

Alcohols, Phenols and Ethers

11.1 Classification

11.2 Nomenclature

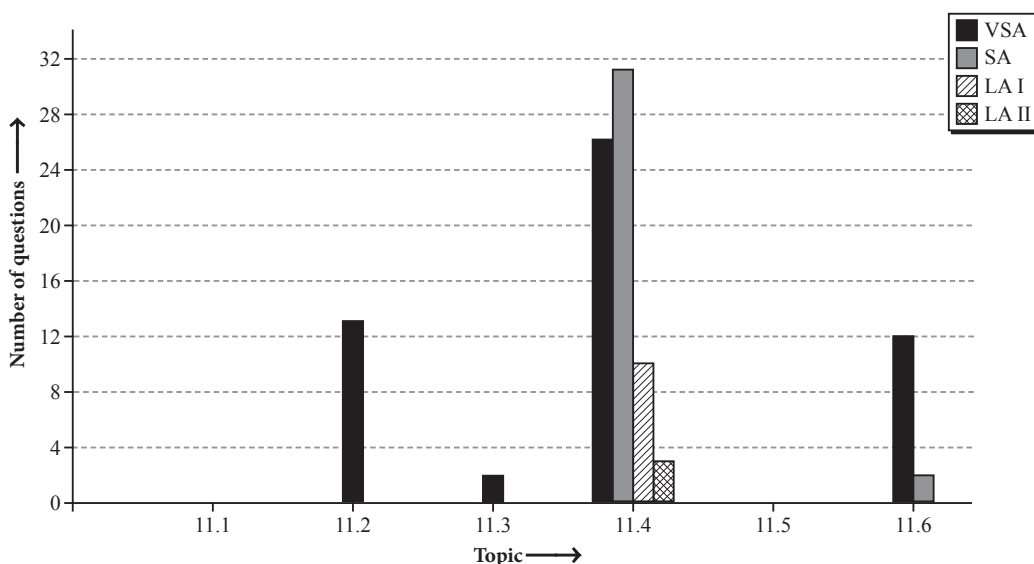
11.3 Structures of Functional Groups

11.4 Alcohols and Phenols

11.5 Some Commercially Important Alcohols

11.6 Ethers

Topicwise Analysis of Last 10 Years' CBSE Board Questions (2020-2011)



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

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

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

QUICK RECAP

ALCOHOLS

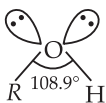
▶▶ **General formula** : Alcohols are the hydroxy derivatives of alkanes having general formula $C_nH_{2n+1}OH$.

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

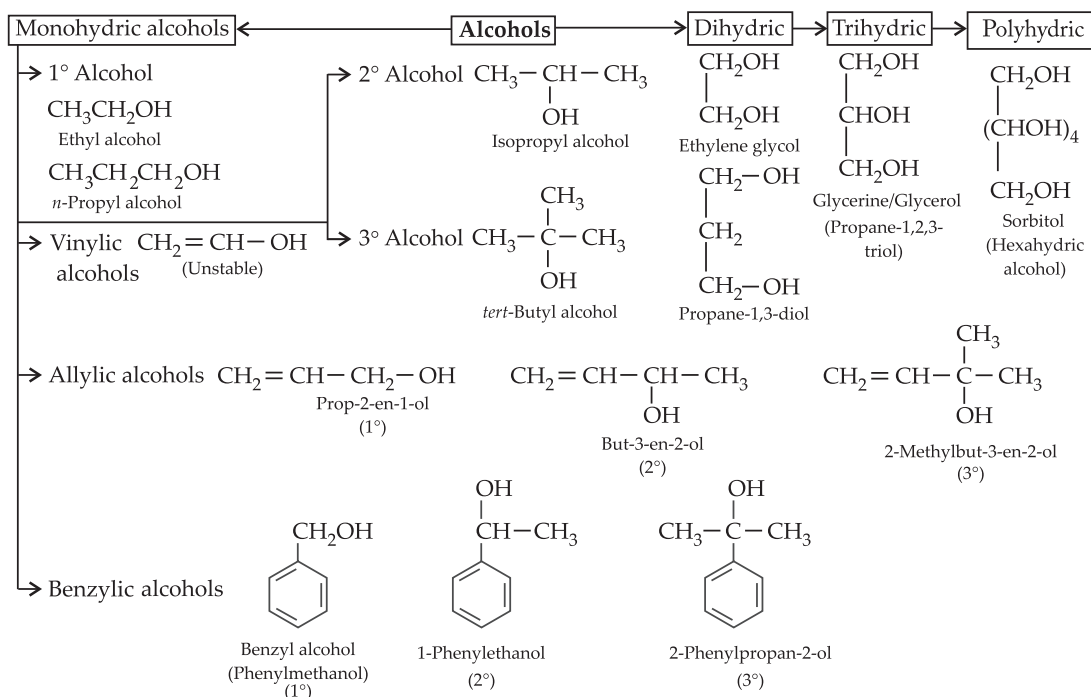
are named as *alkyl alcohol*. According to IUPAC system, alcohols are called '*alkanols*', by replacing '-e' of alkane by '-ol'.

▶▶ **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 sp^3 hybridised orbital of O-atom.



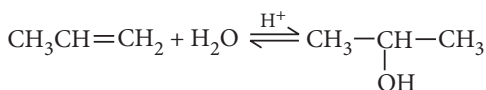
► **Classification :** Alcohols are classified as monohydric, dihydric, trihydric and polyhydric alcohols depending upon the number of hydroxyl ($-\text{OH}$) groups present in the molecule.



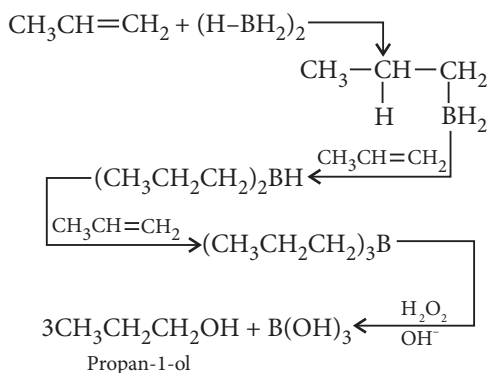
► Preparation :

► From alkenes :

– By acid catalysed hydration :

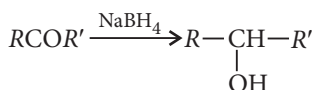
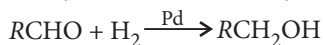


– By hydroboration-oxidation :

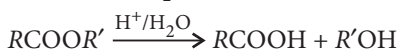
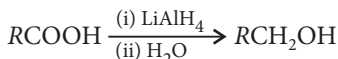


► From carbonyl compounds :

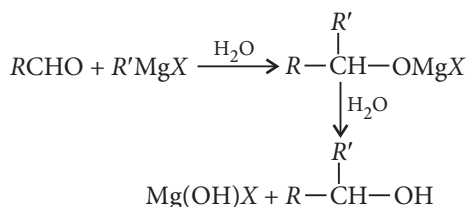
– By reduction of aldehydes and ketones :

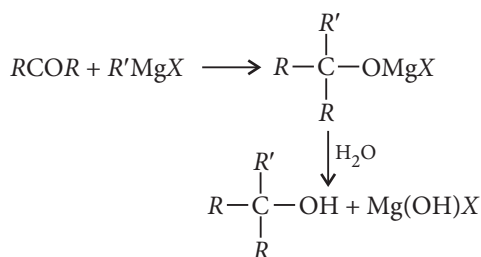


– By reduction of carboxylic acids and esters :



– From Grignard reagents :





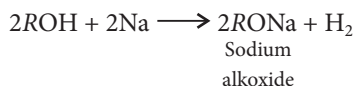
Physical properties :

- **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 $1^\circ > 2^\circ > 3^\circ$.

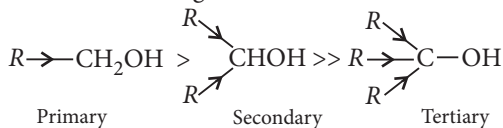
Chemical properties : Alcohols react both as nucleophiles (when the bond between O—H is broken) and electrophiles (when the bond between C—O is broken).

Reactions involving cleavage of O—H bond :

Acidity of alcohols (reaction with metals) :



- The above reaction shows that alcohols are acidic in nature.
- The acid strength of alcohols decreases in the following order :

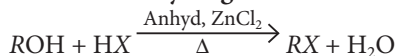


Esterification :



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 .

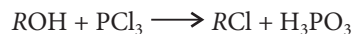
– With Lucas reagent,

Primary alcohols – No cloudiness

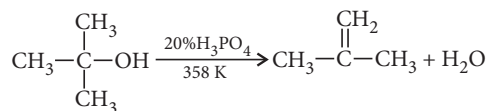
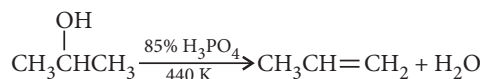
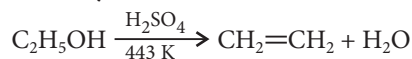
Secondary alcohols – Cloudiness in 5 minutes

Tertiary alcohols – Cloudiness immediately

Reaction with phosphorus trihalides :



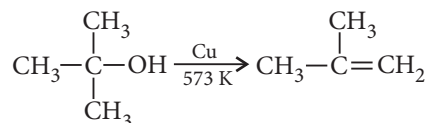
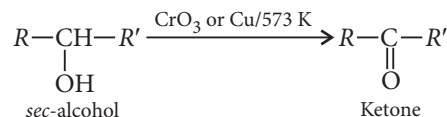
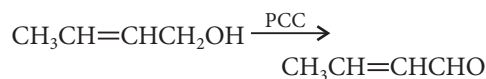
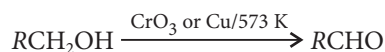
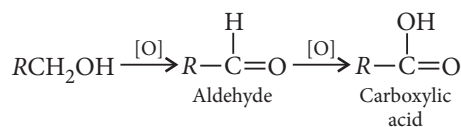
Dehydration :



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

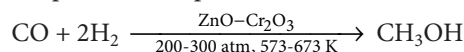
Tertiary > Secondary > Primary

Oxidation :



Some commercially important alcohols :

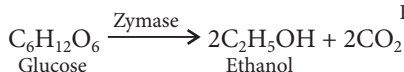
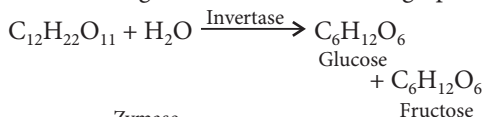
► **Methanol (wood spirit) :** It is produced by catalytic hydrogenation of CO in the presence of $\text{ZnO} - \text{Cr}_2\text{O}_3$ as catalyst at high temperature and pressure.



– 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.



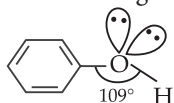
- Ethanol is colourless liquid and is used as a solvent in paint industry and in preparation of a number of carbon compounds.
- Commercial alcohol made unfit for drinking by mixing it with copper sulphate and pyridine, it is called *denatured alcohol*.

PHENOLS

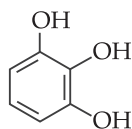
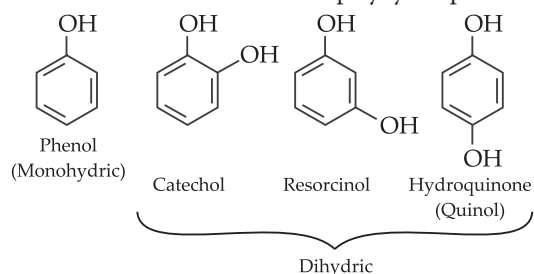
► **General formula** : Phenols are the compounds in which hydroxy (—OH) group is directly linked to aromatic ring having formula, $\text{C}_6\text{H}_5\text{OH}$.

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

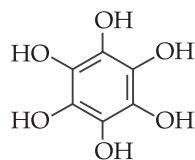
► **Structure** : In phenols, the —OH group is attached to sp^2 hybridised C-atom of an aromatic ring.



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



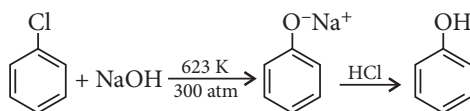
Pyrogallol
(Trihydric)



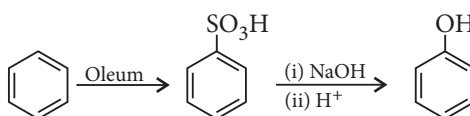
Hexaphenol
(Polyhydric)

► Preparation :

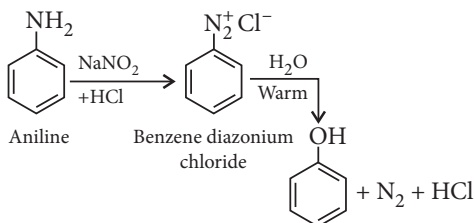
► **From haloarenes** :



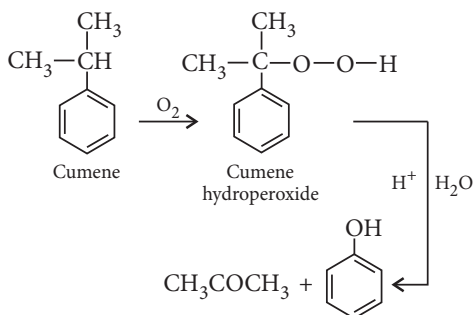
► **From benzenesulphonic acid** :



► **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.

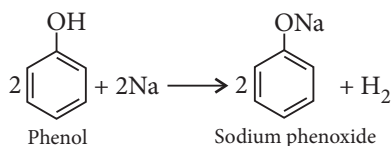
► **Boiling points :** The boiling points of phenols are much higher than the corresponding aromatic hydrocarbons and haloarenes due to intermolecular hydrogen bonding.

► Chemical properties :

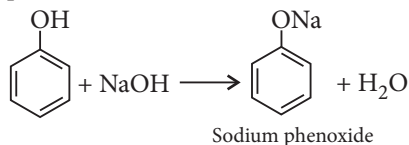
► **Acidity of phenols :** Phenols are weakly acidic in nature due to polar O—H bond directly attached to sp^2 -hybridised C-atom.

- 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.

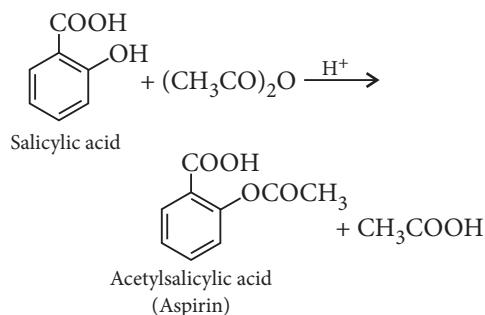
► Reaction with metals :



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

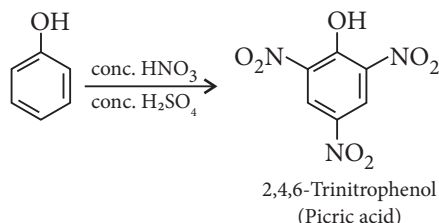
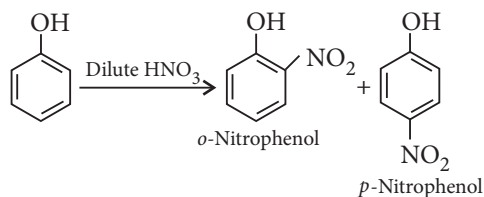


► Esterification :

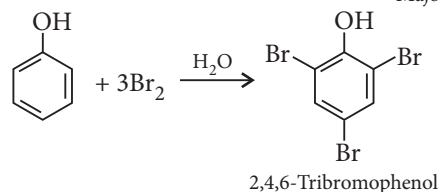
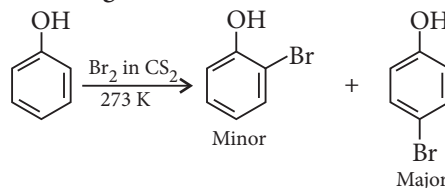


► Electrophilic aromatic substitution :

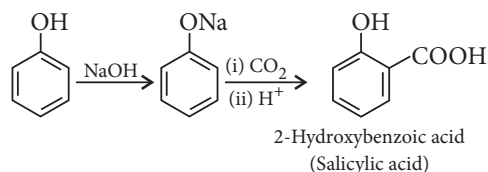
► Nitration :



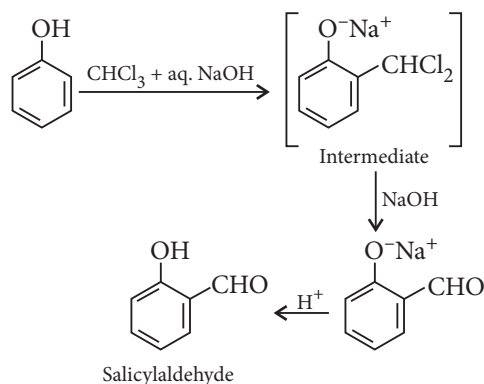
► Halogenation :



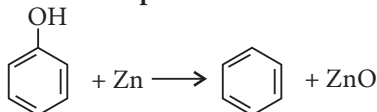
► Kolbe's reaction :



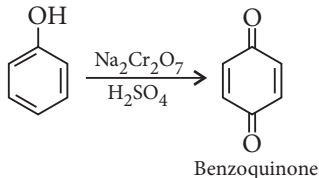
► Reimer-Tiemann reaction :



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

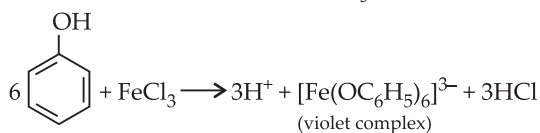


► **Oxidation**

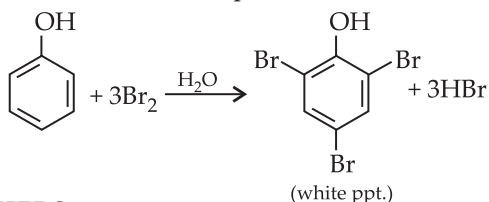


► **Test for phenols :**

- **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

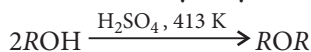
approximately in a tetrahedral arrangement.



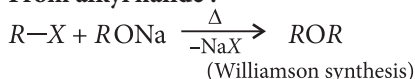
- **Classification :** Ethers can be classified as symmetrical or simple ethers having formula, $R-\text{O}-R$ and unsymmetrical or mixed ethers having formula, $R-\text{O}-R'$.

►► **Preparation :**

- **From alcohols by dehydration :**



- **From alkyl halide :**



- Williamson synthesis 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

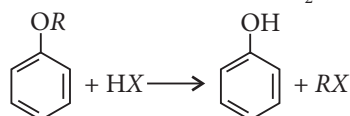
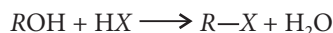
lower boiling points than *n*-alkanes of comparable molecular masses due to weak van der Waals' forces of attraction.

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

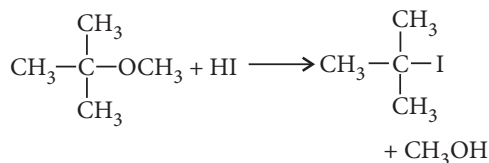


Chemical properties :

► Cleavage of C—O bond in ethers :

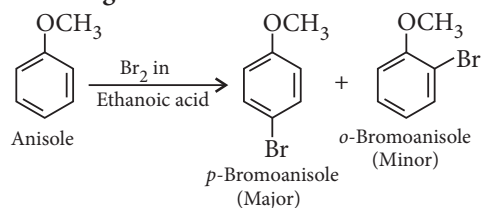


The order of reactivity of hydrogen halides is as follows : HI > HBr > HCl.

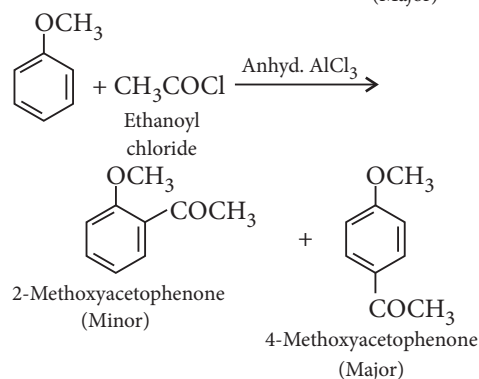
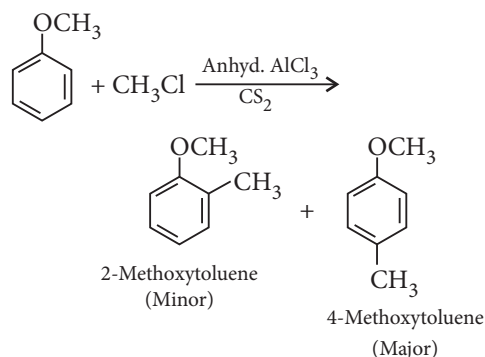


► Electrophilic substitution :

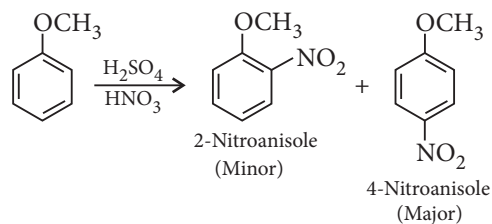
– Halogenation :



– Friedel-Crafts reaction :



– Nitration :

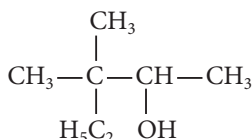


Previous Years' CBSE Board Questions

11.2 Nomenclature

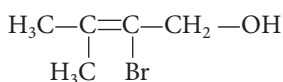
VSA (1 mark)

1. Write the IUPAC name of the following :



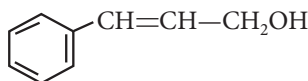
(2018)

2. Write the IUPAC name of the following compound :



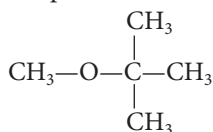
(AI 2017, AI 2012C)

3. Write the IUPAC name of the following compound :



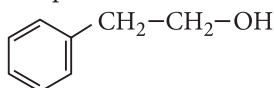
(AI 2017)

4. Write the IUPAC name of the following compound :



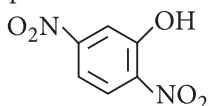
(AI 2017)

5. Write the IUPAC name of the given compound.



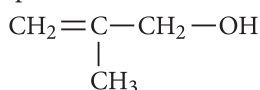
(AI 2016)

6. Write the IUPAC name of the given compound :



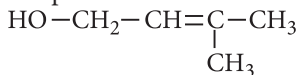
(Delhi 2015)

7. Write the IUPAC name of the given compound :



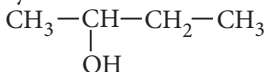
(AI 2015)

8. Write the IUPAC name of the given compound:



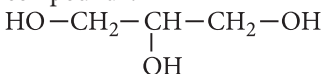
(Foreign 2015)

9. Name the following according to IUPAC system :



(1/2, Delhi 2015C)

10. Write IUPAC name of the following compound :

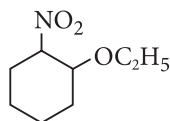


(Foreign 2014)

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

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

13. Write IUPAC name of the following :



(1/3, AI 2012C)

11.3 Structures of Functional Groups

VSA (1 mark)

14. **Assertion (A) :** The C—O—H bond angle in alcohols is slightly less than the tetrahedral angle.

Reason (R) : This is due to the repulsive interaction between the two lone electron pairs on oxygen.

- (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).
 (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).
 (c) Assertion (A) is correct, but Reason (R) is incorrect statement.
 (d) Assertion (A) is incorrect, but Reason (R) is correct statement. (2020)

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

11.4 Alcohols and Phenols

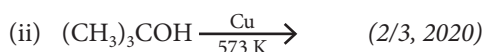
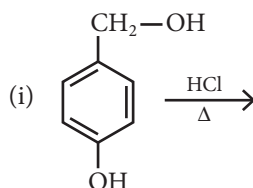
VSA (1 mark)

16. Carry out the following conversion :
Phenol to salicylaldehyde (1/5, 2020)
17. Carry out the following conversion :
Propene to propanol (1/5, 2020)
18. Predict the reagent for carrying out the following conversion :
Phenol to benzoquinone (1/5, 2020)
19. Predict the reagent for carrying out the following conversion :
Phenol to 2,4,6-tribromophenol (1/5, 2020)
20. Write the preparation of phenol from cumene. (1/3, 2020)
21. How can you convert the following :
Phenol to chlorobenzene. (1/3, 2020)
22. How can you convert the following :
Sodium phenoxide to *o*-hydroxybenzoic acid. (1/3, 2020)
23. How can you convert the following?
Ethanol to propanenitrile (1/3, 2020)
24. Write the equation involved in the following reaction : Kolbe's reaction
(1/2, AI 2019, Delhi 2014C, 2013C)
25. Give reason for the following :
Phenol is more acidic than ethanol.
(1/3, AI 2017C, 2015)
26. Write the equation involved in the acetylation of salicylic acid. (Delhi 2015)
27. Which of the following isomers is more volatile :
o-nitrophenol or *p*-nitrophenol?
(Delhi 2014)
28. Write the equation involved in the following reaction :
Reimer – Tiemann reaction.
(1/2, AI 2014, 2013)
29. How is toluene obtained from phenol?
(1/3, Delhi 2013C)
30. Give a chemical test to distinguish between 2-pentanol and 3-pentanol.
(1/2, Delhi 2013C)

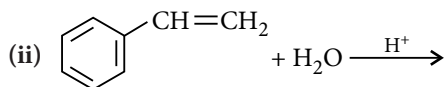
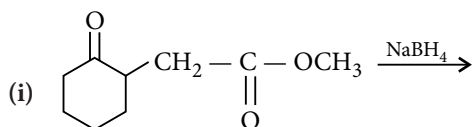
31. Of the two hydroxy organic compounds ROH and *R'*OH, the first one is basic and other is acidic in behaviour. How is *R* different from *R'*? (Delhi 2013C)
32. How would you obtain ethane-1, 2-diol from ethanol ? (AI 2013C)
33. How would you obtain acetophenone from phenol? (AI 2013C)
34. *Ortho*-nitrophenol has lower boiling point than *p*-nitrophenol. Why? (Delhi 2012C)
35. Give a chemical test to distinguish between benzoic acid and phenol. (Delhi 2012C)
36. Illustrate the following name reaction
Reimer-Tiemann Reaction. (Delhi 2012C)
37. Give a chemical test to distinguish between 2-propanol and 2-methyl-2-propanol.
(Delhi 2012C)
38. *Ortho*-nitrophenol is more acidic than *ortho*-methoxyphenol. Why? (1/2, Delhi 2012C)
39. Give the structure and IUPAC name of the product formed when propanone is reacted with methylmagnesium bromide followed by hydrolysis. (AI 2012C)
40. Explain the following giving one example :
Reimer-Tiemann reaction. (1/3, Delhi 2011)
41. How would you convert ethanol to ethene?
(AI 2011)

SA (2 marks)

42. Out of *t*-butyl alcohol and *n*-butanol, which one will undergo acid catalysed dehydration faster and why? (2/5, 2020)
43. Give the mechanism for the formation of ethanol from ethene. (2/5, 2020)
44. Write the major product(s) of the following reactions :

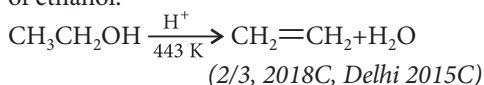


45. Write the structures of the main products in the following reactions :

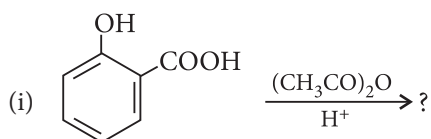


(2/3, 2018)

46. Explain the mechanism of dehydration steps of ethanol.



47. Write the product(s) in the following reactions :



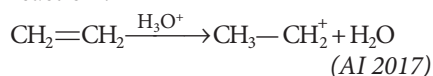
48. Give simple chemical tests to distinguish between the following pairs of compounds:

- (i) Ethanol and phenol
(ii) Propanol and 2-methylpropan-2-ol.
- (2/5, Delhi 2017)

49. (a) Arrange the following compounds in the increasing order of their acid strength :

p-cresol, *p*-nitrophenol, phenol

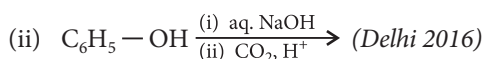
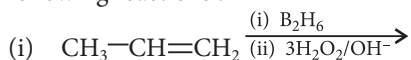
- (b) Write the mechanism (using curved arrow notation) of the following reaction :



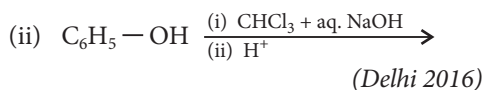
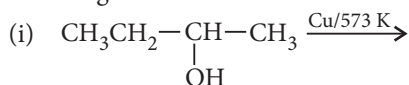
50. Write the structure of the products when Butan-2-ol reacts with the following :

- (a) CrO_3 (b) SOCl_2 (AI 2017)

51. Write the main product(s) in each of the following reactions :



52. Write the final product(s) in each of the following reactions :

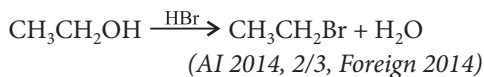


53. How are the following conversions carried out?

- (i) Propene to propan-2-ol
(ii) Benzyl chloride to Benzyl alcohol
- (2/3, Delhi 2015C)

54. Write the mechanism of acid dehydration of ethanol to yield ethene. (AI 2015C)

55. Write the mechanism of the following reaction :



56. 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)

57. 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)

58. How are the following conversions carried out?

- (i) Propene to Propan-2-ol
(ii) Ethyl chloride to Ethanal (Delhi 2014C)

59. Explain the following with an example for each :

- (i) Kolbe's reaction,
(ii) Reimer-Tiemann reaction
- (2/3, AI 2014C)

60. How will you convert :

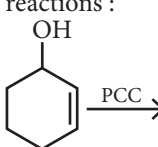
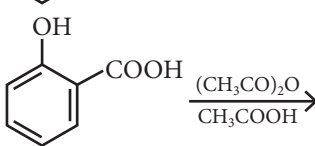
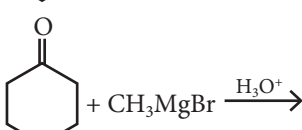
- (i) Propene to propan-2-ol,
(ii) Phenol to 2,4,6-trinitrophenol?
- (Delhi 2013)

61. How will you convert the following :
 (i) Propan-2-ol to propanone
 (ii) Phenol to 2,4,6-tribromophenol.
 (Delhi 2013)
62. 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)
63. Explain the mechanism of acid catalysed hydration of an alkene to form corresponding alcohol.
 (AI 2012)
64. 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)
65. 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)
66. How would you obtain the following :
 (i) 2-methylpentan-2-ol from 2-methyl-1-pentene
 (ii) Acetophenone from phenol.
 (2/3, AI 2012C)
67. How would you obtain
 (i) Picric acid (2, 4, 6-trinitrophenol) from phenol.
 (ii) 2-Methylpropene from 2-methylpropanol?
 (Delhi 2011)
68. How would you obtain the following :
 (i) Benzoquinone from phenol
 (ii) 2-Methylpropan-2-ol from methyl magnesium bromide?
 (AI 2011)
69. 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)
70. 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)

71. 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)
72. Write Reimer-Tiemann reaction giving an example.
 (AI 2011C)

LA I (3 marks)

73. Write the product(s) of the following reactions :
 (i)  $\xrightarrow{\text{PCC}}$
 (ii)  $\xrightarrow[\text{CH}_3\text{COOH}]{(\text{CH}_3\text{CO})_2\text{O}}$
 (iii)  $+ \text{CH}_3\text{MgBr} \xrightarrow{\text{H}_3\text{O}^+}$ (2020)
74. (a) Show how will you synthesise the following alcohol prepared by the reaction of a suitable Grignard reagent on methanal?

$$\text{CH}_3\text{—}\underset{\text{CH}_3}{\text{CH}}\text{—CH}_2\text{—OH}$$

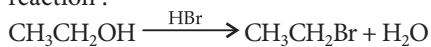
 (b) Write the mechanism of the following reaction:

$$\text{CH}_2\text{=CH}_2 + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}_2\text{OH}$$
 (AI 2019)
75. 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)
76. 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)
77. 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)

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



- (b) Write the equation involved in Reimer-Tiemann reaction. (Delhi 2014)

- 79 (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*-Nitrophenol is more acidic than *o*-methoxyphenol. Explain why.

(AI 2013C)

80. 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-butanol
- (iii) 2-methyl-1-propanol (Delhi 2012)

81. (a) Describe the mechanism of hydration of ethene to yield ethanol.

- (b) Write Kolbe's reaction with an example. (AI 2011C)

82. Acid catalysed dehydration of *tert*-butanol is faster than that of *n*-butanol. Explain.

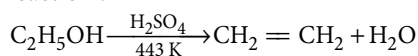
(AI 2011C)

LA II (5 marks)

83. (a) How do you convert the following :

- (i) Phenol to Anisole
- (ii) Ethanol to Propan-2-ol

- (b) Write mechanism of the following reaction :



- (c) Why phenol undergoes electrophilic substitution more easily than benzene?

(Delhi 2019)

84. (a) Account for the following :

- (i) *o*-nitrophenol is more steam volatile than *p*-nitrophenol.
- (ii) *t*-butyl chloride on heating with sodium methoxide gives 2-methylpropene instead of *t*-butylmethylether.

- (b) Write the reaction involved in the following :

- (i) Reimer-Tiemann reaction

- (ii) Friedal-Crafts alkylation of phenol

- (c) Give simple chemical test to distinguish between ethanol and phenol.

(Delhi 2019)

85. (a) Write the formula of reagents used in the following reactions :

- (i) Bromination of phenol to 2,4,6-tribromophenol

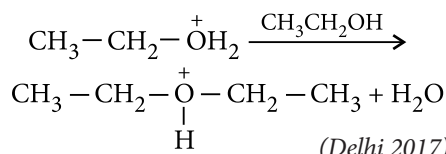
- (ii) Hydroboration of propene and then oxidation to propanol.

- (b) Arrange the following compound groups in the increasing order of their property indicated :

- (i) *p*-nitrophenol, ethanol, phenol (acidic character)

- (ii) propanol, propane, propanal (boiling point)

- (c) Write the mechanism (using curved arrow notation) of the following reaction:



(Delhi 2017)

11.6 Ethers

VSA (1 mark)

86. **Assertion (A) :** $(\text{CH}_3)_3\text{C}-\text{O}-\text{CH}_3$ gives $(\text{CH}_3)_3\text{C}-\text{I}$ and CH_3OH on treatment with HI.

Reason (R) : The reaction occurs by $\text{S}_{\text{N}}1$ mechanism.

- (a) Both Assertion (A) and Reason (R) are correct statements, and Reason (R) is the correct explanation of the Assertion (A).

- (b) Both Assertion (A) and Reason (R) are correct statements, but Reason (R) is not the correct explanation of the Assertion (A).

- (c) Assertion (A) is correct, but Reason (R) is incorrect statement.

- (d) Assertion (A) is incorrect, but Reason (R) is correct statement. (2020)

87. Carry out the following conversion :

t-Butyl chloride to *t*-butyl ethyl ether

(1/3, 2020)

88. Predict the reagent for carrying out the following conversions :

Anisole to *p*-bromoanisole (1/3, 2020)

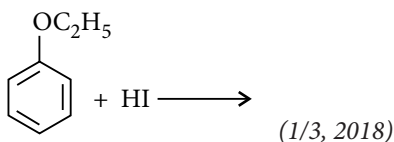
89. Write the equation for the preparation of 2-methyl-2-methoxypropane by Williamson synthesis. (1/3, 2020)

90. Write the equations involved in the following reaction :

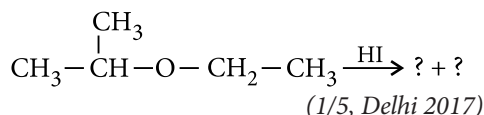
Friedel—Crafts alkylation of anisole.

(1/2, AI 2019, 1/3, Delhi 2011)

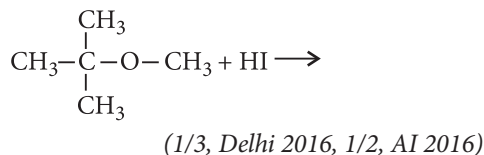
91. Write the structure of the main products in the following reaction :



92. Write the product in the following reaction :



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



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

95. Write the equation involved in the following reaction :

Williamson synthesis

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

1/3, AI 2014C, Delhi 2012C)

96. Account for the following :

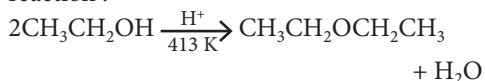
Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. (1/3, Delhi 2011C)

97. Account for the following :

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

SA (2 marks)

98. Write the mechanism of the following reaction :



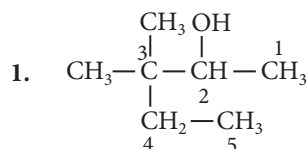
(2/3, 2020, 2/3, AI 2017, Delhi 2016, 2015, 2013, 2013C)

99. Give reasons for the following :

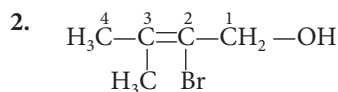
(i) Boiling point of ethanol is higher in comparison to methoxymethane.

(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)

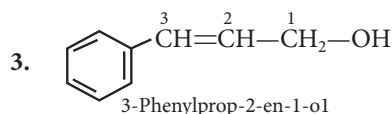
Detailed Solutions



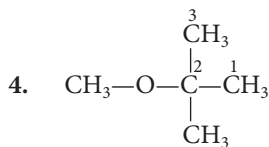
3,3 - Dimethylpentan-2-ol



2-Bromo-3-methylbut-2-en-1-ol



3-Phenylprop-2-en-1-ol



2-Methoxy-2-methylpropane

5. 2-Phenylethanol

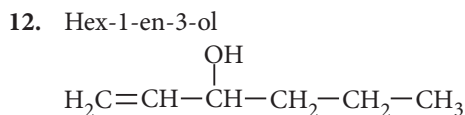
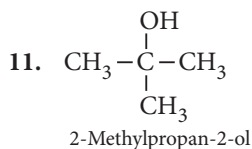
6. 2,5-Dinitrophenol

7. 2-Methylprop-2-en-1-ol

8. 3-Methylbut-2-en-1-ol

9. Butan-2-ol

10. Propane-1,2,3-triol

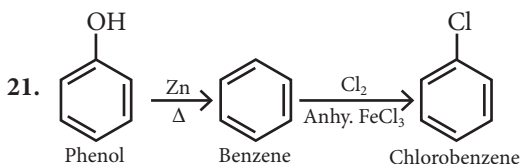
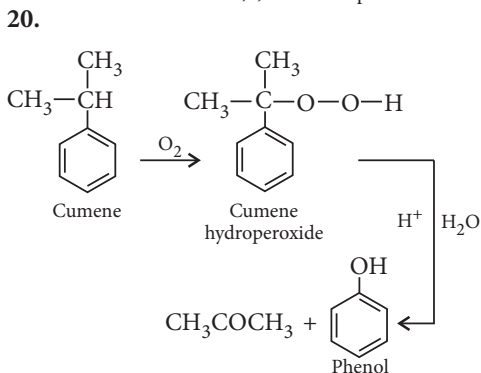
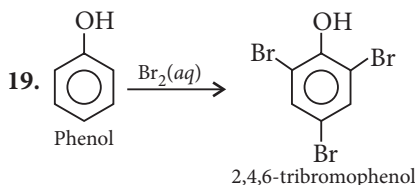
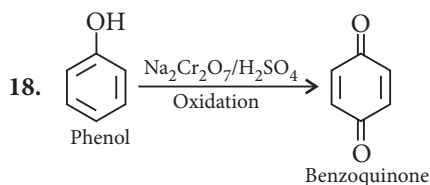
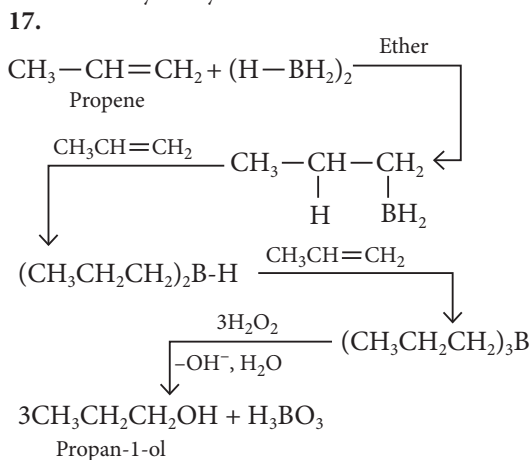
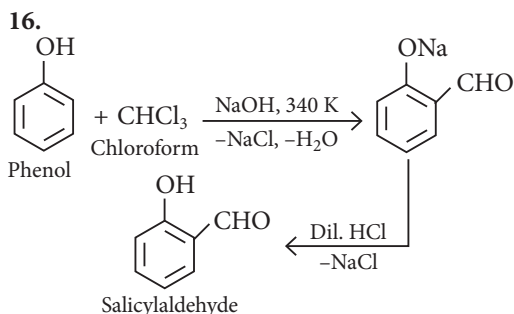


13. 1-Ethoxy-2-nitrocyclohexane.

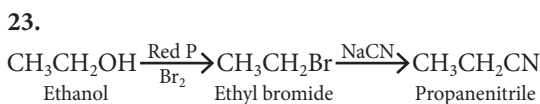
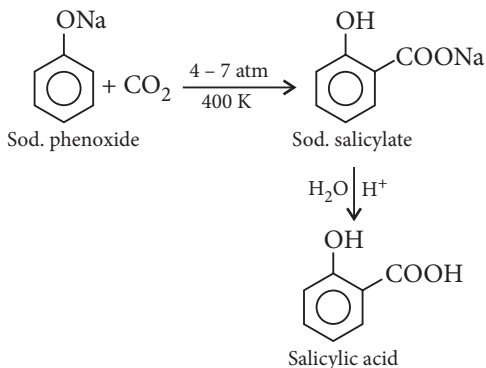
14. (a) : The C—O—H bond angle in alcohols is slightly less than the tetrahedral angle due to greater lone pair-lone pair repulsions than lone pair-bond pair repulsions.

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

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



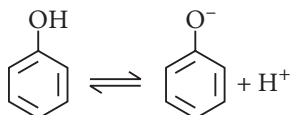
22. **Kolbe's reaction** : When sodium phenoxide is heated with carbon dioxide under pressure, it gives salicylic acid.



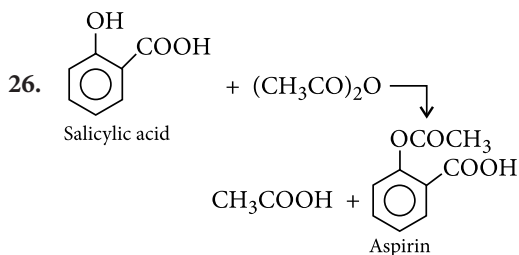
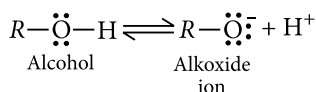
24. Refer to answer 22.

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

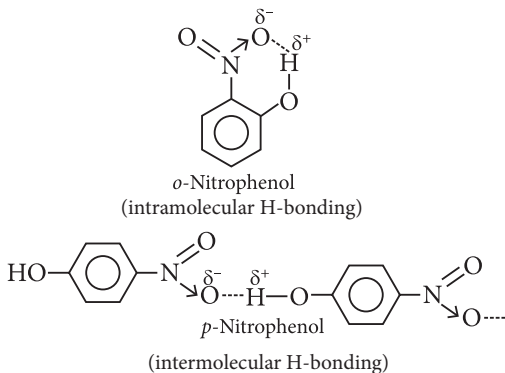
The greater acidity of phenol is due to the stability of the phenoxide ion which is resonance stabilized.



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

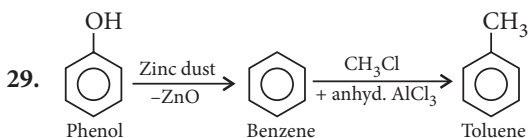
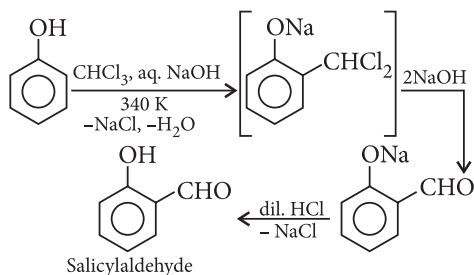


27. *o*-Nitrophenol is more steam volatile than *p*-nitrophenol due to the presence of intramolecular H-bonding. *p*-Nitrophenol shows intermolecular H-bonding.

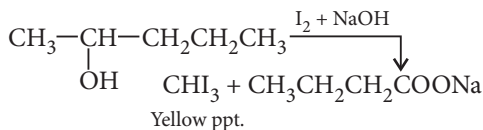


That's why *o*-nitrophenol has lower boiling point than *p*-nitrophenol.

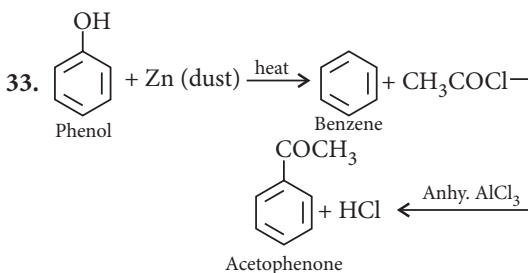
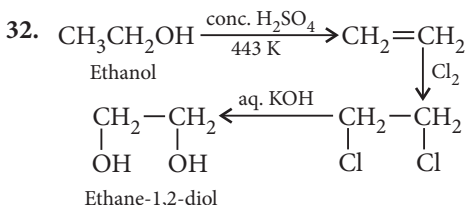
28. Reimer-Tiemann reaction :



30. On adding I₂ and NaOH, 2-pentanol will give yellow precipitate of iodoform whereas 3-pentanol will not give yellow precipitate.



31. *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 behaving +R effect.



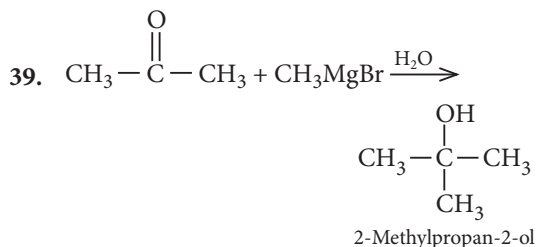
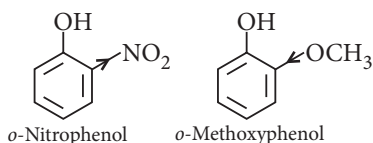
34. Refer to answer 27.

35. Benzoic acid gives brisk effervescence of CO₂ on addition of NaHCO₃ while phenol does not.

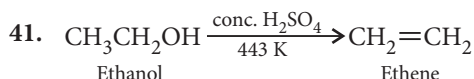
36. Refer to answer 28.

37. 2-Propanol will give yellow precipitate of iodoform on addition of I₂ and NaOH while 2-methyl-2-propanol will not.

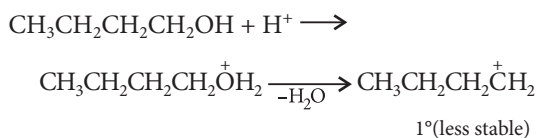
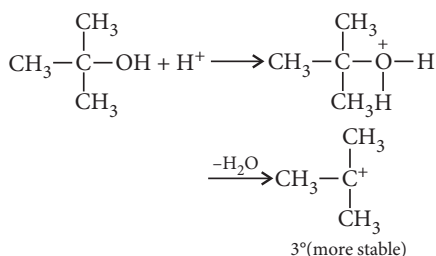
38. As we know that the electron withdrawing groups enhance the acidic character of phenols because they help in the stabilisation of phenoxide ion by dispersing negative charge. Nitro group is an electron withdrawing group whereas methoxy group destabilise the phenoxide ion by intensifying the negative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



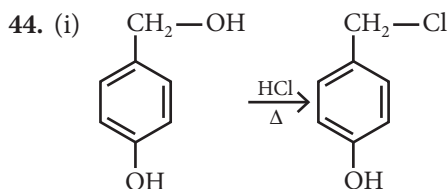
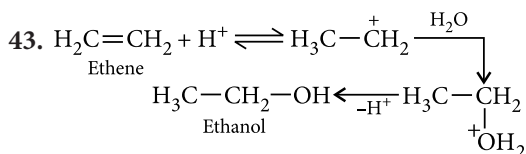
40. Refer to answer 28.



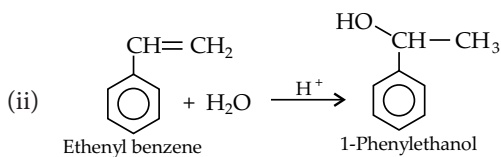
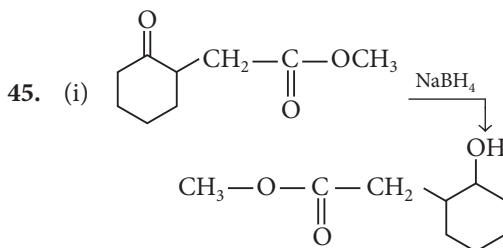
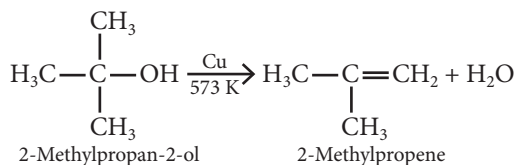
42. Acid catalysed dehydration of alcohols follows carbocation mechanism.



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



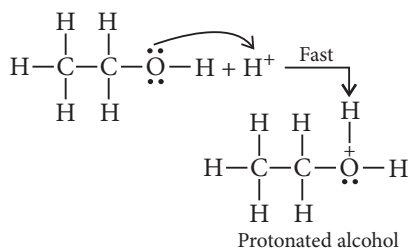
(ii)



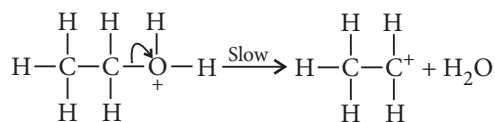
46. Acid catalysed dehydration of alcohols at high temperature takes place with formation of an alkene.

Mechanism : The dehydration of ethanol involves the following steps :

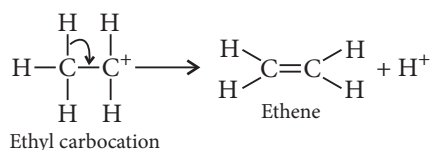
(a) Formation of protonated alcohol.

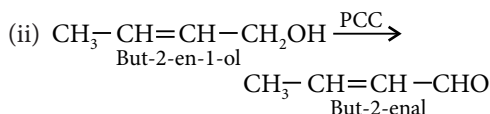
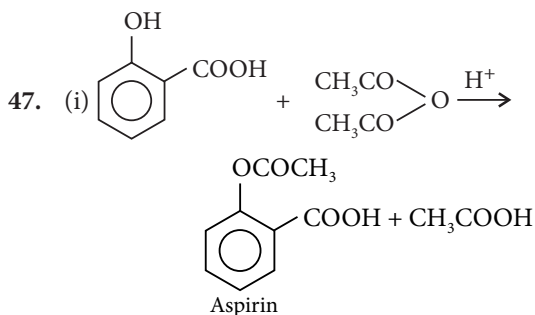


(b) Formation of carbocation.

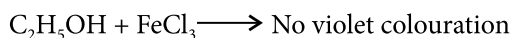
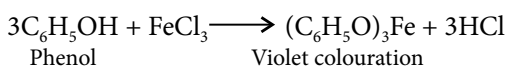


(c) Formation of ethene.

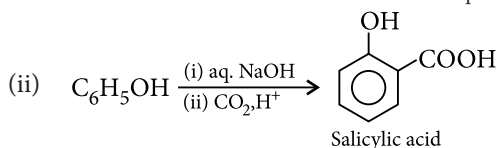
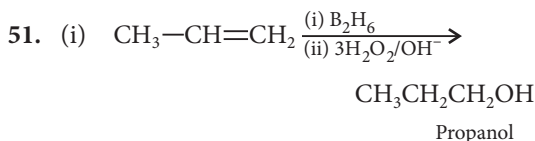
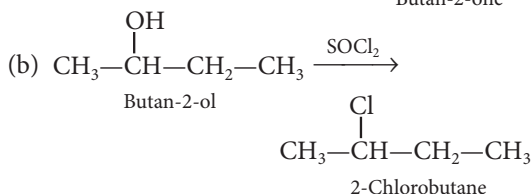
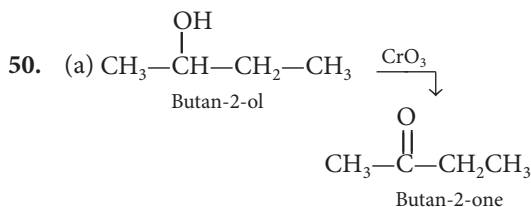
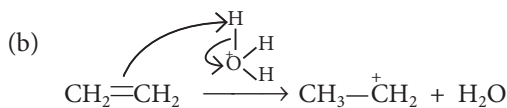
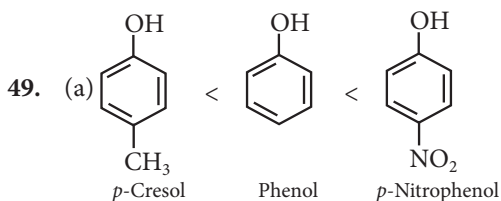




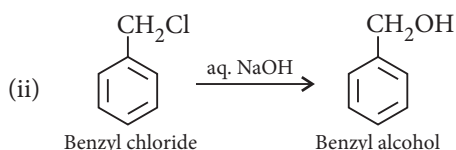
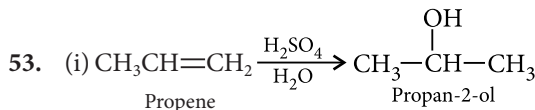
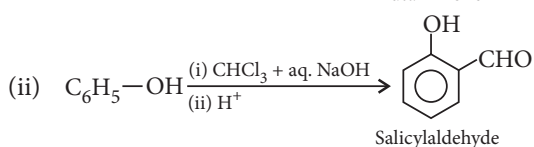
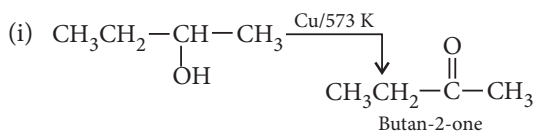
48. (i) Distinction between ethanol and phenol.
 FeCl₃ test : Phenol gives a violet colouration with FeCl₃ solution while ethanol does not.



(ii) On oxidation in presence of acidic KMnO₄, 1° alcohol (propanol) will give aldehyde while 3° alcohol (2-methylpropan-2-ol) will give a ketone.

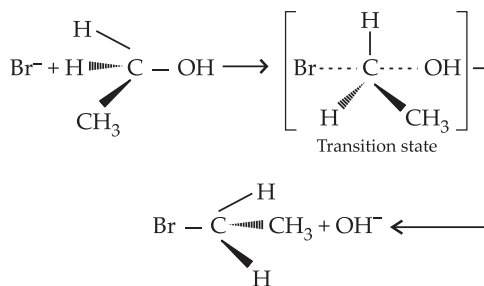


52.



54. Refer to answer 46.

55. The reaction proceeds through nucleophilic substitution bimolecular (S_N2) mechanism, as shown below :



Inversion of configuration takes place during the reaction.

56. (i) Bromine water, (Br_{2(aq)})

(ii) Lithium aluminium hydride, (LiAlH₄) or H₂/Ni

(iii) Alkyl halide in the presence of anhydrous aluminium chloride, CH₃Cl and AlCl₃ (anhy.)

(iv) Acidified potassium permanganate, KMnO_4 , H_3O^+

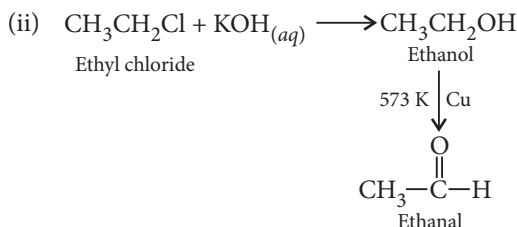
57. (i) Zinc dust

(ii) Concentrated H_2SO_4

(iii) Refer to answer 56(iii).

(iv) $\text{Cu}/573\text{ K}$

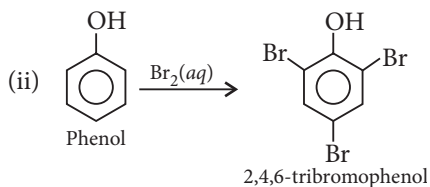
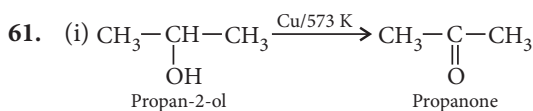
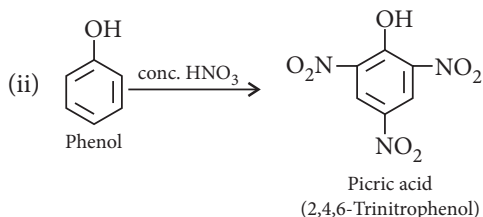
58. (i) Refer to answer 53(i).



59. (i) Refer to answer 22.

(ii) Refer to answer 28.

60. (i) Refer to answer 53(i).



62. Refer to answer 46.

63. Refer to answer 43.

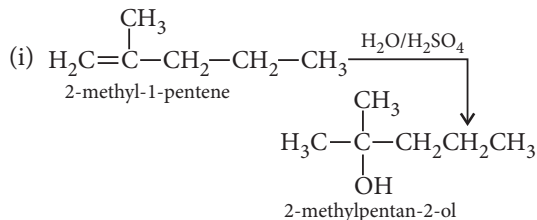
64. (i) The solubility of alcohols in water is due to their ability to form hydrogen bonds with water molecules. Hydrocarbons cannot form such hydrogen bonds, hence they are insoluble in water.

(ii) Refer to answer 38.

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

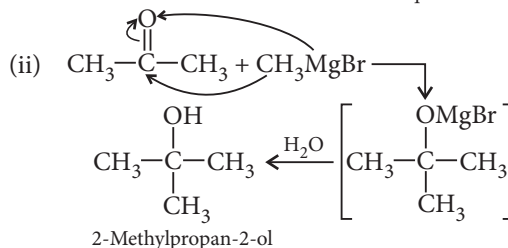
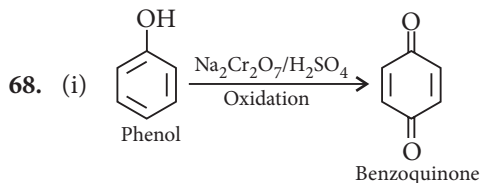
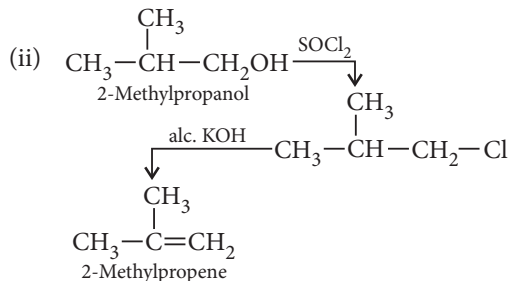
(ii) Refer to answer 30.

66.



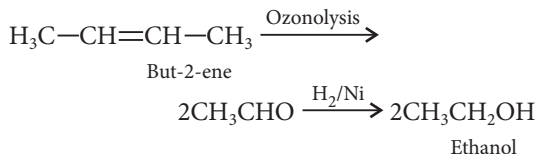
(ii) Refer to answer 33.

67. (i) Refer to answer 60(ii).

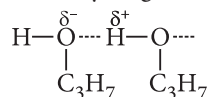


69. (i) Cu at 573 K

(ii) Ozonolysis followed by catalytic hydrogenation



70. (i) 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.

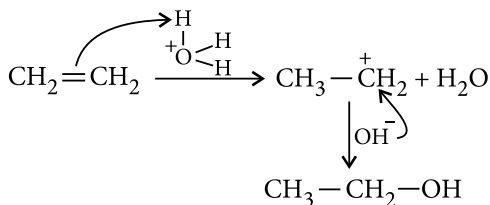
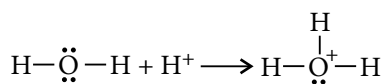
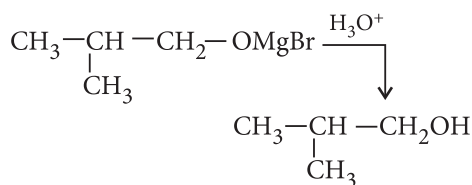
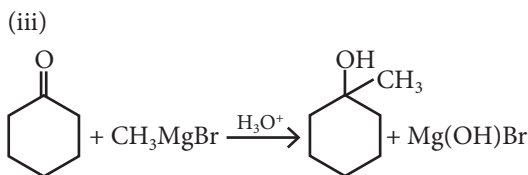
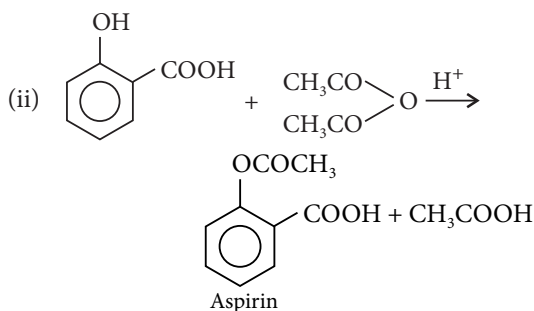
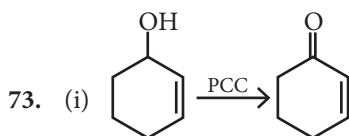


(ii) Refer to answer 38.

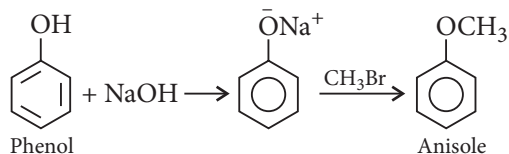
71. (i) It is due to higher molecular weight, more surface area, more van der Waals' forces of attraction in C_2H_5OH than CH_3OH .

(ii) Refer to answer 25.

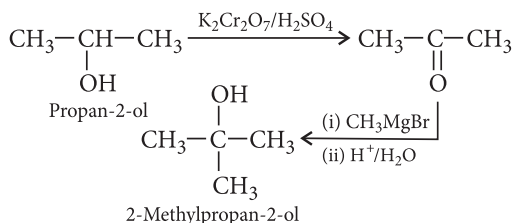
72. Refer to answer 28.



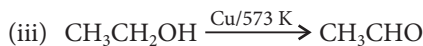
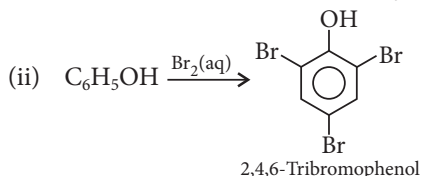
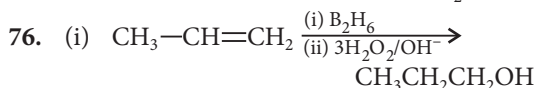
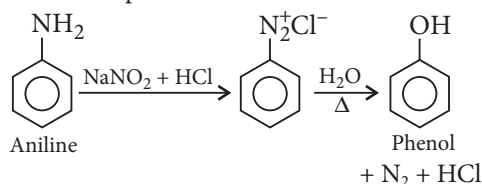
75. (i) Phenol to anisole



(ii) Propan-2-ol to 2-methylpropan-2-ol

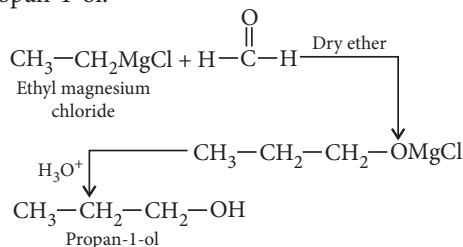


(iii) Aniline to phenol



77. (i) Refer to answer 53(ii).

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



(iii) Refer to answer 53(i).

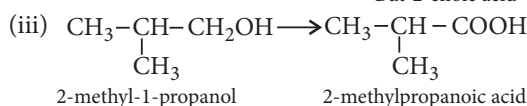
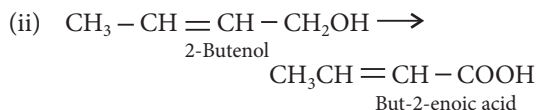
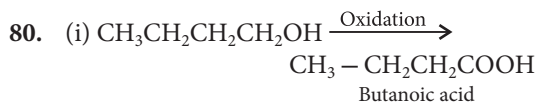
78. (a) Refer to answer 55.

(b) Refer to answer 28.

79. (a) (i) Refer to answer 30.

(ii) Refer to answer 48(i).

(b) Refer to answer 38.

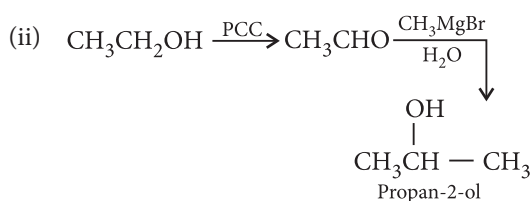


81. (a) Refer to answer 43.

(b) Refer to answer 22.

82. Refer to answer 42.

83. (a) (i) Refer to answer 75(i).

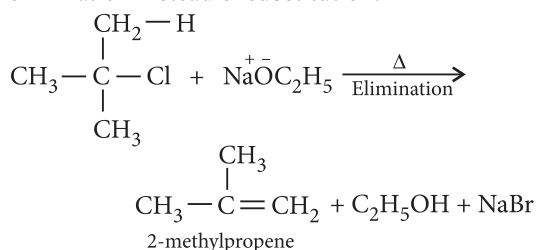


(b) Refer to answer 46.

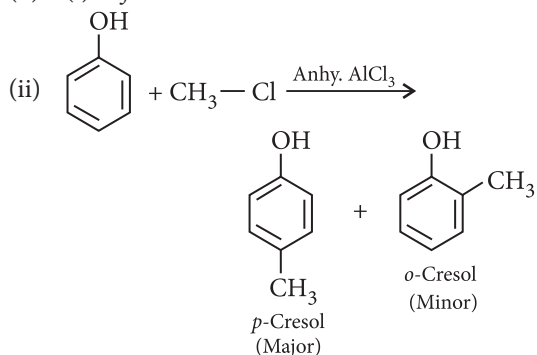
(c) Phenols undergo electrophilic substitution reaction more easily than benzene due to strong activating effect of $-\text{OH}$ group attached to benzene ring.

84. (a) (i) Refer to answer 27.

(ii) This is because *tert*-alkyl halides undergo elimination instead of substitution.



(b) (i) Refer to answer 28.



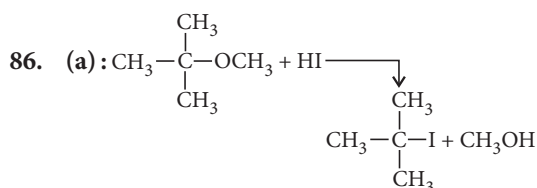
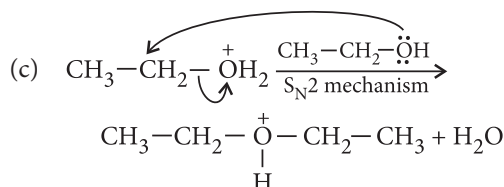
(c) Refer to answer 48(i).

85. (a) (i) $\text{Br}_2/\text{H}_2\text{O}$

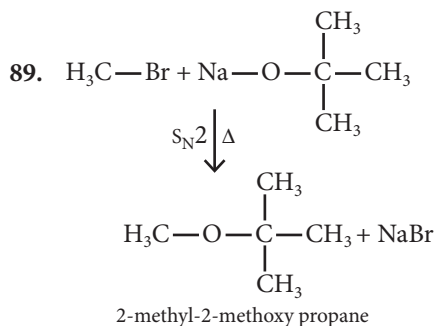
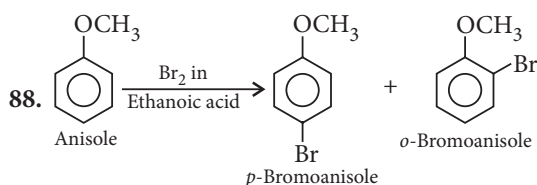
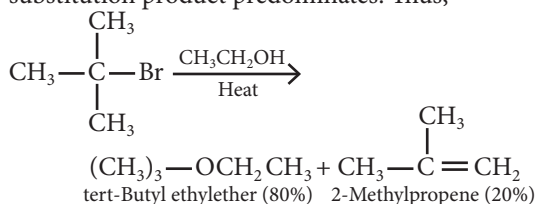
(ii) BH_3 in $\text{THF}/\text{H}_2\text{O}_2$

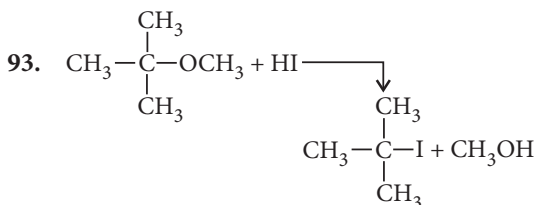
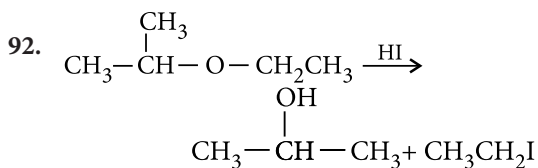
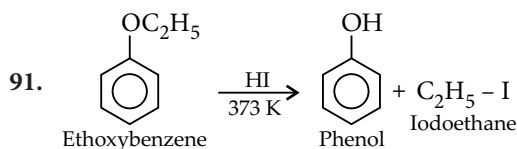
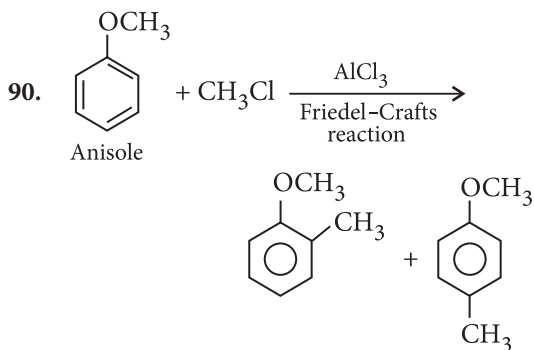
(b) (i) *p*-nitrophenol > phenol > ethanol

(ii) Propanol > propanal > propane



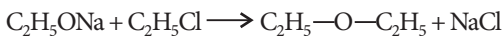
87. The given conversion is not possible by treating sodium ethoxide with *t*-butyl chloride or bromide since, under these conditions an alkene i.e., isobutylene (2-methylpropene) is the main product. If however, *t*-butyl bromide is heated with a weak nucleophile such as pure ethanol both substitution and elimination occur in which substitution product predominates. Thus,





94. Refer to answer 88.

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



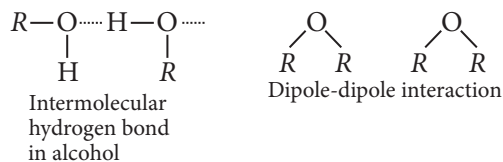
96. Acid dehydration of 2° and 3° alcohols give alkenes rather than ethers.

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

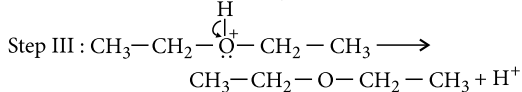
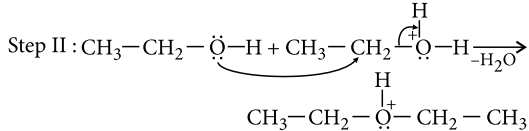
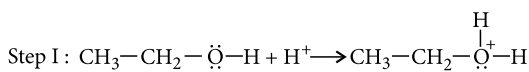
The protonated 2° and 3° alcohols lose water

molecules to form stable 2° and 3° carbocations.

97. 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.



98. Mechanism : The formation of ether is nucleophilic bimolecular reaction.



99. (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 (CH₃-OH) creates a more stable carbocation (3°) and the reaction follows S_N1 mechanism.

