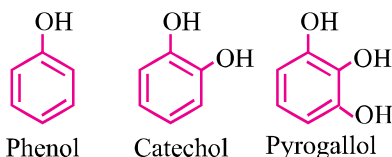


UNIT-11

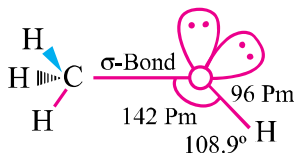
ALCOHOLS, PHENOLS AND ETHERS

Quick Concepts to Remember

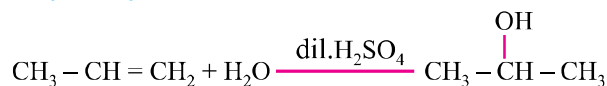
1. Hydroxyl (– OH) derivatives of alkane are called alcohols.
2. Alcohols are classified as 1°, 2° and 3°.
3. –OH group is attached to sp^3 hybridized carbon. Alcohols further may be monohydric, dihydric and polyhydric on the basis of OH group.
4. **Phenols** : Compounds containing – OH group bound directly to benzene ring.



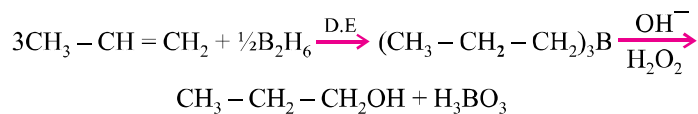
5. **Structure** : Oxygen atom is sp^3 hybridised and tetrahedral geometry of hybrid atomic orbitals ROH bond angle depends upon the R group. R – O – H angle for $\text{CH}_3 - \text{OH}$ is 108.9° .

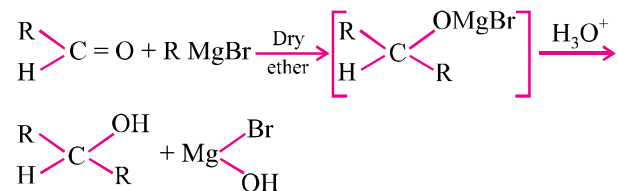


6. **Isomerism** :
 - (i) Functional isomerism
 - (ii) Chain isomerism
 - (iii) Positional isomerism
7. **General Methods of Preparation** :
 - (i) **Acid catalysed hydration of alkenes** :

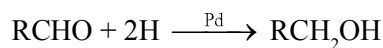
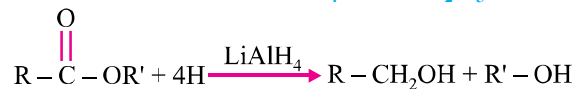
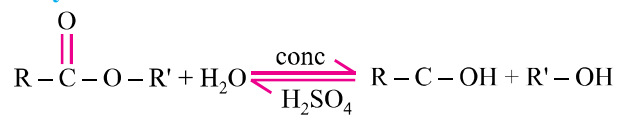
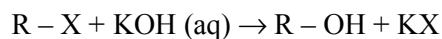
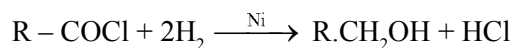
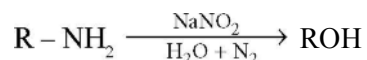


- (ii) **Hydroboration oxidation** :



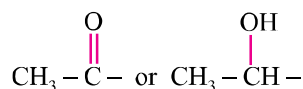
(iii) From carbonyl compounds with Grignard's reagent :

Formaldehyde gives 1° alcohol and ketones gives tertiary alcohol.

(iv) By reduction of carbonyl compounds :**(v) By reduction of esters with LiAlH₄ or Na/C₂H₅OH :****(vi) By hydrolysis of esters :****(vii) From alkyl halides :****(viii) By reduction of acids and their derivatives :****(ix) From 1° amines :**

8. Ethers are dialkyl derivatives of water or monoalkyl derivatives of alcohols with formula
9. Lucas test can be used to distinguish primary, secondary and tertiary alcohols (ZnCl₂ + HCl).
(3° turbidity – instant, 2° - 5 minutes, 1° - heating for 60 minutes)
10. Ethers are relatively inert and hence are used as solvents.

11. 100% ethanol is known as absolute alcohol.
12. 95% ethanol is called rectified spirit.
13. A mixture of 20% ethanol and 80% gasoline is known as power alcohol.
14. Iodoform test is used for distinguishing compounds having the groups



15. Presence of EWGs increase the acid strength of phenols while ERGs decrease the acid strength.

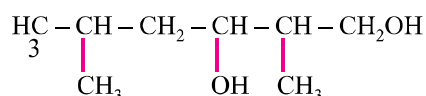
EWG : $-\text{NO}_2$, $-\text{X}$, $-\text{CN}$, $-\text{COOH}$ etc.

ERG : $-\text{R}$, $-\text{OR}$, $-\text{OH}$, $-\text{NH}_2$ etc.

16. 3° alcohols are resistant to oxidation due to lack of α -hydrogen.
17. Intermolecular H-bonds of *p*- and *m*-nitrophenol increases water solubility/acid strength while intramolecular H-bonds in *o*-nitrophenol decreases these properties.
18. In the reaction of alkyl aryl ether (anisole) with HI, the products are always alkyl halide and phenol because O – R bond is weak than O – Ar bond which has partial double character due to resonance.
19. C – O – C bond in ether is bent and hence the ether is always polar molecule even if both alkyl groups are identical.

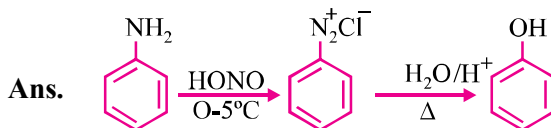
VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

Q. 1. Write IUPAC name of the following compound :



Ans. 2,5-Dimethylhexane-1, 3 diol.

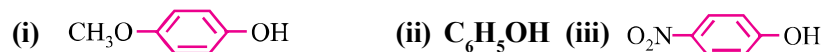
Q. 2. How is phenol obtained from aniline ?



Q. 3. Why phenol is acidic in nature ?

Ans. Due to stability of phenoxide ion by resonance.

Q. 4. Arrange the following in decreasing order of their acidic character :



Ans. (iii) > (ii) > (i)

Q. 5. Among HI, HBr and HCl, HI is most reactive towards alcohols. Why ?

Ans. Due to lowest bond dissociation energy of HI.

Q. 6. Name a compound which is used as antiseptic as well as disinfectant.

Ans. Solution of phenol : 0.2% antiseptic, 2% disinfectant.

Q. 7. What is nitrating mixture ?

Ans. Conc. ($\text{H}_2\text{SO}_4 + \text{HNO}_3$)

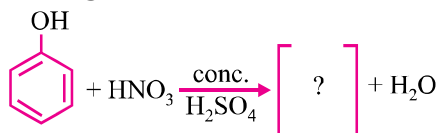
Q. 8. Lower alcohols are soluble in water, higher alcohols are not. Why ?

Ans. Due to formation of hydrogen bonds.

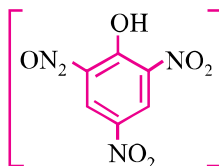
Q. 9. What happens when $\text{CH}_3\text{CH}_2\text{OH}$ heated with red P and HI ?

Ans. $\text{C}_2\text{H}_5\text{OH} + 2\text{HI} \xrightarrow{\text{Red P}} \text{C}_2\text{H}_6 + \text{I}_2 + \text{H}_2\text{O}$

Q. 10. Complete the following reaction :



Ans.



2, 4, 6-Trinitro phenol (Picric acid)

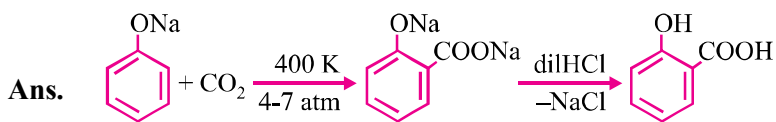
Q. 11. Ethanol has higher boiling point than methoxy methane. Give reason.

Ans. Because of H-bonds.

Q. 12. How could you convert ethanol to ethane ?

Ans. $\text{C}_2\text{H}_5\text{OH} \xrightarrow[443 \text{ K}]{\text{Conc. H}_2\text{SO}_4} \text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O}$

Q. 13. Explain Kolbe's reaction with example.

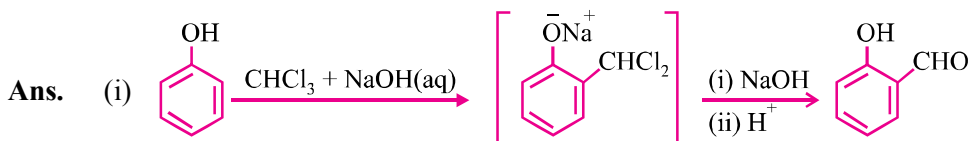


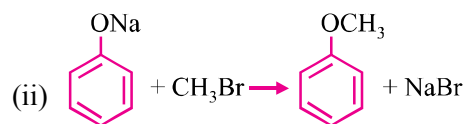
SHORT ANSWER-I TYPE QUESTIONS (2 Marks)

Q. 1. Write one chemical reaction to illustrate the following :

(i) Reimer-Teimann reaction

(ii) Williamson's synthesis





Q. 2. Account for the following :

(i) Phenol has a smaller dipole moment than methanol.

(ii) Phenol goes electrophilic substitution reactions.

Ans. (i) Due to –ve charge on oxygen in delocalized by resonance.

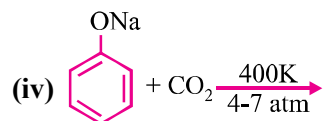
(ii) Due to greater electron density than benzene.

Q. 3. Complete the following equations and name the products :

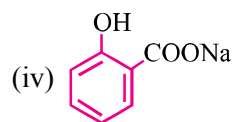
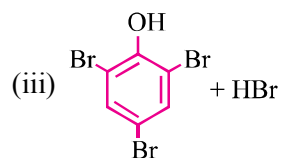
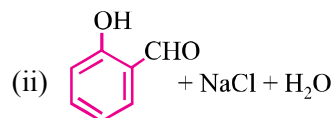
(i) Phenol + $\text{FeCl}_3 \rightarrow$

(ii) $\text{C}_6\text{H}_5\text{OH} + \text{CHCl}_3 + \text{NaOH} \xrightarrow{340\text{ K}}$

(iii) $\text{C}_6\text{H}_5\text{OH} + \text{Br}_2 (\text{aq}) \rightarrow$



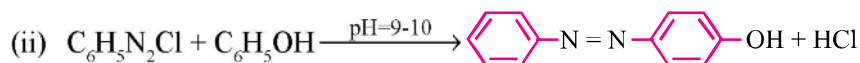
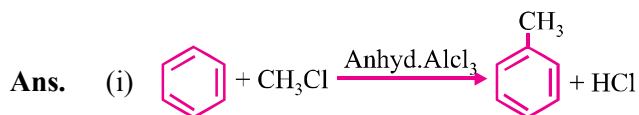
Ans. (i) $[(\text{C}_6\text{H}_5\text{O})_6\text{Fe}]^{3-} + \text{HCl} + \text{H}^+$



Q. 4. Write :

(i) Friedel-Crafts reaction

(ii) Coupling reaction



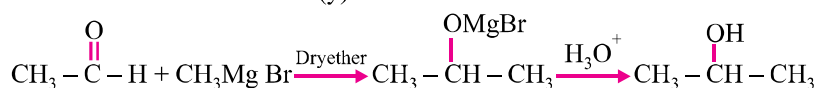
Q. 5. Give two reaction of alcohol involving cleavage of :

- (i) C – O bond
- (ii) O – H bond

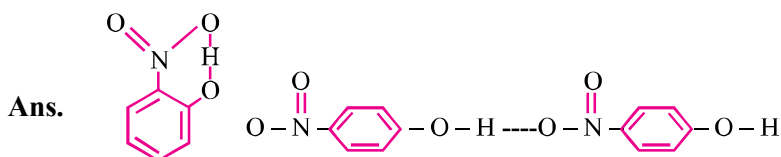
Ans. (i) $\text{CH}_3\text{CH}_2\text{OH} + \text{PCl}_5 \rightarrow \text{CH}_3\text{CH}_2\text{Cl} + \text{POCl}_3 + \text{HCl}$
(ii) $\text{CH}_3\text{CH}_2\text{OH} + \text{Na} \rightarrow \text{CH}_3\text{CH}_2\text{ONa} + \text{H}_2$

Q. 6. Etherial solution of an organic compound 'X' when heated with Mg gave 'Y'. 'Y' on treatment with C_2H_5OH followed by acid hydrolysis gave 2-propanol. Identify the compound 'X'. What is 'Y' known as ?

Ans.
$$\underset{x}{\text{CH}_3\text{Br}} + \text{Mg} \xrightarrow{\text{Dry ether}} \underset{(y)}{\text{CH}_3\text{MgBr}}$$



Q. 7. While separating a mixture of *o*- and *p*-nitrophenols by steam distillation name the isomer which is steam volatile. Give reason.



H-bonding and association of molecules.

Q. 8. Account for the following :

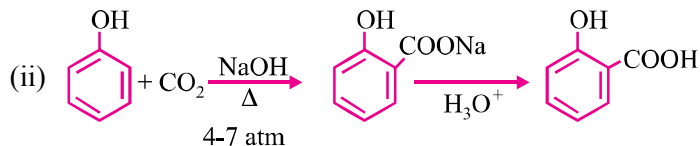
- (i) Phenol has a smaller dipole moment than CH_3OH .
- (ii) Phenol do not give protonation reactions readily.

Ans. (i) Because phenol has electron attracting benzene ring.
(ii) Resonance and +ve charge oxygen does not have tendency to accept a proton.

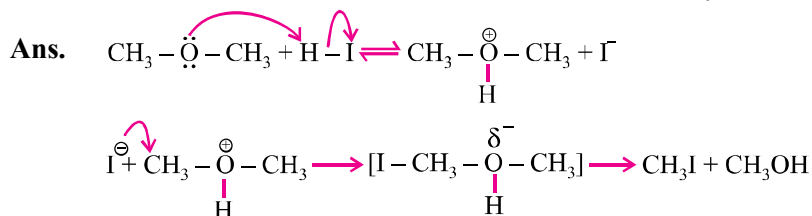
Q. 9. Write the reactions and conditions involved in the conversion of :

- (i) Propene to propan-2-ol.
(ii) Phenol to salicylic acid.

Ans. (i) $\text{CH}_3\text{CH}=\text{CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3 - \underset{\text{OH}}{\underset{|}{\text{CH}}} - \text{CH}_3$



Q. 10. Write mechanism of reaction of HI with methoxymethane.



Q. 11. Arrange in order of boiling points :

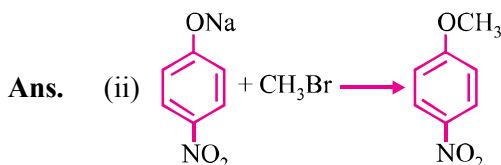
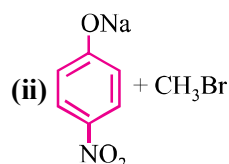
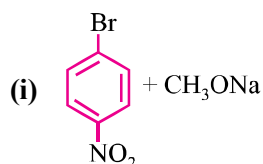
(i) $\text{C}_2\text{H}_5 - \text{O} - \text{C}_2\text{H}_5$, $\text{C}_4\text{H}_9\text{COOH}$, $\text{C}_4\text{H}_9\text{OH}$

(ii) $\text{C}_3\text{H}_7\text{CHO}$, $\text{CH}_3\text{COC}_2\text{H}_5$, $\text{C}_2\text{H}_5\text{COOCH}_3$, $(\text{CH}_3\text{CO})_2\text{O}$

Ans. (i) $\text{C}_4\text{H}_9\text{COOH} > \text{C}_4\text{H}_9\text{OH} > \text{C}_2\text{H}_5 - \text{O} - \text{C}_2\text{H}_5$

(ii) $(\text{CH}_3\text{CO})_2\text{O} > \text{C}_2\text{H}_5\text{COOCH}_3 > \text{CH}_3\text{COC}_2\text{H}_5 > \text{C}_3\text{H}_7\text{CHO}$

Q. 12. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why ?



It is because of double bond character, (C – Br) bond in  due to resonance it is less reactive towards S_N , RXN .

Q. 13. Ethers are relatively inert. Justify.

Ans. Due to absence of any active site in their molecules, divalent oxygen is linked to carbon atoms on both sides $\left(\text{C} - \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} - \text{C} \right)$.

Q. 14. How will you distinguish between CH_3OH and $\text{C}_2\text{H}_5\text{OH}$?

Ans.
$$\text{C}_2\text{H}_5\text{OH} + 4\text{I}_2 + 3\text{Na}_2\text{CO}_3 \xrightarrow{\text{warm}} \text{CHI}_3 + \text{HCOONa} + 5\text{NaI} + 2\text{H}_2\text{O} + 3\text{CO}_2$$

Iodoform (yellow)

CH_3OH does not give this test.

SHORT ANSWER-II TYPE QUESTIONS (3 Marks)

Q. 1. Name the reagents which are used in the following conversions :

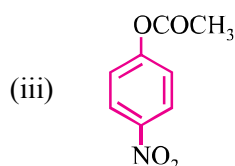
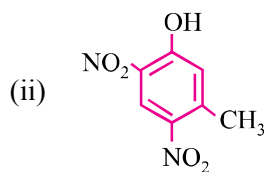
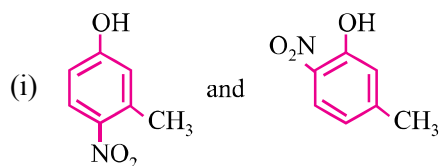
- (i) 1° alcohol to an aldehyde
- (ii) Butan-2-one to butan-2-ol
- (iii) Phenol to 2, 4, 6 tribromophenol

Ans. (i) PCC, a complex of chromium trioxide with pyridine and HCl.
 (ii) NaBH_4 , sodium borohydride.
 (iii) Br_2 (water)

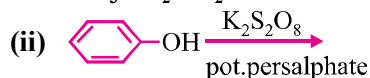
Q. 2. Write structures of the major products of the following :

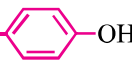
- (i) Mononitration of 3-methylphenol
- (ii) Dinitration of 3-methylphenol
- (iii) Mononitration of phenyl methanoate

Ans. –OH and –CH₃ are *o*- and *p*-directing groups. The products are :



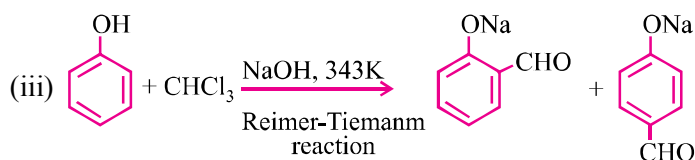
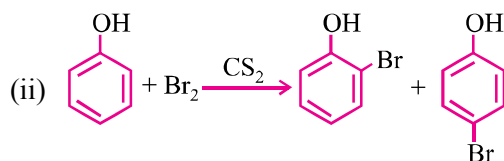
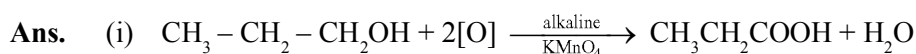
Q. 3. Complete the following reactions :



- Ans.** (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
 (ii) 
 (iii) CH_3I
 (iv) $\text{C}_2\text{H}_5\text{Cl}$
 (v) $\text{CH}_2\text{OH} - \text{CH}_2\text{OH}$
 (vi) $\text{CH}_3\text{CH}_2\text{OH}$

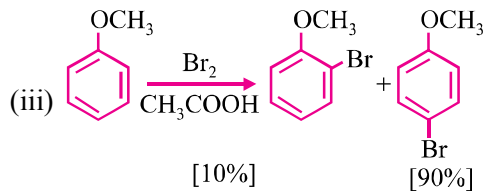
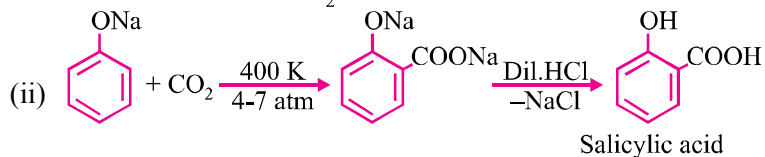
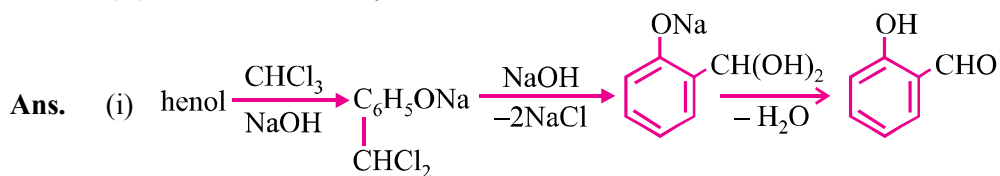
Q. 4. Give equations of the following reactions :

- (i) Oxidation of propan-1-al with alkaline KMnO_4 solution.
 (ii) Bromine in CS_2 with phenol.
 (iii) Treating phenol with chloroform in presence of aqueous NaOH .



Q. 5. Describe the following reactions with examples :

- (i) Reimer-Tiemann reaction
 (ii) Kolbe's reaction
 (iii) Friedel Crafts acylation of anisole



Q. 6. Dehydration of alcohols to form an alkene is always carried out with conc. H_2SO_4 and not with conc. HCl or HNO_3 . Explain.

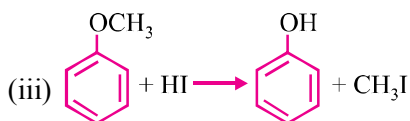
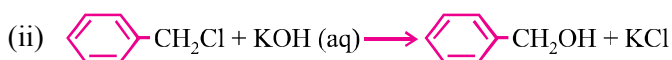
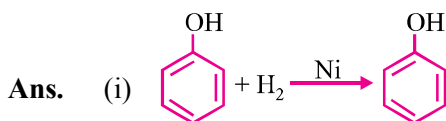
Ans. In acidic medium alcohols protonated then loses H_2O to form a carbo cation. If HCl Cl^- strong nucleophile cause nucleophilic substitution, HNO_3 causes oxidation.

Q. 7. How will you convert :

(i) Phenol to cyclohexanol

(ii) Benzene chloride to benzyl alcohol

(iii) Anisole to phenol



LONG ANSWER TYPE QUESTIONS (5 Marks)

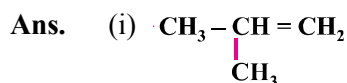
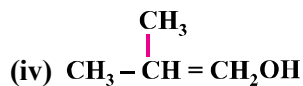
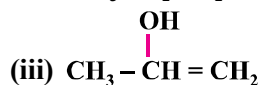
Q. 1. An alcohol A ($\text{C}_4\text{H}_{10}\text{O}$) on oxidation with acidified $\text{K}_2\text{Cr}_2\text{O}_7$ gives carboxylic acid 'B' ($\text{C}_4\text{H}_8\text{O}_2$). Compound 'A' when dehydrated with conc. H_2SO_4 at 443 K gives compound 'C' with aqueous H_2SO_4 . 'C' gives compound 'D' ($\text{C}_4\text{H}_{10}\text{O}$) which is an isomer of 'A'. Compound 'D' is resistant to oxidation but compound 'A' can be easily oxidized. Identify A, B, C and D and write their structure.

Ans. A : $(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{OH}$ B : $\text{CH}_3\text{CH}(\text{CH}_3)\text{COOH}$
C : $(\text{CH}_3)_2\text{C}=\text{CH}_2$ D : $(\text{CH}_3)_3\text{C}-\text{OH}$

Q. 2. An ether 'A' ($\text{C}_5\text{H}_{12}\text{O}$) when heated with excess of hot concentrated HI produced two alkyl halides which on hydrolysis form compounds B and C. Oxidation of B gives an acid D whereas oxidation of C gave a ketone E. Deduce the structures of A, B, C, D and E.

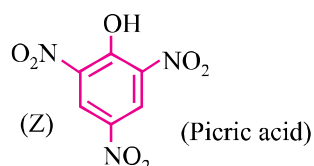
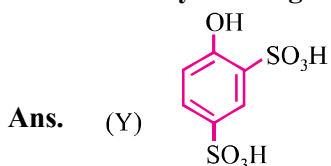
Ans. A : $\text{CH}_3\text{CH}_2\text{OCH}(\text{CH}_3)_2$
B : $\text{CH}_3\text{CH}_2\text{OH}$
C : $\text{CH}_3\text{CHOHCH}_3$
D : CH_3COOH
E : CH_3COCH_3

Q. 3. Which of the following compounds gives fastest reaction with HBr and why ?



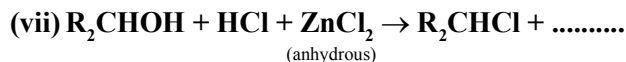
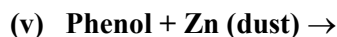
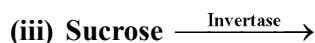
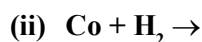
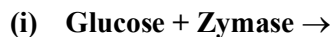
Due to formation of EDG and formation of cation.

Q. 4. Phenol, $\text{C}_6\text{H}_5\text{OH}$ when it first reacts with concentrated sulphuric acid, forms Y. The compound, Y is reacted with concentrated nitric acid to form Z. Identify Y and Z and explain why phenol is not converted commercially to Z by reacting it with conc. HNO_3 .



Phenol is not reacted directly with conc. HNO_3 because the yield of picric acid is very poor.

Q. 5. Fill in the blanks :



- Ans.**
- | | |
|----------------|---|
| (i) C_2H_5OH | (ii) CH_3OH |
| (iii) Glucose | (iv) $C_6H_{12}O_6$ |
| (v) C_6H_6 | (vi) C_6H_5ONa |
| (vii) H_2O | (viii) $R - \overset{\overset{O}{ }}{C} - R$ |
| (ix) SO_2 | (x) $CHCl_3$ |

VALUE BASED QUESTIONS (4 Marks)

- Q. 1.** An owner of a paint company who was using ethanol as solvent noted that his stock of ethanol was misused by his employees. To prevent this, he decided to add small amount of blue coloured compound (A) and another nitrogen containing heterocyclic base (B) which gives a foul smell to alcohol.
- Do you think that he took right decision and mention the values with this decision.
 - Write the names of compound A and B.
 - Consumption of methylated ethanol by person can cause blindness and even death. How is methanol poisoning treated ?
 - Mention values associated with the above decision.
- Q. 2.** Recently Delhi Police launched a special drive to curb the crimes and accidents related to 'Drunken Driving'. An instrument known as alcometer is used to test whether a driver has consumed alcohol or not beyond a certain limit.
- Write the name and chemical formula of the compound used in alcometer.
 - Write the chemistry involved in above test.
 - Write the ionic equation involved in the chemistry of the test.
 - Mention the value shown by Delhi Police.