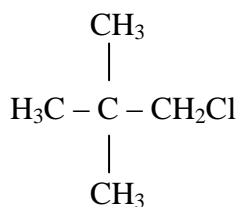


## CHAPTER – 10

### HALOALKANES AND HALOARENES

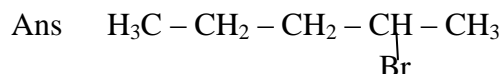
#### 1 Mk Questions:

- 1) Write the IUPAC name of the following compound :

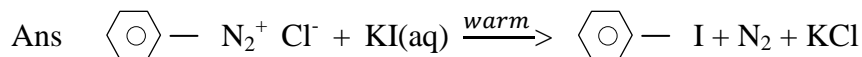


Ans 1 – Chloro – 2, 2 – dimethylpropane

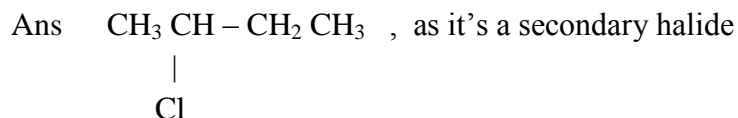
- 2) Draw the structure of 2-bromopentane



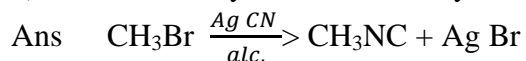
- 3) Write a chemical reaction in which iodide ion replaces the diazonium group in a diazonium salt.



- 4) Out of  $\text{CH}_3\text{CHClCH}_2\text{CH}_3$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$  which one is hydrolysed more easily by aq. KOH?



- 5) How can you convert methylbromide to methylisocyanide in a single step?



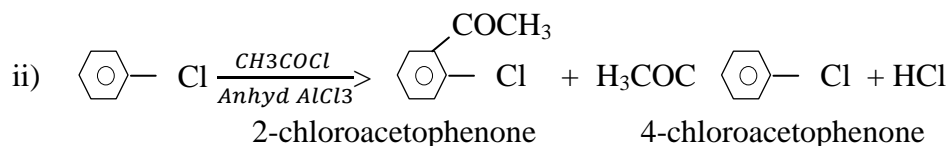
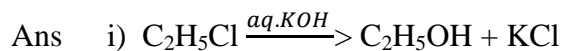
#### 2 Mks Questions

- 1) What are ambident nucleophiles? Explain with an example.

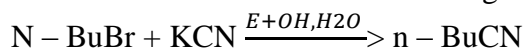
Ans Ambident nucleophiles have two nucleophilic sites through which they can attack.

Eg.  $[\text{C} \equiv \text{N} \leftrightarrow \text{C} = \text{N}^\ominus]$  linking through C results in alkyl cyanides and through N results in isocyanides.

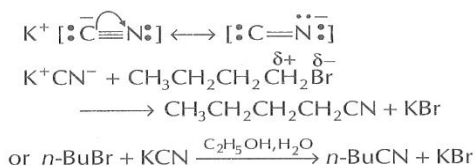
- 2) Write chemical equations when  
 i) ethylchloride is treated with aq.KOH  
 ii) chlorobenzene is treated with  $\text{CH}_3\text{COCl}$  in presence of anhyd. $\text{AlCl}_3$ .



- 3) Write the mechanism of the following reaction:



Ans  $\text{CN}^-$  is an ambident nucleophile  $\therefore$  it can attack through C and N



C-C bond is stronger than C-N bond, cyanide is formed.

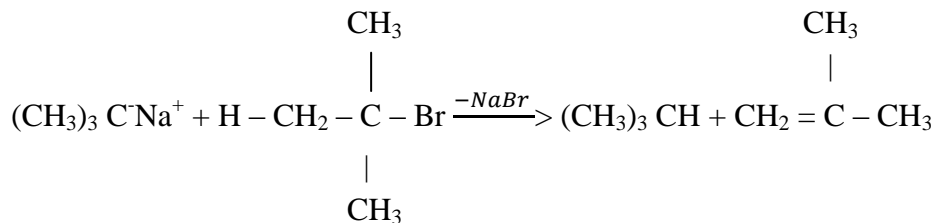
- 4) Give reasons:

- a) The order of reactivity of haloalkanes is  $\text{RI} > \text{RBr} > \text{RCl}$   
 b) Neopentyl chloride,  $(\text{CH}_3)_3\text{C}-\text{CH}_2\text{Cl}$  doesn't follow  $\text{SN}^2$  mechanism.

- Ans a) Larger the size of halogen atom, weaker the C-X bond, R group remaining same i.e; bond strength follows the order  $\text{R-I} < \text{R-Br} < \text{R-Cl}$ , hence reactivity is opposite.  
 b) R - group being bulky, provides steric hindrance to the incoming nucleophile.

- 5) Why does Wurtz reaction fail in case of tertiary halides?

Ans  $3^\circ$  halides prefer to undergo dehydrohalogenation in presence of a base like Na metal.



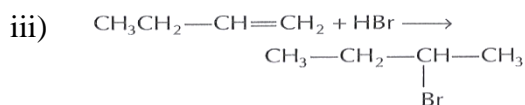
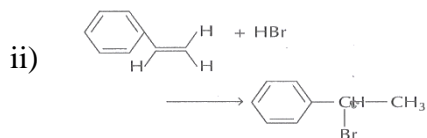
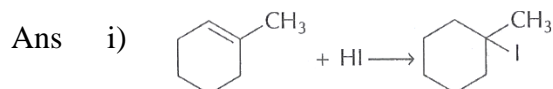
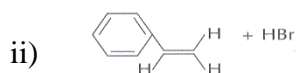
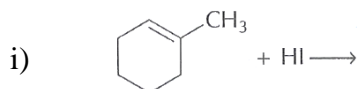
### 3 Mk Questions:

- 1) Write a chemical test to distinguish between
- Chlorobenzene and benzyl chloride
  - Chloroform and carbontetrochloride
  - n-propyl bromide and isopropyl bromide

Ans

- Benzyl chloride gives a white ppt with  $\text{AgNO}_3$  Soln., chlorobenzene does not.
- Chloroform gives offensive smelling isocyanides, on heating with  $1^\circ$  amine and KOH,  $\text{CCl}_4$  doesn't give this test.
- Isopropyl bromide, on treating with aq.KOH, gives Propan-2-ol which gives a yellow ppt. on heating with NaOH and  $\text{I}_2$  n-propyl bromide doesn't answer this test

- 2) Complete the following reactions:



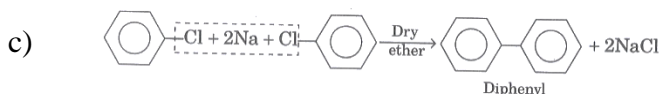
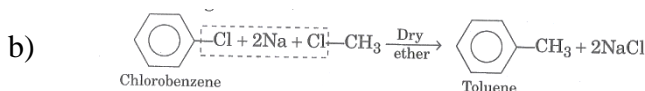
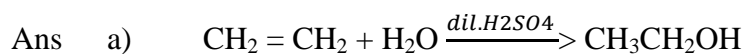
- 3) Give reasons:

- p-dichlorobenzene has higher melting point than o- and m- isomers.
- Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reactions.
- Alkyl chloride gives alcohol with aq.KOH, but alkene with alc. KOH.

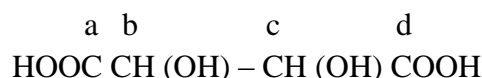
- Ans a) p-isomer has more symmetric structure, so molecules can pack closely.
- b) The C-X bond has partial double – bond character due to resonance. Also, in haloalkanes, X is bonded to  $sp^3 - C$  while in haloarenes, X is bonded to  $sp^2 - C$ .  $sp^3 - C$  is less electronegative, releases electrons to halogen more easily.
- c) In aq. solution, KOH is almost completely ionized to give  $OH^-$  ions, which being a strong nucleophile, gives a substitution product. An alcoholic soln. of KOH contains alkoxide ions ( $RO^-$ ), which being a strong base, preferentially eliminates an HCl molecule to form alkenes.

4) Convert:

- a) Ethene to ethanol
- b) Chlorobenzene to toluene
- c) Chlorobenzene to diphenyl



5) What are enantiomers? Identify the asymmetric carbons in the following molecule:-



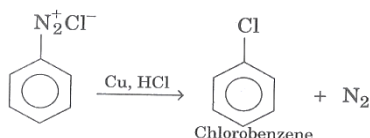
Ans Enantiomers are non-superimposable mirror images of an optically active compound.

b and c are asymmetric carbon atoms as they are bonded to 4 different groups.

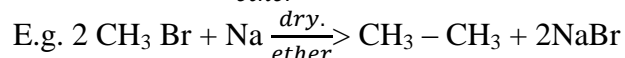
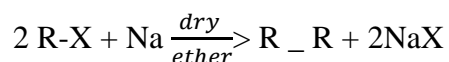
6) Write short notes on :

- a) Gatterman reaction
- b) Wurtz reaction
- c) Peroxide effect or Kharasch effect

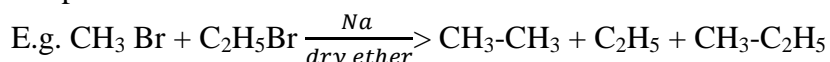
Ans a) Aromatic  $1^\circ$  amines produce benzene diazonium salts with  $HNO_2$  (produced in situ) at 273 K. Chloro arenes and bromoarenes can be prepared using Cu/HCl or Cu/HBr from these diazonium salts.



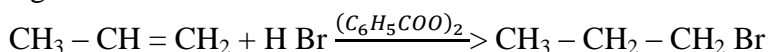
b) Alkyl halides, when treated with sodium in presence of dry ether, produce an alkane with even number of C atoms.



If a mix of two different alkyl halides is taken, then a mixture of alkanes is obtained which is difficult to separate.



c) The addition of Hydrogen bromide to unsymmetrical alkenes in presence of a peroxide takes place in such a way that H goes to that C which has lesser H atoms and Br goes to the C with greater number of H atoms.

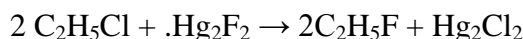
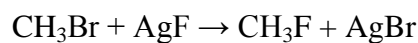


This rule doesn't apply to addition of HCl or HI

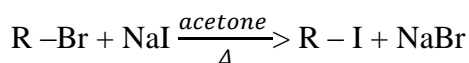
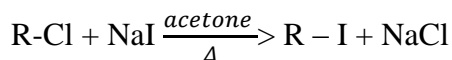
7) Explain the following with an example each

- a) Swarts reaction
- b) Finkelstein reaction
- c) Hunsdiecker reaction

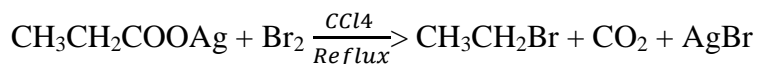
Ans a) Fluorination of hydrocarbons directly with  $\text{F}_2$  occurs explosively due to the large amount of energy released. Hence, they can be conveniently prepared indirectly by halogen exchange with chloro and bromoalkanes.



b) Iodoalkanes can be easily prepared from chloroalkanes or bromoalkanes by heating with NaI in acetone.



c) Bromoalkanes can be prepared by refluxing the silver salt of a carboxylic acid with Bromine in  $\text{CCl}_4$ .



The yield of alkyl bromide is  $1^\circ > 2^\circ > 3^\circ$

- Vinyl chloride is unreactive in nucleophilic substitution reaction
- 3-Bromocyclohexene is more reactive than 4-Bromocyclohexene in hydrolysis with aq. NaOH

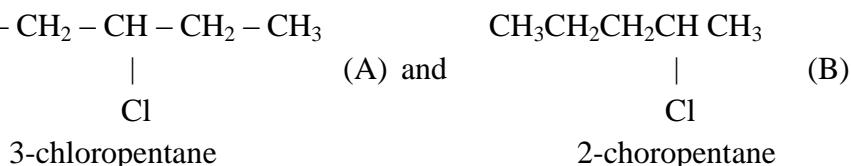
Ans a) Vinyl chloride is unreactive in nucleophilic substitution reactions due to resonance which results in a partial double bond character of C-Cl bond which is difficult to break.



c) Tertiary carbocation is stable, so tert-butyl chloride follows  $\text{SN}^1$  mechanism. N-butyl chloride would form  $1^\circ$  carbocation which isn't that stable. Hence it undergoes  $\text{SN}^2$  mechanism through formation of transition state.

$$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}-\text{CH}_3 + \text{HCl} \rightarrow \text{A} + \text{B}$$

So, products will be  $\rightarrow \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_3$

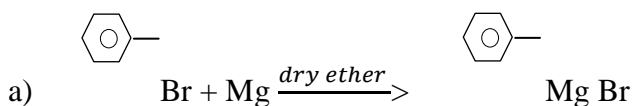


a) n-butyl chloride is treated with alc.KOH

b) Bromobenzene is treated with Mg in presence of dry ether.

c) Chlorobenzene is subjected to hydrolysis.

Ans a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} - \text{alc.KOH} \rightarrow \text{CH}_3\text{-CH}_2\text{-CH=CH}_2 + \text{KCl} + \text{H}_2\text{O}$   
But - 1 - ene



a)  $\text{Cl}_2 + \text{aq. NaOH} \rightarrow \text{no reaction.}$

## CHAPTER – 11

## ALCOHOLS, PHENOLS AND ETHERS

### 1 Mark Questions

1) Write the IUPAC name of  $\text{CH}_3\text{CH}=\text{CH}-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{CH}_3$



A) Hex – 4 – en – 3 – ol

2) Why is the boiling point of  $\text{C}_2\text{H}_5\text{OH}$  higher than that of  $\text{CH}_3\text{OH}$  ?

A) Due to more number of C atoms, van der waal's forces increase.

3) Name the reagent used in bromination of phenol to 2,4, 6 – tribromophenol.

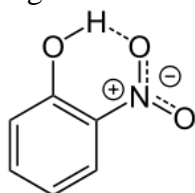
A) Aqueous solution of bromine (Bomine water)

4) Name the alcohol used to prepare the ester  $\text{CH}_3-\text{C}\text{OOCH}(\text{CH}_3)\text{CH}_3$

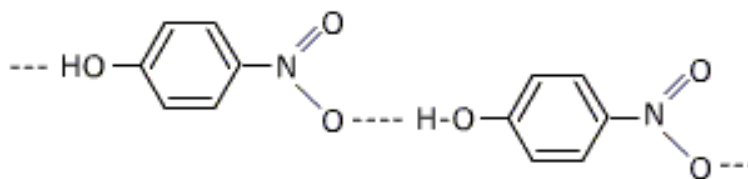
A) Propan-2-ol  $\text{CH}_3\text{-CH}(\text{OH})\text{-CH}_3$

5) Which is more volatile – o-nitrophenol or p-nitrophenol?

A) o-nitrophenol,, as it has intramolecular H-bonding, whereas p-nitrophenol has intermolecular H-bonding.



O-Nitrophenol with intra molecular hydrogen bonding



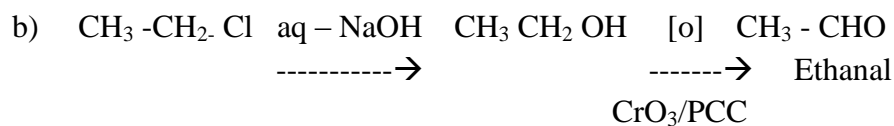
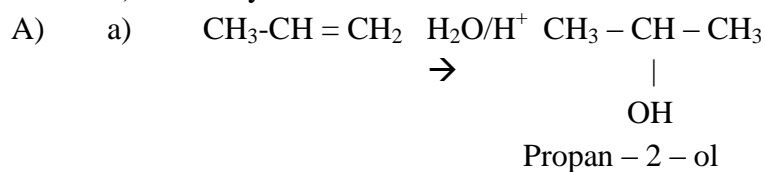
P- Nitrophenol with inter  
molecular hydrogen bonding

## 02 MARKS

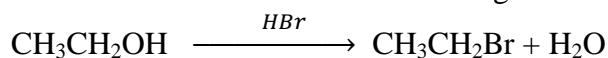
1) How will you convert:

a) Propene to propan-2-ol

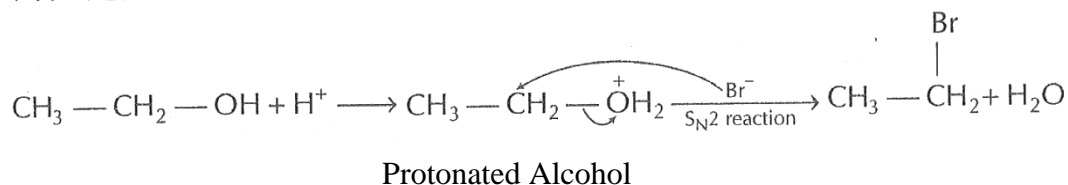
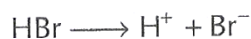
b) Ethyl chloride to ethanol



2) Write the mechanism for the following reaction:



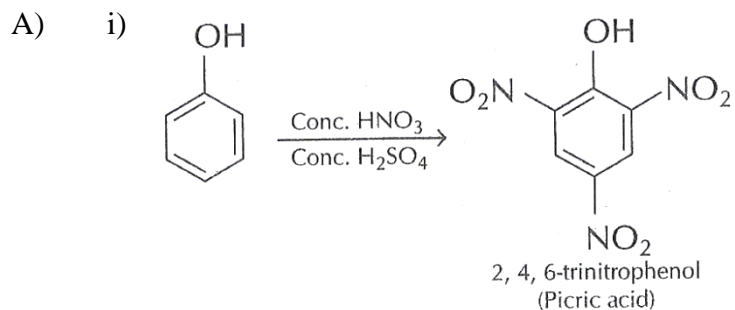
A)  $1^\circ$  alc undergoes the reaction by  $\text{S}_{\text{N}}2$  mechanism



3) How would you obtain

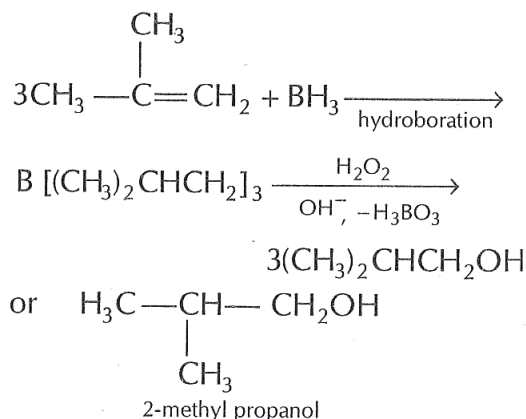
i) Picric acid from phenol?

ii) 2-Methylpropan-2-ol from 2-Methylpropene?





ii)



4) Give reasons :

- a) Boiling points of alcohols decrease with increase in branching of the alkyl chain.
- b) Phenol does not give protonation reaction readily
- A) a) Because increase in branching of the alkyl chain reduces surface area, so intermolecular forces of attraction decrease.
- b) Because the lone pair on oxygen is delocalized over the benzene ring due to resonance, hence not available for protonation easily.

5) Explain why cleavage of phenyl alkyl ether with HBr always gives phenol and alkyl bromide.

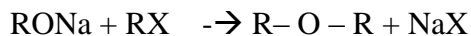
- A) Due to resonance, the O-C bond in phenyl alkyl ether has a partial double bond character, hence it is difficult to break.

Also, phenoxide ion is stabilized by resonance, hence we get phenol and alkyl bromide.

### 03 MARKS

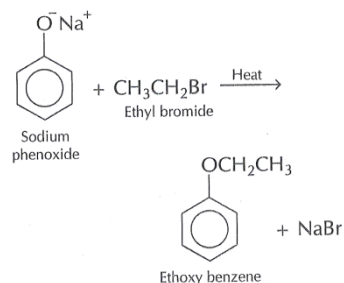
1) Write a short note on Williamson's Synthesis.

- A) An alkyl halide, on treating with a suitable sodium alkoxide gives an ether



Symmetric and unsymmetric ethers can be prepared by this method

Aryl alkyl ethers can be prepared as shown



But there is no reaction if arylhalide and sodium alkoxide are taken

Best yields of unsymmetrical ethers are obtained when alkyl halides are primary with 2° and 3° alkyl halide, dehydrohalogenation occurs to give alkene.

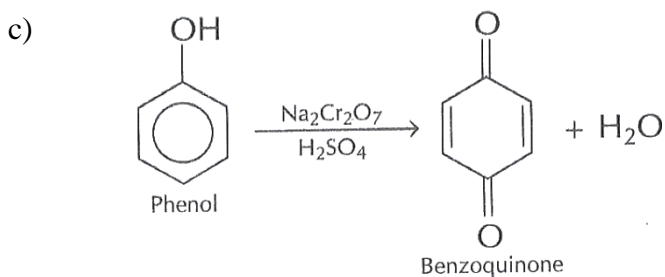
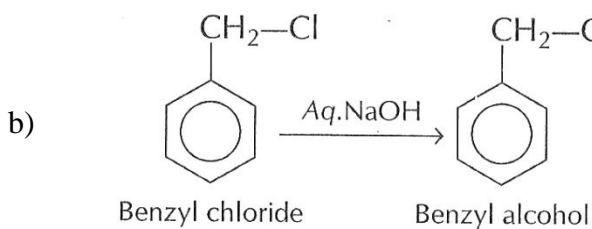
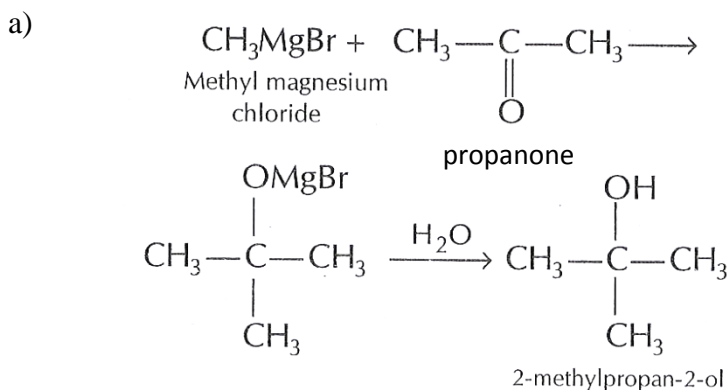
2) Convert:

a) Methyl magnesium chloride  $\rightarrow$  2-methyl propan-2-ol

b) Benzyl chloride  $\rightarrow$  Benzyl alcohol

c) Phenol  $\rightarrow$  benzoquinone

A)



3) **Give reasons :**

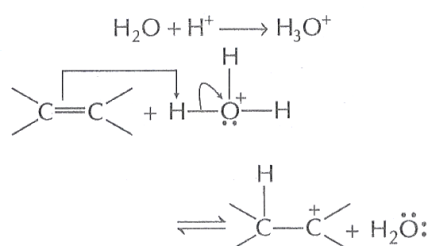
a) The boiling point of ethanol is higher than methoxymethane.

b) Phenol is more acidic than ethanol

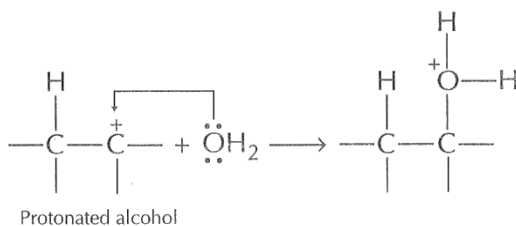
- c) O- and p-nitrophenols are more acidic than phenol.
- A) a) Ethanol has intermolecular H-bonding while methoxymethane only has dipole-dipole forces.
- b) In phenols, O atom acquires a partial positive charge due to resonance, this weakens O-H bond, release of  $\text{H}^+$  is easy. Also, phenoxide ion is stabilised by resonance. On the other hand, alkoxide ion is destabilized due to the +I effect of alkyl group.
- c)  $-\text{NO}_2$  group, being electron-withdrawing, stabilizes the o- and p- nitrophenoxide ions.

4) Describe the mechanism of hydration of ethene to yield ethanol.

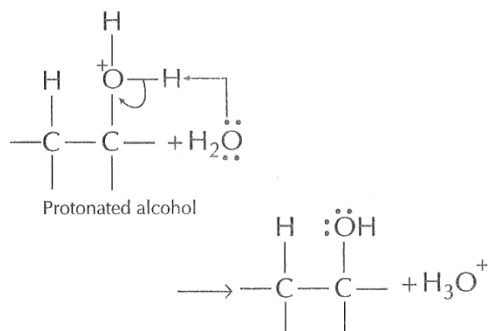
A)



#### Protonation of Alkene



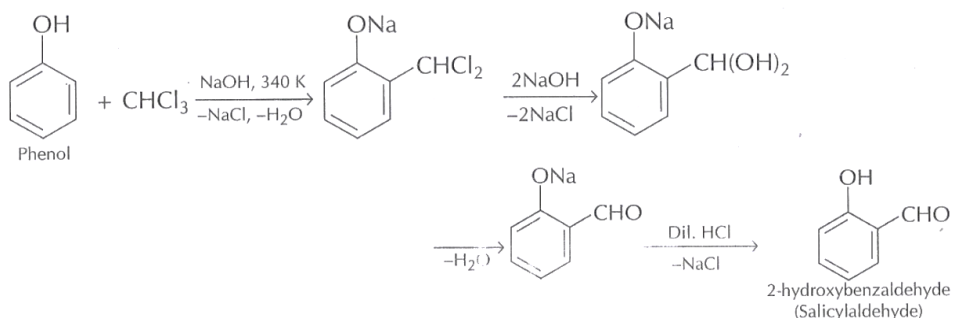
#### Nucleophilic attack by water on the carbocation



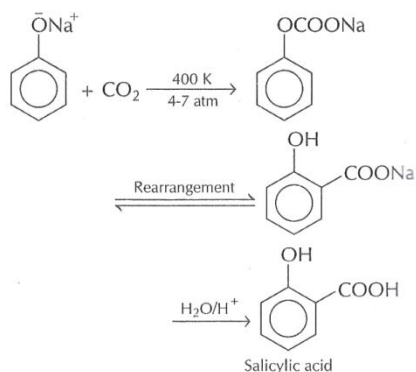
#### Deprotonation

5) Give equations for Reimer Tiemann reaction and Kolbe's reaction.

A) Reimer Tiemann reaction – Phenol reacts with chloroform in the presence of alkali to give o- and p-hydroxy aldehyde.



Kolbe's reaction – Phenoxide ion generated by treating phenol with NaOH undergoes electrophilic substitution with  $\text{CO}_2$



6) Arrange the following compounds in increasing order of their acid strength.

Propan-1-ol, 2, 4, 6-Trinitrophenol, 3 – Nitrophenol,  
3, 5- Dinitrophenol, phenol, 4-Methylphenol, 4-Methoxyphenol

A) Propan-1-ol < 4-Methoxyphenol < 4-Methylphenol < phenol < 3-Nitrophenol  
< 3, 5 – Dinitrophenol < 2, 4, 6 – Trinitro phenol

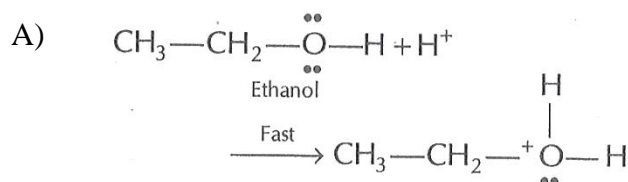
- Propan – 1 ol has R group, which destabilizes the propoxide ion due to +I effect, hence weaker than all phenols.
- All  $e^-$  donating groups reduce acidity of phenols by destabilizing phenoxide ion and  $e^-$  withdrawing groups increase acidity.
- Methoxy group is stronger  $e^-$  - donating groups compared to methyl group.
- Larger the number of  $e^-$  withdrawing groups, greater the acidity.  $\therefore$  2, 4, 6 – Trinitrophenol is strongest, followed by 3, 5 – Dinitrophenol and 3 – Nitrophenol.

7) Give a simple chemical test to distinguish between:

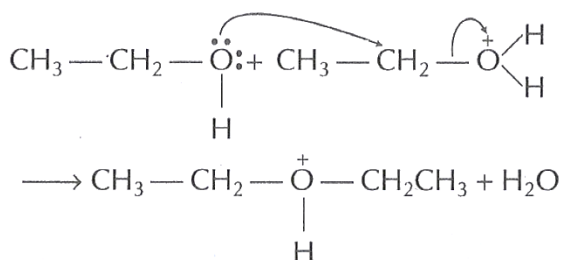
- Phenol and cyclohexanol
- Propan-2-ol and Benzyl alcohol
- Propan-1-ol and 2-Methylpropan-2-ol

- A) a) Phenol produces a deep violet colour with neutral  $\text{FeCl}_3$  solution., cyclohexanol doesn't.  
 b) Propan-2-ol gives yellow ppt of iodoform with  $\text{NaOH}$  and  $\text{I}_2$ , benzyl alcohol doesn't.  
 c) On treating with conc.  $\text{HCl}$  and anhydrous  $\text{ZnCl}_2$  at room temperature, 2-methylpropan-2-ol produces turbidity immediately while propan-1-ol doesn't produce turbidity at room temperature.

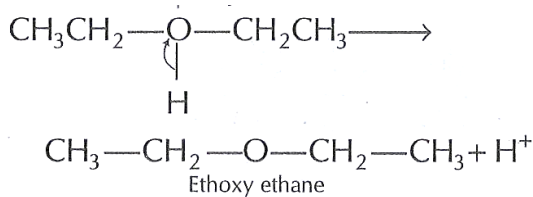
8) Give the mechanism for the reaction:  $2\text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{Dilute } \text{H}_2\text{SO}_4 (413\text{K})} \text{C}_2\text{H}_5\text{O C}_2\text{H}_5$



#### Protonation of Alcohol



#### Nucleophilic attack by Alcohol



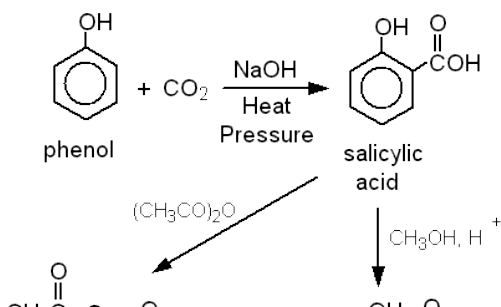
#### Deprotonation

- 9) An organic compound A ( $\text{C}_6\text{H}_6\text{O}$ ) gives a characteristic colour with aq.  $\text{FeCl}_3$  Solution. when (A) is treated with  $\text{CO}_2$  and  $\text{NaOH}$  at 410 K under pressure, it gives compound (B) which on acidification gives compound (C). Compound (C) reacts with acetyl chloride to give (D), which is a popular pain killer. Deduce the structures of A,B,C and D and explain all reactions

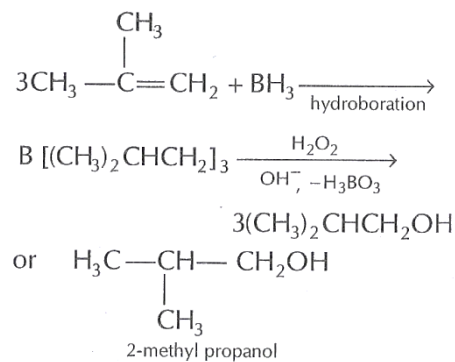
A) (A)  $\text{C}_6\text{H}_6\text{O}$  must be phenol

Phenol gives sodium salicylate with  $\text{CO}_2$  which on acidification gives salicylic acid.

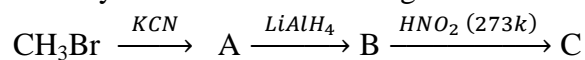
Salicylic acid forms aspirin with acetyl chloride.



- 10) (a) Explain hydroboration-oxidation reaction with an example  
 A Diborane reacts with alkenes to give trialkyl boranes as addition product. This is oxidized by  $\text{H}_2\text{O}_2$  to alcohol, in the presence of aq. NaOH



- (b) Identify A B C in the following reaction.



**A       $\text{CH}_3\text{CN}$**

**B       $\text{CH}_3\text{CH}_2\text{NH}_2$**

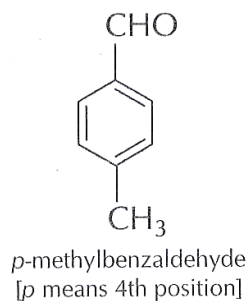
**C       $\text{CH}_3\text{CH}_2\text{N}_2\text{Cl}$  (Unstable, so forms  $\text{CH}_3\text{CH}_2\text{OH} + \text{N}_2 + \text{HCl}$  with Water)**

## CHAPTER – 12

### ALDEHYDES – KETONES AND CARBOXYLIC ACIDS

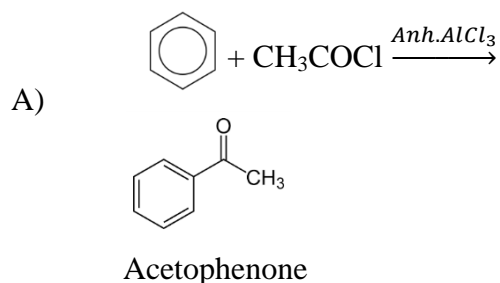
#### 01 MARK

- 1) Write the structure of p-methylbenzaldehyde.



A)

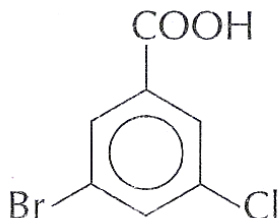
- 2) Complete the reaction :



- 3) Arrange the following in increasing order of their acid strength  $(\text{CH}_3)_2\text{CHCOOH}$ ,  $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$ ,  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$ .

A)  $(\text{CH}_3)_2\text{CHCOOH} < \text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH} < \text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$

- 4) Write IUPAC name of



A) 5 – Bromo -3- chlorobenzoic acid

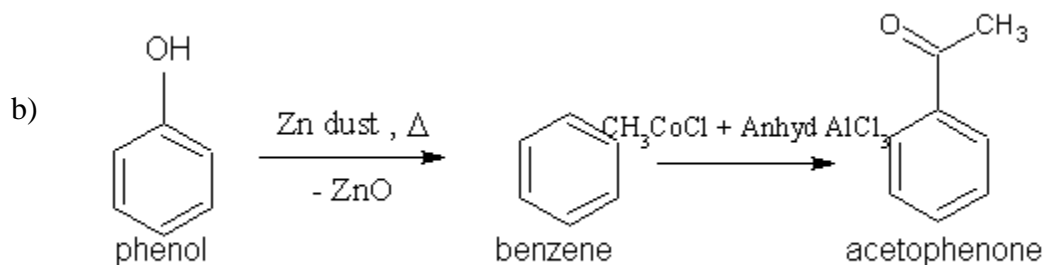
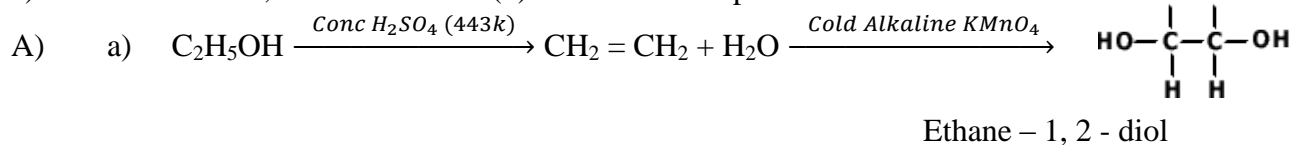
- 5) Give a chemical test to distinguish between acetaldehyde and benzaldehyde.

- A) On heating with Na OH and I<sub>2</sub>, acetaldehyde gives a yellow ppt of iodoform, benzaldehyde doesn't

## **02 MARKS**

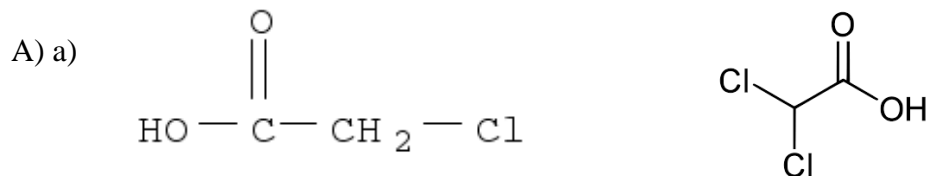
1) Convert:

a) Ethanol to 1,2 Ethanediol (b) Phenol to acetophenone



3) **Give reasons:**

- a) Monochloroethanoic acid is a weaker acid than dichloroethanoic acid.  
b) Benzoic acid is stronger than ethanoic acid



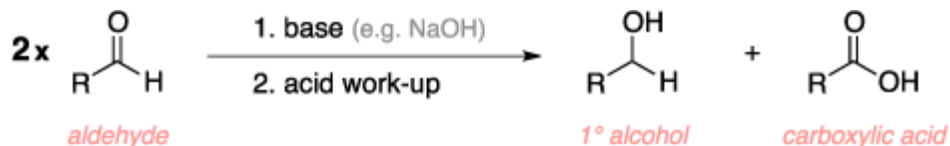
Cl has – I effect, making release of protons easier. Also, it stabilises the carboxylate ion. Monochloroacetic acid has one Cl atom. While dichloroacetic acid has two Cl atoms. Hence it is a stronger acid.



b) Benzene ring is  $e^-$  withdrawing, while  $CH_3$  group is  $e^-$  donating. Hence, release of protons is easier in benzoic acid than ethanoic acid. Also, the benzoate ion is much more stable than ethanoate ion due to  $e^-$  - withdrawing benzene ring.

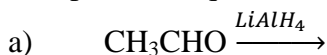
4) Describe Cannizzaro's reaction with example.

A) Aldehydes without  $\alpha$ -H undergo self-oxidation and reduction (disproportionation) on treatment with conc. Alkali. One molecule is reduced to alcohol while the other is oxidized to salt of corresponding carboxylic acid

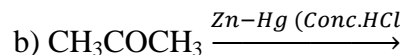


$R = \text{aryl, alkyl (no } \alpha\text{-hydrogens)}$

5) Complete the equations



A) a)  $CH_3CH_2OH$

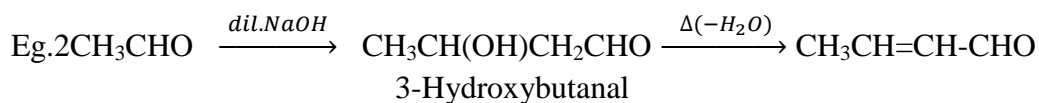


b)  $CH_3CH_2CH_3$

### 03 MARKS

1) Explain Aldol condensation with an example.

A) Aldehydes or ketones having at least one  $\alpha$ -H undergo condensation to produce  $\beta$ -hydroxy aldehyde (aldol) in the presence of a dil. Base.



Eg. If two different molecules of aldehydes and/or ketones undergo aldol condensation, the reaction is called CROSS ALDOL REACTION.

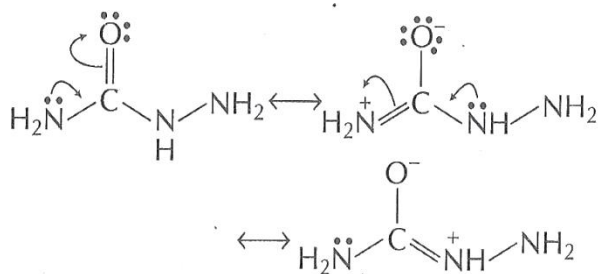
2) Give reasons

a) There are two  $-NH_2$  groups in semicarbazide, but only one is involved in the formation of semicarbazones:

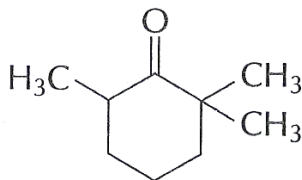
b) Cyclohexanone forms cyanohydrins in good yield, but 2,2,6-Trimethylcyclohexanone doesn't.

c) Aldehydes are more reactive than ketones towards nucleophilic addition.

A) a) One of the  $\text{NH}_2$  groups is involved in resonance, hence it cannot act as a nucleophile. Other one is free,  $\therefore$  it can act as a nucleophile.



b)  $\text{CN}^-$  can attack easily without any steric hindrance in cyclohexanone.



2,2,6-trimethylcyclohexanone

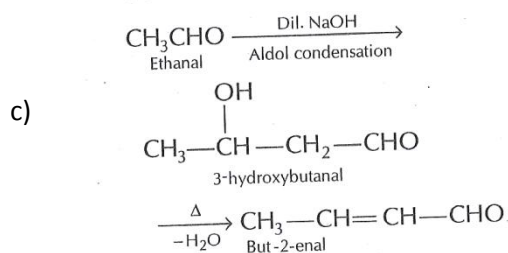
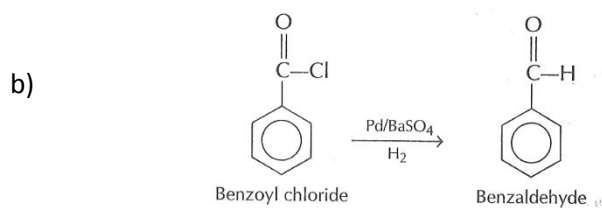
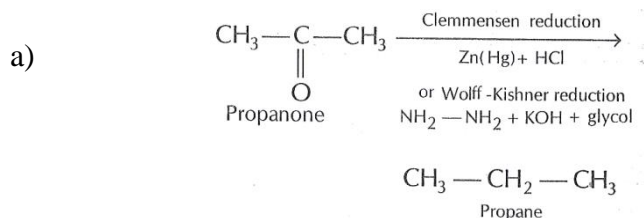
Lot of  $\text{CH}_3$  groups offer too much steric hindrance.

c) Aldehydes have one R group and ketones have two. Two R groups cause more steric hindrance and greater +I effect reduces the electrophilicity of the carbonyl carbon.

3) How will you convert:

- Propanone to propane
- Benzoyl chloride to benzaldehyde
- Ethanal to but-2-enal

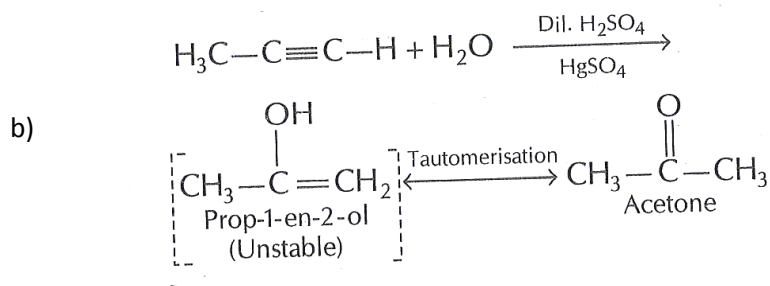
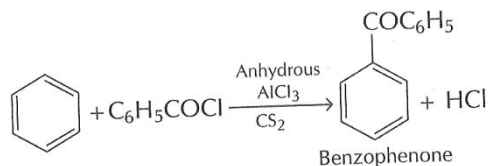
A)

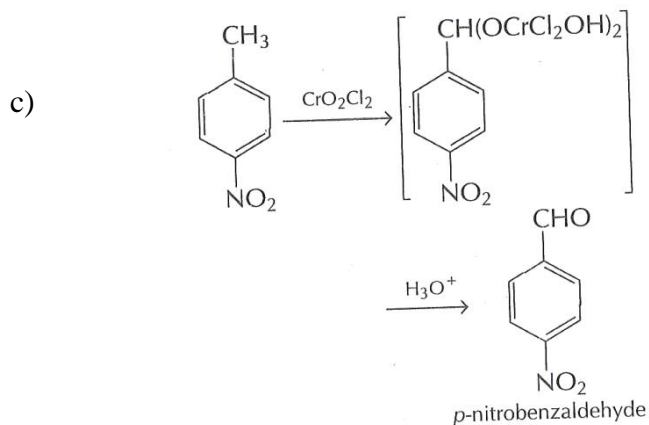


4) How will you bring about the following conversions?

- Benzene to Benzophenone
- Propyne to acetone
- p-nitrotoluene to p-nitrobenzaldehyde

Ans 4 a)





5) An organic compound A contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecules mass of the compound is 86. It doesn't reduce Tollen's reagent but forms an addition compound with sodium hydrogen sulphite and gives positive iodoform test. On vigorous oxidation, it gives ethanoic and propanoic acids. What is the structure of compound A?

Ans	Element	%	Molar Mass	Moles	Simple ratio
	C	69.77	12	5.81	5
	H	11.63	1	11.63	10
	O	18.6	16	1.16	1

Empirical formula  $\text{C}_5\text{H}_{10}\text{O}$

Empirical formula mass =  $5(12) + 10(1) + 1(16) = 86$

$$n = \frac{86}{86} = 1$$

$\therefore$  Molecules formula  $\text{C}_5\text{H}_{10}\text{O}$

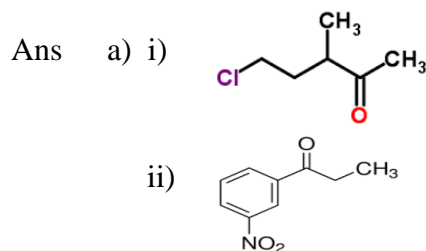
Since it doesn't give Tollen's test but gives positive iodoform test. It is a methyl ketone i.e it has  $-\text{C}-\text{CH}_3$  group. Since on oxidation it gives ethanoic and propanoic acid, it must be pentan-2-one.



Pentan-2-one

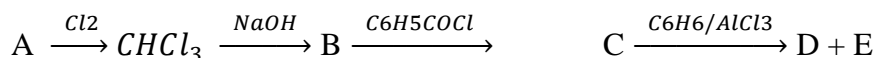
**05 MARKS**

- 1) a) Draw the structures of:
- 5-Chloro-3methyl-pentan-2-one
  - p-nitropropiophenone
- b) Give simple chemical tests to distinguish between:
- Ethanal and propanal
  - Phenol and benzoic acid
  - Benzaldehyde and acetophenone



- b) i)  $\text{CH}_3\text{CHO}$  gives a yellow ppt of iodoform with  $\text{NaOH/I}_2$  (positive iodoform test)  $\text{CH}_3\text{CH}_2\text{CHO}$  doesn't answer this test.
- ii) Phenol produces deep violet colour with aq-neutral  $\text{FeCl}_3$  Soln., benzoic acid doesn't answer the test.
- iii) Acetophenone produces yellow ppt on heating with  $\text{NaOH+I}_2$ , benzaldehyde doesn't.

- 2) Identify A,B,C,D and E in the following sequence:



A)  $\text{A} \rightarrow \text{CH}_4$ ,  $\text{B} \rightarrow \text{HCOONa}$ ,  $\text{C} \rightarrow \text{C}_6\text{H}_5\text{COOCH}_3$ ,



- 3) An organic compound A ( $\text{C}_3\text{H}_8\text{O}$ ) on treatment with Cu at 573 K gives B. B doesn't reduce Fehling's solution. But gives a yellow ppt. of compound C with  $\text{I}_2/\text{NaOH}$ . Deduce the structures of A, B and C.

A) Since compound B gives iodoform test, it must be having  $-\text{CO}-\text{CH}_3$  group i.e it is a ketone.

Since B is obtained by dehydrogenation of A,  $\therefore$  A is a  $2^\circ$  alcohol

∴ A is  $\text{R}-\text{CH}-\text{CH}_3$



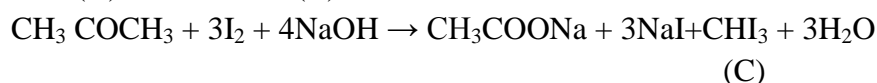
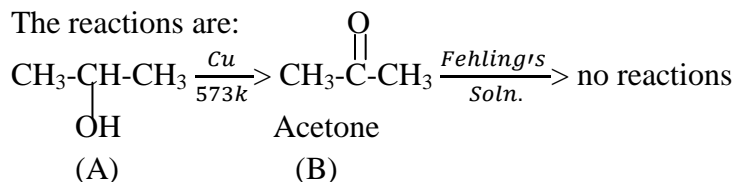
Comparing with the given molecules formula, R is  $-\text{CH}_3$

∴ A is  $\text{CH}_3-\text{CH}-\text{CH}_3$



Propan-2-ol

The reactions are:



So, A =  $\text{CH}_3\text{CHCH}_3$  Propan-2-ol

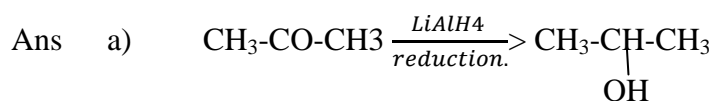


B =  $\text{CH}_3\text{COCH}_3$  Propan-2-one

C =  $\text{CHI}_3$  Iodoform

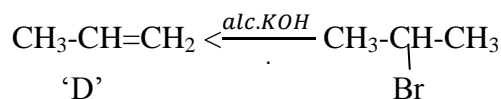
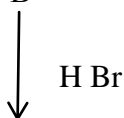
4) a) An organic compound A ( $\text{C}_3\text{H}_6\text{O}$ ) is resistant to oxidation but forms a compound B ( $\text{C}_3\text{H}_8\text{O}$ ) on reduction. B reacts with H Br to form a bromide 'C' which on treatment with alcoholic KOH forms an alkene D ( $\text{C}_3\text{H}_6$ ). Deduce the structures A,B,C and D.

b) Carboxylic acids contain a carbonyl group, but do not show the nucleophilic addition reaction like ketones or aldehydes. Why?



Acetone  
'A'

Propan-2-ol  
'B'



'D'  
Propene

Br  
2-Bromo propane

‘C’

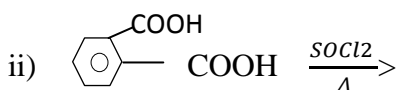
- b) This is due to resonance (for structures refer NCERT)

The carboxyl carbon of the resonance hybrid is less positive and hence less electrophilic than carbonyl ‘C’ of aldehydes and ketones

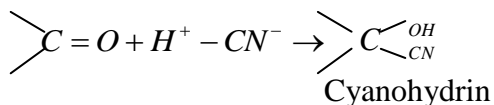
- 5) a) Explain the following :

- i) Cyanohydrin                      ii) Acetal                      iii) 2,4 – DNP derivative

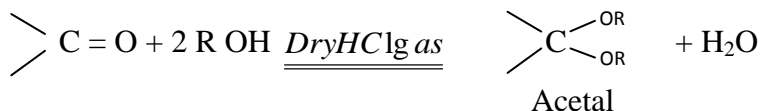
- b) Complete the following:



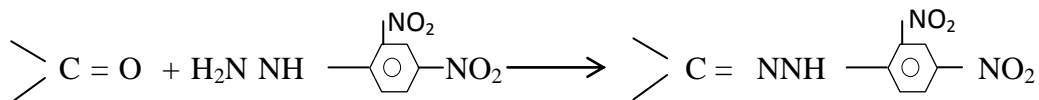
- Ans a) i) Formed addition of HCN to aldehydes or ketones



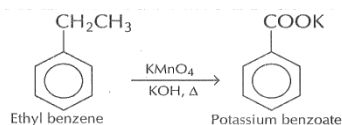
- ii) Formed on addition of two moles of alcohol to an aldehyde or ketone.



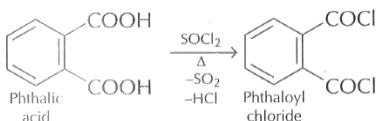
- iii) Addition product of aldehydes or ketones with 2,4 – Dinitro phenyl hydrazine in weakly acidic medium.



- b) i)



- ii)



iii)  $\text{C}_6\text{H}_5\text{CH} = \text{NNHCONH}_2$   
Benzaldehyde semicarbazone



## CHAPTER – 13

### AMINES

#### 01 MARK

1) Draw the structure of prop-2-en-1-amine

Ans  $\text{H}_2\text{C} = \text{CH} - \text{CH}_2 - \text{NH}_2$

2) Give a chemical test to distinguish between ethylamine and aniline.

Ans They can be distinguished by Azo dye test.

On treating with  $\text{HNO}_2$  ( $\text{NaNO}_2 + \text{HCl}$ ) followed by alkaline soln. of 2-naphthol (Temp – 0-5°C) Aniline forms an orange dye, while ethylamine only gives ethanol and  $\text{N}_2$ .

3) Arrange the following in increasing order of their solubility in water :  $\text{C}_6\text{H}_5\text{NH}_2$ ,  $(\text{C}_2\text{H}_5)_2\text{NH}$ ,  $\text{C}_2\text{H}_5\text{NH}_2$

Ans  $\text{C}_6\text{H}_5\text{NH}_2 < (\text{C}_2\text{H}_5)_2\text{NH} < \text{C}_2\text{H}_5\text{NH}_2$

4) Out of  $\text{CH}_3\text{NH}_2$  and  $(\text{CH}_3)_3\text{N}$ , which one has higher boiling point?

Ans  $\text{CH}_3\text{NH}_2$  due to its ability to form Intermolecular H-bonds  $(\text{CH}_3)_3\text{N}$  has no H atoms bonded to N so cannot participate in H bonding.

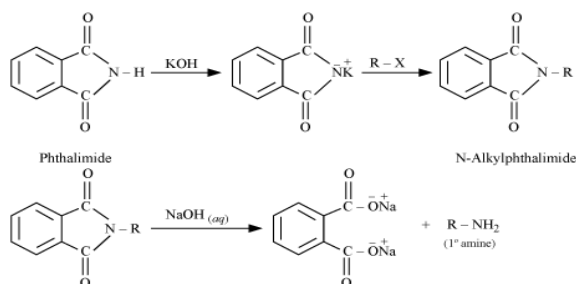
5) Why is the  $\text{pK}_b$  of aniline greater than methylamine?

Ans In aniline, lone pair of N is delocalized over the benzene ring, reducing basicity. In  $\text{CH}_3\text{NH}_2$ , +I effect of  $-\text{CH}_3$  group increases basicity of  $\text{CH}_3\text{NH}_2$ .

#### 02 MARKS

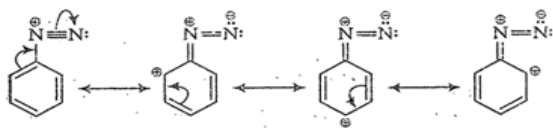
1) Explain Gabriel Pthalimide synthesis.

Ans It is used to prepare pure 1° amine. Aromatic 1° amines can't be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide



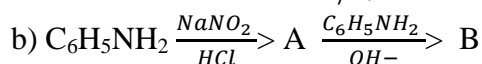
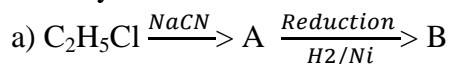
- 2) Give reasons:
- a) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.
- b) Amines are more basic than alcohols of comparable molecular masses.

Ans a) Resonance stabilization of diazonium salts of aromatic amines

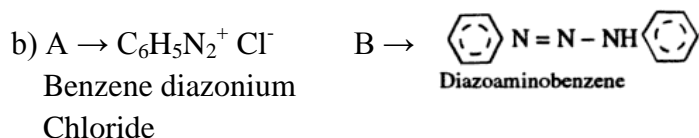


b) N is less electronegative than O,  $\therefore$  lone pair of electrons are easily available. Such resonance stabilization is not possible in diazonium salts of aliphatic amines.

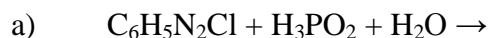
- 3) Identify A and B in each of the following:



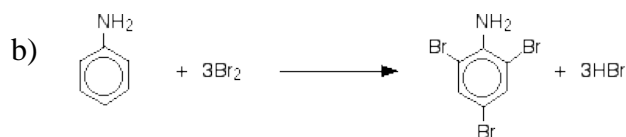
Ans a)  $\text{A} \rightarrow \text{C}_2\text{H}_5\text{CN}$ ,  $\text{B} \rightarrow \text{C}_2\text{H}_5\text{CH}_2\text{NH}_2$   
 Propanenitrile propanamine



- 4) Complete the reactions



Ans a)  $\text{C}_6\text{H}_6 + \text{N}_2 + \text{H}_3\text{PO}_3 + \text{HCl}$



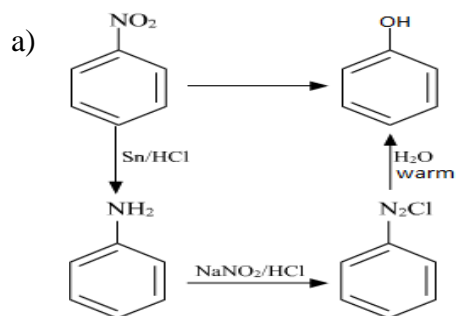
2, 4, 6 – Tribromoaniline

- 5) Convert

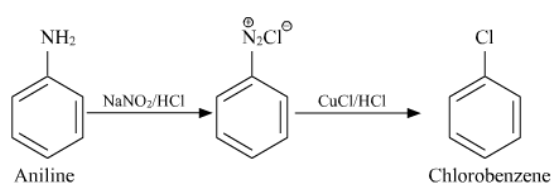
a) Nitrobenzene to phenol

b) aniline to chlorobenzene

Ans

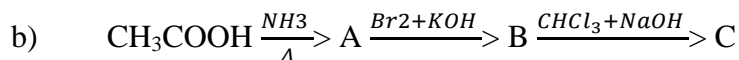


b)



### 03 MARKS

1) Give the structures of A, B, C in the following:



Ans a)  $\text{A} \rightarrow \text{CH}_3\text{CN}$ ,  $\text{B} \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2$ ,  $\text{C} \rightarrow \text{CH}_3\text{CH}_2\text{OH}$

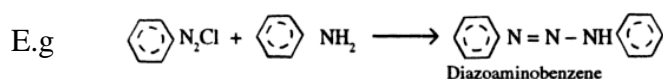


2) Write short notes on :

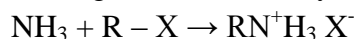
a) Coupling reaction

b) Ammonolysis

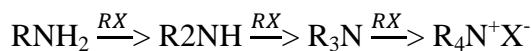
Ans a) Benzene diazonium salts react with  $e^-$  rich aromatic compounds such as phenols and amines to form azo compounds, which are often coloured and are used as dyes.



b) An alkyl or benzyl halide, on reaction with ethanolic soln. of  $\text{NH}_3$  undergoes nucleophilic substitution reaction in which the halogen atom is replaced with  $-\text{NH}_2$  group. This cleavage of C-X bond by ammonia molecule is called AMMONOLYSIS.



Substituted ammonium salt

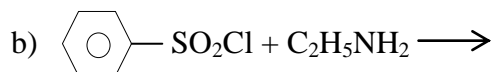
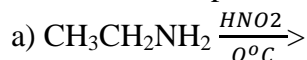


Quarternary Ammonium salt

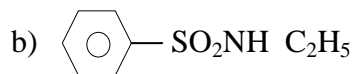
Disadvantage : Mixture of  $1^\circ$ ,  $2^\circ$ ,  $3^\circ$  amines and quarternary ammonium salt is obtained.

Order of reactivity of halides with amines is  $\text{RI} > \text{RBr} > \text{RCl}$

3) Write the main products of the following reactions:



Ans a)  $\text{CH}_3\text{CH}_2\text{OH}$



4) Give reasons:

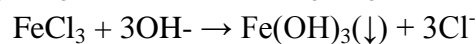
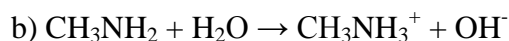
a) Amines are basic while amides are neutral.

b)  $\text{CH}_3\text{NH}_2$  in water reacts with ferric chloride to precipitate  $\text{Fe}(\text{OH})_3$


c) Reactivity of  $-\text{NH}_2$  group gets reduced in acetanilide.

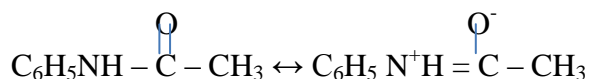
Ans a) In amines, R group increase e- density on N due to +I effects, whereas in amides,

 R - C - group is electron withdrawing.



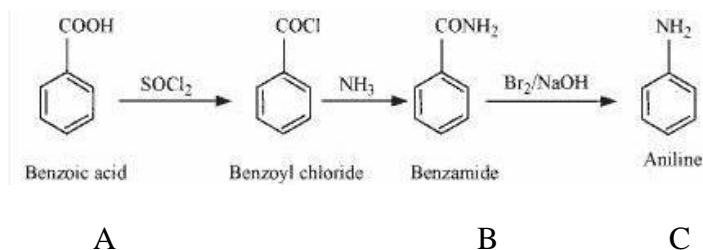
Reddish - brown

c) The lone pair on N is involved in conjugation with R-C-group



5) An aromatic compound 'A' on treatment with ammonia followed by heating forms compound 'B', which on heating with  $\text{Br}_2$  and  $\text{KOH}$  forms a compound 'C' ( $\text{C}_6\text{H}_7\text{N}$ ). Give the structures of A, B and C and write the reactions involved.

Ans 'A' must be benzoic acid

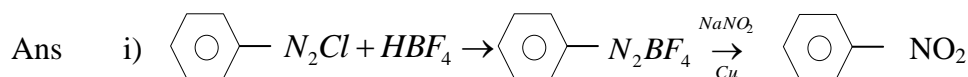


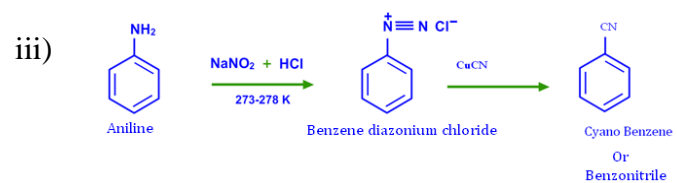
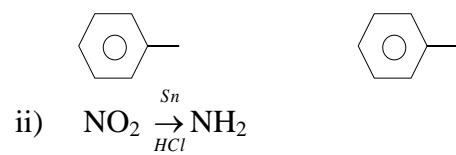
6) Convert

i) Benzene diazonium chloride to nitrobenzene

ii) Nitrobenzene to aniline

iii) Aniline to benzonitrile





7) Give reasons

a) Although amine group is O, P- directly in aromatic substitution reaction, aniline on nitroation gives some amount of m-nitro aniline.

b) Aniline doesn't undergo Friedel-Craft reaction.

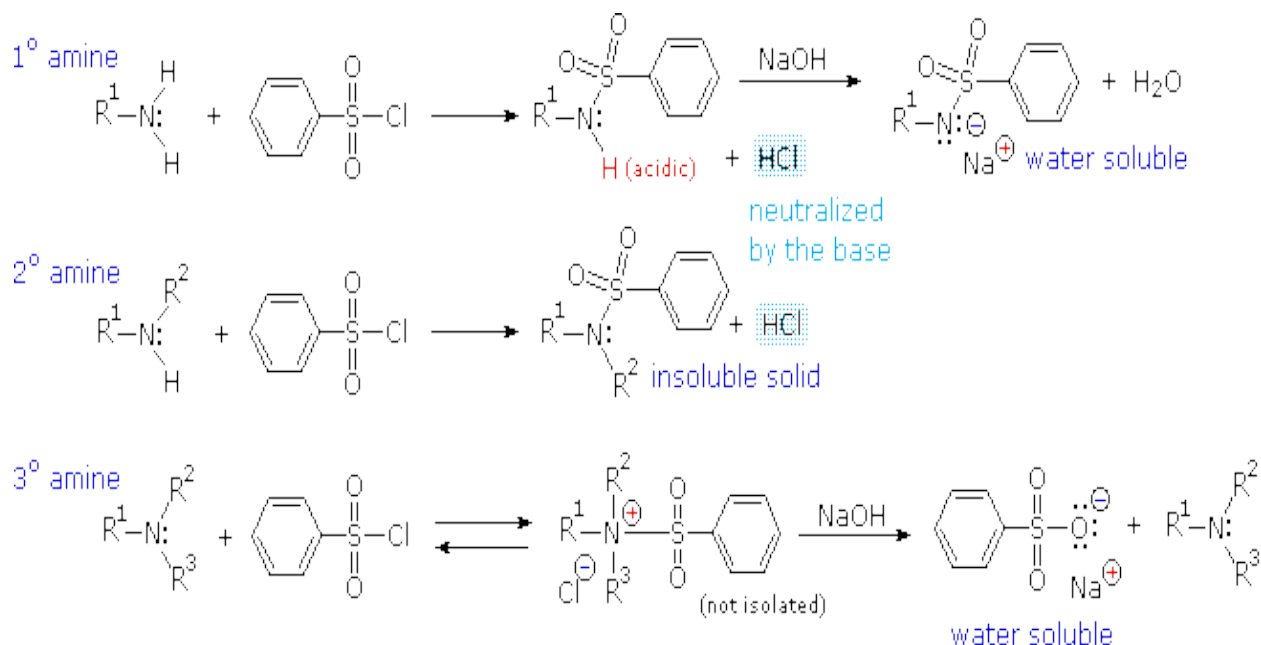
Ans a) Nitration is usually carried out with conc.  $\text{HNO}_3 + \text{con. H}_2\text{SO}_4$ . In presence of these acids, some amount of aniline undergoes protonation to form anilinium ion, so the reaction mixture consists of aniline and anilinium ion,  $-\text{NH}_2$  group in aniline is o- and p- directing and activating while the  $-\text{NH}_3^+$  group in anilinium ion is m-directing and deactivating. Nitration of aniline mainly gives p-nitroaniline (due to steric hindrance at o- position) nitration of anilinium ion gives m-nitroaniline.

b) Aniline being a lewis base reacts with Lewis acid  $\text{AlCl}_3$  to form a salt.  $\text{C}_6\text{H}_5\text{NH}_2^+ \text{Al}^-\text{Cl}_3$ . As a result N acquires a positive charge

8) Describe Hinsberg's test to distinguish between  $1^\circ$ ,  $2^\circ$  and  $3^\circ$  amines.

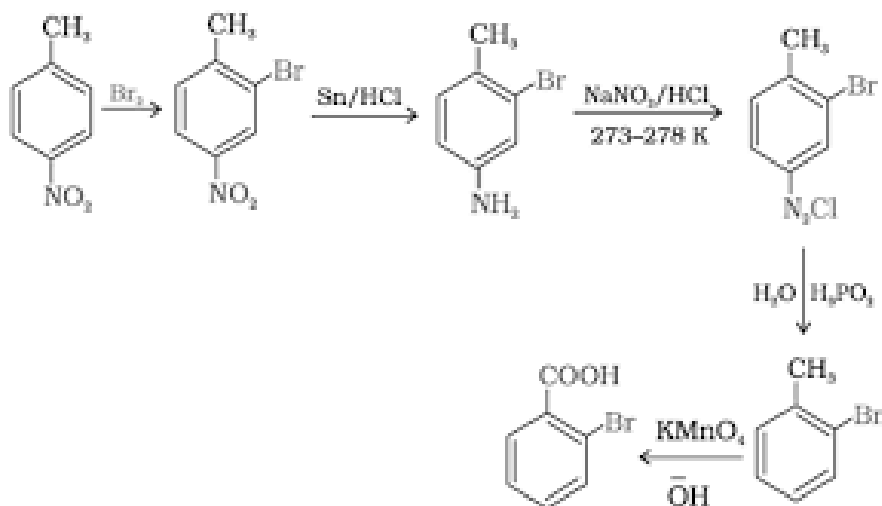
Ans The amine is shaken with benzenesulphonyl chloride (Hinsberg reagent) in presence of aq. KOH soln.

Ans



9) How will you convert 4-Nitrotoluene to 2-Bromobenzoic acid?

Ans



10) a) Predict, with reasons, the order of basicity of the following compounds in gas phase.

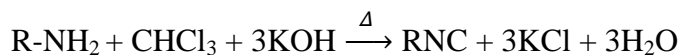
$(\text{CH}_3)_3\text{N}$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{NH}_3$

b) Describe Carbylamine reaction.

Ans a) In gaseous phase, solvation effects are missing. Hence, greater the number of alkyl groups, greater +I effect and stronger the base.

$\therefore (\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3$

b) Aliphatic and aromatic primary amines on heating with  $\text{CHCl}_3$  and ethanolic  $\text{KOH}$  form isocyanides or carbylamines, which are foul-smelling substances. Secondary and tertiary amines do not show this reaction. Hence this reaction is used as a test for primary amines.



Carbylamine

or

Isocyanide

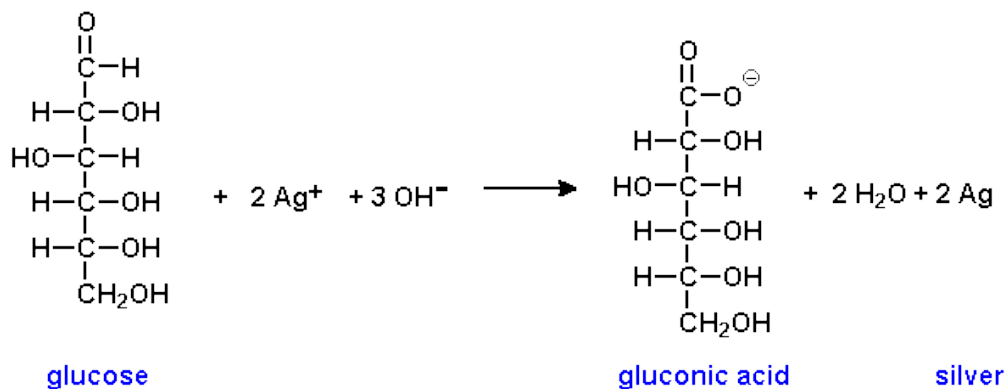


## CHAPTER – 14

## BIOMOLECULES

**01 MARK**

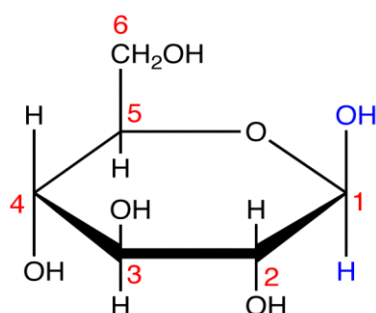
- 1) What are polypeptides?  
A) Polymers of amino acids having peptide linkage ( $-\text{CONH}-$ )
- 2) Which vitamin's deficiency causes pernicious anemia?  
A) Vitamin  $\text{B}_{12}$
- 3) What is the biological effect of denaturation of proteins?  
A) The protein molecule uncoils from an ordered and specific conformation into a more random conformation. Primary structure remains undisturbed.
- 4) In what sense are the two strands of DNA not identical but complementary to each other?  
A) If one strand has the bases A T C G, the other strand has T A G C, i.e. A can only bond with T and C can pair with G. Hence the strands are not identical, but complementary.
- 5) Show the reaction of Glucose with Tollen's reagent.



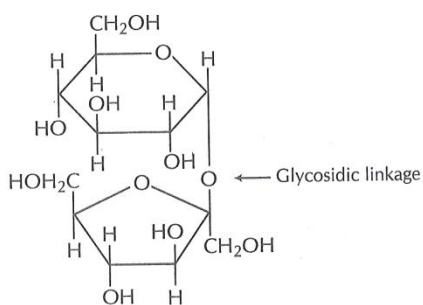
**02 MARKS**

- Q1. What is meant by
- (a) Pyranose structure of glucose
  - (b) Glycosidic linkage

Ans 1 a) Six-membered cyclic structure of glucose, in analogy with pyran



b) Two monosaccharide units are linked through oxygen atom accompanied by loss of a water molecule. This linkage is called glycosidic linkage.



Q2) What is the difference between  $\alpha$  – form of glucose and  $\beta$ -form of glucose?

Ans These two forms differ from each other in orientation of  $\text{-OH}$  group at C-1.  
 $\alpha$  – form is obtained by crystallization from concentrated solution of glucose at 303K while  
 $\beta$  – form (melting point 423 K) is obtained by crystallization from hot saturated soln. at 371 K.

Q3) Mention the type of linkages responsible for the formation of the following:

- Primary structure of proteins
- Cross-linking of polypeptide chains
- $\alpha$  – helix formation

iv)  $\beta$  – sheet structure.

- Ans
- i) Peptide linkage
  - ii) H-bond, sulphide linkage, van der waal's forces
  - iii) H-bond
  - iv) Intermolecular H-bonds.

Q4) Why are carbohydrates generally optically active?

Ans Due to presence of chiral or asymmetric carbon atom and absence of plane of symmetry.

Q5) Give reactions characteristic of  $-\text{CHO}$  group, but not by glucose, as in it, free  $-\text{CHO}$  group is absent.

Ans i) No reaction with Schiff's reagent  
 $\text{CHO}$   
 $|$   
 $(\text{CHOH})_4 + \text{Schiff's reagent} \rightarrow \text{no reaction}$   
 $|$   
 $\text{CH}_2\text{OH}$

ii) No reaction with  $\text{NaHSO}_3$  and  $\text{NH}_3$   
 $\text{CHO}$   
 $|$   
 $(\text{CHOH})_4 + \text{NaHSO}_3/\text{NH}_3 \rightarrow \text{no reaction}$   
 $|$   
 $\text{CH}_2\text{OH}$

### **03 MARKS**

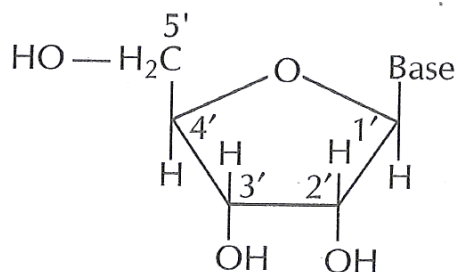
Q1) Define :

- a) Invert sugar      b) Vitamins      c) Nucleosides

Ans a) Hydrolysis of sucrose brings about a change in sign of rotation from dextro (+) to laevo (-), hence it is called invert sugar.

b) Organic compounds which can't be produced by the body and must be supplied in small amounts in diet to perform specific biological functions for normal health, growth and maintenance of body.

c) A unit formed by attachment of a base to 1' position of sugar



Q2) Differentiate between fibrous and globular proteins.

Ans

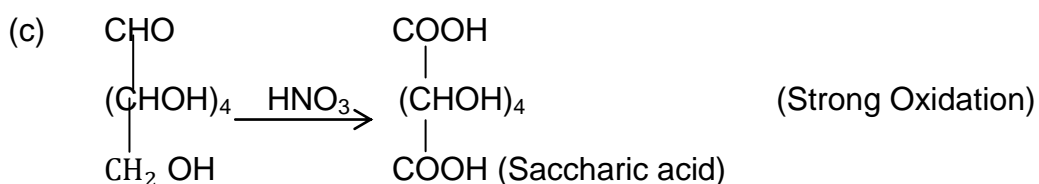
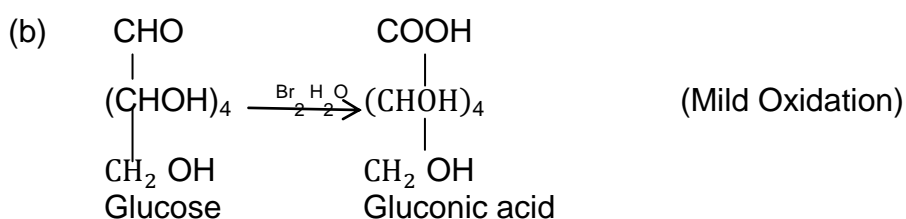
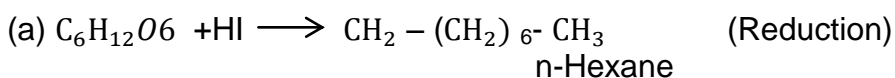
FIBROUS PROTEINS	GLOBULAR PROTEINS
1. Fibre – like structure	1. Polypeptide chains coil around to give a

	spherical shape.
2. Water – insoluble e.g. keratin, myosin, fibrin etc.	2. Water soluble e.g. insulin, haemoglobin, enzymes, hormones.
3. Stable to moderate changes in temperature and pH.	3. Very sensitive even to small changes in temperature and pH.

Q3) What happens when D-Glucose is treated with

- a) HI                      b) Br<sub>2</sub> water                      c) HNO<sub>3</sub>

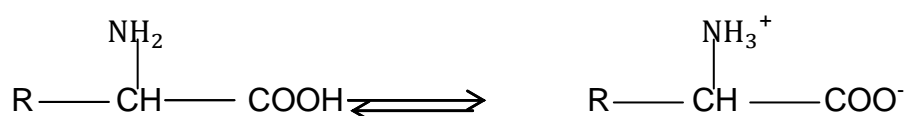
Ans 3



Q7. (a) Define Zwitter ions with examples?

(b) What is the difference between essential amino acids and non-essential amino acids?

A7. (a) Amino acids contain -NH<sub>2</sub> and -COOH groups. These two groups interact by transferring a proton from carboxyl group to amino group within the molecule. Hence, a dipolar ion called ZWITTER ION is formed.



(b)

S No	Essential Amino Acids	Non-Essential Amino Acids
1.	Cannot be synthesized by the body.  Therefore should be supplemented through diet.	Can be synthesized by the body.
2.	Eg Valine, leucine	E.g Glycine, alanine

Q8. Which is the sugar present in

milk? How many monosaccharides are present in it? What are such oligosaccharides called?

A8. Lactose, two monosaccharide units (glucose and galactose) such oligosaccharides are called DISACCHARIDES.

### **05 MARKS**

Q1. Discuss the structure of proteins in detail? What is the difference between  $\alpha$ -helix and  $\beta$ -pleated sheet structures of proteins?

A1. (a) Specific sequence in which various amino acids in a protein are linked to one-another – primary structures.

(b) The conformation adopted by these polypeptide chains as a result of H-bonding – SECONDARY STRUCTURES.

(i)  **$\alpha$ - Helix.** Formed by intra molecular H – bonds, causing the polypeptide chain to coil – up into a spiral structure or right handed helix  
Eg . Fibrous protein like keratin and myosin.

(ii)  **$\beta$ -pleated sheet structures** Polypeptide chains lie side by side held by intermolecular H-bonds , forming sheets. These sheets can then be stacked one over the other forming a 3-D structure. This structure resembles pleated folds of drapery, hence also called  $\beta$ -pleated sheet structures.

(c) **Tertiary Structure.** The secondary structure is further arranged, leading to following two possibilities.

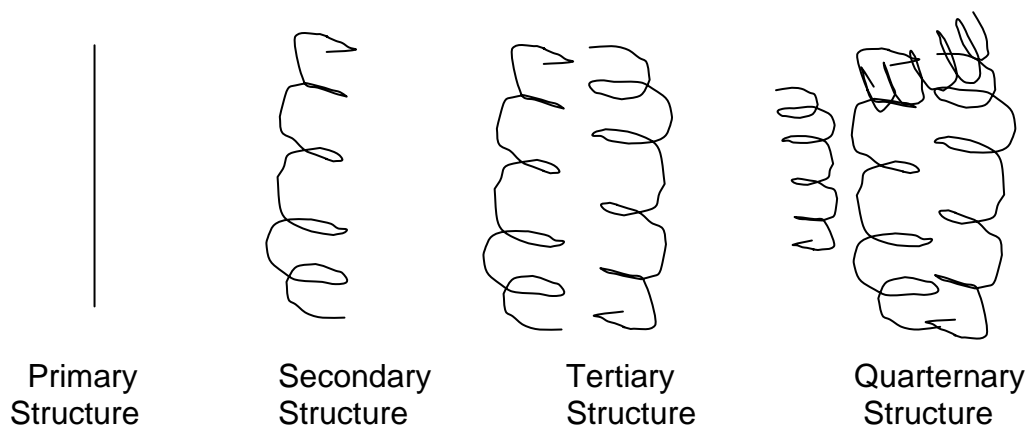
(i) **FIBROUS PROTEIN.** The long linear protein chains form thread like structure. These are insoluble in water and have  $\beta$ -pleated structure.

(ii) **GLOBULAR PROTEINS.** Different segments of the protein fold up to give the entire molecule a spherical shape. The folding involves various

interactions between the side-chains-such as, vander waal's interactions, disulphide bridges ,hydrogen bonding etc.

(d) **Quaternary Structure.** Some proteins exist as assembly of two or more polypeptide chains called **SUBUNITS** or **PROMOTERS**. These subunits may be identical or different and are held together by H-bonds, electrostatic and van der waal's interactions.

The quaternary structure refer to the determination of number of subunits and their spatial arrangement w.r.t each other in an aggregate protein molecule.



Q2. (a) Write important structural and functional differences between DNA and RNA?

S No	Structural Differences	
1.	Sugar present is 2 – deoxy –D-(-) ribose	Sugar present is D-(-) - ribose
2.	Cytosine and thymine are the pyrimidine bases	Cytosine and Uracil are the pyrimidine bases
3.	Double- stranded $\alpha$ - helix	Single- stranded $\alpha$ - helix
4.	Very large molecules ; molecular	Smaller molecules with

	mass may vary from six – sixteen million	molecular mass ranging from 20,000- 40,000 $\mu$
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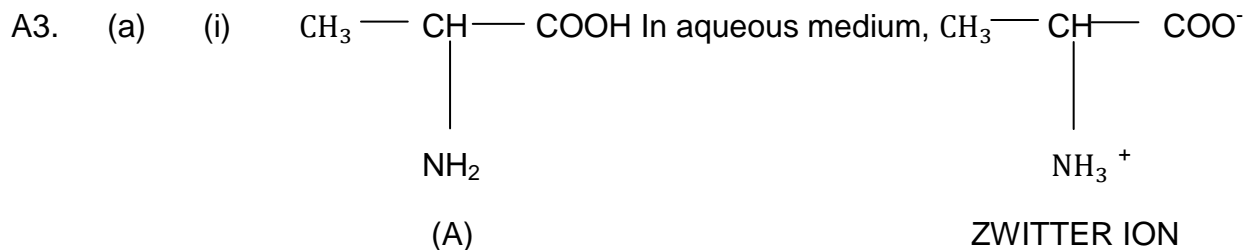
S No	Functional Differences	
1.	Unique property of replication	Usually doesn't replicate
2.	Responsible for transmission of hereditary characteristics	Responsible for protein synthesis

Q2. (b) What deficiency diseases are caused due to lack of vitamins A, B<sub>1</sub>, B<sub>6</sub> and K in human diet?

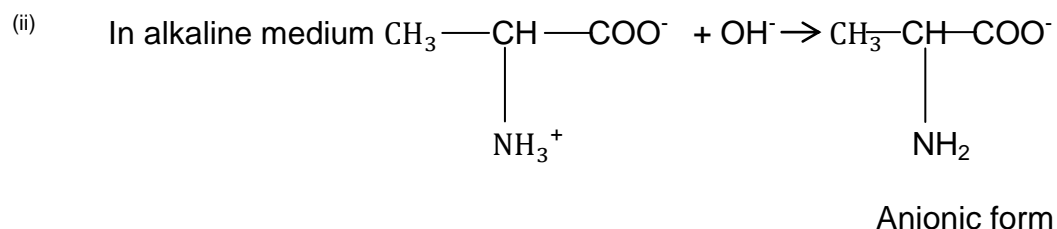
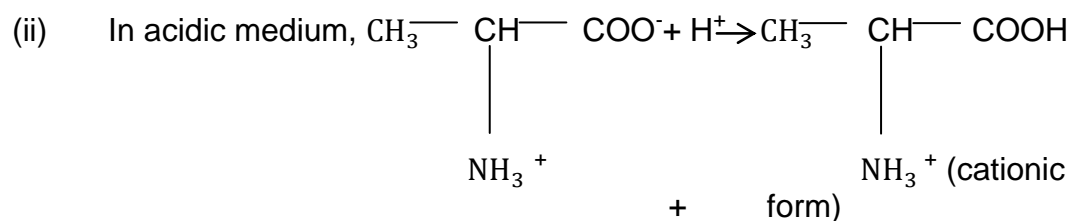
S No	Vitamins	Deficiency disease
1.	A	Xerophthalmia , night blindness
2.	B <sub>1</sub>	Beriberi, loss of appetite
3.	B <sub>6</sub>	Anaemia, general weakness
4.	K	Hemorrhage , slow blood clotting

Q3. (a) An optically active amino acid (A) can exist in three forms depending on the *pH* of the medium. If the molecular formula of (A) is C<sub>3</sub>H<sub>7</sub>NO<sub>2</sub>, write

- Structure of (A) in aqueous medium. What are such ions called?
- In which medium will the cationic form of (A) exist?
- In alkaline medium, towards which electrode will compound (A) migrate?







Therefore the compound in alkaline medium will migrate towards anode.

(b) What are reducing sugars ? How are proteins related to amino acids?

A3 (b) Carbohydrates with free aldehyde group that can reduce Fehling's solution and Tollen's reagent are called reducing sugars. All monosaccharides are reducing sugars. Also, those disaccharides where the linkage between two monosaccharides is not through aldehydic group are also called reducing sugars.

Q4. (a) Write four characteristics features of enzymes. Name a disease caused by the deficiency of a particular enzyme?

(b) What is a peptide bond? Explain its formation with an e.g?

A4. (a) (i) Enzymes are specific in their action.

(ii) Work at specific pH & moderate temperature.

(iii) Activity is high.

(iv) Catalyse biochemical reactions and their deficiency can cause diseases.

Eg Phenylketoneuria is caused by deficiency of phenylalanine hydroxylase and Albinism is caused by deficiency of tyrosinase.

(b) Proteins are polymers of  $\alpha$ -amino acids connected to each other by peptide linkage. Chemically peptide linkage is an amide formed between  $-\text{COOH}$  group and  $-\text{NH}_2$  group.

Q5. (a) Two samples of DNA, A and B have melting points 340K and 350K respectively. What conclusion can you draw from these data regarding their base content?

(b) Discuss the composition of starch.

A5. (a) CG base pair has 3 H- bonds and AT base pair has two H – bonds. Therefore CG base pair is more stable than AT base pair. Since sample B has higher melting point than sample A, therefore sample B has higher CG content than sample A.

(b) Starch is made of two components

(i) Amylose (15 – 20%) – Water – soluble, linear polymer of  $\alpha$ -D Glucose in which  $C_1$  of one glucose unit is attached to  $C_4$  of the other through  $\alpha$  – glycosidic linkage. Aqueous solution of amylose gives blue colour with iodine solution.

(ii) Amylopectin (30-85%) – Highly branched polymer, large number of short chains containing 20-25 glucose units joined through  $\alpha$  – glycosidic linkage involving  $C_1$  of one glucose unit and  $C_4$  of another. The  $C_1$  of terminal glucose unit in each chain is further linked to  $C_6$  of some other glucose unit in the next chain through  $C_1 - C_6$   $\alpha$  – glycosidic linkage.