# **Chapter 11- Alcohols, Phenols and Ethers**

### **Intext Questions Pg-317**

Q. 1A Classify the following as primary, secondary and tertiary alcohols:

$$\begin{array}{c} \operatorname{CH}_3\\ \operatorname{CH}_3- \overset{|}{\underset{\operatorname{C}}{\operatorname{C}}} - \operatorname{CH}_2 \operatorname{OH}\\ \overset{|}{\operatorname{CH}_3}\end{array}$$

Answer: It is primary alcohol because carbon which carries the –OH group is only attached to one alkyl group.

Q.1B Classify the following as primary, secondary and tertiary alcohols:  $H_2C = CH - CH_2OH$ 

Answer: It is primary alcohol because carbon which carries the –OH group is only attached to one alkene group.

Q.1C Classify the following as primary, secondary and tertiary alcohols:  $CH_3 - CH_2 - CH_2 - OH$ 

Answer: It is primary alcohol because the carbon which carries the –OH group is only attached to one propyl group.

Q.1D Classify the following as primary, secondary and tertiary alcohols:



Answer: It is secondary alcohol because the carbon which carries the – OH group is joined directly to methyl and benzene.

Q.1E Classify the following as primary, secondary and tertiary alcohols:

 ${\displaystyle \bigcap^{CH_2-CH-CH_3}}_{OH}$ 

CH<sub>a</sub>

Answer: It is secondary alcohol because the carbon which carries the – OH group is joined directly to two different alkyl groups.

Q.1F Classify the following as primary, secondary and tertiary alcohols:  $CH_{a}$  CH=CH-C-OH

Answer: It is tertiary alcohol because the carbon which carries the –OH group is joined directly to three different alkyl groups. Here two of the alkyl group is methyl and the third one is 1-ethylbenzene.

Q.2 Identify allylic alcohols in the above examples.

Answer: Allylic alcohol is an organic compound which has the structural formula  $CH_2 = CHCH_2OH$ . In other words, in these alcohols, the the -OH group is attached to  $sp^2$  hybridized carbon next to the carbon-carbon double bond, that is to an allylic carbon. Therefore, in the above examples, the following are the allylic alcohols.

(ii)  $H_2C = CH - CH_2OH$  and (vi)  $CH_2CH = CH_2OH$ 

CHa

### **Intext Questions Pg-320**

Q.3 Name the following compounds according to IUPAC system.

 $(i) CH_3-CH_2-CH-CH-CH-CH_3$  $| | | | | CH_2Cl CH_3$ 

(ii) 
$$CH_3 - CH - CH_2 - CH - CH - CH_3$$
  
 $| \qquad | \qquad | \qquad CH_3 \quad OH$ 

(iii)



(iv) 
$$H_2C = CH - CH - CH_2 - CH_2 - CH_3$$

OH

(v) 
$$CH_3 - C = C - CH_2OH$$
  
 $CH_3 Br$ 

# Answer:

- (i) 3-chloroethyl-2-isopropylpentan-1-ol
- (ii) 2,5-Dimethylhexane-1,3-diol
- (iii) 3-Bromocyclohexanol
- (iv) Hex-1-en-3-ol
- (v) 2-Bromo-3-methylbut-2-en-1-ol

### **Intext Questions Pg-325**

Q.4A Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal? CH<sub>3</sub>-CH-CH<sub>2</sub>OH CH<sub>3</sub>

**Answer:** In the Grignard reagent reaction, the first step of the reaction is the nucleophilic addition of Grignard reagent to the carbonyl group to form an adduct, Hydrolysis of adduct results in the formation of alcohol.

Here, is the general reaction with Grignard reagent below:-

HCHO + RMgX 
$$\xrightarrow{H_2O}_{H^+}$$
 RCH<sub>2</sub> + Mg(OH)X

From here, it is clear that HCHO gives  $CH_2OH$  groups, so R of Grignard reagent is the remaining part of given alcohols. Thus, select the suitable Grignard reagent by substituting the value of R. Now we can see the reaction given below:-

Methanal reacts with iso-propyl magnesium bromide, in presence of dry ether gives an additional compound. And this additional compound on reaction with H2O /H+ gives iso-butyl alcohol (i.e., 2-methylpropane-1-ol) as one of the final product.

Q.4B Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal?



Methanal reacts with cyclohexyl magnesium bromide, in presence of dry ether, which gives an intermediate product. This intermediate product when reacts with given reagent, as shown above, gives cyclohexyl methanol as a product.

Q.5A Write structures of the products of the following reactions:

 $CH_3 - CH = CH_2 \xrightarrow{H_2O/H^+}$ 

# Answer:

In this reaction, when propene reacts with the given reagent then the double bond of propene breaks down with charges on them. So, H+ gets placed on the carbon which already has two hydrogen atom and OH- gets substituted on center carbon because it has the more positive charge which attracts OH-. Thus we get propene-2-or as a product.

$$CH_3 - CH = CH_2 \xrightarrow{H_2O/H^+} CH_3 - CH - CH_3$$

Propane

OH

Propane-2-ol

Q.5B Write structures of the products of the following reactions:

NaBH,



#### Answer:

In this reaction, when Methyl (2-oxocyclohexyl) ethanoate reacts with the given reagent then the double bond between the oxygen atom and cyclohexyl gets breaks down, such that O has a negative charge and that particular carbon will have a positive charge on it. So, to neutralize it, H+ gets substituted to that carbon and with O- to form the structure of alcohol. Thus we get Methyl (2-hydroxycyclohexyl) ethanoate as a product.



Q.5C Write structures of the products of the following reactions:  $CH_3 - CH_2 - CH - CHO$ 

 $CH_3 \xrightarrow{NaBH_4} \longrightarrow$ 

Answer: In this reaction, when 2-Methylbutanal reacts with the given reagent NaBH<sub>4</sub>, then the double bond between carbon and oxygen gets to break down in the above aldehyde compound, where carbon has positive

charge and oxygen will have a negative charge on them. So,  $H^+$  gets placed on the carbon to complete its octet and  $H^+$  gets substituted on O<sup>-</sup> to form OH, i.e, an alcohol. Thus we get 2-Methylbutan-1-ol as a product.

#### **Intext Questions Pg-335**

Q.6 Give structures of the products you would expect when each of the following alcohol reacts with

(a) HCl –ZnCl<sub>2</sub>

(b) HBr and

(c) SOCl<sub>2</sub>

(i) Butan-1-or (ii) 2-Methylbutan-2-ol

#### Answer:

(a)

(i) Primary alcohols do no react appreciably with Lucas' reagent (HCl - ZnCl<sub>2</sub>) at room temperature.

 $CH_3 - CH_2 - CH_2 - CH_2 - OH \xrightarrow{HCl+ZnCl_2}$  No reaction Butan- 1 – ol (ii) Tertiary alcohol reacts immediately with Lucas 'reagent.

$$\begin{array}{c} OH \\ (H_{3} - CH_{2} - C - CH_{3} \xrightarrow{HCl - ZnCl_{2}} CH_{3} - CH_{2} - C - CH_{3} + H_{2}O \\ (H_{3} - CH_{3} - CH_{3} - CH_{2} - C - CH_{3} + H_{2}O \\ (H_{3} - CH_{3} -$$

$$CH_{3} - CH_{2} - C - CH_{3} + HBr \rightarrow CH_{3} - CH_{2} - C - CH_{3} + H_{2}O$$

$$CH_{3} - CH_{3} - CH_{3} - CH_{2} - C - CH_{3} + H_{2}O$$

$$CH_{3} - CH_{3} - C$$

(c) (i)

 $\begin{array}{ll} CH_3CH_2CH_2CH_2OH + SOCl_2 \rightarrow CH_3CH_2CH_2CH_2Cl + SO_2 + \text{HCl} \\ \\ \text{Butane} - 1 \text{-ol} & 1 \text{- chlorobutane} \end{array}$ 

$$CH_{3} - CH_{2} - C - CH_{3} + SOCl_{2} \rightarrow CH_{3} - CH_{2} - C - CH_{3} + SO_{2} + HCl$$

$$CH_{3} - CH_{2} - C - CH_{3} + SO_{2} + HCl$$

$$CH_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3} - CH_{3} + SO_{2} + HCl$$

$$CH_{3} - CH_{3} - CH_{3$$

Q.7 Predict the major product of acid catalyzed dehydration of(i) 1-methyl cyclohexanol and (ii) butan-1-olAnswer:



Q.8 Ortho and para nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.

**Answer:** Resonating structures of o-nitrophenoxide ions that are formed by the loss of a proton from o-nitrophenol are as follows:

(ii)



Resonating structures of p-nitrophenoxide ions that are formed by the loss of a proton from p-nitrophenol are as follows:



Resonating structures of phenoxide ions that are formed by the loss of a proton from phenol are as follows:



It is clearly evident from the above structures that due to -R-effect of  $-NO_2NO_2$  group, o-and p-nitrophenoxide ions are more stable than phenoxide ions. Consequently, o- and p-nitrophenols are more acidic than phenols.

Q.9A Write the equations involved in the following reactions:

Reimer - Tiemann reaction

Answer: Phenol on mixing with chloroform and NaOH at 340K followed by Acidic hydrolysis, salicyl aldehyde is formed. When carbon tetrachloride ( $CCl_4$ ) is used at the place of chloroform salicylic acid is formed. This type of reaction is known as Reimer - Tiemann reaction.



Q.9B Write the equations involved in the following reactions:

### Kolbe's reaction

Answer: The sodium phenoxide reacts with CO2 under pressure 4-7 atm at a 400K temperature to form sodium salicylate, which on acidification yields salicylic acid. This type of reaction is known as Kolbe's reaction.



**Intext Questions Pg-342** 

Q.10 Write the reactions of Williamson synthesis of 2-ethoxy-3-methyl pentane starting from ethanol and 3-methyl pentane-2-ol.

Answer: During Williamson synthesis of ethers, an alkyl halide reacts with an alkoxide(ion with –ve charge on the oxygen of alcohol and + ve charge on alkali metal like Na) ion. it is an  $S_N2$  reaction. In the reaction, alkyl halides should be least hindered. Hence, an alkyl halide is obtained from ethanol and alkoxide ion from 3-methylpentan-2-ol. The reactions are shown below:

Step 1: 
$$C_2H_5OH \xrightarrow{HBr} C_2H_5Br$$
  
Ethanol Bromoethane  
Step 2:  $CH_3 - CH_2 - CH - CH - CH_3 \xrightarrow{Na} CH_3 - CH_2 - CH - CH$  -Ona  
 $CH_3 OH CH_3 - CH_2 - CH - CH_3 \xrightarrow{Na} CH_3 - CH_2 - CH - CH$  -Ona  
 $CH_3 OH CH_3 - CH_3 - CH_3 \xrightarrow{CH_3} CH_3$   
3-Methylpentan - 2 - ol Sodium 3-Methylpentan -2- oxide

Step 3:

 $CH_3 - CH_2 - CH - CH - Ona + C_2H_5Br \rightarrow CH_3 - CH_2 - CH - CH - OC_2H_5 + NaBr$ Sodium 3 – Methylpentan – 2 – oxide 2-Ethoxy–3- methylpentane

Q.11 Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?(i)



#### Answer:

Set (ii) is appropriate Because  $CH_3Br$  is only a nucleophile whereas  $CH_3ONa$  is nucleophile as well as strong base, so the elimination reaction





Q.12A Predict the products of the following reactions:  $CH_3 - CH_2 - CH_2 - O - CH_3 + HBr \rightarrow$ 

# Answer:

When N –propyl methyl ether reacts with HBr, it forms propanol and bromomethane, n-propyl methyl ether will cleave at O . and  $H^+$  will attack at O, and  $Br^-$  will attack  $CH_3^+$ 

 $CH_3 - CH_2 - CH_2 - O - CH_3 + HBr \rightarrow CH_3 - CH_2 - CH_2 - OH + CH_3Br$ 

(1-methoxypropane) (Hydrogen bromide) (Propanol) (Bromomethane)

Q.12B Predict the products of the following reactions:

OC<sub>2</sub>H<sub>5</sub> + HBr

**Answer:** When Ethoxybenzene Reacts with HBr, it forms Phenol and bromoethane, Ethoxybenzene cleaves at O.  $H^+$  will attack at O, and Br<sup>-</sup> will attack  $C_2H_5^+$ 



Q.12C Predict the products of the following reactions:



Answer:

When nitrating mixture reacts with ethoxy benzene introduction of nitro group is occurred at para position as it will give the stable product without hindrance.



Ethoxybenzene



4 - Ethoxynitrobenzene (Major) 2 - Ethoxynitrobenzene (Minor)

Q.12D Predict the products of the following reactions:

$$(CH_3)_3$$
C -  $OC_2H_5$  —

Answer:

As HI is a strong nucleophile it will protonate the oxygen , to form a good leaving group. And I- will attack at  $C(CH_3)_3^+$  to give tert- butyl iodide and ethanol.

 $(CH_3)_3$ C -  $OC_2H_5 \xrightarrow{HI} (CH_3)_3$ C -I

tert-Butyl ethyl ether

tert-Butyliodide

+  $C_2H_5OH$ Ethanol

#### **Exercises**

Q.1A Write IUPAC names of the following compounds:

$$CH_{3} - CH - CH - CH - C - CH_{3}$$

$$| \qquad | \qquad |$$

$$CH_{3} \quad OH \quad CH_{3}$$

#### Answer:

2,2,4-Trimethylpentan-3-ol

The naming of the compound usually starts with numbering the carbons in the chain. The lower set of locants are chosen for this purpose, while in this case numbering under this condition is done from the left side. Once the carbons are mentioned, the position of -OH group is numbered and ol is added as the suffix.

Q.1B Write IUPAC names of the following compounds:  $H_3C - CH - CH_2 - CH - CH_2 - CH_3$ OH OH  $C_2H_5$ 

### Answer:

5-Ethylheptane-2,4-diol

Here the longest chain is the straight chain. For such situations, numbering should be such that the functional groups should be denoted by the smallest number. Ethyl group is named at the beginning as it's a side chain.

Q.1C Write IUPAC names of the following compounds:

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CH_3 - CH - CH - CH_3
| | | OH OH
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# Answer:

Butane-2,3-diol

In this system, glycols are called as Diols and their class name is Alkane diols. The two-hydroxyl group position is indicated by Arabic numerals. Firstly, the carbon chain is named, the -OH positions are numbered and suffixed with -diol (depends on the number of -OH groups.

Q.1D Write IUPAC names of the following compounds:

Answer: Propane-1,2,3-triol

Initially carbon chain is named, -OH groups are numbered (can be done from any side as it's a symmetrical compound) and suffixed with triol.

Q.1E Write IUPAC names of the following compounds:



# Answer:

# 2-Methylphenol

In the IUPAC system, the position of the substituent w.r.t –OH group is indicated by an Arabic numeral, with the carbon carrying the OH group being numbered 1. So, methyl is numbered at the minimum position and phenol is added. The common name is o-cresol (ortho-cresol).

Q.1F Write IUPAC names of the following compounds:



# Answer:

4-Methylphenol

Methyl group is numbered 4 w.r.t to -OH position. The compound is symmetrical. The compound is known by its common name p-cresol (para cresol).

Q.1G Write IUPAC names of the following compounds:



Answer:

2,5-Dimethylphenol

The position of the substituent w.r.t –OH group is indicated by an Arabic numeral, with the carbon carrying the OH group being numbered 1. The lowest number chain is further chosen. The positions of the methyl group is 2 and 5.

Q.1H Write IUPAC names of the following compounds:



### Answer:

2,6-Dimethylphenol

The position of the substituent w.r.t –OH group is indicated by an Arabic numeral, with the carbon carrying the OH group being numbered 1. The lowest number chain is further chosen. The positions of the methyl group are 2 and 6 from both sides.

Q.11 Write IUPAC names of the following compounds:

 $\begin{array}{c} CH_3 \ - \mathrm{C} - CH_2 - \mathrm{CH} - CH_3 \\ | \\ CH_3 \end{array}$ 

### Answer:

1-Methoxy-2-methylpropane

Longest carbon chain attached to oxygen is chosen. It is called the principal chain and the other carbon chain is named with -oxy(Alkoxy) suffix at the end. Now the position of alkoxy group is 1 w.r.t the principal chain(propane) and the methyl group Is 2. Further alphabetically methoxy comes before methyl, therefore named as such.

Q.1J Write IUPAC names of the following compounds:

 $C_6H_5 - O - C_2H_5$ 

#### Answer:

Ethoxybenzene

The principal chain is benzene, so the short chain is named as ethoxy and suffixed with benzene.

Q.1K Write IUPAC names of the following compounds:

 $C_6H_5 - O - C_7H_{15}(n-)$ 

Answer: 1-Phenoxyheptane

Principal chain is heptane group having 7 carbon groups. Phenol group is called as substituent alkoxy group and is named.

Q.1L Write IUPAC names of the following compounds:

$$CH_3 - CH_2 - O - CH - CH_2 - CH_3$$

Answer: 2-Ethoxybutane

The longest chain here is butane and the ethyl group is attached to the 2<sup>nd</sup> carbon.

Q.2A Write structures of the compounds whose IUPAC names are as follows:

2-Methylbutan-2-ol

Answer:

$$CH_{3} - CH_{2} - CH_{3} - CH_{3} - CH_{3} - CH_{3}$$

Butane is the longest chain.  $C_2H_5$ 

Q.2B Write structures of the compounds whose IUPAC names are as follows:

1-Phenylpropan-2-ol

Answer:

ОН | СН2-СН-СН3

Propane is principle chain and substituents are numbered accordingly.

Q.2C Write structures of the compounds whose IUPAC names are as follows:

3,5-Dimethylhexane –1, 3, 5-triol

Answer:

HO - 
$$CH_2$$
- $CH_2$ - $CH_2$   $CH_2$   $CH_2$   $CH_3$   $CH_3$ 

Hexane is the longest chain. There are three -OH substituents and 2 methyl groups.

Q.2D Write structures of the compounds whose IUPAC names are as follows:

2,3 – Diethylphenol

Answer:



-OH of phenol is numbered a 1.

Q.2E Write structures of the compounds whose IUPAC names are as follows:

1 – Ethoxypropane

### Answer:

 $CH_3 - CH_2 - O - CH_2 - CH_2 - CH_3$ 

Propane is the principle chain and the alkoxy group is ethyl group.

Q.2F Write structures of the compounds whose IUPAC names are as follows:

2-Ethoxy-3-methylpentane

Answer:

$$CH_3$$

 $CH_3 - CH_2 - o - CH - CH - CH_2 - CH_3$ 

 $CH_{3}$ 

Longest chain is pentane and substituents are numbered accordingly.

Q.2G Write structures of the compounds whose IUPAC names are as follows:

Cyclohexylmethanol

## Answer:



In such cases, cyclo groups are named first, followed by conventional naming methods.

Q.2H Write structures of the compounds whose IUPAC names are as follows:

3-Cyclohexylpentan-3-ol

Answer:

$$CH_3 - CH_2 - C - CH_2 - CH_3$$

The cyclo group is named first, followed by conventional naming methods.

Q.21 Write structures of the compounds whose IUPAC names are as follows:

Cyclopent-3-en-1-ol

Answer:



Cyclo group is named first. Pentane having a double bond is named then with the suffix -OL added to the end.

Q.2J Write structures of the compounds whose IUPAC names are as follows:

4-Chloro-3-ethylbutan-1-ol.

Answer:

 $\begin{array}{c} CH_{2}Cl\\ H_{3}-CH_{2}-CH-CH_{2}-CH_{2}-OH \end{array}$ 

The longest chain is butane when looked for minimum numbering case.

Q.3A Draw the structures of all isomeric alcohols of molecular formula  $C_5H_{12}O$  and give their IUPAC names.

# Answer:

The structures of all isomeric alcohols of  $C_5H_{12}O$  are given below:

(a)

$$5 4 3 2 1CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - OHPentan - 1 - ol$$

Naming is done by the conventional method. The -OH group is attached on the first carbon.

(b) 
$$CH_3 - CH_2 - CH - CH_2 - OH$$

3-Methylbutan-1-ol

Butane is the longest chain and methyl is the substituent group.

(c)

$$CH_3 - CH - CH_2 - CH_2 - OH$$
  
$$CH_3$$
  
3-Methylbutan-1-ol

Longest chain is butane and conventional naming method is used.

#### (d)

$$CH_{3} - C - CH_{2} - OH$$

$$CH_{3} - C - CH_{2} - OH$$

$$CH_{3}$$

2,2-Dimethylpropan-1-ol

Isomer is made by transforming the principal carbon into tertiary type. The longest chain is butane and named accordingly.

(e) 
$$CH_3 - CH_2$$

(e) 
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$$

Pentan-2-ol

Longest chain is pentane and the numbering is chosen from the minimum position.

(f) 
$$CH_3 - CH - CH - CH_3$$

#### 3-Methylbutan-2-ol

Butane is the longest chain, further numbering is done by choosing a minimum position for the -OH group followed by other substituents.

OH  
(g) 
$$CH_3 - CH_2 - CH - CH_2 - CH_3$$
  
Pentan-3-ol

Conventional method of naming is used.

(h) 
$$CH_3 - CH_2 - CH_2 - CH_3$$

2-Methylbutan-2-ol

Butane is the longest chain and substituents are named accordingly by looking into minimum position.

Q.3B Classify the isomers of alcohols in question 3. (i) as primary, secondary and tertiary alcohols.

Answer:

(A) Primary alcohol	Explanation
(i) Pentan-l-ol	The -OH group is attached to
(ii) 2-Methylbutan-l-ol	the carbon that is attached to
(iii) 3-Methylbutan-l-ol	another single carbon.
(iv) 2,2-Dimethylpropan-l-ol	
(B) Secondary alcohol	
(i) Pentan-2-ol	The -OH group is attached to
(ii) 3-Methylbutan-2-ol	the carbon that is attached to
(iii) Pentan-3-ol	another two carbons.
(C) Secondary alcohol	
(i) 2-Methylbutan-2-ol	The -OH group is attached to
	the carbon group that is
	further attached to another
	three carbon atoms.

Q.4 Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

Answer: Here, propanol undergoes intermolecular H-bonding because of the presence of -OH group while butane has no such property.

$$\delta_{+} \quad \delta_{-} \quad \delta_{+} \quad \delta_{-} \quad \delta_{+} \quad \delta_{-}$$
-----H - O -----H - O -----  

$$\begin{vmatrix} & & \\ & &$$

Therefore, extra energy will be required to break those hydrogen bonds which in turn causes higher boiling point for propanol when compared to butane.

Q.5 Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

### Answer:

Due to the presence of –OH group, alcohols form hydrogen-bonds with water but hydrocarbons cannot form hydrogen-bonds with water.



Due to inter moleculer hydrogen bonding between Alcohol and water molecular they remain tightly bounded to water molecules and have higher solubility. Whereas in case of hydrocarbon there is no chance of hydrogen bonding.

Q.6 What is meant by the hydroboration-oxidation reaction? Illustrate it with an example.

Answer: The **hydroboration-oxidation reaction** is a two-step reaction that converts an alkene into a neutral alcohol by the net addition of water across the double bond. The hydrogen and hydroxyl group are added in a syn addition leading to the *cis* configuration. Hydroboration-oxidation is an anti-Markovnikov reaction, with the hydroxyl group attaching to the less substituted carbon. In first step Addition of Hydroborate group is done and in next step, it is oxidized by hydrogen peroxide.

$$H_{3}C \xrightarrow{H} BH_{2} \xrightarrow{H_{2}O_{2}} H_{3}C \xrightarrow{H} OH_{2}$$

$$H_{3}C \xrightarrow{C=CH_{2}} \frac{BH_{3}}{THF}}{CH_{3}} H_{3}C \xrightarrow{C-CH_{2}} \frac{H_{2}O_{2}}{OH^{-}} H_{3}C \xrightarrow{C-CH_{2}} CH_{3}$$

For example: - When propene undergoes hydroboration-oxidation reaction, then it produces propan-1-ol as product. In this reaction diborane i.e.,  $(BH_3)_2$  reacts with propene, which in result generates trialkyl borane as an addition product. Then trialkyl borane is oxidised, by using hydrogen peroxide in the presence of aqueous sodium hydroxide to form alcohol, as final product.

$$\begin{array}{ccc} CH_3 - \mathrm{CH} = & CH_2 + (\mathrm{H} - BH_2)_2 \rightarrow CH_3 - \mathrm{CH} - CH_2 \\ \mathrm{Propane} & \mathrm{Diborane} & & & & & \\ & \mathrm{H} & BH_2 \\ & & & & \\ & & & \\ &$$

$$(CH_3 - CH_2 - CH_2)_3 B \xleftarrow{CH_3 - CH = CH_2} (CH_3 - CH_2 - CH_2)_2 BH$$

$$H_2 O \downarrow 3H_2 O_2 . OH$$

$$3CH_3 - CH_2 - CH_2 - OH + B (OH)_3$$
Propane - 1 - ol

Q.7 Give the structures and IUPAC names of monohydric phenols of molecular formula,  $C_7H_8O$ .

Answer: The different forms of cresol is formed with given molecular formula:

(I) 2-methylphenol

(II) 3-methylphenol

(III) 4-methylphenol



Q.8 While separating a mixture of ortho and para nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

# Answer:

In ortho nitrophenol there is intra-molecular H bonding, whereas in paranitrophenol there is inter-molecular H bonding, as shown below:



And because of that para-nitrophenol get tightly bounded with water and ortho nitrophenol is steam volatile and it will leave the solution.

Q.9 Give the equations of reactions for the preparation of phenol from cumene.

Answer: The conversion of Phenol from Cumene requires the air oxidation of cumene.

The air oxidation of cumene (isopropyl benzene) leads to the production of both phenol and acetone (costlier than phenol).



The air oxidation of cumene gives cumene hydro peroxide as an intermediate which on further hydrolysis  $(H_3O^+)$  gives phenol and acetone.

Q.10 Write chemical reaction for the preparation of phenol from chlorobenzene.

Answer: There are many ways to this conversion. Two of them are given below:-



In the above conversion, the chlorobenzene is treated with a base such as NaOH, KOH etc. (strong base). The base abstracts the hydrogen from the C-2 position (it can also abstract the hydrogen from the C-6 position, as both are equally acidic) leaving the negative charge at that position.

In the next step Cl- leaves, leaving behind the positive charge at that carbon. Both the negative charge and positive charge forms a bond resulting Benzyne as the intermediate.

After the formation of the Benzyne intermediate OH- of the base attacks at the C-1 position and further, the H+ attacks to stabilize the negative charge thus resulting in the phenol.

(b) The second method is as follows:



The reaction can start from benzene also. Chlorination of benzene gives Chlorobenzene. When it is further treated with NaOH and  $H_2O$  at 350°C it results in the formation of sodium phenoxide which on further treatment H+ gives Phenol as the final product.

Q.11 Write the mechanism of hydration of ethene to yield ethanol.

Answer:

Step 1:- Protonation of ethene to form carbocation by electrophilic attack of  $H_3O^+$ .



Step 2:-Nucleophilic attack of water on carbocation.



Step 3:- Deprotonation to form ethanol.



Q.12 You are given benzene, conc.  $H_2SO_4$  and NaOH. Write the equations for the preparation of phenol using these reagents.

Answer:

The reaction given below is:



Benzene reacts with concern.  $H_2SO_4$  and undergoes the following mechanism:-

Step 1: The equilibrium produces  $SO_3$  in concentrated  $H_2SO_4$ , as shown below:

 $2H_2SO_4 \rightleftharpoons SO_3 + H_3O^+ + HSO_4^-$ 

Step 2:  $SO_3$  is the electrophile which reacts with benzene to form arenium ion, as shown below:



Step 3: A proton is removed from the arenium ion to form benzenesulfonate ion.



Step 4: The benzenesulfonate ion accepts a proton to become benzenesulphonic acid, as shown below:

Step 5: The benzene sulphonic acid then reacts with NaOH to give phenol as the final product, as shown below:


Q.13A Show how will you synthesise:

1-phenylethanol from a suitable alkene.

Answer: 1-phenylethanol from a suitable alkene.



The addition of water takes place according to Markovnikov rule. The alkene taken is styrene. And According to the rule, the positive charge i.e.  $H^+$  goes to the carbon of the double bond which has more number of hydrogens and the negative part i.e. OH- goes to the carbon that has less number of hydrogens. Therefore resulting the final product as 1-phenyl ethanol.

Q.13B Show how will you synthesise:

cyclohexylmethanol using an alkyl halide by an SN2 reaction. Answer:



In the above conversion, NaOH gets dissociated into Na<sup>+</sup> and OH<sup>-</sup>and Na<sup>+</sup> then combines with Cl of chloromethylcyclohexane forming NaCl and thus the final product Cyclohexylmethanol is obtained.

Q.13C Show how will you synthesise: pentan-1-ol using a suitable alkyl halide? Answer:  $CH_3CH_2CH_2CH_2CH_2Cl + NaOH \rightarrow CH_3CH_2CH_2CH_2OH + NaCl$ 1-Chloropentane Pantan – 1 - ol

In this conversion also, Na forms the compound with Cl i.e. NaCl and to compensate the negative charge formed by Cl, OH attacks at that position resulting in pentan-1-ol.

Q.14 Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol

Answer: The acidic nature of phenol can be represented by the following two reactions:-

(a) Phenols react with sodium to give sodium phenoxide, liberating  $H_2$ .



(b) Phenols react with sodium hydroxide to give sodium phenoxide and water as a by-product.



The acidity of phenol is more than that of ethanol. This is because phenol after losing a proton becomes phenoxide ion which undergoes resonance and is stabilized whereas ethoxide ion does not.



phenoxide ion

The resonating structures of phenoxide ion are shown as below:



The lone pair of electrons on oxygen delocalizes into the benzene (mesomeric effect) which reduces the electron density in the O-H bond. The O-H bonds are weaker and therefore breaks easily whereas in ethanol the electron releasing inductive effect of the alkyl group increases the electron density on the O-H bond. This strengthens the bond so the bond does not break easily. Therefore making ethanol less acidic than phenol.

Q.15 Explain why is ortho nitrophenol more acidic than ortho methoxyphenol?

**Answer:** *ortho*-nitro phenol is more acidic than ortho-methoxy phenol.

Explanation: Due to strong -R and -I effect of NO<sub>2</sub> group, electron density in the O-H bond decreases and hence the loss of a proton becomes easy.



Now after the loss of a proton, the o-nitrophenoxide ion left behind is stabilized by resonance and thus making o-nitro phenol a stronger acid.

In contrast, due to the +R effect of methoxy group increases the electron density in the O-H bond. Thereby making the loss of proton difficult.

Now, the o-methoxyphenoxide ion left after the loss of a proton is destabilized by resonance. The two negative charges repel each other, thereby destabilizing the o-methoxyphenoxide ion.



Therefore, o-nitrophenol is more acidic than o-methoxyphenyl.

Q.16 Explain how does the –OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?

Answer: The –OH group is an electron donating group. Thus, it increases the electron density in the benzene ring as shown by its resonating structure of phenol.



As a result benzene ring is activated towards electrophilic substitution.

Q.17A Give equations of the following reactions:

Oxidation of propan-1-ol with an alkaline KMnO<sub>4</sub> solution.

Answer: Oxidation of propane-1-ol with alkaline  $KMnO_4$  solution gives propanoic acid as the product. As the oxidation of primary alcohol gives carboxylic acid as the major product in the presence of a strong oxidizing reagent. And here  $KMnO_4$  is a very strong oxidizing agent.

$$R - CH_2 - OH \xrightarrow{[0]} R - C \xrightarrow{OH}$$

Primary alcoholcarboxylic acid $[O] = KMnO_4$ , jones oxidation, PDC in DMF,<br/>Heyns oxidation,  $RuO_4$  or TEMPO

Q.17B Give equations of the following reactions: Bromine in  $CS_2$  with phenol.

Answer: A mixture of o-bromo phenol and p-bromo phenol is formed. The formation of 2 products depends totally on the reaction conditions.



Q.17C Give equations of the following reactions:

Dilute HNO<sub>3</sub> with phenol.

Answer: Dilute HNO<sub>3</sub> with phenol.

Only dilute acid will be required for the nitration of phenol, nitric acid contains a small amount of nitrous acid which because of the activation of the ring will be more than enough to nitrate the phenol. Two products are formed 2-nitrophenol (ortho) and 4-nitrophenol (para).



Q.17D Give equations of the following reactions: Treating phenol with chloroform in presence of aqueous NaOH Answer: Treating Phenol with chloroform in presence of aqueous NaOH results in the formation of salicylaldehyde(Reimer-Tiemann reaction)



Q.18A Explain the following with an example.

Kolbe's reaction.

Answer: Kolbe's Reaction: it is a carboxylation chemical reaction that proceeds by heating sodium phenoxide(the sodium salt of phenol)with carbon dioxide under pressure(100 atm,125°C), then treating the product with a sulphuric acid. The final product is salicylic acid (the precursor to aspirin).

The reaction is given as:



The mechanism is given below:



Q.18B Explain the following with an example. Reimer-Tiemann reaction.

Answer: **<u>Reimer-Tiemann reaction:</u>** The Reimer Tiemann reaction is a chemical reaction used for the ortho-formylation of phenols, with the simplest example being the conversion of phenol to salicylaldehyde.

When phenol is treated at 340K with chloroform and alkali, it forms salicylaldehyde.



Q.18C Explain the following with an example.

Williamson ether synthesis.

Answer: Williamson ether synthesis: It is an organic reaction forming ether from an organohalide and a deprotonated alcohol (alkoxide). Typically it involves the reaction of an alkoxide ion with primary alkyl halide via  $S_N 2$  reaction.



During this reaction, the main bonds broken is the C-Br bond and the new bonds formed are "C-O" bond.

Q.18D Explain the following with an example.

Unsymmetrical ether

Answer: Unsymmetrical ether: It is an ether in the molecule of which the two ligands on the ether group are different.

Eg.



Q.19 Write the mechanism of acid dehydration of ethanol to yield ethene **Answer:** The mechanism of acid dehydration of ethanol to yield ethane involves three steps:

Step 1:- Protonation of ethanol to form ethyl oxonium ion.



Step 3:-Elimination of a proton to form ethane



The acid consumed in step 1 is released in step 3. After the formation of ethane, it is removed to shift the equilibrium in a forward direction.

Q.20A How are the following conversions carried out? Propene  $\rightarrow$  Propane-2-ol.

Answer: The conversion of Propene to propane-2-ol takes place according to markovnikoff rule. The positive part of  $H_2O$  that is H+ goes to the carbon which has more hydrogen and the negative part that is OH-goes to carbon that has less number of carbons.

$$CH_3 - CH = CH_2 \xrightarrow{H_2O} CH_3 - CH - CH_3$$

Propane

OH Propane-2-ol

Q.20B How are the following conversions carried out? Benzyl chloride  $\rightarrow$  Benzyl alcohol.

Answer: NaOH act as a base in the conversion of benzyl chloride to benzyl alcohol. On hydrolysis removal of NaCl takes place and OH is inserted in place of Cl.



Q.20C How are the following conversions carried out? Ethyl magnesium chloride  $\rightarrow$  Propane-1-ol. Answer:

Ethyl magnesium chloride (Grignard reagent) attacks on the carbon of the formaldehyde.(The partial positive and negative charge is because of the electronegativity difference). After the formation of the addition product, hydrolysis takes place which further results in the formation of propane-1-ol and Mg(OH)Cl as the byproduct.

Dry ether CH3CH2-MgCl CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OMgC Addition product Formaldehyde CH3CH2CH2OH+Mg(OH)Cl Propan-1-ol

Q.20D How are the following conversions carried out? Methyl magnesium bromide  $\rightarrow$  2-Methylpropan-2-ol Answer: Attack of methyl magnesium bromide (Grignard reagent) on

carbonyl carbon results in the formation of adduct, which has partial charges due to electronegativity differences. The adduct on hydrolysis yields 2-methylpropan2-ol.

$$H_{3}C = O + CH_{3} - MgBr \longrightarrow \begin{bmatrix} CH_{3} \\ -I \\ CH_{3} - C \\ -OMgBr \\ CH_{3} \end{bmatrix}$$
Adduct
$$H_{2}O \qquad OH$$

$$Mg (OH) Br + CH_{3} - C \\ -CH_{3} \\ CH_{3} \end{bmatrix}$$

$$2 - Methylpropan - 2 - ol$$

**Q.21A** Name the reagents used in the following reactions: Oxidation of a primary alcohol to carboxylic acid. Answer: Acidified  $KMnO_4$ (potassium permanganate)

Potassium permanganate is a strong oxidant and is able to react with many functional groups. Here KMnO4 will readily react with primary carbon (where hydrogen is attached) and transforms that to acid.

Q.21B Name the reagents used in the following reactions:

Oxidation of a primary alcohol to an aldehyde.

Answer: PCC (Pyridinium Chlorochromate)

This is actually a milder version of chromic acid. This works as a sort of elimination reaction. The formation of aldehyde occurs because of the action chromium (a good leaving group) which will be replaced when the C-H bond is broken.

Q.21C Name the reagents used in the following reactions: Bromination of phenol to 2,4,6-tribromophenol.

Answer: Bromine water

Bromine water is actually an aqueous form of bromine. Here in aqueous solution, phenol ionizes to form phenoxide ion due to the presence of negative charge, the oxygen of phenoxide ion donates electron on benzene ring to a large extent, as a result, the ring gets highly activated and hence tri-substituion occurs.

Q.21D Name the reagents used in the following reactions: Benzyl alcohol to benzoic acid.

# Answer: Acidified KMnO<sub>4</sub>

(potassium permanganate)

Potassium permanganate is a strong oxidant and oxidizes benzyl alcohol to benzoic acid. The compound is used due to its high oxidation power and the reaction proceeds due to the presence of hydrogen attached to the carbon group (Benzylic position)

Q.21E Name the reagents used in the following reactions:

Dehydration of propan-2-ol to propene.

**Answer:** Conc.Sulphuric acid or concentrated Phosphoric acid Alcohols are amphoteric. So, the lone pair of oxygen atoms makes the -OH group weakly basic. Thus, in the presence of a strong acid, R—OH acts as a base and protonates into the very acidic alkyloxonium ion +OH2.This basic characteristic of alcohol necessarily helps in conversion to propene when dehydrated with a strong acid.

Q.21F Name the reagents used in the following reactions:

Butan-2-one to butan-2-ol.

Answer: L<sub>i</sub>AlH<sub>4</sub> (lithium aluminum hydride) or NaBH<sub>4</sub>.

Both compounds are best-reducing agents containing 4 Hydrogen atoms each. In reaction with a ketone, the double bond is reduced and hydrogen atoms are substituted to form alcohol.

Q.22 Give a reason for the higher boiling point of ethanol in comparison to methoxymethane.

Answer: Due to the presence of -OH group, ethanol undergoes intermolecular hydrogen bonding which results in the association of molecules.



Therefore, extra energy is required to break those hydrogen bonds. Whereas methoxymethane does not undergo those hydrogen bonding which implies ethanol has a higher boiling point than that of methoxymethane.

Q.23A Give IUPAC names of the following ethers:

$$C_2H_5OCH_2 - CH - CH_3$$
$$CH_3$$

#### Answer :

1-Ethoxy-2-methylpropane

The carbonyl group takes precedence over alkyl groups and halogen substituents, as well as double bonds, in the numbering of the parent chain. When there is a choice the parent chain is numbered to give the substituents the lowest number at the first point of difference.

Q.23B Give IUPAC names of the following ethers:

## CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>Cl

Answer: 2-Chloro-1-methoxyethane

The carbonyl group takes precedence over alkyl groups and halogen substituents, as well as double bonds, in the numbering of the parent chain. Q.23C Give IUPAC names of the following ethers:

```
O<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-OCH<sub>3</sub>(p)
```

# Answer:

4-Nitroanisole

In cyclic ketones, the carbonyl group is assigned location position 1, and this number is not included in the name unless more than one carbonyl group are present. The rest of the ring is numbered to give substituents the lowest possible location numbers.

Q.23D Give IUPAC names of the following ethers:

```
CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>
```

# Answer:

1-Methoxypropane

The carbonyl group takes precedence over alkyl groups and halogen substituents, as well as double bonds, in the numbering of the parent chain.

Q.23E Give IUPAC names of the following ethers:



Answer: 1-Ethoxy-4,4-dimethylcyclohexane

In cyclic ketones, the carbonyl group is assigned location position 1, and this number is not included in the name unless more than one carbonyl group is present. The rest of the ring is numbered to give substituents the lowest possible location numbers.

Q.23F Give IUPAC names of the following ethers:



Answer: Ethoxy benzene.

In cyclic ketones, the carbonyl group is assigned location position 1, and this number is not included in the name unless more than one carbonyl group is present. The rest of the ring is numbered to give substituents the lowest possible location numbers.

Q.24A Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

1-Propoxypropane.

## Answer:

 $\begin{array}{ll} CH_3CH_2\text{CHONa} + CH_3CH_2CH_2Br \rightarrow C_2H_5CH_2 - O - CH_2C_2H_5 + \text{NaBr} \\ \text{Sodium propoxide} & 1\text{-Bromopropane} & 1\text{-Propoxypropane} \\ \text{During the reaction, an alkoxide ion is formed which is then added to an} \\ \text{alkyl halide to form the ether via } S_N2 \text{ mechanism.} \end{array}$ 

In the primary step, the nucleophile is formed  $(O^-)$  which will the approach to the alkyl halide and after the transition stage, the substitution takes place.

Q.24B Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

Ethoxybenzene

Answer:



During the reaction, an alkoxide ion is formed which is then added to an alkyl halide to form the ether via  $S_N 2$  mechanism.

Q.24C Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

2-Methoxy-2-methylpropane

Answer;

$$CH_{3} \longrightarrow CH_{3} \longrightarrow C$$

During the reaction, an alkoxide ion is formed which is then added to an alkyl halide to form the ether via  $S_N 2$  mechanism.

Q.24D Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

1-Methoxyethane

Answer:

 $CH_3CH_2 - ONa + CH_3 - Br \rightarrow CH_3CH_2 - O - CH_3 + NaBr$ 

Sodium ethoxide Bromomethane 1-Methoxyethane

During the reaction, an alkoxide ion is formed which is then added to an alkyl halide to form the ether via  $S_N 2$  mechanism.

Q.25 Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.

#### Answer:

Williamson synthesis is basically a  $S_N 2$  reaction of a primary alkyl halide with an alkoxide ion. The basic mechanism for this reaction is



Now consider this reaction,

 $CH_{3} - \overset{CH_{3}}{\underset{l}{\overset{l}{\underset{CH_{3}}{\overset{l}{\underset{CH_{3}}{\overset{d}{\underset{CH_{3}{I}{\underset{CH_{3}}{\\{L}{1}{L}{1}{L}{1}{L}{1}{L}}{L}{1}{L}{1}{L}{1}{L}{1}{L}{1}{L}{1}{L}{1}{L}{1}{L}{1}{L}{1$ 

This reaction proceeds as conventional Williamson synthesis. But if secondary or tertiary alkyl halides are taken in place of primary alkyl halides, then elimination would compete over substitution reaction, which will result in the formation of alkenes. The reason is alkoxides are better nucleophiles as well as strong bases. Therefore, they react with alkyl halides resulting in an elimination reaction.

$$CH_{3} - \overset{CH_{3}}{\overset{l}{\underset{CH_{3}}{\leftarrow}}} - CI + Na\overset{\widetilde{O}}{\overset{O}{\underset{CH_{3}}{\leftarrow}}} - CH_{3} \longrightarrow CH_{3} - \overset{C}{\underset{CH_{3}}{\leftarrow}} CH_{2} + CH_{3}OH + NaCI$$

Q.26 How is 1-proposypropane synthesized from propan-1-ol? Write mechanism of this reaction.

Answer:

According to the question we have to perform the following conversion: -

$$H_3C - c - c - OH \longrightarrow H_3C - c - c - o - c - c - CH_3$$
  
Propan - 1-ol 1 - Propoxypropane

The above conversion can be done easily by dehydrating 1- propanol with  $conc.H_2SO_4$  at 413 K.

 $H_{3}C \longrightarrow C \longrightarrow C \longrightarrow OH \xrightarrow{Conc.H_{2}SO_{4}} H_{3}C - C - C - O - C - C - CH_{3}$   $H_{2} \qquad H_{2}$   $H_{2} \qquad H_{2}$   $Propan - 1 - ol \qquad 1- Proposypropane$ 

The mechanism of the above reaction is as follows : -

The mechanism is given below: -

In the first step, the alcohol gets protonated by the acid present to give a protonated alcohol.



In the second step, the nucleophilic attack of another alcohol molecule on the protonated alcohol gives us 1-propoxypropane as the desired product.



Q.27 Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

Answer:

The preparation of ether by acid dehydration of primary alcohol involves the nucleophilic addition of alcohol molecule to the protonated alcohol molecule as shown below: -



However, under these conditions secondary and tertiary alcohols forms alkenes rather than ethers. The reason for this being that due to stearic hindrance, nucleophilic attack by the alcohol molecule on the protonated alcohol molecule does not take place. Instead protonated  $2^0$  and  $3^0$  alcohols lose a molecule of water to form stable carbocations. The stable carbocations so formed prefers to lose a proton to form alkenes instead of forming ethers by undergoing nucleophilic attack by another alcohol molecule. This could be seen clearly from the following reactions :-





Q.28A Write the equation of the reaction of hydrogen iodide with:

#### 1-propoxypropane

Answer: 1-propoxypropane reacts with hydrogen iodide to give propan-1-ol and 1-iodopropane as the products.



Q.28B Write the equation of the reaction of hydrogen iodide with:

methoxybenzene and

Answer: Methoxybenzene reacts with hydrogen iodide to give phenol and iodomethane.



Q.28C Write the equation of the reaction of hydrogen iodide with: benzyl ethyl ether.

#### Answer:

Benzyl ethyl ether reacts with hydrogen iodide to give benzyl iodide and ethanol.



Q.29 Explain the fact that in aryl alkyl ethers (i) the alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming substituents to ortho and para positions in the benzene ring.

Answer:

(i) In aryl alkyl ethers the +R effect of the alkoxy group leads to an increase in the electron density of the benzene ring as they push electrons into the ring making the benzene ring activated towards electrophilic substitution reactions. This could be understood more clearly from the following resonating structures : -



(ii) It could be clearly seen from the above resonating structures that the electron density increases more at the ortho and para positions as compared to the meta positions. Hence, we can conclude that the alkoxy group directs the incoming substituents to ortho and para positions in the benzene ring.

For example -



Q.30 Write the mechanism of the reaction of HI with methoxymethane.

#### Answer:

The reaction of HI with methoxymethane yields two different sets of products depending upon the initial amount of HI taken.

(i) When equal moles of HI and methoxymethane are taken, a mixture of methyl alcohol and methyl iodide is formed.

The mechanism is given below:

In the first step, methoxymethane reacts with hydrogen iodide to extract a proton to give the dimethyloxonium ion.



In the second step of the reaction, the Dimethyloxonium ion reacts with the iodide ion present to yield methyl iodide and methyl alcohol as the product via  $SN^2$  pathway.



(ii) If an excess of HI is used the methyl alcohol formed in Step II is also converted into methyl iodide by the following mechanism : -

In the first step, methoxymethane reacts with hydrogen iodide to extract a proton to give the dimethyloxonium ion.



In the second step of the reaction the Dimethyloxonium ion reacts with the iodide ion present to yield methyl iodide and methyl alcohol as the product via SN2 pathway.



In the third step of the reaction Methyl alcohol formed above reacts with hydrogen iodide to extract a proton to give the protonated methyl alcohol which finally reacts in the fourth step with the iodide ion via SN2 pathway to give methyl iodide and water as the product.



Q.31A Write equations of the following reactions:

Friedel-Crafts reaction – alkylation of anisole.

Answer: The driving force of all the reactions given to the question is that the alkoxy group is an ortho and para directing group because it exerts its +R effect in the benzene ring. Para position being comparatively more stable than the ortho position is usually preferred because ortho position leads to stearic hindrance, hence the major product is mostly the parasubstituted compound.



As seen from the resonating structures above the structure in which the negative charge is in the para position will form a more stable product when attacked by an electrophile. Hence in the following reactions, we will be considering that resonating structure as the starting material.

The Friedel-Crafts alkylation of anisole gives p-methylanisole as the major product.



# The mechanism is given below:

Step - I



Q.31B Write equations of the following reactions: Nitration of anisole.

**Answer;** The driving force of all the reactions given to the question is that the alkoxy group is an ortho and para directing group because it exerts its +R effect in the benzene ring. Para position being comparatively more stable than the ortho position is usually preferred because ortho position leads to stearic hindrance, hence the major product is mostly the parasubstituted compound.



As seen from the resonating structures above the structure in which the negative charge is in the para position will form a more stable product when attacked by an electrophile. Hence in the following reactions, we will be considering that resonating structure as the starting material.

Nitration of anisole gives p-nitroanisole as the major product.



#### The mechanism is given below:

Step-I

#### Step- II



Q.31C Write equations of the following reactions:

Bromination of anisole in ethanoic acid medium.

Answer: The driving force of all the reactions given to the question is that the alkoxy group is an ortho and para directing group because it exerts its +R effect in the benzene ring. Para position being comparatively more stable than the ortho position is usually preferred because ortho position leads to stearic hindrance, hence the major product is mostly the parasubstituted compound.



As seen from the resonating structures above the structure in which the negative charge is in the para position will form a more stable product when attacked by an electrophile. Hence in the following reactions, we will be considering that resonating structure as the starting material.

Bromination of anisole in ethanoic acid medium gives p-bromoanisole as the major product.



Q.31D Write equations of the following reactions: Friedel-Craft's acetylation of anisole.

#### Answer:

The driving force of all the reactions given to the question is that the alkoxy group is an ortho and para directing group because it exerts its +R effect in the benzene ring. Para position being comparatively more stable than the ortho position is usually preferred because ortho position leads to stearic hindrance, hence the major product is mostly the para-substituted compound.



As seen from the resonating structures above the structure in which the negative charge is in the para position will form a more stable product when attacked by an electrophile. Hence in the following reactions, we will be considering that resonating structure as the starting material.

The Friedel-Craft's acetylation of anisole gives 4- methoxyacetophenone as the major product.



The mechanism is given below:



Q.32A Show how would you synthesise the following alcohols from appropriate alkenes?

# ОН ОН

Answer: We know that the addition and elimination reactions are opposite of each other.Hence, for solving the above questions our approach should be to first dehydrate a suitable alcohol to give either a single alkene or a mixture of an alkene, if we obtain a mixture of alkene then we would have to detect which of the alkene will give us the desired alcohol. Wherever required the acid-catalyzed addition of water to alkenes will follow Markovnikov's rule.



Addition of H<sub>2</sub>O to both of these alkenes gives us the desired alcohol.



1-methylcyclohexan-1-ol

Q.32B Show how would you synthesise the following alcohols from appropriate alkenes?

OH

Answer: We know that the addition and elimination reactions are opposite of each other. Hence, for solving the above questions our

approach should be to first dehydrate a suitable alcohol to give either a single alkene or a mixture of an alkene, if we obtain a mixture of alkene then we would have to detect which of the alkene will give us the desired alcohol. Wherever required the acid-catalyzed addition of water to alkenes will follow Markovnikov's rule.



Q.32C Show how would you synthesise the following alcohols from appropriate alkenes?



Answer: We know that the addition and elimination reactions are opposite of each other.Hence, for solving the above questions our approach should be to first dehydrate a suitable alcohol to give either a single alkene or a mixture of an alkene, if we obtain a mixture of alkene then we would have to detect which of the alkene will give us the desired alcohol. Wherever required the acid-catalyzed addition of water to alkenes will follow Markovnikov's rule.


Now, upon addition of H<sub>2</sub>O to pent-1-ene we obtain the desired product.



But the addition of  $H_2O$  to pent-2-ene gives us a mixture of two alcohols out of which one is desired and the other one undesired.



Hence, the alkene to be chosen to arrive at the desired alcohol as the product should be pent-1-ene as it gives only a single product which is the desired alcohol.

Q.32D Show how would you synthesise the following alcohols from appropriate alkenes?



## Answer:

We know that the addition and elimination reactions are opposite of each other.Hence, for solving the above questions our approach should be to first dehydrate a suitable alcohol to give either a single alkene or a mixture of an alkene, if we obtain a mixture of alkene then we would have to detect which of the alkene will give us the desired alcohol. Wherever required the acid-catalyzed addition of water to alkenes will follow Markovnikov's rule.

As addition is the reverse of elimination we first dehydrate our required product to obtain –



Now, if we add  $H_2O$  to either of the three alkenes in presence of an acid we get the desired alcohol.



Q.33 When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place:

$$\begin{array}{cccc} & & & & & & & & \\ CH_3 - CH - CH - CH_3 & CH_3 & \xrightarrow{HBr} & CH_3 - C - CH_3 - CH_3 \\ & & & CH_3 & OH & CH_3 \end{array}$$

Give a mechanism for this reaction.

(Hint: The secondary carbocation formed in step II rearranges to a more stable tertiary carbocation by a hydride ion shift from 3rd carbon atom.)

## Answer:

The first step in the mechanism of the given reaction is protonation of the alcohol followed by loss of water to give a  $2^0$  carbocation.



The next step is a rearrangement of the  $2^{0}$  carbocations formed in the above step is less stable it rearranges by a 1,2-hydride shift to form more stable  $3^{\circ}$  carbocations.



The last step of the reaction is the nucleophilic attack of  $Br^-$  ion on the  $3^\circ$  carbocations giving the final product.

