

Alcohols, Phenols and Ethers

Topic 1

Alcohols and Phenols

Previous Years' Examination Questions

Practice the Real Questions

1 Mark Questions

- Write the equations involved in the following reaction:
Reimer-Tiemann reaction
[All India 2012]
- Draw the structure of hex-1-en-3-ol compound. [Delhi 2012]
- Draw the structural formula of 2-methylpropan-2-ol molecule. [Delhi 2012]
- Write the IUPAC name of the following compound:

$$\text{CH}_3-\text{CH}=\text{CH}-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{CH}_3$$
[Foreign 2012]
- How could you convert ethanol to ethene? [All India 2011]
- Draw the structure of 2, 6-dimethyl phenol. [All India 2011]
- Write the chemical equation for the preparation of phenol from benzene using oleum and sodium hydroxide. [Delhi 2011]
- Write Reimer-Tiemann reaction giving an example. [All India 2011]
- Write the structure of the molecule of compound whose IUPAC name is 1-phenyl propan-2-ol. [All India 2010]
- Give IUPAC name of the following compound:

$$\text{H}_2\text{C}=\text{CH}-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{CH}_2-\text{CH}_3$$
[All India 2009]
- Write the IUPAC name of

$$\text{H}_3\text{C}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2\text{OH}$$
[Delhi 2008]

2 Marks Questions

- Explain the mechanism of the following reaction?

$$\text{CH}_3-\text{CH}_2-\text{OH} \xrightarrow[443\text{ K}]{\text{H}^+} \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}$$
[All India 2013]
- How will you convert the following?
 (i) Propan-2-ol to propanone
 (ii) Phenol to 2, 4, 6-tribromophenol
 [Delhi 2013]
- How will you convert:
 (i) Propene to propan-1-ol?
 (ii) Ethanal to propan-2-ol? [Delhi 2013]
- How will you convert:
 (i) Propene to propan-2-ol?
 (ii) Phenol to 2, 4, 6-trinitrophenol?
 [Delhi 2013]
- Explain the following behaviours.
 (i) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.
 (ii) Ortho-nitrophenol is more acidic than ortho-methoxyphenol. [All India 2012]
- Explain the mechanism of acid catalysed hydration of an alkene to form corresponding alcohol. [All India 2012]
- How would you obtain [Delhi 2011]
 (i) picric acid from phenol?
 (ii) 2-methyl propanol from 2-methyl propene?
- Account for the following [Delhi 2011C, 2008C]
 (i) Propanol has higher boiling point than butane.
 (ii) Ortho-nitrophenol is more acidic than ortho-methoxy phenol.

20. How are the following conversions carried out? [Delhi 2010]

- (i) Benzyl chloride to benzyl alcohol
 (ii) Methyl magnesium bromide to 2-methyl propane-2-ol

21. How are the following conversions carried out? [Delhi 2010; 2006C]

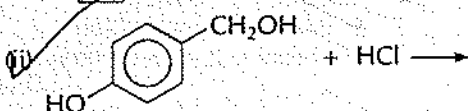
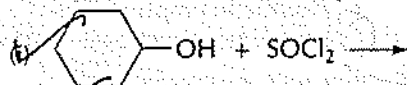
- (i) Propene to propan-2-ol
 (ii) Ethyl magnesium chloride to propan-1-ol

22. Write the mechanism of hydration of ethene to ethanol. [Foreign 2010, 2009]

23. Give one chemical test to distinguish between the following pairs of compounds.

- (i) Phenol and benzoic acid
 (ii) 1-propanol and 2-propanol [Delhi 2010C, 2009C]

24. Complete the following reaction equations. [Delhi 2009]



25. Give reason for the following.

- (i) *m*-amino phenol is a stronger acid than *o*-amino phenol.
 (ii) Alcohols act as weak bases. [Delhi 2008C]

26. Describe the mechanism of alcohols reacting both as nucleophiles and as electrophiles in their reactions. [Foreign 2008]

27. Write the reactions and conditions involved in the conversion of

- (i) propene to propan-1-ol
 (ii) phenol to salicylic acid [Delhi 2008]

3 Marks Questions

28. Draw the structure and name the product formed if the following alcohols are oxidized. Assume that an excess of oxidizing agent is used.

- (i) CH₃CH₂CH₂CH₂OH
 (ii) 2-butanol
 (iii) 2-methyl-1-propanol [Delhi 2012]

29. How would you obtain the following?

- (i) Benzoquinone from phenol.
 (ii) 2-methylpropan-2-ol from methyl magnesium bromide
 (iii) Propan-2-ol from propene [All India 2011; Foreign 2011]

30. Account for the following.

- (i) The boiling point of ethanol is higher than that of methanol.
 (ii) Phenol is a stronger acid than an alcohol.
 (iii) The boiling point of ethers are lower than isomeric alcohols. [Delhi 2011C; All India 2009]

31. Account for the following.

- (i) Propanol has higher boiling point than butane
 (ii) *Ortho*-nitrophenol is more acidic than *ortho*-methoxy phenol.
 (iii) Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. [Delhi 2011C]

32. (i) Describe the mechanism of hydration of ethene to yield ethanol.

- (ii) Write Kolbe's reaction with an example. [All India 2011C]

33. A compound A (C₂H₆O) on oxidation by PCC gave B, which on treatment with aqueous alkali and subsequent heating furnished C. B on oxidation by KMnO₄ forms a monobasic carboxylic acid with molar mass 60 g mol⁻¹. Deduce the structure of A, B and C. [All India 2011C]

34. Account for the following.

- (i) The boiling points of alcohols decrease with increase in branching of the alkyl chain. [Delhi 2011C]
 (ii) Phenol does not give protonation reaction readily. [All India 2008]

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(iii) Phenyl methyl ether reacts with HI to give phenol and methyl iodide and not iodobenzene and methyl alcohol.

[NCERT]

35. How would you convert
- phenol to benzoquinone
 - propanone to 2-methylpropan-2-ol
 - propene to propan-2-ol? [All India 2010]

36. (i) Describe the mechanism of acid catalyzed dehydration of ethanol to yield ethene.

(ii) Describe the chemical test to distinguish between ethanol and phenol.

[Delhi 2008C; All India 2010C, 2009]

37. Explain the mechanism of the following reactions.

(i) Addition of Grignard's reagent to the carbonyl group of compound forming an adduct followed by hydrolysis.

[Delhi 2009]

(ii) Acid catalyzed dehydration of an alcohol forming an alkene.

[All India 2010C, Foreign 2010]

(iii) Acid catalysed hydration of an alkene forming an alcohol. [All India 2012]

38. Explain the following observations:

(i) The boiling point of ethanol is higher than of methoxy methane

(ii) Phenol is more acidic than ethanol.

(iii) *o*- and *p*-nitro phenols are more acidic than phenol. [All India 2009]

39. Name the reagents which are used in the following conversions.

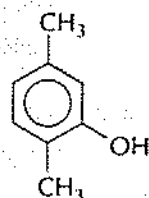
(i) A primary alcohol to an aldehyde

(ii) Butan-2-one to butan-2-ol

(iii) Phenol to 2, 4, 6 - tribromophenol.

[Delhi 2008]

40. Write the IUPAC name of the following.



(i) Give reason for

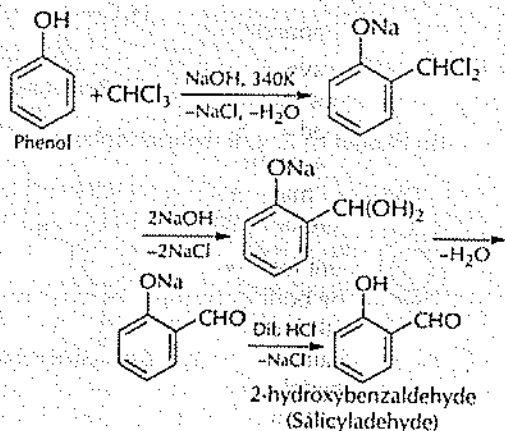
(a) Phenol is a stronger acid than alcohol.

(b) Alcohols are comparatively more soluble in water than the corresponding hydrocarbons.

[All India 2008C]

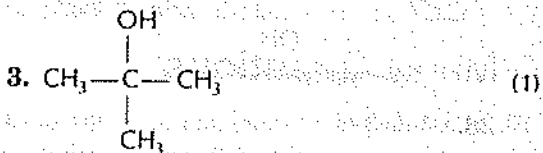
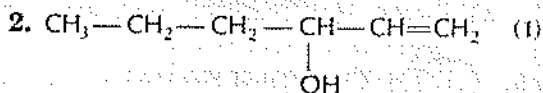
Step-by-Step Solutions

1. (i) Reimer-Tiemann reaction

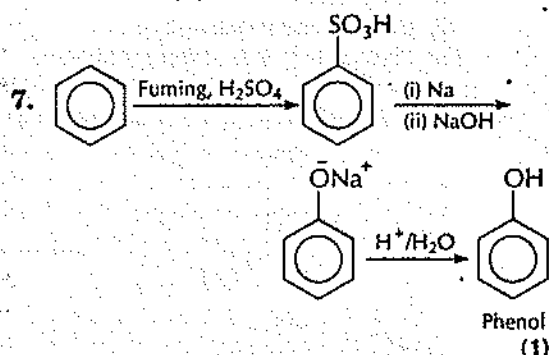
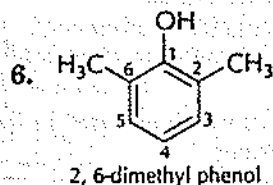
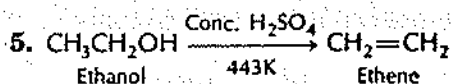


A small amount of *p*-hydroxy benzaldehyde is also formed.

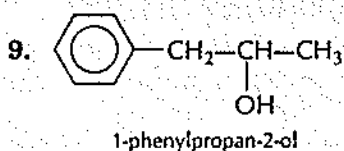
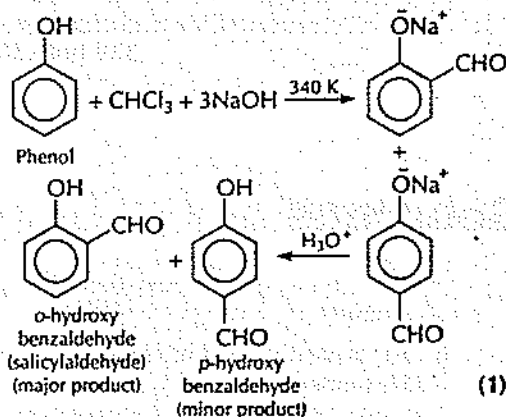
It CCl_3 is used instead of chloroform salicylic acid is formed. (1)



Chapterwise CBSE Solved Papers Chemistry

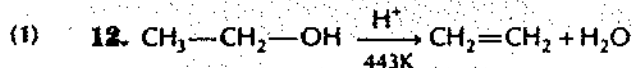


8. The reaction of phenol with chloroform in the presence of alkali to give *o*- and *p*-hydroxy aldehyde is known as Reimer-Tiemann reaction. e.g.,



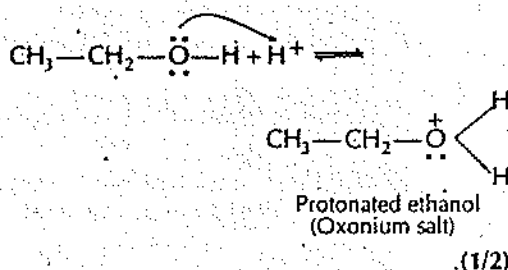
10. Hex-1-en-3-ol

11. 2,5-dimethylhexan-1, 3-diol

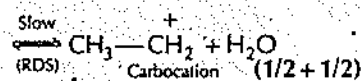
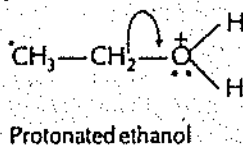


Mechanism This reaction involves the following steps :

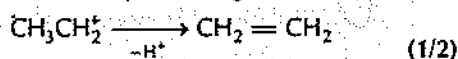
Step I Formation of protonated alcohol



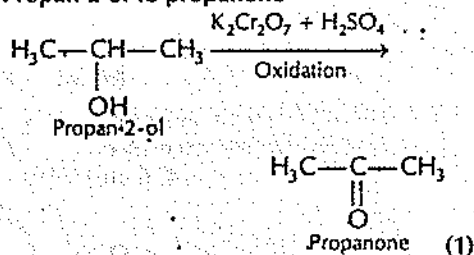
Step II Formation of carbocation



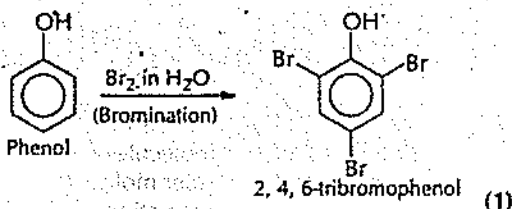
Step III Loss of proton to give alkene



13. (i) Propan-2-ol to propanone

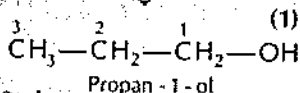
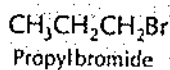
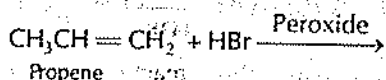


(ii) Phenol to 2, 4, 6-tribromophenol

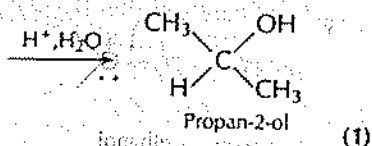
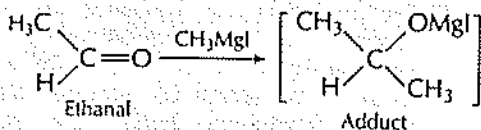


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14. (i) Propene to propan-1-ol

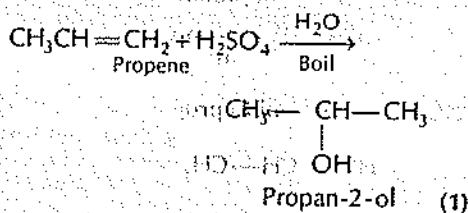


(ii) Ethanal to propan-2-ol



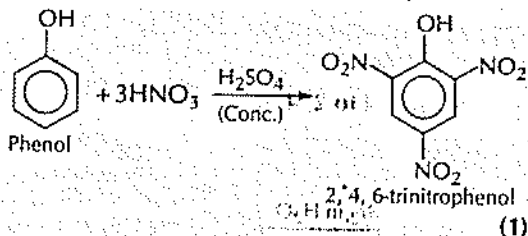
15. (i) Propene to propan-2-ol

Addition of H_2SO_4 takes place (in accordance with Markownikoff's rule) while converting propene to propan-2-ol.



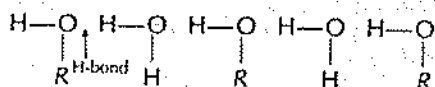
(ii) Phenol to 2, 4, 6 trinitrophenol

Nitration of phenol in the presence of conc. H_2SO_4 and conc. HNO_3 yields 2, 4, 6 - trinitrophenol.



16. (i) Because of the presence of polar —OH bond, alcohol molecules can form H-bonds with the water molecules and the water-alcohol interaction becomes

stronger than the water-water or alcohol-alcohol interactions. That's why alcohols are soluble in water.

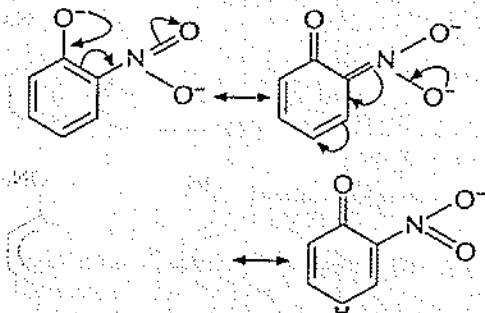


Intermolecular H-bonding between alcohol and water

Hydrocarbons, on the other hand, have no polar bond and hence, the water-hydrocarbon interaction remains weaker as compared to water-water or hydrocarbon-hydrocarbon interactions, i.e., hydrocarbons do not form H-bond with water. Thus, they remain insoluble in water. (1)

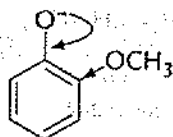
(ii) Acidity is the tendency to give a proton. It depends upon the stability of phenoxide ion formed (in case of phenols). Higher the stability of phenoxide ion, more will be the acidic character.

NO_2 group, being electron withdrawing, stabilises the phenoxide ion by dispersing negative charge.



and so on.

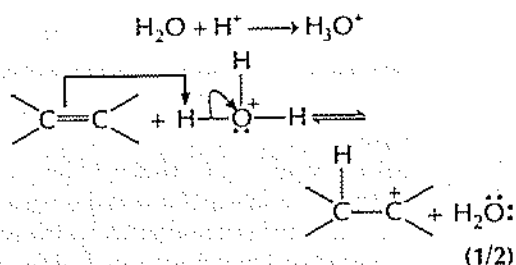
Methoxy group ($-\text{OCH}_3$) on the other hand destabilises the phenoxide ion by intensifying the negative charge.



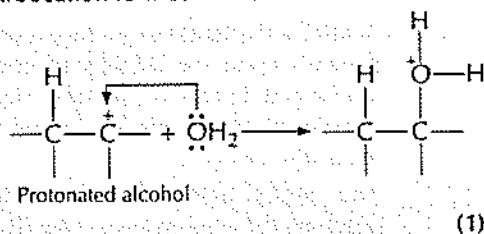
Thus, *o*-nitrophenol is more acidic than *ortho*-methoxyphenol. (1)

17. Following steps are involved in the acid catalysed hydration of ethene.

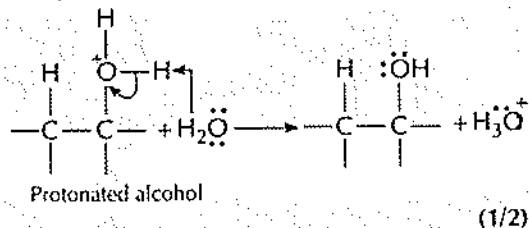
Step I Protonation of alkene to give carbocation by electrophilic attack of H_3O^+ as shown below



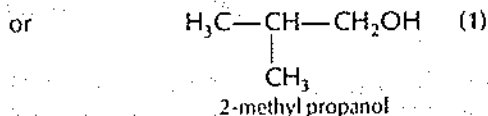
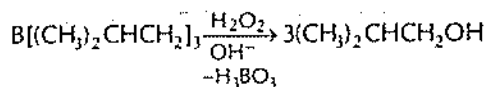
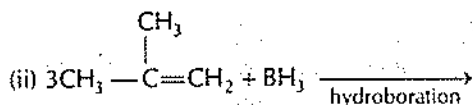
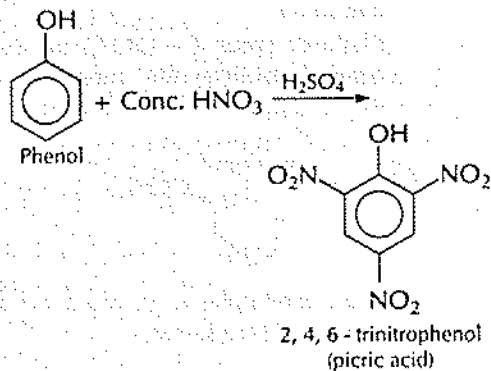
Step II Attack of nucleophile water on carbocation formed



Step III Deprotonation to give an alcohol

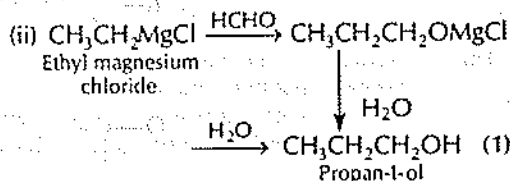
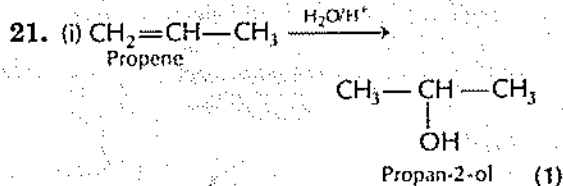
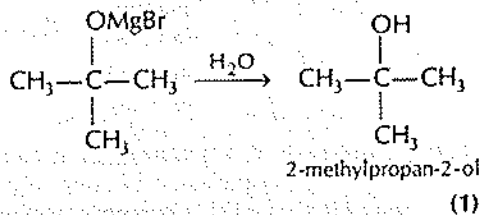
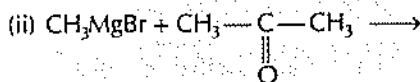
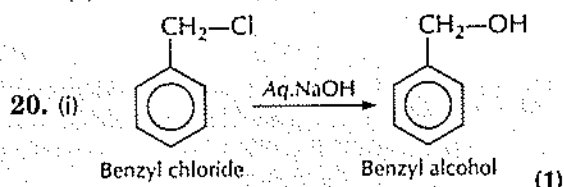


18. (i) Phenol when treated with concentrated nitric acid is converted into 2,4,6-trinitrophenol (picric acid). (1)



19. (i) The molecules of propanol are held together by intermolecular hydrogen bonding while butane has only weak forces of interaction i.e., van der Waals' forces. Hydrogen bonds are much stronger so the boiling point of propanol is much higher. (1)

(ii) Refer ans. 16 (ii). (1)

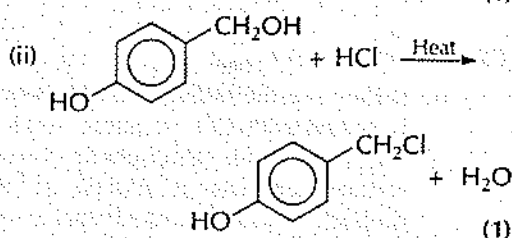
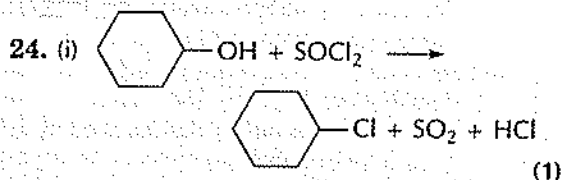


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22. Refer ans. 17. (2)

23. (i) Phenol gives a violet colouration with neutral FeCl_3 solution while benzoic acid gives buff coloured ppt. (1)

(ii) Propane-2-ol on reaction with sodium hydroxide and I_2 (warm) gives a yellow precipitate of iodoform while propane-1-ol gives no such test. (1)

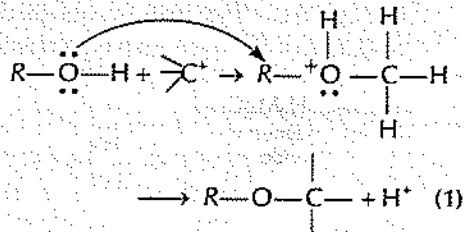


25. (i) Amino group being electron releasing, intensify the charge if present at ortho position and thus makes the phenol less acidic. However, at *m*-position it does not interfere in the dispersal of charge and hence, has no effect over the acidity of phenol. Thus, *m*-aminophenol is more acidic than *o*-amino phenol. (1)

(ii) Alcohols act as bronsted bases due to the presence of lone pair of electrons on oxygen, which makes them proton acceptors. (1)

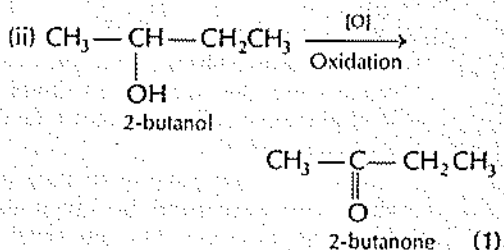
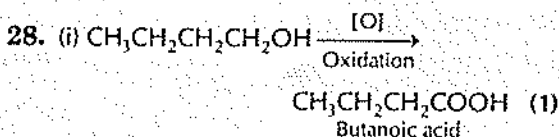
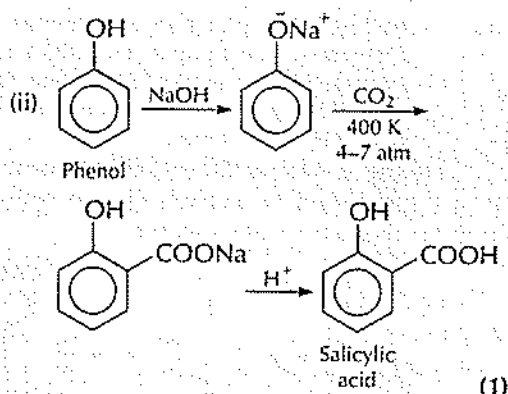
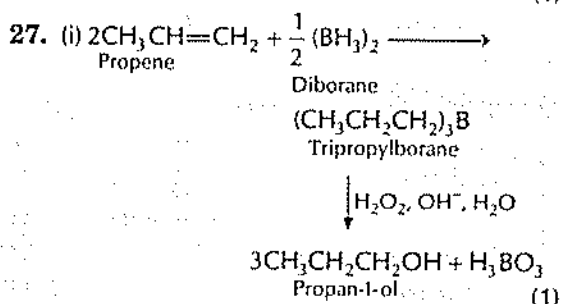
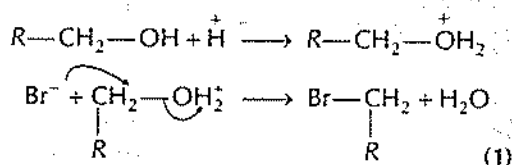
26. Alcohols are versatile compounds. They react both as nucleophiles and electrophiles

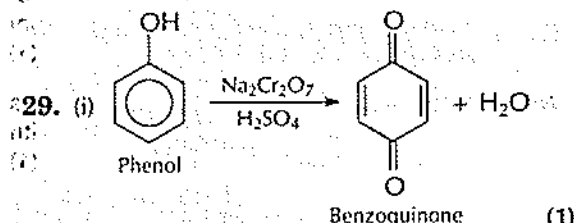
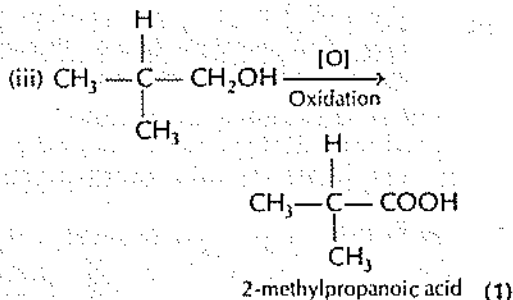
(i) The bond between 'O' and 'H' (O—H) is broken when alcohols react as nucleophiles. Alcohols as nucleophiles:



(ii) The C—O bond between is broken when they react as electrophiles. Protonated alcohols react in this manner.

Protonated alcohols as electrophiles



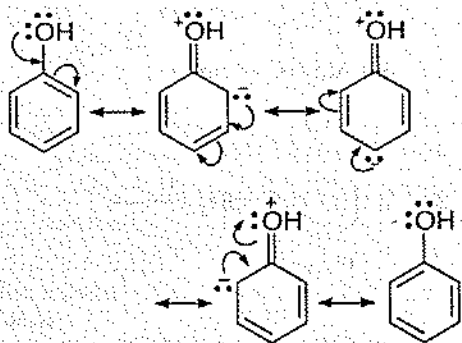


(ii) Refer ans. 20 (ii). (1)

(iii) Refer ans. 21 (i). (1)

30. (i) Boiling point of alcohols increases with increase in the number of carbon atoms (increase in van der Waals' forces). That's why boiling point of ethanol is higher than that of methanol. (1)

(ii) The greater acidic nature of phenols as compared to alcohols can be explained on the basis of resonance.



Due to positive charge on oxygen atom, it attracts the electron pair of O—H bond strongly towards itself and thus, facilitates the release of H⁺. (1)

(iii) Ethers have low polarity, so they do not show any association by intermolecular hydrogen bonding. On the other hand their isomeric alcohols have strong H-bonding and so their boiling points are high. (1)

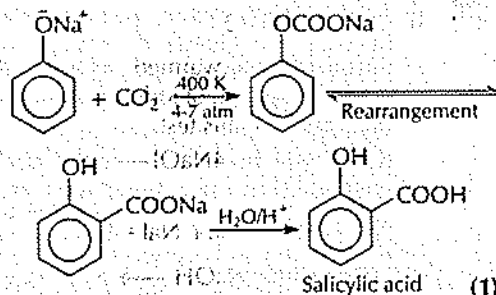
31. (i) Since alcohols can form H-bonds with water molecule, whereas hydrocarbons do not therefore, propanol has higher boiling point than butane. $\left(1\frac{1}{2}\right)$

(ii) It is because, —NO₂ group is electron withdrawing group, whereas —OCH₃ group is electron releasing group. Therefore, o-nitrophenoxide ion is more stable than o-methoxyphenoxide ion.

(iii) Secondary and tertiary alcohols on dehydration lead to the formation of alkene but not ethers due to stability of 2° and 3° carbocation. $\left(1\frac{1}{2}\right)$

32. (i) Refer ans. 17 (ii). (2)

(ii) Kolbe's reaction: When sodium phenoxide is heated with CO₂ at about 400 K and under 4 to 7 atmospheric pressure, sodium salicylate is formed as major product, which on acidification gives salicylic acid, e.g.,



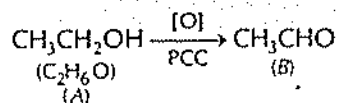
33. A monobasic carboxylic acid has the formula RCOOH.

Given, molar mass of RCOOH = 60 g mol⁻¹

$$x + 12 + 16 + 16 + 1 = 60$$

$$x = 60 - 45 = 15 \quad (1)$$

Thus, R = CH₃ (molar mass 15) and the acid is CH₃COOH. The acid is obtained by the oxidation of aldehyde, so B is an aldehyde, i.e., CH₃CHO and A is CH₃CH₂OH (an alcohol). The reactions are as



6. Aromatic ethers like anisole can be prepared by the reaction of sodium phenoxide with alkyl halides.
7. Ethers are inert and thus are used as solvents in many reactions.
8. Ethers on cleavage by acids give back alcohols and alkyl halides.
9. Aromatic ethers on cleavage give phenol and alkyl halide.
10. The order of reactivity of alkyl halides for Williamson's synthesis reaction is
Primary > Secondary > Tertiary

Previous Years' Examination Questions

Practice the Real Questions

1 Mark Questions

1. Write the equation involved in the reaction of Williamson's ether synthesis.

[All India 2013]

2. Phenyl methyl ether reacts with HI to give phenol and methyl iodide and not iodo benzene and methyl alcohol. Why?

[Delhi 2010C]

3. Write the structure of the following compound: 2-methyl-2-ethoxypentane.

[Delhi 2009C]

4. Write the IUPAC name of

$$\text{CH}_3-\text{O}-\text{CH}_2-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_2-\text{CH}_3$$

[All India 2008]

5. Why is the preparation of ether by acid catalysed dehydration of secondary alcohol not a suitable method? [All India 2008C]

6. How can you convert anisole to phenol? [All India 2007]

2 Marks Questions

7. Explain the following giving one example for each.

(i) Reimer-Tiemann reaction

(ii) Friedel-Crafts acetylation of anisole [Delhi 2011, 2010; All India 2009C]

8. Illustrate the following reaction by giving a chemical equation for each.

(i) Kolbe's reaction

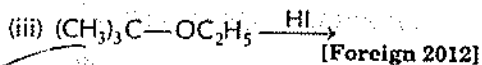
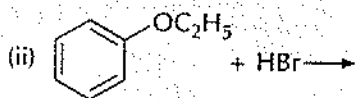
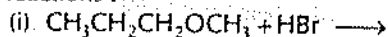
(ii) Williamson's synthesis

[Delhi 2010; All India 2010; 2009C
Foreign 2010, 2009]

Alcohols, Phenols and Ethers

3 Marks Questions

9. State the products of the following reactions:



10. (i) Name the reagents and write the chemical equation for the preparation of the following compounds by Williamson's synthesis.

(a) Ethoxy benzene

(b) 2-methyl-2-methoxy propane

(iii) Why do phenols not give the protonation reaction readily?

[All India 2008]

11. How could you account for:

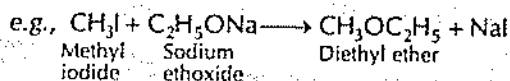
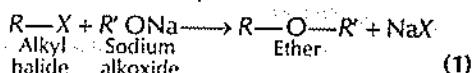
(i) phenols are more acidic than alcohols?

(ii) the boiling points of ethers are much lower than those of the alcohols of comparable molar masses?

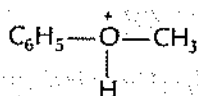
[Delhi 2007]

Step-by-Step Solutions

1. Williamson's ether synthesis

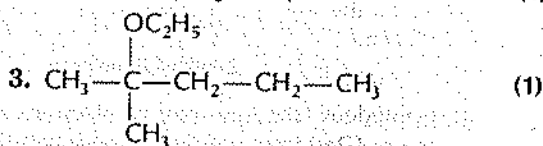


2. Protonation of anisole (Phenyl methyl ether) gives methyl phenyl oxonium ion.



In this ion the stronger bond is $\text{O}-\text{C}_6\text{H}_5$. Therefore, attack by I^- ion exclusively breaks the weaker $\text{O}-\text{CH}_3$ bond forming methyl iodide and phenol. The phenol formed do not react further to give aryl halides.

(1)

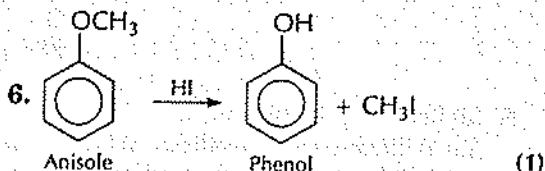


4. 2-methyl-1-methoxy butane. (1)

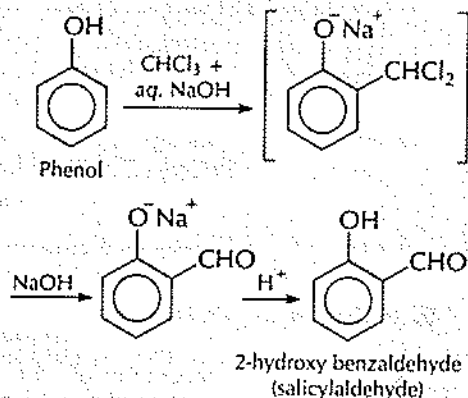
5. 2° and 3° alcohols are sterically hindered and due to steric hindrance, the nucleophilic attack by the alcohol molecule on the protonated alcohol molecule does not occur. The protonated 2° and 3° alcohols readily lose a

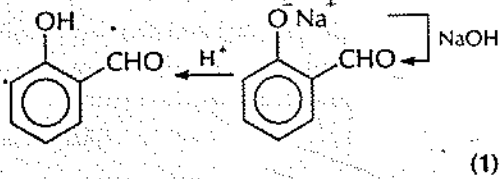
molecule of water to form stable 2° and 3° carbocations, which after losing a proton give alkane. Thus, acid catalysed dehydration of 2° and 3° alcohols gives alkenes rather than ethers.

(1)

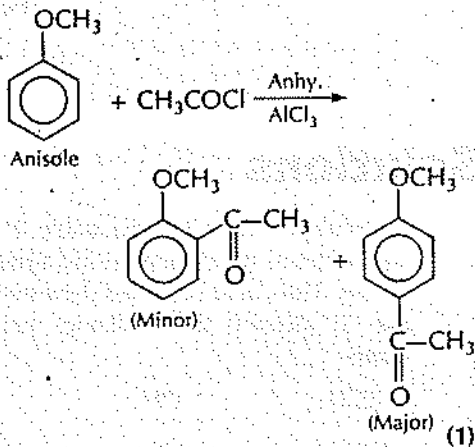


7. (i) Reimer-Tiemann reaction Chloroform reacts with phenol in aqueous sodium hydroxide at 340K to give salicylaldehyde.

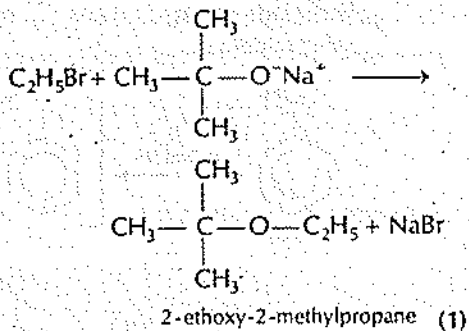




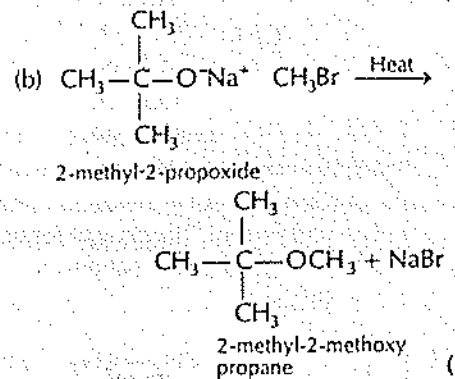
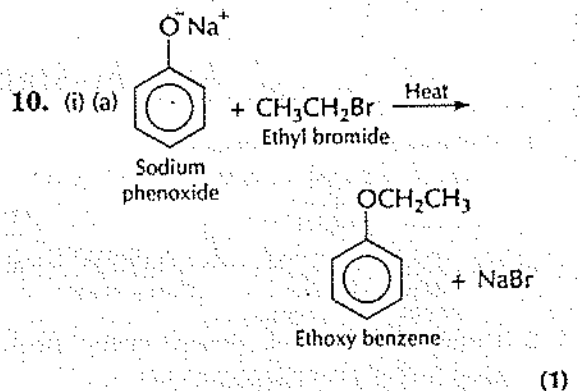
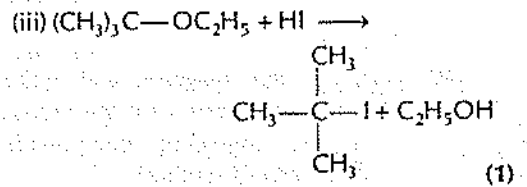
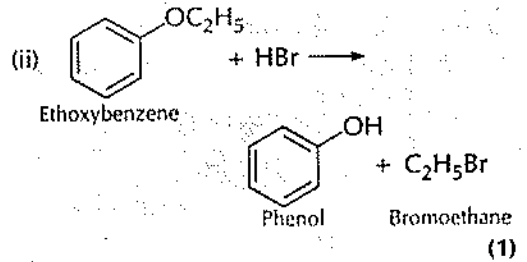
- (ii) Friedel-Crafts acetylation of anisole
When anisole reacts with acetyl chloride in the presence of anhydrous AlCl_3 , the acyl group is introduced at *ortho* and *para*-positions.



8. (i) Refer ans. 32 (ii) topic 1. (1)
(ii) Williamson's synthesis When alkyl halide reacts with sodium alkoxide, ethers are formed. This reaction is known as Williamson's synthesis.



9. (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3 + \text{HBr} \longrightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{CH}_3\text{Br}$ (1)



- (ii) In phenols, the lone pair of electrons on the oxygen atom are delocalised over the benzene ring due to resonance and hence, are not easily available for protonation. (1)

11. (i) Refer ans. 30 (ii) of topic 1. $\left(\frac{1}{2}\right)$
(ii) Refer ans. 30 (iii) of topic 1. $\left(\frac{1}{2}\right)$