



 $CH_{3} \longrightarrow O \longrightarrow CH_{2} \longrightarrow CH_{2} \longrightarrow CH_{3}$ $\downarrow \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{3} \\ CH_{5} \longrightarrow C_{2}H_{5}$

Q 2 Write IUPAC names of the following compounds:

(xi)
$$\begin{array}{c} C_{6}H_{5} - O - C_{7}H_{15}(n-) \\ CH_{3} - CH_{2} - O - CH_{7} - CH_{2} - CH_{3} \\ \\ \\ H_{3} - CH_{2} - CH_{3} \end{array}$$

(xii)

Answer 2

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

Q 3 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.

Answer3



Q 4 Draw the structures of all isomeric alcohols of molecular formula C₅H₁₂O and give their IUPAC names.

<u>Answer4</u> The structures of all isomeric alcohols of molecular formula, $C_5H_{12}O$ are shown below:

(a) Pentan-1-ol (1°)

$$CH_{3} - CH_{2} - CH_{1} - CH_{2} - OH_{1}$$

$$(b) CH_{3}$$

$$2-Methylbutan-1-ol (1^{\circ}) CH_{3} - CH_{2} - CH_{2} - OH_{1}$$

$$(c) CH_{3}$$

$$3-Methylbutan-1-ol (1^{\circ})$$

CH₃ CH₃ CH₃ CH₃ CH₂ OH CH₃ CH₂ OH CH₃ CH₂ OH (1°)

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

Pentan-2-ol (2°)

СН₃ ОН | | (f) СН₃—СН—СН—СН₃

3-Methylbutan-2-ol (2°)

Pentan-3-ol (2°)

2-Methylbutan-2-ol (3°)

Q 5 Give the IUPAC name of the following compound

$$CH_3 - C = C - CH_2OH$$
$$| \\CH_3 Br$$

Answer 2 – Bromo-3-methyl-but-2-ene-1-ol.

Q 6

Draw the structure of 2, 6-Dimethylphenol. Answer



INCOMPLETE REACTIONS

Q1 Write structures of the products of the following reactions:



Answer





Q 2 Predict the products of the following reactions:

(i)
$$CH_3 - CH_2 - CH_2 - O - CH_3 + HBr \rightarrow$$



(iv)
$$(CH_3)_3 C - OC_2 H_5 \longrightarrow$$

Answer



$$(CH_3)_3 C - OC_2H_5 \longrightarrow (CH_3)_3 C - I + C_2H_5OH$$

(iv) *tert*-Butyl ethyl ether *tert*-Butyliodide Ethanol

Complete the following reaction equations:



$$\bigcirc$$
 OH + SOCl₂ $\xrightarrow{\text{Pyridine}}$ \bigcirc Cl + SO₂ \uparrow + HCl \uparrow

(ii)



reactions:

- (a) Mononitration of 3-methylphenol
- (b) Dinitration of 3-methylphenol
- (c) Mononitration of phenyl methanoate.



 $(i) CH_{3}-CH_{2}-CH-CH_{2}-O-CH_{2}-CH_{3}$ $(i) CH_{3}-CH_{2}-CH_{2}-O-C-CH_{2}-CH_{3}$ $(ii) CH_{3}-CH_{2}-CH_{2}-O-C-CH_{2}-CH_{3}$ $(iii) CH_{3}-CH_{2}-CH_{2}-O-CH_{2}-CH_{3}$

Answer

```
(i) CH_3-CH_2-CH-CH_2OH + CH_3CH_2I

CH_3

(ii) CH_3CH_2CH_2OH + CH_3CH_2-C-I

CH_3

(iii) CH_3CH_2CH_2OH + CH_3CH_2-C-I

CH_3
```

(iii)
$$\sim$$
 CH₂I + \sim OH

Q 5 Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane\starting from ethanol and 3methylpentan-2-ol.

Answer

$$\begin{array}{c} \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{CH}-\mathrm{CH}-\mathrm{CH}_{3} \xrightarrow{\mathrm{Na}} \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{CH}-\mathrm{CH}-\mathrm{CH}-\mathrm{ONa}\\ & & | & | \\ \mathrm{CH}_{3} & \mathrm{OH} & \mathrm{CH}_{3}-\mathrm{CH}_{3} & \mathrm{CH}_{3} \end{array}$$

$$\begin{array}{c} \mathrm{C}_{2}\mathrm{H}_{5}\mathrm{OH} \xrightarrow{\mathrm{HBr}} \mathrm{C}_{2}\mathrm{H}_{5}\mathrm{Br}\\ \mathrm{C}_{3}-\mathrm{CH}_{2}-\mathrm{CH}-\mathrm{CH}-\mathrm{ONa} + \mathrm{C}_{2}\mathrm{H}_{5}\mathrm{Br} \xrightarrow{\mathrm{CH}_{3}} \mathrm{CH}_{3} - \mathrm{CH}_{2}-\mathrm{CH}-\mathrm{CH}-\mathrm{OC}_{2}\mathrm{H}_{5}\\ & | & | \\ \mathrm{CH}_{3} & \mathrm{CH}_{3} \end{array}$$

$$\begin{array}{c} \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{CH}-\mathrm{CH}-\mathrm{OC}_{2}\mathrm{H}_{5}\\ \mathrm{CH}_{3} & \mathrm{CH}_{3} \end{array}$$

$$\begin{array}{c} \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{CH}-\mathrm{CH}-\mathrm{OC}_{2}\mathrm{H}_{5}\\ \mathrm{CH}_{3} & \mathrm{CH}_{3} \end{array}$$

$$\begin{array}{c} \mathrm{CH}_{3}-\mathrm{CH}_{2}-\mathrm{CH}-\mathrm{CH}-\mathrm{OC}_{2}\mathrm{H}_{5}\\ \mathrm{CH}_{3} & \mathrm{CH}_{3} \end{array}$$

Q 4 Give the major products that are formed by heating each of the followingethers with HI.

Q 6 Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?



INTER CONVERSIONS

Q 1 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. <u>Answer</u>

(i) If propene is allowed to react with water in the presence of an acid as a catalyst, then 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 (followed by acidification) then benzyl alcohol is produced.



(iii) When ethyl magnesium chloride is treated with methanal, an adduct is the produced which gives propan-1-ol on hydrolysis.





Q2 Show how would you synthesise the following alcohols from appropriate alkenes?



The given alcohols can be synthesized by applying Markovnikov's rule of acid-catalyzed hydration of appropriate alkenes.

(i)



(ii)



Q3

Give names of the reagents to bring about the following transformations:

(i) Hexan-1-ol to hexanal

(ii) Cyclohexanol to cyclohexanone

(iii) Allyl alcohol to propenal

A3

(i) $C_5H_5NH^+CrO_3Cl^-(PCC)$ (ii) $K_2Cr_2O_7$ in acidic medium (iii) PCC

Q4 How would you obtain

(i) Picric acid (2, 4, 6-trinitrophenol) from phenol,

(ii) 2-Methylpropene from 2-methylpropanol?



5 How are the following conversions carried out?(i) Benzyl chloride to benzyl alcohol,(ii) Methyl magnesium bromide to 2-methylpropan-2-ol

Solution:





How would you obtain the following:

- (i) Benzoquinone from phenol
- (ii) 2-Methylpropan-2-ol from methylmagnesium bromide
- (iii) Propan-2-ol from propane



NAMED REACTIONS

1 Hydroboration-oxidation

Diborane (B₂H₆)reacts with alkenesto give trialkyl boranes as addition

product. This is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.

$$\begin{array}{cccc} \mathrm{CH}_{3}\text{-}\mathrm{CH}=\mathrm{CH}_{2} & + & (\mathrm{H}-\mathrm{BH}_{2})_{2} \longrightarrow & \mathrm{CH}_{3}\text{-}\mathrm{CH}-\mathrm{CH}_{2} \\ & & & & & & \\ \mathrm{I} & & & \mathrm{I} \\ \mathrm{H} & & \mathrm{BH}_{2} \end{array}$$

$$(\mathrm{CH}_{3}\text{-}\mathrm{CH}_{2}\text{-}\mathrm{CH}_{2})_{3}\mathrm{B} & \xleftarrow{\mathrm{CH}_{3}-\mathrm{CH}=\mathrm{CH}_{2}} & (\mathrm{CH}_{3}\text{-}\mathrm{CH}_{2}\text{-}\mathrm{CH}_{2})_{2}\mathrm{BH}$$

$$\mathrm{H}_{2}\mathrm{O} \downarrow \mathrm{3H}_{2}\mathrm{O}_{2}, \ \bar{\mathrm{O}}\mathrm{H} \\ \mathrm{3CH}_{3}\text{-}\mathrm{CH}_{2}\text{-}\mathrm{CH}_{2}\text{-}\mathrm{OH} + & \mathrm{B}(\mathrm{OH})_{3} \\ & & & & & \\ \mathrm{Propan-1-ol} \end{array}$$

The product so formed looks as if it were formed by the addition of water to the alkene in a <u>way opposite to Markovnikov's rule.</u>

2 Kolbe's Reaction : When phenol is treated with sodium hydroxide, sodium phenoxide is produced. 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.



3 Reimer-Tiemann Reaction

When phenol is treated with chloroform (CHCl₃) in the presence of sodium hydroxide, a –CHO group is introduced at the ortho position of the benzene ring



Intermediate . This reaction is known as the

Reimer-Tiemann reaction. The intermediate is hydrolyzed in the presence of alkalis to produce salicyclaldehyde.



4 :Williamson ether synthesis Williamson ether synthesis is a laboratory method to prepare symmetrical and unsymmetrical ethers by allowing alkyl halides to react with sodium alkoxides.



This reaction involves $S_N 2$ attack of the alkoxide ion on the alkyl halide. Better results are obtained in case of primary alkyl halides.



Explain the following giving one example

Friedel Craft's acetylation of anisole. **Friedel-Crafts acetylation of anisole:** Friedel-Crafts acetylation of anisole involves the treatment of anisole with either acetyl chloride or

acetic anhydride to give 2-methoxyacetophenone



WORD MAP

Q1An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene.Write equations for the reactions involved.

<u>Answer</u>

An organic compound A with molecular formula $C_8H_{16}O_2$ gives a carboxylic acid (B) and an alcohol (C) on hydrolysis with dilute sulphuric acid. Thus, compound A must be an ester. Further, alcohol C gives acid B on oxidation with chromic acid. Thus, B and C must contain equal number of carbon atoms.

Since compound A contains a total of 8 carbon atoms, each of B and C contain 4 carbon atoms.

Again, on dehydration, alcohol C gives but-1-ene. Therefore, C is of straight chain and hence, it is butan-1-ol.

o On oxidation, Butan-1-ol gives butanoic $CH_3CH_2CH_2 - C - OCH_2CH_2CH_2$ Butylbutanoate On oxidation, Butan-1-ol gives butanoic acid. Hence, acid B is butanoic acid. Hence, the ester with molecular formula C₈H₁₆O₂ is butylbutanoate.

All the given reactions can be explained by the following equations.



 $3^{\circ} \rightarrow$ Formation of turbidity \rightarrow immediate $2^{\circ} \rightarrow$ Formation of turbidity within 5 minutes. $1^{\circ} \rightarrow$ No turbidity appears –

2 Phenolic group

[i]Phenol gives violet colour with alc. FeCl₃

[ii] Phenol gives white precipitate with Br2water

3 The Iodoform Test

Methyl ketones, Acetaldehyde and α -Methyl secondary alcohols undergo the iodoform reaction and give yellow crystalline precipitate confirms the presence of a methyl secondary alcohol or a methyl ketone or acetaldehyde RCH(CH₃)OH + 6 OH⁻ + 4 I₂ \longrightarrow CHI₃ + RCOO⁻ + 5 I⁻ + 5 H₂O 4 important pairs and test applicable

Methyl alcohol and	Iodoform	Yellow ppt with ethyl
ethyl alcohol	test[NaOH+I ₂]	alcohol
Ethyl alcohol and n-	Iodoform	Yellow ppt with ethyl
propyl alcohol	test[NaOH+I ₂]	alcohol
n-Propyl alcohol and	Iodoform	Yellow ppt with iso-propyl
iso-propyl alcohol	test[NaOH+I ₂]	alcohol
Butane-1-oland	Iodoform	Yellow ppt with Butane-2-
Butane-2-ol	test[NaOH+I ₂]	ol
Phenol and Benzoic	Neutral FeCl ₃	Violet colour with phenol
acid		

CHEMICAL TEST

- **1** OH–group [alcohol, phenol and carboxylic acid]
 - (i) Na -metal : evolves H₂ gas with.
 - (ii) Lucas test: (anhydrous ZnCl₂ / fConcentrated

HCI)

Q1 Give chemical tests to distinguish between the following pairs of compounds:

- (i) Ethanol and Propanol
- (ii) Phenol and Benzoic acid
- ANSWER

(i) Ethanal and propanal can be distinguished by iodoform test.(ii)Phenol and benzoic acid can be distinguished by ferric chloride test.

Phenol reacts with neutral FeCl₃ to form ferric phenoxide complex giving violet colouration.

$$6 C_6 H_5 OH + FeCl_3 \longrightarrow \left[Fe (OC_6 H_5)_6\right]^{3-} + 3H^+ + 3Cl^-$$
Phenol Iron-phenol complex (Violet colour)

But benzoic acid reacts with neutral FeCl₃ to give a buff coloured precipitate of ferric benzoate.

3 C₆H₅OH + FeCl₃ → (C₆H₅COO)₃Fe + 3 HCl Benzoic acid Ferric benzoate (Buff coloured ppt)

REACTION MECHANISM

1 Hydration of alkene [electrophilic addition]

Step 1 – Protonation of alkene by electrophilic attack of H_3O^+ to form carbocation $H_2O+H^+ \longrightarrow H_3O^+$



$$CH_3CH_2 - CH_2 - OH_2 - OH_1 + H_2O \rightarrow CH_3CH_2 - CH_2 - OH_1 + H_3O^+$$

4 Dehydration of alcohols [E-1elimination]



Therefore, the reactivity order for dehydration can be observed as $1^{\circ} < 2^{\circ} < 3^{\circ}$

5 Reaction of HI with ether having 3° alkyl and 1°



$$CH_3 \overset{\bullet}{\square} CH_2 CH_2 CH_3 + H^+ \iff CH_3 \xrightarrow{H} CH_2 CH_2 CH_2 CH_3 \xrightarrow{S_N 2} CH_3 \overset{\bullet}{\square} + CH_3 CH_2 CH_2 OH$$

6 the reaction of HI with methoxymethane.

The mechanism of the reaction of HI with methoxymethane involves the following steps:

Step1: Protonation of methoxymethane:

Step2: Nucleophilic attack of I^{-:}

$$I^- + CH_3 \longrightarrow \begin{bmatrix} I & \cdots & H_3 \\ I & \cdots & H_3 \\ \vdots & \vdots \\ & & & \downarrow \\ CH_3 & \cdots & I + CH_3 & \cdots \\ & & & \downarrow \\ CH_3 & \cdots & I + CH_3 & \cdots \\ Iodomethane & methanol \end{bmatrix}^-$$

Step3:

When HI is in excess and 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

$$CH_3 \longrightarrow \overset{H}{\textcircled{0}} H + H \longrightarrow \overset{H}{\textcircled{1}} \underset{CH_3}{\longleftarrow} CH_3 \longrightarrow \overset{H}{\textcircled{0}} H + I^-$$

$$\mathbf{I}^- + \mathbf{C}\mathbf{H}_3 - \overset{+}{\mathbf{O}}\mathbf{H}_2 \longrightarrow \mathbf{C}\mathbf{H}_3 - \mathbf{I} + \mathbf{H}_2\mathbf{O}$$

7 Electrophilic substitution

mechanism for nitration



mechanism for bromination



alkoxy (**-OR**) **-X** , **_OH** , **NH**₂ group is *ortho*- and *para*directing, and activates the aromatic ring towards electrophilic substitution due to resonance.



7 Explain the mechanism of the following reactions:

(i) Addition of Grignard's reagent to the carbonyl group of a compound forming an adduct followed by hydrolysis.
(ii) Acid catalysed dehydration of an alcohol forming an alkene.
(iii) Acid catalysed hydration of an alkene forming an alcohol.

Solution:

(i) Grignard's reagent is an alkyl magnesium halide. The alkyl group has a partial negative charge, whereas the magnesium group has a partial positive charge. The alkyl group attacks the carbon of the carbonyl group to form an addition compound.



Grignard's reagent acts as a nucleophilic agent and attacks electrophilic carbon atoms to yield a carbon – carbon bond. The addition to the nucleophile is an irreversible process due to the high pk_a value of the alkyl group.



(ii) When heated with concentrated sulphuric acid, phosphoric acid or boric acid, alcohols undergo dehydration to form alkenes. The mechanism of this reaction involves the protonation of alcohol, followed by loss of a water molecule and a proton.

$$CH_{3} - CH_{2} - OH + H^{+} \xleftarrow{\text{protonation}} CH_{3} - CH_{2} - \overset{+}{O}H_{2}$$
(a) Oxonium ion

(b)

$$CH_3 - CH_2 - \overset{+}{O}H_2 \xleftarrow{-H_2O} CH_2 - \overset{+}{C}H_2$$

Carbo cation



During the dehydration of alcohol, the intermediate carbocation may undergo re-arrangement, resulting in the formation of a stable carbocation.

(iii) Some reactive alkenes like 2 – methyl propene undergo direct hydration in the presence of mineral acids which act as catalysts. The addition of water to the double bond takes place in accordance with Markonikoff's rule.



ACIDITY OF PHENOLS

Acidic strength of Phenols : Phenols are stronger acids than alcohols AND WATER.

Reason: Phenoxide ion is more stable than R - O - Halkoxide ion due its resonance stabilisation. Alcohol





Therefore, phenol is more acidic than alcohol.



Electron-withdrawing substituents (especially at *ortho*- and *para*-positions) increase the acidity of phenols whereas electron-donating substituents decrease acidity.

Q 1

Which phenol in each of the following pairs is more acidic? Justify your choice.

- (a) 2,4,6-Trimethylphenol or 2,4,6-trinitrophenol
- (b) 2-Nitro phenol or 4- Nitro phenol
- (c) 3-Nitrophenol or 4-nitrophenol
- (d) Phenol or 4-methoxyphenol
- (e) 2,5-Dinitrophenol or 2,6-dinitrophenol

ANSWER

- (a) 2,4,6-trinitrophenol
- (b) 4- Nitro phenol [H-BOND in -2-Nitro phenol]
- (c) 4-nitrophenol
- (d) Phenol
- (e) 2,6-dinitrophenol

PHYSICAL PROPERTIES

Boiling point

• Increase with the increase in number of carbon atoms

Reason – With the increase in the number of carbon atoms, van der Waals forces increase.

• Decrease with increase of branching

Reason – With the increase in branching, surface area decreases and hence, van der Waals forces decrease.

Alcohols and phenols have higher boiling points than other classes of compounds (hydrocarbons, ethers, haloalkanes, and haloarenes) of comparable molecular masses.

 Reason – They undergo extensive intermolecular hydrogen bonding resulting in aggregation of molecules.



- Alcohols are Soluble in Water
 - Reason They undergo H-bonding with water molecules.

- Boiling points of aldehydes and ketones are lower than those of alcohols of similar molecular masses.
 - Reason: Absence of intermolecular hydrogen bonding
- Lower members of aldehydes and ketones are miscible with water in all proportions.
 - \circ $\;$ Reason: They form hydrogen bonds with water.

Order of boiling points of isomeric amines is

Primary > Secondary > Tertiary

REASONING

- Q 1 Explain why propanol has higher boiling point than that of the hydrocarbon, butane?
- A1 Propanol undergoes intermolecular H-bonding because of the presence of -OH group. On the other hand, butane does not



Therefore, extra energy is required to break hydrogen bonds. For this reason, propanol has a higher boiling point than hydrocarbon butane.

- Q 2Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.
- **A2** Alcohols form H-bonds with water due to the presence of –OH group. However, hydrocarbons cannot form H-bonds with water.



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

Q3 Arrange the following compounds in the increasing order of their boiling points:

 $\mathrm{CH_3CH_2CH_2CHO}, \mathrm{CH_3CH_2CH_2CH_2OH}, \mathrm{H_5C_2}\text{-}\mathrm{O}\text{-}\mathrm{C_2H_5}, \mathrm{CH_3CH_2CH_2CH_2CH_3}$

A 3The molecular masses of these compounds are in the range of 72 to74. Since only butan-1-ol molecules are associated due to extensive intermolecular hydrogen bonding, therefore, the boiling point of butan-1-ol would be the highest. Butanal is more polar than ethoxyethane. Therefore, the intermolecular dipole-dipole attraction is stronger in the former. n-Pentane molecules have only weak van der Waals forces Hence increasing order of boiling points of the given compounds is as follows:

 $\mathrm{CH_3CH_2CH_2CH_3CH_3} < \mathrm{H_5C_2}\text{-}\mathrm{O}\text{-}\mathrm{C_2H_5} < \mathrm{CH_3CH_2CH_2CHO} < \mathrm{CH_3CH_2CH_2CH_2OH}$

- Q 4 While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.
- **A 4** Intramolecular H-bonding is present in *o*-nitrophenol and *p*-nitrophenol. In *p*-nitrophenol, the molecules are strongly associated due to the presence of intermolecular bonding. Hence, *o*-nitrophenol is steam volatile.



Q5 Give reason for the higher boiling point of ethanol in comparison to methoxymethane.

A5 Ethanol undergoes intermolecular H-bonding due to the presence of -OH group, resulting in the association of molecules. Extra energy is required to break these hydrogen bonds. On the other hand, methoxymethane does not undergo H-bonding. Hence, the boiling point of ethanol is higher than that of methoxymethane.



Q6 Arrange the following sets of compounds in order of their increasing boiling points:

(a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.

(b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.

A6 (a) Methanol, ethanol, propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol.

(b) n-Butane, ethoxyethane, pentanal and pentan-1-ol

Q7 Arrange the following compounds in increasing order of their boiling points.

CH₃CHO, CH₃CH₂OH, CH₃OCH₃, CH₃CH₂CH₃

A7 $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$

Q8 Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

A8 The formation of ethers by dehydration of alcohol is a bimolecular reaction ($S_N 2$) involving the attack of an alcohol molecule on a protonated alcohol molecule. In the method, the alkyl group should be unhindered. In case of secondary or tertiary alcohols, the alkyl group is hindered. As a result, elimination dominates substitution. Hence, in place of ethers, alkenes are formed.

Q9 The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

A9 In an aqueous solution, KOH almost completely ionizes to give OH⁻ ions. OH⁻ ion is a strong nucleophile, which leads the alkyl chloride to undergo a substitution reaction to form alcohol.

 $R - Cl + KOH_{(aq)} \longrightarrow R - OH + KCl$

Alkyl

Alcohol

chlorideOn the other hand, an alcoholicsolution of KOH contains alkoxide (RO⁻) ion, which is a strong base.Thus, it can abstract a hydrogen from the β-carbon of the alkylchloride and form an alkene by eliminating a molecule of HCI.

$$R - \underset{\beta}{C}H_2 - \underset{\alpha}{C}H_2 - CI + KOH(alc) \longrightarrow R - CH = CH_2 + KCI + H_2O$$

Alkyl chloride Alkene

 OH^{-} ion is a

much weaker base than RO⁻ ion. Also, OH⁻ ion is highly solvated in an aqueous solution and as a result, the basic character of OH⁻ ion decreases. Therefore, it cannot abstract a hydrogen from the β -carbon.

Q 10 Explain why is *ortho* nitrophenol more acidic than *ortho* methoxyphenol?



A10 The nitro-group is an electron-withdrawing group. The presence of this group in the ortho position decreases the electron density in the O–H bond. As a result, it is easier to lose a proton. Also,

the *o*-nitrophenoxide ion formed after the loss of protons is stabilized by resonance. Hence, *ortho* nitrophenol is a stronger acid.

On the other hand, methoxy group is an electron-releasing group. Thus, it increases the electron density in the O–H bond and hence, the proton cannot be given out easily.

For this reason, ortho-nitrophenol is more acidic than orthomethoxyphenol.

Q11 Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

A11 The formation of ethers by dehydration of alcohol is a bimolecular reaction ($S_N 2$) involving the attack of an alcohol molecule on a protonated alcohol molecule. In the method, the alkyl group should be unhindered. In case of secondary or tertiary alcohols, the alkyl group is hindered. As a result, elimination dominates substitution. Hence, in place of ethers, alkenes are formed.

Q12 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.



In aryl alkyl ethers, due to the +R effect of the alkoxy group, the electron density in the benzene ring increases as shown in the following resonance structure.



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

(ii) It can also be observed from the resonance structures that the electron density increases more at the ortho and para positions than at the meta position. As a result, the incoming substituents are directed to the ortho and para positions in the benzene ring.

Q13 The following is not an appropriate reaction for the preparation of

t-butyl ethyl ether.

$$C_{2}H_{5}ONa + CH_{3} - \begin{array}{c}CH_{3} & CH_{3} \\ | \\ C_{2}H_{5}ONa + CH_{3} - \begin{array}{c}C-C-Cl \\ | \\ CH_{3} \end{array} \rightarrow CH_{3} - \begin{array}{c}C-OC_{2}H_{5} \\ | \\ CH_{3} \end{array}$$

(i) What would be the major product of this reaction ?(ii) Write a suitable reaction for the preparation of t-butylethyl ether.

A13 (i) The major product of the given reaction is 2-methylprop-1ene. It is because sodium ethoxide is a strong nucleophile as well as a strong base. Thus elimination reaction predominates over substitution.



Q14 The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

A14 In an aqueous solution, KOH almost completely ionizes to give OH⁻ ions. OH⁻ ion is a strong nucleophile, which leads the alkyl chloride to undergo a substitution reaction to form alcohol.

 $R - Cl + KOH_{(aq)} \longrightarrow R - OH + KCl$ Alkyl Alcohol chloride

On the other hand, an alcoholic solution of KOH contains alkoxide (RO⁻) ion, which is a strong base. Thus, it can abstract a hydrogen from the β -carbon of the alkyl chloride and form an alkene by eliminating a molecule of HCl.

$R - CH_{\beta}H_{2} - CH_{\alpha}H_{2} - CH + KOH(alc)$	\longrightarrow R - CH = CH ₂ + KCI + H ₂ O
Alkyl chloride	Alkene

OH⁻ ion is a much weaker base than RO⁻ ion. Also, OH⁻ ion is highly solvated in an aqueous solution and as a result, the basic character of OH⁻ ion decreases. Therefore, it cannot abstract a hydrogen from the β -carbon.

Q15 Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?



A15 Set (ii) is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene.



In set (i), sodium methoxide (CH_3ONa) is a strong nucleophile as well as a strong base. Hence, an elimination reaction predominates over a substitution reaction.

Q16 Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?

A16 Resonance structures of phenoxide ion are:



It can be observed from the resonance structures of phenoxide ion that in II, III and IV, less eliminated. Only structures I and V carry a negative charge on the more electronegative oxygen atom.



Q17 Arrange the following compounds in increasing order of their acid strength: Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5dinitrophenol, phenol, 4-methylphenol.

A17 Propan-1-ol, 4-methylphenol, phenol, 3 nitrophenol, 3,5-dinitrophenol, 2,4, 6-trinitrophenol.

18 Which one is more acidic – ethanol or phenol? Explain you answer.

A18

Phenol is more acidic than ethanol. This is because the phenoxide ion formed after the loss of a proton from phenol is resonance stabilised, whereas the alkoxide ion formed after the loss of a proton from alcohol is not.









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