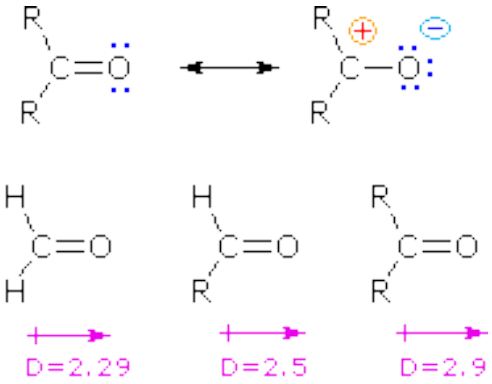
UNIT - 12

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Nature of carbonyl group:- The Pi electron cloud of >C=O is unsymmetrical therefore, partial positive charge develop over carbon of carbonyl group while negative charge develop over oxygen of carbonyl group and dipole moment is approximate 2.6D.



- They are highly polar molecule
- They boil at higher temperatures than the corresponding hydrocarbons and weakly polar compounds such as ethers. This is due to the weak molecular association in aldehydes and ketones arising out of the dipole dipole interactions.
- Solubility of aldehydes and ketones decreases rapidly on increasing the length of the alkyl chain.
- Lower members are soluble in water because they can form H-bond with water
- Higher members are insoluble in water due to large size of their hydrophobic group

POINTS TO REMEMBER

- Aldehydes, Ketones and Carboxylic acids are important classes of organic compounds containing carbonyl groups.
- They are highly polar molecules.
- They boil at higher temperatures than the corresponding hydrocarbons and weakly polar compounds such as ethers.
- Lower members are soluble in water because they can form H-bond with water.
- Higher members are insoluble in water due to large size of their hydrophobic group.

Method of Preparation

Aldehydes are prepared by-

a. Dehydrogenation of primary alcohols

b. Controlled oxidation of primary alcohols.

c. Controlled and selective reduction of acylhalides

Aromatic aldehydes can be prepared by-

a. Oxidation of toluene with chromyl chloride or CrO_3in the presence of acetic anhydride.

b. Formylation of arenes with carbon monoxide and Hydrochloric acid in thepresence of

anhydrous aluminium chloride / Cuprous chloride.
c. Hydrolysis of benzal chloride.

Ketones are prepared by-

a. oxidation of secondary alcohols
b. Hydration of alkenes
c. Reaction acyl chlorides with dialkyl cadmium
d. By Friedel Crafts reaction

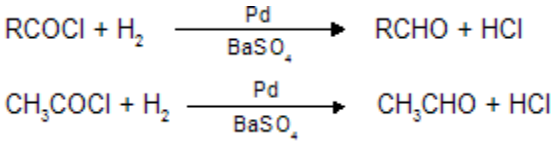
Carboxylic acids are prepared by –

a. Oxidation of primary alcohols, aldehydes and alkenes
b. Hydrolysis of nitriles
c. Treatment of Grignard reagent with carbondioxide.

NAME REACTIONS

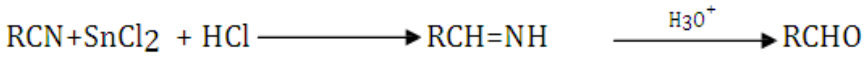
1. ROSENMUND REDUCTION

Acylchlorides when hydrogenated over catalyst, palladium on barium Sulphate yield aldehydes. Sulphur and Quinolene can be used as poison.



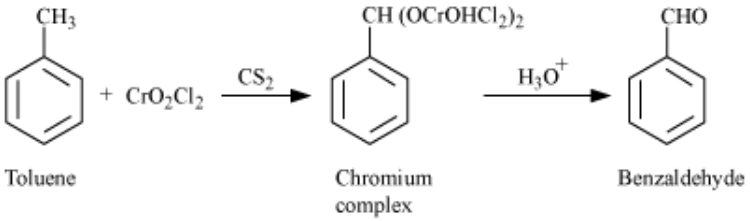
2. STEPHEN REACTION

Nitriles are reduced to corresponding imines with stannous chloride in the presence of Hydrochloric acid, which on hydrolysis give corresponding aldehyde.



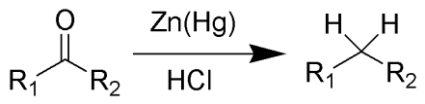
3. ETARD REACTION

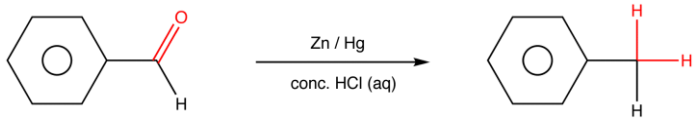
On treating toluene with chromylchloride CrO_2Cl_2, them ethyl group is oxidized to achromium complex, which on hydrolysis gives corresponding benzaldehyde.



4.CLEMMENSON REDUCTION

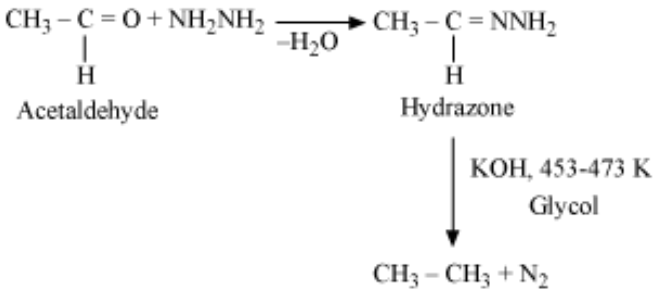
The carbonyl group of aldehydes and ketone is reduced to–CH_2 group on treatment with zinc amalgam and conc.Hydrochloric acid.





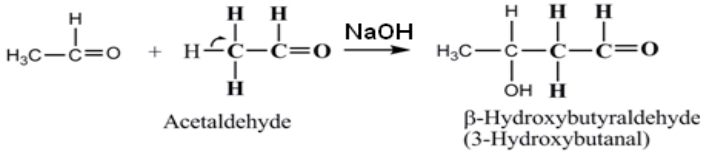
5.WOLFF-KISHNER REDUCTION

On treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent like ethylene glycol



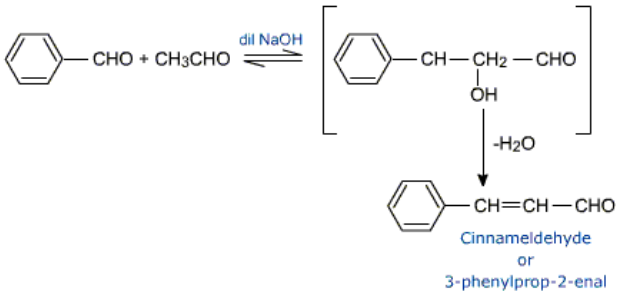
6.ALDOL CONDENSATION

Aldehydes and ketones having atleast one α-hydrogen condense in the presence of dilute alkali as catalyst to form β-hydroxy aldehydes (aldol)or β-hydroxy ketones (ketol).



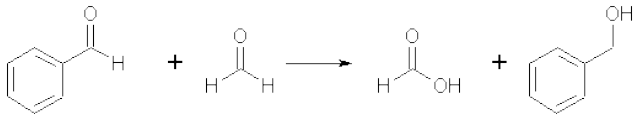
7.CROSS-ALDOL CONDENSATION

When aldol condensation is carried out between two different aldehydes and/ orketones, a mixture of self and cross-aldol products are obtained.



8.CANNIZARO REACTION

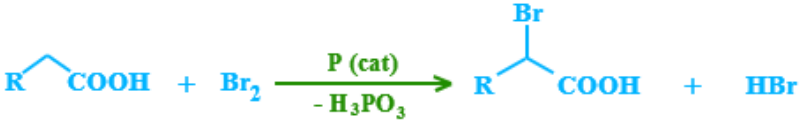
Aldehydes which do not have a α-hydrogen atom undergo self oxidation and reduction (dispropotionation) reaction on treatment **with concentrated alkali**, to yield carboxylioc acid salt and an alcohol respectively.



Reactions of Carboxylic Acid:

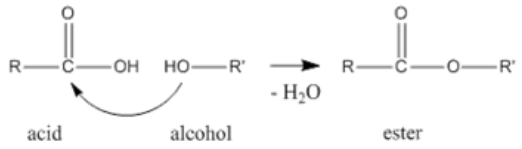
1. **HELL-VOLHARD-ZELINSKY REACTION(HVZ)**

Carboxylic acids having an α –hydrogen are halogenated at the α–position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α –halo carboxylic acids.



2. **ESTERIFICATION**

Carboxylic acids react with alcohols or phenols in the presence of a mineral acid such as conc.H_2SO_4 as catalyst to form esters.



3. **DECARBOXYLATION**:

Carboxylic acids lose carbondioxide to form hydrocarbons when their sodium salts are heated with soda lime NaOH and CaO in the ratio 3:1.

$$RCOONa \xrightarrow{NaOH \text{ and } CaO/\Delta} R\text{-}H + Na_2CO_3$$

DISTINGUISH

Q1:-Distinguish between the following:-

(a)Phenol and alcohol
(b)Benzaldehyde and Propanal
(c)Acetic acid and formic acid
(d)Benzo phenone and acetophenone
(e)Ethanal and propanal
(f)Propanol and ethanol
(g)Pentanone-2 and pentanone-3
(h) 2Alcohol and 3alcohol
(i) 1, 2, 3 amine
(j)Benzoic acid and benzene
(k) Phenol and benzoic acid
(l) Anilineandethyl amine
(m)Aniline and nitrobenzene
(n)Benzaldehyde and acetophenone
(o)Methanol and benzaldehyde
(p)Chloro benzene and benzylchloride

ANSWERS

a	Phenol	It gives $FeCl_3$ test(violet colour)
	Alcohol	It doesn't give this test
b	Benzaldehyde	It gives tollen's test It doesn't give Fehling test
	Propanal	It also give tollen's reagent test It gives fehling solution test
c	Acetic acid	It doesn't gives tollen's reagent . It doesn't give fehling's test
	Formicacid	It gives tollen's test It gives fehling test
d	Benzophenone	It doesn't give iodoform test
	Acetophenone	It gives iodoform test
e	Ethanal	It gives iodoform test

	Propanal	It doesn't gives iodoform test
f	1-Propanol	It doesn't give iodoform test
	Ethanol	It gives iodoform test
g	2-pentanone	It gives iodoform test
	3-pentanone	It doesn't gives iodoform test
h	2^0alcohol	Lucas Test – HCl and an.$ZnCl_2$ It takes 5 minutes to form the turbidity
	3^0alcohol	Lucas Test – HCl and an.$ZnCl_2$ turbidity is formed within no seconds
i	1^0amine	On treating with Hinsberg reagent ($C_6H_5SO_2Cl$) gives white precipitate which dissolves in alkali.
	2^0amine	On treating with Hinsberg reagent ($C_6H_5SO_2Cl$) gives white precipitate which is insoluble in alkali.
	3^0amine	No reaction with Hinsberg reagent
j	Benzoic acid	Add $NaHCO_3$, effervescence obtained (CO_2)
	Benzene	no effervescence obtained
k	Phenol	It gives violet colour with neutral $FeCl_3$ test It doesn't give effervescences of CO_2
	Benzoicacid	It doesn't give violet colour with neutral $FeCl_3$ Effervescence of CO_2evolve when $NaHCO_3$ is added
l	Aniline	It gives azo-dye test(orange dye)
	Ethylamine	It doesn't give azo-dye
m	Aniline	It gives azo-dye test
	Nitrobenzene	It doesn't give azo dye test
n	Benzaldehyde	It gives Tollen's test It doesn't give iodoform test
	Acetophenone	It doesn't give Tollen's test It gives iodoform test
o	Methanal	It gives fehling solution test
	Benzaldehyde	It doesn't give Fehling's test
p	Chlorobenzene	Does't give white curdy ppt on hydrolysisNaOH followed by addition of $AgNO_3$
	Benzylchoride	Gives white curdy ppt on hydrolysis with NaOH followed by addition of $AgNO_3$

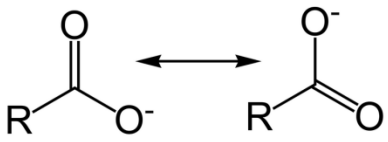
CONCEPTUAL QUESTIONS

GIVE REASONS

Q1) Phenoxide ion has more no. of resonating structures than carboxylate ion, carboxylic acid is a stronger acid why?

Ans:- The phenoxide ion has non equivalent resonance structures in which–vecharge is at less electro negative C atom and +ve charge as at more electronegative O-atom.

In carboxylate ion –ve charge is delocalized on two electronegative O-atoms hence resonance is more effective and a stronger acid.

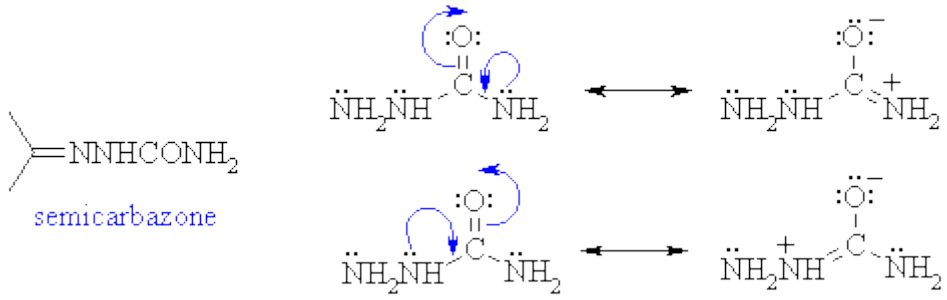


Q.2 Why Carboxylic acid have higher boiling point than alcohols as alcohol forms strongest intermolecular hydrogen bonding?

Ans. As Carboxylic acid forms adimer due to which their surface area increases and forms strong intermolecular H-bonding. It is having higher boiling point than alcohols.

Q.3 There are two-NH_2 groups in semi carbazide. However **only one is involved in formation of semi carbazones. Why?**

Ans.



Due to resonance one NH_2 group undergoes or involved in resonance and hence can't participate in the formation of semicarhazone. Lone pair of NH_2 group is not involved in resonance and is available for nucleophillic attack

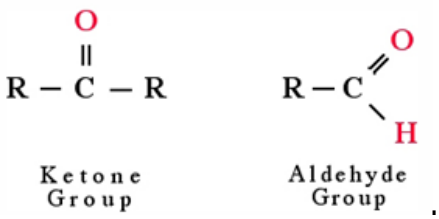
Q.4 Why does solubility decreases with increasing molecular mass in carboxylic acid?

Ans. Because of increase in alkyl chain length which is hydrophobic in nature.Hence solubility decreases.

Q.5 Why are aldehydes are more reactive than ketones when undergo nucleophillic addition reaction?

Ans (a) + I effect:- The alkyl group in Ketones due to their e-releasing character decrease the +ve charge on C-Atom and thus reduce its reactivity.

(b) Steric hindrance :- Due to sterichindrance in ketones they are less reactive.



Q.6 Why PCC cannot oxidize methanol to methanoic acid and while $KMnO_4$ can?

Ans. This is because PCC is a mild oxidising agent and can oxide methanol to methanal only.While $KMnO_4$ being strong oxidising agent oxidises it to methanoic acid.

Q.7 During preparation of esters from a carboxylic acid and an alcohol in the presence of acid catalyst water or ester formed should be removed as soon as it is formed.

Ans. The formation ofesters from a carboxylic acid and an alcohol in the presence of

acid catelyst in a reversible reaction.

$$R\text{–}COOH + R'OH \rightleftharpoons R\text{–}COOR' + H_2O$$

To shift the equilibrium in forward direction, the water or ester formed should be removed as fast as it is formed.

Q.8 Why HCOOH does not give HVZ reaction while CH_3COOHdoes?

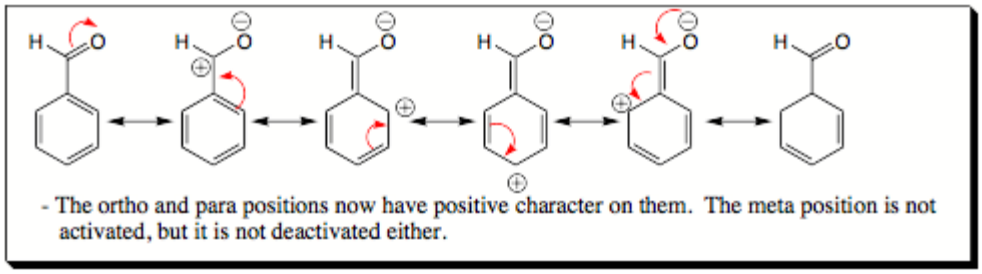
Ans. CH_3COOH contains α-hydrogens and hence give HVZ reaction but HCOOH does not contain α-hydrogen and hence does not give HVZ reaction.

Q.9 Suggest a reason for the large difference in the boling point of butanol and butanal although they have same solubility in water.

Ans. Because Butanol has strong inter molecular H-bonding while butanal has weak dipole-dipole interaction. However both of them form H-bonds with water and hence are soluble.

Q.10 Would you expect benzaldehyde to be more reactive or less reactive in nuderophillic addition reaction than propanol. Explain.

Ans. C-atom of Carbonyl group of benzaldehyde is less electrophilic than C- atom of Carbonyl group in propanol. Polarity of Carbonyl group is in benzaldehyde reduced due to resonance making it less reactive in nucleophillic addition reactions.



Q.11 Why does methanal not give aldol condensation while ethanol gives?

Ans. This is because only those compounds which have α-hydrogen atoms can undergo aldol reaction ethanol pessess α-hydrogen and undergo esaldol condensation Methanal has no alpha hydrogen atoms hence does not undergo aldol condensation.

Q.12 Why does methanal undergo cannizaro's reaction?

Ans. Because it does not possesses α-hydrogen atom.

Q.13 Which acid is stronger and why?

$F_3C\text{-}C_6H_4COOH$ and $CH_3C_6H_4COOH$

Ans . CF_3-has strong (-I) effect where as, CH_3-has strong (+I)effect

Due to greater stability of $F_3CC_6H_4COO$ ion over $CH_3\text{-}C_6H_4COO$ ion

$CF_3C_6H_4COOH$ is much stronger acis than $CH_3\text{-}C_6H_4COOH$.

Q.14 Explain why O-hydroxybenzaldehyde is a liquid at room temperature while p- hydroxybenzaldehyde is a high melting solid.

Ans. Due to intra molecular H-bonding in O-hydroxy benzaldehyde exists as discrete molecule whereas due to intermolecular H-bonding p-hydroxy benzaldehyde exists as associated molecules.

To break this intermolecular H-bonds a large amount of energy is needed. Consequently P-isomer has a much higher m.p. and b.p. than that of O-isomer. As a result O-hydroxy benzaldehyde is liquid.

Q.15Why is the boiling point ofan acid anhydride higher than the acid from which it is derived?

Ans. Acid an hydrides are bigger in size than corresponding acids have more surface area more van der Waals. Force of attraction hence have higher boiling point.

Q.16y do Carboxylic acids not give the characteristic reactions of a carbonyl group?

Ans. Due to resonance, it doesn't give the characteristics reactions of carbonyl group. It does not have free

\
C=O group
/

Q.17 Cyclohexanone forms cyanohydrin in good yield but 2,2,6 tri methyl cyclo-hexanone does not. Why?

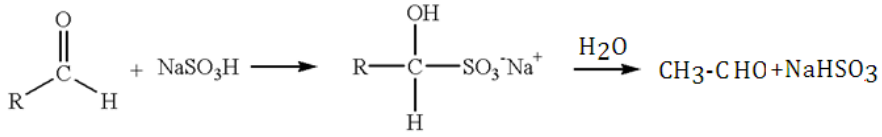
Ans. In 2,2,6 trimethyl cyclohexaunone there is streric hindrance of 3 methyl groups, It does not form cynohydrin in good yield.

Q.18 Why is carboxyl group in benzoic acid meta directing?

Ans. In benzoic acid the Carboxyl group is meta directing because it is electron-withdrawing There is +ve charge on ortho acid para positions Electrophillic substitution takes place at meta-position.

Q.20 Sodium Bisulphite is used for the purification of aldehydes and Ketones. Explain.

Ans. Aldehydes and Ketones form addition compounds with $NaHSO_3$ where as impurities do not. On hydrolysis we get pure aldehydes and Ketones back.



Q.21 Why pH of reaction should be carefully controlled while preparing ammonia derivatives of carbonyl compound?

Ans. In strongly acidic medium ammonia derivatives being basic will react with acids and will not react with carbonyl compound. In basic mesium, OH^- will attack carbonyl group. pHofa reaction should be carefully controlled.

Q.22 Why formic acid is stronger acid than acetic acid?

Ans. Due to +I effect, CH_3- group in acetic acid increases e^- density on carbon atom which makes it. Weak acid.While in formic acid no such pushing group is present, hence is more stronger acid than acetic acid.

Q.23 Why isoxidation of alcohals to get aldehydes carried out under controlled conditions?

Ans. It is because aldehydes get further oxidized to acids, oxidation of alcohals to aldehydes needs to be controlled.

Q.24 Why the oxidation of toluene to benzaldehyde with CrO3 is carried out in

the presence of acetic anhydride.

Ans. If acetic anhydride is not used we will get benzoic acid.

Acetic anhydride used to prevent oxidation of benzaldehyde to benzoic acid.

Q.25 Melting point of an acid with even no. of carbon atoms is higher than those of its neighbour with odd no. of carbon atoms.

Ans. They fit into crystal lattice more readily than odd ones that is why they have higher lattice energy and higher melting point.

Q.26 Why do aldehydes havelower boiling point than corresponding alcohols?

Ans. alcohols have lower boiling point as they are not associated with intermolecular where as alcohals are associated with intermoleculer H-bonding. Aldehydes have lower B.p.

Q.27 Why do aldehydes behave like polar compounds?

Ans. Due to presence of =C=O group which is polar

Q.28 Most aromatic acids are solids while acetic acid and others of this series are liquids. Explain why?

Ans. Aromatic acids have higher molecular weight, more van-der waals force of attraction as compared to aliphalic acids They are solids.

Q.29 Ethers possess a dipole moment ever if the alkyl radicals in the molecule are identical. Why?

Ans. It is because ethers are bent molecles, dipole do not get cancelled.

Q.30 Why does acyl chorides have lower boling point than corresponding acids?

Ans. Acyl chlorides are not associated with intermolecular H-bonding. They have lower boiling point.

Q.31 Why ethers are stored in coloured bottles?

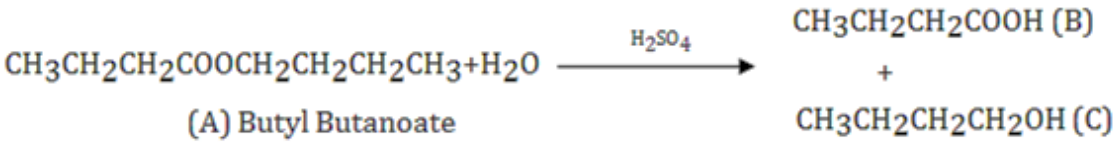
Ans. They are stored in coloured bottles. In presence of sunlight they react with oxygen to form peroxides which may cause explosion.

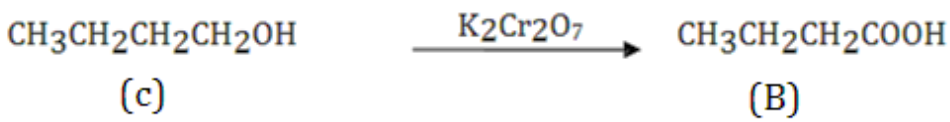
Q.32 Why formaldehyde cannot be prepared by Rosenmund's reduction?

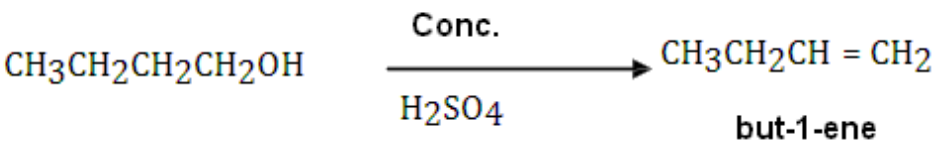
Ans. Because the formyl chloride thus formed is unstable at room temperature.Cannot be prepared by Rosenmund reduction.

STEP REACTIONS

Q1. An organic compound (A) {$C_8H_{16}O_2$} was hydrolysed with dilute sulphuric acid to give a carboxylicacid(B)and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene.Identity A, B, C







IDENTIFY A, B, C

Q1. $CH_3COOH \xrightarrow[NH_3]{\Delta} A \xrightarrow[NaOBr]{} B \xrightarrow[NaNO_2]{HCl} C$

Q2. $C_6H_5NO_2 \xrightarrow{Fe/HCl} A \xrightarrow{NaNO_2/HCl} B \xrightarrow{H_2O/H^+} C^+$

Q3. $CH_3CH_2Br \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow{HNO_2} C$

Q4. $C_6H_5N_2^+Cl^- \xrightarrow{CuCN} A \xrightarrow{H_2O/H^+} B \xrightarrow{\Delta\ NH_3} C$

Q5. $CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow{OH^-} B \xrightarrow{NaOH} C$

Q6 $C_6H_5NH_2 + (CH_3CO_2)_2O \longrightarrow A$

Q7. $C_6H_5N_2^+Cl^- \xrightarrow[HBF_4]{NaNO_2/Cu\ \Delta} A$

Q8. $A \xrightarrow[Br_2]{NaOH} B \xrightarrow{HNO_2} C \xrightarrow[I_2]{Red\ P} D \quad (CH_3I)$

ONE MARK QUESTIONS

Q1. Name the reaction and the reagent used for the conversion of acid chlorides to the corresponding aldehydes.

A. Name: Rosenmund's reaction Reagent: H_2 in the presence of Pd (supported over $BaSO_4$) and partially poisoned by addition of Sulphur or quinoline.

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

$$CH_3COCl + H_2 \xrightarrow[BaSO_4]{Pd} CH_3CHO + HCl$$

Q2. Suggest a reason for the large difference in the boiling points of butanol and butanal, although they have same solubility in water

.A. The b.p. of butanol is higher than that of butanal because butanol has strong intermolecular H-bonding while butanal has weak dipole-dipole interaction. However both of them form H-bonds with water and hence are soluble.

Q3.What type of aldehydes undergo Cannizaro reaction?

Aromatic and aliphatic aldehydes which do not contain α-hydrogens.

Q4.Out of acetophenone and benzophenone, which gives iodoform test? Write the reaction involved. (The compound should have CH_3CO-group to show the iodoform test.)

A. Aceto phenone ($C_6H_5COCH_3$) contains the grouping (CH_3CO attached to carbon) and hence given iodoform test while benzophenone does not contain this group and hence does not give iodoform test.

$$\underset{\text{Acetophenane}}{C_6H_5COCH_3} + 3I_2 + 4NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + C_6H_5COONa + 3NaI + 3H_2O$$

$$C_6H_5COC_6H_5 \xrightarrow{I_2/NaOH} \text{No reaction}$$

Q5. Give Fehling solution test for identification of aldehyde gp (only equations). Name the aldehyde which does not give Fehling's soln. test. A.

$$R—CHO—2Cu^{2+} + 5OH^- \longrightarrow RCOO^- + Cu_2O + 3H_2O$$

Benzaldehyde does not give Fehling soln. test.(Aromatic aldehydes do not give this test.)

Q6. What makes acetic acid a stronger acid than phenol?

A. Greater resonance stabilization of acetate ion over phenoxide ion.

Q7. Why HCOOH does not give HVZ (HellVolhardZelinsky) reaction but CH_3COOH does?

A. CH_3COOH contains α-hydrogens and hence give HVZ reaction but HCOOH does not contain α-hydrogen and hence does not give HVZ reaction

Q8.During preparation of esters from a carboxylic acid and an alcohol inthe presence of an acid catalyst, water or the ester formed should be removed as soon as it is formed.

A. The formation of esters from a carboxylic acid and an alcohol in the presence of acid catalyst in a reversible reaction.

$$\underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{alcohol}}{R'OH} \xleftrightarrow{H_2SO_4} \underset{\text{Ester}}{RCOOR'} + H_2O$$

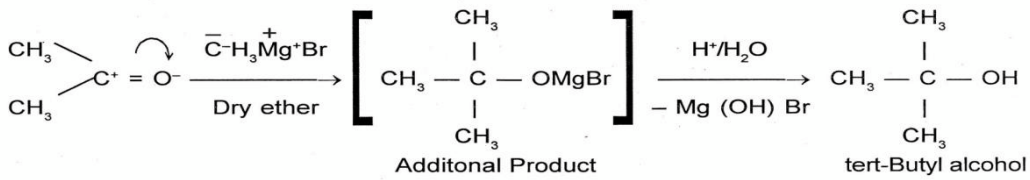
To shift the equilibrium in the forward direction, the water or ester formed should be removed as fast as it is formed

Q9. **Arrange the following compounds in increasing order of their acid strength. Benzoic acid, 4Nitrobenzoic acid, 3, 4dinitro benzoic acid, 4methoxy benzoic cacid.**

A. 4-methoxybenzoicacid<benzoic acid<4-nitrobenzoic acid<4, dinitrobenzoic acid.

2/3 MARKS QUESTIONS

1. How is tert-butyl alcohol obtained from acetone? A.



2. **Arrange the following compounds in increasing order of their boiling points. Explain by giving reasons.**

CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$.

A. The molecular masses of all these compounds are comparable: CH_3CHO(44), CH_3CH_2OH(46), CH_3COCH_3(46), $CH_3CH_2CH_3$(44). CH_3CH_2OH exists as associated molecule due to extensive intermolecular hydrogen bonding and hence its boiling point is the highest (351K). Since dipole-dipole interaction are stronger in CH_3CHO than in CH_3OCH_3, hence boiling point

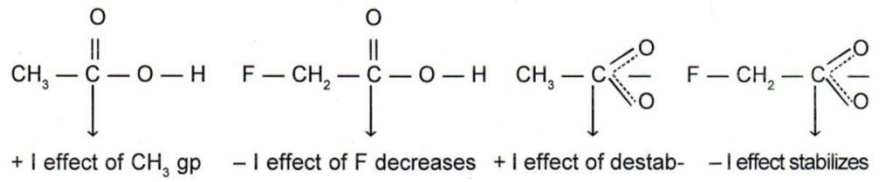
Of CH_3CHO(293K)is much higher than that of CH_3OCH_3(249K).Further, molecules of $CH_3CH_2CH_3$ have only weak Vander Waals forces while the molecules of CH_3OCH_3 have little stronger dipole-dipole interactions and hence the boiling point of CH_3OCH_3 is higher (249K)than that of $CH_3CH_2CH_3$(231K).

Thus the overall increasing order of boiling points is:

$CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2O$

3. **Which acid of each pair shown here would you expect to be stronger?**

CH_3CO_2H or FCH_2CO_2H



Thus due to lesser electron density in the O—H bond and greater stability of FCH_2COO^-ion over CH_3COO^-ion FCH_2COOH is a stronger acid than CH_3COOH.

4. **Which acid is stronger and why?**

$F_3C—C_6H_4—COOH$, $CH_3—C_6H_4—COOH$

$F_3C—C_6H_4—COOH$	**$CH_3—C_6H_4—COOH$**
CF3 has a strong(–I) effect	CH3 has a weak(+I) effect
It stabilizes the carboxylate ion	It stabilizes the carboxylate ion
By dispersing the–vecharge	By intensifying the–ve charge

Therefore due to greater stability of $F_3C—C_6H_4—COO^-$(p) ion over $CH_3—C_6H_4COO^-$(p)ion,$F_3C—C_6H_4—COOH$ is a much stronger acid than $CH_3—C_6H_4—COOH$.

5. **Explain why o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxy benzaldehyde is a high melting solid.**

Due to intera molecular H-bonding or tho-hydroxybenzaldehyde exists as discrete molecule where as due to intermolecular H-bonding, p-hydroxybenzaldehyde exists as associated molecules. To break these intermolecular H-bonds, a large amount of energy is needed. Consequently, p-hydroxy benzaldehyde has a much higher m.p. and b.p. than that of o-hydroxybenzaldehyde. As a result, o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a high melting solid.

5MARKSQUESTIONS

1. **Arrange the following compounds in order of their property as indicated-**

i) Acetaldehyde, Acetone, di-tert-butylketone, Methyltert-butyl ketone reactivity towards HCN

- di-tert-butylketone< Methyltert-butylketone<Acetone<Acetaldehyde
- Aldehydes are more reactive towards nucleophilic addition across the >C= O due to steric and electronic reasons.
- Sterically the presence of two relatively large substituents in ketone shinders the approach of nucleophile to carbonyl carbon than in aldehydes having only one such substituent.
- Electronically, the presence of two alkyl groups reduces the electrophilicity of the carbonyl carbon in ketones.

ii) $CH_3CH_2CHBrCOOH$, $CH_3CHBrCH_2COOH$, $(CH_3)_2CHCOOH$, $CH_3CH_2CH_2COOH$ acid strength

- $(CH_3)_2CHCOOH < CH_3CH_2CH_2COOH < CH_3CHBrCH_2COOH < CH_3CH_2CHBrCOOH$
- Electron withdrawing groups like –Br increases the acidity of carboxylic acids by stabilizing the conjugate base through delocalisation of negative charge by negative inductive effect. The closer the electron withdrawing group to the–COOH group, greater is the stabilizing effect.
- Electron donating groups decrease the acidity by destabilizing the conjugate base. Greater the number of –CH3 groups, greater the destabilizing effect and lower the acidity.

iii) Benzoic acid, 4-Nitrobenzoic acid, 3, 4-Dinitrobenzoic acid, 4-Methoxybenzoicacid (acid strength)

- 4-Methoxybenzoic acid < Benzoicacid <4 –Nitrobenzoic acid< 3, 4-Dinitrobenzoic acid
- Benzoic acid is a stronger acid than aliphatic carboxylic acid due to stabilization of the conjugate base due to resonance.
- Presence of electron withdrawing group-NO_2 on the phenyl ring of aromatic carboxylic acid increases their acidity while electron donating groups-OCH_3 decreases their acidity.

Additional Questions

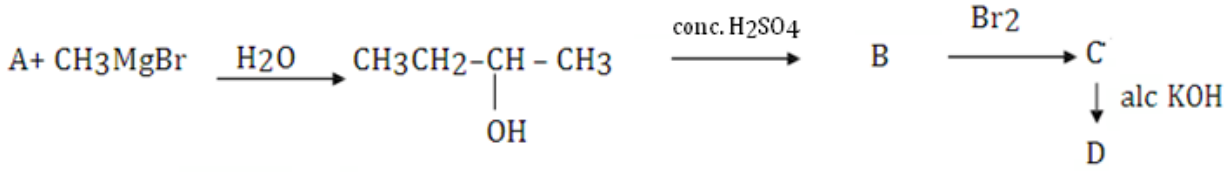
1. An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4DNP derivative reduces tollens reagent and undergoes cannizaro reaction . On vigorous oxidation, it gives 1, 2 benzene carboxylic acid. Identify the compound.
2. An organic compound (A) with molecular formula C_8H_8O forms an orange-red precipitate with2,4 DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces tollen's or fetiling's reagent , nor does it decolourise bromine water or baeyer's reagents .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).
3. Two moles of organic compound A on treatment with a strong base gives two compounds B

and C. Compound B on dehydration with cu gives A while acidification of C yields carboxylic acid D having molecular formula of CH_2O_2 . Identify the compounds A, B, C, D

4. An aliphatic compound A' with a molecular formula of C_3H_6 O reacts with phenylhydrazine to give compound B' .Reaction of A' with I_2in alkaline medium on warming gives a yellow precipitate C'. Identify the component A, B, C

5. A component A' with molecular formula $C_5H_{10}O$ gave a positive2,4 DNP test but a negative tollen's reagents test . It was oxidised to carboboxylic acid B' with molecular formula $C_3H_6O_2$ when treated with alkalines KMnO4 under vigorous condition . Sodium salt of B' gave hydrocarbon C' on Kolbe eletrolysis reduction . Identify A,B,C and D.
6. An organic compound A' has the molecular formula $C_5H_{10}O$. It does not reduce Fehling's solution but forms abisulphite compound .It also gives positive Iodoform test. What are possible structure of A'?Explain your reasoning.
7. An organic compound A' which has characterstic odour, on treatment with NaOH forms two compounds B' and C'. Compound B' has the molecular formula C_7H_8O which on oxidation gives back compound A'. Compound'C' is the sodium salt of an acid which when heated with soda lime yields an aromatic hydrocarbon D'. DeduceA, B, C, D
8. An organic compound A' is resistant to oxidation forms an oxidation forms a compound 'B (C_3H_80) on reduction. B' reacts with HBr to form a bromide C' which on treatment with alcoholic KOH forms an alkene D' (C_3H_6). Deduce A, B, C, D.
9. Eherial solution of an organic compound 'A' when heated with magnesium gave 'B' on treatment with ethanal followed by acid hydrolysis gave 2-propanol. Identify the compound 'A .What is 'B' known as?

10. Identify A, B, C, D



11. Primary alkyl halide C_4H_9Br(A) reacted with alcoholic KOH to give compound (B) is reacted with HBr to give (C) which is an isomer of (A).When (A) is reacted with sodium metal it gives compound (D) C_8H_{18}that was different from the compound formed when n-butyl bromide is reacted with sodium . Give the formula of (A) and write equations.
12. An organic compound 'A' having molecular formula C_4H_8 on treatment with dil.H_2SO_4 gives 'B . B on treatment with conc. HCL and an hydrous $ZnCl_2$ gives C and on treatment with sodium ethoxide gives back A. Identify A, B, C.

13. An aromatic compound A on treatment with aqueous ammonia and heating forms compound B which on heating with Br_2 and KOH forms a compound C of molecular formula C_6H_7N. Identify A, B, C .

14. Two isomeric compound A and B having molecular formula $C_{15}H_{11}N$, both lose N_2on treatment with HNO_2 and gives compound C and D. C is resistant to oxidation but immediately responds to oxidation to lucas reagent after 5 minutes and gives a positive Iodoform test. Identify A and B.
15. An organic compound A' having molecular formula $C_2H_5O_2N$ reacts with HNO_2 and gives $C_2H_4O_3N_2$.On reduction A' gives a compound 'B' with molecular formula C_2H_7N. C' on treatment with HNO2gives C' which gives positive idoform test. Identify A, B, C.
16. An organic compound A' having molecular formula C_3H_5N on reduction gave another compound B'. The compound B on treatment with HNO_2 gave propyl alcohol . B on warming with $CHCl_3$ and alcohalic caustic potash give the offensive smelling C .Identify A, B, C
17. Idomethane reacts with KCN to form a major product A. Compound A' on reduction in presence of $LiAlH_4$ forms a higher amine 'B'. Compound B on treatment with $CuCl_2$ forms a blue colour complex C . Identify A, B, C
18. An aliphatic compound A with molecular formula C_2H_3Cl on treatment with AgCN gives two isomeric compounds of unequal amount with the molecular formula C_3H_3N. The minor of these two products on complete reduction with H_2 in the presence of Ni gives a compound 'B' with molecular formula C_3H_9N. Identify the compounds.
19. A compound 'X' having molecular formula C_3H_7NO reacts with Br_2in presence of KOH to give another compound Y. the compound Y reacts with $HNO_2$to form ethanol N_2gas. Identify X, Y,
20. A compound A' of molecular formula $C_3H_7O_2N$ reaction with Fe and conc, HCl gives a compound B' OF molecular formula C_3H_9N. Compound B' on treatment with $NaNO_2$ and HCl gives another compound C' of molecular formula C_3H_8o. The compound C' gives effervescences with Na on oxidation with CrO_3.The Compound C' gives a saturated aldehyde containing three carbon atom deduce A,B,C.

A Chloro compound A' on reduction with Zn– Cu and alcohol gives the hydro carbon (B) with five carbon atom. When A' is dissolved in ether and treated with sodium 2,2,5,5 tetramethyl hexhane is formed structure of A