8. ALDEHYDES KETONES AND CARBOXYLIC ACIDS

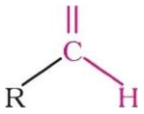
These are compounds containing carbon-oxygen double bond [>C=O, called carbonyl group]. In aldehydes, the carbonyl group is bonded to a carbon and hydrogen while in ketones, it is bonded to two carbon atoms. The carbonyl compounds in which carbonyl group is bonded to oxygen are known as carboxylic acids, and their derivatives (e.g. esters, anhydrides) while in compounds where carbon is attached to nitrogen and to halogens are called amides and acyl halides respectively. The general formulas of these compounds are as follows:

O

O

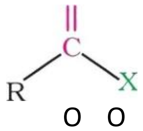
O

o

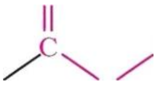


R R' R OH R OR'

Aldehyde Ketone Carboxylic acid Ester



O O O o c



R O R'

RAmideNH2 Acyl halide; X = (Halogen) Acid anhydride Aldehydes and Ketones

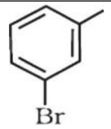
Nomenclature:

The common names of most aldehydes are derived from the common names of the corresponding carboxylic acids by replacing the ending —ic acid with aldehyde. The position of the substituent in the carbon chain is indicated by Greek letters a, ß, V, 5, etc.

The common names of ketones are derived by naming two alkyl or aryl groups bonded to the carbonyl group and by suffixing ketone. The positions of the substituents are indicated by Greek letters, a a', ß ß' and so on.

The IUPAC names of open chain aliphatic aldehydes and ketones are derived from the names of the corresponding alkanes by replacing the ending —e with '—al' and '—one' respectively. In case of aldehydes the longest carbon chain is numbered starting from the carbon of the aldehyde group while in case of ketones the numbering begins from the end nearer to the carbonyl group. Some examples are:

Compound	Common name	IUPAC name
	ALDEHYDES	
$HCHO$	Formaldehyde	Methanal
$CH3CHO$	Acetaldehyde	Ethanal
$(CH3)2CHCHO$	Isobutyraldehyde	2-Methylpropanal

$CH_3CH(OCH_3)CHO$	a-Methoxypropionaldehyde	2-Methoxypropanal
CH3CH2CH2CH2CHO	Valeraldehyde	Pentanal
CHFCHCHO	Acrolein	Prop-2-enal
CHO CHO	Phthalaldehyde	Benzene-I,2-dicarbaldehyde
 CHO	m-Bromobenzaldehyde	3-Bromobenzenecarbaldehyde Or, 3-Bromobenzaldehyde
KETONES		
CH3-CO-CH3	Acetone	Propanone
CH3-CO-CH2-CH3	Ethyl methyl ketone	Butanone
CH3-CO-CH2-CH2-CH3	Methyl n-propyl ketone	Pentan-2-one
CH3-CH2-CO-CH2-CH3	Diethyl ketone	Pentan-3-one
	Diisopropyl ketone	2,4-Dimethylpentan-3-one
	Mesityl oxide	4-Methylpent-3-en-2-one
O CH3	a-Methylcyclohexanone	2-Methylcyclohexanone

Preparation of Aldehydes and Ketones

1. By oxidation of alcohols: Primary alcohols on oxidation with mild oxidising agents like Cr03 to give aldehydes while secondary alcohols give ketones.

[0]
R-CH20H — R-CHO
[0]
R2CHOH R2CO

2. By dehydrogenation of alcohols: Alcohols when heated with copper or silver catalyst at 573K, we get carbonyl compounds. Primary alcohols give aldehydes, while secondary alcohols give ketones.

hot cu/573 K
R-CH20H — — * R_CHO hot
cu/573 K1
311
R2CHOH 9———— R2C0

3. By ozonolysis of alkenes: Alkenes add ozone followed by hydrolysis with zinc dust and water, we get aldehydes or ketones.

CH2

Propene O CH3CHO + HCHO

Propene ozonide Ethanal Methanal

4. By hydration of alkynes: Alkynes add water in the presence of H2S04 and HgS04 to give carbonyl compounds. Ethyne (acetylene) gives acetaldehyde and all other alkynes give ketones.

H2S04/HgS04

CH CH + 1-420 CH3-CHO

Ethyne Acetaldehyde

H2S04/HgS04

CH3-C = CH + H20 CH3_co-CH3

Propyne Acetone

<u>Preparation of Aldehydes</u>

1. From acyl chloride or, acid chloride [Rosenmund's Reduction]:

Acid chlorides react with hydrogen in presence of palladium (Pd) supported on barium sulphate (BaS04), we get aldehydes. This reaction is called Rosenmund's reduction.

Pd/BaS04

R-COCI + H2 R_ CHO + HCI o

CHO

Pd - BaS04

Benzoyl chloride Benzaldehyde

2. From nitriles and esters:

Nitriles when reduced with stannous chloride in the presence of hydrochloric acid, we get imines, which on hydrolysis give corresponding aldehyde. This reaction is called Stephen reaction.

$$\text{RCN + SnC12 + HCI R-CH=NH} \xrightarrow{\text{H30}} \text{R-CHO}$$

Nitriles can also be selectively reduced by diisobutylaluminium hydride (DIBAL-H) to imines followed by hydrolysis to aldehydes. DIBAL-H does not affect other reducable groups like double bonds.

$$\text{ROI} \xrightarrow{\text{(i) AlH(i–Bu)}_2\text{ (ii) H20}} \text{R-CHO}$$

$$CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CN \xrightarrow{\text{(i) DIBAL-H (ii) H20}} CH_3\text{-}CH{=}CH\text{-}CH_2\text{-}CHO$$

Esters are also reduced to aldehydes with DIBAL-H.

$$\text{CH3-CH2COOCH3+} \xrightarrow{\text{(i) DIBAL-H (ii) H20}} CH_3\text{-}CH_2\text{-}CHO$$

<u>Preparation of Aromatic aldehydes</u>:

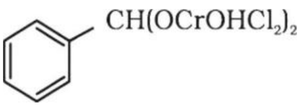
1. By oxidation of methylbenzene:

Methyl benzenes when oxidised by using mild oxidising agents like chromyl chloride (Cr02C12) or chromic oxide (Cr03) in acetic anhydride, we get benzaldehyde.

Chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde. This reaction is called Etard reaction.

CH3CHO

+ Cr02 12



Toluene Chromium complex Benzaldehyde

On treating with chromic oxide in acetic anhydride, methyl benzene is converted to benzylidene diacetate which on acidification gives benzaldehyde.

CH3CHO

273-283K

Benzaldehyde

2. **By side chain chlorination followed by hydrolysis [Manufacture of Benzaldehyde]**

Side chain chlorination of toluene gives benzal chloride, which on hydrolysis gives benzaldehyde. This method is used for the manufacture of benzaldehyde.

CH3 CHC12 CHO

H20

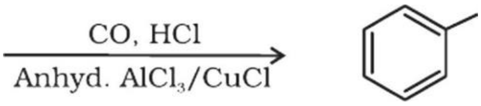
373 K

Toluene Benzal chloride Benzaldehyde

3. By Gatterman - Koch reaction:

When benzene is treated with carbon monoxide and hydrogen chloride in the presence of anhydrous aluminium chloride or cuprous chloride, we get benzaldehyde. This reaction is known as Gatterman-Koch reaction.

CHO



Benzene Benzaldehyde

Preparation of Ketones

1. From acyl chlorides: Acid chlorides react with dialkylcadmium, we get ketones. Dialkyl cadmium is prepared by the reaction of cadmium chloride with Grignard reagent.

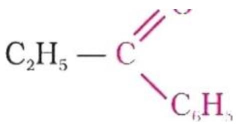
2 R-Mgx + CdC12 →------→ R2Cd +2Mg(X)Cl

2 R'-COCI + R2Cd 9-----*2 R'-CO-R + CdC12

2. From nitriles: Nitriles add Grignard reagent followed by hydrolysis gives ketones.

/ NMgBr o ether H30+

CH_3— CH2 C N + CcH5MgBr-------> CHgCH2 — C



Propiophenone
(I -Phenylpropanone)

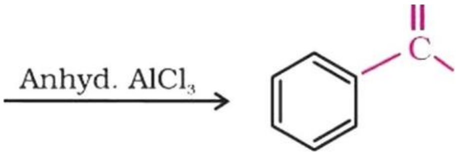
3. From benzene or substituted benzenes [Friedel — Crafts acylation reaction]

When benzene or substituted benzene is treated with acid chloride (R-COCI) in the presence of anhydrous aluminium chloride, we get a ketone. This reaction is known as Friedel-Crafts acylation reaction.

O

O

+ Ari/ R — C
— C I



Ar/R

Physical Properties of Aldehydes and Ketones

1. Boiling Point:

The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses. It is due to dipole-dipole interactions which results in weak molecular association. But their boiling points are lower than those of alcohols of similar molecular masses due to absence of intermolecular hydrogen bonding.

2. Solubility:

The lower members of aldehydes and ketones are miscible with water in all proportions, because they form hydrogen bond with water. But the solubility decreases rapidly on increasing the length of alkyl chain.

3. Physical state:

Methanal is a gas at room temperature, ethanal and acetone are volatile liquids and other aldehydes and ketones are liquid or solid at room temperature.

Structure of the Carbonyl group

The carbonyl carbon atom is sp ^{2}-hybridised and forms three sigma (o) bonds. The fourth valence electron of carbon forms a Tt-bond with oxygen. In addition, the oxygen atom also has two non bonding electron pairs. Thus, the carbonyl carbon and the three atoms attached to it lie in the same plane and the Tlelectron cloud is above and below this plane. The bond angles are approximately 120^0 .

The carbon-oxygen double bond is polarised due to higher electronegativity of oxygen. Hence, the carbonyl carbon is an electrophilic (Lewis acid), and carbonyl oxygen, a nucleophilic (Lewis base) centre. The high polarity of the carbonyl group is explained on the basis of resonance as follows: 101 O

⟷

c

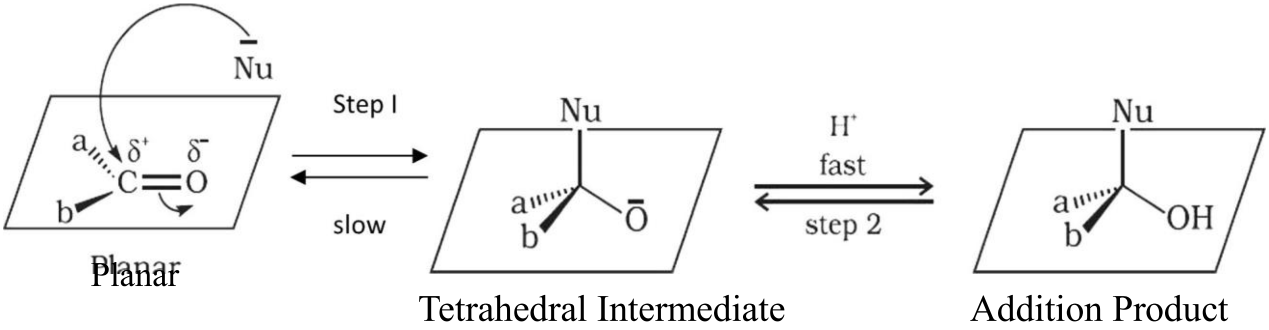
(B)

Chemical Reactions of Aldehydes and Ketones

Since aldehydes and ketones contain a carbonyl group, they undergo similar chemical reactions. The important reactions of aldehydes and ketones are:

1. Nucleophilic addition reactions:

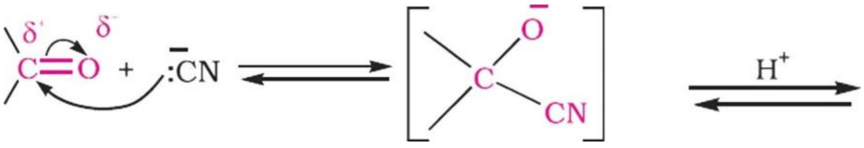
A nucleophile attacks the electrophilic carbon atom of the polar carbonyl group from a direction approximately perpendicular to the plane of sp ^{2} hybridised orbitals of carbonyl carbon. As a result, the hybridisation of carbon changes from sp ^{2} to sp ^{3} and a tetrahedral alkoxide intermediate is produced. This intermediate captures a proton from the reaction medium to give the product.



Aldehydes are generally more reactive than ketones in nucleophilic addition reactions due to steric and electronic reasons. Sterically, the presence of two bulky alkyl groups in ketones hinders the approach of nucleophile to carbonyl carbon than in aldehydes. Electronically, ketones are less reactive because of the electron releasing nature of the two alkyl groups reduces the electrophilicity of the carbonyl carbon.

Some important nucleophilic addition reactions of aldehydes and ketones are:

a) Addition of hydrogen cyanide (HCN): Aldehydes and ketones react with hydrogen cyanide (HCN) in presence of a base to give cyanohydrins.



CN

c

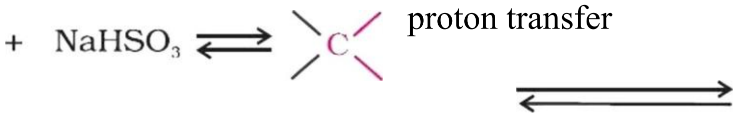
011

Intermediate Cyanohydrin

Aldehydes give aldehyde cyanohydrins and ketones give ketone cyanohydrins. The cyanohydrins are useful synthetic intermediates since it can be converted to carboxylic acids, amines, amides etc.

b) Addition of sodium hydrogensulphite: Aldehydes and ketones add sodium hydrogensulphite to form the addition products (bisulphite adduct).

OS02H



proton transfer

OSO,.Na

C=O

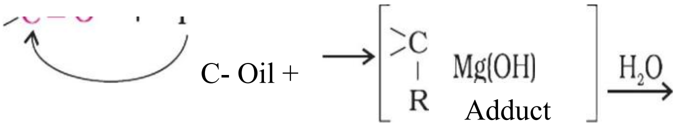
ONa

OH

Bisulphite addition compound

The bisulphite adduct are water soluble and can be converted back to the original aldehyde or ketone by treating it with dilute mineral acid or alkali. Therefore, this reaction is used for the separation and purification of aldehydes and ketones.

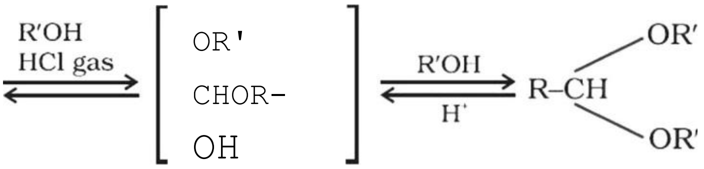
c) Addition of Grignard reagents: Carbonyl compounds add Grignard reagent followed by hydrolysis give alcohols. Formaldehyde gives primary alcohols, other aldehydes give secondary alcohols and ketones give tertiary alcohols. c=o + R-+Mg—X C- (j Mg-x



C- Oil +

d) Addition of alcohols: Aldehydes react with monohydric alcohol in the presence of dry HCI to give alkoxyalcohol intermediate (known as hemiacetals), which further react with one molecule of alcohol to give a gem-dialkoxy compound known as acetal.

R-



OR'

CHOR-

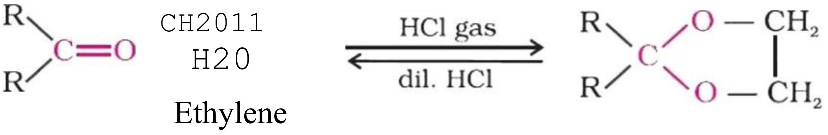
OH

CHH20

Hemiacetal Acetal

Ketones react with ethylene glycol in presence of dry HCI to form cyclic products known as ethylene glycol ketals.

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



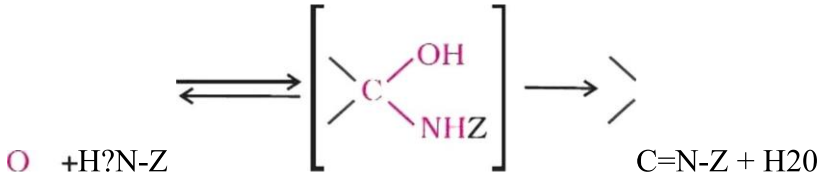
CH2011

H20

\+ CH20H

Ethylene glycol ketal

e) Addition of ammonia and its derivatives: Nucleophiles like ammonia and its derivatives H2N-Z are added to the carbonyl group of aldehydes and ketones. The reaction is reversible and catalysed by acid.



i) Addition of ammonia: Aldehydes and ketones add ammonia followed by elimination of a water molecule to give imines.

R_CHO + NH3 →------→ R-CH(OH)NH$_2$ →------→ R-CH=NH + H20

(imines)

R2CO + NH3 →------→ R$_2$C(OH)NH$_2$ →------→ R2C=NH + 1420

*ii)*Addition ofAmine: Carbonyl compounds add amines to give substituted imines (Schiff's bases).

R-CHO + →------→ R-CH(OH)NHR' →------→ R-CH=NR' R'-NH2+ 1-120

R2CO+ →------→ R$_2$C(OH)NHR' →------→ R$_2$C=NR' + H: R'-NH2*- + 1-420

iii) Addition of hydroxyl amine (NH2-OH): Carbonyl compounds condensed with hydroxyl amine to give oximes.

R-CHO + NH20H 9-----+ R-CH=N-OH + H20

(aldoxime)

R2CO + NH 201-4 →------→ R2C=N-OH + 1-120 iv) Addition of hydrazine (NH2-NH2): Carbonyl compounds condensed with hydrazine to give hydrazone.

R_CHO + NH$_2$-NH$_2$ →------→ R-CH=N-NH$_2$+ 1--120

(hydrazone)

R2CO + NH2-NH2 →------→ R$_2$C=N-NH$_2$+ 1-120

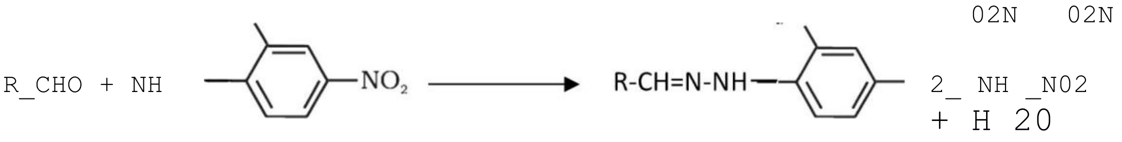
v) Addition of phenyl hydrazine (NH2-NH-C6H5): Carbonyl compounds condensed with phenyl hydrazine to give phenyl hydrazone.

R-CHO + NH2-NH-C6H5 9-----* R-CH=N-NH-C6H5 + H20

(phenyl hydrazone)

R2CO + NH$_2$-NH-C$_6$H$_5$ →------→ R$_2$C=N-NH-C$_6$H$_5$ + H20

vi) Addition of2,4-dinitrophenyl hydrazine (2,4-DNP): Carbonyl compounds condensed with 2,4dinitrophenyl hydrazine to give 2,4-dinitrophenyl hydrazone.



2,4-dinitrophenyl hydrazine2,4-dinitrophenyl hydrazone

2,4-dinitrophenyl hydrazine is also known as Borsches reagent. 2,4-DNP-derivatives are yellow, orange or red solids and hence this reaction is used for the characterisation of aldehydes and ketones.

vii) Addition of Semicarbazide (NHrNH-CO-NH2): Carbonyl compounds condensed with semicarbazide to yield samicarbazone.

IR-CHO + NH2-NH-CO-NH2 9-----+ R-CH=N-NH-CO-NH2 + 1-120
(semicarbazone)
R2CO + NH2-NH-CO-NH2 9-----* R2C=N-NH-CO-NH2 + 1-420

2. <u>Reduction</u>:

i) Reduction to alcohols: When reduced using sodium borohydride (NaBH4) or lithium aluminium hydride (LiAlH4) or 1-12 in presence of Ni, Pd or Pt catalyst (Catalytic hydrogenation), aldehydes give primary alcohols, while ketones give secondary alcohols.

$$R-\ J\xrightarrow{[H]} CHOR\_CH2OH$$
$$\xrightarrow{[H]} R$$
R2CO R2CHOH ii)

Reduction to Hydrocarbons:

<u>Clemmensen reduction</u>: Aldehydes and ketones can be reduced to alkanes on treatment with zinc amalgam and concentrated hydrochloric acid. During this reaction, the carbonyl group is reduced to CH2 (methylene) group.

<u>Zn-Hg </u>c=o CH2
+ H20
HCI /
Zn/Hg

CH3-CHO + [H] →------→ CH3-CH3
Acetaldehyde Ethane
Zn/Hg
CH3-CO-CH3 + [H]→------→ CH_3-CH_2-CH_3
Acetone Propane

<u>Wolff-Kishner reduction</u>: Carbonyl group can also be reduced to methylene group, by treating with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol.

NH2NH2 KOH/cthylcne glycol
C =NNH2 -...-...>heat CIL + N2

(i) NH2-NH2 (ii) KOH/Ethylene glycol/A
CH3-CH0 CH3CH3
(i) NH2-NH2 (ii)KOH/Ethylene glycol/A
CH3-CO-CH3 CH3-CH2-CH3

3. <u>Oxidation</u>:

Aldehydes are easily oxidised to carboxylic acids on treatment with common oxidising agents like nitric acid, potassium permanganate, potassium dichromate etc. Mild oxidising agents like Cr03, Tollens' reagent and Fehlings' reagent can also oxidise aldehydes.

$$R-CHO \xrightarrow{[0]} R-COOH$$

$$CH3-CHO \xrightarrow{[0]} CH3-COOH$$

Ketones when oxidised using strong oxidising agents and at high temperatures, we get a mixture of carboxylic acids having lesser number of carbon atoms. During this reaction carbon-carbon bond cleavage occurs.

1 2 CH2COOH + R'-COOH

[01

R—C112—C—CI 12-R' ⟶ R_COOII + R'-CI 12COOII +

(By cleavage of Cl-C2 bond) (By cleavage of Cz-C, bond)

E.g. CH3-CH2-CO-CH2-CH2-CH3 9-------*2 CH3-CH2-COOH + CH3-COOH + CH3-CH2-CH2-COOH

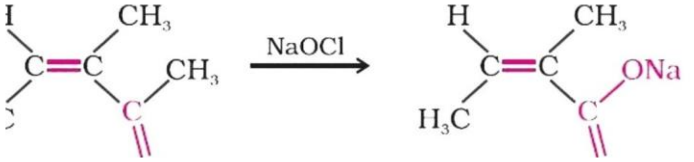
Hexan-3-one Propanoic acidEthanoic acidButanoic acid

4. Haloform Reaction:

Aldehydes or ketones having CH3-CO- group or CH3-CHOH- group, when treated with sodium hypohalite or halogen in presence of NaOH, we get a haloform (CHX3). This reaction is called haloform reaction. During this reaction, the methyl group is converted to haloform. This reaction does not affect a carbon-carbon double bond, if present in the molecule.

NaOX

R-CO-CH3 →--------+ R-COONa + (where X = Cl, Br or l)



\+ H CHC1g

113C

O O

The reaction with sodium hypoiodite gives an yellow precipitate of iodoform and this reaction is used for the detection of CH3-CO- group or CH3-CHOH- group in a compound (Iodoform Test).

E.g.: 2-pentanone and 3-pentanone can be distinguished by iodoform reaction. 2-pentanone gives this reaction.

5. Aldol condensation Reaction:

Aldehydes and ketones having at least one a-hydrogen atom when treated with dilute alkali, we get ß-hydroxy aldehydes (aldol) or B-hydroxy ketones (ketol) respectively. This is known as Aldol reaction. The product formed contains both aldehydic (ketonic) and alcoholic group. So the name aldol or ketol is used.

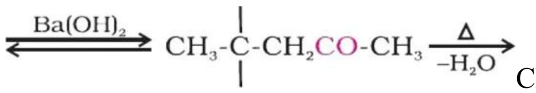
The aldol or ketol on heated undergo dehydration to give a,ß-unsaturated aldehyde or ketone. This reaction is called Aldol condensation.

dil.NaOH

2CH3-CHO →⇌--------→ CH_3-CH(OH)-CH_2-CHO →------→ CH_3-CH=CH-CHO

Ethanal 3-Hydroxybutanal (aldol) But-2-enal (Crotanaldehyde)

CH3 CH3



$\xrightleftharpoons{Ba(OH)_2} CH_3\text{-}\overset{|}{\underset{|}{C}}\text{-}CH_2CO\text{-}CH_3 \xrightarrow[-H_2O]{\Delta}$

2CH3-CO-CH3 CH3-C=CH-CO-CH3

Propanone 011

4-Methylpent-3-en-2-one

(Ketol) (Aldol condensation

4-Hydroxy-4-methylpentan-2-one product)

6. Cross aldol condensation: When aldol condensation is carried out between two different aldehydes or ketones, it is called cross aldol condensation. If both of them contain a-hydrogen atoms, we get a mixture of four products.

NaOH/A

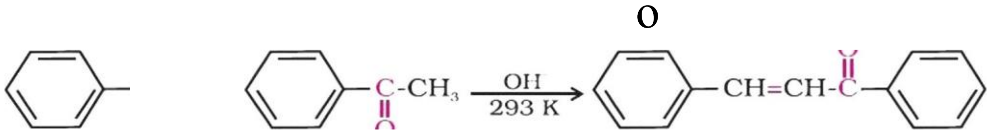
CH3-CHO + CH2-CH2-CHO→-------→CH3-CH=CH-CHO +

$H_3-CH_2-CH=C(CH_3)-CHO + CH_3-CH=C(CH_3)-CHO$

Ethanal Propanal But-2-enal 2-methylpent-2-enal 2-methylbut-2-enal

+ $CH_3-CH_2-CH=CH-CHO$

Pent-2-enal



CHO +

+ C6Hs-C = CH
-C6H5

CH3

1, 3-Diphcnylprop-2-cn-1 -one 1,2-Diphenylprop-1-ene

(Benzalacetophenone)

7. Cannizzaro Reaction:

Aldehydes having no a-hydrogen atom (e.g. HCHO, C6H5-CHO, CC13-CHO etc), when treated with conc. alkali (NaOH or KOH) undergo self oxidation and reduction (disproportionation) to form one molecule of the alcohol and one molecule of carboxylic acid salt. This reaction is called Cannizzaro reaction.

Conc.KOH

2 HCHO →---------→ CH_3-OH + H-COOK

Formaldehyde methanol potassium formate

Conc.KOH

2 C6H5-CHO →-------—9 C6H5_CH20H +C6H5-COOK

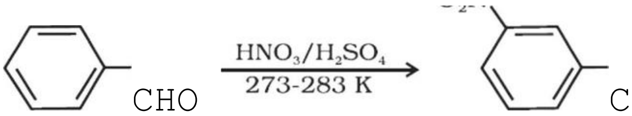
Benzaldehyde benzyl alcohol potassium benzoate

8. Electrophilic Substitution Reactions:

Aldehydic and ketonic groups are meta directing and deactivating. So on electrophilic substitution reactions, they give meta-derivatives.

e.g. Nitration:

02N



CHO CHO

Benzaldehyde m-Nitrobenzaldehyde Tests to distinquish Aldehydes and Ketones

1 . Tollens' test:

Tollen's reagent is freshly prepared ammoniaca/ Silver nitrate. On warming Tollens' reagent, aldehydes give a bright silver mirror. During this reaction, the aldehyde is oxidised to corresponding carboxylate ion and silver nitrate is reduced to silver metal. R-CHO + $2[Ag(NH_3)_2]^+$ + 30H- →------→ R-COO-+ 2 Ag + 2 1-120 + 4 NH3

2. Fehling's test:

Fehling reagent is a mixture of two solutions, Fehling solution A and Fehling solution B. Fehling solution A is aqueous copper sulphate and Fehling solution B is alkaline sodium potassium tartarate (Rochelle salt). On heating with Fehling's reagent, aldehyde gives a reddish brown precipitate of cuprous oxide (CU20). Aromatic aldehydes do not give this test.

R-CHO + 2Cu2+ + 501-1 - →------→ R_COO-+ C1120 + 31-120
(Cuprous oxide)

The above tests are not answered by ketones.

CARBOXYLIC ACIDS

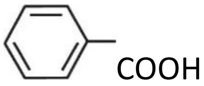
Carbon compounds containing a carboxyl functional group (—COOH) are called carboxylic acids. The carboxyl group consists of a carbonyl group attached to a hydroxyl group, hence its name carboxyl. Aliphatic carboxylic acids containing 12 to 18 C atoms are called fatty acids. They occur in natural fats as esters of glycerol.

Nomenclature

The common names of carboxylic acids end with the suffix —ic acid and have been derived from Latin or Greek names of their natural sources. For example, formic acid (HCOOH) was first obtained from red ants (Latin: formica means ant), acetic acid (CH3COOH) from vinegar (Latin: acetum, means vinegar), butyric acid (CH3CH2CH2COOH) from rancid butter (Latin: butyrum means butter).

In the IUPAC system, aliphatic carboxylic acids are named by replacing the ending —e in the name of the corresponding alkane with —oic acid. In numbering the carbon chain, the carboxylic carbon is numbered one. For naming compounds containing more than one carboxyl group, the ending —e of the alkane is retained. The number of carboxyl groups is indicated by adding the prefixes di, tri, etc. to the term oic. Some examples are:

Compound	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH3COOH	Acetic acid	Ethanoic acid
CH3CH2COOH	Propionic acid	Propanoic acid
CH3CH2CH2COOH	Butyric acid	Butanoic acid

(CH3)2CHCOOH	Isobutyric acid	2-Methylpropanoic acid
CH3CH2CH2CH2COOH	Valeric acid	Pentanoic acid
CH3CH2CH2CH2CH2COOH	Caproic acid	Hexanoic acid
HOOC-COOH	Oxalic acid	Ethanedioic acid
HOOC -CH2-COOH	Malonic acid	Propanedioic acid
HOOC -(CH2)2-COOH	Succinic acid	Butanedioic acid
HOOC -(CH2)3-COOH	Glutaric acid	Pentanedioic acid
HOOC -(CH2)4-COOH	Adipic acid	Hexanedioic acid
HOOC $-CH_2-CH(COOH)-CH_2-COOH$		Propane-I, 2, 3tricarboxylic acid
	Benzoic acid	Benzenecarboxylic acid (Benzoic acid)
CH2COOH	Phenylacetic acid	2-Phenylethanoic acid
cooll cooll	Phthalic acid	Benzene-I, 2-dicarboxylic acid

Methods of Preparation of Carboxylic acids

1. From primary alcohols and aldehydes:

Primary alcohols are readily oxidised to carboxylic acids with common oxidising agents such as potassium permanganate (KMn04) in neutral, acidic or alkaline media or by potassium dichromate (1<2Cr207) and chromium trioxide (Cr03) in acidic media.

$$R-CH2OH \xrightarrow{\text{Alkaline KMn04/H30+}} R-COOH$$

$$CH3-CH2-OH \xrightarrow{\text{Cr03/H2S04}} CH3-COOH$$

Aldehydes on oxidation with mild oxidising agents like Cr03 or Tollen's reagent to give carboxylic acids.

$$R-CHO \xrightarrow{[0]} R-COOH$$

$$CH3-CHO \xrightarrow{[0]} CH3-COOH$$

2. From alkylbenzenes:

Aromatic carboxylic acids can be prepared by vigorous oxidation of alkyl benzenes with chromic acid or acidic or alkaline potassium permanganate. Primary and secondary alkyl groups are oxidised in this manner while tertiary group is not affected.

E.g.: Toluene when oxidized using alkaline KMn04 followed by acidification we get benzoic acid.

CH3 COOK COOI 1

KMn04-KOH
Heat
H30+

Toluene Potassium Benzoate Benzoic acid

Here the entire side chain is oxidised to the carboxyl group irrespective of length of the side chain.

CH2CH2CH3 COOK COO! I

$\xrightarrow[\triangle]{\text{KMn04-KOH}}$ H30'

I-phenylpropane Potassium benzoate Benzoic acid

3. From nitriles and amides:

Hydrolysis of nitriles in presence of acid or alkali as catalyst first give amides, which on further give carboxylic acids. Mild reaction conditions are used to stop the reaction at the amide stage.

O

H or
öH

OHH or

RCOOH

1420

H30

CHßCONH2 CH$COOH + NH,

Ethanamide Ethanoic acid

CONH2 COOH

+ NH3

Benzamide Benzoic acid

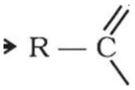
4. From Grignard reagents:

Grignard reagents react with carbon dioxide (dry ice) in dry ether to form salts of carboxylic acids which on acidification give corresponding carboxylic acids.

O

Dry ether

R-Mg-X +O=C=



Hgo.

O-MgX+

Grignard reagents and nitriles can be prepared from alkyl halides. So the above two reactions are used for converting alkyl halides into corresponding carboxylic acids having one carbon atom more than that present in alkyl halides.

5. From acyl halides and anhydrides:

Acid chlorides and anhydrides when hydrolysed with water give carboxylic acids. The rate of hydrolysis increases in alkaline medium.

FLO RCOOII + Cl

RCOCI

ÖH/H20

C̄l $\xrightarrow{H_3O}$ RCOOH

H30+

RC00 +

H20

Benzoic anhydride Benzoic acid

H20

C6H5COC)COCH3 -.1...> CGH5CC)OI I + CH3COOl 1

Benzoic ethanoic Benzoic acid Ethanoic acid

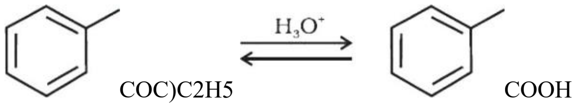
anhydride

6. <u>From esters:</u>

Acidic hydrolysis of esters gives directly carboxylic acids while basic hydrolysis gives salt of carboxylic acids which on acidification give corresponding carboxylic acids.

$$CH3\text{-}CH2\text{-}COOCH3 \xrightarrow{NaOH} CH3\text{-}CH2\text{-}COONa + CH30H$$

CH3-CH2-COOH + NaOH



Ethyl benzoate Benzoic acid

Physical Properties

1. <u>Physical state</u>: Aliphatic carboxylic acids upto nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids and are practically odourless due to their low volatility.
2. <u>Boilinq point</u>: Carboxylic acids are higher boiling liquids than aldehydes, ketones and alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. Most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.
3. <u>Solubility</u>: Simple aliphatic carboxylic acids having upto four carbon atoms are miscible in water due to the formation of hydrogen bonds with water. The solubility decreases with increasing number of carbon atoms. The simplest aromatic carboxylic acid, benzoic acid, is nearly insoluble in cold water. Carboxylic acids are also soluble in less polar organic solvents like benzene, ether, alcohol, chloroform, etc.

Chemical Reactions

(A) Reactions Involving Cleavage of O—H Bond:

1. Acidity:

Reactions with metals and alkalies: Like alcohols and phenols, carboxylic acids react with electropositive metals and liberate hydrogen gas.

2 R-COOH + 2 Na 9-----*2 R-COONa + 1-12

R-COOH + NaOH *- R_C00Na + 1-120

Carboxylic acids react with sodium carbonates and bicarbonates and give brisk effervescence of carbon dioxide. This reaction is not given by alcohols and phenols. So this reaction is used to distinguish carboxylic acids from alcohols and phenols.

R-COOH + NaHC03 *------→ R_COONa + 1-120 + C02

Carboxylic acids dissociate in water to give resonance stabilized carboxylate anions and hydronium ion.

R-COOH + H20 9-----+ R-COO - + 1-130

Due to the formation of hydronium ion in water, carboxylic acids are acidic in nature.

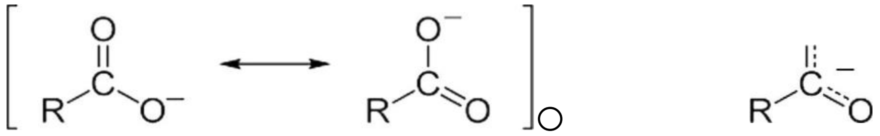
The acidity of a substance is expressed in terms of pl<a value, which is the negative logarithm of Ka.

i.e. pl<a = - logl<a

Greater the value of Ka, smaller will be pl<a and stronger will be the acid. Comparison of acidic character

Carboxylic acids are weaker than mineral acids, but they are stronger acids than other organic compounds like alcohols and many simple phenols. The higher acidity of carboxylic acids as compared to phenols can be explained as follows:

The carboxylate ion formed from the ionization of carboxylic acid is stabilised by two equivalent resonance structures in which the negative charge is at the more electronegative oxygen atom. But the phenoxide ion formed from the ionization of phenol has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom.



Also the negative charge is delocalised over two electronegative oxygen atoms in carboxylate ion, whereas it is less effectively delocalised over one oxygen atom and less electronegative carbon atoms in phenoxide ion. Therefore carboxylate ion is more stable than phenoxide ion and hence carboxylic acids easily donate 1-4+ ion and form carboxylate ion. So it is more acidic.

Effect of substituents on the acidity of carboxylic acids:

Electron withdrawing groups increase the acidity of carboxylic acids by stabilising the carboxylate ion through delocalisation of the negative charge by inductive and resonance effects. But electron donating groups decrease the acidity by destabilising the carboxylate ion.

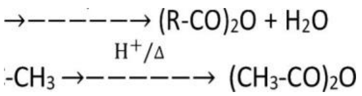
The effect of the following groups in increasing acidity order is

$Ph < I < Br < Cl < F < CN < NO_2 < CF_3$

Direct attachment of groups such as phenyl or vinyl to the carboxylic acid, increases the acidity of corresponding carboxylic acid. This is because of greater electronegativity of sp ^{2} hybridised carbon to which carboxyl carbon is attached. The presence of electron withdrawing group on the phenyl of aromatic carboxylic acid increases their acidity while electron donating groups decrease their acidity.

A) Reactions Involving Cleavage of C—OH Bond

1. Formation of anhydride: Carboxylic acids on heating with mineral acids like H2S04 or with P205 undergo dehydration to give acid anhydrides.



$\rightarrow$------$\rightarrow$ $(R\text{-}CO)_2O + H_2O$

H^+/Δ

-CH_3 $\rightarrow$-------$\rightarrow$ $(CH_3\text{-}CO)_2O$

P205/A R-

COOH + HOOC-R

CH3-COOH + HOOC-CH3*- + H 20 Acetic acid
Acetic anhydride

2. Esterification: Carboxylic acids when heated with alcohols or phenols in the presence of a mineral acid like concentrated 142504 or HCI gas, we get esters. This reaction is reversible and is known as esterification.

RCOOH + R'C)H— RCOOR' + H20

H^+

CH3-COOH + CH3-OH $\rightleftharpoons$ CH3-COO-CH3+ H20

Acetic acid methanol methyl acetate

3. Reactions with PCL, PC15 and SOC12: Carboxylic acids on treating with PC13, PC15 or SOC12, we get acid chlorides.
Reaction with thionyl chloride (SOC12) is preferred because the byproducts are gases and are easily escaped from the reaction mixture so that we get pure acid chloride.

R-COOH + PC13$\rightarrow$-------$\rightarrow$ R_COCI + H3P03

R-COOH + PC15 -5-----* R-COCI + POC13+ HCI

R-COOH + SOC12 9-----+ R-COCI + + I-ICI

4. Reaction with ammonia: Carboxylic acids react with ammonia to give ammonium salts which on further heating at high temperature give amides.

R-COOH + NH3$\rightarrow$-------$\rightarrow$ $R\text{-}COO^-NH_4^+$ $\rightarrow$---R$\rightarrow$ R_CONH2+ 1-120

CH3C0011 + NH3 $\rightleftharpoons$ CH3COON114 $\xrightarrow[-1120]{\Delta}$ H C O N 1 12

Ammonium acetate Acetamide

COOII COONIL CONIU

+ NIL $\rightleftharpoons$

_H20

Benzoic acid Ammonium benzoate Benzamide

COOH COONIII CONIU

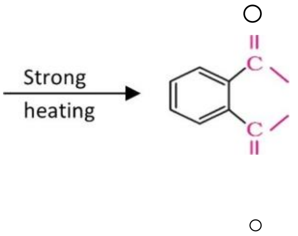
+ NH_3 ⇌

_ +-2H20 NH

COOI 1 COONH, CON112

Phthalamide

Phthalic acid Ammonium phthalate



Phthalimide

B) Reactions Involving-COOH Group

1. Reduction: Carboxylic acids when reduced with lithium aluminium hydride or with diborane, primary alcohols are formed. Diborane does not reduce functional groups like ester, nitro, halo, etc. Sodium borohydride does not reduce the carboxyl group.

(i) LiAIH4/ether or B2H6 (ii)H30+

R-COOH →---------------------------→ R-CH20H

(i) LiAIH4/ether or B2H6 (ii)H30+

CHÆOOH ----- – - – --___________________ CH3-CH20H

2. Decarboxylation:

i) When sodium salts of carboxylic acid are heated with sodalime (a mixture of NaOH and CaO), they undergo decarboxylation (elimination of C02) to form alkanes. ca0/A

R-COONa + NaOH →-----→ R-H +

Na2C03 ca0/A

CH3-COONa + NaOH +-— CH4 + Na2C03 ii) Kolbe's electrolysis: When an aqueous solution of sodium or potassium salt of carboxylic acid is electrolysed, we get alkanes having twice the number of carbon atoms that present in the alkyl group of the acid. This reaction is known as Kolbe electrolysis.

Electrolysis

2 R-COOK + 2H20 9-----------+ R-R + 21<01-1 + H2 + 2C02

Electrolysis

2 CFL-COOK + 2 H20 9----------* CH3-CH3 + 21<01-1 + H2 + 2C02

C) Substitution Reactions in the Hydrocarbon Part:

1 . HgLgeng.tien...LH.Y.Z...Regcgien1

Carboxylic acids having an a-hydrogen atom, when treated with halogen (chlorine or bromine) in the presence of red phosphorus, we get a-halocarboxylic acids. This reaction is known as Hell-VolhardZelinsky(HVZ) reaction.

(i) X2/Red phosphorus

IR-CFL-COOH ____________________ IR-CH-COOH

(ii)H20

X

X = Cl, Br

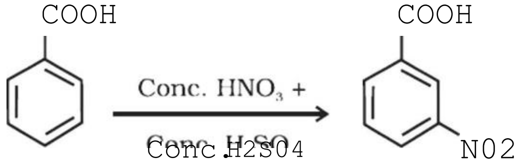
a-halocarboxylic acid

CH3-CH2-COOH i) P ii) H20 CH3-CHCl-COOH + HCI
Propanoic acid 2-chloropropanoic acid

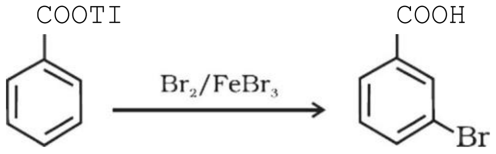
This reaction is synthetically important since the halogen atom can be replaced by other groups.

2. <u>Electrophilic substitution reactions:</u>

The —COOH group is a deactivating group and meta-directing. So on electrophilic substitution reactions, we get meta derivatives. E.g. 1. Nitration



2. Bromination



But carboxylic acids do not undergo Friedel-Crafts reactions because the carboxyl group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group to form salts.