

ALCOHOL, PHENOL AND ETHER

This particular chapter is divided in the following parts with the exam point of view.

1. Reasoning
2. IUPAC Naming
3. Mechanisms
4. Name Reactions
5. Distinguish between two compounds
6. Conversions

REASONING

Q1. Arrange the following compounds increasing order of boiling point pentanol, butanol, butan-2-ol, propan-1-ol, methanol

Ans. Methanol < ethanol < propanol < butan-2-ol (branch) < butanol < pentanol. B.P is directly related to molecular mass and indirectly to branching.

Q2. Arrange the following in the increasing order of property given:

- (a) $\text{CH}_3\text{CH}_2\text{OH}$, $\text{CF}_3\text{CH}_2\text{OH}$, $\text{CCl}_3\text{CH}_2\text{OH}$ — Acid strength.
- (b) 2-methyl-2-propanol, 1-butanol and 2-butanol-reactivity towards Na.

Ans. (a) Due to –I effect of the halogen the O – H bonds weaken and release of a proton. F is more electronegative than Cl.

- (b) Reactivity depends on strength of Acidity of Alcohols with Na
 $1\text{-butanol} > 2\text{-butanol} > 2\text{-methyl-2-propanol}$ (+I effect)

Q3. Unlike phenols, alcohols are easily protonated.

Ans. Due to resonance, the lone pairs of electrons on O atoms are delocalised over the benzene ring while in alcohols, they are easily available for protonation.

Q4. How do you account for the fact that unlike phenol, 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol are soluble in Na_2CO_3 (aq) solution.

Ans. Presence of 2 NO_2 and 3 NO_2 (strong EWG) in above nitro compound which makes them more acidic and will easily be soluble in Na_2CO_3 .

Q5. Alcohols react with halogen acid or phosphorous halides to form haloalkanes but phenol does not form halobenzene.

Ans. $\text{ROH} \xrightarrow{\text{H}^+} \text{RX} + \text{H}_2\text{O}$ (ROH → In aliphatic alcohol carbon atom has sp^3 hybridisation,

Phenol has sp^2 hybridisation at C – OH bond which is also given double bond character by resonance. So it cannot give Nucleophilic substitution reactions.

Q6. Explain why dehydration of alcohols to form alkenes is always carried out with conc. H_2SO_4 and not with conc. HCl or HNO_3 .

Ans. Reaction with acid will give carbocation. In case HSO_4^- being non-nucleophile cannot substitute the Halogen group but in case Cl^- will give substitution rx. in presence of HNO_3 as NO_3^- is a nucleophile. HCl being oxidising agent, and oxidise alcohol to aldehyde then to acid.

Q7. Di-tert-butyl ether cannot be made by Williamson's synthesis.

Ans. For preparation of di-tert butyl ether requires tert butyl bromide which prefers to undergo elimination rather than substitution reaction.

Q8. Explain why ethers are cleaved only by acids and not by bases.

Ans. Acids can weaken C-O-C bond by protonating oxygen atom which can be attacked by a strong nucleophile to cleavage C - O-C bond.

Q9. Explain why anisole is less reactive than phenol towards electrophilic substitution.

Ans. Both shows +R effect. But in case phenol, it is further more stabilising by releasing a proton.

Q10. Ortho and para nitrophenol are more acidic than phenol.

Ans. NO_2 is EWG group which stabilise phenoxide ion by $-R$ effect.

Q11. Which of the following is an appropriate set of reactant for the preparation of 1-methoxy 4 nitrobenzene and why.

Ans. Try Yourself.

Q12. Why Alcohols has higher B.P than ether or Alkanes.

Ans. Alcohols form strong intermolecular H bonding. ethers form polar-polar bonds while alkanes form weak Vander walls force.

Q13. Alcohols are more soluble than alkane.

Ans. Alcohols can form intermolecular H bonding with H_2O molecules.

Q14. While separating a mixture of ortho and para nitrophenol by steam distillation, name the isomers which is steam volatile?

Ans. O-nitrophenol forms intermolecular H-bonding and can be separated by steam distillation as p-nitrophenol forms strong intermolecular H-bonding.

Q15. Why phenol is more acidic than Alcohols.

Ans. In phenol, the phenoxide ion after losing H^+ gets stabilised by resonance but in alcohols there is no such arrangement.

Q17. Preparation of ethers by acid catalysed dehydration of 2° and 3° Alcohols is not suitable method.

Ans. In above method 2° and 3° Alcohols give alkenes in SN^2 condition due to steric hindrance effect.

Q18. Define :-

(a) Rectified spirit (b) absolute alcohols (c) denaturation of Alcohols (d) Fermentation.

Q19. Phenol has smaller dipole moment than methanol.

Q20. Diethyl ether does not react with sodium. Explain.

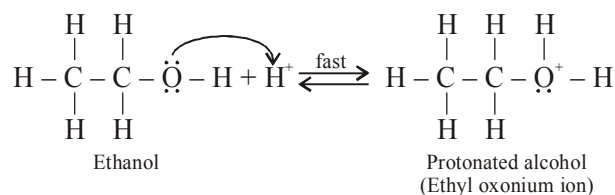
Q21. Dimethyl ether is completely miscible with H_2O but diethyl ether is soluble in water to small extent.

Q22. Explain why cleavage of Alkyl phenyl ethers with HBr always produces phenol and Alkyl bromides.

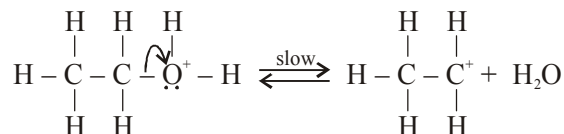
MECHANISMS

1. Acidic dehydration of Alcohol

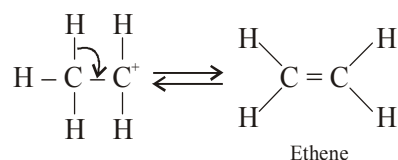
Step 1: Formation of protonated alcohol.



Step 2: Formation of carbocation. It is the slowest step and hence, the rate determining step of the reaction.

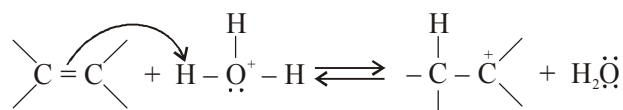


Step 3: Formation of ethene by elimination of a proton.

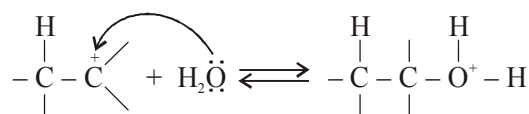


2. Acid Catalysed Hydration of Alkene -

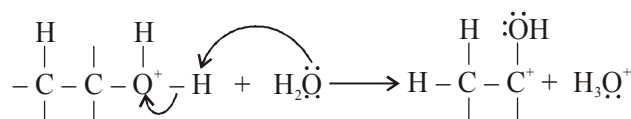
Step 1: Protonation of alkene to form carbocation by electrophilic attack of H_3O^+ .



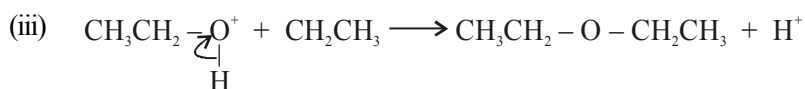
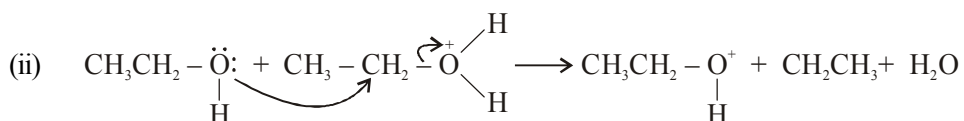
Step 2: Nucleophilic attack of water on carbocation.

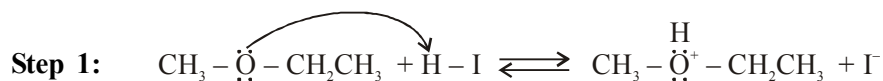


Step 3: Deprotonation to form an alcohol.

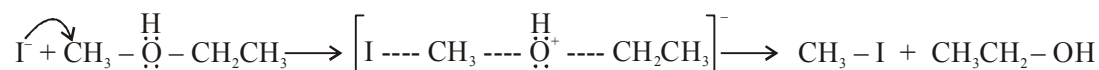


3. Dehydration of Alcohol to form Ether

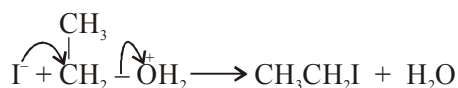
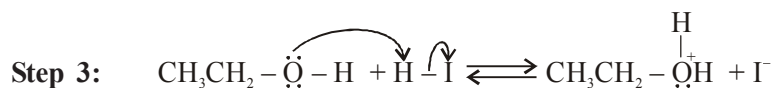
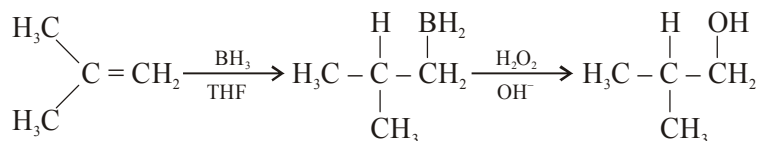
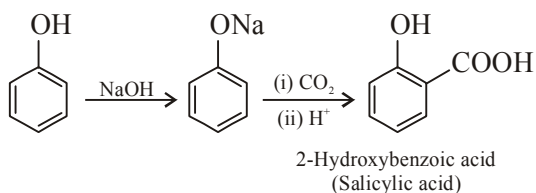
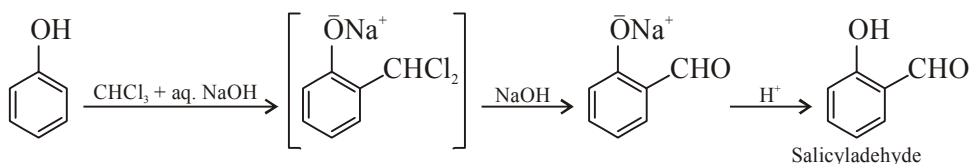


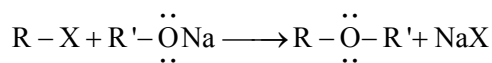
4. Reaction of Ether with HI

Step 2: Iodide is a good nucleophile. It attacks the least substituted carbon of the oxonium ion formed in step 1 and displaces an alcohol molecule by $\text{S}_\text{N}2$ mechanism. Thus, in the cleavage of mixed ethers with two different alkyl groups, the alcohol and alkyl iodide formed, depend on the nature of alkyl groups. When primary or secondary alkyl groups are present, it is the lower alkyl group that forms alkyl iodide ($\text{S}_\text{N}2$ reaction).

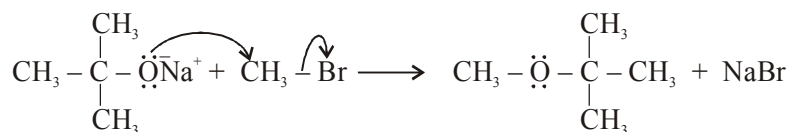


If HI is more and the temp is high then, all products will form be haloalkanes.

**NAME REACTIONS****1. Hydroboration Oxidation Reaction****2. Kolbe's reaction****3. Reimer-Tiemann reaction****4. Williamson synthesis**

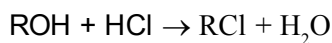


The reaction involves SN₂ attack of an alkoxide ion on primary alkyl halide. Better results are obtained if the alkyl halide is primary. In case of secondary and tertiary alkyl halides, elimination competes over substitution.



Distinguish Between Two Compounds

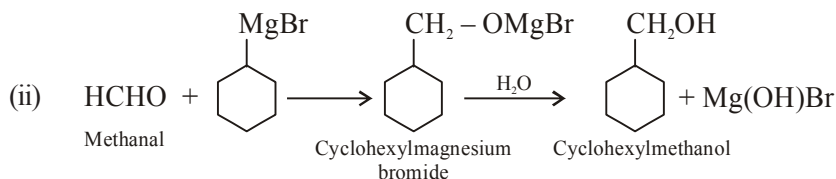
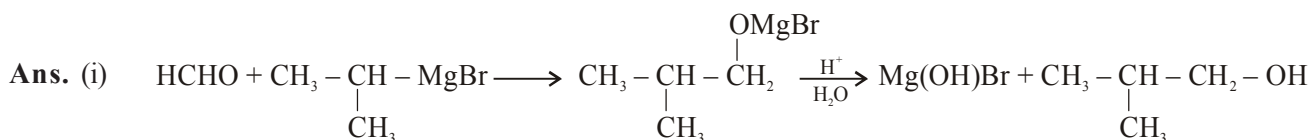
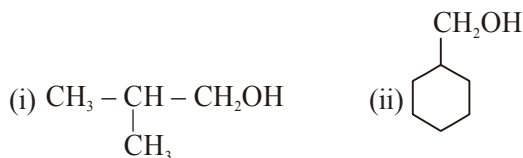
Lucas Test : This test is used for distinguish between primary, secondary and tertiary alcohol. In this reaction, Lucas' reagent is a solution of zinc chloride in concentrated hydrochloric acid. A positive test is indicated by a change from colourless to turbid, signalling formation of a chloroalkane. It is based on the difference in reactivity of the three classes of alcohols with hydrogen halides



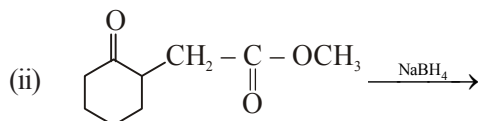
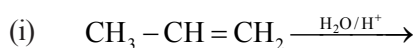
Tertiary alcohols react immediately with Lucas reagent as evidenced by turbidity owing to the low solubility of the organic chloride in the aqueous mixture. Secondary alcohols react within five or so minutes (depending on their solubility). Primary alcohols do not react appreciably with Lucas reagent at room temperature.

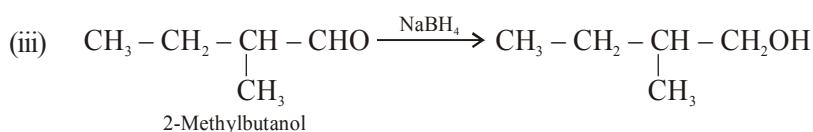
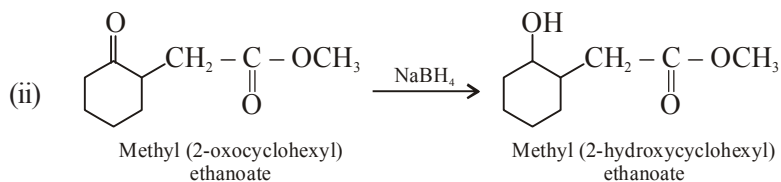
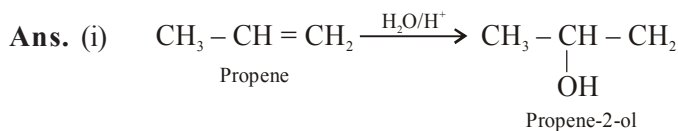
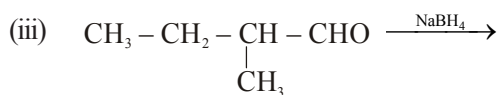
CONVERSIONS

Q1. Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal ?



Q2. Write structures of the products of the following reactions:

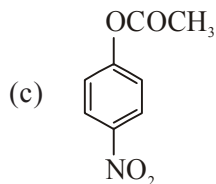
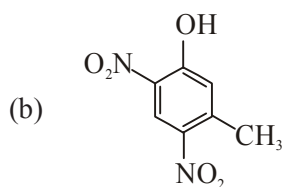
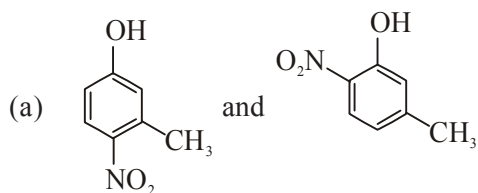




Q3. Write the structures of the major products expected from the following reactions:

- Mononitration of 3-methylphenol
- Dinitration of 3-methylphenol
- Mononitration of phenyl methanoate.

Ans. The combined influence of -OH and -CH₃ groups determine the position of the incoming group.



Q4. (a) Give structures of the products you would expect when each of the following alcohol reacts with

(a) HCl-ZnCl₂ (b) HBr and (c) SOCl₂.

(i) Butan-1-ol

(ii) 2-Methylbutan-2-ol

Ans. (a) (i) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH} \xrightarrow{\text{HCl-ZnCl}_2} \text{No reaction.}$
Butan-1-ol

(ii) $\text{CH}_3 - \text{CH}_2 - \underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}} - \text{CH}_3 \xrightarrow{\text{HCl-ZnCl}_2} \text{CH}_3 - \text{CH}_2 - \underset{\text{CH}_3}{\overset{\text{Cl}}{\text{C}}} - \text{CH}_3 + \text{H}_2\text{O}$
2-Methylbutan-2-ol (3°) 2-Chloro-2-Methylbutane
(White turbidity)

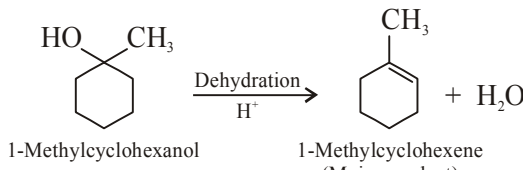
(b) (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{HBr} \xrightarrow{-\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$
Butan-1-ol 1-Bromobutane

(ii) $\text{CH}_3 - \text{CH}_2 - \underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}} - \text{CH}_3 + \text{HBr} \longrightarrow \text{CH}_3 - \text{CH}_2 - \underset{\text{CH}_3}{\overset{\text{Br}}{\text{C}}} - \text{CH}_3 + \text{H}_2\text{O}$
2-Methylbutan-2-ol (3°) 2-Chloro-2-Methylbutane
(White turbidity)

(b) Predict the major product of acid catalysed dehydration of

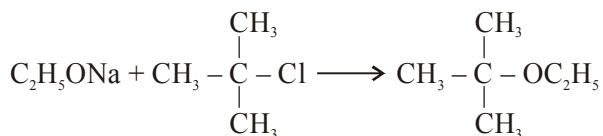
(i) 1-methylcyclohexanol and

(ii) butan-1-ol

Ans. (i) 
1-Methylcyclohexanol 1-Methylcyclohexene
(Major product)

(ii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \xrightarrow[\text{H}^+]{\text{Dehydration}} \text{CH}_3\text{CH}=\text{CHCH}_3 + \text{H}_2\text{O}$
Butan-1-ol But-2-ene
(Major Product)

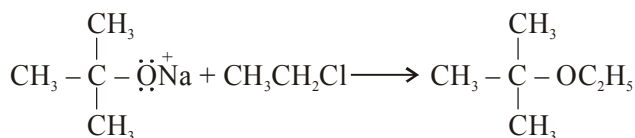
Q5. The following is not an appropriate reaction for the preparation of t-butyl ethyl ether.



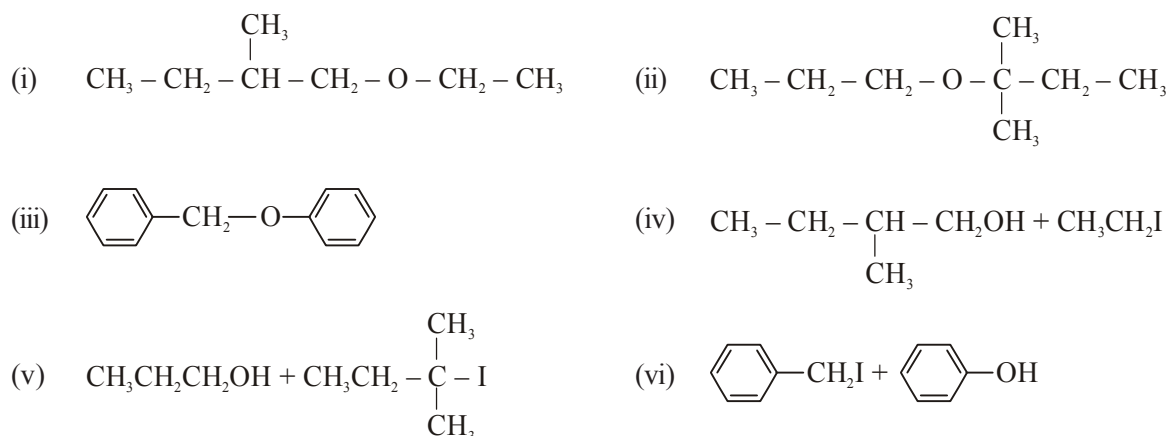
(i) What would be the major product of this reaction ?

(ii) Write a suitable reaction for the preparation of t-butylethyl ether.

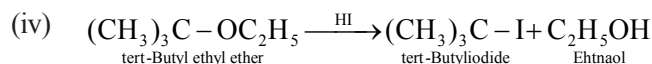
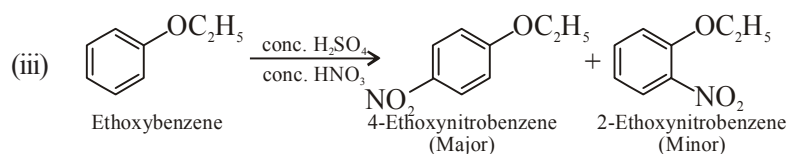
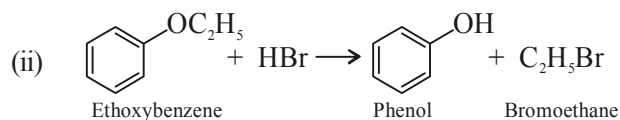
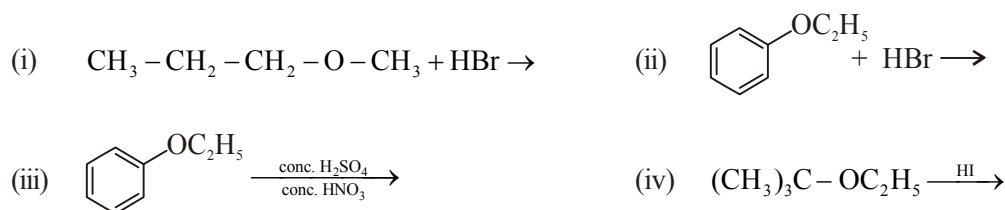
Ans. (i) The major product of the given reaction is 2-methylprop-1-ene. It is because sodium ethoxide is a strong nucleophile as well as a strong base. Thus elimination reaction predominates over substitution.



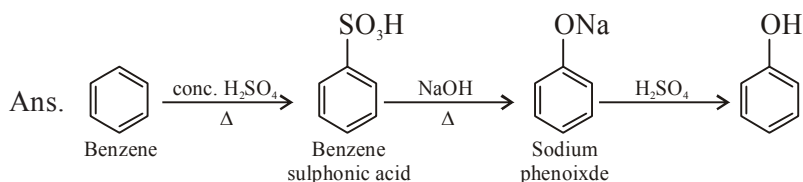
Q6. Give the major products that are formed by heating each of the following ethers with HI.



Q7. Predict the products of the following reactions:



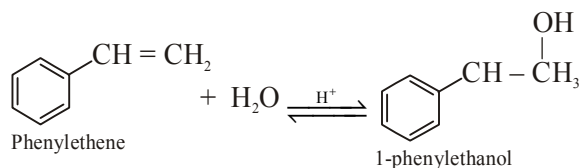
Q8. You are given benzene, conc. H_2SO_4 and NaOH . Write the equations for the preparation of phenol using these reagents.



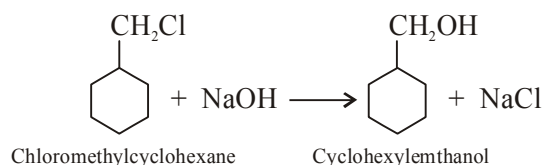
Q9. Show how will you synthesise:

- 1-phenylethanol from a suitable alkene.
- cyclohexylmethanol using an alkyl halide by an S_N2 reaction.
- pentan-1-ol using a suitable alkyl halide?

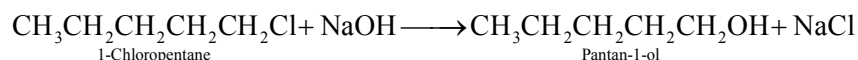
Ans. (i) By acid-catalyzed hydration of ethylbenzene (styrene), 1-phenylethanol can be synthesized.



- When chloromethylcyclohexane is treated with sodium hydroxide, cyclohexylmethanol is obtained.

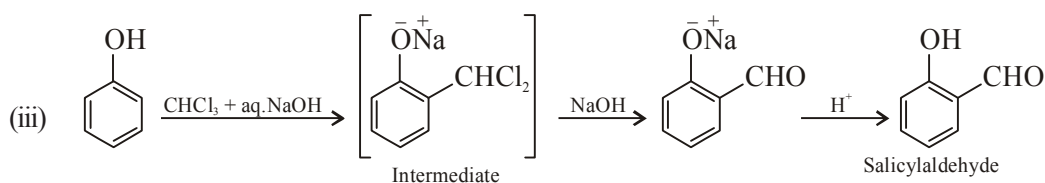
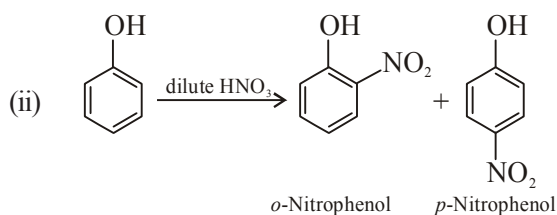
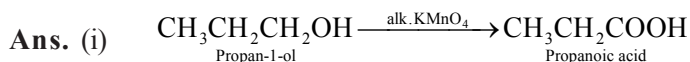


- When 1-chloropentane is treated with NaOH, pentan-1-ol is produced.



Q10. Give equations of the following reactions:

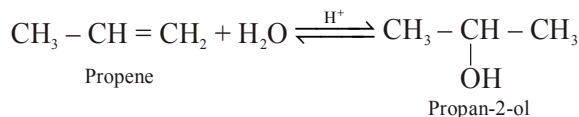
- Oxidation of propan-1-ol with alkaline KMnO_4 solution.
- Bromine in CS_2 with phenol.
- Dilute HNO_3 with phenol.
- Treating phenol with chloroform in presence of aqueous NaOH.



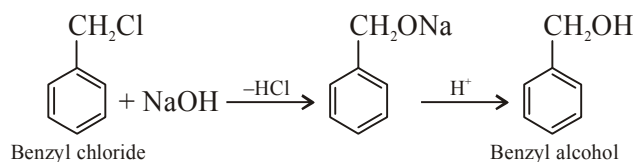
Q11. How are the following conversions carried out?

- (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.

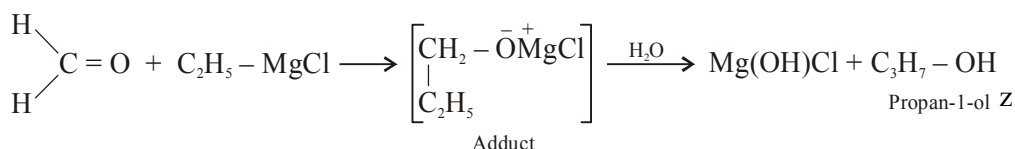
Ans. (i) If propene is allowed to react with water in the presence of an acid as a catalyst, then propan-2-ol is obtained.



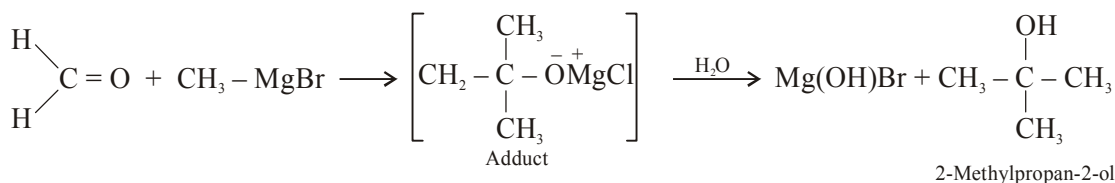
- (ii) If benzyl chloride is treated with NaOH (followed by acidification) then benzyl alcohol is produced.



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



- (iv) When methyl magnesium bromide is treated with propane, an adduct is the product which gives 2-methylpropan-2-ol on hydrolysis.



Q12. Name the reagents used in the following reactions:

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

- Ans. (i) Acidified potassium permanganate
- (ii) Pyridinium chlorochromate (PCC)
- (iii) Bromine water
- (iv) Acidified potassium permanganate
- (v) 85% phosphoric acid

(vi) NaBH_4 or LiAlH_4

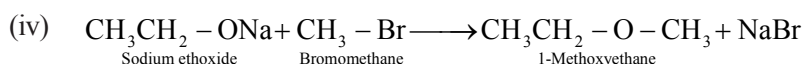
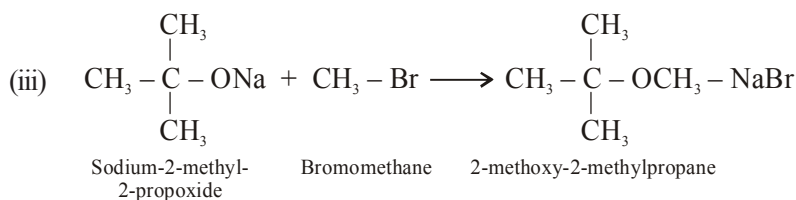
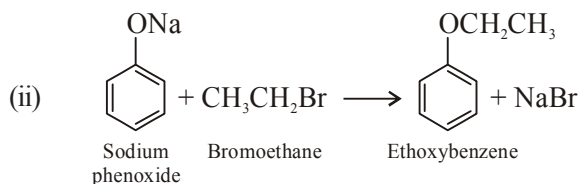
Q13. Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

(i) 1-Propoxypropane

(ii) Ethoxybenzene

(iii) 2-Methoxy-2-methylpropane

(iv) 1-Methoxyethane

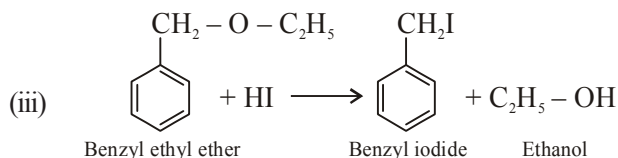
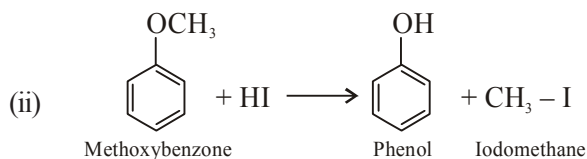
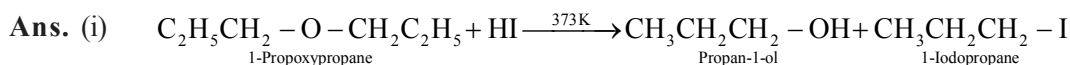


Q14. Write the equation of the reaction of hydrogen iodide with:

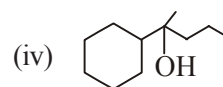
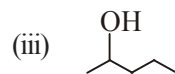
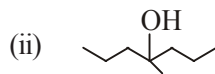
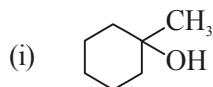
(i) 1-propoxypropane

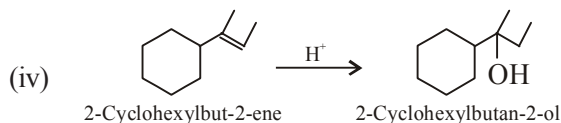
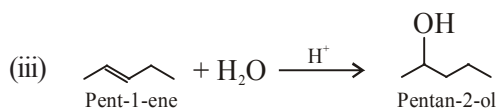
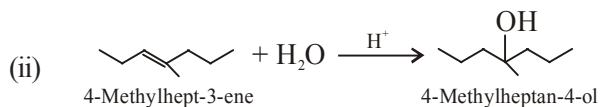
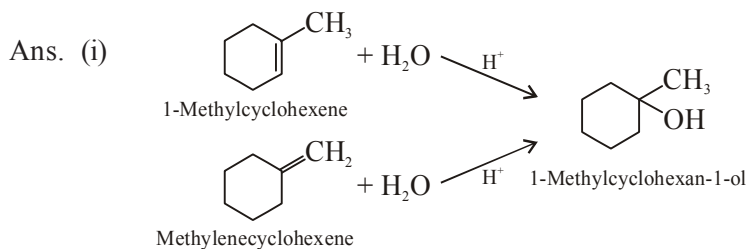
(ii) methoxybenzene and

(iii) benzyl ethyl ether.-

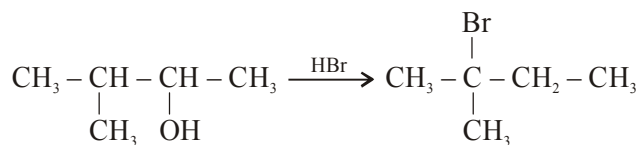


Q15. Show how would you synthesise the following alcohols from appropriate alkenes?

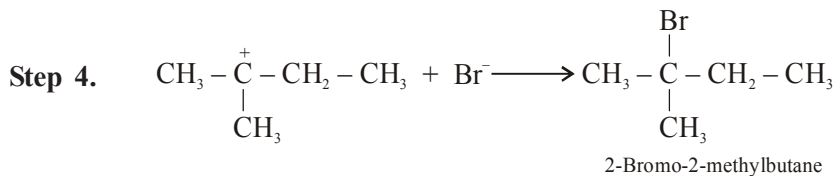
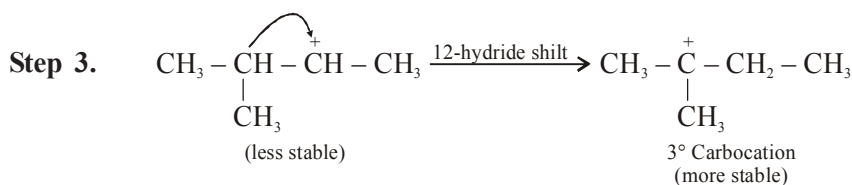
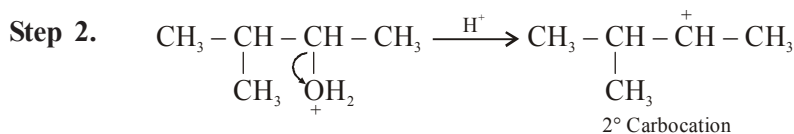
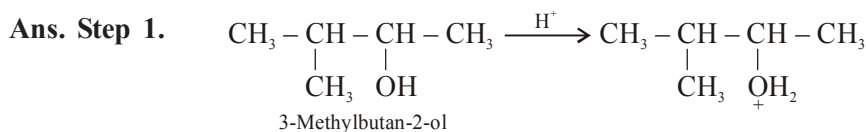




Q16. When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place:



Give a mechanism for this reaction.



Previous Years Questions**2011**

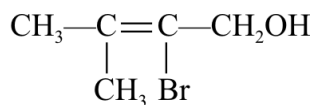
- Explain the following giving one example for each :
 - Reimer-Tiemann reaction.
 - Friedel Craft's acetylation of anisole.
- How would you obtain :
 - Picric acid (2, 4, 6-trinitrophenol) from phenol,
 - 2-Methylpropene from 2-methylpropanol ?
- How would you obtain
 - But-2-enal from ethanal,
 - Butanoic acid from butanol
 - Benzoic acid from ethylbenzene ?

2010

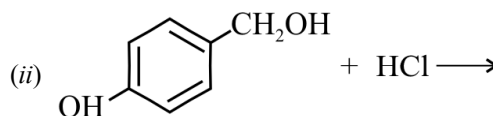
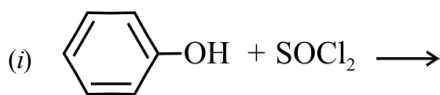
- Illustrate the following reactions giving a chemical equation for each :
 - Kolbe's reaction
 - Williamson synthesis.

2009

- Give the IUPAC name of the following compound:



- Complete the following reaction equations:

(2 Marks)

- Explain the mechanism of the following reactions:
 - Addition of Grignard's reagent to the carbonyl group of a compound forming an adduct followed by hydrolysis.
 - Acid catalysed dehydration of an alcohol forming an alkene.
 - Acid catalysed hydration of an alkene forming an alcohol.
- An organic compound A contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollen's reagent but forms an addition compound with sodium hydrogen sulphite and gives positive iodoform test. On vigorous oxidation it gives ethanoic and propanoic acids. Derive the possible structure of compound A.

2008

- Name the reagents which are used in the following conversions: **(3 Marks)**
 - A primary alcohol to an aldehyde
 - Butan-2-one to butan-2-ol
 - Phenol to 2, 4, 6-tribromophenol

2007

- How would you account for the following : **(2 Marks)**
 - Phenols are much more acidic than alcohols.
 - The boiling points of ethers are much lower than those of the alcohols of comparable molar masses.

2. How are the following conversions be carried out : (2 Marks)
(a) Propene to propan-2-ol (b) Anisole to phenol
(Write the reaction only.)
3. Write chemical reaction equations to illustrate the following reactions : (2 Marks)
(a) Williamson synthesis of ethers (b) Reimer-Tiemann reaction

2006

1. Write the reactions and the conditions involved in the conversion of:
(a) Propene to 1-Propanol (b) Phenol to Salicylic acid (2 Marks)
2. Give reasons for the following:
(a) Ortho-nitrophenol is more acidic than ortho-methoxyphenol. (1 Mark)
(b) Glycerol is used in cosmetics. (1 Mark)
3. How are the following conversions carried out?
(a) Benzyl chloride to benzyl alcohol (b) Ethyl magnesium bromide to propan-1-ol
(2 Marks)

2005

1. Give an illustration of Reimer-Tiemann reaction. (2 Marks)

2004

1. Write the names of the reagents and equations in the conversion of (2 Marks)
(a) phenol to salicyl aldehyde (b) anisole to p-methoxyacetophenone
2. How are the following conversions carried out? (2 Marks)
(a) Ethanol to 1, 2 Ethane-diol
(b) Phenol to Acetophenone
3. Explain the following giving suitable examples: (2 Marks)
(a) Kolbe's reaction (b) Williamson synthesis