7

CHAPTER

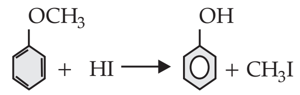
Alcohols Phenols & Ethers

Level - 1 CORE SUBJECTIVE QUESTIONS

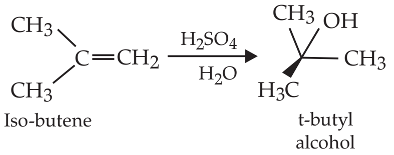
MULTIPLE CHOICE QUESTIONS (MCQs)

(1 Mark)

1. **Option (D) is correct.**
   Explanation: This is because the chlorine atom in para chlorophenol withdraws density which stabilizes the conjugate base (phenoxide ion) due to inductive and resonance effect combined.
2. **Option (A) is correct.**
   Explanation:



3. **Option (C) is correct.**
   Explanation:
   $2C_2H_5OH \xrightarrow{conc.H_2SO_4} C_2H_5 - O - C_2H_5 + H_2O$
4. **Option (D) is correct.**
   Explanation: pKa is inversely proportional to the acidity of phenols.
   A lower pKa value indicates increase in acidity and vice versa.
   Electron withdrawing groups in substituted phenols increase its acidity implying lower pKa and electron donating groups decrease the acidity implying higher pKa.
   As 2, 4, 6-trinitrophenol has 3 electron withdrawing NO_2 groups, its pKa is the lowest.
5. **Option (B) is correct.**
   Explanation:
   $(CH_3)_2CH—O—CH_3 + HI \longrightarrow (CH_3)_2\,CH — OH + CH_3 — I$
6. **Option (C) is correct.**
   Explanation: Weakest acid ROH has the strongest conjugate base RO^-. Therefore the strongest base is RO^-
7. **Option (A) is correct.**
   Explanation: PCC oxidises alchol to aldehyde
   $NaBH_4$ – Reduces ketones to alcohol
   Br_2 Water – Help in bromination
   85% H_3PO_4 - dehydrating agent
8. **Option (D) is correct.**
   Explanation:



9. **Option (D) is correct.**
   Explanation: The oxidation of secondary alcohol gives ketone
10. **Option (A) is correct.**
    Explanation: The ease of dehydration of alcohol is determined by the stability of the intermediate carbocation. As tert- carbocations are most stable due to electron donating effect of the alkyl groups, they are easily dehydrated by conc. sulphuric acid.
11. **Option (D) is correct.**
    Explanation: Williamsons' synthesis of preparing dimethyl ether is an S_N2 reaction which is type of nucleophilic subsitution involving reaction of primary alkyl halide with alkoxide ion.
    $R—O— + R'—X \longrightarrow R—O—R' + X—.$
12. **Option (A) is correct.**
    Explanation: *t*-butoxide give Williamson synthesis with alkyl halide while *t*-butyl chloride gives elimination reaction with alkoxide base due to stearic hinderance present in *t*-butyl chloride.
13. **Option (D) is correct.**
    Explanation: This reaction involves cleavage of the C-O bond in the ether by HI, resulting in the formation of two moles of ethyl iodide.
    $CH_2CH_2 — O — C_2H_5 \xrightarrow{conc.\ HI} 2CH_3CH_2 — I$
14. **Option (C) is correct.**
    Explanation: 2-Methylbutan-2-ol will not undergo oxidation because it does not have a hydrogen atom attached to the carbon bearing hydroxyl group. As it is a tertiary alcohol.
15. **Option (A) is correct.**
    Explanation: Tertiary alcohol react faster with Lucas reagent as the tert carbocation produced as an intermediate is more stable hence formed faster showing immediate reaction.
16. **Option (A) is correct.**
    Explanation: Presence of electron withdrawing group at ortho position increase the acidic strength of 0-nitrophenol compared to given options.

ASSERTION-REASON QUESTIONS (1 Mark)

1. **Option (A) is correct.**

   Explanation: Ethanol has a higher boiling point than dimethylether due to presence of hydrogen bonding present in ethanol and absent in ether.

2. **Option (D) is correct.**

   Explanation: *p*-nitrophenol is more acidic than phenol. As nitro being an electron withdrawing group stablises the phenoxide ion negative charge by resonance as well as inductive effect more than the phenol.

3. **Option (D) is correct.**

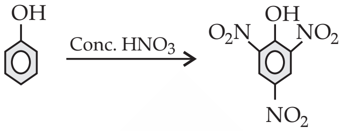
   Explanation: Methoxyphenol is a weaker acid than *p*-nitrophenol.

   Nitro group is an electron withdrawing group which stablises the phenoxide ion by pulling electrons away from oxygen atom hence facilitating removal of H^+.

   However, $-OCH_3$ methoxy group is an electron donating group which increases electron density on oxygen atom making it harder for H^+ ion to leave and thus decreasing its acidity.

4. **Option (C) is correct.**

   Explanation:

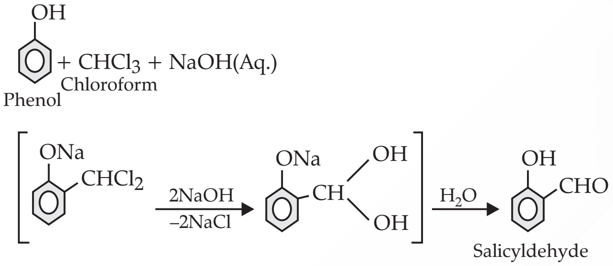


2, 4, 6-Trinitro phenol

—OH group in phenol is o-p directing group.

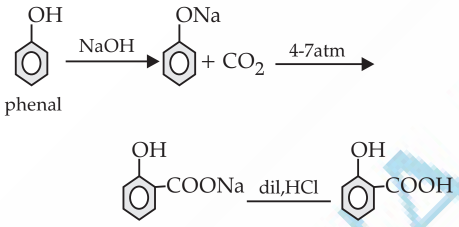
VERY SHORT ANSWER TYPE QUESTIONS (2 Marks)

1. (i) Riemer — Tiemann reaction



Salicyldehyde

   (ii) Kolbe's reaction



Salicylic acid

2. (i) Phenol is stronger acid than alcohol because the phenoxide ion is stablised by resonance.

   (ii) The boiling point of alcohol decreases with increasing branching of the alkyl chain due to decrease in surface area and van der Waal forces of attraction.

3. (i) Phenol is more acidic as its conjugate anion while cyclohaxane does not have resonance.

   (ii) $FeCl_3$ Test: phenol react with neutral Ferric chloride ($FeCl_3$) it form a violet coloured complex where as cyclo hexanol give no change in colour on reacting with ferric chloride.

4. $CH_2 = CH_2 + H_2O \xrightarrow[443K]{H^+} CH_3CH_2OH$

   This is an example of electrophilic addition of water molecule to alkene to form alcohol.

   Step 1: In step I a carbocation is formed by protonation of ethene.

   $CH_2 = CH_2 + H^+ \longrightarrow CH_3 - C + H_2$ (a carbocation is formed)

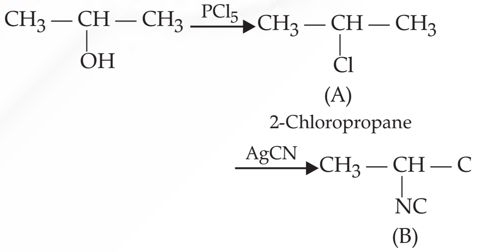
   Step 2: A water molecule attacks the carbocation to form an oxonium ion intermediate

   $CH_3 - C + H_2 + H_2O \longrightarrow CH_3 - CH_2 - OH_2{}^+$

   Step 3: Oxonium ion loses a proton to form ethanol as a product and regenerating the acid catalyst

   $CH_3 - CH_2 - OH_2{}^+ \longrightarrow CH_3 - CH_2 - OH + H^+$

5. (i)



$$\underset{\displaystyle OH}{CH_3 - \overset{}{CH} - CH_3} \xrightarrow{PCl_5} \underset{\displaystyle\underset{\displaystyle 2\text{-Chloropropane}}{(A)}}{\underset{\displaystyle Cl}{CH_3 - CH - CH_3}} \xrightarrow{AgCN} \underset{\displaystyle NC}{CH_3 - CH - C}$$

(A)

2-Chloropropane

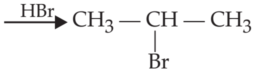
(B)

Iso propyl isocyanide

   (ii) $CH_3CH_2CH_2Cl + KOH \xrightarrow{Ethanol} CH_3CH{=}CH_2$

(A)

propene



$$\xrightarrow{HBr} \underset{\displaystyle Br}{CH_3 - CH - CH_3}$$

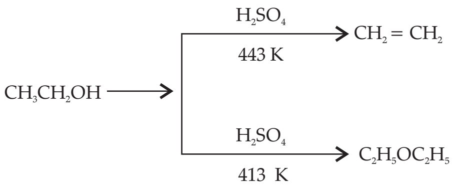
(B)

2-bropropene

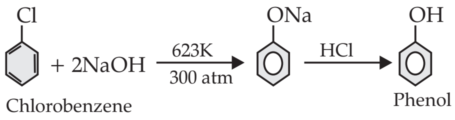
SHORT ANSWER TYPE QUESTIONS (3 Marks)

1. (i) Ethanol undergoes a dehydration reaction. At 140°C, diethyl ether is formed. The formation of ether is a nucleophilic substitution S_N2 bimolecular reaction.

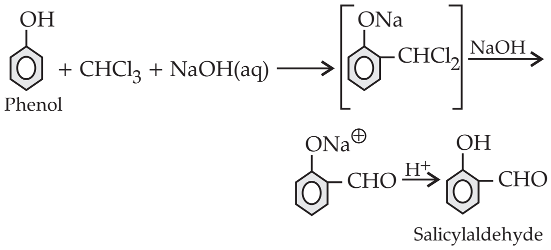
   (ii) When the temperature exceeds 170°C, ethene is the major product. Nucleophilic substitution S_N1 unimolecular reaction.



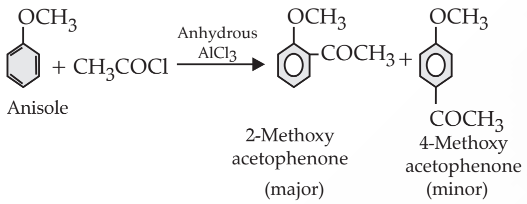
2. (i)



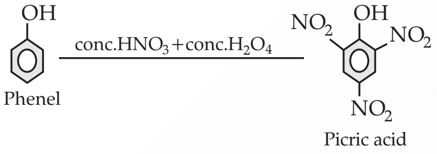
(ii)



(iii)



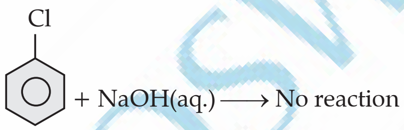
(iv)



3. (i) $R—X + AgCN \longrightarrow RNC + AgX$

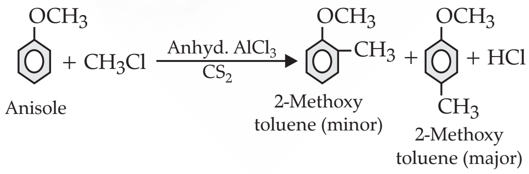
(ii) Allylic chloride forms stable carbocation due to this it gives S_N1 type nucleophilic substitution Reaction

(iii)

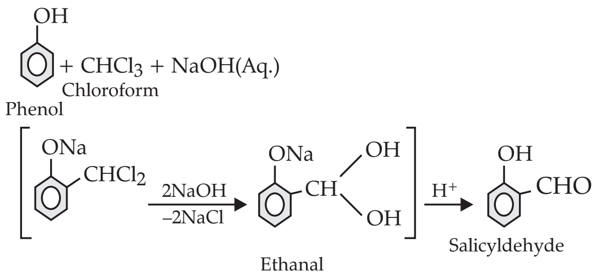


Halo arenas does not give nucleophilic substitution reaction due to partial double bond between C – X bond.

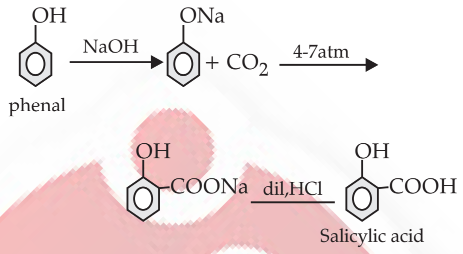
(iv) Friedal craft alkylation reaction



4. (i) (1) Riemer — Tiemann reaction

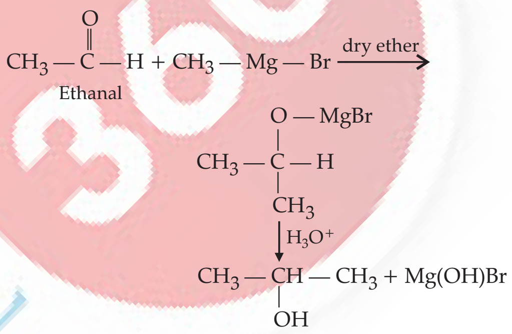


(2) Kolbe's reaction

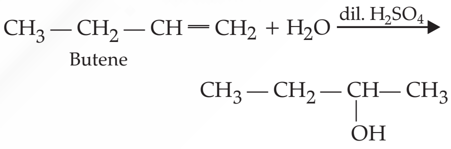


(ii) Br_2 water

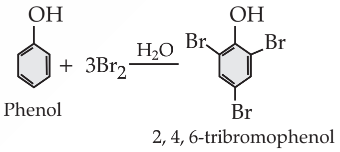
5. (i) 2-propanol



(ii) Butan-2-ol



(iii) 2,4,6, Tribromophenol

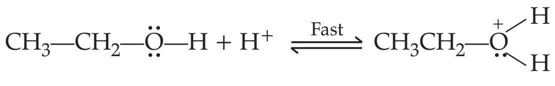


6. (i) Mechanism of the following reaction

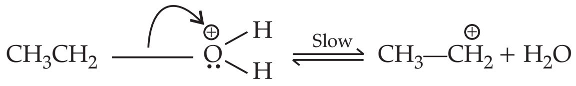
$$CH_3CH_2OH \xrightarrow{H^+,\ 443K} CH_2 = CH_2$$

Mechanism Ethene

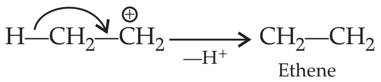
(a) Protonation



(b) Formation of Carbocation



(c) Loss of proton



$$H-CH_2-\overset{\oplus}{C}H_2 \xrightarrow[-H^+]{} CH_2-CH_2$$

Ethene

(ii) (1) Butan -1--ol

$$CH_3-CH_2-CH=CH_2 \xrightarrow[\text{(b) } H_2O_2/OH^-]{\text{(a) } B_2H_6}$$

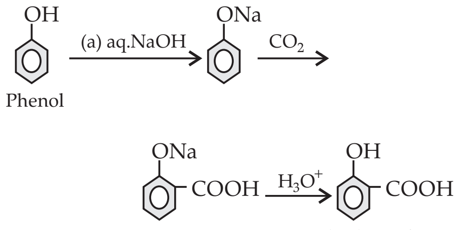
Butene

Hydroboration-oxidation reaction

$$CH_3CH_2CH_2CH_2-OH$$

1-Butanol

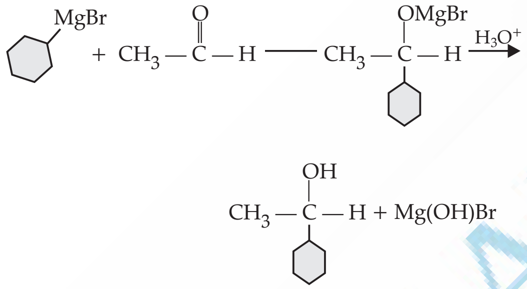
(2) Salicylic acid



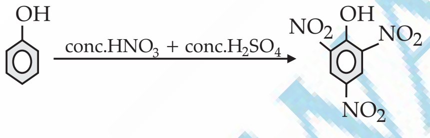
Salicylic acid

7. It decreases electron density at 0- and *p*- positions due to its inductive effect making them ideal sites for a nucleophilic substitution.

8. (i) Cyclohexyl ehtnaol is formed

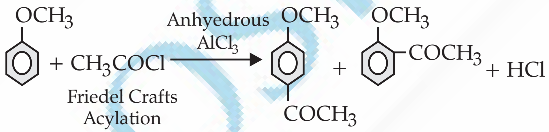


(ii) Picric acid is formed



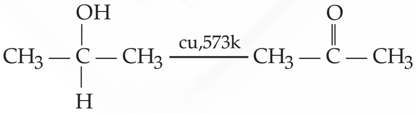
picric acid

(iii) *p*-methoxyacetophenone



4-methoxyacetophenone

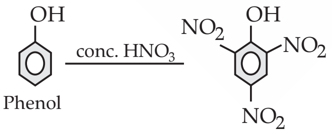
(iv) Acetone is formed



$$CH_3-\underset{H}{\overset{OH}{C}}-CH_3 \xrightarrow{cu,573k} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

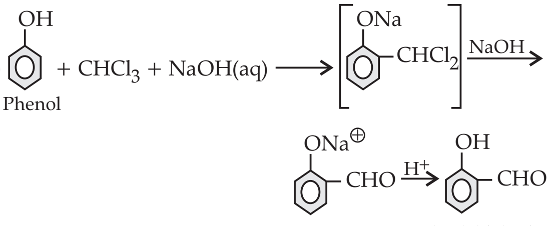
9. (i)

(1)



Picric acid

(2)



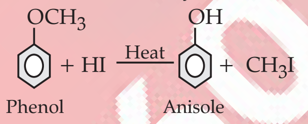
Salicylaldehyde

(ii) The reaction of CH_3ONa with $(CH_3)_3C$ Br produces 2-Methyl propene instead of $(CH_3)_3$ $COCH_3$ because alkoxides are strong bases and nucleophiles which lead to the elimination reaction of alkyl halide.

10. (i) This is due to partial double bond character in phenol between C — O bond. The lone pair of electrons on oxygen atom get delocalised on the phenyl ring due to resonance, thus giving C-O bond a partial double bond character.

(ii) *n*-butane <ethoxyethane < butanal < butanol

(iii)



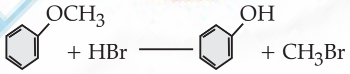
11. (i) The addition of borane followed by oxidation is known as hydroboration oxidation reaction For example propan-1-ol is produced by the hydroboration oxidation reaction of propene.

$$3CH_3-CH=CH_2+BH_3 \longrightarrow (CH_3-CH_2-CH_2)_8$$

$$\xrightarrow{3H_2O_2/\bar{O}H} 3CH_3CH_2CH_2OH + B(OH)_3$$

Propan-1-ol

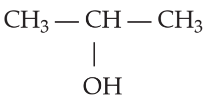
(ii)



(iii) The nitro group is an electron withdrawing group The presence of this group on para position decreases the electron density in the —OH bond As a result it is easier to lose a proton. Hence, para nitro phenols are stronger acid then phenol.

12. (i) $CH_3-CH=CH_2+H_2O \xrightarrow{\text{dil.}H_2SO_4}$

propene



$$CH_3-\underset{OH}{\underset{|}{C}H}-CH_3$$

2-propanol

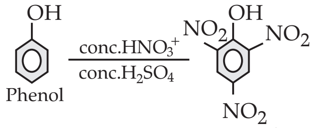
(ii) $C_2H_5Br + NaOC_2H_5 \longrightarrow C_2H_5-O-C_2H_5 + NaBr$

Diethyl ether

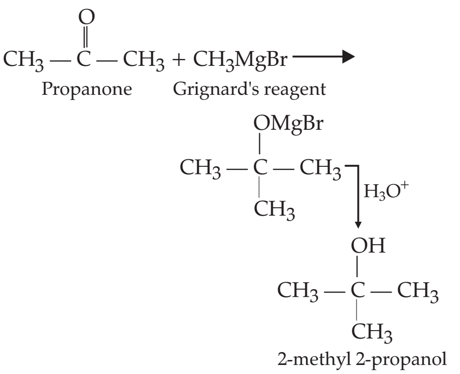
(iii) $CH_3-O-CH_3 + HI \longrightarrow CH_3-OH + CH_3-I$

Methanol methyl iodide

13. (i)



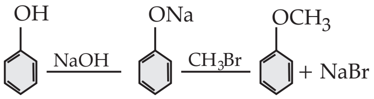
Picric acid

(ii) 

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3MgBr \longrightarrow CH_3-\underset{CH_3}{\overset{OMgBr}{C}}-CH_3 \xrightarrow{H_3O^+} CH_3-\underset{CH_3}{\overset{OH}{C}}-CH_3$$

Propanone Grignard's reagent

2-methyl 2-propanol

(iii) 

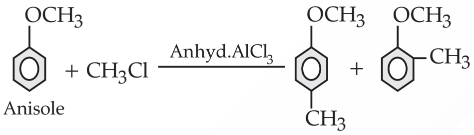
Anisole

(iv) $CH_3-CH=CH_2 + HBr \xrightarrow{Peroxide} CH_3CH_2CH_2-Br \xrightarrow{KOH(aq)} CH_3CH_2CH_2-OH$

Propene

Propan-1-ol

14. (i) 4-Methoxy Toluene is formed

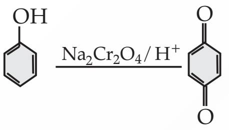


Anisole

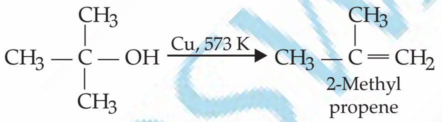
4-Methory toluene (major)

2- Methory Toluene (minor)

(ii) Benzo quinone is formed



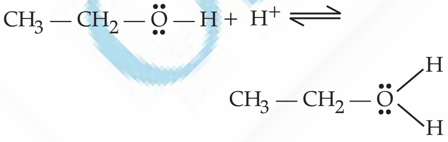
(iii) 2-Methyl propene is formed



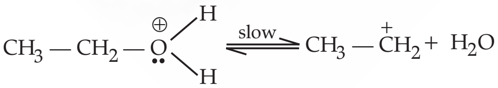
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow{Cu,\ 573\ K} CH_3-\overset{CH_3}{C}=CH_2$$

2-Methyl propene

15. (i) **Step I:** Formation of protonated alcohol



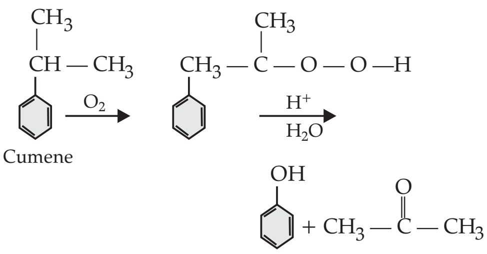
Step II: Formation of carbocation



Step III: Elimination of a proton to form ethene

$$H-CH_2-\overset{\oplus}{C}H_2 \overset{fast}{\rightleftharpoons} CH_3=CH_2 + H^+$$

Ethene

(ii) 

Cumene

Phenol

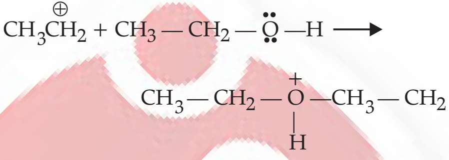
16. (i) Step I: Protonation of alcohol

$$CH_3-CH_2-OH \overset{H^+}{\rightleftharpoons} CH_3-CH_2-\overset{+}{\underset{\cdot\cdot}{O}}H_2$$

Step II: Removal of water

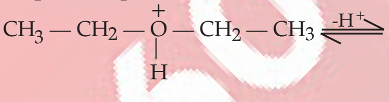
$$CH_3-CH_2-\overset{+}{\underset{\cdot\cdot}{O}}H_2 \overset{-H_2O}{\rightleftharpoons} CH_3-\overset{+}{C}H_2$$

Step III: Attack of nucleophile



$$CH_3\overset{\oplus}{C}H_2 + CH_3-CH_2-\ddot{\underset{\cdot\cdot}{O}}-H \longrightarrow CH_3-CH_2-\underset{H}{\overset{+}{O}}-CH_3-CH_2$$

Step IV: Deprotonation



$$CH_3-CH_2-\underset{H}{\overset{+}{O}}-CH_2-CH_3 \overset{-H^+}{\rightleftharpoons}$$

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

(ii) The addition of borane followed by oxidation is known as hydroboration oxidation reaction For example propan-1-ol is produced by the hydroboration oxidation. reaction of prepene.

$$3CH_3-CH=CH_2 + BH_3 \longrightarrow (CH_3-CH_2-CH_2)_3B$$

$$\xrightarrow{3H_2O_2/\bar{O}H} 3CH_3CH_2CH_2OH + B(OH)_3$$

Propan-1-ol

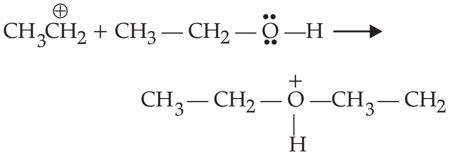
17. (i) Step I: Protonation of alcohol

$$CH_3-CH_2-OH \overset{H^+}{\rightleftharpoons} CH_3-CH_2-\overset{+}{\underset{\cdot\cdot}{O}}H_2$$

Step II: Removal of water

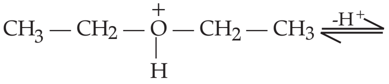
$$CH_3-CH_2-\overset{+}{\underset{\cdot\cdot}{O}}H_2 \overset{-H_2O}{\rightleftharpoons} CH_3-\overset{+}{C}H_2$$

Step III: Attack of nucleophile



$$CH_3\overset{\oplus}{C}H_2 + CH_3-CH_2-\ddot{\underset{\cdot\cdot}{O}}-H \longrightarrow CH_3-CH_2-\underset{H}{\overset{+}{O}}-CH_3-CH_2$$

Step IV: Deprotonation

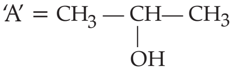


$$CH_3-CH_2-\underset{H}{\overset{+}{O}}-CH_2-CH_3 \overset{-H^+}{\rightleftharpoons}$$

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

(ii) In ortho-nitrophenol, the nitro group ($-NO_2$) is close to the hydroxyl group (–OH) resulting in intramolecular hydrogen bonding between –OH group hydrogen with one of the oxygen atoms of $-NO_2$ group. This internal bonding reduces the molecule's ability to form hydrogen bonds with other molecules, leading to weaker intermolecular forces. Hence, it has a lower boiling point and can be steam distilled.

On the other hand *p*-nitrophenol has strong intermolecular hydrogen bonds as well as compactly packed, which increases its boiling point and makes it unsuitable for steam distillation.

18. 
$$'A' = CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

Compound A with formula C_3H_8O on treatment with Cu gives compound B, which does not reduce Fehling's solution.

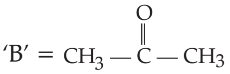
We know that ketones do not give Fehling's test whereas aldehydes do. So B could be a ketone.

As secondary alcohols on oxidation with Cu yield ketones- compound A has to be a secondary alcohol.

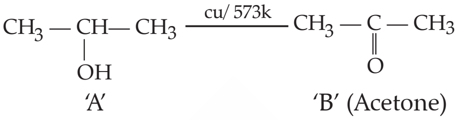
As compound B give a positive Iodoform test, it indicates presence of methyl group- B has to be a methyl ketone.

C has to be the yellow *ppt* -iodoform CHI_3.

Hence,


$$'B' = CH_3-\overset{\overset{O}{\|}}{C}-CH_3$$

$'C' = CHI_3$


$$\underset{'A'}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3} \xrightarrow{cu/\ 573k} \underset{'B'\ (Acetone)}{CH_3-\underset{\underset{O}{\|}}{C}-CH_3}$$

$$CH_3COCH_3 \xrightarrow[\text{Solution}]{\text{Fehling}} \text{No reaction}$$

$$CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow CH_3COONa + 3NaI + CHI_3\downarrow + 3H_2O$$

'C' (Iodoform)

LONG ANSWER TYPE QUESTIONS (5 Marks)

1. (i) (a) The reaction of ethanol with acetyl chloride is carried out in the presence of pyridine as ethanol (CH_3CH_2OH) reacts with acetyl chloride (CH_3COCl) to produce ethyl acetate ($CH_3COOCH_2CH_3$) and HCl. Pyridine is a strong organic base. The function of pyridine is to neutralise HCl formed in the reaction. Removal of HCl supports the forward reaction and formation of ester.

(b) In phenols the lone pair of oxygen atom is delocalised on the phenyl ring. This makes phenoxide ion resonance stablised and it is easier for phenol to lose a proton.

On the other hand, the electron releasing group in Cresol is $-CH_3$ which increases the negative charge on oxygen atom attached to the ring making losing of a proton difficult. Thus making cresol less acidic than phenol.

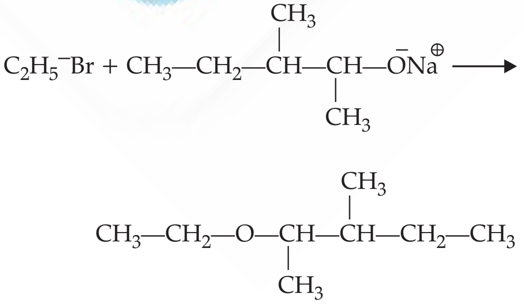
(ii) C_2H_5Br and $CH_3CH_2CH(CH_3)CH(CH_3)ONa$ yields 2-ethoxy-3-methylpentane.

The desired ether (2-ethoxy-3-methylpentane) has a 2-carbon ethoxy group (CH_3CH_2O-) and a 3-methylpentyl group.

Williamson's synthesis involves a S_N2 nucleophilic attack by alkoxide ion on alkyl halide.

As primary alkyl halides yield the desired results in Williamson's synthesis whereas secondary and tertiary alkyl halides lead to elimination reactions- the alkyl halide has to be Ethyl Bromide.

The alkoxide contains a 3-methyl pentane group.


$$C_2H_5^-Br + CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-\overset{-}{O}\overset{\oplus}{Na} \longrightarrow$$
$$CH_3-CH_2-O-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3$$

2. (i) Isomers of butanol are:

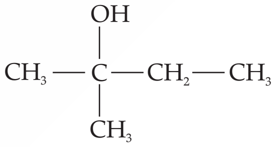
Butan-1-ol, butan-2-ol, 2-methylpropanol, 2-methylpropan-2-ol.

Acidic strength in isomeric alcohols varies as follows:

The acidic character of alcohols is due to the polar nature of O–H bond. An electron-releasing group ($-CH_3$, $-C_2H_5$) increases electron density on oxygen tending to decrease the polarity of O-H bond. So, their increasing order of acidity will be: 2-methylpropan-2-ol< 2-methylpropanol < butan-2-ol <Butan-1-ol.

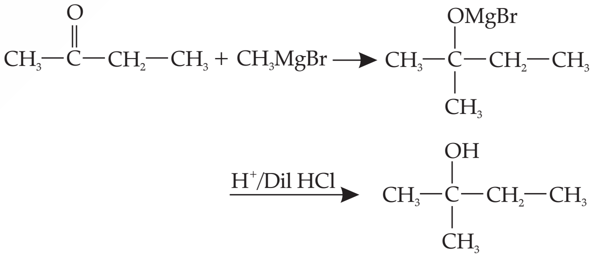
(ii) An organic compound A is a Grignard reagent: RMgX.B is a ketone RCOR'

A + B ⟶


$$CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$$

(2-methylbutan-2-ol)

Ketones lead to the formation of tertiary alcohol, so the compound B– Butan-2-one and A ' is CH_3MgBr


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 + CH_3MgBr \longrightarrow CH_3-\overset{\overset{OMgBr}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$$
$$\xrightarrow{H^+/Dil\ HCl} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3$$

3. (i) (1) Aqueous Br_2

(2) B_2H_6, H_2O_2 and OH^-

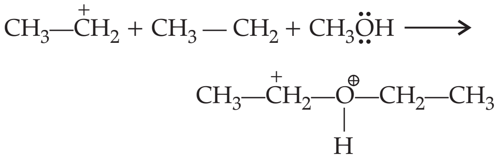
(ii) (1) ethanol < phenol < *p*-nitrophenol

(2) propane < propanal < propanol

(iii) Removal of water:

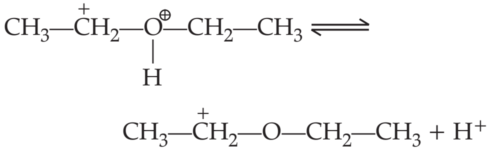
$$CH_3-CH_2-\overset{+}{O}H_2 \overset{H^+}{\rightleftharpoons} CH_3-\overset{+}{C}H_2 + H_2O$$

Attacking of nucleophile:



$$CH_3-\overset{+}{C}H_2 + CH_3-CH_2 + CH_3\ddot{O}H \longrightarrow CH_3-\overset{+}{C}H_2-\underset{H}{\underset{|}{\overset{\oplus}{O}}}-CH_2-CH_3$$

Deprotonation:



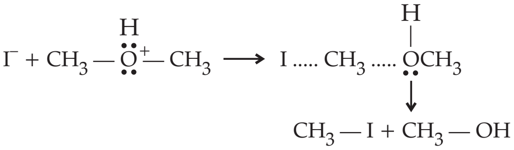
$$CH_3-\overset{+}{C}H_2-\underset{H}{\underset{|}{\overset{\oplus}{O}}}-CH_2-CH_3 \rightleftharpoons CH_3-\overset{+}{C}H_2-O-CH_2-CH_3 + H^+$$

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

Step 1: Protonation of methoxymethane

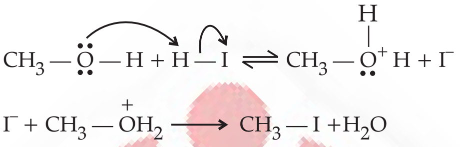
$$CH_3-\ddot{O}-CH_3 + H-I \rightleftharpoons CH_3-\ddot{O}-CH_3 + I^-$$

Step 2: Nucleophilic attack of I^-:



$$I^- + CH_3-\overset{H}{\ddot{O}^+}-CH_3 \longrightarrow I \ldots\ldots CH_3 \ldots\ldots \overset{H}{\overset{|}{\ddot{O}}}CH_3 \downarrow CH_3-I + CH_3-OH$$

Step 3: When HI is in excess and the reaction is carried out at a high temperature, the product formed is the second step reacts with another HI molecule and gets converted to methyliodide.



$$CH_3-\ddot{O}-H + H-I \rightleftharpoons CH_3-\overset{H}{\overset{|}{\ddot{O}^+}}H + I^-$$

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

Level - 2 ADVANCED COMPETENCY FOCUSED QUESTIONS

MULTIPLE CHOICE QUESTIONS (MCQs)

(1 Mark)

1. **Option (A) is correct.**

   Explanation: On oxidation primary alcohol oxidises to aldehyde which reduces tollen's reagent.

2. **Option (B) is correct.**

   Explanation: Dichlorocarbene ($:CCl_2$) electrophile is formed as a reaction intermediate in this reaction. Dichlorocarbe $:CCl_2$ which is formed by reaction of chloroform $CHCl_3$ and aqueous NaOH acts as an electrophile in the Reimer Tiemann reaction.

3. Option (C) is correct

   Explanation: Ethanol is added to petrol (forming gasohol) because it is miscible with petrol, ensuring uniform mixing. It has a high octane number, which reduces engine knocking and improves performance. It burns more cleanly, reducing carbon monoxide emissions.

4. Option (C) is correct

   Explanation: Phenol is effective as an antiseptic because it denatures proteins in microbial cells, leading to cell death. It disrupts the cell membrane integrity and inactivates enzymes, making it effective in formulations like Dettol.

5. Option (B) is correct

   Explanation: Glycerol (also called glycerin) is a triol (contains three –OH groups), which makes it hygroscopic, i.e., it absorbs moisture from the air. This property makes it effective in moisturising creams, lotions, and soaps, keeping skin soft and hydrated.

6. Option (D) is correct

   Explanation: Ethylene glycol ($HO–CH_2–CH_2–OH$) is a diol (contains two –OH groups) widely used as an antifreeze agent in car radiators (lowers the freezing point of water). It is also used as an industrial solvent in the manufacture of polyesters and plastics.

7. Option (C) is correct

   Explanation: Methanol (CH_3OH) is highly toxic when ingested because in the human liver, methanol is metabolised by the enzyme alcohol dehydrogenase into Formaldehyde (HCHO) — a toxic compound, which is further converted into formic acid (HCOOH) — a compound that can cause metabolic acidosis, blindness, permanent nervous system damage and even death, if untreated.

8. Option (A) is correct

   Explanation: Anisole ($C_6H_5OCH_3$) is a methoxybenzene, widely used in perfume industries because it has a pleasant, sweet odour, which makes it suitable as a fragrance base. The ether functional group ($–OCH_3$) contributes to its volatility and stability, allowing it to be effectively used in perfumes and aromatic blends.

ASSERTION-REASON QUESTIONS

(1 Mark)

1. Option (C) is correct.

   Explanation: Assertion is true. The shorter C-O bond length in phenol is due to the partial double bond character of the bond. This arises due to the resonance of the lone pair on oxygen with the aromatic ring of phenol.

   Reason is not true. The carbon atom attached to oxygen in phenol is sp^2 hybridised not sp^3 hybridised.

2. Option (A) is correct.

   Explanation: Assertion is true and Reason is also true. Hydroboration is an addition reaction between an alkene and a borane (neutral species containing a B-H bond). In hydroboration, a C-C pi bond is broken, and a C-H bond as well as a C-B bond is formed. Oxidation of the resulting organoborane with hydrogen peroxide (H_2O_2) then replaces the C-B bond with a C-OH bond resulting in formation of alcohols.

3. Option (A) is correct

Explanation: Assertion is true. Tertiary alcohols have the –OH group attached to a carbon atom that is bonded to three other carbon atoms. Since there is no hydrogen on the α-carbon (the carbon bonded directly to the –OH group), oxidation is difficult. Under mild oxidising agents, tertiary alcohols generally do not undergo oxidation.

Reason is also true. In tertiary alcohols, the carbon bearing the –OH group is bonded to three other carbon atoms, and thus lacks any hydrogen atom directly attached to it. This absence of α-hydrogens makes oxidation difficult.

4. Option (A) is correct

Explanation: Assertion is true. Phenol is more acidic than ethanol because the phenol molecule can lose a proton (H^+) more easily. This is due to the stabilisation of the phenoxide ion through delocalisation (resonance). In contrast, ethanol forms an ethoxide ion, which is not resonance stabilised and thus less stable. Therefore, phenol has a greater tendency to donate a proton, making it more acidic than ethanol.

Reason is also true. When phenol loses a proton (H^+), it forms a phenoxide ion. This ion has its negative charge delocalised over the aromatic ring through resonance, which stabilises the ion significantly.

5. Option (A) is correct

Explanation: Assertion is true. Ethers have lower boiling points than alcohols of similar molecular mass. This is because alcohols can form intermolecular hydrogen bonds, which require more energy (heat) to break, resulting in higher boiling points. Ethers lack this kind of bonding between their own molecules, so their boiling points are lower.

Reason is also true. Ethers have an oxygen atom, but no hydrogen directly bonded to oxygen, so they cannot form hydrogen bonds among themselves. Only alcohols have an –OH group capable of such bonding.

6. Option (A) is correct

Explanation: Assertion is true. When ethanol (C_2H_5OH) is heated with concentrated sulphuric acid (H_2SO_4) at about 443 K, it undergoes dehydration (loss of water) to form ethene (C_2H_4). This is an elimination reaction, where a molecule of water is removed from ethanol.

Reason is also true. Concentrated H_2SO_4 is a strong dehydrating agent. It protonates the –OH group of ethanol, making it a better leaving group, and facilitates the removal of a water molecule, leading to the formation of a double bond (ethene).

VERY SHORT ANSWER TYPE QUESTIONS (2 Marks)

1. This is not a good method for the preparation of *n*-propyl ethyl ether.

The reaction will produce a mixture of three different ether which would be difficult to separate.

2. Tertiary alcohols give a positive Lucas test immediately because they form tertiary carbocations quickly through the S_N1 mechanism, which are highly stable due to inductive and hyperconjugation effects. This leads to rapid formation of the corresponding alkyl halide, causing turbidity.

In contrast, primary alcohols form unstable primary carbocations, so the reaction is either very slow or does not occur at room temperature, showing no turbidity.

3. Phenol reacts with bromine water to give a white precipitate of 2, 4, 6-tribromophenol, even at room temperature:

$C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr$

This reaction is useful in detecting phenol because the formation of a white precipitate is a visual confirmation of phenol's presence. It is a specific test, as few other compounds react with bromine water this rapidly or form such a distinctive product.

4. Ethanol is commonly used as a solvent in medicines and perfumes due to the following physical and chemical properties:

(1) Good Solubility (Polarity): Ethanol has both a hydrophilic –OH group and a hydrophobic ethyl group, allowing it to dissolve both polar and non-polar substances. This makes it an excellent medium for dissolving active medicinal ingredients and aromatic compounds.

(2) Volatility: Ethanol has a moderate boiling point (78.5°C) and evaporates easily at room temperature. This helps perfumes disperse quickly and leave no residue, making it ideal for fragrance delivery.

(3) Non-toxicity in small amounts: Ethanol is safe in low concentrations, making it suitable for internal medicinal preparations like tinctures, cough syrups, and tonics.

(4) Antiseptic nature: Ethanol has antibacterial and antifungal properties, enhancing its use in medicinal formulations like hand sanitisers and disinfectants.

5. Ethers are highly volatile and can form explosive peroxides on prolonged exposure to air and light. Dark-coloured bottles reduce light-induced peroxide formation, and tightly closed containers prevent vapour leakage and contact with oxygen. Heat sources can ignite ether vapours, so they must be kept away to avoid fire or explosions.

6. Phenol is a weak acid and does not have enough acidity to release CO_2 from sodium carbonate (Na_2CO_3) or sodium bicarbonate ($NaHCO_2$). Carboxylic acids are stronger acids than phenol, so they react with these carbonates to form carbon dioxide (CO_2), water, and a salt. Thus, only carboxylic acids can displace CO_2 from carbonates and bicarbonates.

SHORT ANSWER TYPE QUESTIONS (3 Marks)

1. The acid-catalysed hydration of ethene is an electrophilic addition reaction that proceeds in the following steps:

Step 1: Protonation of Ethene: Ethene (C_2H_4) has a double bond with high electron density. The π-electrons attack a proton (H^+) from the acid (H_2SO_4), forming a carbocation intermediate.

$CH_2 = CH_2 + H^+ \rightarrow CH_3–CH_2^+$

Step 2: Nucleophilic Attack by Water: Water, acting as a nucleophile, attacks the carbocation, forming a protonated ethanol molecule.

$CH_3–CH_2^+ + H_2O \rightarrow CH_3–CH_2–OH_2^+$

Step 3: Deprotonation: The protonated alcohol loses a proton to form ethanol.

$CH_3–CH_2–OH_2^+ \rightarrow CH_3–CH_2–OH + H^+$

Overall Reaction:

$$CH_2 = CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3–CH_2–OH$$

H_2SO_4 acts as a catalyst. It provides H^+ ions to initiate the reaction. Dilution ensures water is in excess, shifting the equilibrium toward ethanol formation. Concentrated H_2SO_4 could lead to side reactions (e.g., dehydration back to ethene), hence dilute H_2SO_4 ensures hydration predominates.

2. Phenol reacts readily with aqueous bromine (Br_2 in water) to give a white precipitate of 2, 4, 6-tribromophenol. This is a characteristic test for phenol.

$C_6H_5OH + 3Br_2 \rightarrow C_6H_2Br_3OH + 3HBr$

Phenol + Bromine → 2, 4, 6-Tribromophenol (white ppt.) + Hydrogen bromide

Role of Activating Groups:

The –OH group in phenol is an activating group. It increases the electron density on the benzene ring, especially at the ortho (2, 6) and para (4) positions, due to +R (resonance donating) effect. This makes the ring more reactive toward electrophilic substitution reactions like bromination (Bromine when dissolved in water acts as an electrophile). Hence, bromine substitutes easily at all three activated positions without the need for a catalyst.

3.

	Properties	Alcohols	Ethers
(i)	Boiling points	Have higher boiling points than ethers of similar molecular mass due to strong intermolecular hydrogen bonding.	Have lower boiling points. Lack intermolecular hydrogen bonding between ether molecules.
(ii)	Hydrogen bonding	Can form hydrogen bonds with other alcohol molecules (intermolecular) and with water (intermolecular). –OH group is a strong hydrogen bond donor.	Cannot form hydrogen bonds with themselves. Can form hydrogen bonds with water due to lone pairs on oxygen (intermolecular only with water).
(iii)	Solubility in water	Generally more soluble in water, especially lower alcohols, due to hydrogen bonding with water.	Also soluble in water to some extent (especially lower ethers), but less than alcohols.

4. The Williamson Synthesis is a method to prepare ethers by reacting a sodium alkoxide with a primary alkyl halide in an S_N2 reaction.

Using sodium ethoxide (C_2H_5ONa) and bromoethane (C_2H_5Br):

$C_2H_5ONa + C_2H_5Br \rightarrow C_2H_5OC_2H_5 + NaBr$

The product formed is diethyl ether.

Mechanism:

The ethoxide ion ($C_2H_5O^–$) acts as a nucleophile and attacks the electrophilic carbon of the bromoethane, displacing $Br^–$. This is a bimolecular nucleophilic substitution (S_N2) reaction.

Primary alkyl halides are less hindered, so the S_N2 mechanism proceeds faster and more efficiently. Secondary or tertiary halides tend to undergo elimination (E2) instead of substitution, which reduces the ether yield.

5. Lucas reagent is a mixture of concentrated hydrochloric acid (HCl) and anhydrous zinc chloride ($ZnCl_2$). It is used to differentiate primary, secondary, and tertiary alcohols based on their reactivity in forming alkyl halides.

Type of Alcohol	Observation with Lucas Reagent	Time Taken
Secondary alcohol	Cloudiness appears slowly	5–10 minutes
Tertiary alcohol	Immediate cloudiness or turbidity	Within seconds

Reason for Difference:

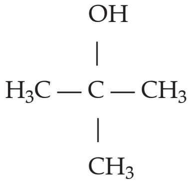
Tertiary alcohols form stable tertiary carbocations quickly when reacted with $\frac{HCl}{ZnCl_2}$, facilitating fast S_N1 substitution to form alkyl chlorides, which are insoluble in the aqueous medium, hence turbidity appears instantly.

Secondary alcohols form less stable secondary carbocations, so the reaction is slower, and turbidity appears after some time.

CASE BASED QUESTIONS

(4 Mark)

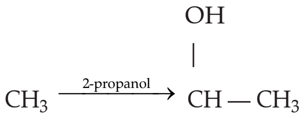
1. (i)



$$H_3C-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

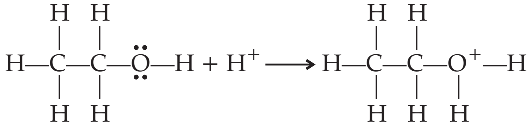
2-methyl propan-2-ol

(ii) $CH_3 \xrightarrow{\text{propene}} CH = CH_2 + H_2O \xrightarrow{H^+}$

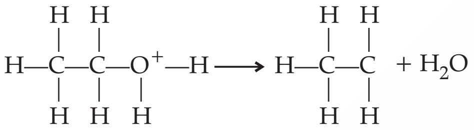


$$CH_3 \xrightarrow{\text{2-propanol}} \overset{\overset{OH}{|}}{CH}-CH_3$$

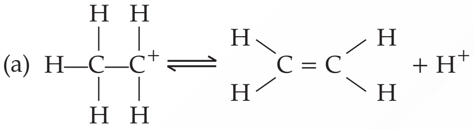
(iii) (a) **Step 1:**



Step 2:



Step 3:



OR

(b) (1) Because of H-bond formation between alcohol and water molecule.

(2) Nitro being the electron with drawing group stabilises the phenoxide ion formed after deprotonation, thus increasing its acidity.

However, the methoxy group ($-OCH_3$) is an electron-donating group (through both inductive and resonance effects), which destabilises the phenoxide ion, hence decreasing its acidity.

2. (i) Yes, he took the right decision.

(ii) The compound A and B are copper sulphate ($CuSO_4$) and pyridine (C_5H_5N), respectively. This process is called denaturation of alcohol.

(iii) (a) A 10% ethanol solution administered intravenously is a safe and effective antidote for severe methanol poisoning. Both methanol and ethanol are oxidised in the body first to methanal and ethanal and then to methanoic acid and ethanoic acid, respectively.

OR

(b) The addition of the nitrogen- containing heterocyclic base (B) helps in deterring the misuse of ethanol in the paint company by imparting a foul smell to the alcohol. This unpleasant odour makes the ethanol less desirable for unauthorised purposes, thereby discouraging employees from using it.

LONG ANSWER TYPE QUESTIONS

(5 Marks)

1. (i) (1) Ethanol is a clean-burning fuel with a high octane number.

(2) It is volatile, easily combustible, and produces fewer harmful emissions.

(3) It is renewable and biodegradable.

(ii) Ethanol contains oxygen, which promotes more complete combustion of petrol. This reduces the emission of carbon monoxide (CO), unburnt hydrocarbons, and particulate matter. It helps lower greenhouse gas emissions compared to pure petrol.

(iii) **Economic challenge:** Diverting food crops (like corn, sugarcane) for fuel can raise food prices and impact food security.

Environmental challenge: Large-scale farming for ethanol leads to deforestation, soil erosion, and increased water use.

(iv) Using second-generation biofuels from agricultural waste, lignocellulosic biomass (like crop residues), or algae helps reduce environmental burden and avoids food vs. fuel issues.

(v) (1) Ethanol combustion produces CO_2 and water with minimal soot.

(2) It generates fewer toxic pollutants (like NO_x and SO_2) compared to fossil fuels.

(3) It has a lower energy content per litre but burns cleaner and more efficiently in blends.

2. (i) Phenol has germicidal properties due to its ability to denature microbial proteins and disrupt cell membranes.

(ii) The –OH group attached to the aromatic ring increases phenol's ability to form hydrogen bonds with amino acid side chains. This disrupts protein structure, causing coagulation of proteins in microbial cells, leading to their death.

(iii) Undiluted phenol is corrosive and can cause skin burns and tissue damage. It is diluted (e.g., in products like Dettol) to reduce toxicity while retaining antimicrobial activity.

(iv) Overexposure to phenol can cause skin irritation, respiratory problems, and in some cases, systemic toxicity upon absorption through the skin.

(v) Chlorhexidine is a widely used safer antiseptic that has broad-spectrum antimicrobial activity and is less toxic than phenol.

3. (i) Diethyl ether was used due to its strong anesthetic effect, rapid action, and ability to induce unconsciousness safely at controlled doses.

(ii) Ether vapours are highly flammable and can form explosive mixtures with air, posing serious fire and explosion hazards in surgical environments.

(iii) Diethyl ether has a low boiling point (~35°C), so it evaporates easily at room temperature. It must be stored in airtight containers, away from heat or open flames, and often under an inert atmosphere to prevent peroxide formation.

(iv) Compounds like halothane and isoflurane have replaced ether. They are non-flammable, have fewer side effects, and are easier to control during surgeries.

(v) Ethers do not form hydrogen bonds between their molecules, resulting in weaker intermolecular forces and hence low boiling points, making them volatile.

4. (i) Glycerol has three hydroxyl (–OH) groups, which make it highly hygroscopic (ability to absorb moisture from the air). This triol structure enables it to attract and retain water.

(ii) (1) It acts as a humectant, drawing moisture from the environment into the skin.

(2) It also forms a protective layer on the skin, preventing water loss through evaporation.

(iii) Unlike methanol or ethanol, glycerol is non-toxic and non-irritating. It does not dry out the skin, while alcohols can remove natural oils and cause irritation.

(iv) Glycerol is used in cough syrups as a sweetening and soothing agent. It also serves as a laxative and in suppositories for treating constipation.

(v) The three –OH groups in glycerol can form strong hydrogen bonds with water and biological molecules. This enhances its solubility, moisture-retaining ability, and compatibility with skin and body fluids.

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