# CARBONYL COMPOUNDS AND CARBOXYLIC ACIDS



# Adolf von Baeyer

Adolf Von Baever, German research chemist who synthesized indigo (1880) and formulated its structure (1883). He was awarded the Nobel Prize for Chemistry in 1905. Notable among Baeyer's many achievements were the discovery of the phthalein dyes and his investigations of uric acid derivatives, polyacetylenes, and oxonium salts. One derivative of uric acid that he discovered was barbituric acid, the parent compound of the sedative-hypnotic drugs known as barbiturates.



# **O** Learning Objectives

After studying this unit the student will be able to

- describes the important methods of preparation and reactions of Carbonyl compounds
- explains the mechanism of Nucleophilic addition reaction of carbonyl compounds
- describes the preparation and chemical reactions of carboxylic acids and its derivatives
- list the uses of aldehydes, ketones and carboxylic acids

# **INTRODUCTION**

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

# 12.1 Nomenclature of Aldehydes and ketones

Compound	IUPAC Name				
(common name, Structural formula, IUPAC Name)	Prefix with position number	Root used	Primary suffix	Secondary Suffix	
Formaldehyde H – CHO methanal	_	meth	an¢	al	
Acetaldehyde CH <sub>3</sub> – CHO ethanal	_	eth	an¢	al	
Acrolein $CH_2 = CH - CHO$ prop – 2- enal	_	prop	2-en¢	al	
Crotonaldehyde $CH_3 - CH = CH - CHO$ but - 2 - enal	_	but	2-en¢	al	
Glyceraldehyde HO – CH <sub>2</sub> – CH – CHO   OH 2, 3 – dihydroxy propanal	2, 3 dihydroxy	prop	an¢	al	

We have already learnt the IUPAC system of nomenclature of organic compounds in XI<sup>th</sup> standard. Let us apply the rules to name the following compounds.



Benzaldehyde	phenyl	meth	an¢	al
Acetone / Dimethyl ketone $CH_3 - CO - CH_3$ propanone		prop	an¢	one
Mesityl oxide $(CH_3)_2C = CHCOCH_3$ 4 – methylpent-3-en-2-one	4 – methyl	pent	3-en¢	2-one
Methyl Phenyl ketone $C_6H_5 - C - CH_3$ 0 Acetophenone (PIN)* 1-phenylethan-1-one	1-phenyl	eth	an¢	1-one
Diphenyl ketone $C_6H_5 - C - C_6H_5$ $\ $ O Benzophenone (PIN)* Diphenylmethanone	Diphenyl	meth	an¢	one
$CH_3 - CH_2 - C - CH_2 - CHO$ 3 - oxopentanal	3 - oxo	pent	an¢	al
COOH 2 - formylbenzoicacid	2 – formyl	benz	-	oicacid
CH <sub>3</sub> 3 -methylcyclopent–2,4-dien-1-one	3 -methyl	cyclopent	2, 4 dien¢	1-one

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\* PIN– Preferred IUPAC name



# 12.2 Structure of carbonyl group

similar to carbon – carbon double bond in alkenes. The carbonyl carbon forms three  $\sigma$  bonds using their three sp<sup>2</sup> hybridised orbital. One of the sigma bond is formed with oxygen and the other two with hydrogen and carbon (in aldehydes) or with two carbons (in ketones). All the three ' $\sigma$ ' bonded atoms are lying on the same plane as shown in the fig (12.1). The fourth valence electron of carbon remains in its unhybridised '2p' orbital which lies perpendicular to the plane and it overlaps with 2p orbital of oxygen to form a carbon – oxygen  $\pi$  bond. The oxygen atom has two nonbonding pairs of electrons, which occupy its remaining two p-orbitals. Oxygen, the second most electro negative atom attracts the shaired pair of electron between the carbon and oxygen towards itself and hence the bond is polar. This polarisation contributes to the reactivity of aldehydes and ketones.



# 12.3 General methods of preparation of aldehydes and ketones

# A. Preparation of aldehydes and ketones

#### 1.) Oxidation and catalytic dehydrogenation of alcohols

We have already learnt that the oxidation of primary alcohol gives aldehydes and secondary alcohol gives a ketone. Oxidising agents such as acidified  $Na_2Cr_2O_7$ ,  $KMnO_4$ , PCC are used for oxidation. Oxidation using PCC yield aldehydes. Other oxidising agents further oxidise the aldhydes / ketones in to carboxylic acids (Refer Unit No. - 11 Oxidation of alcohols)

When vapours of alcohols are passed over heavy metal catalyst such as Cu, Ag, alcohols give aldehydes and ketons. (Refer Unit No. - 11 Catalytic dehydrogenation of alcohols

#### 2.) Ozonolysis of alkenes

We have already learnt in XI th standard that the reductive ozonolysis of alkenes gives aldehydes and ketones.

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

$$CH_{3}-CH = CH - CH_{3} + O_{3} \longrightarrow CH_{3}-CH \xrightarrow{CH_{3}-CH} CH^{-}CH_{3} \xrightarrow{Zn / H_{2}O} 2 CH_{3} CHO + H_{2}O_{2}$$
  
but - 2- ene  

$$O \xrightarrow{CH_{3}} O \xrightarrow{CH_{3}-CHO} CH_{3} - CHO + CH_{3}-C-CH_{3} + H_{2}O_{2}$$
  

$$CH_{3}-CH = C - CH_{3} + O_{3} \longrightarrow CH_{3}-CH \xrightarrow{C} C - CH_{3} \xrightarrow{Zn / H_{2}O} CH_{3} - CHO + CH_{3}-C - CH_{3} + H_{2}O_{2}$$
  

$$CH_{3}-CH = C - CH_{3} + O_{3} \longrightarrow CH_{3}-CH \xrightarrow{C} C - CH_{3} \xrightarrow{Zn / H_{2}O} CH_{3} - CHO + CH_{3}-C - CH_{3} + H_{2}O_{2}$$
  

$$CH_{3}-CH = C - CH_{3} + O_{3} \longrightarrow CH_{3}-CH \xrightarrow{C} C - CH_{3} \xrightarrow{Zn / H_{2}O} CH_{3} - CHO + CH_{3}-C - CH_{3} + H_{2}O_{2}$$
  

$$CH_{3}-CH = C - CH_{3} + O_{3} \longrightarrow CH_{3}-CH \xrightarrow{C} C - CH_{3} \xrightarrow{Zn / H_{2}O} CH_{3} - CHO + CH_{3}-C - CH_{3} + H_{2}O_{2}$$
  

$$CH_{3}-CH = C - CH_{3} + O_{3} \longrightarrow CH_{3}-CH \xrightarrow{C} C - CH_{3} \xrightarrow{Zn / H_{2}O} CH_{3} - CHO + CH_{3}-C - CH_{3} + H_{2}O_{2}$$
  

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$$CH_{3}-CH = C - CH_{3} + O_{3} \longrightarrow CH_{3}-CH \xrightarrow{C} C - CH_{3} \xrightarrow{Zn / H_{2}O} CH_{3} - CHO + CH_{3}-C - CH_{3} + H_{2}O_{2}$$
  

$$CH_{3}-CH = C - CH_{3} + O_{3} \longrightarrow CH_{3}-CH \xrightarrow{C} C - CH \xrightarrow{C} C$$

Terminal olefines give formaldehyde as one of the product.

#### Evaluate yourself - 1

What happens when the following alkenes are subjected to reductive ozonolysis.

1) propene 2) 1 – Butene 3) Isobutylene

#### 3. Hydration of alkynes

We have already learnt in XI standard that the hydration of alkynes in presence of 40% dilute sulpuric acid and 1%  $HgSO_4$  to give the corresponding aldehydes / ketones.

#### a) Hydration of acetylene yields acetaldehyde

$$HC = CH + H - OH - HgSO_4 \rightarrow H_2SO_4 = H - C = C - OH - OH - HgSO_4 = H - C = C - OH - HgSO_4 = Hanal$$

b) Hydration of alkynes, other than acetylene gives ketones

$$CH_{3}-C = CH + H - OH \xrightarrow{HgSO_{4}}_{H_{2}SO_{4}} \qquad CH_{3}-C = CH_{2}$$

$$CH_{3}-C = CH_{2}$$

$$CH_{3}-C - CH_{3}$$

$$CH_{3}-C - CH$$

#### 4. From calcium salts of carboxylic acids

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

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



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



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Calcium ethanoate

# **B.** Preparation of aldehydes

# 1) Rosenmund reduction

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

Example  
O  

$$CH_3 - C - Cl + H_2 \xrightarrow{Pd/BaSO_4} CH_3 - C - H + HCl$$
  
Acetyl chloride Acetaldehyde

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

Formaldehyde and ketones cannot be prepared by this method.

# 2. Stephen's reaction

When alkylcy anides are reduced using  $SnCl_2/HCl$ , imines are formed, which on hydrolysis gives corresponding ald ehyde.

$$CH_{3} C \equiv N \xrightarrow{SnCl_{2}/HCl} CH_{3} CH = NH \xrightarrow{H_{3}O^{+}} CH_{3} CHO + NH_{3}$$

# 3. Selective reduction of cyanides

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

$$CH_{3}-CH = CH-CH_{2}-CH_{2}-CN \xrightarrow{i) AlH(iso-butyl)_{2}} CH_{3}-CH = CH-CH_{2}-CH_{2}-CH_{2}-CHO$$
  
hex - 4- ennitrile hex - 4- enal

# C) Preparation of benzaldehyde

1. Side chain oxidation of toluene and its derivatives by strong oxidising agents such as KMnO<sub>4</sub> gives benzoic acid.

When chromylchloride is used as an oxidising agent, toluene gives benzaldehyde. This reaction is called **Etard reaction**. Acetic anhydride and CrO<sub>3</sub> can also be used for this reaction.



methylbenzene

benzaldehyde

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

# 2) Gattermann – Koch reaction

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



# 3) Manufacture of benzaldehyde from toluene

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



This is the commercial method for the manufacture of benzaldehye.

# D) Preparation of ketones

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



# 2) Preparation of phenyl ketones Friedel – Crafts acylation

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



# 12.4 Physical properties of aldehydes and ketones

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

# 2. Boiling points

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

$$\sum_{C=0}^{\delta_{+}} \sum_{C=0}^{\delta_{-}} \sum_{C=0}^{\delta_{+}} \sum_{C=0}^{\delta_{-}} \sum_{C=0}^{\delta_{+}} \sum_{C=0}^{\delta_{-}} \sum_{C=0}^{\delta_{$$

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

Compound	Molar mass	Boiling point (K)	Compound	Molar mass	Boiling point (K)
$CH_3(CH_2)_3CH_3$ Pentane	72	309	$CH_3CH_2COCH_3$ butan - 2- one	72	353
$CH_3(CH_2)_2CHO$ butanal	72	349	CH <sub>3</sub> CH <sub>2</sub> COOH Propanoicacid	74	414
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> OH butanol	74	391			

# 3. Solubility

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

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

$$R = 0 = 0 = C = R$$

#### 4. **Dipolemoment:**

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

$$>_{C^{+}=0}^{\delta}$$

# 12.5 Chemical properties of aldehydes and ketones

### A) Nucleophilic addition reactions

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



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



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

# Examples

# 1) Addition of HCN

Attack of CN<sup>-</sup>on carbonyl carbon followed by protonation gives cyanohydrins.



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

# 2) Addition of NaHSO<sub>3</sub>



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

# 3) Addition of alcohol

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

#### example

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







# 4) Addition of ammonia and its derivatives

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

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



G	Ammonia derivatives	Carbonyl derivatives	Product name
OH	Hydroxyl amine	C = N - OH	Oxime
$-NH_2$	Hydrazine	$\sum C = N - NH_2$	Hydrazone
$- HN - C_6H_5$	Phenyl hydrazine	$C = N - NH - C_6H_5$	Phenyl hydrazone



# i) Reaction with hydroxyl amine

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

Example:



# ii) Reaction with hydrazine

Aldehydes and ketones react with hydrazine to form hydrazone.

Example:



# iii) Reaction with phenyl hydrazine

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



# 5) Reaction with NH<sub>3</sub>

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



Acetaldehyde

Acetaldehyde ammonia

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

 $6HCHO + 4 NH_3 \longrightarrow (CH_2)_6 N_4 + 6 H_2O$ 

Formaldehyde

Hexamethylene tetramine

Structure



# Uses

- (i) Urotropine is used as a medicine to treat urinary infection.
- (ii) Nitration of Urotropine under controlled condition gives an explosive RDX (Research and development explosive). It is also called cyclonite or cyclotri methylene trinitramine.
- iii) Acetone reacts with ammonia to form diacetone amine.



iv) Benzaldehyde form a complex condensation product with ammonia.



# B) Oxidation of aldehydes and ketones

#### a) Oxidation of aldehydes

Aldehydes are easily oxidised to carboxylic acid containing the same number of carbon atom, as in parent aldehyde. The common oxidising agents are acidified  $K_2Cr_2O_7$ , acidic or alkaline KMnO<sub>4</sub> or chromic oxide.

#### Example



#### b) Oxidation of ketone

Ketones are not easily oxidised. Under drastic condition or with powerful oxidising agent like Con.HNO<sub>3</sub>, H<sup>+</sup>/KMnO<sub>4</sub>, H<sup>+</sup>/K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, cleavage of carbon-carbon bond takes place to give a mixture of carboxylic acids having less number of carbon atom than the parent ketone.

 $\begin{array}{c} CH_3 - C - CH_3 \xrightarrow{(O)} HCOOH + CH_3COOH \\ O Formic acid & Acetic acid \end{array}$ 

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

$$CH_{3} - CH_{2} - CH_{2} - CH_{2} - CH_{3} \xrightarrow{(O)}{Con HNO_{3}} CH_{3}CH_{2} - COOH + CH_{3}COOH$$
pentan - 2 - one Propanoic acid ethanoic acid

# C) Reduction reactions

# (i) Reduction to alcohols

We have already learnt that aldehydes and ketones can be easily reduced to primary and secondary alcohols respectively. The most commonly used reducing agents are Lithium Aluminium hydride (LiAlH<sub>4</sub>), and Sodium borohydride (NaBH<sub>4</sub>).

# a) Aldehyde are reduced to primary alcohols.

Example

$$CH_{3} - \begin{matrix} H \\ CH_{3} - \begin{matrix} CH_{2} - OH_{3} - \begin{matrix} CH_{3} - \end{matrix} \\ CH_{3} - \begin{matrix} CH_{3} - \end{matrix} \\ CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \end{matrix} \\ CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \end{matrix} \\ CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \end{matrix} \\ CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \end{matrix} \\ CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \end{matrix} \\ CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \end{matrix} \\ CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \end{matrix} \\ CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \end{matrix} \\ CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \end{matrix} \\ CH_{3} - \end{matrix} \\ CH_{3} - \begin{matrix} CH_{3} - \end{matrix} \\ CH_{3} - \begin{matrix} CH_{3} - \end{matrix} \\ CH_{3} - \end{matrix} \\ CH_{3} - \begin{matrix} CH_{3} - \end{matrix} \\ CH_{3} - \end{matrix} \\ CH_{3} - \begin{matrix} CH_{3} - \end{matrix} \\ CH_{3} - \end{matrix} \\ CH_{3} - \end{matrix} \\ CH_{3} - \end{matrix} \\ CH_{3} - \begin{matrix} CH_{3} - \begin{matrix} CH_{3} - \end{matrix} \\ CH_{$$

b) Ketone are reduced to Secondary alcohols.

Example

The above reactions can also be carried out with hydrogen in the presence of metal catalyst like Pt, Pd, or Ni. LiAlH<sub>4</sub> and NaBH<sub>4</sub> do not reduce isolated carbon – carbon double bonds and double bond of benzene rings. In case of  $\alpha$ ,  $\beta$  unsaturated aldehyde and ketones, LiAlH<sub>4</sub> reduces only C = O group leaving C = C bond as such.

#### ii) Reduction to hydrocarbon

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

$$- \underset{O}{\text{C}} - \underset{\text{agent}}{\overset{4(\text{H})}{\text{-}}} - CH_2 - H_2O$$

#### a) Clemmensen reduction

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

Example

$$\begin{array}{c} CH_{3}-C-H+4(H) & \underline{Zn-Hg} \\ 0 & CH_{3}-CH_{3}+H_{2}O \\ Con HCl & Ethane \\ CH_{3}-C-CH_{3}+4(H) & \underline{Zn-Hg} \\ 0 & CH_{3}CH_{2}CH_{3}+H_{2}O \\ 0 & Con HCl \\ 0 & Acetone \\ \end{array}$$

**b)** Wolf Kishner reduction Aldehydes and Ketones when heated with hydrazine (NH<sub>2</sub>NH<sub>2</sub>) and sodium ethoxide, hydrocarbons are formed Hydrazine acts as a reducing agent and sodium ethoxide as a catalyst.

#### Example

$$\begin{array}{ccc} CH_{3}-C-H+4(H) & \underbrace{\frac{NH_{2} NH_{2}}{C_{2}H_{5}ONa}}_{C_{2}H_{5}ONa} & CH_{3}-CH_{3}+H_{2}O+N_{2} \\ & \\ H_{0} & \\ CH_{3}-C-CH_{3}+4(H) & \underbrace{\frac{NH_{2} NH_{2}}{C_{2}H_{5}ONa}}_{C_{2}H_{5}ONa} & CH_{3}CH_{2}CH_{3}+H_{2}O+N_{2} \\ & \\ H_{0} & \\ Acetone & \\ \end{array}$$

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

(iii) **Reduction to pinacols:** Ketones, on reduction with magnesium amalgam and water, are reduced to symmetrical diols known as pinacol.

$$CH_{3} - C = O + O = C - CH_{3} + 2(H) \xrightarrow{Mg - Hg} CH_{3} - CH_{3} + CH_{3}$$

$$CH_{3} - CH_{3} + CH_{3}$$

$$CH_{3} - CH_{3} + CH_{3}$$

$$CH_{3} - CH_{3} + CH_{3}$$

$$OH OH$$

$$2,3 \text{ dimethyl butane } 2,3 - diol$$

$$(pinacol)$$

#### D) Haloform reaction

Acetaldehyde and methyl ketones, containing  $CH_3$ -C- group, when treated with O

halogen and alkali give the corresponding haloform. This is known as Haloform reaction.

$$\begin{array}{c} CH_{3}-C-CH_{3} \xrightarrow{3Cl_{2}} & CCl_{3}-C-CH_{3} \xrightarrow{NaOH} & CHCl_{3} + & CH_{3}-C-ONa \\ \parallel & & & \\ O & & & & \\ O & & & & \\ \end{array}$$

# E) Reaction involving alkylgroup

#### i) Aldol condensation

The carbon attached to carbonyl carbon is called  $\alpha$  - **carbon** and the hydrogen atom attached to  $\alpha$  - carbon is called  $\alpha$  - hydrogen.

In presence of dilute base NaOH, or KOH, two molecules of an aldehyde or ketone having  $\alpha$  - hydrogen add together to give  $\beta$ - hydroxyl aldehyde (aldol) or  $\beta$  - hydroxyl ketone (ketol). The reaction is called **aldol condensation reaction**. The aldol or ketol readily loses water to give  $\alpha$ , $\beta$  – unsaturated compounds which are aldol condensation products.

a) Acetaldehyde when warmed with dil NaOH gives  $\beta$  - hydroxyl butyraldehyde (acetaldol)

$$\begin{array}{c} H \\ CH_{3}-C \\ H \\ O \\ O \\ Acetaldehyde \\ Acetaldol \\ (3 - Hydroxy butanal) \end{array} CH_{3}-CH-CH_{2} - CHO \\ H \\ Acetaldol \\ (3 - Hydroxy butanal) \end{array}$$

#### Mechanism

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

#### **Step 1 :**

The carbanion is formed as the  $\alpha$  - hydrogen atom is removed as a proton by the base.

$$HO^{-} + H^{-} CH_{2} - CHO \longrightarrow CH_{2} - CHO + H_{2}O$$

#### **Step 2 :**

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

$$CH_3 - \bigcup_{C+\Theta}^{H} CH_2 - CHO \longrightarrow CH_3 - CH - CH_2 - CHO$$

# Step 3:

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



The aldol rapidly undergoes dehydration on heating with acid to form  $\alpha$  -  $\beta$  unsaturated aldehyde.

#### ii) Crossed aldol condensation

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

Example :



# F) Some important reactions of benzaldehyde

#### i) Claisen – Schmidt Condensation

Benzaldehye condenses with aliphatic aldehyde or methyl ketone in the presence of dil. alkali at room temperature to form unsaturated aldehyde or ketone. This type of reaction is called Claisen – Schmidt condensation.

#### Example



#### ii) Cannizaro reaction

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

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

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This reaction is an example disproportionation reaction

#### Mechanism of Cannizaro reaction

Cannizaro reaction involves three steps. **Step 1 :** Attack of OH<sup>-</sup> on the carbonyl carbon.



Step 2 : Hydride ion transfer



**Step 3 :** Acid – base reaction.

$$C_{6}H_{5} - \overset{O}{C} - OH + C_{6}H_{5} CH_{2}O^{-} \xrightarrow{\text{Proton}}_{\text{exchange}} C_{6}H_{5} - \overset{O}{C} - \overset{O}{O}_{\text{benzoate}} + C_{6}H_{5}CH_{2}O$$

Cannizaro reaction is a characteristic reaction of aldehyde having no  $\alpha$  – hydrogen.

#### **Crossed Cannizaro reaction**

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

C <sub>6</sub> H <sub>5</sub> CHO	+	HCHO	NaOH	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	+	HCOONa	
Benzaldehyde	F	Formaldehyd	e	Benzyl alcohol		sodium formate	

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

#### 3) Benzoin condensation

The Benzoin condensation involves the treatment of an aromatic aldehyde with aqueous alcoholic KCN. The products are  $\alpha$  hydroxy ketone.

#### Example

Benzaldehyde reacts with alcoholic KCN to form benzoin

Benzaldehyde

Benzoin 2-hydroxy – 1, 2 – diphenyl ethanone

### 4) Perkins' reaction

When an aromatic aldehyde is heated with an aliphatic acid anhydride in the presence of the sodium salt of the acid corresponding to the anhydride, condensation takes place and an  $\alpha$ ,  $\beta$  unsaturated acid is obtained. This reaction is known as **Perkin's reaction**.

۲

**Example:** 



#### 5) Knoevenagal reaction



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

#### 6) Reaction with amine

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

#### Example

$$C_{6}H_{5} - CH = O + H_{2} N - C_{6}H_{5} - H_{5} - CH = N - C_{6}H_{5} + H_{2}O$$
  
Benzaldehyde Aniline Benzal aniline (Schiff's base)

#### 7) Condensation with tertiary aromatic amines

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



lellyde



Malachite green dye



# 8) Electrophilic substitution reactions of benzaldehyde

Electrophilic substitution reaction of acetophenone

Acetophenone reacts with Nitrating mixture to form m – nitroacetophenone.

#### 12.6 **Test for Aldehydes**



m - nitro acetophenone

# i) Tollens Reagent Test

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

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

# ii) Fehling's solution Test

Fehling's solution is prepared by mixing equal volumes of Fehling's solution 'A' containing aqueous copper sulphate and Fehling's solution 'B' containing alkaline solution of sodium potassium tartarate (Rochelle salt)

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

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

#### iii) Benedict's solution Test:

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

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

#### iv) Schiffs' reagent Test

Dilute solution of aldehydes when added to schiffs' reagent (Rosaniline hydrochloride dissolved in water and its red colour decolourised by passing SO<sub>2</sub>) yields its red colour. This is known as **Schiffs' test** for aldehydes . Ketones do not give this test. Acetone however gives a positive test but slowly.

# 12.7 Uses of Aldehydes and Ketones

#### Formaldehyde

- (i) 40% aqueous solution of formaldehyde is called **formalin**. It is used for preserving biological specimens.
- (ii) Formalin has hardening effect, hence it is used for tanning.
- (iii) Formalin is used in the production of thermo setting plastic known as bakelite, which is obtained by heating phenol with formalin.

### Acetaldehye

- (i) Acetaldehyde is used for silvering of mirrors
- (ii) Paraldehyde is used in medicine as a hypnotic.
- (iii) Acetaldehyde is used in the commercial preparation of number of organic compounds like acetic acid, ethyl acetate etc.,

# Acetone

- (i) Acetone is used as a solvent, in the manufacture of smokeless gun powder (cordite)
- (ii) It is used as a nail polish remover.
- (iii) It is used in the preparation of sulphonal, a hypnotic.
- (iv) It is used in the manufacture of thermosoftening plastic **Perspex**.

# Benzaldehyde is used

- (i) as a flavoring agent (ii) in perfumes (iii) in dye intermediates
- (iv) as starting material for the synthesis of several other organic compounds like cinnamaldehyde, cinnamic acid, benzoyl chloride etc.

### **Aromatic Ketones**

- (i) Acetophenone has been used in perfumery and as a hypnotic under the name **hypnone**.
- (ii) Benzophenone is used in perfumery and in the preparation of **benzhydrol eye drop.**

# **CARBOXYLIC ACIDS**

# Introduction

Carbon compounds containing a carboxyl function group, -COOH are called carboxylic acids. The Carboxyl group is the combination of carbonyl group -C - and the hydroxyl group (-OH).

However, carboxyl group has its own characteristic reaction. Carboxylic acids may be aliphatic (R – COOH) or aromatic (Ar – COOH) depending on the alkyl or aryl group attached to carboxylic carbon. Some higher members of aliphatic carboxylic acids ( $C_{12}$  to  $C_{18}$ ) known as fatty acids occur in natural fats as esters of glycerol.

# 12.8 IUPAC nomenclature of Carboxylic acids

Compound	IUPAC Name				
(common name, Structural formula, IUPAC Name)	Prefix with position number	Root used	Primary suffix	Secondary Suffix	
Formic acid HCOOH methanoicacid	_	meth	an¢	oicacid	
Acetic acid CH <sub>3</sub> COOH Ethanoic acid	_	eth	an¢	oicacid	
Isobutyric acid (CH <sub>3</sub> ) <sub>2</sub> CHCOOH 2 – methylpropanoic acid	2 – methyl	prop	an¢	oicacid	
Phenyl acetic acid CH <sub>2</sub> COOH 2-phenyl ethanoic acid	2-phenyl	eth	an¢	oicacid	
Oxalic acid HOOC - COOH ethane–1, 2 – dioicacid	_	eth	ane	1, 2 – dioicacid	



Malonic acid HOOC-CH <sub>2</sub> -COOH Propane-1,3-dioic acid	_	prop	ane	1, 3 – dioicacid
Succinic acid HOOC- $(CH_2)_2$ -COOH Butane-1,4-dioic acid	_	but	ane	1, 4 – dioicacid
Glutaric acid HOOC- $(CH_2)_3$ -COOH Pentane-1,5-dioic acid	_	pent	ane	1,5 – dioicacid
Adipic acid HOOC- $(CH_2)_4$ -COOH Hexane-1,6-dioic acid	_	hex	ane	1,6 – dioicacid

# 12.9 Structure of carboxyl group:

The carboxyl group represent a planar arrangement of atoms. In – COOH group, the centre carbon atom and both the oxygen atoms are in  $sp^2$  hybridisation. The three  $sp^2$  hybrid orbitals of the carbon atom overlap.

The two sp<sup>2</sup> – hybridised orbitals of the carboxyl carbon overlap with one sp<sup>2</sup> hybridised orbital of each oxygen atom while the third sp<sup>2</sup> hybridised orbital of carbon overlaps with either a s -orbital of H – atom or a sp<sup>3</sup> – hybridised orbital of C –atom of the alkyl group to form three  $\sigma$ - bonds. Each of the two oxygen atoms and the carbon atom are left with one unhybridised p – orbital which is perpendicular to the  $\sigma$ - bonding skeleton.

All these three p – orbitals being parallel overlap to form a  $\pi$ - bond which is partly delocalized between carbon and oxygen atom on one side, and carbon and oxygen of the OH group on the other side. In other words, RCOOH may be represented as a resonance hybrid of the following two canonical structures.



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

# 12.10 Methods of Preparation of carboxylic acids

Some important methods for the preparation of carboxylic acids are as follows :

# 1. From Primary alcohols and aldehydes

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

# Example

 $\begin{array}{ccc} CH_{3}CH_{2}OH & \xrightarrow{H^{+}/K_{2}Cr_{2}O_{7}} & CH_{3}CHO & & CH_{3}COOH \\ Ethyl alcohol & (O) & Acetaldehyde & (O) & Acetic acid \end{array}$ 

### 2. Hydrolysis of Nitriles

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

# Example



# 3. Acidic hydrolysis of esters

Esters on hydrolysis with dilute mineral acids yield corresponding carboxylic acid

# Example

$$\begin{array}{c} O \\ H_{3}-C \\ CH_{3}-C \\ CH_{5}+H_{2}O \\ \end{array} \xrightarrow{H^{+}} CH_{3}-C \\ CH_{3}-C \\ CH_{5}-OH \\ H^{+} \\ CH_{5}OH \\ \end{array}$$
Ethyl acetate   
Ethyl acetate   
Ethyl alcohol

# 4. From Grignard reagent

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

# Example

$$\begin{array}{c} O \\ C = O + CH_3MgBr \xrightarrow{dry} CH_3 - \overrightarrow{C} - OMgBr \xrightarrow{H_2O} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} Br \\ Methyl Magnessium \\ Bromide \end{array}$$

$$\begin{array}{c} O \\ C = O + \swarrow MgBr \xrightarrow{dry} CH_3 - \overrightarrow{C} - OMgBr \xrightarrow{H_2O} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} Br \\ Acetic acid \\ C = O + \swarrow MgBr \xrightarrow{dry} CH_3 - \overrightarrow{C} - OMgBr \xrightarrow{H^+} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} Br \\ H^+ \\ H_2O \xrightarrow{OH} C - OH + Mg \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} Br \\ H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} Br \\ H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} Br \\ H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} H^+ \\ H_2O \xrightarrow{OH} CH_3 - \overrightarrow{C} - OH + Mg \xrightarrow{OH} H^+ \\ H_2O \xrightarrow{OH} H^+ \\ H$$

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

# 5. Hydrolysis of acylhalides and anhydrides

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

# Example



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



#### 6. Oxidation of alkyl benzenes

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

#### Example



# **Evaluate yourself**

1) What happens when n-propyl benzene is oxidised using  $H^+$  / KMnO<sub>4</sub>?

2) How will you prepare benzoic acid using Grignard reagent.

# 12.11 Physical Properties of carboxylic acids.

- i) Aliphatic carboxylic acid upto nine carbon atoms are colour less liquids with pungent odour. The higher members are odourless wax like solids.
- ii) Carboxylic acids have higher boiling point than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more association of carboxylic acid molecules through intermolecular hydrogen bonding.



Inter molecular hydrogen bonding

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

- iii) Lower aliphatic carboxylic acids (up to four carbon) are miscible with water due to the formation of hydrogen bonds with water. Higher carboxylic acid are insoluble in water due to increased hydrophobic interaction of hydrocarbon part. The simplest aromatic carboxylic acid, benzoic acid is insoluble in water.
- iv) Vinegar is 6 to 8% solution of acetic acid in water. Pure acetic acid is called glacial acetic acid. Because it forms ice like crystal when cooled. When aqueous acetic acid is cooled at 289.5 K, acetic acid solidifies and forms ice like crystals, where as water remains in liquid state and removed by filtration. This process is repeated to obtain glacial acetic acid.

# 12.12 Chemical properties of carboxylic acids.

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

The reactions of carboxylic acids can be classified as follows:

- A) Reactions involving cleavage of O H bond.
- B) Reactions involving cleavage of C OH bond.
- C) Reactions involving COOH group.
- D) Substitution reactions involving hydrocarbon part.

# A) Reactions involving cleavage of O – H bond.

# 1) Reactions with metals

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

#### Example

$$2 CH_3 - C - OH + 2Na \longrightarrow 2 CH_3 - C - ONa + H_2$$
  
Acetic acid Sodium acetate

### 2) Reaction with alkalies

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





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

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

# Example

$$\begin{array}{c} O \\ \parallel \\ 2CH_3 - C - OH + Na_2CO_3 \longrightarrow 2CH_3 - C - ONa + CO_2 + H_2O \\ Acetic acid & Sodium acetate \end{array}$$

#### 4) All Carboxylic acids turn blue litmus red

### B) Reactions involving cleavage of C-OH bond

# 1) Reactions with PCl<sub>5</sub>, PCl<sub>3</sub> and SOCl<sub>2</sub>

The hydroxyl group of carboxylic acids behaves like that of an alcoholic group and is easily replaced by chlorine atom on treating with PCl<sub>5</sub>, PCl<sub>3</sub> or SOCl<sub>2</sub>.

#### Example

$$CH_{3}-C-OH + PCl_{5} \longrightarrow CH_{3}-C-Cl + POCl_{3} + HCl$$
Acetic acid
$$C_{6}H_{5}-C-OH + SOCl_{2} \longrightarrow C_{6}H_{5}-C-Cl + SO_{2} + HCl$$
Benzoic acid
Benzoyl chloride

### 2) Reactions with alcohols (Esterification)

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

#### Example

$$C_{6}H_{5} - C - OH + C_{2}H_{5}OH \xrightarrow{H^{+}} C_{6}H_{5} - C - OC_{2}H_{5} + H_{2}O$$
  
Benzoic acid ethyl benzoate

# Mechanism of esterification:

The Mechanism of esterification involves the following steps.



# C) Reactions involving – COOH group

# 1) Reduction

# i) Partial reduction to alcohols

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

#### Example

$$\begin{array}{c} O \\ H_{3} - C - OH \end{array} \xrightarrow{\text{LiAlH}_{4}} CH_{3}CH_{2}OH + H_{2}O \\ \text{ethanoicacid} \end{array} ethanol$$

### ii) Complete reduction to alkanes

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

# Example

$$CH_3 - C - OH + 6 HI \xrightarrow{\text{Red P}} CH_3 - CH_3 + 3I_2 + 2H_2O$$
Acetic acid Ethane

#### 2) Decarboxylation

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

#### Example



### 3) Kolbe's electrolytic decarboxylation

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



Sodium formate solution on electrolysis gives hydrogen

# 4) Reactions with ammonia

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

#### Example



# 5) Action of heat in the presence of $P_2O_5$

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

#### Example



# D) Substitution reactions in the hydrocarbon part

# 1) $\alpha$ - Halogenation

Carboxylic acids having an  $\alpha$  - hydrogen are halogenated at the  $\alpha$  - position on treatment with chlorine or bromine in the presence of small amount of red posphorus to form  $\alpha$  halo carboxylic acids. This reaction is known as **Hell – Volhard – Zelinsky reaction** (HVZ reaction) The  $\alpha$  - Halogenated acids are convenient starting materials for preparing  $\alpha$  - substituted acids.

$$CH_{3} - COOH \xrightarrow[H_{2}O]{Cl_{2} / red P_{4}} CH_{2} - COOH$$

$$\downarrow Cl$$
Acetic acid
Mono Chloro acetic acid

# 2) Electrophilic substitution in aromatic carboxylic acids

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

# i) Halogenation



iv) Benzoic acid does not undergo friedal craft's reaction. This is due to the strong deactivating nature of the carboxyl group.

# E) Reducing action of Formic acid

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



Aldehyde group

allowylic acid group

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

HCOO<sup>-</sup> +  $2Ag^+$  +  $3OH^ \longrightarrow$  2Ag +  $CO_3^2$  +  $2H_2O$ (Tollens reagent) Silver mirror

ii) Formic acid reduces Fehling's solution. It reduces blue coloured cupric ions to red coloured cuprous ions.

HCOO<sup>-</sup> + 2Cu<sup>2+</sup> + 5 OH<sup>-</sup>  $\longrightarrow$  Cu<sub>2</sub>O + CO<sub>3</sub><sup>2-</sup> + 3 H<sub>2</sub>O (Fehlings solution) red precipitate

# Tests for carboxylic acid group

- i) In aqueous solution carboxylic acid turn blue litmus red.
- ii) Carboxylic acids give brisk effervescence with sodium bicarbonate due to the evolution of carbon-di -oxide.
- iii) When carboxylic acid is warmed with alcohol and Con  $H_2SO_4$  it forms an ester, which is detected by its fruity odour.

# 12.13 Acidity of Carboxylic acids

Carboxylic acids undergo ionisation to produce  $H^+$  and carboxylate ions in aqueous solution. The carboxylate anion is stabilised by resonance which make the Carboxylic acid to donate the proton easily.

$$\begin{array}{c} O \\ \parallel \\ R - C - OH \end{array} \xrightarrow{O} \\ R - C - O^{-} + H^{+} \\ Carboxylic acid \end{array}$$

The resonance structure of carboxylate ion are given below.

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

$$R-COOH + H_2O \longrightarrow RCOO^- + H_3O^+$$
$$Ka = \frac{[RCOO^-] [H_3O^+]}{[RCOOH]}$$

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

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

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

Ka and pKa values of some Carboxylic acids of 298 K

Carboxy		
Name of acid	Molecular formula	pKa value
Trichloroacetic acid	Cl <sub>3</sub> CCOOH	0.64
Dichloroacetic acid	Cl <sub>2</sub> CHCOOH	1.26
Fluoroacetic acid	FCH <sub>2</sub> COOH	2.59
Chloroacetic acid	ClCH <sub>2</sub> COOH	2.87
Bromoacetic acid	BrCH <sub>2</sub> COOH	2.90
Iodoacetic acid	ICH <sub>2</sub> COOH	3.17
Formic acid	НСООН	3.75
Benzoic acid	C <sub>6</sub> H₅COOH	4.20
Acetic acid	СН <sub>3</sub> СООН	4.76
Propionic acid	CH <sub>3</sub> CH <sub>2</sub> COOH	4.88
o – nitrobenzoic acid	o-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COOH	2.17
m-nitrobenzoic acid	m-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COOH	3.49
p- nitrobenzoic acid	p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> COOH	3.44

# Effect of substituents on the acidity of carboxylic acid.

# i) Electron releasing alkyl group decreases the acidity

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

$$\begin{array}{c} O \\ H - C \\ - OH \\ > CH_3 \\ - C \\ - OH \\ > CH_3 \\ - CH_3 \\ - CH_2 \\ - CH_2 \\ - CH_2 \\ - OH \\$$

# ii) Electron withdrawing substituents increases the acidity

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

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

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

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

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

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

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

The relative acidities of various organic compounds are

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

# 12.14 Functional derivatives of carboxylic acids

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

Group replacing - OH	Name	Structure	Example
-Cl	Acid chloride	$\mathbf{R} - \mathbf{C} - \mathbf{C}\mathbf{I}$	$CH_3 - C - Cl$ Acetyl chloride
-NH <sub>2</sub>	Acid amide	$\mathbf{R} - \mathbf{C} - \mathbf{N}\mathbf{H}_2$	$ \begin{array}{c}     O \\     \parallel \\     CH_3 - C - NH_2 \\     Acetamide \end{array} $
-OR'	ester	$\mathbf{R} = \mathbf{C} = \mathbf{O}\mathbf{R}'$	$ \begin{array}{c} O \\ \parallel \\ CH_3 - C - OCH_3 \\ Methyl acetate \end{array} $
-OOCR	Acid anhydride	$\begin{array}{c} 0 & 0 \\ \parallel & \parallel \\ R - C - O - C - R \end{array}$	$ \begin{array}{c} O & O \\ \parallel & \parallel \\ CH_3 - C - O - C - R \\ Acetic anhydride \end{array} $

# **Relative reactivity of Acid derivatives**

The reactivity of the acid derivatives follows the order

$$\begin{array}{ccccc} O & O & O & O & O \\ \| & \| & \| & \| & \| \\ R - C - Cl > & R - C - O - C - R > & R - C - OR' > & R - C - NH_2 \end{array}$$

The above order of reactivity can be explained in terms of

i) Basicity of the leaving group ii) Resonance effect

# (i) Basicity of the leaving group

Weaker bases are good leaving groups. Hence acyl derivatives with weaker bases as leaving groups (L) can easily rupture the bond and are more reactive. The correct order of the basicity of the leaving group is  $H_2N$  :> : OR > RCOO :> : C1 Hence the reverse is the order of reactivity.

# (ii) Resonance effect

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

This effect makes the molecule more stable and reduces the R - C reactivity of the acyl compound. The order of electronegativity of the leaving groups follows the order –  $Cl > - OCOR > - OR > - NH_2$ 

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

acid halide > acid anhydride > esters > acid amides

# 12.14.1 Nomenclature

Compound	IUPAC Name			
(common name, Structural formula, IUPAC Name)	Prefix with position number	Root used	Primary suffix	Secondary Suffix
Acetyl chloride				
$CH_3 - C - Cl$	_	eth	an¢	oyl chloride
Ethanoylchloride				
Propionyl chloride				
$C_2H_5 - C - Cl$	_	prop	an¢	oyl chloride
Propanoylchloride				
Benzoyl chloride				
$C_6H_5 - C - Cl$	-	Benz	an¢	oyl chloride
Benzoylchloride				



Acetic anhydride $CH_3 - C - O - C - CH_3$ $\parallel \qquad \parallel$ $O \qquad O$ Ethanoic anhydride	_	eth	an¢	oic anhydride		
Propionic anhydride $CH_3 - CH_2 - C - O - C - CH_2 - CH_3$ $\  \qquad \  \qquad 0$ Propanoic anhydride	-	prop	an¢	oic anhydride		
Benzoic anhydride $C_6H_5-C-O-C-C_6H_5$ $\ $ $\ $ $\ $ O $OBenzoic anhydride$	_	Benz		oic anhydride		
Esters						
Methyl acetate $CH_3-C-O-CH_3$ $\parallel$ O Methyl ethanoate Ethyl acetate $CH_3-C-O-C_2H_5$	Methyl	eth	an¢	oate		
∥ O Ethyl ethanoate	Ethyl	eth	an¢	oate		
Phenyl acetate $CH_3 - C - O - C_6H_5$ $\parallel$ O Phenyl ethanoate	Phenyl	eth	an¢	oate		
Acid Amides						
Acetamide $CH_3 - C - NH_2$ $\ $ O Ethanamide	_	eth	an¢	amide		

|\_\_\_\_

Propionamide				
$C_2H_5 - C - NH_2$	_	prop	an¢	amide
Propanamide				
Benzamide				
$C_6H_5 - C - NH_2$	_	benz	-	amide
Benzamide				

#### 12. 14. 2. Acid Halides:

#### Methods of Preparation of acid chloride:

Acid chlorides are prepared from carboxylic acid by treating it with anyone of the chlorinating agent such as SOCl<sub>2</sub>, PCl<sub>5</sub>, or PCl<sub>3</sub>

# 1) By reaction with thionyl Chloride (SOCl<sub>2</sub>)



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

### **Physical properties:**

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

#### **Chemical properties:**

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

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



2) Reaction with Alcohols (Alcoholysis) gives esters.



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

$$CH_3 - C - Cl + H - NH_2 \longrightarrow CH_3 - C - NH_2 + HC$$
Acetyl chloride Ammonia Acetamide

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



### (5) Reduction.

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

$$CH_{3} \xrightarrow{O} C \xrightarrow{O} Cl_{+}H_{2} \xrightarrow{Pd - BaSO_{4}} CH_{3} \xrightarrow{O} CH_{3} \xrightarrow{O} H_{+}HCl$$
Acetyl chloride Acetaldehyde

(b) When reduced with LiAlH<sub>4</sub> gives primary alcohols.

$$CH_3 - CH_3 - CH_2 - CH_4 + 4(H) \xrightarrow{\text{LiAlH}_4} CH_3 - CH_2 - OH + HCl$$
  
Ethyl alcohol

### 12.14.3 Acid anhydride

### Methods of preparation

# 1. Heating carboxylic acid with P<sub>2</sub>O<sub>5</sub>

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

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

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



# **Chemical properties**

# 1. Hydrolysis

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



# 2. Reaction with alcohol

Acid anhydride reacts with alcohols to form esters.



# 3. Reaction with ammonia

Acid anhydride reacts with ammonia to form amides.



# 4. Reaction with PCl<sub>5</sub>

Acid anhydride reacts with PCl<sub>5</sub> to form acyl chlorides.



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Acetic anhydride

Acetyl chloride

# 12.14.4 Esters Methods of preparation

# 1. Esterification

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

# 2. Alcoholysis of Acid chloride or Acid anhydrides

ii) Treatment of acid chloride or acid anhydride with alcohol also gives esters

# **Physical Properties**

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

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

# **Chemical Properties**

# 1. Hydrolysis

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

# 2. Reaction with alcohol (Transesterification)

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



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

# 3. Reaction with ammonia (Ammonolysis)

Esters react slowly with ammonia to form amides and alcohol.

$$\begin{array}{c} O \\ H \\ CH_3 - C - OC_2H_5 + H - NH_2 \longrightarrow CH_3 - C - NH_2 + C_2H_5OH \\ Ethyl acetate & Acetamide & Ethyl alcohol \end{array}$$

#### 4. Claisen Condensation

Esters containing at least one  $\infty$ - hydrogen atom undergo self condensation in the presence of a strong base such as sodium ethoxide to form  $\beta$ - keto ester.



# 5. Reaction with PCl<sub>5</sub>

Esters react with PCl<sub>5</sub> to give a mixture of acyl and alkyl chloride

$$CH_{3} - C - OC_{2}H_{5} + PCl_{5} \longrightarrow CH_{3} - C - Cl + C_{2}H_{5}Cl + POCl_{3}$$
  
Ethyl acetate Acetyl chloride Ethyl chloride

#### **Evaluate yourself**

Why is acid anhydride preferred to acyl chloride for carrying out acylation reactions ?

# 12.14.5 Acid Amides

Acid amides are derivatives of carboxylic acid in which the – OH part of carboxyl group has been replaced by – NH<sub>2</sub> group. The general formula of amides are given as follows.

O || Now, we shall focus our attention mainly on the study of chemistry of acetamide.  $R-C-NH_2$ 

# **Methods of Preparation**

# 1. Ammonolysis of acid derivatives

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



#### Acetic anhydride

Acetamide

# 2) Heating ammonium carboxylates

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

$$CH_3 - \overset{O}{C} - O^- NH_4^+ \xrightarrow{\Delta} CH_3 - \overset{O}{C} - NH_2 + H_2O$$

Ammonium acetate

Acetamide

# 3) Partial hydrolysis of alkyl cyanides (Nitriles)

Partial hydrolysis of alkyl cyanides with cold con HCl gives amides

$$CH_3 - C \equiv N \xrightarrow[H_2O/OH]{Conc HCl} CH_3 - C - NH_2$$

$$Methyl cyanide Acetamide$$

# **Chemical Properties**

### 1. Amphoteric character

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

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

$$CH_3 - C - NH_2 + HCl \longrightarrow CH_3 - C - NH_3 Cl$$

Acetamide

Acetamide hydrochloride

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

$$2CH_3 - C - NH_2 + 2Na \longrightarrow 2CH_3 - C - NHNa + H_2$$
  
Acetamide Sodium acetamide

# 2) Hydrolysis

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

$$CH_{3} - C - NH_{2} + H_{2}O \xrightarrow{dil HCl} CH_{3} - C - OH + NH_{4}Cl$$
Acetamide
$$CH_{3} - C - NH_{2} \xrightarrow{NaOH} CH_{3} - C - ONa + NH_{3}$$
Acetamide
Sodium acetate

# 3) Dehydration

A mides on heating with strong dehydrating agents like  $\rm P_2O_5$  get dehydrated to form cyanides.

$$\begin{array}{c} O \\ H_{3}-C \\ H_{2}-NH_{2} \end{array} \xrightarrow{P_{2}O_{5}} CH_{3}-C \equiv N+H_{2}O \\ Acetamide \\ Acetamide \\ (aceto nitrile) \end{array}$$

### 4) Hoff mann's degradation

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

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

Acetamide

Methyl amine

# 5) Reduction

Amides on reduction with LiAlH<sub>4</sub> or Sodium and ethyl alcohol to form corresponding amines.

$$CH_3 - C - NH_2 + 4 (H) \xrightarrow{\text{LiAIH}_4} CH_3 - CH_2 - NH_2 + H_2O$$
  
Acetamide Ethyl amine

# 12.15 Uses of carboxylic acids and its derivatives

# Formic acid

It is used

- i) for the dehydration of hides.
- ii) as a coagulating agent for rubber latex
- iii) in medicine for treatment of gout
- iv) as an antiseptic in the preservation of fruit juice.

#### Acetic acid

It is used

- i) as table vinegar
- ii) for coagulating rubber latex
- iii) for manufacture of cellulose acetate and poly vinylacetate

# Benzoic acid

It is used

- i) as food preservative either in the pure form or in the form of sodium benzoate
- ii) in medicine as an urinary antiseptic

#### iii) for manufacture of dyes

#### **Acetyl Chloride**

It is used

- i) as acetylating agent in organic synthesis
- ii) in detection and estimation of OH, NH, groups in organic compounds

# Acetic anhydride

It is used

- i) acetylating agent
- ii) in the preparation of medicine like asprin and phenacetin
- iii) for the manufacture plastics like cellulose acetate and poly vinyl acetate.

#### Ethyl acetate is used

- i) in the preparation of artificial fruit essences.
- ii) as a solvent for lacquers.
- iii) in the preparation of organic synthetic reagent like ethyl acetoacetate.



# Choose the correct answer:

1. The correct structure of the product 'A' formed in the reaction

 $H_2$  (gas, 1 atm) A is Pd / C, ethanol OH OH b) c) d) a)



(NEET)

- 2. The formation of cyanohydrin from acetone is an example of
  - a) nucleophilic substitution b) electrophilic substitution
  - c) electrophilic addition d) Nucleophilic addition
- 3. Reaction of acetone with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is

d) Fehling solution test

a) Grignard reagent

b) Sn / HCl

- c) hydrazine in presence of slightly acidic solution d) hydrocyanic acid
- 4. In the following reaction,

HC=CH 
$$\xrightarrow{H_2SO_4}$$
 X Product 'X' will not give

- a) Tollen's test b) Victor meyer test
- c) Iodoform test

5. 
$$CH_2 = CH_2 \xrightarrow{i) O_3} X \xrightarrow{NH_3} Y 'Y' is$$
  
a) Formaldelyde b) di acetone ammonia

- c) hexamethylene tetraamine d) oxime
- 6. Predict the product Z in the following series of reactions с II OU M.D

Ethanoic acid 
$$\xrightarrow{PCl_5} X \xrightarrow{C_6H_6} Y \xrightarrow{II(CH_3MgBF)} Z$$
.  
a)  $(CH_3)_2C(OH)C_6H_5$  b)  $CH_3CH(OH)C_6H_5$ 

c) CH<sub>3</sub>CH(OH)CH<sub>2</sub>-CH<sub>3</sub>

7. Assertion: 2,2 – dimethyl propanoic acid does not give HVZ reaction. Reason: 2 – 2, dimethyl propanoic acid does not have  $\alpha$  - hydrogen atom

d)



b) if both assertion and reason are true but reason is not the correct explanation of assertion.

- c) assertion is true but reason is false
- d) both assertion and reason are false.
- 8. Which of the following represents the correct order of acidity in the given compounds

a)FCH<sub>2</sub>COOH > CH<sub>3</sub>COOH > BrCH<sub>2</sub>COOH > ClCH<sub>2</sub>COOH b)FCH<sub>2</sub>COOH > ClCH<sub>2</sub>COOH > BrCH<sub>2</sub>COOH > CH<sub>3</sub>COOH c) CH<sub>3</sub>COOH > ClCH<sub>2</sub>COOH > FCH<sub>2</sub>COOH > Br-CH<sub>2</sub>COOH d) Cl CH,COOH > CH,COOH > BrCH,COOH > ICH,COOH 9. Benzoic acid  $\xrightarrow{i) \text{ NH}_3} A \xrightarrow{\text{NaOBr}} B \xrightarrow{\text{NaNO}_2/\text{HCl}} C$  'C' is a) anilinium chloride b) O – nitro aniline c) benzene diazonium chloride d) m – nitro benzoic acid 10. Ethanoic acid  $\xrightarrow{P/Br_2} 2$  – bromoethanoic acid. This reaction is called b) Haloform reaction a) Finkelstein reaction c) Hell – Volhard – Zelinsky reaction d) none of these 11. CH<sub>2</sub>Br $\xrightarrow{\text{KCN}}$ (A) $\xrightarrow{\text{H}_3O^+}$ (B) $\xrightarrow{\text{PCl}_5}$ (C) product (C) is b) chloro acetic acid a) acetylchloride c)  $\alpha$  - chlorocyano ethanoic acid d) none of these 12. Which one of the following reduces tollens reagent a) formic acid b) acetic acid c) benzophenone d) none of these i) Mg, ether  $H_3O^+$ - **B** 'B' is 13. ii)  $CO_2$ COOH COOH a) b) c) d) The IUPAC name of 14. OH



16. In which case chiral carbon is not generated by reaction with HCN



- 17. Assertion : p N, N dimethyl aminobenzaldehyde undergoes benzoin condensation Reason : The aldehydic (-CHO) group is meta directing
  - a) if both assertion and reason are true and reason is the correct explanation of assertion.
  - b) if both assertion and reason are true but reason is not the correct explanation of assertion.
  - c) assertion is true but reason is false d) both assertion and reason are false.
- 18. Which one of the following reaction is an example of disproportionation reaction
  - a) Aldol condensation b) cannizaro reaction
  - c) Benzoin condensation d) none of these
- 19. Which one of the following undergoes reaction with 50% sodium hydroxide solution to give the corresponding alcohol and acid
  - a) Phenylmethanal b) ethanal c) ethanol d) methanol

- 20. The reagent used to distinguish between acetaldehyde and benzaldehyde is
  - a) Tollens reagent b) Fehling's solution
  - c) 2,4 dinitrophenyl hydrazine d) semicarbazide
- 21. Phenyl methanal is reacted with concentrated NaOH to give two products X and Y. X reacts with metallic sodium to liberate hydrogen X and Y are
  - a) sodiumbenzoate and phenol b) Sodium benzoate and phenyl methanol
  - c) phenyl methanol and sodium benzoate d) none of these
- 22. In which of the following reactions new carbon carbon bond is not formed?
  - a) Aldol condensation b) Friedel craft reaction
  - c) Kolbe's reaction d) Wolf kishner reduction
- 23. An alkene "A" on reaction with  $O_3$  and  $Zn H_2O$  gives propanone and ethanal in equimolar ratio. Addition of HCl to alkene "A" gives "B" as the major product. The structure of product "B" is

a) 
$$CI-CH_2-CH_2-CH_1$$
  
 $CH_3$   
 $CH_2CI$   
 $I$   
 $CH_2CI$   
 $I$   
 $CH_2-CH_2-CH_3$   
 $CH_3$   
 $CH_3C-CH_2-CH_2-CH_3$   
 $CH_3$   
 $CH_3C-CH_2-CH_3$   
 $CH_3$   
 $CH_3C-CH_2-CH_3$   
 $CH_3$   
 $CH_3C-CH_3$   
 $CH_3C-CH_3C-CH_3$   
 $CH_3C-$ 

- 24. Carboxylic acids have higher boiling points than aldehydes, ketones and even alcohols of comparable molecular mass. It is due to their (NEET)
  - a) more extensive association of carboxylic acid via van der Waals force of attraction
  - b) formation of carboxylate ion
  - c) formation of intramolecular H-bonding
  - d) formation of intermolecular H bonding

# **Short Answer Questions**

- 1. How is propanoic acid is prepared starting from
  - (a) an alcohol (b) an alkylhalide
- (c) an alkene
- 2. A Compound (A) with molecular formula C<sub>2</sub>H<sub>3</sub>Non acid hydrolysis gives(B) which reacts with thionylchloride to give compound(C). Benzene reacts with compound (C) in presence of anhydrous AlCl<sub>3</sub> to give compound(D). Compound (D) on reduction with Zn/Hg and Conc.HCl gives (E). Identify (A), (B), (C), (D) and (E). Write the equations.
- 3. Identify X and Y.

 $\mathrm{CH}_{3}\mathrm{COCH}_{2}\mathrm{CH}_{2}\mathrm{COOC}_{2}\mathrm{H}_{5} \xrightarrow{\mathrm{CH}_{3}\mathrm{MgBr}} \mathrm{X} \xrightarrow{\mathrm{H}_{3}\mathrm{O}^{+}} \mathrm{Y}$ 

4. Identify A, B and C



5. Identify A, B, C and D

ethanoic acid  $\xrightarrow{\text{SOCl}_2}$  A  $\xrightarrow{\text{Pd/BaSO}_4}$  B  $\xrightarrow{\text{NaOH}}$  C  $\xrightarrow{\Delta}$  D

- 6. An alkene (A) on ozonolysis gives propanone and aldehyde (B). When (B) is oxidised (C) is obtained. (C) is treated with Br<sub>2</sub>/P gives (D) which on hydrolysis gives (E). When propanone is treated with HCN followed by hydrolysis gives (E). Identify A, B, C, D and E.
- 7. How will you convert benzaldehyde into the following compounds?

(i) benzophenone (ii) benzoic acid

(iii)  $\alpha$ -hydroxyphenylaceticacid.

- 8. What is the action of HCN on
  - (i) propanone (ii) 2,4-dichlorobenzaldehyde. iii) ethanal
- 9. A carbonyl compound A having molecular formula  $C_5H_{10}O$  forms crystalline precipitate with sodium bisulphite and gives positive iodoform test. A does not reduce Fehling solution. Identify A.
- 10. Write the structure of the major product of the aldol condensation of benzaldehyde with acetone.
- 11. How are the following conversions effected
  - (a) propanal into butanone (b) Hex-3-yne into hexan-3-one.
  - (c) phenylmethanal into benzoic acid (d) phenylmethanal into benzoin
- 12. Complete the following reaction.

$$\begin{array}{c} CH_3-CH_2-CH_2-C-CH_3 \xrightarrow{HO-CH_2-CH_2-CH_2-OH} \\ 0 \\ dry HCl \end{array}?$$

13. Identify A, B and C



- 14. Oxidation of ketones involves carbon carbon bond cleavage. Name the product (s) is / are formed on oxidising 2,5 dimethyhexan 3- one using strong oxidising agent.
- 15. How will you prepare
  - i. Acetic anhydride from acetic acid
  - ii. Ethylacetate from methylacetate
  - iii. Acetamide from methylcyanide
  - iv. Lactic acid from ethanal
  - v. Acetophenone from acetylchloride
  - vi. Ethane from sodium acetate
  - vii. Benzoic acid from toluene
  - viii. Malachitegreen from benzaldehyde
    - ix. Cinnamic acid from benzaldehyde
    - x. Acetaldehyde from ethyne



# **CARBONYL COMPOUNDS**