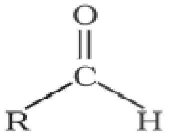
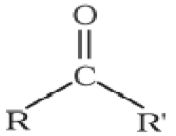
ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Aldehydes and Ketones: The organic compounds containing carbon-oxygen double bond (>C=O) called carbonyl group, which is one of the most important functional groups in organic chemistry.

In aldehydes, the carbonyl group is bonded to a carbon and hydrogen while in the ketones; it is bonded to two carbon atoms.



Aldehyde



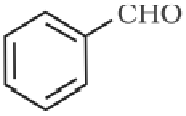
Ketone

Nomenclature: There are two systems of nomenclature of aldehydes and ketones.

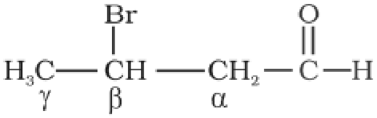
(a) Common names: Acetaldehyde, Benzaldehyde and β-Bromo-butyraldehyde

CH_3CHO

Acetaldehyde



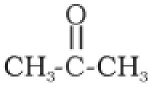
Benzaldehyde



$H_3C-\overset{Br}{CH}-CH_2-\overset{O}{\overset{||}{C}}-H$ (γ, β, α)

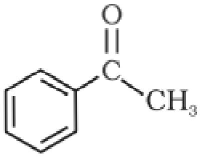
β-Bromobutyraldehyde

Acetone, Acetophenone, Propiophenone and Benzophenone

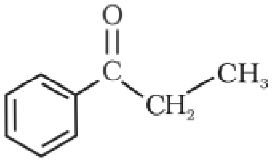


$CH_3-\overset{O}{\overset{||}{C}}-CH_3$

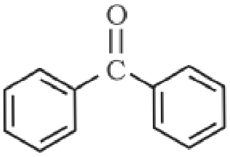
Acetone



Acetophenone

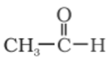


Propiophenone



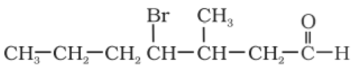
Benzophenone

(b) IUPAC names: 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.



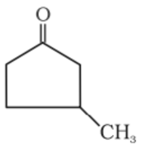
$CH_3-\overset{O}{\overset{||}{C}}-H$

Ethanal

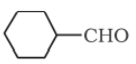


$CH_3-CH_2-CH_2\,\overset{Br}{CH}-\overset{CH_3}{CH}-CH_2-\overset{O}{\overset{||}{C}}-H$

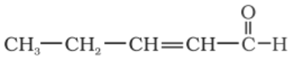
4-Bromo-3-methylheptanal



3-Methylcyclopentanone

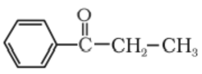


Cyclohexanecarbaldehyde

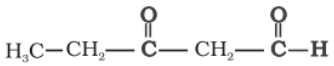


$CH_3-CH_2-CH=CH-\overset{O}{\overset{||}{C}}-H$

Pent-2-enal

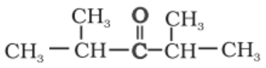


1-Phenylpropan-1-one



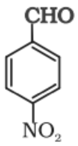
$H_3C-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-H$

3-Oxopentanal

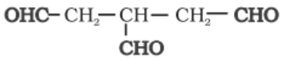


$CH_3-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{CH}}-CH_3$

2,4-Dimethylpentan-3-one



4-Nitrobenzenecarbaldehyde
or
4-Nitrobenzaldehyde



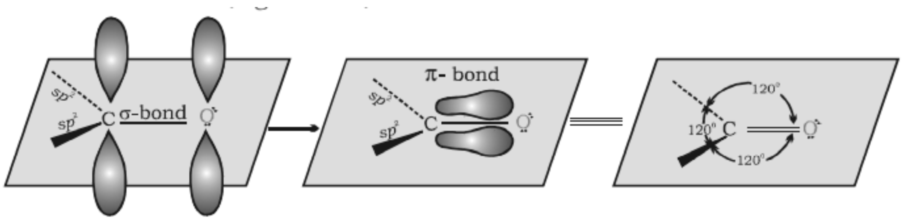
$OHC-CH_2-\underset{CHO}{\underset{|}{CH}}-CH_2-CHO$

Propane–1,2,3-tricarbaldehyde

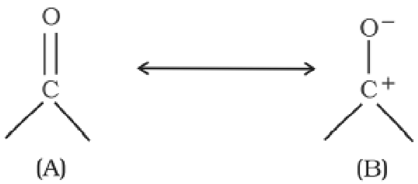
Note: To give identical treatment to all aldehydic groups, the compound is named as shown above.

Structure of the Carbonyl Group: The carbonyl carbon atom is sp^2 -hybridized and forms three sigma (σ) bonds. The fourth valence electron of carbon remains in its p-orbital and forms a π-bond with oxygen by overlap with p-orbital of oxygen. In addition, the oxygen atom also has two nonbonding electron pairs. Thus, the carbonyl carbon and the three atoms attached to it lie in the same plane and the π-electron cloud is above and below this plane. The bond angles are approximately 120° as expected of a Trigonal coplanar structure.

Orbital diagram for the formation of carbonyl group:



The carbon-oxygen double bond is polarized due to higher electronegativity of oxygen relative to carbon. Hence, the carbonyl carbon is an electrophilic (Lewis acid), and carbonyl oxygen, a Nucleophilic (Lewis base) centre. Carbonyl compounds have substantial dipole moments and are polar than ethers. The high polarity of the carbonyl group is explained on the basis of resonance involving a neutral (A) and a dipolar (B) structure as shown.



Preparation of Aldehydes and Ketones:

1. **By oxidation of alcohols:** Aldehydes and ketones are generally prepared by oxidation of primary and secondary alcohols, respectively.
   $CH_3CH_2OH \xrightarrow{\text{K2Cr2O7 + dil H2SO4}} CH_3CHO$
   By dehydrogenation of alcohols: This method is suitable for volatile alcohols and is of industrial application. In this method alcohol vapours are passed over heavy metal

catalysts (Ag or Cu). Primary and secondary alcohols give aldehydes and ketones, respectively and Tertiary alcohol gives 2-methyl propene.

$CH_3CH_2OH \xrightarrow{\text{Cu, 573 K}} CH_3CHO + H_2$

$CH_3CH\ (OH)\ CH_3 \xrightarrow{\text{Cu, 573 K}} CH_3COCH_3 + H_2$

$(CH_3)_3COH \xrightarrow{\text{Cu, 573 K}} (CH_3)_2C = CH_2 + H_2$

2. **From hydrocarbons:**
   - (i) By ozonolysis of alkenes: Ozonolysis of alkenes followed by reaction with zinc dust and water gives aldehydes, ketones or a mixture of both depending on the substitution pattern of the alkene.

     $CH_2 = CH_2 + O_3 \rightarrow$ Ethene ozonide $\xrightarrow{\text{Zn, H2O}}$ $2HCHO + H_2O_2$

     $CH_3CH = CH_2 + O_3 \rightarrow$ Propene ozonide $\xrightarrow{\text{Zn, H2O}}$ $CH_3CHO + HCHO$

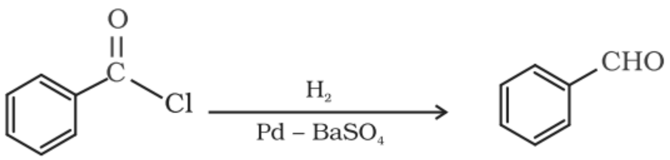
   - (ii) By hydration of alkynes: Addition of water to Ethyne in the presence of H_2SO_4 and $HgSO_4$ gives acetaldehyde. All other alkynes give ketones in this reaction.

     Ethyne + $H_2O \xrightarrow{\text{H2SO4 (dil), HgSO4}} CH_3CHO$

     Propyne + $H_2O \xrightarrow{\text{H2SO4 (dil), HgSO4}} CH_3COCH_3$

Preparation of Aldehydes:

1. From acyl chloride (acid chloride): Acyl chloride (acid chloride) is hydrogenated over catalyst, palladium on barium sulphate. This reaction is called **Rosenmund's reduction.**



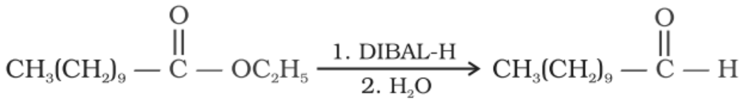
Benzoyl chloride

Benzaldehyde

2. From nitriles: Nitriles are reduced to corresponding imine with stannous chloride in the presence of hydrochloric acid, which on hydrolysis give corresponding aldehyde. This reaction is called **Stephen reaction.**

RCN +$SnCl_2$ +HCl --------> RCH = NH ----------> RCHO

3. From esters: Esters are reduced to aldehydes with DIBAL-H.

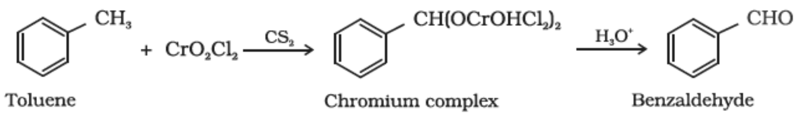


$$CH_3(CH_2)_9 - \overset{\overset{O}{\|}}{C} - OC_2H_5 \xrightarrow[\text{2. } H_2O]{\text{1. DIBAL-H}} CH_3(CH_2)_9 - \overset{\overset{O}{\|}}{C} - H$$

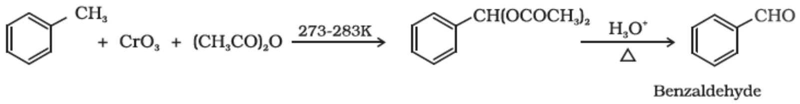
4. **From hydrocarbons:**

(i) By oxidation of methylbenzene

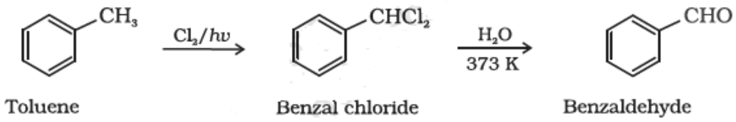
(a) Use of chromyl chloride (CrO_2Cl_2): This reaction is called Etard reaction.



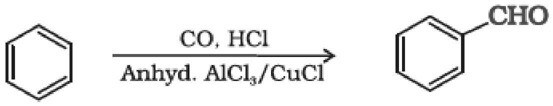
(b) Use of chromic oxide (CrO_3):



(ii) By side chain chlorination followed by hydrolysis:

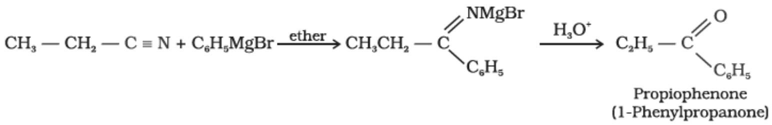


(iii) By Gatterman – Koch reaction:

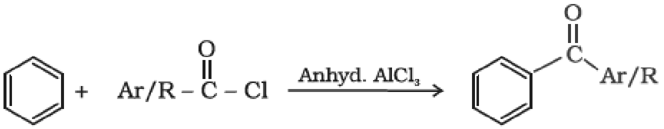


Preparation of Ketones:

1. **From acyl chlorides:**
   $2RMgX + CdCl_2$ ------> $R_2Cd + 2Mg(X)\,Cl$
   $2R'\,CO\,Cl + R_2Cd$ ------> $2R'\,CO\,R + CdCl_2$
2. **From nitriles:**



3. **From benzene or substituted benzenes:**



This reaction is known as Friedel-Crafts acylation reaction.

Physical Properties:

Methanal is a gas at room temperature. Ethanal is a volatile liquid. Other aldehydes and ketones are liquid or solid at room temperature.

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

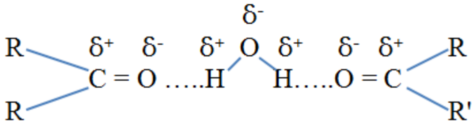
The following compounds of molecular masses 58 and 60 are ranked in order of increasing boiling points.

n-Butane < Methoxyethane < Propanal < Acetone < Propan-1-ol

The following compounds of molecular masses 72 and 74 are ranked in order of increasing boiling points.

$CH_3CH_2CH_2CH_3 < H_5C_2\text{-}O\text{-}C_2H_5 < CH_3CH_2CH_2CHO < CH_3CH_2CH_2CH_2OH$

The lower members of aldehydes and ketones such as Methanal, Ethanal and Propanone are miscible with water in all proportions, because they form hydrogen bond with water.



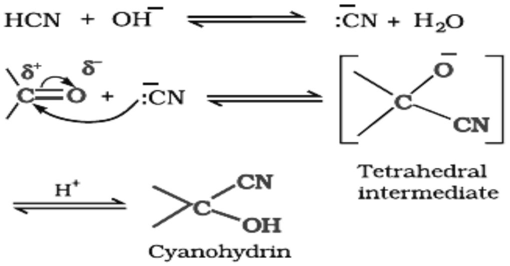
However, the solubility of aldehydes and ketones decreases rapidly on increasing the length of alkyl chain. All aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, methanol, chloroform, etc.

The lower aldehydes have sharp pungent odours. As the size of the molecule increases, the odour becomes less pungent and more fragrant. In fact, many naturally occurring aldehydes and ketones are used in the blending of perfumes and flavouring agents.

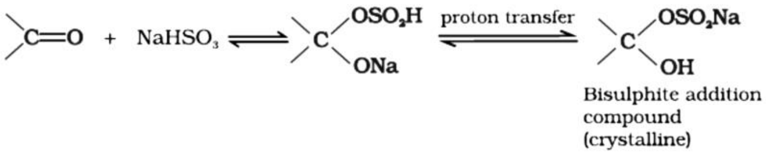
Chemical Properties:

1. **Nucleophilic addition and Nucleophilic addition-elimination reactions:**

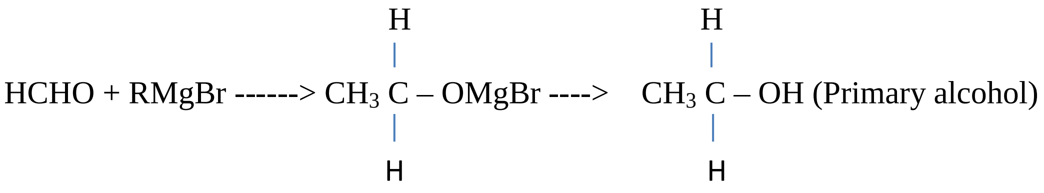
(a) Addition of hydrogen cyanide (HCN):



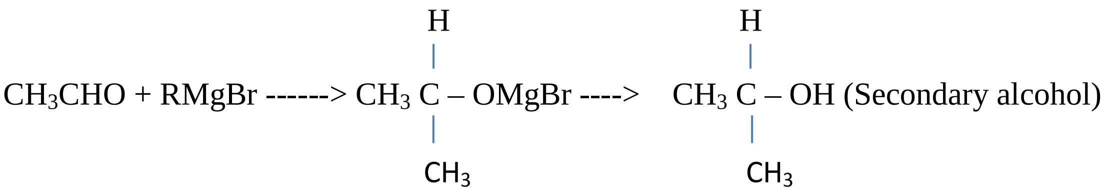
(b) Addition of sodium hydrogensulphite:



(c) Addition of Grignard reagents:

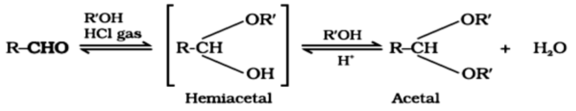


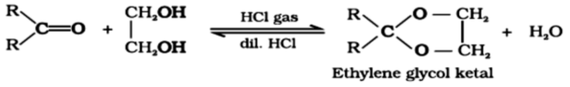
$$HCHO + RMgBr \text{ ------> } CH_3\,\underset{H}{\overset{H}{C}} - OMgBr \text{ ----> } CH_3\,\underset{H}{\overset{H}{C}} - OH \text{ (Primary alcohol)}$$



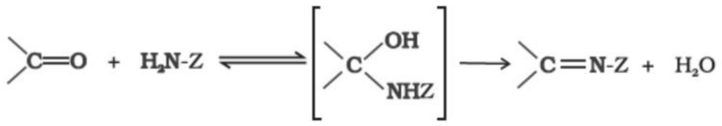
$$CH_3CHO + RMgBr \text{ ------> } CH_3\,\underset{CH_3}{\overset{H}{C}} - OMgBr \text{ ----> } CH_3\,\underset{CH_3}{\overset{H}{C}} - OH \text{ (Secondary alcohol)}$$

(d) Addition of alcohols:





(e) Addition of ammonia and its derivatives:



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

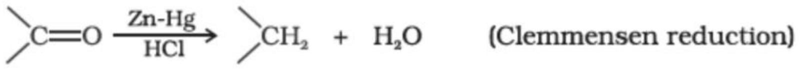
2. Reduction

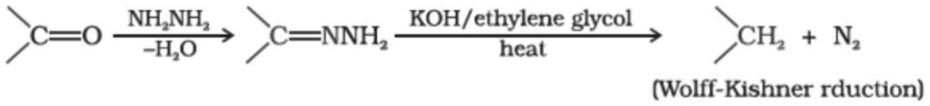
(i) Reduction to alcohols:

$$RCHO \xrightarrow{\text{H2(Ni or Pt or Pd) Na/C2H5OH, LiAlH4 or NaBH4}} RCH_2OH \text{ (Primary alcohol)}$$

$$RCOR' \xrightarrow{\text{H2(Ni or Pt or Pd) Na/C2H5OH, LiAlH4 or NaBH4}} RCH(OH)R' \text{ (Secondary alcohol)}$$

(ii) Reduction to hydrocarbons:





3. Oxidation:

$$RCHO \xrightarrow{[O]} RCOOH$$

The mild oxidising agents mainly Tollen's' reagent and Fehling's' reagent are used to distinguish aldehydes from ketones:

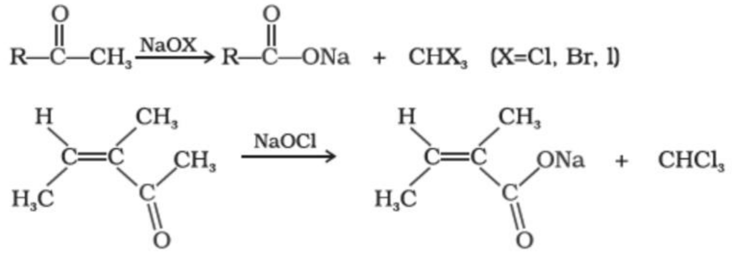
(i) Tollen's' test: On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollen's' reagent), a bright silver mirror is produced due to the formation of silver metal.

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

(ii) Fehling's test: On heating an aldehyde with Fehling's reagent, a reddish brown precipitate is obtained.

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

(iii) Oxidation of methyl ketones by haloform reaction:



4. Reactions due to a-hydrogen: (i) Aldol condensation: Aldehydes and ketones having at least one α-hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes (Aldol) or β-hydroxy ketones (ketol), respectively. This is known as Aldol reaction.

$2CH_3CHO \xrightarrow{\text{dil.NaOH}} CH_3–CH(OH)-CH_2-CHO \text{ (Aldol)} \xrightarrow{\text{heat}} CH_3-CH = CH-CHO$

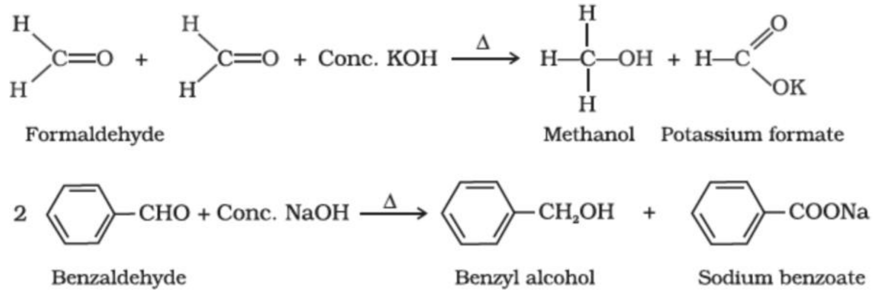
$2CH_3COCH_3 \xrightarrow{\text{Ba(OH)2}} CH_3–C(CH_3)(OH)-CH_2-CO-CHO \xrightarrow{\text{heat}} CH_3–C(CH_3) = CH–CO–CHO$

(Ketol)

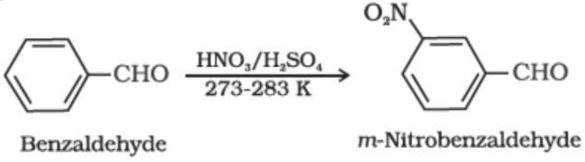
(ii) Cross Aldol condensation: When Aldol condensation is carried out between two different aldehydes and / or ketones; it is called cross Aldol condensation.

5. Other reactions

(i) Cannizzaro reaction:



(ii) Electrophilic substitution reaction: Aromatic aldehydes and ketones undergo electrophilic substitution at the ring in which the carbonyl group acts as a deactivating and meta-directing group.

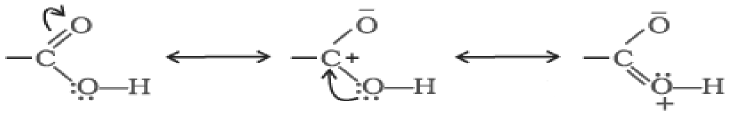


Uses of Aldehydes and Ketones:

Formaldehyde is well known as formalin (40%) solution used to preserve biological specimens and to prepare bakelite (a phenol-formaldehyde resin), urea-formaldehyde glues and other polymeric products.

Acetaldehyde is used primarily as a starting material in the manufacture of acetic acid, ethyl acetate, vinyl acetate, polymers and drugs.
Benzaldehyde is used in perfumery and in dye industries.
Acetone and ethyl methyl ketone are common industrial solvents.
Many aldehydes and ketones, e.g., butyraldehyde, vanillin, acetophenone, camphor, etc. are well known for their odours and flavours.

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. Carboxylic acids may be aliphatic (RCOOH) or aromatic (Ar COOH) depending on the group, (R, alkyl or Ar, aryl group) attached to carboxylic carbon.
Structure of Carboxyl Group: In carboxylic acids, the bonds to the carboxyl carbon lie in one plane and are separated by about 120°. The carboxylic carbon is less electrophilic than carbonyl carbon because of the possible resonance structure shown below:



Methods of Preparation of Carboxylic Acids:

1. From primary alcohols:

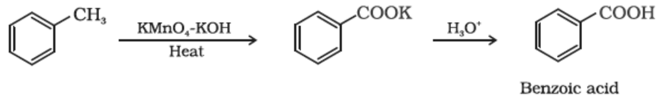
$$RCH_2OH \xrightarrow[2.\ H_3\overset{+}{O}]{1.\ \text{alkaline } KMnO_4} RCOOH$$

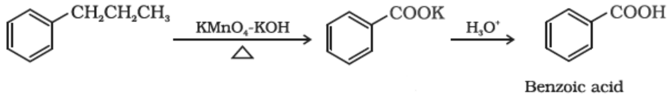
$$\underset{\text{1-Decanol}}{CH_3(CH_2)_8CH_2OH} \xrightarrow[\text{Jones reagent}]{CrO_3\text{-}H_2SO_4} \underset{\text{Decanoic acid}}{CH_3(CH_2)_8COOH}$$

2. From aldehydes:

$$RCHO \xrightarrow{[O]} RCOOH$$

3. From alkyl benzenes:



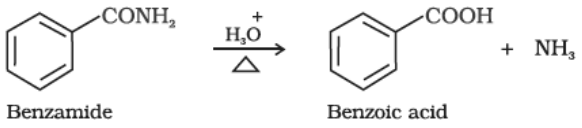


4. From nitriles:

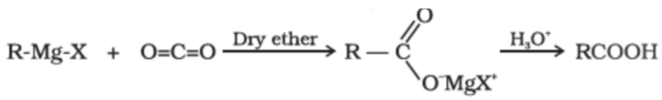
$$RCN \xrightarrow{H+\ or\ OH-} RCONH_2 \xrightarrow{H+\ or\ OH-} RCOOH$$

5. From amides:

$$CH_3CONH_2 \xrightarrow{H3O+} CH_3COOH + NH_3$$

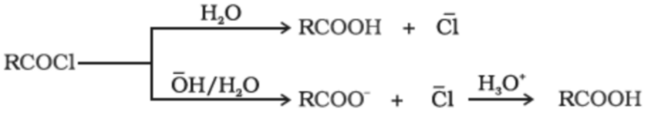


6. From Grignard reagents:



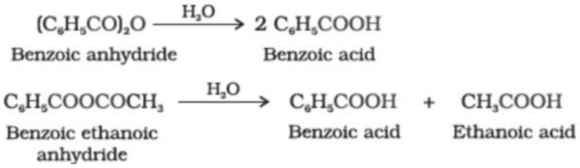
$$R\text{-}Mg\text{-}X + O{=}C{=}O \xrightarrow{\text{Dry ether}} R-C(=O)O^-MgX^+ \xrightarrow{H_3O^+} RCOOH$$

7. From acyl halides:



$$RCOCl \xrightarrow{H_2O} RCOOH + \bar{C}l$$
$$RCOCl \xrightarrow{\bar{O}H/H_2O} RCOO^- + \bar{C}l \xrightarrow{H_3O^+} RCOOH$$

8. From anhydrides:



$$\underset{\text{Benzoic anhydride}}{(C_6H_5CO)_2O} \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{2\ C_6H_5COOH}$$
$$\underset{\text{Benzoic ethanoic anhydride}}{C_6H_5COOCOCH_3} \xrightarrow{H_2O} \underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Ethanoic acid}}{CH_3COOH}$$

6. From esters: Acidic hydrolysis of ethyl benzoate gives benzoic acid.

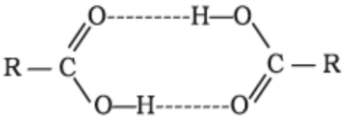
$$C_6H_5\,COO\,C_2H_5 \xrightarrow{H3O+} C_6H_5\,COOH + C_2H_5OH$$

Physical Properties:

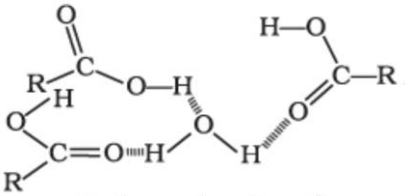
Aliphatic carboxylic acids up to nine carbon atoms are colourless liquids at room temperature with unpleasant odours. The higher acids are wax like solids and are practically odourless due to their low volatility.

Carboxylic acids are higher boiling liquids than aldehydes, ketones and even alcohols of comparable molecular masses. This is due to more extensive association of carboxylic acid molecules through intermolecular hydrogen bonding. The hydrogen bonds are not broken completely even in the vapour phase.

In fact, most carboxylic acids exist as dimer in the vapour phase or in the aprotic solvents.



dimer



Hydrogen bonding of RCOOH with H_2O

Simple aliphatic carboxylic acids having up to 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. Higher carboxylic acids are practically insoluble in water due to the increased hydrophobic interaction of hydrocarbon part. Benzoic acid, the simplest aromatic carboxylic 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:

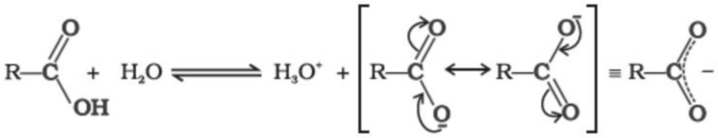
Reactions Involving Cleavage of O–H Bond:

Acidity:

Reactions with metals: $2RCOOH + 2Na \text{ ---> } 2RCOO^-Na^+ + H_2$

Reactions with alkalies: $RCOOH + NaOH \text{ ---> } RCOO^-Na^+ + H_2O$

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



For the above reaction:

$$K_{eq} = \frac{[\overset{+}{H_3O}]\,[RCO\overset{-}{O}]}{[H_2O]\,[RCOOH]} \qquad K_a = K_{eq}\,[H_2O] = \frac{[\overset{+}{H_3O}]\,[RCO\overset{-}{O}]}{[RCOOH]}$$

where K_{eq}, is equilibrium constant and K_a is the acid dissociation constant.

The dissociation constant is called acidity constant. The stronger the acid, the larger will be its K_a value.

$$pK_a = -\ \log K_a$$

Smaller the value of pKa, stronger the acid is.

The acids have pKa values < 1. Strong acids.

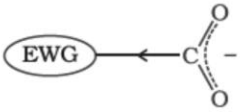
The acids with pKa values between 1 and 5 are considered to be moderately strong acids.

The acids have pKa values between 5 and 15 are extremely weak acids have pKa values >15.

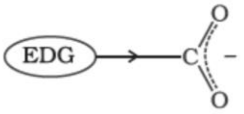
Effect of substituents on the acidity of carboxylic acids:

Electron withdrawing group’s increase the acidity of carboxylic acids by stabilizing the conjugate base through delocalization of the negative charge by inductive and/or resonance effects.

Conversely, electron donating groups decrease the acidity by destabilizing the conjugate base.



Electron withdrawing group (EWG) stabilises the carboxylate anion and strengthens the acid



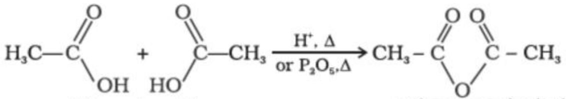
Electron donating group (EDG) destabilises the carboxylate anion and weakens the acid

The effect of the following groups in increasing acidity order is

Phenyl < I < Br < Cl < F < CN < NO_2 < CF_3

Reactions Involving Cleavage of C–OH Bond:

1. Formation of anhydride:



2. Esterification:

RCOOH + R'OH ----> RCOOR' + H_2O

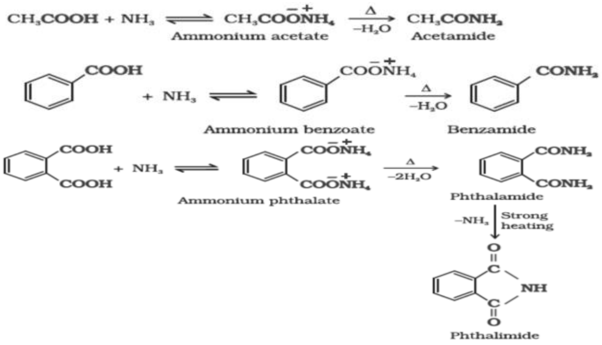
3. Reactions with PCl_5, PCl_3 and $SOCl_2$:

RCOOH + PCl_5 ---> RCOCl + $POCl_3$ + HCl

$3RCOOH + PCl_3 \text{--->} 3RCOCl + H_3PO_3$

$RCOOH + SOCl_2 \text{--->} RCOCl + SO_2 + HCl$

4. Reaction with ammonia:



Reactions Involving –COOH Group:

1. Reduction:

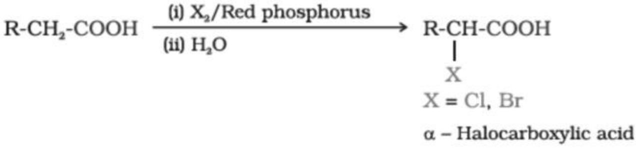
$$RCOOH \xrightarrow{\text{(i) LiAlH4/Ether or B2H6 (ii) H3O+}} RCH_2OH$$

2. Decarboxylation:

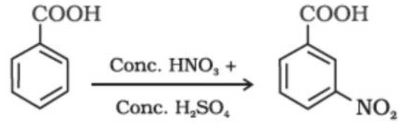
$$RCOONa \xrightarrow{\text{NaOH \& CaO, heat}} R - H + Na_2CO_3$$

Substitution Reactions in the Hydrocarbon Part:

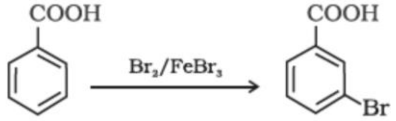
Hell-Volhard-Zelinsky reaction



2. Ring substitution:



m-Nitrobenzoic acid



m-Bromobenzoic acid

Uses of Carboxylic Acids:

Methanoic acid is used in rubber, textile, dyeing, leather and electroplating industries.

Ethanoic acid is used as solvent and as vinegar in food industry.

Hexanedioic acid is used in the manufacture of nylon-6, 6.

Esters of benzoic acid are used in perfumery.

Sodium benzoate is used as a food preservative.

Higher fatty acids are used for the manufacture of soaps and detergents.

ASSIGNMENTS:

Q1. Name the following compounds according to IUPAC system of nomenclature:

(i) $CH_3CH(CH_3)\ CH_2CH_2CHO$
(ii) $CH_3CH_2COCH(C_2H_5)\ CH_2CH_2Cl$
(iii) $CH_3CH=CHCHO$
(iv) $CH_3COCH_2COCH_3$
(v) $CH_3CH(CH_3)\ CH_2C(CH_3)_2COCH_3$
(vi) $(CH_3)_3CCH_2COOH$
(vii) $OHCC_6H_4CHO$-p

Ans. (i) 4-methyl pentanal

(ii)6-chloro-4-ethyl hexan-3-one

(iii) But-2-enal
(iv) Pentane-2,4-dione
(v) 3,3,5-trimethyl hexane-2-one
(vi) 3,3-dimethyl butanoic acid
(vii) Benzene-1,4-dicarbaldehyde

Q2. Give names of the reagents to bring about the following transformations:

(i) Hexan-1-ol to hexanal
(ii) Cyclohexanol to cyclohexanone
(iii) p-Fluorotoluene to p-Fluoro benzaldehyde
(iv) Ethanenitrile to ethanal
(v) Allyl alcohol to propenal
(vi) But-2-ene to ethanal

Ans.

(i) $C_5H_5NH^+CrO_3Cl^-$ (PCC)
(ii) Anhydrous CrO_3 or $K_2Cr_2O_7$ in acidic medium
(iii) CrO_3 in the presence of acetic anhydride or 1. CrO_2Cl_2 2. H_2O
(iv) (Di isobutyl) Aluminium hydride (DIBAL-H)
(v) PCC
(vi) O_3 /H_2O-Zn dust

Q3. Arrange the following compounds in the increasing order of their boiling points: $CH_3CH_2CH_2CHO$, $CH_3CH_2CH_2CH_2OH$, H_5C_2 -O-C_2H_5 and CH3CH2CH2CH3

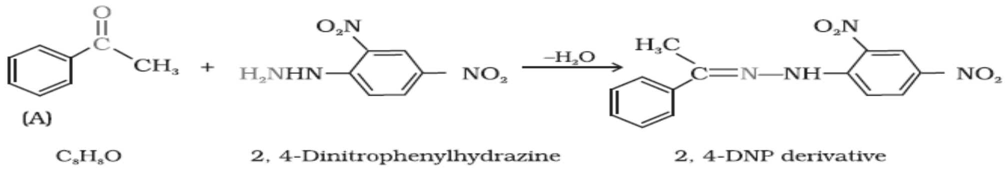
Ans. Increasing order of boiling points of the given compounds is as follows:

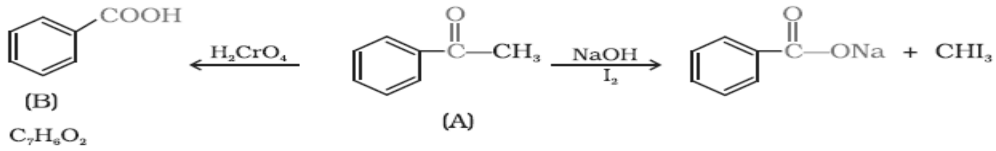
$CH_3CH_2CH_2CH_3 < H_5C_2\text{-O-}C_2H_5 < CH_3CH_2CH_2CHO < CH_3CH_2CH_2CH_2OH$

Q4. Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?
Ans. The electronic charge in the carboxylate ion is more dispersed in comparison to phenate ion. Carboxylate ion is more stable as compared to phenate ion. The release of H^+ ion is easier from carboxylic acid. It behaves as stronger acid than phenol.

Q5. An organic compound (A) with molecular formula C_8H_8O forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehlings' reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula $C_7H_6O_2$. Identify the compounds (A) and (B) and explain the reactions involved.

Ans. Reactions are as follows:





Q6. Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

(i) Ethanal, Propanal, Propanone, Butanone.
(ii) Benzaldehyde, p-Tolualdehyde, p-Nitrobenzaldehyde, Acetophenone.

Ans. (i) Butanone < Propanone < Propanal < Ethanal

(ii) Acetophenone < p-Tolualdehyde < Benzaldehyde < p-Nitrobenzaldehyde

Q7. An organic compound with the molecular formula $C_9H_{10}O$ forms 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.

Ans. 2-Ethyl benzaldehyde

Q8. An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolyzed with dilute Sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.

Ans. A = Butyl butanoate, B = Butanoic acid, C = Butanol

Q9. Arrange the following compounds in increasing order of their property as indicated:

(i) Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone (reactivity towards HCN)
(ii) $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ (acid strength)
(iii) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)

Ans. (i) Acetaldehyde > Acetone > Methyl tert-butyl ketone > Di-tert-butyl ketone

(ii) $(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH < CH_3\,CH\,(Br)\,CH_2\,COOH < CH_3CH_2CH\,(Br)\,COOH$

(iii) 4-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3, 4-Dinitrobenzoic acid

Q10. Give plausible explanation for each of the following:

(i) Cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethylcyclohexanone does not.
(ii) There are two $–NH_2$ groups in semicarbazide. However, only one is involved in the formation of semicarbazones.
(iii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

Ans. (i) Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6-trimethylcyclohexanone does not because of presence of three methyl groups at α-position w.r.t carbonyl group which hinder the Nucleophilic attack of CN^- group due steric hindrance. No such steric hindrance in Cyclohexanone.

(ii) Semicarbazide has two $–NH_2$ groups but one of these which is directly attached to C=O is involved in resonance. Electron density on NH_2 group decreases hence it does not act as nucleophile.

(iii)It is a reversible reaction. Therefore, to shift the equilibrium in the forward direction, the water or the ester should be removed as fast as it is formed.