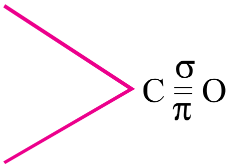
UNIT 12

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Points to Remember

1. Aldehydes, ketones, carboxylic acids and their derivatives are commonly called as carbonyl compounds.
2. In Rosemund's reduction, poisoning of Pd with $BaSO_4$ prevent reduction of R – CHO to R – CH_2OH.
3. In the reaction of toluene with CrO_3, acetic anhydride is used to protect benzaldehyde by forming benzylidenediacetate to avoid its oxidation to benzoic acid.
4. Order of reactivity of aldehydes and ketones towards nucleophilic addition is :
   (i) $HCHO > CH_3CHO > CH_3CH_2CHO$.
   (ii) $HCHO > RCHO > R\,CO\,R$.
   (iii) $ArCHO > Ar\,COR > Ar\,CO\,Ar$.
5. Benzaldehyde does not reduce Fehling's reagent.
6. Aldehydes and ketones with atleast one α–H atom get condensed in presence of a base. This is known as Aldol condensation.
7. Aldol condensation involves carbanion as intermediate.
8. Aldehydes with no α–H atoms under Cannizzaro's reaction.
9. Ketones react with dihydric alcohols to form cyclic ketals.
10. Monocarboxylic acids having (C_{12}–C_{18}) carbon atoms, are called fatty acids.
11. Boiling points of carboxylic acids is greater than corresponding alcohols.
12. Presence of EWGs enhances the acidic character of carboxylic acids.
13. –COOH group is *m*-directing in electrophilic substitution reactions.
14. Compounds containing – CHO group are named as carbaldehydes if – CHO groups are three or more.
15. Isomerism : Chain, position and functional.

16. Structure of –CHO group sp^2 hybridised.



17. General Methods of Preparation :

(i) Controlled oxidation of 1° alcohols :

$$RCH_2OH \xrightarrow{PCC/CrO_3} RCHO$$

(Collin's reagent)

(ii) Dehydration of 1° alcohols :

$$RCH_2OH \xrightarrow{Cu/573\ K} RCHO + H_2$$

(iii) From Rosemund reaction/reduction :

$$RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

(iv) Hydration of alkynes :

$$CH \equiv CH \xrightarrow[40\%\ H_2SO_4]{1\%\ HgSO_4} [CH = CH - OH] \xrightarrow{Tautomerism} CHCHO$$

(v) Reductive ozonolysis of alkenes :

$$R - OH = CH - R \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3} 2RCHO + H_2O_2$$

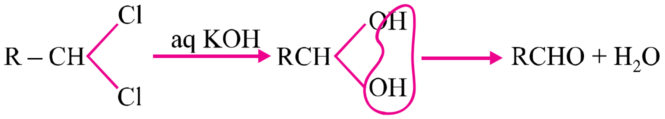
(vi) From salts of fatty acids :

$$(RCOO)_2Ca + (HCOO)_2Ca \xrightarrow{D\ Dist.} 2RCHO + 2CaCO_3$$

(vii) Stephen's reduction of nitrile compounds :

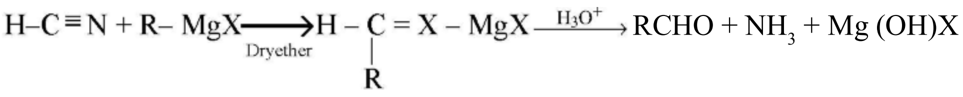
$$R - C \equiv N \xrightarrow{SnCl_2/HCl} [R - CH = NH.HCl] \xrightarrow{H_3^+O} RCHO + NH_4Cl$$

(viii) Hydrolysis of germinal halides :



$$R - CH\begin{matrix} Cl \\ Cl \end{matrix} \xrightarrow{aq\ KOH} RCH\begin{matrix} OH \\ OH \end{matrix} \longrightarrow RCHO + H_2O$$

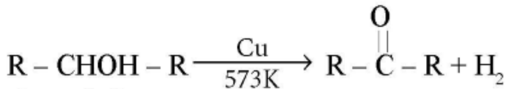
(ix) From Grignard's reagent :



$$H{-}C \equiv N + R{-}\ MgX \xrightarrow[Dryether]{} H - \underset{\substack{| \\ R}}{C} = X - MgX \xrightarrow{H_3O^+} RCHO + NH_3 + Mg\ (OH)X$$

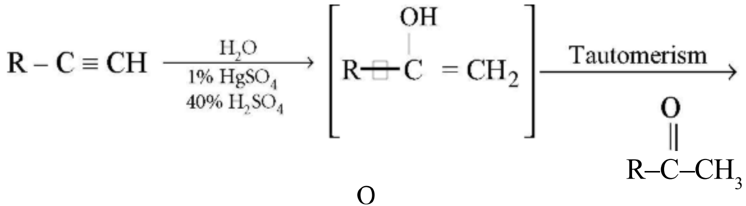
General Methods of Preparation of Ketones only

(i) Dehydrogenation of 2° alcohols :



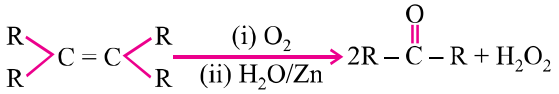
$$R-CHOH-R \xrightarrow[573K]{Cu} R-\overset{\overset{O}{||}}{C}-R + H_2$$

(ii) Hydration of alkynes :



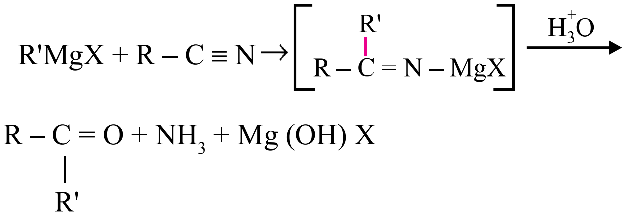
$$R-C\equiv CH \xrightarrow[\substack{1\%\ HgSO_4 \\ 40\%\ H_2SO_4}]{H_2O} \left[R-\overset{\overset{OH}{|}}{C}=CH_2 \right] \xrightarrow{\text{Tautomerism}} R-\overset{\overset{O}{||}}{C}-CH_3$$

(iii)



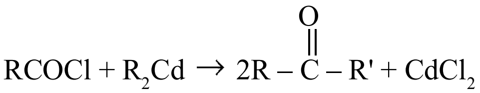
$$\begin{matrix} R \\ R \end{matrix}\!\!>C=C<\!\!\begin{matrix} R \\ R \end{matrix} \xrightarrow[\text{(ii) } H_2O/Zn]{\text{(i) } O_2} 2R-\overset{\overset{O}{||}}{C}-R + H_2O_2$$

(iv) From Grignard's reagents :



$$R'MgX + R-C\equiv N \rightarrow \left[R-\overset{\overset{R'}{|}}{C}=N-MgX \right] \xrightarrow{H_3\overset{+}{O}} R-\underset{\underset{R'}{|}}{C}=O + NH_3 + Mg(OH)X$$

(iv) From acid chlorides :



$$RCOCl + R_2Cd \rightarrow 2R-\overset{\overset{O}{||}}{C}-R' + CdCl_2$$

Physical Properties :

HCHO is a gas at normal temperature. Formalin is 40% as solution of HCHO. Due to polarity they have high values of boiling point. Solubility in water is only for lower members.

Reactivity :

(i) + I effect of alkyl groups decreases the +ve charge on carbonyl carbon.

(ii) Steric hindrance : Bulky group hinder approach of nucleophile.

(iii) α-hydrogen atom is acidic due to resonance.

18. Vinegar is 8 to 10% solution of CH_3COOH.

19. α-hydrogen atoms in carboxylic acid are acidic in nature and can be easily replaced by halogen atoms in HVZ reaction.

21. Relative acid strength of $RCOOH > HOH > ROH > HC \equiv CH > NH_3$. It is because a strong acid has weak conjugate base.

22. Some dicarboxylic acids bearing general formula $HOOC - (CH_2)_n - COOH$ where n – 0, 1, 2, ...etc.

$HOOC - COOH$	Oxalic acid	1, 2 ethanedioic acid
$HOOC - CH_2 - COOH$	Malonic acid	1, 3 propanedioic acid
$HOOC - (CH_2)_2 - COOH$	Succinic acid	1, 4 butanedioic acid
$HOOC - (CH_2)_3 - COOH$	Glutonic acid	1, 5 pentamdioic acid
$HOOC - (CH_2)_4 - COOH$	Adipic acid	1, 6 hexanedioic acid

23. Melting points : Higher : Even carbon atoms than next lower or higher homologues containing even number of carbon atoms due to symmetry and closer packing of molecules in the crystal lattice.

VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

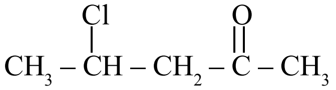
Q. 1. Arrange the following compounds in increasing order of their acid strengths :

$(CH_3)_2CHCOOH$, $CH_3CH_2CH(Br)COOH$, $CH_3CH(Br)CH_2COOH$

Ans. $(CH_3)_2CHCOOH < CH_3CH(Br)CH_2COOH < CH_3CH_2CH(Br)COOH$

Q. 2. Draw the structure of the compound whose IUPAC name is 4-chloropentan-2-one.

Ans.



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

Q. 3. Which type of aldehyde can go Cannizzaro reaction ?

Ans. Aromatic and aliphatic aldehydes which do not contain α-hydrogen.

Q. 4. Name the aldehyde which does not give Fehling's solution test.

Ans. Benzaldehyde.

Q. 5. Arrange the following in order of their increasing reactivity towards HCN :

CH_3CHO, CH_3COCH_3, $HCHO$, $C_2H_5COCH_3$

Ans. $C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

Q. 6. Mention industrial product obtained from HCHO.

Ans. Bakelite

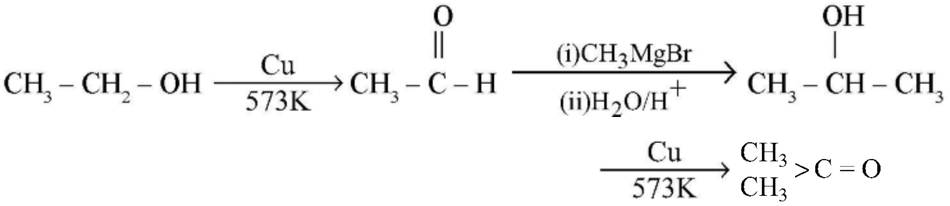
Q. 7. Arrange the following compounds in increasing order of their boiling point :

$$CH_3CHO,\ CH_3CH_2OH,\ CH_3-O-CH_3,\ CH_3-CH_2-CH_3$$

Ans. $CH_3-CH_2-CH_3 < CH_3-O-CH_3 < CH_3CHO < CH_3CH_2OH$

Q. 8. How is acetone obtained from ethanol ?

Ans.



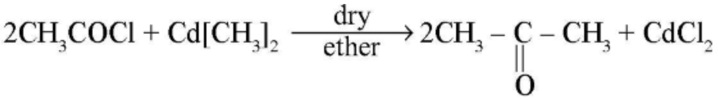
$$CH_3-CH_2-OH \xrightarrow[573K]{Cu} CH_3-\overset{\overset{O}{\|}}{C}-H \xrightarrow[(ii)H_2O/H^+]{(i)CH_3MgBr} CH_3-\overset{\overset{OH}{|}}{C}H-CH_3 \xrightarrow[573K]{Cu} \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C=O$$

Q. 9. Why do aldehydes and ketones have lower boiling point than alcohols ?

Ans. Due to presence of associated molecules with H-bonding in alcohols.

Q. 10. Write reaction between acetyl chloride and dimethyl cadmium.

Ans.

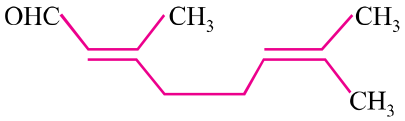


$$2CH_3COCl + Cd[CH_3]_2 \xrightarrow[ether]{dry} 2CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + CdCl_2$$

Q. 11. What happens when CH_3CHO is treated with $K_2Cr_2O_7$ in presence of H_2SO_4 ?

Ans. $CH_3CHO + [O] \xrightarrow{K_2Cr_2O_7+H_2SO_4} CH_3COOH$

Q. 12. Write the IUPAC name of



Ans. 3, 7-Dimethylocta-2, 6 dien-1-al

Q. 13. Give balanced equation and name of products when CH_3COOH is treated with PCl_5 ?

Ans. $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

Q. 14. Write the name of ester which gives the flavor of pineapple.

Ans. Ethyl butanoate.

Q. 15. What product is obtained when ethyl benzene is oxidized with alkaline $KMnO_4$?

Ans. Benzoic acid (C_6H_5COOH) is obtained.

Q. 16. What is RDX ?

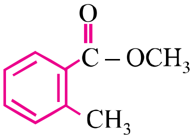
Ans. RDX is Research and Development Explosive which is prepared by the nitration of hexamethylene under controlled conditions.

Q. 17. Write IUPAC names of the following compound :

HOOC – CH = CH - COOH

Ans. But-2-ene-1, 4-dioic acid

Q. 18. Write the IUPAC name of



Ans. Methyl-2-methylbenzoate.

Q. 19. Why does benzoic acid not undergo Friedel-Craft reaction ?

Ans. – COOH group in C_6H_5COOH is an E. W. G. which deactivates the benzene ring. Hence electrophilic substitution becomes difficult.

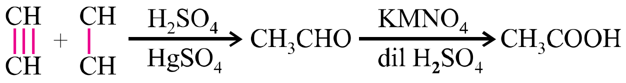
SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. How will you convert :

(i) $C_2H_2 \rightarrow CH_3COOH$

(ii) $C_6H_5CONH_2 \rightarrow C_6H_5COOH$

Ans. (i)

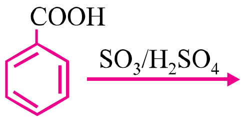


$$\begin{matrix}CH\\|||\\CH\end{matrix} + \begin{matrix}CH\\|\\CH\end{matrix} \xrightarrow[HgSO_4]{H_2SO_4} CH_3CHO \xrightarrow[\text{dil } H_2SO_4]{KMNO_4} CH_3COOH$$

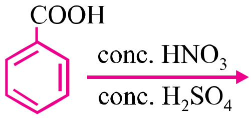
(ii) $C_6H_5CONH_2 + HNO_2 \rightarrow C_6H_5COOH + N_2 + H_2O$

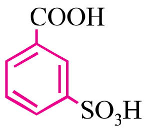
Q. 2. Complete the following :

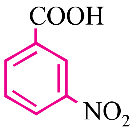
(i)



(ii)

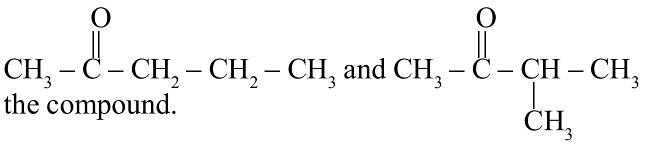


Ans. (i) 

(ii) 

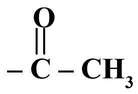
Q. 3. An organic compound X has molecular formula $C_5H_{10}O$. It does not reduce Fehling's solution but forms a bisulphate compound. It also gives positive Iodoform test. What are possible structures of X ? Explain your reasoning relating structure.

Ans. Ketone give +ve test with Iodoform. It is methyl-ketone.



$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3$ and $CH_3-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{CH}-CH_3$ are possible structures of the compound.

Q. 4. Give the chemical test to distinguish between :

(i) CH_3CHO and  $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

(ii) CH_3CHO and C_6H_5CHO

Ans. (i) CH_3CHO gives Tollen's reagent test.

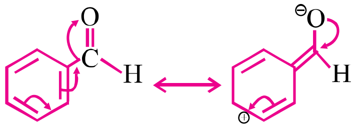
$$CH_3CHO + 2AgNO_3 + 2NH_4OH \rightarrow CH_3COOH + \underset{\text{Silver mirror}}{2Ag} + 2NH_4NO_3 + 2H_2O$$

(ii) CH_3CHO gives brick red ppt.

$$CH_3CHO + 2CuSO_4 + 4NaOH \rightarrow CH_3COOH + \underset{\text{Brick red ppt.}}{Cu_2O} + Na_2SO_4 + 2H_2O$$

Q. 5. Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal ? Explain your answer.

Ans. Carbon atom of carbonyl is C_6H_5CHO is less reactive than that of propanal. C_6H_5CHO less polar due to resonance.

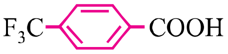


Q. 6. Which acid of each pair shown here would you expect to be stronger ?

(i) CH_3CO_2H or CH_2FCO_2H

(ii) CH_2FCO_2H or CH_2ClCO_2H

(iii) $CH_2FCH_2CH_2CO_2H$ or $CH_3CHFCH_2CO_2H$

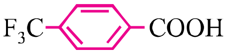
(iv)  **or** 

Ans. (i) FCH_2COOH

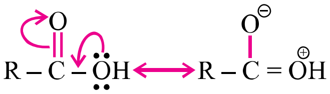
(ii) CH_2FCOOH

(iii) 

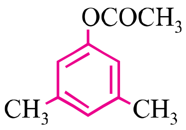
$CH_3-\overset{F}{\underset{|}{C}}H-CH_2COOH$

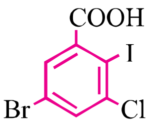
(iv) 

Q. 7. Carboxylic acids do not give reactions of aldehydes and ketones why ?

Ans. It is due to resonance  Position of $> C = O$ group keep changing.

Q. 8. Write IUPAC name of the following :

(i) 

(ii) 

Ans. (i) 3, 5 Dimethylphenylethanoate

(ii) 5 bromo 3-chloro-2-iodobenzoic acid

Q. 9. Account for the following :

(i) Oxidation of toluene to C_6H_5CHO with CrO_3 is carried out in presence of acetic anhydride.

(ii) Melting point of an acid with even number is higher than those of its neighbours with odd number of carbon atoms.

Ans. (i) It is used to prevent oxidation to benzoic acid.

(ii) Acids with even number of carbon atoms fit into crystal lattice.

Q. 10. Distinguish between :

(i) C_2H_5OH and CH_3CHO

(ii) $C_6H_5COCH_3$ and $C_6H_5CH_2CHO$

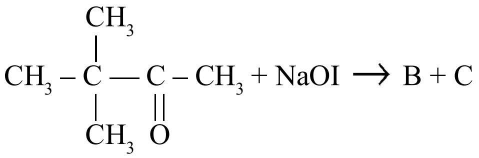
Ans. (i) C_2H_5OH evolves H_2 gas with Na, CH_3CHO not.

(ii) Acetophenone will give yellow ppt. of iodoform while $C_6H_5CH_2CHO$ will not.

Q. 11. Complete the following reactions by identifying A, B and C :

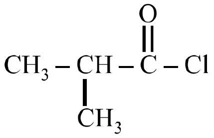
(i) **A + Hydrogen (g)** $\xrightarrow{Pd/BaSO_4}$ **$(CH_3)_2CH-CHO$**

(ii)



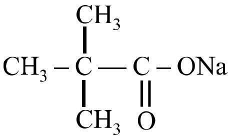
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{O}{||}}{C}-CH_3 + NaOI \rightarrow B + C$$

Ans. (i) ‘A’ is



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

(ii) ‘B’ is CHI_3 and ‘C’ is



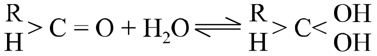
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{O}{||}}{C}-ONa$$

Q. 12. Benzaldehyde gives a positive test with Tollen’s reagent but not with Fehling’s and Benedict solutions. Why ?

Ans. It is due to stronger oxidizing nature of Tollen’s reagent as compared to Fehling and Benedict’s solution and cannot oxidise benzaldehyde to benzoic acid. In general, all these three can oxidise aliphatic acids.

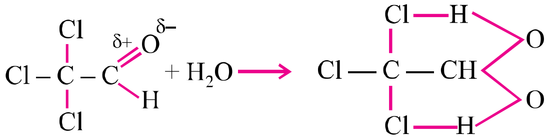
Q. 13. Aldehydes usually do not form stable hydrates but chloral normally exists as chloral hydrate. Give reason.

Ans. In case of aldehyde reaction is reversible.



$$\genfrac{}{}{0pt}{}{R}{H}>C=O+H_2O \rightleftharpoons \genfrac{}{}{0pt}{}{R}{H}>C<\genfrac{}{}{0pt}{}{OH}{OH}$$

In case of CCl_3CHO, Cl atoms increases +ve charge on carbonyl carbon. Therefore, weak nucleophiles like water readily added to the carbonyl group.



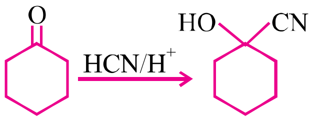
Chloralhydrate

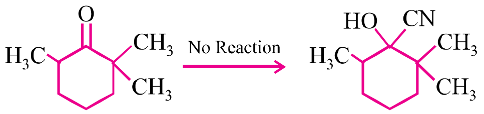
Q. 14. Give possible explanation for the following :

(i) **Cyclohexanone forms cyanohydrins in good yield but 2, 2, 6 trimethylcyclohexanone does not.**

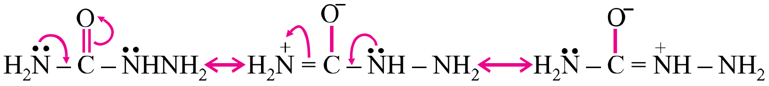
(ii) **There are two – NH_2 groups in semicarbazide. However, only one is involved in formation of semi carbozone.**

Ans. (i) Due to steric hindrance for CN^- at C = O and not of 3-methyl groups at α-position but in case of





(ii) Only one – NH_2 group attached to C = O is involved in resonance. As result electron density on theis NH_2 group decreases and hence does not act as nucleophile.



$$H_2\ddot{N}-\overset{O}{\overset{\|}{C}}-\ddot{N}HNH_2 \longleftrightarrow H_2\overset{+}{N}=\overset{O^-}{\overset{|}{C}}-\ddot{N}H-NH_2 \longleftrightarrow H_2\ddot{N}-\overset{O^-}{\overset{|}{C}}=\overset{+}{N}H-NH_2$$

Q. 15. Aldehydes are easily oxidisable yet propanal can conveniently be prepared by the oxidation of propanol by acidic $K_2Cr_2O_7$.

Ans. Aldehydes having boiling points less than 373 K can be removed by distillation therefore propanal 323 can easily be prepared from propanol-1 by distillation from the alcohol acid dichromate solution.

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. Illustrate the following name reactions :

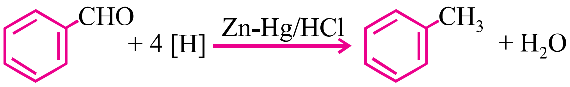
(i) Clemmensen's Reduction

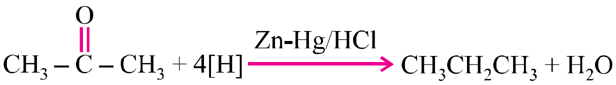
(ii) Beckmann Rearrangement

(iii) Benzoin Condensation

Ans. (i) Both aldehydes and ketones are reduced to hydrocarbons.

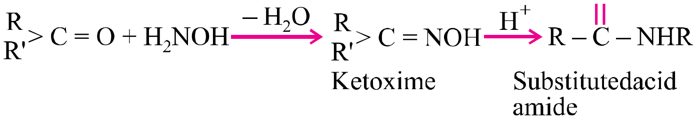
$$CH_3CHO + 4[H] \xrightarrow{\text{Zn-Hg/HCl}} CH_3CH_3 + H_2O$$



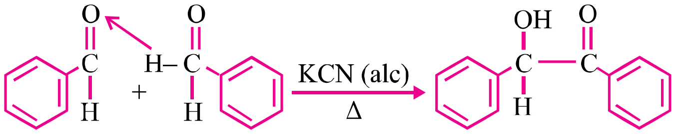


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + 4[H] \xrightarrow{\text{Zn-Hg/HCl}} CH_3CH_2CH_3 + H_2O$$

(ii) Formation of ketoximes on treatment with an acid (H_2SO_4) or reagents like PCl_5, $SOCl_2$ etc.



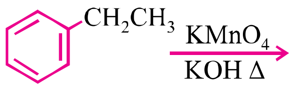
$$\overset{R}{\underset{R'}{}}{>}C=O + H_2NOH \xrightarrow{-H_2O} \underset{\text{Ketoxime}}{\overset{R}{\underset{R'}{}}{>}C=NOH} \xrightarrow{H^+} \underset{\text{Substitutedacid amide}}{R-\overset{\overset{O}{\parallel}}{C}-NHR}$$

(iii) 

Benzaldehyde

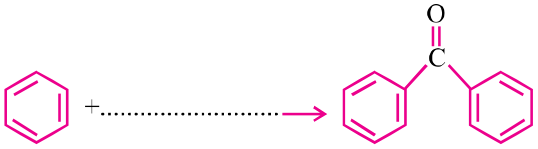
Benzoin

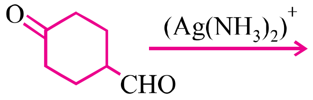
Q. 2. Predict the organic products of the following reactions :

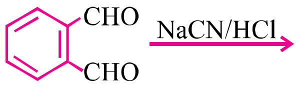
(i) 

(ii) 

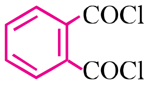
(iii) $C_6H_5CHO \xrightarrow{H_2NCONHNH_2}$

(iv) 

(v) 

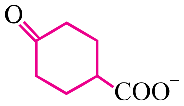
(vi) 

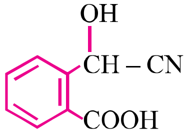
Ans. (i) C_6H_5-COOK

(ii) 

(iii) $C_6H_5CN=N-NHCONH_2$

(iv) $C_6H_5COCl/AlCl_3$

(v) 

(vi) 

Q. 3. Write chemical reaction to affect the following transformations :

(i) Butan-1-ol → Butanoic acid

(ii) Benzyl alcohol to pheynylethanoic acid

(iii) 3-Nitrobromobenzene to 3-nitrobenzoic acid

(iv) 4-methylacetophenone to Terephthalic acid

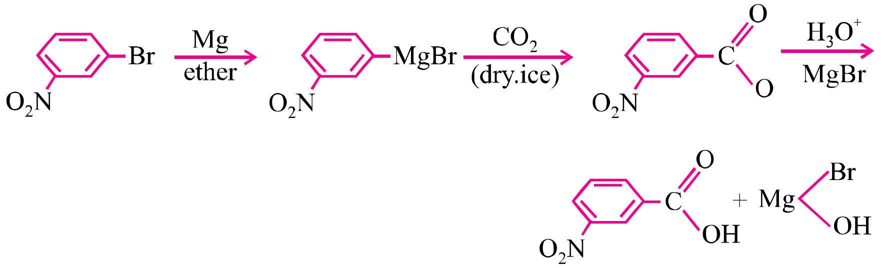
(v) Cyclohexene → Hexane-1, 6 dioic acid

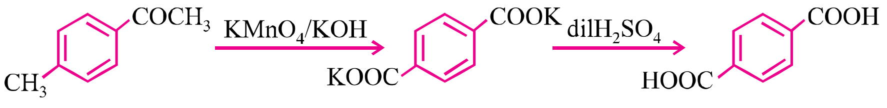
(vi) Butanal → Butanoic acid

Ans. (i) $CH_3CH_2CH_2CH_2OH \xrightarrow[\text{Jones reagent}]{CrO_3+H_2SO_4} CH_3CH_2CH_2COOH$

(ii) $C_6H_5CH_2OH \xrightarrow{HBr} C_6H_5CH_2Br \xrightarrow{KCN} C_6H_5OH_2CN$

$$\xrightarrow[H_3O^+]{\Delta} C_6H_5CH_2COOH$$

(iii) 

(iv) 

Dipotassium benzene
1, 4 dicarboxylate

Terephthalic acid

(v) 

Cyclohexene

Hexane-1, 6-dioicacid (adipic acid)

(vi) $CH_3CH_2CH_2CHO \xrightarrow[\text{Tollen's reagent}]{\text{Amm. AgNO}_3} CH_3CH_2CH_2COOH$

Q. 4. Draw the structure of the following derivatives :

(i) 2, 4-dinitrophenylhydrazone of C_6H_5CHO

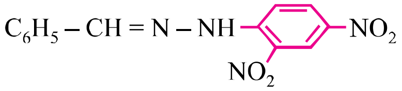
(ii) Cyclopropanone oxime

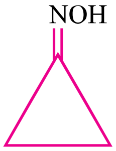
(iii) Acetaldehydedimethylacetal

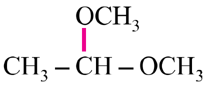
(iv) Semicarbazone to cyclobutanone

(v) Ethylene ketal of hexan-3-one

(vi) Methylhemiacetal of formaldehyde

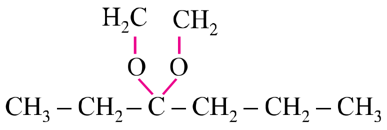
Ans. (i) 

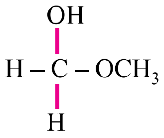
(ii) 

(iii) 

$$CH_3-\overset{\overset{\displaystyle OCH_3}{|}}{CH}-OCH_3$$

(iv) 

(v) 

(vi) 

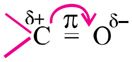
$$H-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-OCH_3$$

Q. 5. Draw the structure of a carbonyl group and indicate :

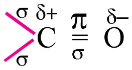
(i) hybridized state of carbon

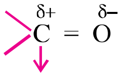
(ii) the σ and π bonds

(iii) the electrophilic and nucleophilic centres

Ans. (i) 

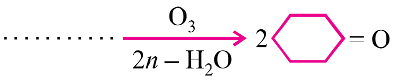
hybridized state of 'C' is sp^2

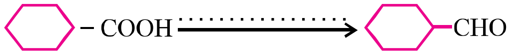
(ii) 

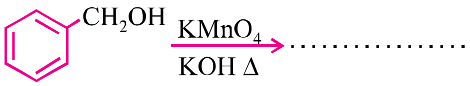
(iii) 

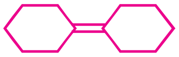
Nucleophilic centre

Q. 6. Complete the following as missing starting material, reagent or products :

(i) 

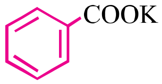
(ii) 

(iii) 

Ans. (i)  (Ozonolysis)

1, 2 Dicyclohexylethene

(ii) B_2H_6/THF, PCC (Hydroboration)

(iii) 

(Oxidation)

Potassium benzoate

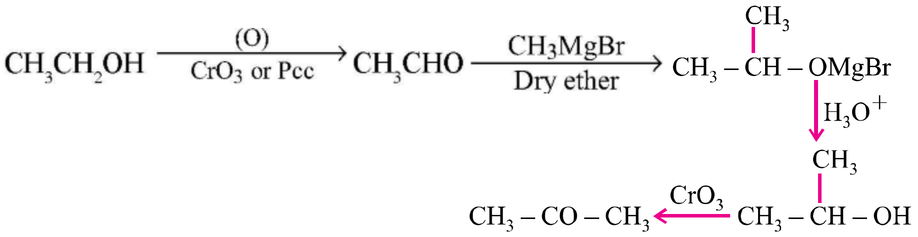
Q. 7. How can the following converted :

(i) Ethanol → Acetone

(ii) Benzene → Acetophenone

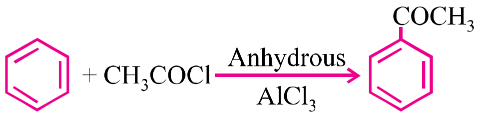
(iii) Benzoic acid → Benzaldehyde

Ans. (i)



$$CH_3CH_2OH \xrightarrow[CrO_3 \text{ or Pcc}]{(O)} CH_3CHO \xrightarrow[\text{Dry ether}]{CH_3MgBr} CH_3-\overset{\overset{CH_3}{|}}{C}H-OMgBr \xrightarrow{H_3O^+} CH_3-\overset{\overset{CH_3}{|}}{C}H-OH \xrightarrow{CrO_3} CH_3-CO-CH_3$$

(ii)



$$C_6H_6 + CH_3COCl \xrightarrow[AlCl_3]{\text{Anhydrous}} C_6H_5COCH_3$$

(iii) $C_6H_5COOH \xrightarrow{PCl_5} C_6H_5COCl + H_2 \xrightarrow{Pd/BaSO_4} C_6H_5CHO + HCl$

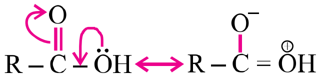
Q. 8. Give reasons for the following :

(i) Carboxylic acids do not give characteristic reactions of carbonyl group.

(ii) Treatment of C_6H_5CHO with HCN gives a mixture of two isomers which cannot be separated even by fractional distillation.

(iii) Sodium bisulphate is used for purification of ketones and aldehydes.

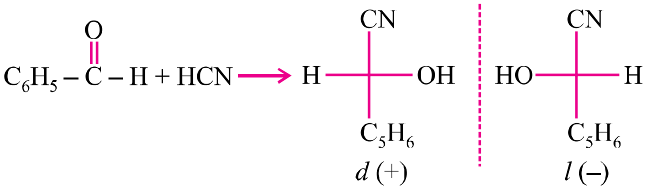
Ans. (i)



$$R-\overset{\overset{O}{\|}}{C}-\ddot{O}H \longleftrightarrow R-\overset{\overset{O^-}{|}}{C}=\overset{\oplus}{\ddot{O}}H$$

Because of resonance, the position of $>C=O$ group is changing.

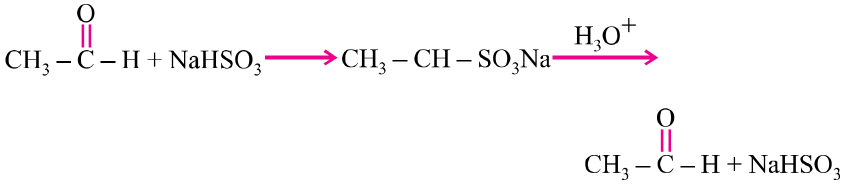
(ii) Due to two optical isomers fractional distillation is not possible.



$$C_6H_5-\overset{\overset{O}{\|}}{C}-H + HCN \longrightarrow$$

d (+) l (–)

(iii) Due to formation of additional compound with $NaHCO_3$ whereas impurities do not.



$$CH_3-\overset{\overset{O}{\|}}{C}-H + NaHSO_3 \longrightarrow CH_3-CH-SO_3Na \xrightarrow{H_3O^+} CH_3-\overset{\overset{O}{\|}}{C}-H + NaHSO_3$$

Q. 9. Write tests to distinguish between :

(i) CH_3CHO and C_6H_5CHO

(ii) C_6H_5-OH and CH_3COOH

(iii) Pentanal and Pentan-2-one

Ans. (i) CH_3CHO gives brick red ppt. with Fehling, C_6H_5CHO not.

(ii) Phenol does not give brisk effervescence but CH_3COOH gives this test with $NaHCO_3$.

(iii) Pentanal forms silver mirror but pentan-2-one does not.

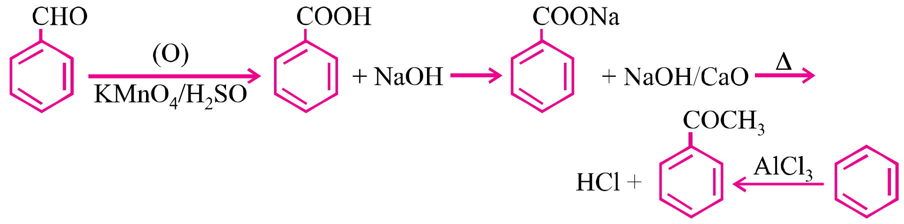
Q. 10. Convert :

(i) Benzaldehyde to acetophenone

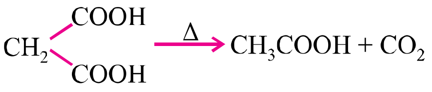
(ii) Malonic acid to acetic acid

(iii) Acetaldehyde to 2-butanol

Ans. (i)



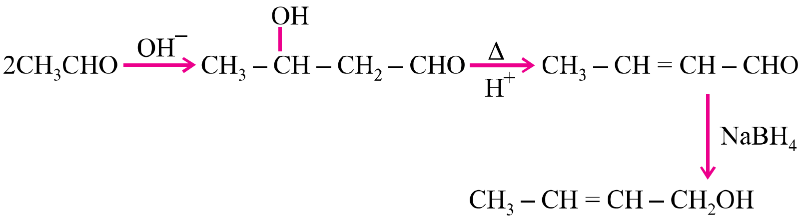
(ii)



$$CH_2\begin{cases}COOH\\COOH\end{cases} \xrightarrow{\Delta} CH_3COOH + CO_2$$

Malonic acid

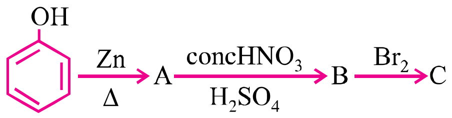
(iii)



$$2CH_3CHO \xrightarrow{OH^-} CH_3-\underset{}{\overset{OH}{\overset{|}{C}H}}-CH_2-CHO \xrightarrow[H^+]{\Delta} CH_3-CH=CH-CHO \xrightarrow{NaBH_4} CH_3-CH=CH-CH_2OH$$

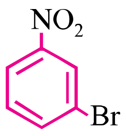
2-Butanol

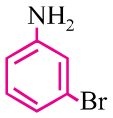
Q. 11. Write the structures of organic compound A to F in the following sequence of reactions :

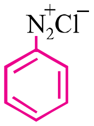


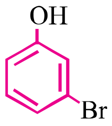
$$C \xrightarrow{H_2/pt\text{-}v} D \xrightarrow[HCl]{HNO_2} E \xrightarrow{H_3O^+} F$$

Ans. $A = C_6H_6$ $B = C_6H_5NO_2$ C =



D = 

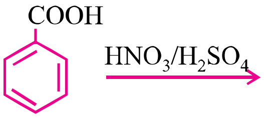
E = 

F = 

Q. 12. Complete the following :

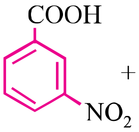
(i) $CH_3CONH_2 + HNO_2 \rightarrow$

(ii) $CH_3CONH_2 + NaOH + Br_2 \rightarrow$

(iii) 

Ans. (i) $CH_3COOH + N_2 + H_2O$

(ii) $CH_3NH_2 + Na_2CO_3 + NaBr + H_2O$

(iii) 

$+ H_2O$

LONG ANSWER TYPE QUESTIONS (5 Marks)

Q. 1. Which of the following compounds would undergo Aldol condensation, which the Cannizzaro reaction and which neither ? Write the structures of the expected products of aldol condensation and Cannizzaro reaction :

(i) Methanal	**(ii) 2-Methylpentanal**
(iii) Benzaldehyde	**(iv) Benzophenone**
(v) Cyclohexanone	**(vi) 1-Phenylpropanone**
(vii) Phenylacetaldehyde	**(viii) Butan-1-ol**
(ix) 2, 2 Dimethylbutanal	

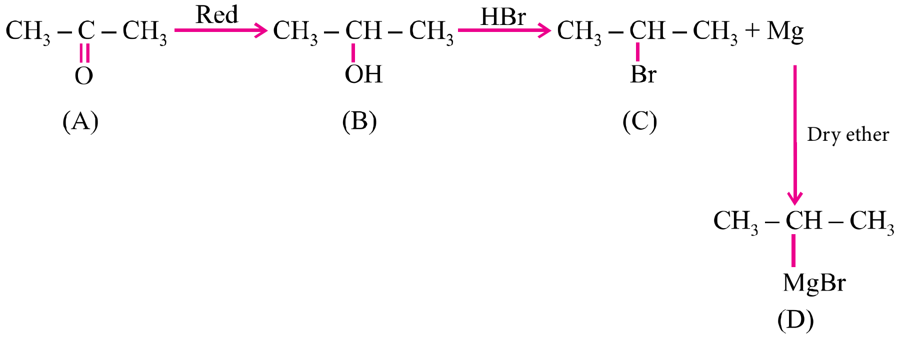
Ans. (i), (iii) and (ix) will give Cannizzaro reaction due to absence of α-hydrogen.

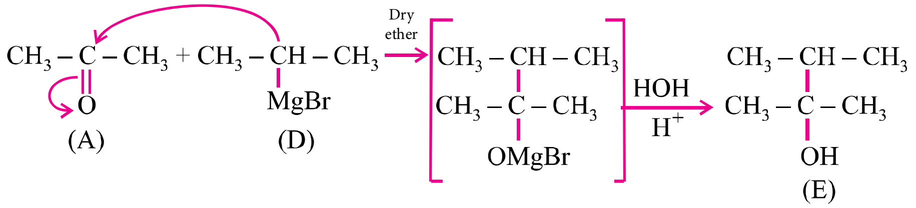
(ii), (v), (vi) and (vii) will give aldol condensation due to presence of α-hydrogen.

(iv) and (viii) will neither undergo Cannizzaro's reaction nor Aldol condensation because benzophenone does not give α-hydrogen and butanol is alcohol, not aldehyde which cannot undergo aldol condensation.

Q. 2. An organic compound 'A' (C_3H_6O) is resistant to oxidation but forms compound 'B' (C_3H_8O). On reduction 'B' reacts with HBr to form the compound 'C'. 'C' with Mg forms Grignard's reagent 'D' which reacts with 'A' to form a product which on hydrolysis gives 'E'. Identify 'A' to 'E'.

Ans. 'A' must be ketone.





2, 3 Dimethylbutan-2-al

Q. 3. Give structure of the following compounds :

(i) 2-methoxypropionaldehyde

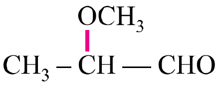
(ii) 3-hydroxy butanal

(iii) 2-hydroxy cyclopentanecarbaldehyde

(iv) 4-oxopentanal

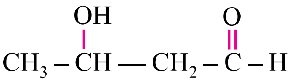
(v) Di-seebutyl ketone

Ans. (i)



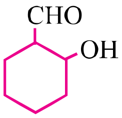
$$CH_3-\overset{\overset{\displaystyle OCH_3}{|}}{CH}-CHO$$

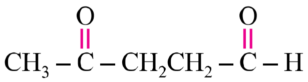
(ii)



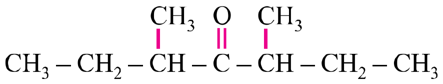
$$CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$$

(iii)



(iv) 

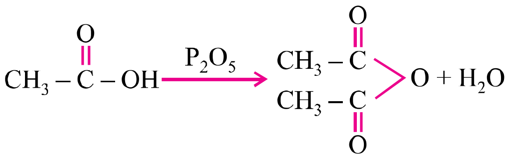
$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H$

(v) 

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

Q. 4. (i) How will you prepare (a) acetic anhydride and (b) acetyl chloride from CH_3COOH ? Write the equation involved in each case.

(ii) Why is the boiling point of acid anhydride higher than the acid from which it is obtained ?

Ans. (i) (a) 

(b) 

$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

(ii) Acid anhydride bigger size than corresponding acids and stronger van der Waal's forces of attraction than their corresponding acids.

Q. 5. Complete the following reactions and write main products :

(i) $CH_3CONH_2 + HNO_2 \rightarrow$ **(ii) $CH_3COCl + H_2O$ (steam) $\rightarrow$**

(iii) $CH_3MgBr \xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) } CO_2/H^+}$ **(iv) $CH_3COOH + NH_3 \xrightarrow{\Delta}$**

(v) $CH_3COOH + C_2H_5OH \xrightarrow{\text{conc. } H_2SO_4}$ **(vi) $HCHO + NH_3 \rightarrow$**

(vii) $CH_3CHO \xrightarrow{LiAlH_4}$ **(viii) $CH_3CHO \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} \xrightarrow{H^+}$**

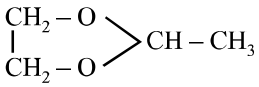
(ix) $CH_3COR + NaOI \rightarrow$ **(x) $C_6H_5CHO + NH_2-NH_2 \rightarrow$**

Ans. (i) CH_3COOH (ii) CH_3COOH

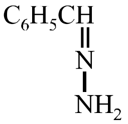
(iii) CH_3COOH (iv) CH_3CONH_2

(v) $CH_3COOC_2H_5$ (vi) $(CH_2)_6N_4$ (Urotropine)

(vii) CH_3CH_2OH

(viii) 

(ix) CHI_3

(x) 

$C_6H_5CH{=}N{-}NH_2$

Q. 6. Give reasons for the following :

(i) C_6H_5COOH is weaker than formic acid.

(ii) HCOOH and CH_3COOH differentiated by Tollen's reagent.

(iii) R – COOH do not give characteristic reaction with > C = O.

(iv) Carboxylic acids are stronger acids than phenols.

(v) Acid amides are weakly basic in nature.

Ans. (i) Due to disabilities of carboxylate anion due to conjugation.

(ii) HCOOH acid is a stronger acid than CH_3COOH.

(iii) > C = O group is sterically hindered in carboxylic acid.

(iv) Dispersal of –ve charge on carboxylate ions than phenate ion.

(v) Acid amides are basic due to lone pair of electrons on nitrogen atom.