

11

Alcohols, Phenols and Ethers

11.1 Classification

11.2 Nomenclature

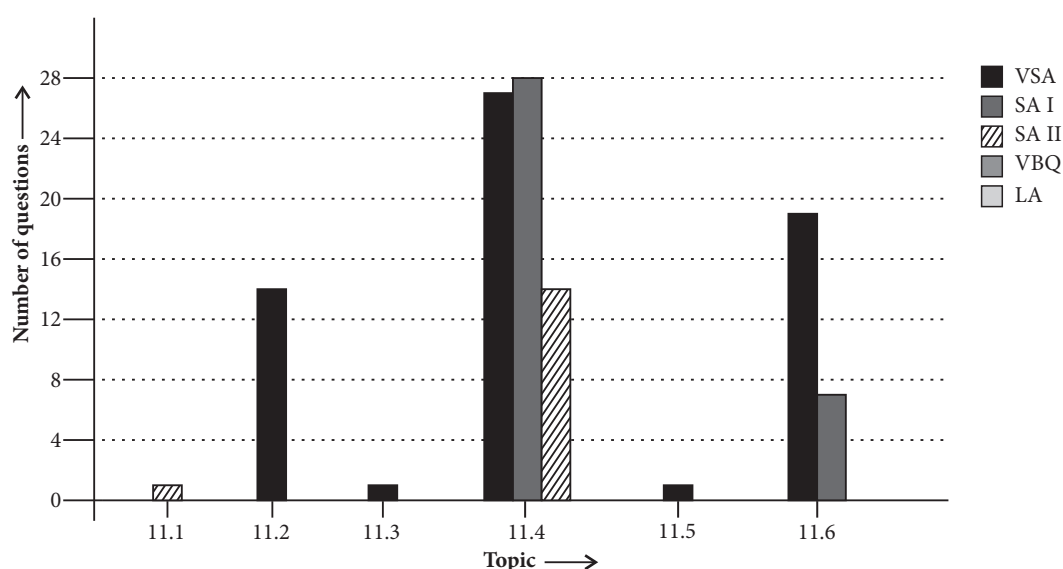
11.3 Structures of Functional Groups

11.4 Alcohols and Phenols

11.5 Some Commercially Important Alcohols

11.6 Ethers

Topicwise Analysis of Last 10 Years' CBSE Board Questions



▶▶ Maximum total weightage is of *Alcohols and Phenols*.

▶▶ Maximum VSA type questions were asked from *Alcohols and Phenols*.

▶▶ Maximum SA I and SA II type questions were asked from *Alcohols and Phenols*.

QUICK RECAP

ALCOHOLS

▶▶ **General formula :** Alcohols are the hydroxy derivatives of alkanes having general formula $C_nH_{2n+1}OH$.

▶▶ **Nomenclature :** In common system, alcohols

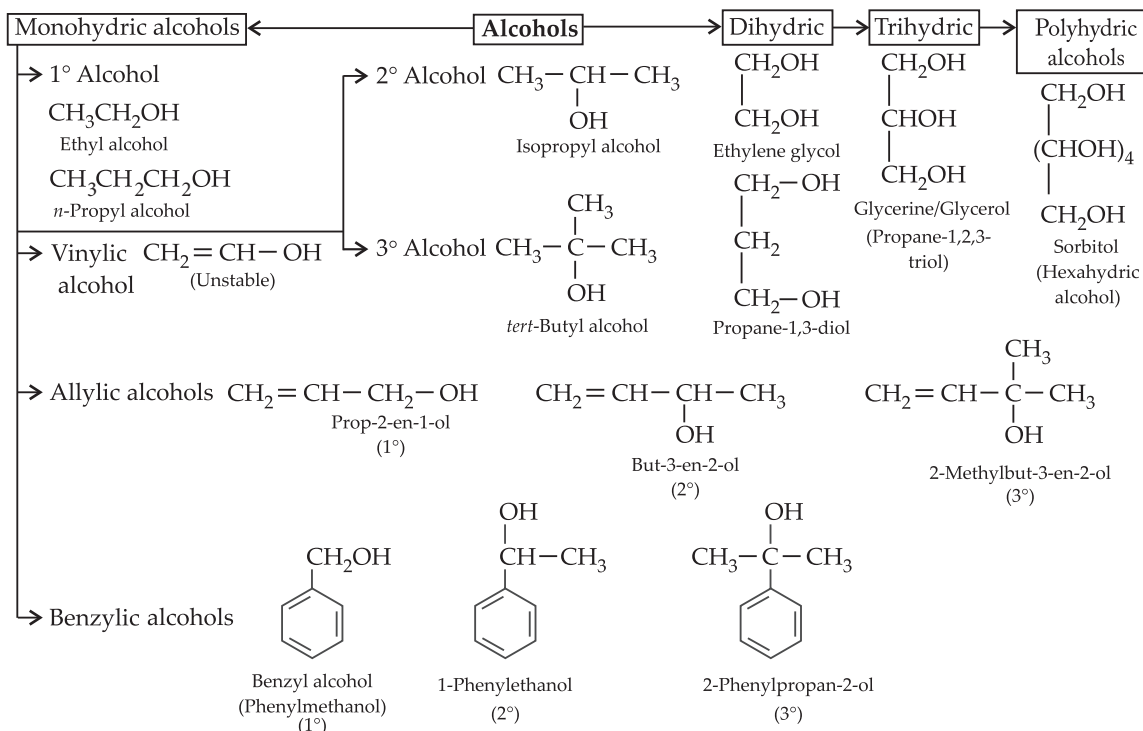
are named as *alkyl alcohol*. According to IUPAC system, alcohols are called '*alkanols*', by replacing '-e' of alkane by '-ol'.

▶▶ **Structure :** In alcohols, $R-OH$, the O atom of hydroxyl group is attached to C-atom

by a sigma (σ) bond formed by the overlap of sp^3 hybridised orbital of C-atom with



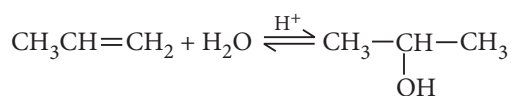
►► **Classification** : Alcohols are classified as monohydric, dihydric, trihydric and polyhydric alcohols depending upon the number of hydroxyl (—OH) groups present in the molecule.



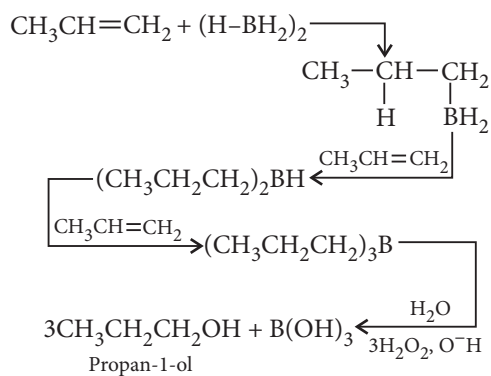
► Preparation :

► From alkenes :

- By acid catalysed hydration :

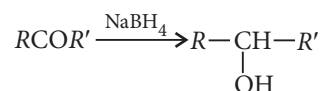
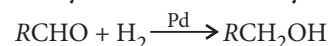


— **By hydroboration-oxidation :**

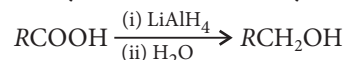


► **From carbonyl compounds :**

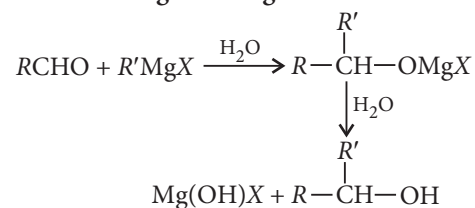
— **By reduction of aldehydes and ketones :**

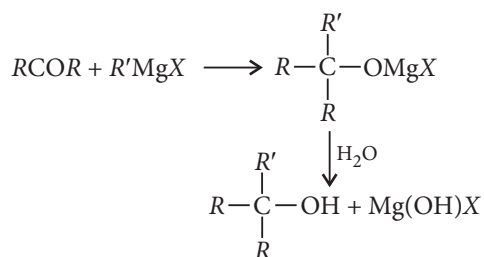


– By reduction of carboxylic acids and esters :



— From Grignard reagents :





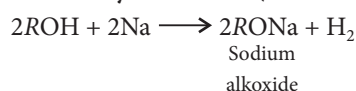
►► **Physical properties :**

- **Physical state :** Lower alcohols are colourless liquids with characteristic smell while higher alcohols are colourless, odourless waxy solids.
- **Solubility :** Solubility of alcohols in water is due to their ability to form hydrogen bonds with water molecules. The solubility decreases with increase in size of alkyl groups and solubility increases with increase in branching and the order is $1^\circ < 2^\circ < 3^\circ$.
- **Boiling points :** The boiling points of alcohols increase with increase in the number of carbon atoms as van der Waals forces increase and the boiling points decrease with increase of branching in carbon chain due to decrease in van der Waals forces with decrease in surface area and the order is $1^\circ > 2^\circ > 3^\circ$.

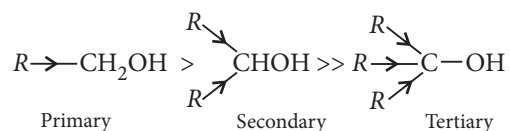
►► **Chemical properties :** Alcohols react both as nucleophiles (when the bond between O—H is broken) and electrophiles (when the bond between C—O is broken).

► **Reactions involving cleavage of O—H bond :**

— **Acidity of alcohols (reaction with metals) :**



- The acid strength of alcohols decreases in the following order :

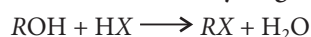


— **Esterification :**



► **Reactions involving cleavage of C—O bond :**

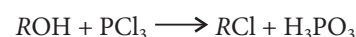
— **Reaction with hydrogen halides :**



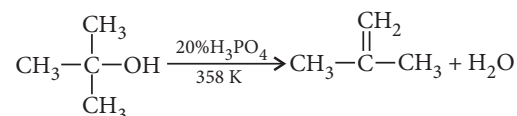
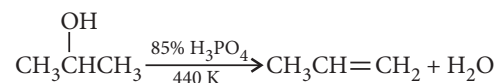
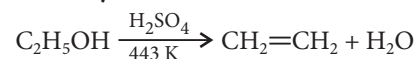
- **Lucas test :** Lucas reagent is a solution of conc. HCl with anhyd. ZnCl_2 .

- With Lucas reagent,
Primary alcohols – No cloudiness
Secondary alcohols – Cloudiness in 5 minutes
Tertiary alcohols – Cloudiness immediately

— **Reaction with phosphorus trihalides :**



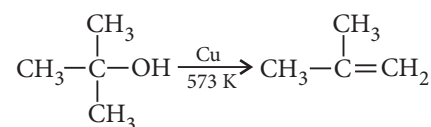
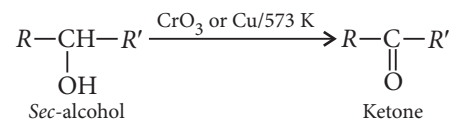
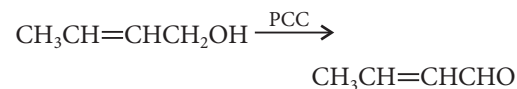
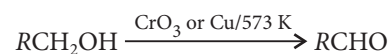
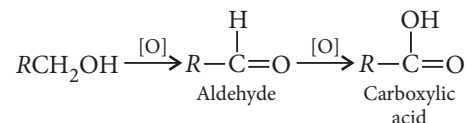
— **Dehydration :**



Thus, the relative ease of dehydration of alcohols follows the following order :

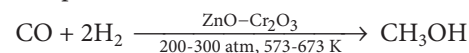
Tertiary > Secondary > Primary

— **Oxidation :**



►► **Some commercially important alcohols :**

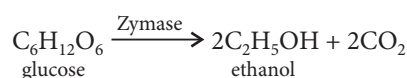
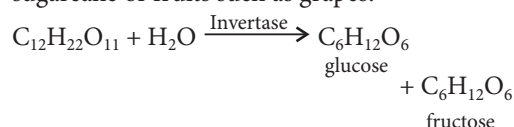
- **Methanol (wood spirit) :** It is produced by catalytic hydrogenation of CO in the presence of $\text{ZnO} - \text{Cr}_2\text{O}_3$ as catalyst at high temperature and pressure.



- Methanol is a colourless liquid and is highly poisonous in nature.

- Ingestion of small quantities can cause blindness while large quantities can cause death.
- It is used as a solvent in paints, varnishes and for making formaldehyde.

► **Ethanol** : It is commercially manufactured by using fermentation of sugar present in molasses, sugarcane or fruits such as grapes.



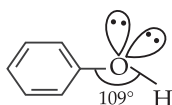
- Ethanol is colourless liquid and is used as a solvent in paint industry and in preparation of a number of carbon compounds.
- Commercial alcohol made unfit for drinking by mixing it with copper sulphate and pyridine is called *denatured alcohol*.

PHENOLS

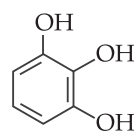
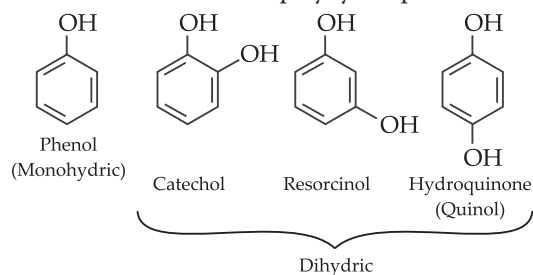
► **General formula** : Phenols are the compounds in which hydroxy (—OH) group is directly linked to aromatic ring having formula $\text{C}_6\text{H}_5\text{OH}$.

► **Nomenclature** : The simplest hydroxy derivative of benzene is phenol also called *carbolic acid*. It is its common name and also an accepted IUPAC name.

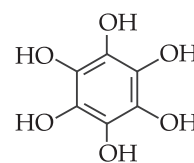
► **Structure** : In phenols, the —OH group is attached to sp^2 hybridised C-atom of an aromatic ring.



► **Classification** : Like alcohols, phenols are also classified as mono and polyhydric phenols.



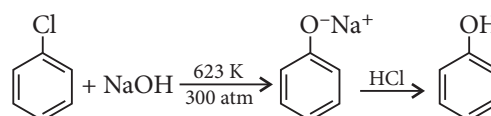
Pyrogallol
(Trihydric)



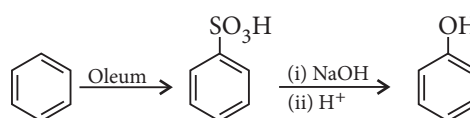
Hexaphenol
(Polyhydric)

► **Preparation** :

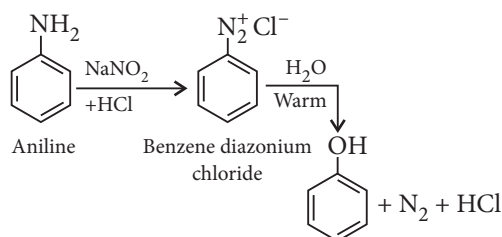
► **From haloarenes** :



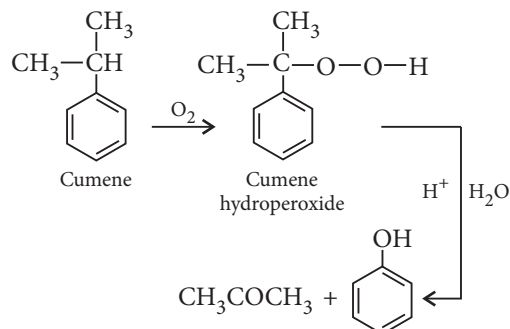
► **From benzenesulphonic acid** :



► **From diazonium salts** :



► **From cumene** :



► **Physical properties** :

► **Physical state** : Phenols are colourless crystalline solids or liquids.

► **Odour** : They have characteristic phenolic odours.

► **Solubility** : Like alcohols, phenols are soluble in water due to the formation of hydrogen bonding with water.

- Phenols are less soluble than alcohols due to large hydrocarbon (benzene ring) part.

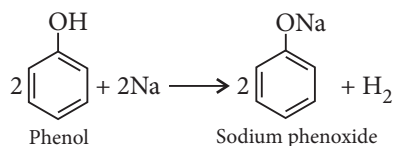
- Phenols are soluble in alcohols, ethers and also in NaOH.

- **Boiling points** : Much higher than the corresponding aromatic hydrocarbons and haloarenes due to intermolecular hydrogen bonding.

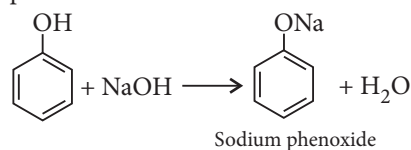
► **Chemical properties :**

- **Acidity of phenols** : Phenols are weakly acidic in nature due to polar O—H bond directly attached to sp^2 -hybridised C-atom.
- They turn blue litmus red and react with alkali metals and alkalies to form their salts.
 - Phenol is weaker acid than carboxylic acid. It does not react with sodium carbonate (Na_2CO_3) and sodium bicarbonate (NaHCO_3).
 - Phenols are more acidic than alcohols which can be explained on the basis of resonance.
 - Electron withdrawing groups increase the acidic strength of phenols.
 - Electron releasing groups decrease the acidic strength of phenols.

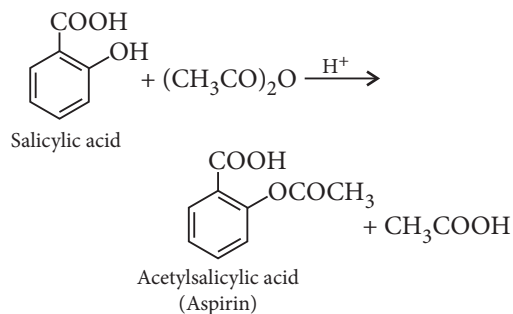
— **Reaction with metals :**



In addition to this, phenols react with aqueous sodium hydroxide to form sodium phenoxides.

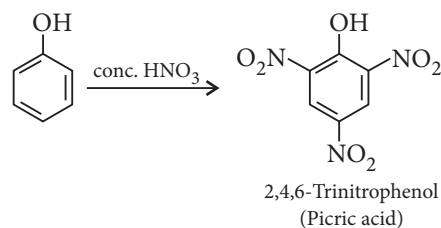
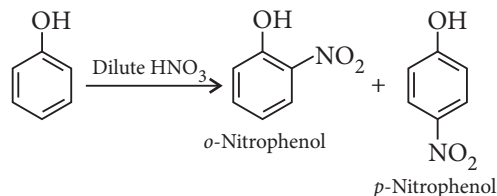


► **Esterification :**

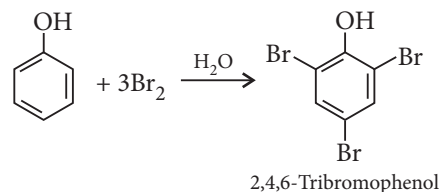
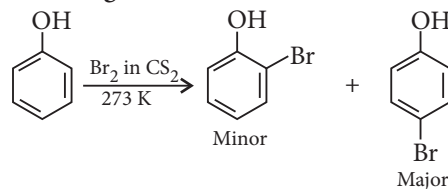


► **Electrophilic aromatic substitution :**

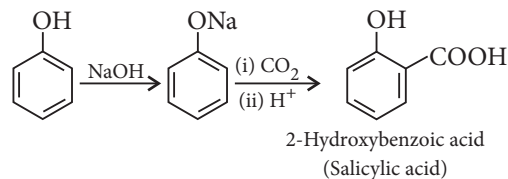
— **Nitration :**



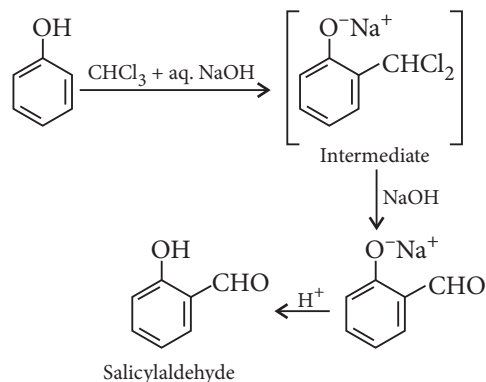
— **Halogenation :**



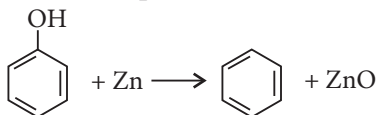
► **Kolbe's reaction :**



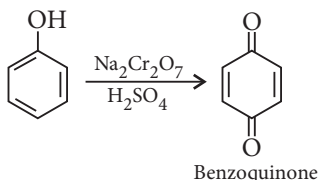
► **Reimer-Tiemann reaction :**



► **Reaction of phenol with zinc dust :**

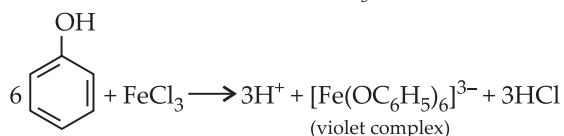


► **Oxidation**

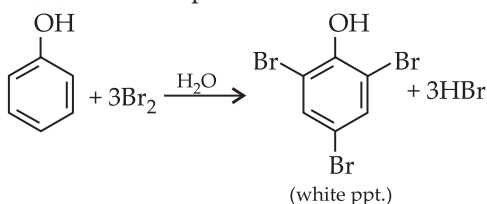


► **Test for phenols :**

- **Ferric chloride test :** Phenol gives violet colour with neutral FeCl_3 solution.



- **Bromine water test :** Phenol gives white ppt. with Br_2 -water due to the formation of 2, 4, 6-tribromophenol.



ETHERS

- **General formula :** Ethers are the compounds having general formula $\text{C}_n\text{H}_{2n+2}\text{O}$ where n is always greater than 1.

- **Nomenclature :** Common names of ethers are derived from the names of alkyl/aryl groups written as separate words in alphabetical order and adding the word 'ether' at the end. If both the alkyl groups are the same, the prefix 'di' is added before the alkyl group. According to IUPAC system of nomenclature, ethers are regarded as hydrocarbon derivatives in which a hydrogen atom is replaced by an $-\text{OR}$ or $-\text{OAr}$ group, where R and Ar represent alkyl and aryl groups, respectively. The larger R group is chosen as the parent hydrocarbon.

- **Structure :** In ethers, the four electron pairs, i.e., the two bond pairs and two lone pairs of

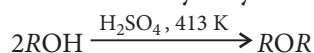
electrons on O atom are arranged approximately in a tetrahedral arrangement.



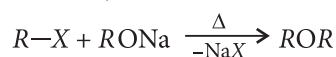
- **Classification :** Ethers can be classified as symmetrical or simple ethers having formula, $R-\text{O}-R$ and unsymmetrical or mixed ethers having formula, $R-\text{O}-R'$.

► **Preparation :**

- **From alcohols by dehydration :**



- **From alkyl halide :**



(Williamson synthesis)

- Williamson synthesis can be used to prepare ethers containing 2° or 3° alkyl groups through $\text{S}_{\text{N}}2$ mechanism. In this case, the alkyl halide must be 1° . In the case of 2° and 3° alkyl halides, elimination takes place. It cannot be used to prepare diaryl ethers.
- Dehydration of alcohols for the formation of ethers follows the order : $1^\circ > 2^\circ > 3^\circ$

► **Physical properties :**

- **Physical state and odour :** Dimethyl ether and ethyl methyl ether are exceptionally gases at room temperature while all other ethers are colourless liquids with characteristic ethereal smell.

- **Solubility :** Ethers are soluble in water to a certain extent due to hydrogen bonding.

- Solubility decreases with increase in molecular mass.
- Ethers are fairly soluble in all organic solvents such as alcohol, chloroform, benzene, etc.

- **Boiling points :** Ethers have lower boiling points than isomeric alcohols due to their inability to form hydrogen bonds and get associated.

- But lower ethers have slightly higher boiling points than n -alkanes of comparable molecular masses due to dipole-dipole interactions.
- Higher ethers (containing carbon atom more than four) have slightly lower boiling points than n -alkanes of comparable molecular

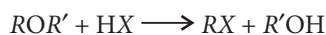
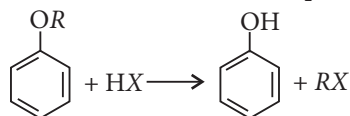
masses due to weak van der Waals forces of attraction.

- **Polarity** : Ethers are polar in nature.
- **Density** : Ethers have low density. All ethers are lighter than water.

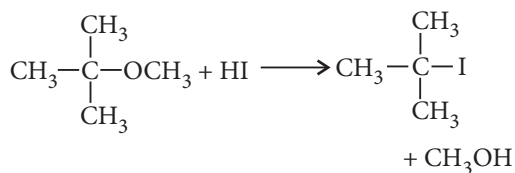


Chemical properties :

► Cleavage of C—O bond in ethers :

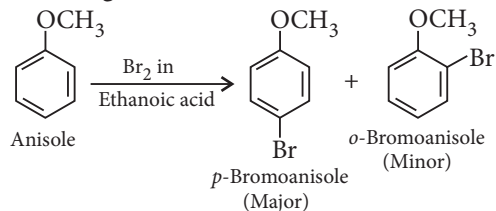


The order of reactivity of hydrogen halides is as follows : HI > HBr > HCl.

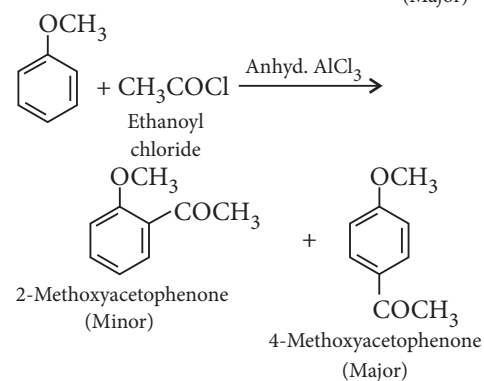
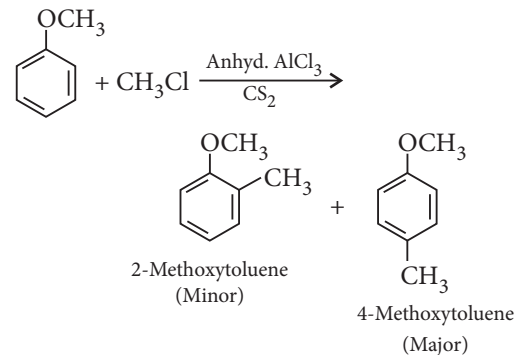


► Electrophilic substitution :

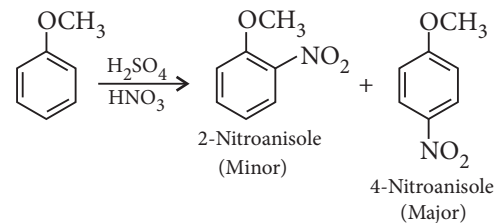
– Halogenation :



– Friedel-Crafts reaction :



– Nitration :



Previous Years' CBSE Board Questions

11.1 Classification

SA II (3 marks)

- Classify the following as primary, secondary and tertiary alcohols :
 - $$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{C}-\text{CH}_2\text{OH} \\ | \\ \text{CH}_3 \end{array}$$
 - $\text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{OH}$
 - $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{OH}$ (AI 2009)

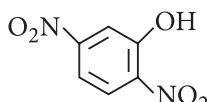
11.2 Nomenclature

VSA (1 mark)

- Write the IUPAC name of the given compound.


 $\text{CH}_2-\text{CH}_2-\text{OH}$

 (AI 2016)
- Write the IUPAC name of the given compound :



 (Delhi 2015)
- Write the IUPAC name of the given compound :

$\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_2-\text{OH} \\ | \\ \text{CH}_3 \end{array}$

 (AI 2015)
- Write the IUPAC name of the given compound:

$\text{HO}-\text{CH}_2-\text{CH}=\text{C}-\text{CH}_3$

$\begin{array}{c} \text{CH}_3 \end{array}$

 (Foreign 2015)
- Name the following according to IUPAC system :

$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3 \\ | \\ \text{OH} \end{array}$

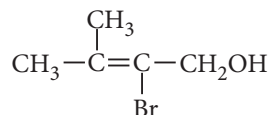
 (1/2, Delhi 2015C)
- Write IUPAC name of the following compound :

$\begin{array}{c} \text{HO}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{OH} \\ | \\ \text{OH} \end{array}$

 (Foreign 2014)
- Draw the structural formula of 2-Methylpropan-2-ol molecule. (Delhi 2012)

- Draw the structure of hex-1-en-3-ol compound. (Delhi 2012)

- Write the IUPAC name of the following :



(AI 2012C)

- Give the structure and IUPAC name of the product formed when propanone is reacted with methylmagnesium bromide followed by hydrolysis. (AI 2012C)
- Write the structure of the molecule of compound whose IUPAC name is 1-Phenylpropan-2-ol (AI 2010)
- Give the IUPAC name of the following compound :

$\begin{array}{c} \text{H}_2\text{C}=\text{CH}-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \\ | \\ \text{OH} \end{array}$

 (AI 2009)
- Write the structure of the following compound : 2-Methyl-2-ethoxypentane. (Delhi 2009C)
- Write the IUPAC name of the following compound :

$\begin{array}{c} \text{CH}_3-\text{O}-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$

 (AI 2008)

11.3 Structures of Functional Groups

VSA (1 mark)

- The C—O bond is much shorter in phenol than in ethanol. Give reason. (Delhi 2012C)

11.4 Alcohols and Phenols

VSA (1 mark)

- Write the equation involved in the acetylation of Salicylic acid. (Delhi 2015)
- Give reason for the following : Phenol is more acidic than ethanol. (1/3, AI 2015)
- Which of the following isomers is more volatile : *o*-nitrophenol or *p*-nitrophenol? (Delhi 2014)

20. Write the equation involved in the following reaction :
Reimer –Tiemann reaction (1/2, AI 2014, 2013)
21. Write the equation involved in the following reaction :
Kolbe's reaction (1/2, Delhi 2014C, 2013C)
22. How is toluene obtained from phenol?
(1/3, Delhi 2013C)
23. Give a chemical test to distinguish between 2-Pentanol and 3-Pentanol. (1/2, Delhi 2013C)
24. Of the two hydroxy organic compounds ROH and R'OH, the first one is basic and other is acidic in behaviour. How is R different from R'? (Delhi 2013C)
25. How would you obtain ethane-1, 2-diol from ethanol ? (AI 2013C)
26. How would you obtain acetophenone from phenol? (AI 2013C)
27. *Ortho*-nitrophenol has lower boiling point than *p*-nitrophenol. Why? (Delhi 2012C)
28. Give a chemical test to distinguish between Benzoic acid and Phenol. (Delhi 2012C)
29. Illustrate the following name reaction
Reimer-Tiemann Reaction. (Delhi 2012C)
30. Give a chemical test to distinguish between 2-propanol and 2-methyl-2-propanol.
(Delhi 2012C)
31. *Ortho*-nitrophenol is more acidic than *ortho*-methoxyphenol. Why? (1/2, Delhi 2012C)
32. Explain the following giving one example :
Reimer-Tiemann reaction.
(1/3, Delhi 2011, 2010, AI 2009C)
33. How would you convert ethanol to ethene?
(AI 2011)
34. Illustrate the following reaction giving a chemical equation :
Kolbe's reaction (Delhi 2010)
35. Give one chemical test to distinguish between the following pairs of compounds.
1-Propanol and 2-Propanol. (1/2, Delhi 2009C)
36. Describe the following with an example :
Kolbe's reaction (AI 2009C)
37. Give reasons for the following :
Propanol has higher boiling point than that of the hydrocarbon butane. (AI 2009C)

38. Why do phenols not give the protonation reaction readily? (1/3, AI 2008)
39. How would you account for the following :
Phenols are much more acidic than alcohols.
(1/2, Delhi 2007)

SA I (2 marks)

40. Write the main product(s) in each of the following reactions :
(i) $\text{CH}_3-\text{CH}=\text{CH}_2 \xrightarrow[\text{(ii) } 3\text{H}_2\text{O}_2/\text{OH}^-]{\text{(i) B}_2\text{H}_6}$
(ii) $\text{C}_6\text{H}_5-\text{OH} \xrightarrow[\text{(ii) CO}_2, \text{H}^+]{\text{(i) aq. NaOH}}$ (Delhi 2016)
41. Write the final product(s) in each of the following reactions :
(i) $\text{CH}_3\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_3 \xrightarrow{\text{Cu/573 K}}$
(ii) $\text{C}_6\text{H}_5-\text{OH} \xrightarrow[\text{(ii) H}^+]{\text{(i) CHCl}_3 + \text{aq. NaOH}}$ (Delhi 2016)
42. Explain the mechanism of dehydration steps of ethanol :
 $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow[443 \text{ K}]{\text{H}^+} \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}$
(Delhi 2015C)
43. How are the following conversions carried out?
(i) Propene to propane-2-ol
(ii) Benzyl chloride to Benzyl alcohol
(2/3, Delhi 2015C)
44. Write the mechanism of acid dehydration of ethanol to yield ethene. (AI 2015C)
45. Write the mechanism of the following reaction :
 $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{HBr}} \text{CH}_3\text{CH}_2\text{Br} + \text{H}_2\text{O}$
(AI 2014, 2/3 Foreign 2014)
46. Name the reagents used in the following reactions :
(i) Bromination of phenol to 2, 4, 6-tribromophenol
(ii) Butan-2-one to Butan-2-ol
(iii) Friedel-Crafts alkylation of anisole
(iv) Oxidation of primary alcohol to carboxylic acid (Foreign 2014)
47. Name the different reagents needed to perform the following reactions :
(i) Phenol to Benzene
(ii) Dehydration of propan-2-ol to propene

- (iii) Friedel-Crafts alkylation of anisole
(iv) Dehydrogenation of ethanol to ethanal
(Foreign 2014)
48. How are the following conversions carried out?
(i) Propene to Propan-2-ol
(ii) Ethyl chloride to Ethanal (Delhi 2014C)
49. Explain the following with an example for each :
(i) Kolbe's reaction
(ii) Reimer-Tiemann reaction (2/3, AI 2014C)
50. How will you convert :
(i) Propene to propan-2-ol?
(ii) Phenol to 2,4,6-trinitrophenol?
(Delhi 2013)
51. How will you convert the following :
(i) Propan-2-ol to propanone.
(ii) Phenol to 2,4,6-tribromophenol.
(Delhi 2013)
52. Explain the mechanism of the following reaction :

$$\text{CH}_3\text{—CH}_2\text{—OH} \xrightarrow[443\text{ K}]{\text{H}^+} \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}$$
 (AI 2013)
53. Explain the mechanism of acid catalysed hydration of an alkene to form corresponding alcohol. (AI 2012)
54. 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. (AI 2012)
55. Give a separate chemical test to distinguish between the following pairs of compounds :
(i) Ethanol and Phenol
(ii) 2-Pentanol and 3-Pentanol (Delhi 2012C)
56. How would you obtain the following :
(i) 2-methylpentan-2-ol from 2-methyl-1-pentene
(ii) Acetophenone from phenol (2/3, AI 2012C)
57. How would you obtain
(i) Picric acid (2, 4, 6-trinitrophenol) from phenol.
(ii) 2-Methylpropene from 2-methylpropanol?
(Delhi 2011)
58. 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? (AI 2011)
59. Give the names of the reagents of bringing about the following transformations :
(i) Hexan-1-ol to hexanal
(ii) But-2-ene to ethanol (Delhi 2011C)
60. Account for the following :
(i) Propanol has higher boiling point than butane.
(ii) *Ortho*-nitrophenol is more acidic than *ortho*-methoxyphenol. (2/3, Delhi 2011C)
61. 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. (Delhi 2011C)
62. Write Reimer-Tiemann reaction giving an example. (AI 2011C)
63. How are the following conversions carried out?
(i) Benzyl chloride to benzyl alcohol.
(ii) Methyl magnesium bromide to 2-methylpropan-2-ol. (Delhi 2010)
64. Describe the mechanism of hydration of ethene to yield ethanol. (AI 2010C)
65. Describe a chemical test each to distinguish between the following pairs :
(i) Ethanol and Phenol
(ii) 1-Propanol and 2-Propanol
(Delhi 2008C, AI 2008)

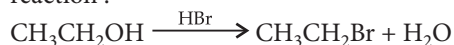
SA II (3 marks)

66. How do you convert the following?
(i) Phenol to anisole
(ii) Propan-2-ol to 2-methylpropan-2-ol
(iii) Aniline to phenol (Delhi 2015)
67. Predict the products of the following reactions :
(i) $\text{CH}_3\text{—CH=CH}_2 \xrightarrow[\text{(ii) } 3\text{H}_2\text{O}_2/\text{OH}^-]{\text{(i) B}_2\text{H}_6} ?$
(ii) $\text{C}_6\text{H}_5\text{OH} \xrightarrow{\text{Br}_2(\text{aq})} ?$
(iii) $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{Cu}/573\text{ K}} ?$ (Foreign 2015)

68. How are the following conversions carried out?
 (i) Benzyl chloride to benzyl alcohol
 (ii) Ethyl magnesium chloride to Propan-1-ol
 (iii) Propene to Propan-2-ol.

(AI 2015C, 2014C)

69. (a) Write the mechanism of the following reaction :



- (b) Write the equation involved in Reimer-Tiemann reaction. (Delhi 2014)
70. (a) Give chemical tests to distinguish between the following pairs of compounds :
 (i) Pentan-2-ol and Pentan-3-ol
 (ii) Methanol and Phenol
 (b) *o*-nitro phenol is more acidic than *o*-methoxy phenol. Explain why.

(AI 2013C)

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

- (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
 (ii) 2-butenol
 (iii) 2-methyl-1-propanol (Delhi 2012)

72. (a) Describe the mechanism of hydration of ethene to yield ethanol.
 (b) Write Kolbe's reaction with an example.

(AI 2011C)

73. Acid catalysed dehydration of *t*-butanol is faster than that of *n*-butanol. Explain. (AI 2011C)

74. How would you convert the following :
 (i) Phenol to benzoquinone
 (ii) Propanone to 2-methylpropan-2-ol
 (iii) Propene to propan-2-ol. (AI 2010)

75. (i) Describe the mechanism of acid dehydration of ethanol to yield ethene.
 (ii) Describe a chemical test to distinguish between ethanol and phenol.

(Delhi 2010C)

76. Explain the mechanism of the following reactions :

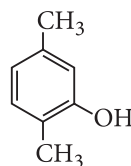
- (i) Addition of Grignard's reagent to the carbonyl group of a compound forming an adduct followed by hydrolysis.
 (ii) Acid catalysed dehydration of an alcohol forming an alkene.

- (iii) Acid catalysed hydration of an alkene forming an alcohol. (Delhi 2009)

77. 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)

78. (a) Write the IUPAC name of the following :



- (b) Give reasons for the following :
 (i) Phenol is a stronger acid than alcohol.
 (ii) Alcohols are comparatively more soluble in water than the corresponding hydrocarbons. (AI 2008C)

11.5 Some Commercially Important Alcohols

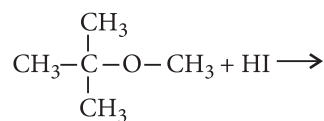
VSA (1 mark)

79. Name a substance that can be used as an antiseptic as well as a disinfectant. (Delhi 2008)

11.6 Ethers

VSA (1 mark)

80. Write the main product(s) in the following reaction :



(1/3, Delhi 2016, 1/2, AI 2016)

81. How is the following conversion carried out? Anisole to *p*-bromoanisole (1/3, Delhi 2015C)

82. Write the equations involved in the following reaction :

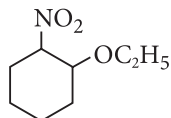
Williamson synthesis
 (1/2, AI 2014, 2013, 1/2, Delhi 2014C)

83. Explain the following with an example : Williamson ether synthesis. (1/3, AI 2014C, 2009C)

84. Illustrate the following name reaction :
Williamson Synthesis

(1/3, Delhi 2012C, 1/2 Delhi 2010)

85. Write IUPAC name of the following :



(1/3, AI 2012C)

86. Explain the following giving one example :
Friedel Craft's acetylation of anisole.

(1/3, Delhi 2011)

87. Account for the following :

Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. (1/3, Delhi 2011C, 1/2, Delhi 2008)

88. Account for the following :

The boiling points of ethers are lower than isomeric alcohols. (1/3, AI 2011C)

89. Phenylmethyl ether reacts with HI to give phenol and methyl iodide and not iodobenzene and methyl alcohol. Why? (Delhi 2010C)

90. Describe the following :

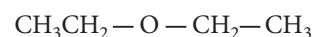
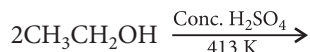
Unsymmetrical ether (1/2, AI 2009C)

91. Why is the preparation of ether by acid dehydration of secondary alcohol not a suitable method? (AI 2008C)

92. The boiling points of ethers are much lower than those of the alcohols of comparable molar masses. (1/3, Delhi 2007)

SAI (2 marks)

93. Write the mechanism of the following reaction :



(Delhi 2016, 2015, 2013)

94. Give reasons for the following :

(i) Boiling point of ethanol is higher in comparison to methoxymethane.

(ii) $(\text{CH}_3)_3\text{C}-\text{O}-\text{CH}_3$ on reaction with HI gives CH_3OH and $(\text{CH}_3)_3\text{C}-\text{I}$ as the main products and not $(\text{CH}_3)_3\text{C}-\text{OH}$ and CH_3I . (2/3, AI 2015)

95. Give mechanism of preparation of ethoxy ethane from ethanol. (Delhi 2013C)

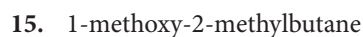
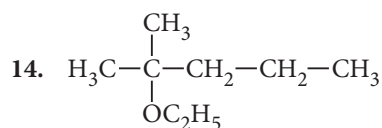
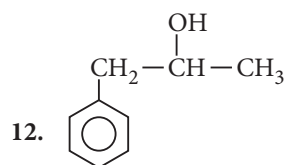
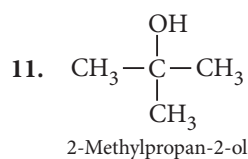
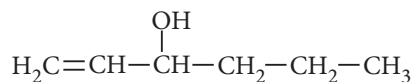
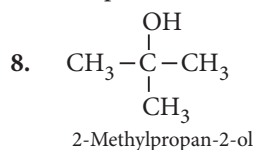
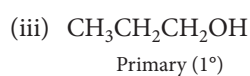
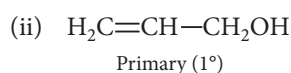
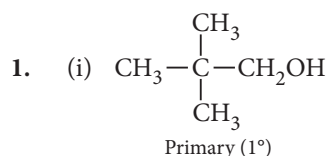
96. How is 1-propoxypropane synthesised from propan-1-ol? (Delhi 2010)

97. Name the reagents and write the chemical equations for the preparation of the following compounds by Williamson's synthesis :

(i) Ethoxybenzene

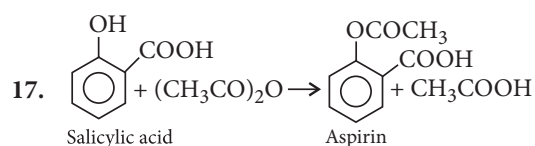
(ii) 2-Methyl-2-methoxypropane (AI 2008)

Detailed Solutions



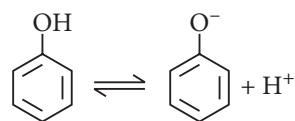
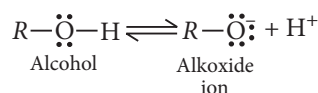
16. Due to resonance C—O bond acquires some partial double bond character.

So, in phenol C—O bond length is smaller than ethanol.



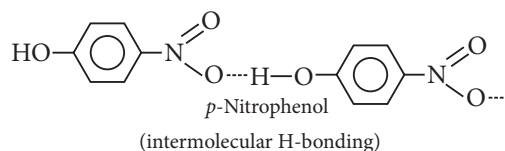
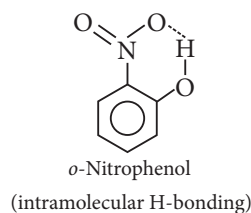
18. Phenols are more acidic than alcohols. It can be explained on the basis that alcohol on losing H^+ ions form alkoxide ion and phenol forms phenoxide ion.

The greater acidity of phenol is due to the stability of the phenoxide ion which is resonance stabilized as shown below.

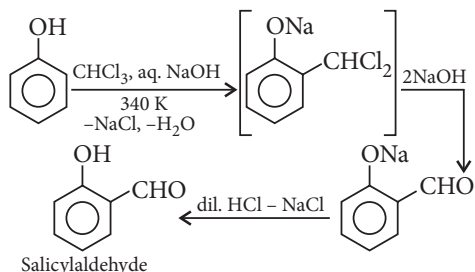


On the other hand, alkoxide ion shows no such resonance stabilisation and is unstable.

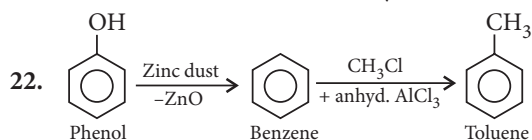
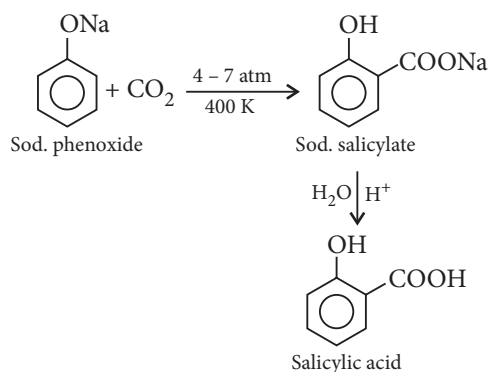
19. *o*-Nitrophenol is more steam volatile than *p*-Nitrophenol due to the presence of intramolecular H-bonding. *p*-nitrophenol shows intermolecular H-bonding.



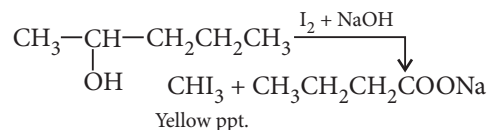
That's why *o*-nitrophenol has lower boiling point than *p*-nitrophenol.

20. Reimer-Tiemann reaction

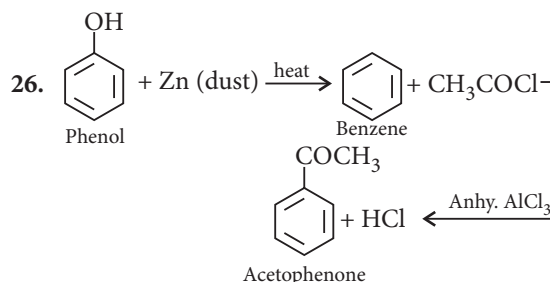
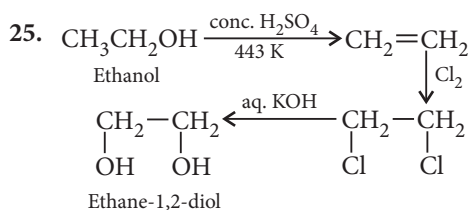
21. Kolbe's reaction : When sodium phenoxide is heated with carbon dioxide under pressure, it gives salicylic acid.



23. On adding I_2 and NaOH , 2-pentanol will give yellow precipitate of iodoform whereas 3-pentanol will not give yellow precipitate.



24. R is alkyl group and R' is aryl group. R must be a group having more electron density than H , i.e., having $+I$ effect whereas R' must be having $-I$ effect.



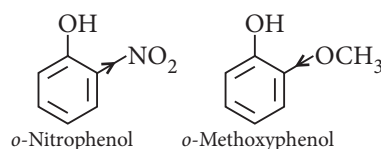
27. Refer to answer 19.

28. Benzoic acid gives brisk effervescence of CO_2 on addition of NaHCO_3 while phenol does not.

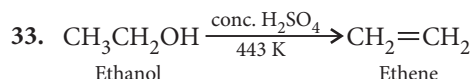
29. Refer to answer 20.

30. 2-propanol will give yellow precipitate of iodoform on addition of I_2 and NaOH while 2-methyl-2-propanol will not.

31. As we know that the electron withdrawing groups enhance the acidic character of phenols because they help in the stabilisation of phenoxide ion by dispersing negative charge. Nitro group is an electron withdrawing group whereas methoxy group destabilises the phenoxide ion by intensifying the negative charge. Thus, *o*-nitrophenol is more acidic than *o*-methoxyphenol.



32. Refer to answer 20.

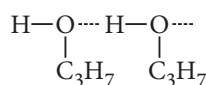


34. Refer to answer 21.

35. On adding I_2 and NaOH 2-Propanol will give yellow ppt. of iodoform, whereas 1-propanol will not give yellow ppt.

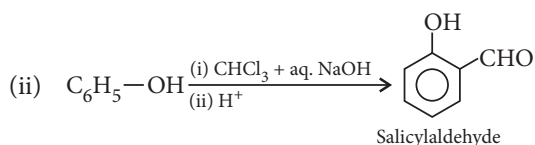
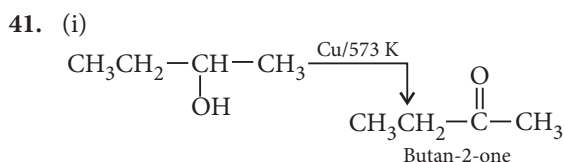
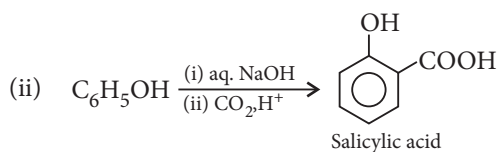
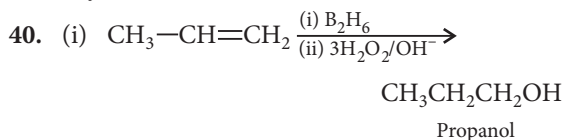
36. Refer to answer 21.

37. The molecules of butane are held together by weak van der Waals forces of attraction while those of propanol are held together by stronger intermolecular hydrogen bonding.

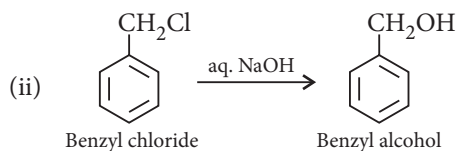
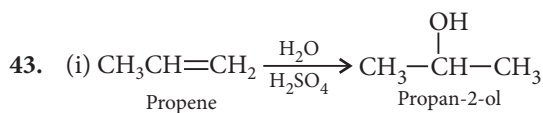
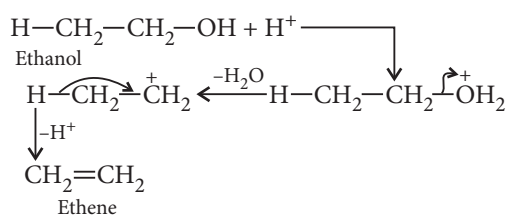


38. Due to electron withdrawing effect of phenyl group the electron density on the oxygen atom of -OH group in phenol is less. Hence, phenols do not undergo protonation.

39. Refer to answer 18.

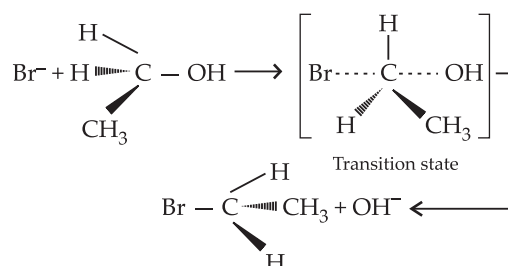


42. Acid catalysed dehydration of alcohols at high temperature takes place with formation of an alkene.



44. Refer to answer 42.

45. The reaction proceeds through nucleophilic substitution bimolecular ($\text{S}_{\text{N}}2$) mechanism, as shown below :

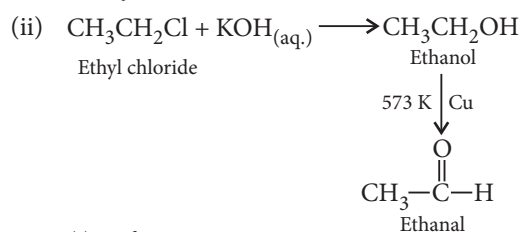


Inversion of configuration takes place during the reaction.

46. (i) Bromine water, ($\text{Br}_{2(\text{aq})}$)
(ii) Lithium aluminium hydride, (LiAlH_4) or H_2/Ni
(iii) Alkyl halide in the presence of anhydrous aluminium chloride, CH_3Cl and AlCl_3 (anhy.)
(iv) Acidified potassium permanganate, KMnO_4 , H_3O^+

47. (i) Zinc dust
(ii) Concentrated H_2SO_4
(iii) Refer to answer 46(iii).
(iv) $\text{Cu}/573\text{ K}$

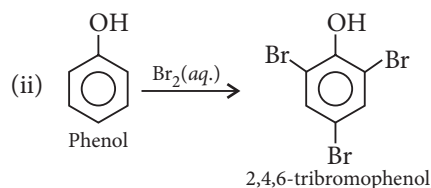
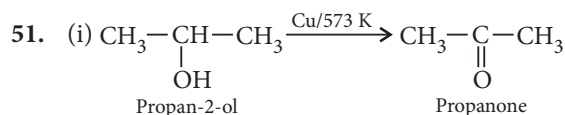
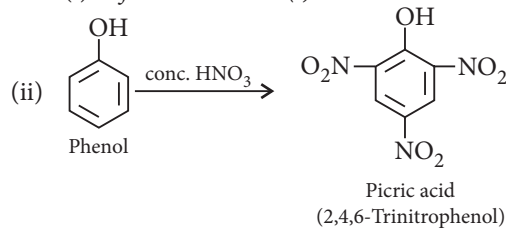
48. (i) Refer to answer 43(i).



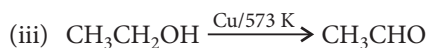
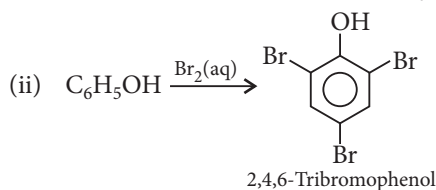
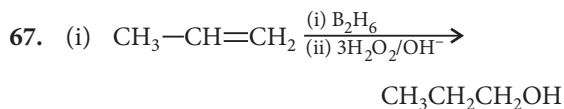
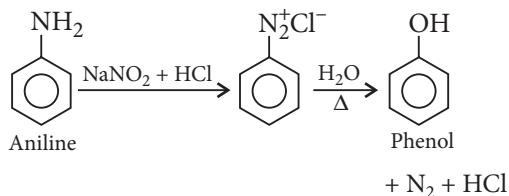
49. (i) Refer to answer 21.

(ii) Refer to answer 20.

50. (i) Refer to answer 43(i).

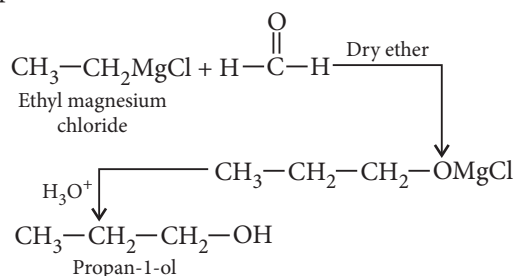


(iii) Aniline to phenol



68. (i) Refer to answer 43(ii).

(ii) Ethyl magnesium chloride on addition to formaldehyde followed by hydrolysis gives propan-1-ol.



(iii) Refer to answer 43(i).

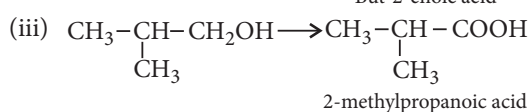
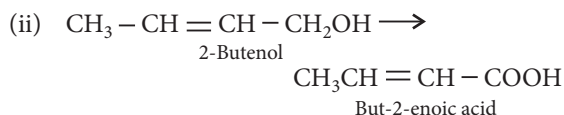
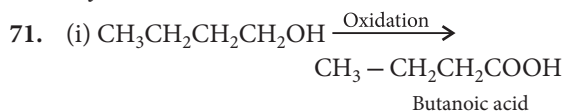
69. (i) Refer to answer 46.

(ii) Refer to answer 20.

70. (a) (i) Refer to answer 23.

(ii) Refer to answer 55(i).

(b) Refer to answer 31.

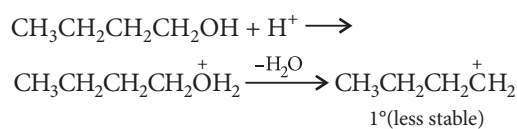
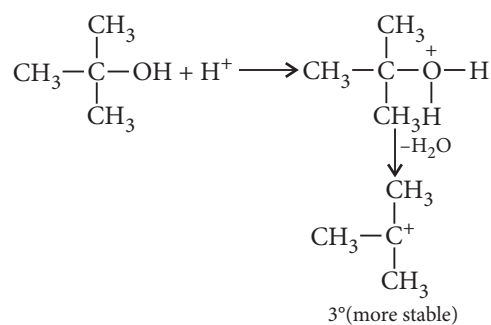


72. (a) Refer to answer 53.

(b) Refer to answer 21.

73. Acid catalysed dehydration of alcohols follows carbocation mechanism.

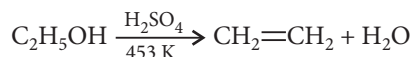
Hence, dehydration of *t*-butanol which form 3° carbocation is faster than *n*-butanol which form primary carbocation.



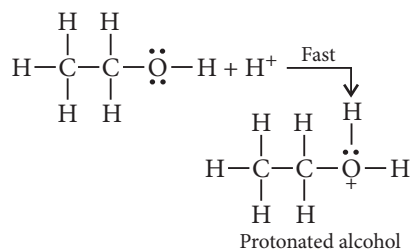
74. (i) Refer to answer 58(i).

(ii) Refer to answer 58(ii).

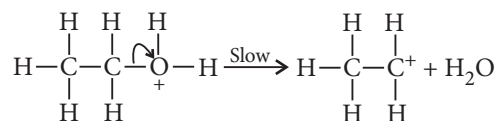
(iii) Refer to answer 43(i).

75. (i) Ethanol undergoes dehydration by heating it with concentrated H_2SO_4 at 453 K.**Mechanism :** The dehydration of ethanol involves the following steps :

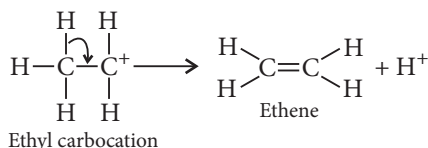
(a) Formation of protonated alcohol.



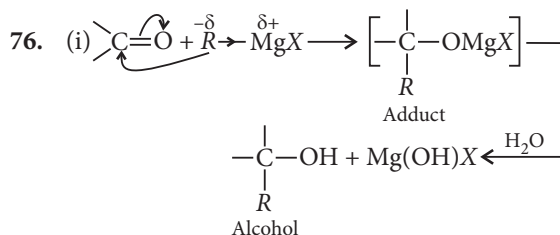
(b) Formation of carbocation.



(c) Formation of ethene.



(ii) Refer to answer 55(i).



(ii) Refer to answer 42.

(iii) Refer to answer 53.

77. (i) Copper at 573 K

(ii) Sodium borohydride (NaBH_4)

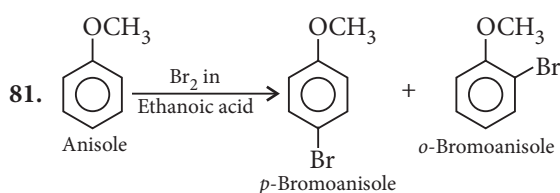
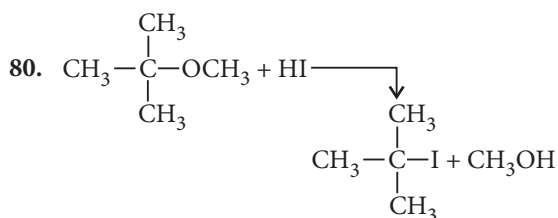
(iii) Bromine water ($\text{Br}_2(\text{aq})$)

78. (a) 2,5-Dimethylphenol

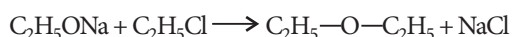
(b) (i) Refer to answer 18.

(ii) Refer to answer 54(i).

79. **Phenol**: 0.2% solution of phenol is an antiseptic while 2% solution is used as disinfectant.



82. **Williamson ether synthesis**: Alkyl halide when treated with sodium alkoxide gives dialkyl ether.

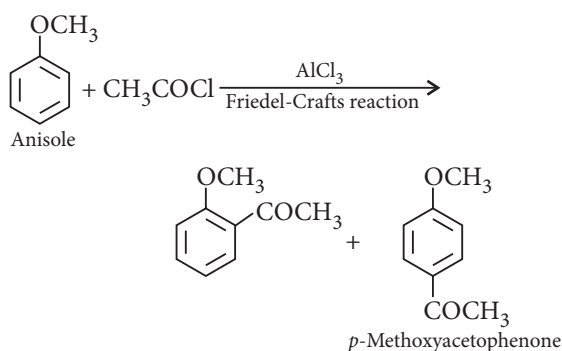


83. Refer to answer 82.

84. Refer to answer 82.

85. 1-Ethoxy-2-nitrocyclohexane.

86. **Reagents**: Acetyl chloride and Lewis acid catalyst.

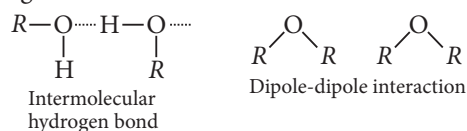


87. Acid dehydration of 2° and 3° alcohols give alkenes rather than ethers.

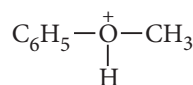
Due to steric hindrance the nucleophilic attack by the alcohol molecule on the protonated alcohol molecule does not occur.

The protonated 2° and 3° alcohols lose water molecules to form stable 2° and 3° carbocations.

88. The boiling points of ethers are much lower than, those of alcohol of comparable molar masses because like alcohols they cannot form intermolecular hydrogen bonds.



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



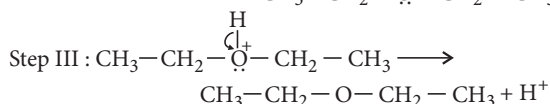
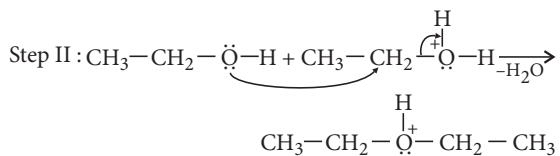
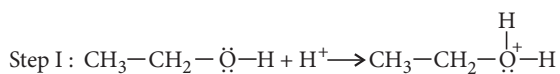
In this ion, the stronger bond is $\text{O}-\text{C}_6\text{H}_5$. Therefore, attack by I^- ion exclusively breaks the weaker $\text{O}-\text{CH}_3$ bond forming methyl iodide and phenol. The phenol formed does not react further to give aryl halides.

90. **Unsymmetrical ether**: Ethers in which two alkyl groups are different are known as unsymmetrical ether. e.g., $\text{CH}_3\text{OCH}_2\text{CH}_3$ Methoxyethane.

91. Refer to answer 87.

92. Refer to answer 88.

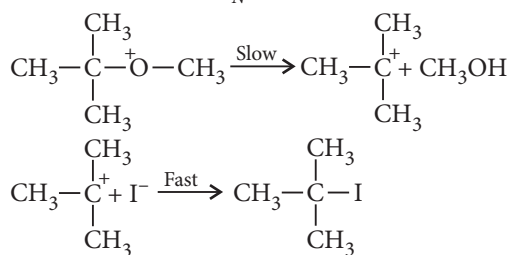
93. **Mechanism**: The formation of ether is nucleophilic bimolecular reaction.



94. (i) Ethanol has higher boiling point because of strong intermolecular hydrogen bonding whereas in methoxymethane, molecules are held by dipole-dipole interaction.

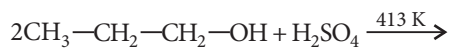
(ii) When one alkyl group is a tertiary group the halide formed is tertiary halide.

In step II the departure of leaving group (CH_3-OH) creates a more stable carbocation (3°) and the reaction follows $\text{S}_{\text{N}}1$ mechanism.

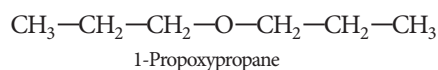


95. Refer to answer 93.

96. Propan-1-ol on treatment with conc. H_2SO_4 at 413 K would yield 1-propoxypropane. In this method, the alcohol is continuously added to keep its concentration in excess.



Propan-1-ol



Mechanism :

