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## Chapter-11 Alcohols, Phenols & Ethers Class-XII Subject-Chemistry

#### 11.1 Write IUPAC names of the following compounds:



**(ii)** 

| H <sub>3</sub> С—СН— | H <sub>2</sub> —CH—CH—CH <sub>2</sub> —CH <sub>3</sub> |
|----------------------|--|
| ОН                   | I I<br>ОН С <sub>2</sub> н <sub>5</sub>                |

(iii)

(iv)

**(v)** 



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(vi)



(vii)



(viii)



(ix)

$$C_6H_5 - O - C_2H_5$$

(xi)

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$$C_{6}H_{5} - O - C_{7}H_{15}(n -)$$

(xii)



#### Answer 11.1

- (i) 2, 2, 4-Trimethylpentan-3-ol
- (ii) 5-Ethylheptane-2, 4-diol
- (iii) Butane-2, 3-diol
- (iv) Propane-1, 2, 3-triol
- (v) 2-Methylphenol
- (vi) 4-Methylphenol
- (vii) 2, 5-Dimethylphenol
- (viii) 2, 6-Dimethylphenol

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- (ix) 1-Methoxy-2-methylpropane
- (x) Ethoxybenzene
- (xi) 1-Phenoxyheptane
- (xii) 2-Ethoxybutane

#### 11.2 Write structures of the compounds whose IUPAC names are as follows:

- (i) 2-Methylbutan-2-ol
- (ii) 1-Phenylpropan-2-ol
- (iii) 3,5-Dimethylhexane –1, 3, 5-triol
- (iv) 2,3 Diethylphenol
- (v) 1 Ethoxypropane
- (vi) 2-Ethoxy-3-methylpentane
- (vii) Cyclohexylmethanol
- (viii) 3-Cyclohexylpentan-3-ol
- (ix) Cyclopent-3-en-1-ol
- (x) **3-Chloromethylpentan-1-ol.**

#### Answer 11.2

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(i) 2-Methylbutan-2-ol



(ii) 1-Phenylpropan-2-ol



(iii) 3,5-Dimethylhexane –1, 3, 5-triol



(iv) 2,3 – Diethylphenol



(v) 1 – Ethoxypropane

$${\rm CH}_{3}-{\rm CH}_{2}-{\rm O}-{\rm CH}_{2}-{\rm CH}_{2}-{\rm CH}_{3}$$

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(vi) 2-Ethoxy-3-methylpentane



(vii) Cyclohexylmethanol



(viii) 3-Cyclohexylpentan-3-ol



(ix) Cyclopent-3-en-1-ol



(x) 3-Chloromethylpentan-1-ol



### 11.3

- (i) Draw the structures of all isomeric alcohols of molecular formula  $C_5H_{12}O$ and give their IUPAC names.
- (ii) Classify the isomers of alcohols in question 11.3 (i) as primary, secondary and tertiary alcohols.

#### Answer 11.3

(i) The structures of isomers of  $C_5H_{12}O$  are:





#### (ii) **Primary alcohol**:

Pentan-1-ol; 2-Methylbutan-1-ol; 3-Methylbutan-1-ol; 2, 2-Dimethylpropan-1-ol

#### Secondary alcohol:

Pentan-2-ol; 3-Methylbutan-2-ol; Pentan-3-ol

#### **Tertiary alcohol**:

2-methylbutan-2-ol

# 11.4 Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

#### Answer 11.4

Propanol contains intermolecular H-bonding because of the presence of –OH group. But in butane, there is no hydrogen bonding is present.



Thus, to break hydrogen bonds, extra energy is required. Hence, propanol has a higher boiling point than butane.

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

#### Answer 11.5

In case of alcohol, Hydrogen-bonding is formed with water because of the presence of –OH group. But in hydrocarbons, it is not possible.

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As a result, alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses.

#### 11.6 What is meant by hydroboration-oxidation reaction? Illustrate it with an example.

#### Answer 11.6

Hydroboration-oxidation reaction: Addition of borane followed by oxidation is known as the hydroboration-oxidation reaction. For example: propan-1-ol is produced by the hydroboration-oxidation reaction of Propene.



11.7 Give the structures and IUPAC names of monohydric phenols of molecular formula, C<sub>7</sub>H<sub>8</sub>O.



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Simplifying Test Prep

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

#### Answer 11.8

In *o*-nitrophenol, intramolecular Hydrogen-bonding is present. On the other hand, in case of *p*-nitrophenol, the molecules are strongly associated due to the presence of intermolecular bonding. Thus, *o*-nitrophenol is steam volatile.



#### 11.9 Give the equations of reactions for the preparation of phenol from cumene.

#### Answer 11.9

Preparation of phenol:

Step 1: Cumene is first oxidized in the presence of air & forms cumene hydroperoxide.



Step 2: Cumene hydroxide is treated with dilute acid to prepare phenol.

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#### 11.10 Write chemical reaction for the preparation of phenol from chlorobenzene.

#### **Answer 11.10**

Preparation of phenol: Chlorobenzene is fused with NaOH (at 623 K and 320 atm pressure) to produce sodium phenoxide, which gives phenol on acidification.



#### 11.11 Write the mechanism of hydration of ethene to yield ethanol.

#### **Answer 11.11**

Mechanism of hydration of ethene:

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



Step 2: Nucleophilic attack of water on carbocation

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Step 3: Deprotonation to form ethanol



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

#### **Answer 11.12**

Preparation of phenol:



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11.13 Show how you will synthesize:

- (i) 1-phenylethanol from a suitable alkene.
- (ii) Cyclohexylmethanol using an alkyl halide by an  $S_N 2$  reaction.
- (iii) Pentan-1-ol using a suitable alkyl halide?

#### **Answer 11.13**

(i) Acid-catalyzed hydration of ethylbenzene :



(ii) Reaction with sodium hydroxide:



(iii) When 1-chloropentane is treated with NaOH, pentan-1-ol is produced.

 $CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}Cl + NaOH \rightarrow CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}OH + NaCl$ 1-Chloropentane Pantan-1-ol

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

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#### **Answer 11.14**

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

(i) On reaction with sodium, phenol forms sodium phenoxide.



(ii) On reaction with sodium hydroxide, phenol produces sodium phenoxide.



Acidity of phenol is more than that of ethanol because after losing a proton, the phenoxide ion undergoes resonance and gets stabilized. But ethoxide ion does not.



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Simplifying Test Prep

#### 11.15 Explain why is *ortho* nitrophenol more acidic than *ortho* methoxyphenol?

**Answer 11.15** 



We know that, nitro-group is an electron-withdrawing group. Its presence in the ortho position decreases the electron density in the O–H bond. Because of which, it loses proton easily. Also, this ion is stabilized by resonance. Hence, *ortho* nitrophenol is a stronger acid.

On the other hand, methoxy group is an electron-releasing group. Hence, it increases the electron density in the O–H bond. Because of this, the proton cannot be releases easily.

Hence, ortho-nitrophenol is more acidic than ortho-methoxyphenol.

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

#### **Answer 11.16**



We know that, -OH group is an electron-donating group. Hence, it increases the electron density on the benzene ring.

As a result, the benzene ring is activated towards electrophilic substitution.

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**11.17** Give equations of the following reactions:

- (i) Oxidation of propan-1-ol with alkaline KMnO<sub>4</sub> solution.
- (ii) Bromine in  $CS_2$  with phenol.
- (iii) Dilute HNO<sub>3</sub> with phenol.
- (iv) Treating phenol with chloroform in presence of aqueous NaOH.

#### **Answer 11.17**

(i) 
$$\begin{array}{c} CH_{3}CH_{2}CH_{2}OH \xrightarrow{\text{Alk. } KMnO_{4}} CH_{3}CH_{2}COOH \\ Propan-1-ol Propanoic acid \end{array}$$



(iii)



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#### 11.18 Explain the following with an example.

- (i) Kolbe's reaction
- (ii) Reimer-Tiemann reaction
- (iii) Williamson ether synthesis
- (iv) Unsymmetrical ether

#### **Answer 11.18**

#### (i) Kolbe's reaction:

Step 1: Phenol is treated with sodium hydroxide & produces sodium phenoxide.

Step 2: This sodium phenoxide when treated with carbon dioxide, followed by acidification, undergoes electrophilic substitution to give ortho-hydroxybenzoic acid as the main product.

This reaction is known as Kolbe's reaction.

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#### (ii) Reimer-Tiemann reaction:

In the presence of sodium hydroxide, phenol is treated with chloroform & introduces –CHO group at the ortho position of the benzene ring.



This reaction is known as the Reimer-Tiemann reaction.

The intermediate is hydrolyzed in the presence of alkalis to produce salicyclaldehyde.



#### (iii) Williamson ether synthesis:

It is a laboratory method to prepare symmetrical and unsymmetrical ethers.

Alkyl halide is reacted with sodium alkoxides & forms ether.

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 $R'-O-Na + R-X \rightarrow R-O-R'+NaX$ Sodium alkoxide Alkyl Ether halide

This reaction involves S<sub>N</sub>2 attack of the alkoxide ion on the alkyl halide.

$$\begin{array}{c} \begin{array}{c} CH_{3} \\ I \\ CH_{3} - CH - \overset{}{\overset{}{\underset{0}{0}}} \overset{}{\overset{}{\underset{n}{n}}} \overset{}{\overset{}{\underset{0}{n}}} \overset{}{\underset{n}{n}} \overset{}{\underset{n}{n}{n}} \overset{}{\underset{n}{n}} \overset{}{\underset{n}{n}} \overset{}{\underset{n}{n}} \overset{}{\underset{n}{n}}$$

If the alkyl halide is secondary or tertiary, then elimination competes over substitution.

#### (iv) Unsymmetrical ether:

It is the ether where two groups on the two sides of an oxygen atom differ means unequal number of carbon atoms. For example: ethyl methyl ether  $(CH_3-O-CH_2CH_3)$ .

#### 11.19 Write the mechanism of acid-catalysed dehydration of ethanol to yield ethene.

#### **Answer 11.19**

Mechanism of acid dehydration of ethanol:

**Step 1:** Protonation of ethanol to form ethyl oxonium ion:



Step 2: Formation of carbocation (rate determining step):

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**Step 3:** Elimination of a proton to form ethene:



The acid which got consumed in step 1 is released in Step 3. For increasing the formation of ethene, it is removed to shift the equilibrium in a forward direction.

#### 11.20 How are the following conversions carried out?

- (i) **Propene**  $\rightarrow$  **Propan-2-ol**
- (ii) Benzyl chloride  $\rightarrow$  Benzyl alcohol
- (iii) Ethyl magnesium chloride  $\rightarrow$  Propan-1-ol
- (iv) Methyl magnesium bromide  $\rightarrow$  2-Methylpropan-2-ol.

#### **Answer 11.20**

(i) Propene react with water in the presence of acid & forms propan-2-ol is obtained.

$$CH_3 - CH = CH_2 + H_2O \xrightarrow{H^+} CH_3 - CH - CH_3$$
  
|  
OH  
Propene Propan - 2 - ol

(ii) If benzyl chloride is treated with NaOH, benzyl alcohol is produced.

#### 

(iii) Ethyl magnesium chloride is treated with methanol & adduct is the produced which gives propan-1-ol on hydrolysis.



(iv) Methyl magnesium bromide is treated with propane & adduct is formed which on hydrolysis gives 2-methylpropane-2-ol.



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**11.21** Name the reagents used in the following reactions:

- (i) Oxidation of a primary alcohol to carboxylic acid.
- (ii) Oxidation of a primary alcohol to aldehyde.
- (iii) Bromination of phenol to 2, 4, 6-tribromophenol.
- (iv) Benzyl alcohol to benzoic acid.
- (v) Dehydration of propan-2-ol to propene.
- (vi) Butan-2-one to butan-2-ol.

#### **Answer 11.21**

- (i) Acidified potassium permanganate
- (ii) Pyridinium chlorochromate (PCC)
- (iii) Bromine water
- (iv) Acidified potassium permanganate
- (v) 85% phosphoric acid
- (vi) NaBH<sub>4</sub> or LiAlH<sub>4</sub>

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# **11.22** Give reason for the higher boiling point of ethanol in comparison to methoxymethane.

#### **Answer 11.22**

Ethanol forms intermolecular H-bonding because of the presence of –OH group. It results in the association of molecules. Extra energy is required to break these hydrogen bonds. In the case of methoxymethane, H-bonding is absent. Thus, the boiling point of ethanol is higher than that of methoxymethane.



#### **11.23** Give IUPAC names of the following ethers:

(i)

(ii)

(iii)

$$O_2N - C_6H_4 - OCH_3(p)$$

(iv)



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#### **Answer 11.23**

- (i) 1-Ethoxy-2-methylpropane
- (ii) 2-Chloro-1-methoxyethane
- (iii) 4-Nitroanisole
- (iv) 1-Methoxypropane
- (v) 1-Ethoxy-4, 4-dimethylcyclohexane
- (vi) Ethoxybenzene



Simplifying Test Prep

- **11.24** Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:
  - (i) **1-Propoxypropane**
  - (ii) Ethoxybenzene
  - (iii) 2-Methoxy-2-methylpropane
  - (iv) 1-Methoxyethane

#### **Answer 11.24**



(iv)

$$CH_{3}CH_{2} - ONa + CH_{3} - Br \rightarrow CH_{3}CH_{2} - O - CH_{3} + NaBr$$
  
Sodium ethoxide 1-methoxyethane



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

#### **Answer 11.25**

Williamson synthesis:

It involves  $S_N 2$  attack of an alkoxide ion on a primary alkyl halide.

$$CH_{3} - \overset{CH_{3}}{\underset{CH_{3}}{\overset{l}{\leftarrow}}} - \overset{CH_{3}}{\overset{n}{\overset{o}{o}}} \overset{R}{\underset{Na}{\overset{h}{\rightarrow}}} + CH_{3} - Cl \longrightarrow CH_{3} - \overset{CH_{3}}{\underset{CH_{3}}{\overset{l}{\leftarrow}}} - \overset{CH_{3}}{\underset{CH_{3}}{\overset{l}{\leftarrow}}} + NaC$$

But if secondary or tertiary alkyl halides are taken, then elimination competes over substitution. As a result of which alkenes are produced.

This happens because alkoxides are nucleophiles as well as strong bases.

$$\begin{array}{c} CH_{3} \\ CH_{3} - \overset{I}{C} - CI \\ \downarrow \\ CH_{3} \\ \end{array} \xrightarrow{} CH_{3} - CH_{3} \xrightarrow{} CH_{3} - CH_{3} \xrightarrow{} CH_{3} - CH_{2} + CH_{3}OH + NaCl \\ \downarrow \\ CH_{3} \\ \end{array}$$
Tertiary alkyl halide Alkene

# 11.26 How is 1-propoxypropane synthesised from propan-1-ol? Write mechanism of this reaction.

#### **Answer 11.26**

In the presence of protic acids, Propan-1-ol undergoes dehydration reaction

 $2CH_{3}CH_{2}CH_{2} - OH \xrightarrow{H^{+}} CH_{3}CH_{2}CH_{2} - O - CH_{2}CH_{2}CH_{3}$ Propan-1-ol 1-Propoxypropane

Mechanism:

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Step 1: Protonation



**Step 2:** Nucleophilic attack



Step 3: Deprotonation



# **11.27** Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

#### **Answer 11.27**

Acid dehydration: Formation of ethers by dehydration of alcohol is a bimolecular reaction ( $S_N$ 2). It involves the attack of an alcohol molecule on a protonated alcohol molecule. In this method, alkyl group should be unhindered.

In case of secondary or tertiary alcohols, the alkyl group is hindered. Because of which, elimination dominates substitution. Thus, in spite of ether alkenes are formed

#### 11.28 Write the equation of the reaction of hydrogen iodide with:

- (i) 1-propoxypropane
- (ii) Methoxybenzene and
- (iii) Benzyl ethyl ether

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#### **Answer 11.28**

(i)







#### 11.29 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 benzene ring.

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#### **Answer 11.29**

(i)



+R effect of the alkoxy group increases the electron density in the benzene ring.



Thus, benzene is activated towards electrophilic substitution by the alkoxy group.

(ii) We can observe from the resonance structures that the electron density increases more at the ortho and para positions than at the meta position.

It directs the incoming substituents at the ortho and para positions in the benzene ring.

#### 11.30 Write the mechanism of the reaction of HI with methoxymethane.

#### **Answer 11.30**

Mechanism of the reaction:

Step1: Protonation of methoxymethane

$$CH_3 - \ddot{O} - CH_3 + H - I \Longrightarrow CH_3 - \ddot{O}^+ - CH_3 + I^-$$

**Step2:** Nucleophilic attack of I<sup>-</sup>

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**Step3:** When HI is present in excess & the reaction is carried out at a high temperature, the methanol formed in the second step reacts with another HI molecule and gets converted to methyl iodide

$$CH_3 \longrightarrow \ddot{\mathbf{Q}} \longrightarrow H + H \longrightarrow I \implies CH_3 \longrightarrow \dot{\mathbf{Q}}^+H + I^-$$

$$I^- + CH_3 - \overset{+}{O}H_2 \rightarrow CH_3 - I + H_2O$$

#### **11.31** Write equations of the following reactions:

- (i) Friedel-Crafts reaction-alkylation of anisole.
- (ii) Nitration of anisole.
- (iii) Bromination of anisole in ethanoic acid medium.
- (iv) Friedel-Craft's acetylation of anisole.

#### **Answer 11.31**



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OCH<sub>3</sub> OCH<sub>3</sub> OCH<sub>3</sub> **(ii)** NO<sub>2</sub> H<sub>2</sub>SO HNO<sub>3</sub> NO<sub>2</sub> Anisole 2 - Nitroanisole 4 - Nitroanisole (Minor) (Major) (iii) OCH<sub>3</sub> OCH<sub>3</sub> OCH3 Br Br<sub>2</sub> in Ethanoic acid Br Anisole p - Bromoanisole o-Nitroanisole (Major) (Minor) (iv) OCH3 OCH<sub>3</sub> OCH3 COCH3 + CH<sub>3</sub>COCI Anhyd.AlCl<sub>3</sub> COCH<sub>3</sub> Anisole Ethanoyl chloride 2 - Methoxy -4 - Methoxy acetophenone acetophenone (Minor) (Major)

#### 11.32 Show how would you synthesise the following alcohols from appropriate alkenes?



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(iii)



(iv)



#### **Answer 11.32**

By applying Markovnikov's rule in acid-catalyzed hydration of alkenes, given alcohols can be synthesized



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Simplifying Test Prep

Acid-catalyzed hydration of pent-2-ene also produces pentan-2-ol but along with pentan-3-ol.



Hence, the first reaction is preferred over the second one to get pentan-2-ol.



#### 11.33 When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place:

$$\begin{array}{c} CH_{3} - CH - CH - CH_{3} \xrightarrow{HBr} CH_{3} - \begin{matrix} Br \\ | \\ CH_{3} & CH_{3} \end{matrix} \xrightarrow{CH_{3}} CH_{2} - CH_{2} - CH_{3} \\ CH_{3} & CH_{3} \end{array}$$

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 11.33**

Mechanism of the reaction:

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Step 1: Protonation

$$\begin{array}{c} CH_{3} \longrightarrow CH \longrightarrow CH_{2} \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{2} \longrightarrow CH_{3} \longrightarrow$$

Step 2: Formation of 2° carbocation by the elimination of a water molecule

$$\begin{array}{c} CH_{3} - CH - CH - CH_{3} \xrightarrow{-H_{2}O} CH_{3} - CH - \stackrel{+}{C}H - CH_{3} \\ | \\ CH_{3} \xrightarrow{|}{} OH_{2} \\ CH_{3} \\ 2^{\circ} Carbocation \end{array}$$





Step 4: Nucleophilic attack



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