.3 Solubility of aldehydes and ketones :

The oxygen atom of ($>$C=O) can involve in hydrogen bonding with water molecule (Fig 12.2). 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.

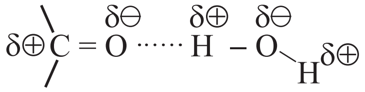


Fig. 12.2 : Hydrogen bonding in carbonyl compound and water

12.6.4 Physical state, boiling points and solubilities 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. Boiling points of lower carboxylic acids are listed in Table 12.5.

Carboxylic acids have higher boiling points than those of alkanes, ethers, alcohols aldehydes and ketones of comparable mass (Table 12.6). The reason is that , in liquid phase, carboxylic acids form dimer in which two molecules are held by two hydrogen bonds. Acidic hydrogen of one molecule form hydrogen bond with carbonyl oxygen of the other molecule (Fig.12.3). This doubles the size of the molecule resulting in increase in intermolecular van der Waals forces, which in turn results in high boiling point. In the case of acetic acid dimers exist even in the gas phase (Fig.12.3).

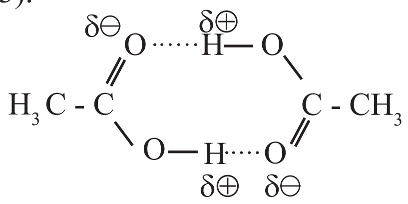


Fig. 12.3 : Dimer of acetic acid (Two molecules held by two hydrogen bonds)

Table 12.5 Increasing boiling points of carboxylic acids

Name	Formula	Boiling point in K
Formic acid	$HCOOH$	373 K
Acetic acid	CH_3COOH	391 K
Propionic acid	CH_3CH_2COOH	414 K
Butyric acid	$CH_3CH_2CH_2COOH$	437 K
Valeric acid	$CH_3CH_2CH_2CH_2COOH$	460 K

Table 12.6 : Variation of boiling point with functional group

Compound	Family	Molecular mass	Boiling point	Strength of intermolecular forces
CH_3-CH_2-CH_2-CH_3	Alkane	58	272 K	increases ↓
CH_3-O-CH_2-CH_3	Ether	60	281 K	
CH_3-CH_2-CHO	Aldehyde	58	322 K	
CH_3-CO-CH_3	Ketone	58	329 K	
CH_3-CH_2-CH_2-OH	Alcohol	60	370 K	
CH_3-COOH	Carboxylic acid	60	391 K	

Remember...

Relative strength of intermolecular force : H-Bond > dipole-dipole attraction > van der Waals force. **Hence, Boiling points :** Carboxylic acids > Alcohols > Ketones > Aldehydes > ether > Alkanes

Do you know ?

Commercially available forms of formaldehyde and acetaldehyde:

i. Formaldehyde is available commercially as solid polymer called paraformaldehyde $HO{+}CH_2 - O{+}_n\ H$ and trioxane $(CH_2O)_3$ (Trioxane has cyclic structure). These are convenient for use in chemical reactions as source of formaldehyde.

ii. Aqueous solution of formaldehyde gas is called formalin, which is used for preservation of biological and anatomical specimens.

iii. When dry formaldehyde is required, it is obtained by heating paraformaldehyde or trioxane.

iv. Acetaldehyde is also conveniently used as solid trimer (paraldehyde) and tetramer (metaldehyde).

Lower aliphatic carboxylic acids containing upto four carbons are miscible with water due to formation of intermolecular hydrogen bonds between carboxylic acid molecules and solvent water molecules. The solubility of carboxylic acids in water decreases with increase in molecular mass. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic (water hating) interaction of hydrocarbon part with water. Aromatic acids like benzoic acid are also practically insoluble in water at room temperature. Water insoluble carboxylic acids are soluble in less polar organic solvents like ether, alcohol, benzene, and so on.

12.7 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 in Fig. 12.4.

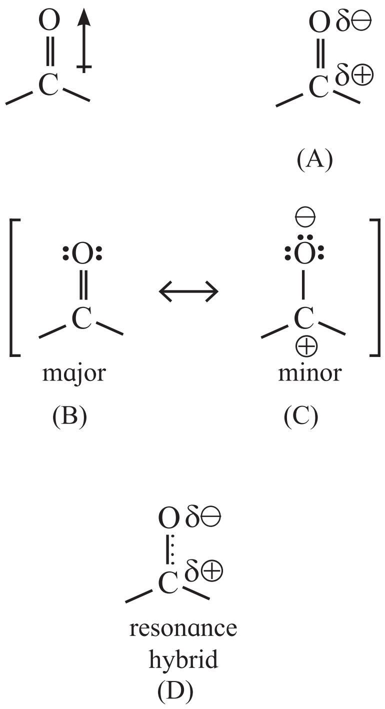


Fig. 12.4 : Polarity of carbonyl group

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 ($Nu:^{\ominus}$).

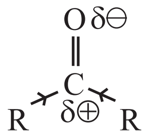
12.7.1 Reactivity of aldehydes and ketones :

Reactivity of aldehydes and ketones is due to the polarity of carbonyl group which results in electrophilicity of carbon. In general, aldehydes are more reactive than ketones toward nucleophilic attack. This can be well explained in terms of both the electronic effects and steric effect.

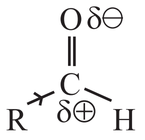
1. Influence of electronic effects : Alkyl groups have electron donating inductive effect (+I). A ketone has two electron donating alkyl groups bonded to carbonyl carbon which are responsible for decreasing its positive polarity and electrophilicity. In contrast, aldehydes have only one electron donating group bonded to carbonyl carbon. This makes aldehydes more electrophilic than 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.



(Ketone)



(Aldehyde)

Remember...

Aromatic aldehydes are less reactive than aliphatic aldehydes in nucleophilic addition reactions. This is due to electron-donating resonance effect of aromatic ring which makes carbonyl carbon less electrophilic.

Try this...

Draw structure of propanone and indicate its polarity.

12.8 Chemical properties of aldehydes and ketones :

12.8.1 Laboratory tests for aldehydes and ketones :

Aldehydes are easily oxidized to carboxylic acids and 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. On the basis of this difference in the reactivity, aldehydes and ketones are distinguished by the following tests:

a. Tests given by only aldehydes :

1. Schiff 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 $Ag^{\oplus}$ ion is reduced to Ag.

$$\underset{\text{(aldehyde)}}{R-CHO} + \underbrace{2\,Ag(NH_3)_2^{\oplus} + 3OH^{\ominus}}_{\text{Tollens reagent}} \xrightarrow{\Delta}$$

$$\underset{\text{(carboxylate)}}{R-COO^{\ominus}} + \underset{\text{(Silver mirror)}}{2\,Ag\downarrow} + 4NH_3\uparrow + 2H_2O$$

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.

$$\underset{\text{(Aldehyde)}}{R-CHO} + \underbrace{2Cu^{2\oplus} + 5OH^{\ominus}}_{\text{(Fehling solution)}} \xrightarrow{\text{boil}} \underset{\text{(carboxylate ion)}}{R-COO^{\ominus}} + \underset{\text{red ppt}}{Cu_2O\downarrow} + 3H_2O$$

Can you tell ?

Simple hydrocarbons, ethers, ketones and alcohols do not get oxidized by Tollens' reagent. Explain, Why ?

Use your brain power

Why is benzaldehyde NOT oxidized by Fehling solution ?

b. Laboratory test for ketonic group : Sodium nitroprusside test :

When a freshly prepared sodium nitroprusside solution is added to a ketone, mixture is shaken well and basified by adding sodium hydroxide solution drop by drop, red colour appears in the solution, which indicates the presence of ketonic (>C=O) group.

$$\underset{\text{(Acetone)}}{CH_3-CO-CH_3} + OH^{\ominus} \longrightarrow CH_3-CO-CH_2^{\ominus} + H_2O$$

$$\underset{\text{(Nitroprusside ion)}}{[Fe(CN)_5NO]^{2\ominus}} + CH_3-CO-CH_2^{\ominus} \longrightarrow \underset{\text{Red colouration}}{[Fe(CN)_5NO(CH_3-CO-CH_2)]^{3\ominus}}$$

The anion of ketone formed by alkali reacts with nitroprusside ion to form a red coloured complex which indicates the presence of ketonic group.

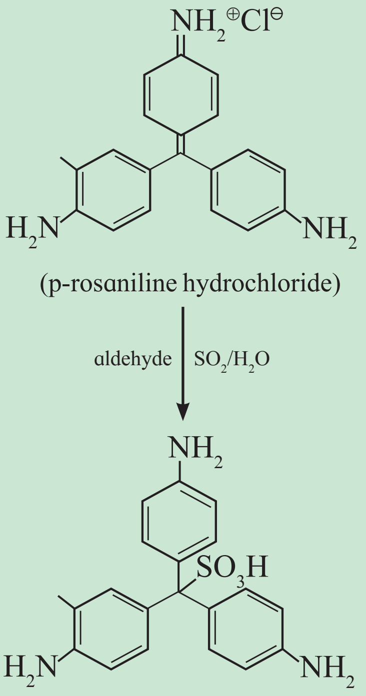
12.8.2 Chemical reactions of aldehydes and ketones with nucleophile :

In all these reactions the nucleophilic reagent brings about reactions by attacking 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

Do you know ?

1. **Schiff 's reagent** is a colourless solution obtained by passing sulfur dioxide gas (oxidant) through magenta coloured solution of p-rosaniline hydrochloride .



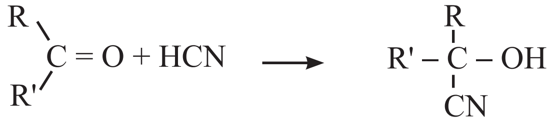
(p-rosaniline hydrochloride)

(Schiff 's reagent)

2. **Tollens' reagent** is prepared by mixing a few drops of $AgNO_3$ solution and a few mL of dilute sodium hydroxide solution. A brown precipitate is formed which is then dissolved by adding dilute ammonium hydroxide.

3. **Fehling solution** is a mixture of two solutions Fehling A and Fehling B. **Fehling A** is prepared by dissolving crystals of copper sulfate in concentrated sulfuric acid. **Fehling B** is prepared by dissolving sodium potassium tartarate in sodium hydroxide solution.

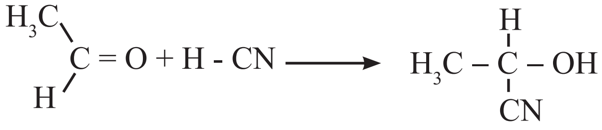
cyanohydrins. The negative part of the reagent ($^{\ominus}$CN) attacks the electrophilic carbon of carbonyl group. The reaction requires either acid or base as catalyst.



(Aldehyde when R' = H
Ketone : R' = alkyl/aryl group)

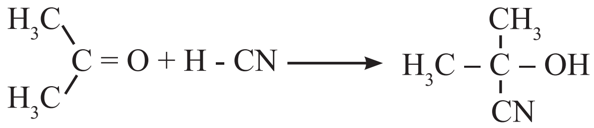
(cyanohydrin)

For example ,



(Acetaldehyde)

(acetaldehyde cyanohydrin)



(Acetone)

(Acetone cynohydrin)

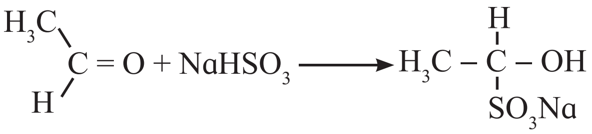
Remember...

i. Cyanohydrin formation is a 'step-up' reaction as a new carbon - carbon single bond is formed.

ii. The - C ≡ N group can be converted to –COOH, - CH_2 - NH_2 and so on.

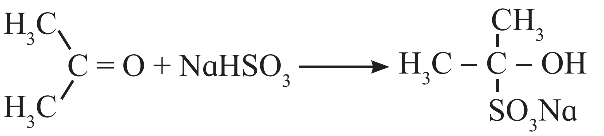
iii. Therefore, cyanohydrins are used as intermediate in step up synthesis.

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 ,



(Acetaldehyde)

(Acetaldehyde sodium bisulfite adduct)



(Acetone)

(Acetonesodium bisulfite adduct)

Use your brain power

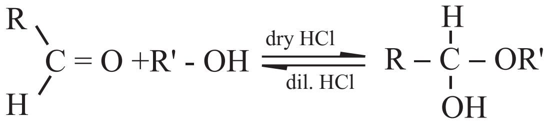
Sodium bisulfite is sodium salt of sulfurous acid, write down its detailed bond structure .

Do you know ?

Sodium bisulfite addition product so formed can be split easily to regenerate aldehydes and ketones on treatment with dilute acid or base. Thus, this reaction is used to separate and purify the aldehydes and ketones from other organic compounds.

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

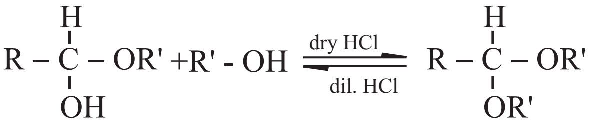
Step 1 :



(Aldehyde)

(Hemiacetal) unstable

Step 2 :



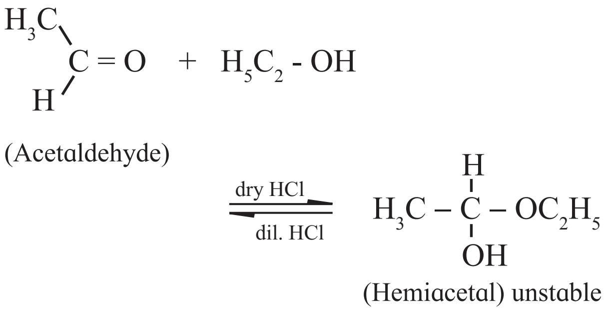
(Hemiacetal)

(Acetal) stable

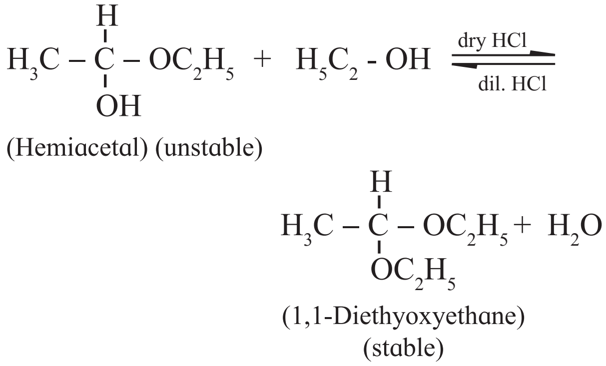
+ H_2O

For example ,

Step 1 :

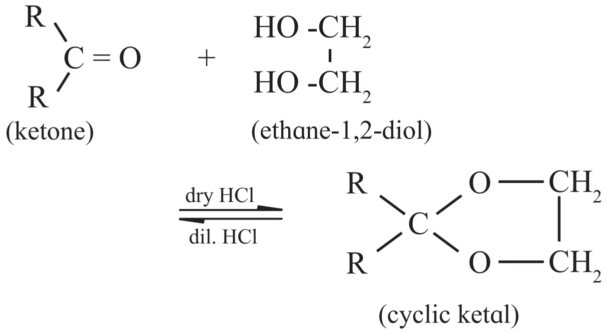


Step 2 :



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 .



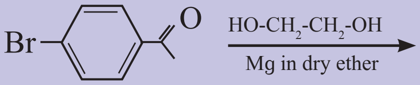
The reaction can be reversed by treating the cyclic ketal with aqueous HCl to regenerate the ketone.

Do you know ?

Cyclic ketal is used as protecting group for ketone in reactions of multifunctional compound to which ketone is sensitive.

Use your brain power

Predict the product of the following reaction :



Acetals and ketals are hydrolysed with aqueous mineral acids to give corresponding aldehydes and ketones respectively.

Remember...

Organic molecule containing an alcohol and carbonyl group can undergo intramolecular reaction with dry HCl to form cyclic hemiacetals/hemiketals.

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.)

e. Nucleophilic addition –elimination of aldehydes and ketones with ammonia derivatives : Aldehydes and ketones undergo addition elimination with some ammonia derivatives (NH_2-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**.

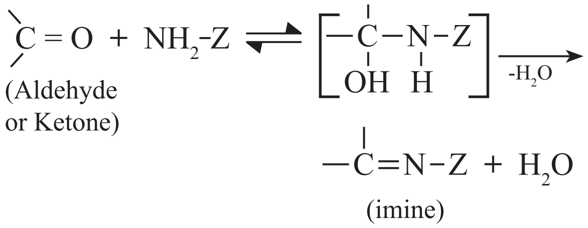
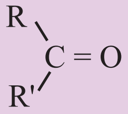
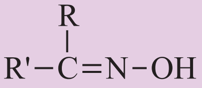
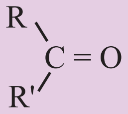
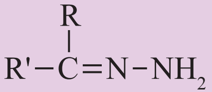
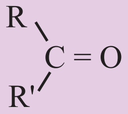
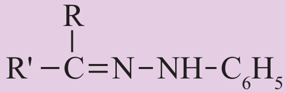
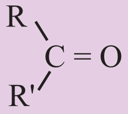
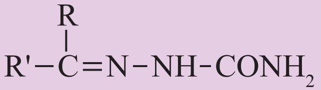
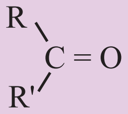
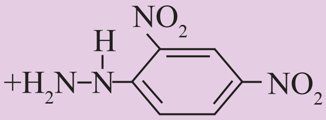
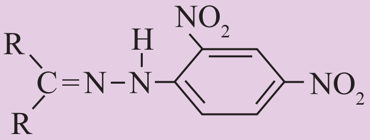
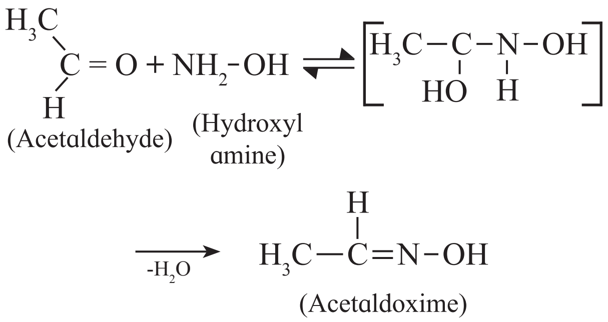


Table 12.7 Nucleophilic addition – elimination reactions of aldehydes and ketones with ammonia derivatives

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

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

For example,


(Acetaldehyde) (Hydroxyl amine)

(Acetaldoxime)

All aldehydes and ketones give similar reactions .Some important reactions are listed in Table 12.7. The resulting products have high molecular mass and are crystalline solids. These reactions are, therefore, useful for characterization of the original aldehydes and ketones.

Remember...

In strong acidic medium, nitrogen atom of ammonia derivative H_2N-Z is protonated to form (H_3N^+ – Z) ion which is no longer a nucleophile.

Use your brain power

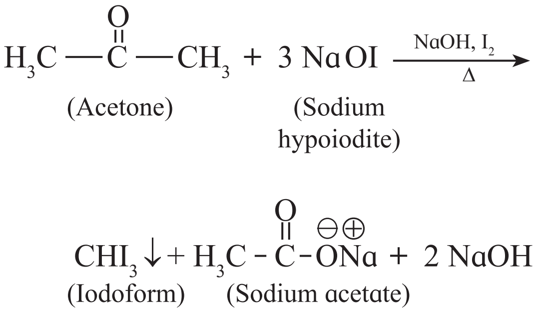
Draw the structures of

i. The semicarbazone of cyclohexanone

ii. The imine formed in the reaction between 2-methylhexanal and ethyl amine

iii. 2, 4 - dinitrophenylhydrazone of acetaldehyde.

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



$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + 3\,NaOI \xrightarrow[\Delta]{NaOH,\ I_2}$$

(Acetone) (Sodium hypoiodite)

$$CHI_3\downarrow + H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\ominus}{O}\overset{\oplus}{Na} + 2\,NaOH$$

(Iodoform) (Sodium acetate)

Remember...

1. If C=C bond is present in a given aldehyde or ketone or methyl ketone, it is not attacked by hypohalite.
2. Non methyl ketones do not give a positive iodoform test.
3. Secondary alcohols having CH_3-CHOH- group give positive iodoform test because the reagent first oxidizes it to a CH_3-CO- group which subsequently forms iodoform.

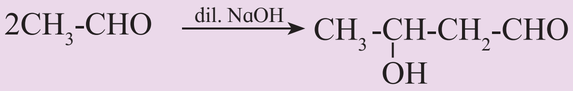
Try this...

Write chemical reactions taking place when propan-2-ol is treated with iodine and sodium hydroxide.

g. Aldol condensation :

Try this...

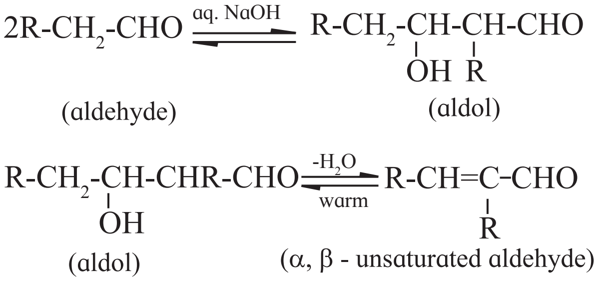
When acetaldehyde is treated with dilute NaOH, the following reaction is observed.



$$2CH_3\text{-}CHO \xrightarrow{\text{dil. NaOH}} CH_3\text{-}\underset{\underset{\displaystyle OH}{|}}{CH}\text{-}CH_2\text{-}CHO$$

- What are the functional groups in the product ?
- Will there be another product formed during the same reaction ? (Deduce the answer by doing atomic audit of reactant and product)
- Is this an addition reaction or condensation reaction ?

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



$$2R\text{-}CH_2\text{-}CHO \underset{}{\overset{\text{aq. NaOH}}{\rightleftharpoons}} R\text{-}CH_2\text{-}\underset{\underset{\displaystyle OH}{|}}{CH}\text{-}\underset{\underset{\displaystyle R}{|}}{CH}\text{-}CHO$$

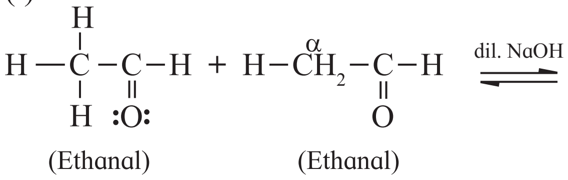
(aldehyde) (aldol)

$$R\text{-}CH_2\text{-}\underset{\underset{\displaystyle OH}{|}}{CH}\text{-}CHR\text{-}CHO \underset{\text{warm}}{\overset{-H_2O}{\rightleftharpoons}} R\text{-}CH{=}\underset{\underset{\displaystyle R}{|}}{C}\text{-}CHO$$

(aldol) (α, β - unsaturated aldehyde)

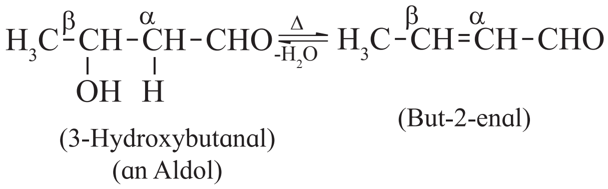
For example :

(i)



$$H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-\underset{\underset{\displaystyle :O:}{\|}}{C}-H + H-\overset{\alpha}{C}H_2-\underset{\underset{\displaystyle O}{\|}}{C}-H \overset{\text{dil. NaOH}}{\rightleftharpoons}$$

(Ethanal) (Ethanal)



$$H_3\overset{\beta}{C}-\underset{\substack{|\\OH}}{CH}-\underset{\substack{|\\H}}{\overset{\alpha}{CH}}-CHO \xrightarrow[-H_2O]{\Delta} H_3C-\overset{\beta}{CH}=\overset{\alpha}{CH}-CHO$$

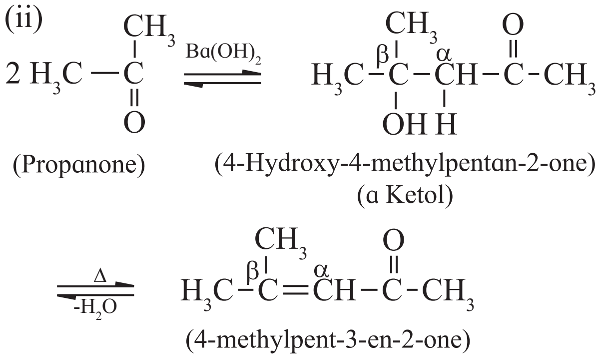
(3-Hydroxybutanal)
(an Aldol)

(But-2-enal)

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

Ketones containing at least two α- hydrogen also undergo aldol condensation reaction and give an α, β - unsaturated ketone. For example:

(ii)



$$2\,H_3C-\underset{\substack{\|\\O}}{\overset{\substack{CH_3\\|}}{C}} \xrightleftharpoons{Ba(OH)_2} H_3C-\overset{\beta}{\underset{\substack{|\\OH}}{\overset{\substack{CH_3\\|}}{C}}}-\underset{\substack{|\\H}}{\overset{\alpha}{CH}}-\overset{\substack{O\\\|}}{C}-CH_3$$

(Propanone)

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

$$\xrightleftharpoons[-H_2O]{\Delta} H_3C-\overset{\beta}{\overset{\substack{CH_3\\|}}{C}}=\overset{\alpha}{CH}-\overset{\substack{O\\\|}}{C}-CH_3$$

(4-methylpent-3-en-2-one)

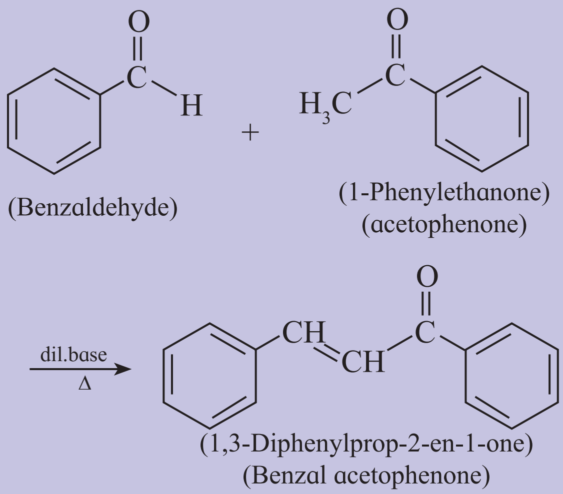
Cross aldol condensation : Cross aldol condensation refers to the aldol condensation that takes place in between two different aldehydes or ketones . If both aldehydes or ketones contain two α-hydrogen atoms each, then a mixture of four products, is formed.

For example, a mixture of ethanal and propanal on reaction with dilute alkali followed by heating gives a mixture of four products (Fig.12.5).

Ketones can also be used as one of the components in cross aldol condensation .

Use your brain power

- Observe the following reaction.



(Benzaldehyde)

(1-Phenylethanone)
(acetophenone)

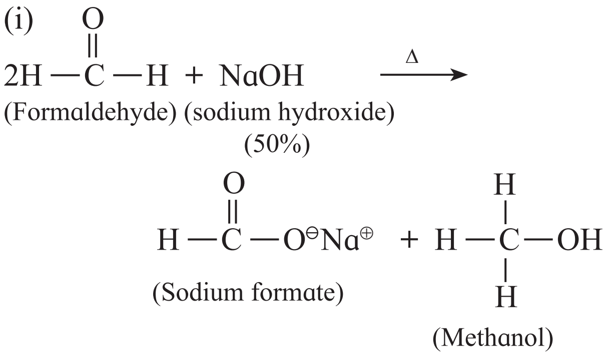
dil.base, Δ

(1,3-Diphenylprop-2-en-1-one)
(Benzal acetophenone)

- Will this reaction give a mixture of products like a cross aldol reaction ?

h. Cannizzaro reaction : This reaction is given only by aldehydes having no α-hydrogen atom. Aldehydes undergo self -oxidation and reduction reaction on heating with concentrated alkali. This is an example of **disproportionation reaction**. 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. For example, Formaldehyde and benzaldehyde

(i)



$$2H-\overset{\substack{O\\\|}}{C}-H + NaOH \xrightarrow{\Delta} H-\overset{\substack{O\\\|}}{C}-O^{\ominus}Na^{\oplus} + H-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-OH$$

(Formaldehyde) (sodium hydroxide)
(50%)

(Sodium formate)

(Methanol)

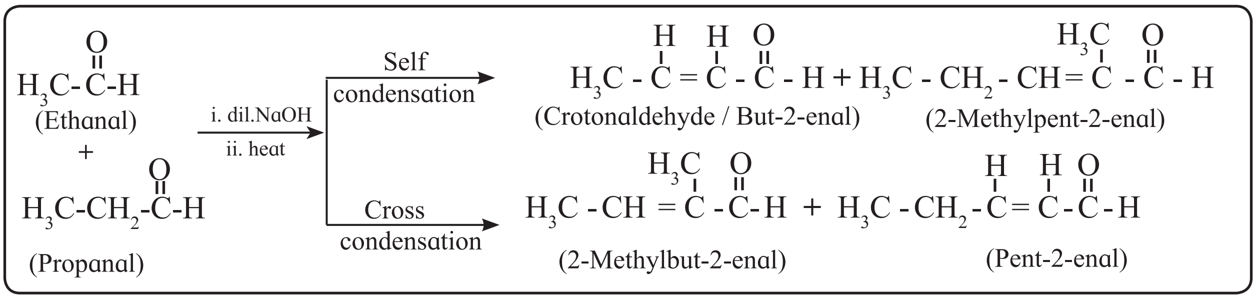
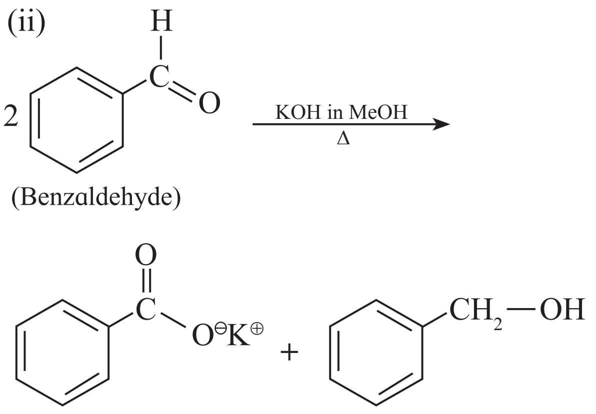


Fig. 12.5 : Cross aldol condensation

(ii)



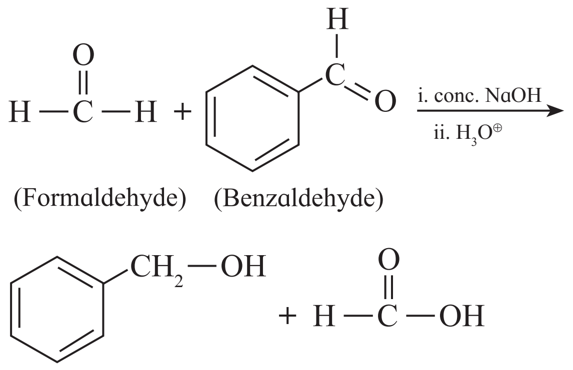
(Benzaldehyde)

(Potassium benzoate) (Phenylmethanol / benzyl alcohol)

Use your brain power

Can isobutyraldehyde undergo Cannizzaro reaction ? Explain.

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 :



(Formaldehyde) (Benzaldehyde)

(Phenylmethanol) (formic acid)

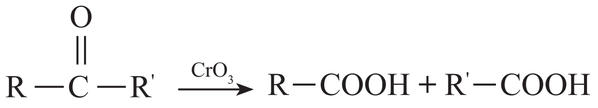
12.8.3 Oxidation and reduction reactions of aldehydes and ketones ;

a. Oxidation of aldehydes and ketones by dilute HNO_3, $KMnO_4$ and $K_2Cr_2O_7$: 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.

$$R-CHO \xrightarrow[\text{dil. } H_2SO_4]{K_2Cr_2O_7} R-COOH$$

(Aldehyde) (Carboxylic acid)

Ketones resist oxidation due to strong CO-C bond ,but they are oxidized by strong oxidizing agents such as CrO_3, alkaline $KMnO_4$ 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.

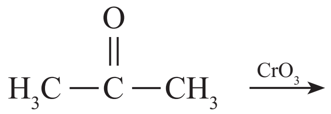


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-R' \xrightarrow{CrO_3} R-COOH + R'-COOH$$

(Ketone) (Carboxylic acids)

For example,

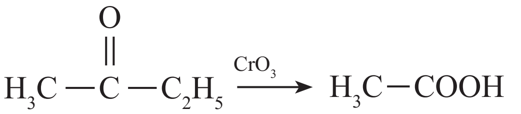
(i)



$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{CrO_3} H_3C-COOH$$

(Acetone) (Acetic Acid)

(ii)



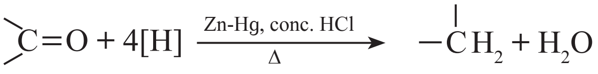
$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-C_2H_5 \xrightarrow{CrO_3} H_3C-COOH + H_5C_2-COOH$$

(Butan-2-one) (Ethanonic acid) (Propanoic acid)

b. Clemmensen and Wolf-Kishner reduction: The carbonyl group of aldehydes and ketones is reduced to methylene group ($-CH_2-$) 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.

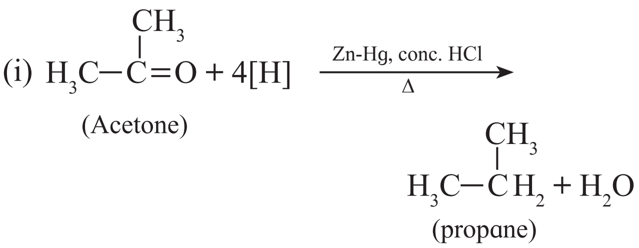
Clemmensen reduction :



$$>C=O + 4[H] \xrightarrow[\Delta]{\text{Zn-Hg, conc. HCl}} -\overset{|}{C}H_2 + H_2O$$

(Carbonyl group in aldehydes and ketones) (Methylene group)

For example :

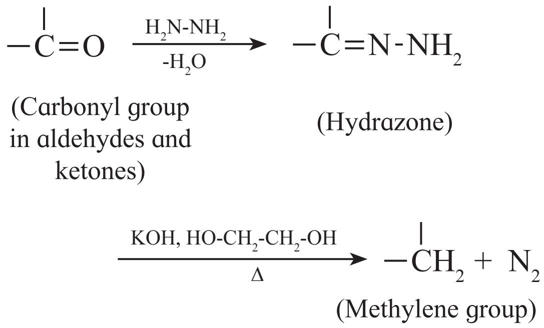

$$\text{(i) } H_3C-\overset{\overset{\displaystyle CH_3}{|}}{C}=O + 4[H] \xrightarrow[\Delta]{\text{Zn-Hg, conc. HCl}} H_3C-\overset{\overset{\displaystyle CH_3}{|}}{C}H_2 + H_2O$$

(Acetone) (propane)

$$\text{(ii) } CH_3-CH_2-CHO + 4[H] \xrightarrow[\Delta]{\text{Zn-Hg, conc. HCl}} CH_3-CH_2-CH_3 + H_2O$$

(Propanal) (Propane)

Wolf-Kishner reduction :


$$-\overset{|}{C}=O \xrightarrow[-H_2O]{H_2N\text{-}NH_2} -\overset{|}{C}=N\text{-}NH_2 \xrightarrow[\Delta]{\text{KOH, HO-}CH_2\text{-}CH_2\text{-OH}} -\overset{|}{C}H_2 + N_2$$

(Carbonyl group in aldehydes and ketones) (Hydrazone) (Methylene group)

For example :

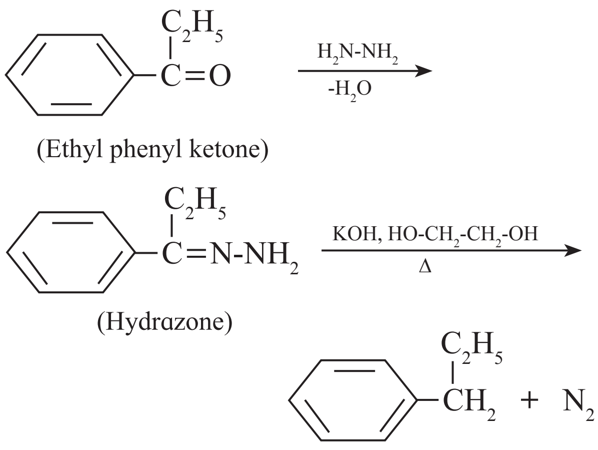
$$\text{(i) } C_2H_5-CHO \xrightarrow[-H_2O]{H_2N\text{-}NH_2} C_2H_5-CH=N\text{-}NH_2$$

(Propanal) (Hydrazone)

$$\xrightarrow[\Delta]{\text{KOH, HO-}CH_2\text{-}CH_2\text{-OH}} CH_3-CH_2-CH_3 + N_2$$

(Propane)

(ii)

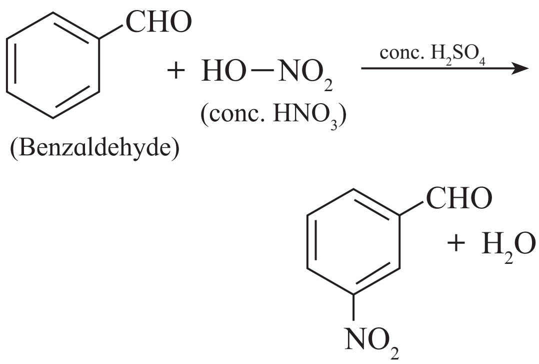


(Ethyl phenyl ketone) (Hydrazone) (n-Propyl benzene)

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

12.8.4 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 ,



(Benzaldehyde) (conc. HNO_3) (m-Nitrobenzaldehyde)

12.9 Chemical properties of carboxylic acids :

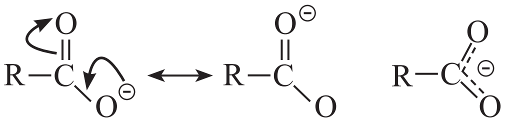
12.9.1 Acidic character of carboxylic acids:

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,

$$R\text{ - }COOH + H_2O \rightleftharpoons R\text{ - }COO^{\ominus} + H_3O^{\oplus}$$

(carboxylate ion)

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



(i) (ii) resonance hybrid

Carboxylate ion has two resonance structures (i) and (ii) and both of them are equivalent to each other (Refer to Std. XI Chemistry Textbook Chapter 14). This gives good resonance stabilization to carboxylate ion, which in turn gives acidic character to carboxylic acids.

Can you recall ?

What is the numerical parameter to express acid strength?

Remember...

Lower K_a value, higher pK_a: Weaker acid.

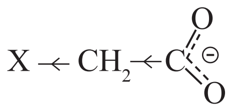
Higher K_a value, lower pKa : stronger acid.

Influence of electronic effects on acidity of carboxylic acids : All the carboxylic acids do not have the same pK_a value. The structure of 'R' in R-COOH has influence on the acid strength of carboxylic acids. Various haloacetic acids illustrate this point very well (Tables 12.8 and 12.9).

Table 12.8 : pK_a values of haloacetic acids

Acid	pK_a	Acid strength
F-CH_2-COOH	2.56	decreases ↓
Cl-CH_2-COOH	2.86	
Br-CH_2-COOH	2.90	
I-CH_2-COOH	3.18	
CH_3-COOH	4.76	

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



$$X \leftarrow CH_2 \leftarrow C\overset{O}{\underset{O}{\lesssim}}{}^{\ominus}$$

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

Problem 12.1

Alcohols (R-OH), phenols (Ar-OH) and carboxylic acids (R-COOH) can undergo ionization of O-H bond to give away proton $H^{\oplus}$; yet they have different pK_a values, which are 16, 10 and 4.5 respectively. Explain

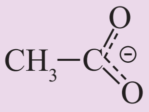
Solution : pK_a value is indicative of acid strength. Lower the pK_a value stronger the acid. Alcohols, phenols and carboxylic acids, all involve ionization of an O-H bond. But their different pK_a values indicate that their acid strength are different. This is because the resulting conjugate bases are stabilized to different extent.

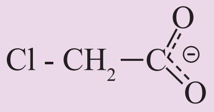
Acid(HA)	Conjugate base($A^{\ominus}$)	Electronic effect	Stabilization/destabilization
R-O-H	$R \rightarrow O^{\ominus}$	+I effect of R group	destabilization of conjugate base
Ar-O-H	$Ar\text{-}O^{\ominus}$	-R effect or Ar group	stabilization of conjugate base is moderate because all the resonance structures are not equivalent to each other
$R-\overset{\overset{O}{\parallel}}{C}-O-H$	$R-\overset{\overset{O}{\parallel}}{C}-\overset{\ominus}{O}$	-R effect of C = O group	stabilization is good because all the resonance structures are equivalent to each other

As the conjugate base of carboxylic acid is best stabilized, among the three, carboxylic acids are strongest and have the lowest pK_a value. As conjugate base of alcohols is destabilized, alcohols are weakest acids and have highest pK_a value. As conjugate base of phenols is moderately stabilized phenols are moderately acidic and have intermediate pK_a value.

Try this...

Compare the following two conjugate bases and answer.


(a)


(b)

- Indicate the inuctive effects of CH_3 - group in (a) and Cl - group in (b) by putting arrowheads in the middle of appropriate covalent bonds.
- Which species is stabilized by inductive effect, (a) or (b) ?
- Which species is destabilized by inductive effect, (a) or (b) ?

Use your brain power

- Compare the pK_a values and arrange the following in an increasing order of acid strength.

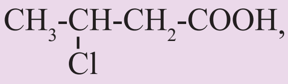
  Cl_3CCOOH, $ClCH_2COOH$, CH_3COOH, $Cl_2CHCOOH$
- Draw structures of conjugate bases of monochloroacetic acid and dichloroacetic acid. Which one is more stabilized by -I effect ?

Acidity of aromatic carboxylic acids : Benzoic acid is the simplest aromatic acid. From the pK_a value of benzoic acid (4.2) we understand that it is stronger than acetic acid (pK_a 4.76). The sp^2 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.

Table 12.9 illustrates that more the number of electron withdrawing substituents higher is the acid strength.

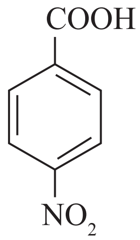
Try this...

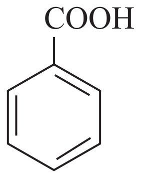
Arrange the following acids in order of their decreasing acidity.

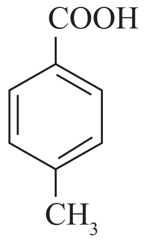

$CH_3\text{-}\underset{\displaystyle Cl}{CH}\text{-}CH_2\text{-}COOH$, $CCl_3\text{-}CH_2\text{-}COOH$,

CH_3COOH

Electron–withdrawing groups like -Cl, -CN, and $-NO_2$ 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)

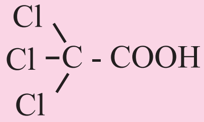

(4-Methylbenzoic acid)
(pK_a = 4.4)

Try this...

Arrange the following carboxylic acids in order of increasing acidity.

m-Nitrobenzoic acid, Trichloroacetic acid, benzoic acid, α-Chlorobutyric acid.

Table 12.9 pK_a values of chloroacetic acids

Name	Structure	pK_a	Acid strength
Monochloroacetic acid	Cl - CH_2 - COOH	2.86	increases ↓
Dichloroacetic acid	 $Cl\text{-}\underset{\displaystyle Cl}{CH}\text{-}COOH$	1.26	
Trichloroacetic acid		0.6	

12.9.2 Laboratory tests for carboxyl (-COOH) group :

The presence of -COOH group in carboxylic acids is identified by the following tests:

a. Litmus test : (valid for water soluble substances)

Aqueous solution of Organic compound containing –COOH group turns blue litmus red which indicates the presence of acidic functional group. (It may be noted that aqueous solutions of water soluble phenols also turn blue litmus red.)

b. Sodium bicarbonate test :

When sodium bicarbonate is added to an organic compound containing –COOH group, a brisk effervescence of carbon dioxide gas is evolved. Water insoluble acid goes in solution and gives precipitate on acidification with conc.HCl. This indicates the presence of –COOH group.

$$\underset{\text{(water insoluble)}}{R\text{ - }COOH} + NaHCO_3(aq) \xrightarrow[-H_2O]{-CO_2}$$

$$R\text{ - }COONa(aq) \xrightarrow{HCl} R\text{ - }COOH\downarrow + NaCl(aq)$$

(Phenol does not evolve CO_2 gas with sodium bicarbonate. Hence, carboxylic acid and phenol are distinguished by this test.)

c. Ester test : One drop of concentrated sulfuric acid is added to a mixture of given organic compound containing –COOH group and one mL of ethanol, the reaction mixture is heated for 5 minutes in hot water bath. After this , hot solution is poured in a beaker containing water, fruity smell of ester confirms the presence of carboxylic acid.

$$R\text{ - }COOH + C_2H_5OH \xrightarrow[\text{warm}]{H^{\oplus}} \underset{\text{(ester)}}{R\text{ - }COO\text{ - }C_2H_5} + H_2O$$

12.9.3 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 .**

$$\underset{\text{(Carboxylic acid)}}{R-COOH} + SOCl_2 \xrightarrow{\Delta} \underset{\text{(acyl chloride)}}{R-COCl} + SO_2\uparrow + HCl\uparrow$$

$$3\ R-COOH + PCl_3 \xrightarrow{\Delta} 3\ R-COCl + P(OH)_3$$

$$R-COOH + PCl_5 \xrightarrow{\Delta} R-COCl + POCl_3 + HCl$$

Use your brain power

Fill in the blanks and rewrite the balanced equations.

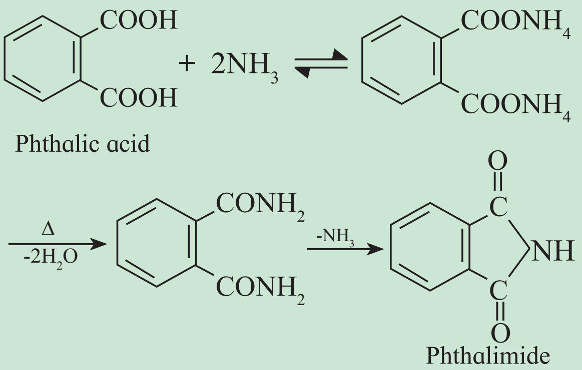
- CH_3COOH + thionyl chloride $\xrightarrow{\Delta}$ ...... + ... + ...
- CH_3-CH_2-COOH + ... $\xrightarrow{\Delta}$ ...... + ... + H_3PO_3
- C_6H_5-COOH + ... $\xrightarrow{\Delta}$ ...... + phosphorous oxylchloride + HCl
- CH_3-COOH + phosphorous trichloride $\xrightarrow{\Delta}$ ...... + ...
- CH_3-COOH $\underset{}{\overset{NH_3}{\rightleftharpoons}}$ ...... $\xrightarrow{\Delta}$ ......
- ...... $\overset{NH_3}{\rightleftharpoons}$ ...... $\xrightarrow{\Delta}$ C_6H_5-$CONH_2$

12.9.4 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.

$$\underset{\text{(Carboxylic acid)}}{R-COOH} + NH_3 \rightleftharpoons \underset{\text{(ammonium carboxylate)}}{R-CO\overset{\curvearrowleft\ominus\oplus}{O}NH_4} \xrightarrow[-H_2O]{\Delta} \underset{\text{(Acid amide)}}{R-CONH_2}$$

Do you know ?



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

$$R-COCl + NH_3 \longrightarrow R-CONH_2 + HCl$$

(Acyl chloride) (Acid amide)

12.9.5 Formation of acid anhydride :

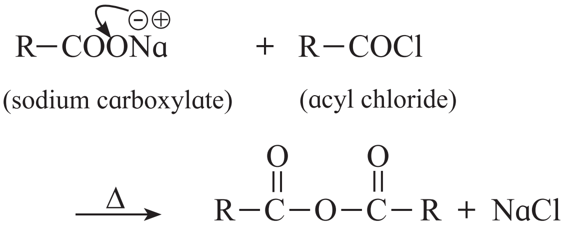
Can you tell ?

What is the term used for elimination of water molecule ?

Mono carboxylic acids on heating with strong dehydrating agent like P_2O_5 concentrated H_2SO_4 give acid anhydrides. The reaction is reversible. Anhydrides are readily hydrolyzed back to acids on reaction with water.

(Carboxylic acid) (Acid anhydride)

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



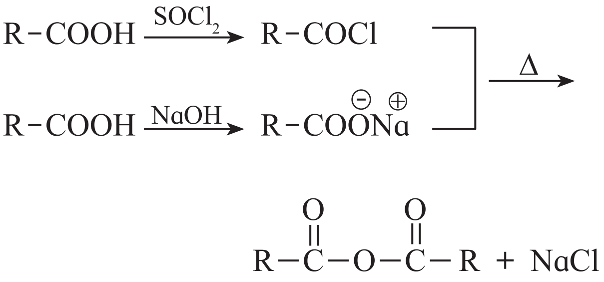
$$R-CO\overset{\ominus}{O}\overset{\oplus}{Na} + R-COCl$$

(sodium carboxylate) (acyl chloride)

$$\xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + NaCl$$

(acid anhydride)

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



$$R-COOH \xrightarrow{SOCl_2} R-COCl$$

$$R-COOH \xrightarrow{NaOH} R-CO\overset{\ominus}{O}\overset{\oplus}{Na}$$

$$\xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + NaCl$$

(Anhydride)

Can you recall ?

Which molecule is eliminated in a decarboxylation ?

12.9.6 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,

$$R-CO\overset{\ominus}{O}\overset{\oplus}{Na} + NaOH \xrightarrow[\Delta]{CaO} R-H + Na_2CO_3$$

$$CH_3-CO\overset{\ominus}{O}\overset{\oplus}{Na} + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

(Sodium acetate) (Methane)

12.9.7 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).

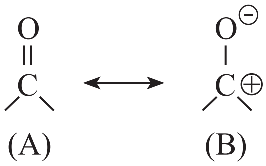
(Note : Sodium borohydride ($NaBH_4$)does not reduce-COOH group).

$$R-COOH + LiAlH_4 \xrightarrow[\text{ether}]{\text{dry}} R-CH_2OH$$

Exercises

1. Choose the most correct option.

i. In the following resonating structures A and B, the number of unshared electrons in valence shell present on oxygen respectively are



a. 2, 4 b. 2, 6

c. 4, 6 d. 6, 4

ii. In the Wolf -Kishner reduction, alkyl aryl ketones are reduced to alkyl benzenes. During this change, ketones are first converted into

a. acids b. alcohols

c. hydrazones d. alkenes

iii. Aldol condensation is

a. electrophilic substitution reaction

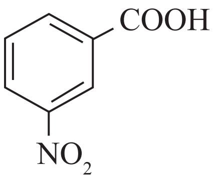
b. nucleophilic substitution reaction

c. elimination reaction

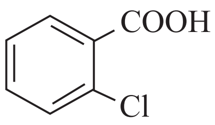
d. addition - elimination reaction

iv. Which one of the following has lowest acidity ?

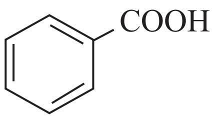
a.



b.



c.



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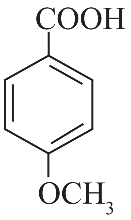


v. Diborane reduces

a. ester group b. nitro group

c. halo group d. acid group

vi. Benzaldehyde does NOT show positive test with

a. Schiff reagent

b. Tollens' ragent

c. Sodium bisulphite solution

d. Fehling solution

2. Answer the following in one sentence

i. What are aromatic ketones?

ii. Is phenyl acetic acid an aromatic carboxylic acid ?

iii. Write reaction showing conversion of ethanenitrile into ethanol.

iv. Predict the product of the following reaction:

$$CH_3-CH_2-COOCH_3 \xrightarrow[\text{ii. } H_3O^{\oplus}]{\text{i. AlH (i-Bu)}_2} ?$$

v. Name the product obtained by reacting toluene with carbon monoxide and hydrogen chloride in presence of anhydrous aluminium chloride.

vi. Write reaction showing conversion of Benzonitrile into benzoic acid.

vii. Name the product obtained by the oxidation of 1,2,3,4-tetrahydronaphthalene with acidified potassium permanganate .

viii. What is formalin ?

ix. Arrange the following compounds in the increasing order of their boiling points :

Formaldehyde, ethane, methyl alcohol.

x. Acetic acid is prepared from methyl magnesium bromide and dry ice in presence of dry ether. Name the compound which serves not only reagent but also as cooling agent in the reaction.

3. Answer in brief.

i. Observe the following equation of reaction of Tollens' reagent with aldehyde. How do we know that a redox reaction has taken place. Explain.

$$R-CHO + 2\ Ag(NH_3)_2^+ + OH^- \xrightarrow{\Delta} R-COO^- + 2\ Ag\downarrow + 4\ NH_3 + 2\ H_2O$$

ii. Formic acid is stronger than acetic acid. Explain.

iii. What is the action of hydrazine on cyclopentanone in presence of ---.

KOH in ethylene glycol ?

iv. Write reaction showing conversion of Acetaldehyde into acetaldehyde dimethyl acetal.

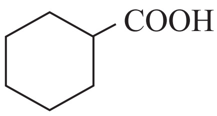
v. Aldehydes are more reactive toward nucleophilic addition reactions than ketones. Explain.

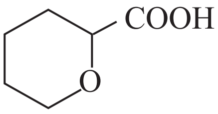
vi. Write reaction showing the action of the following reagent on propanenitrile –

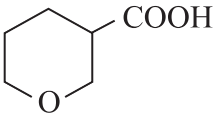
a. Dilute NaOH

b. Dilute HCl ?

vi. Arrange the following carboxylic acids with increasing order of their acidic strength and justify your answer.







4. Answer the following

i. Write a note on –

a. Cannizaro reaction

b. Stephen reaction.

ii. What is the action of the following reagents on toluene ?

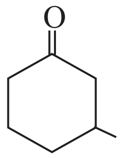
a. Alkaline $KMnO_4$, dil. HCl and heat

b. CrO_2Cl_2 in CS_2

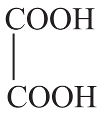
c. Acetyl chloride in presence of anhydrous $AlCl_3$.

iii. Write the IUPAC names of the following structures :

a.



b.

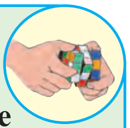


$$\begin{array}{c} COOH \\ | \\ COOH \end{array}$$

iv. Write reaction showing conversion of p- bromoisopropyl benzene into p-Isopropyl benzoic acid (3 steps).

v. Write reaction showing aldol condensation of cyclohexanone.

Activity :



Draw and complete the following reaction scheme which starts with acetaldehyde. In each empty box, write the structural formula of the organic compound that would be formed.