Alcohols, Phenols and Ethers

1. The reaction of an alkyl halide with sodium alkoxide forming ether is known as: (2024)

(A) Wurtz reaction

(B) Reimer-Tiemann reaction

(C) Williamson synthesis

(D) Kolbe reaction

Ans. (C) Williamson synthesis

2. The correct order of the ease of dehydration of the following alcohols by the action of conc. H_2SO_4 is: (2024)

(A) $(CH_3)_3C — OH > (CH_3)_2CH — OH > CH_3CH_2 — OH$

(B) $(CH_3)_2CH — OH > CH_3CH_2 — OH > (CH_3)_3C — OH$

(C) $CH_3CH_2 — OH > (CH_3)_2CH — OH > (CH_3)_3C — OH$

(D) $(CH_3)_2CH — OH > (CH_3)_3C — OH > CH_3CH_2 — OH$

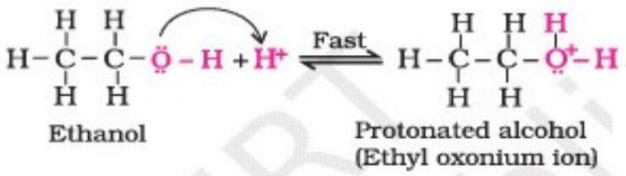
Ans. (A) $(CH_3)_3C — OH > (CH_3)_2CH — OH > CH_3CH_2 — OH$

3. Write the mechanism of the following reaction : (2024)

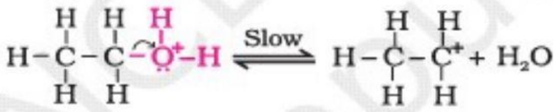
$$CH_3CH_2OH \xrightarrow[443\ K]{H^+} CH_2 = CH_2$$

Ans.

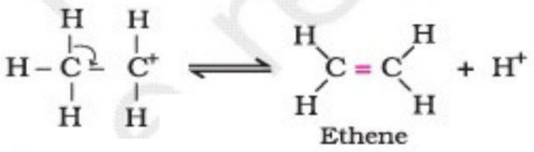
Step 1: Formation of protonated alcohol.



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



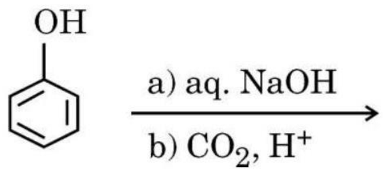
Step 3: Formation of ethene by elimination of a proton.



4. Write the main product in each of the following reactions : (2024)

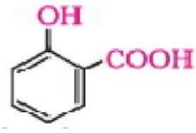
(i) $CH_3 - CH_2 - CH = CH_2 \xrightarrow[\text{b) } 3H_2O_2/OH^-]{\text{a) } B_2H_6}$

(ii)



Ans. (i) $CH_3 - CH_2 - CH_2 - CH_2 - OH$

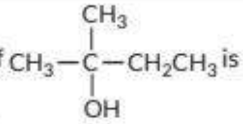
(ii)



Previous Years' CBSE Board Questions

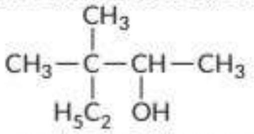
7.2 Nomenclature

MCQ

1. The correct IUPAC name of  $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_2CH_3$ is
   (a) *tert*-butyl alcohol
   (b) 2,2-Dimethylpropanol
   (c) 2-Methylbutan-2-ol
   (d) 3-Methylbutan-3-ol *(2020)*

VSA **(1 mark)**

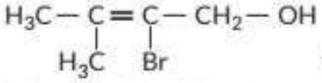
2. Write the IUPAC name of the following :



$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H_5C_2}{|}}{C}}-\underset{\underset{OH}{|}}{CH}-CH_3$

(2018) Ap

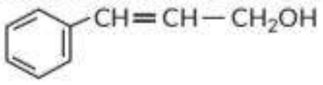
3. Write the IUPAC name of the following compound :



$H_3C-\underset{\underset{H_3C}{|}}{C}=\underset{\underset{Br}{|}}{C}-CH_2-OH$

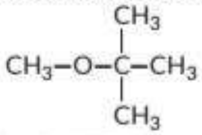
(AI 2017)

4. Write the IUPAC name of the following compound :



(AI 2017) Ap

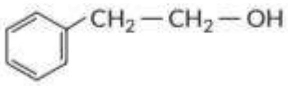
5. Write the IUPAC name of the following compound :



$CH_3-O-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

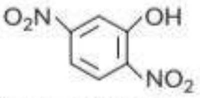
(AI 2017)

6. Write the IUPAC name of the given compound.



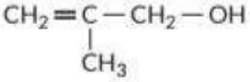
(AI 2016)

7. Write the IUPAC name of the given compound :



(Delhi 2015) Ap

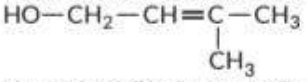
8. Write the IUPAC name of the given compound :



$CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-OH$

(AI 2015)

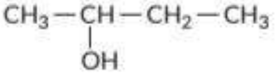
9. Write the IUPAC name of the given compound:



$HO-CH_2-CH=\underset{\underset{CH_3}{|}}{C}-CH_3$

(Foreign 2015)

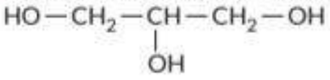
10. Name the following according to IUPAC system :



$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3$

(1/2, Delhi 2015C)

11. Write IUPAC name of the following compound :



$HO-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-OH$

(Foreign 2014)

7.3 Structures of Functional Groups

MCQ

12. The C—O—H bond angle in alcohol is
    (a) slightly greater than 109°28′
    (b) slightly less than 109°28′
    (c) slightly greater than 120°
    (d) slightly less than 120° *(Term I, 2021-22)* U

13. **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)* Ap

7.4 Alcohols and Phenols

MCQ

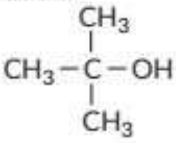
14. Which of the following alcohols will not undergo oxidation?
    (a) Butanol
    (b) Butan-2-ol
    (c) 2-Methylbutan-2-ol
    (d) 3-Methylbutan-2-ol
    (2023)

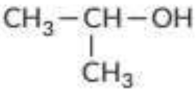
15. In the reaction $R-OH + HCl \xrightarrow{ZnCl_2} RCl + H_2O$, what is the correct order of reactivity of alcohol?
    (a) 1° < 2° < 3°
    (b) 1° > 3° > 2°
    (c) 1° > 2° > 3°
    (d) 3° > 1° > 2°
    (2023)

Read the passage given below and answer the following questions (Q. No. 16 to 18) :

Alcohols and phenols are acidic in nature. Electron withdrawing groups in phenol increase its acidic strength and electron donating groups decrease it. Alcohols undergo nucleophilic substitution with hydrogen halides to give alkyl halides. On oxidation primary alcohols yield aldehydes with mild oxidising agents and carboxylic acids with strong oxidising agents while secondary alcohols yield ketones. The presence of — OH groups in phenols activates the ring towards electrophilic substitution. Various important products are obtained from phenol like salicylaldehyde, salicylic acid, picric acid etc.

16. Which of the following alcohols is resistant to oxidation?

(a) 
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH$

(b) 
$CH_3-\underset{CH_3}{CH}-OH$

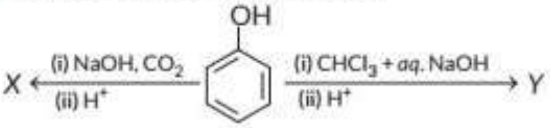
(c) CH_3-CH_2-OH (d) CH_3-OH An

17. Which of the following groups increases the acidic character of phenol?

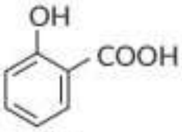
(a) CH_3O- (b) CH_3-

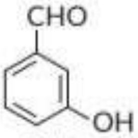
(c) NO_2- (d) All of these An

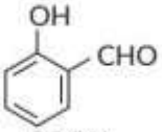
18. Consider the following reaction:

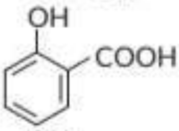


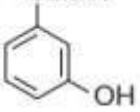
the products X and Y are

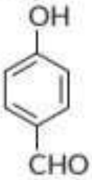
(a) X = 

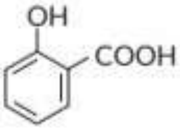
Y = 

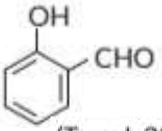
(b) X = 

Y = 

(c) X = 

Y = 

(d) X = 

Y = 

(Term I, 2021-22)

19. In the following reaction,
$CH_3-CH=CH-CH_2-OH \xrightarrow{PCC}$
the product formed is

(a) CH_3-CHO and CH_3CH_2OH
(b) $CH_3-CH=CH-COOH$
(c) $CH_3-CH=CH-CHO$
(d) $CH_3-CH_2-CH_2-CHO$

(Term I, 2021-22) U

20. Which of the following acids reacts with acetic anhydride to form aspirin?

(a) Benzoic acid (b) Salicylic acid

(c) Phthalic acid (d) Acetic acid

(Term I, 2021-22)

21. **Assertion (A) :** *o*-nitrophenol is a weaker acid than *p*-nitrophenol.

Reason (R) : Intramolecular hydrogen bonding makes *ortho* isomer weaker than *para* isomer.

(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)*

22. The conversion of an alkyl halide into an alcohol by aqueous NaOH is classified as

(a) a dehydrohalogenation reaction
(b) a substitution reaction
(c) an addition reaction
(d) a dehydration reaction *(2020)*

23. **Assertion (A) :** Alcohols have higher boiling point than alkanes of comparable molecular mass.

Reason (R) : Alcohols have intramolecular hydrogen bond.

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

VSA (1 mark)

24. Carry out the following conversion :
Phenol to salicylaldehyde *(1/5, 2020)*

25. Carry out the following conversion :
Propene to propanol *(1/5, 2020)* Cr

26. Predict the reagent for carrying out the following conversion :
Phenol to benzoquinone *(1/5, 2020, 2019)*

27. Predict the reagent for carrying out the following conversion :
Phenol to 2,4,6-tribromophenol *(1/5, 2020)*

28. Write the preparation of phenol from cumene. *(1/3, 2020)*

29. How can you convert the following?
Phenol to chlorobenzene. *(1/3, 2020)* Cr

30. How can you convert the following?
Sodium phenoxide to *o*-hydroxybenzoic acid. *(1/3, 2020)*

OR

Write the equation involved in the following reaction:
Kolbe's reaction *(1/2, AI 2019, Delhi 2014C)*

31. How can you convert the following?
Ethanol to propanenitrile. *(1/3, 2020)*

32. Give reason for the following:
Phenol is more acidic than ethanol.
(1/3, AI 2017C, 2015) An

33. Write the equation involved in the acetylation of salicylic acid.
(Delhi 2015)

34. Which of the following isomers is more volatile: *o*-nitrophenol or *p*-nitrophenol?
(Delhi 2014) An

35. Write the equation involved in the following reaction:
Reimer -Tiemann reaction. *(1/2, AI 2014)*

SA I (2 marks)

36. Predict the products of the following reactions:
(i) $CH_3CH_2OH \xrightarrow{Cu/573\,K}$
(ii) $C_6H_5OH \xrightarrow{Br_{2(aq)}}$ *(2023)*

37. For the pair phenol and cyclohexanol, answer the following:
(a) Why is phenol more acidic than cyclohexanol?
(b) Give one chemical test to distinguish between the two. *(2023)*

38. Account for the following:
(i) Phenol is a stronger acid than an alcohol.
(ii) The boiling point of alcohols decreases with increase in branching of alkyl chain.

OR

(i) Write the mechanism of the following reaction
$CH_3CH_2OH \xrightarrow[443\,K]{H^+} CH_2{=}CH_2 + H_2O$
(ii) Write the equation involved in Reimer-Tiemann reaction. *(2023)*

39. Write structures of the products formed when:
(i) Propan-2-ol is heated with Cu at 573 K.
(ii) Salicylic acid is treated with $(CH_3CO)_2O/H^+$.
(2021C)

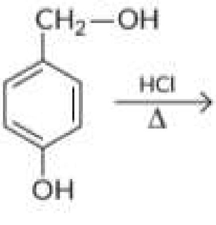
40. Carry out the following conversions:
(i) Phenol to Anisole
(ii) Aniline to Phenol *(2021C)*

41. Out of *t*-butyl alcohol and *n*-butanol, which one will undergo acid catalysed dehydration faster and why?
(2/5, 2020) An

42. How are the following conversions carried out?
(i) Propene to propan-2-ol
(ii) Benzyl chloride to benzyl alcohol
(2020C, 2/3, Delhi 2015C) Ap

43. Give the mechanism for the formation of ethanol from ethene.
(2/5, 2020, AI 2015)

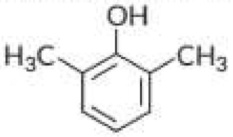
44. Write the major product(s) of the following reactions:

(i)  ; (ii) $(CH_3)_3COH \xrightarrow[573\,K]{Cu}$

(2/3, 2020) U

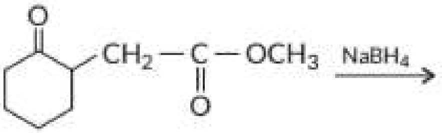
45. How do you convert the following?
(a) Phenol to Toluene
(b) Ethanol to Ethanal *(2019)*

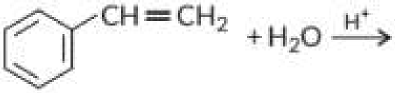
46. (a) Show the chemical reaction with bond movements and arrows for the nucleophilic attack of water on carbocation in acid catalysed hydration of alkenes.
(b) Give IUPAC name for the following:



(2019C)

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

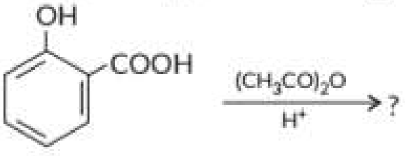
(i) 

(ii) 

(2/3, 2018) Ap

48. Explain the mechanism of dehydration steps of ethanol.
$CH_3CH_2OH \xrightarrow[443\,K]{H^+} CH_2{=}CH_2{+}H_2O$
(2/3, 2018C, Delhi 2015C)

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

(i) 

(ii) $CH_3{-}CH{=}CH{-}CH_2{-}OH \xrightarrow{PCC} ?$
(2/5, Delhi 2017)

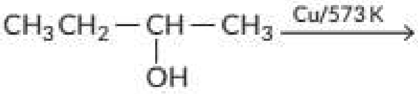
50. Give simple chemical tests to distinguish between the following pairs of compounds:
(i) Ethanol and phenol
(ii) Propanol and 2-methylpropan-2-ol.
(2/5, Delhi 2017)

51. (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:
$CH_2{=}CH_2 \xrightarrow{H_3O^+} CH_3{-}\overset{+}{C}H_2{+}H_2O$ *(AI 2017)*

52. Write the structure of the products when butan-2-ol reacts with the following:
(a) CrO_3
(b) $SOCl_2$ *(AI 2017)* Ap

53. Write the main product(s) in each of the following reactions:
(i) $CH_3{-}CH{=}CH_2 \xrightarrow[\text{(ii) } 3H_2O_2/OH^-]{\text{(i) } B_2H_6}$
(ii) $C_6H_5{-}OH \xrightarrow[\text{(ii) } CO_2,\, H^+]{\text{(i) aq. NaOH}}$ *(Delhi 2016)*

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

(i) 
$CH_3CH_2-\underset{OH}{CH}-CH_3 \xrightarrow{Cu/573\,K}$

(ii) $C_6H_5-OH \xrightarrow[(ii)\ H^+]{(i)\ CHCl_3 + aq.\ NaOH}$ *(Delhi 2016)*

55. Write the mechanism of the following reaction :

$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$

(AI 2014, 2/3, Foreign 2014)

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) Cr

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)* R

SA II (3 marks)

60. (i) Why is the C—O bond length in phenol less than that in methanol?

(ii) Arrange the following in order of increasing boiling point:

Ethoxyethane, Butanal, Butanol, *n*-Butane

(iii) How can phenol be prepared from anisole? Give reaction. *(2023)*

61. How do you convert the following : (Any three)

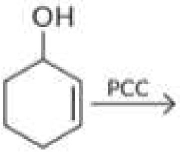
(a) Phenol to picric acid

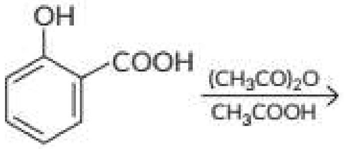
(b) Propanone to 2-methylpropan-2-ol

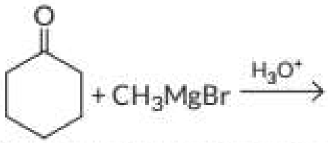
(c) Phenol to anisole

(d) Propene to propan-1-ol *(2023)*

62. Write the product(s) of the following reactions :

(i) 

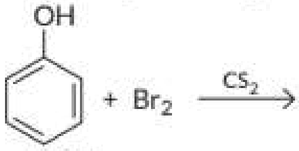
(ii) 

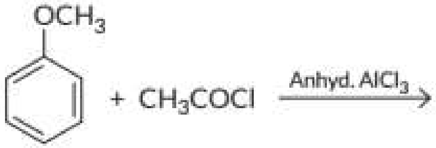
(iii) 

(2020) Ap

63. Write the products of the following reactions :

(i) $CH_3-CH_2-O-CH_3 + HI \longrightarrow$

(ii) 

(iii) 

(2019)

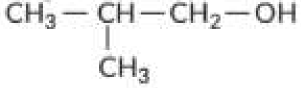
64. Give one chemical test to distinguish between the following :

(a) Phenol and 1-propanol

(b) Ethanol and dimethyl ether

(c) 1-propanol and 2-methyl-2-propanol *(2019)*

65. (a) Show how will you synthesise the following alcohol prepared by the reaction of a suitable Grignard reagent on methanal?


$CH_3-\underset{CH_3}{CH}-CH_2-OH$

(b) Write the mechanism of the following reaction :

$CH_2{=}CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2OH$ *(AI 2019)*

66. (a) How will you convert the following :

(i) Phenol to benzoquinone

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

(b) Why does propanol have higher boiling point than that of butane ? *(2019C)*

67. 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)*

68. Predict the products of the following reactions :

(i) $CH_3-CH{=}\,CH_2 \xrightarrow[(ii)\ 3H_2O_2/OH^-]{(i)\ B_2H_6} ?$

(ii) $C_6H_5OH \xrightarrow{Br_2(aq)} ?$

(iii) $CH_3CH_2OH \xrightarrow{Cu/573K} ?$ *(Foreign 2015)*

69. 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)*

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

$CH_3CH_2OH \xrightarrow{HBr} CH_3CH_2Br + H_2O$

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

LA (5 marks)

71. (a) How do you convert the following :
    (i) Phenol to anisole
    (ii) Ethanol to propan-2-ol?

    (b) Write mechanism of the following reaction :

$$C_2H_5OH \xrightarrow[443\text{ K}]{H_2SO_4} CH_2{=}CH_2 + H_2O$$

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

(Delhi 2019)

72. (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.

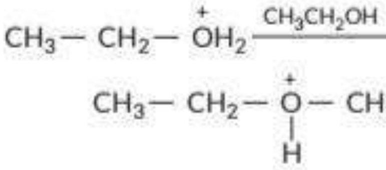
    (b) Write the reaction involved in the following :
    (i) Reimer–Tiemann reaction
    (ii) Friedal–Crafts alkylation of phenol

    (c) Give simple chemical test to distinguish between ethanol and phenol. *(Delhi 2019)* An

73. (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:



$$CH_3-CH_2-\overset{+}{O}H_2 \xrightarrow{CH_3CH_2OH} ?$$

$$CH_3-CH_2-\underset{\displaystyle H}{\overset{+}{O}}-CH_2-CH_3 + H_2O$$

(Delhi 2017) Ap

7.6 Ethers

MCQ

74. **Assertion (A) :** $(CH_3)_3C-O-CH_3$ gives $(CH_3)_3C-I$ and CH_3OH on treatment with HI.
Reason (R) : The reaction occurs by S_N1 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)*

75. **Assertion (A) :** The C-O-C bond angle in ethers is slightly less than tetrahedral angle.
Reason (R) : Due to the repulsive interaction between the two alkyl groups in ethers.
    (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 wrong statement.
    (d) Assertion (A) is wrong, but Reason (R) is correct statement. *(2020)* Ap

VSA (1 mark)

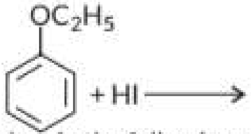
76. Carry out the following conversion :
t-Butyl chloride to *t*-butyl ethyl ether *(1/3, 2020)* Cr

77. Predict the reagent for carrying out the following conversions :
Anisole to *p*-bromoanisole *(1/3, 2020)*

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

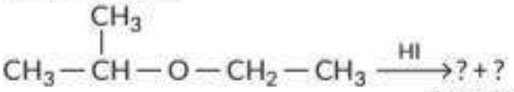
79. Write the equations involved in the following reaction :
Friedel–Crafts alkylation of anisole. *(1/2, AI 2019)*

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



(1/3, 2018)

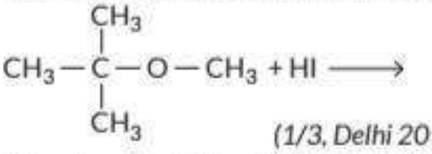
81. Write the product in the following reaction :



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}H}-O-CH_2-CH_3 \xrightarrow{HI} ? + ?$$

(1/5, Delhi 2017)

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



$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}-O-CH_3 + HI \longrightarrow$$

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

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

84. Write the equation involved in the following reaction : Williamson synthesis
(1/2, AI 2014, Delhi 2014C, 1/3, AI 2014C)

SA I (2 marks)

85. Write the mechanism of the following reaction :

$$2CH_3CH_2OH \xrightarrow[413\text{ K}]{H^+} CH_3CH_2OCH_2CH_3 + H_2O$$

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

86. Predict the major product obtained when *t*-butyl

bromide reacts with sodium methoxide. Also, give its IUPAC name. *(2019C)*

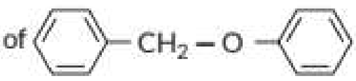
87. Give reasons for the following :
    (i) Boiling point of ethanol is higher in comparison to methoxymethane.
    (ii) $(CH_3)_3C-O-CH_3$ on reaction with HI gives CH_3OH and $(CH_3)_3C-I$ as the main products and not $(CH_3)_3C-OH$ and CH_3I. *(2/3, AI 2015)* An

SA II **(3 marks)**

88. (i) Give mechanism of the following reaction

$$CH_3CH_2OH \xrightarrow[413\,K]{H_2SO_4} CH_3CH_2-O-CH_2CH_3 + H_2O$$

(ii) Illustrate hydroboration - oxidation reaction with an example. *(2023)*

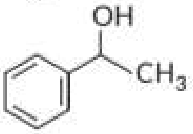
89. Give the structures of final products expected from the following reactions :
    (i) Hydroboration of propene followed by oxidation with H_2O_2 in alkaline medium.
    (ii) Dehydration of $(CH_3)_3C$-OH by heating it with 20% H_3PO_4 at 358 K.
    (iii) Heating of  with HI.

(2020) An

CBSE Sample Questions

7.2 Nomenclature

MCQ

1. Identify the secondary alcohols from the following set:
   (i) $CH_3CH_2CH(OH)CH_3$
   (ii) $(C_2H_5)_3COH$
   (iii) 
   (iv) 
   (a) (i) and (iv) (b) (i) and (iii)
   (c) (i) and (ii) (d) (i), (iii) and (iv)

(Term I, 2021-22)

7.4 Alcohols and Phenols

MCQ

2. The major product of acid catalysed dehydration of 1-methylcyclohexanol is
   (a) 1-methylcyclohexane
   (b) 1-methylcyclohexene
   (c) 1-cyclohexylmethanol
   (d) 1-methylenecyclohexane. *(2022-23)*

3. The boiling points of alcohols are higher than those of hydrocarbons of comparable masses due to
   (a) hydrogen bonding
   (b) ion-dipole interaction
   (c) dipole-dipole interaction
   (d) van der Waals' forces. *(Term I, 2021-22)*

4. During dehydration of alcohols to alkenes by heating with concentrated H_2SO_4, the initiation step is
   (a) protonation of alcohol molecule
   (b) formation of carbocation
   (c) elimination of water
   (d) formation of an ester. *(Term I, 2021-22)*

5. Which of the following reactions is used to prepare salicylaldehyde?
   (a) Kolbe's reaction
   (b) Etard reaction
   (c) Reimer- Tiemann reaction
   (d) Stephen's reduction *(Term I, 2021-22)*

6. Lower molecular mass alcohols are
   (a) miscible in limited amount of water
   (b) miscible in excess of water
   (c) miscible in water in all proportions
   (d) immiscible in water. *(Term I, 2021-22)*

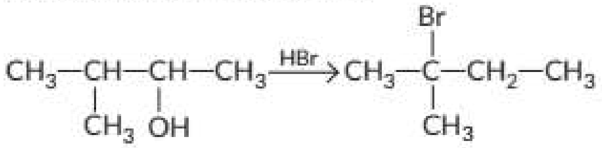
7. Phenol does not undergo nucleophilic substitution reaction easily due to
   (a) acidic nature of phenol
   (b) partial double bond character of C—OH bond
   (c) partial double bond character of C—C bond
   (d) instability of phenoxide ion. *(Term I, 2021-22)*

8. What would be the reactant and reagent used to obtain 2,4-dimethylpentan-3-ol?
   (a) Propanal and propyl magnesium bromide
   (b) 3-Methylbutanal and 2-methyl magnesium iodide
   (c) 2-Dimethylpropanone and methyl magnesium iodide
   (d) 2-Methylpropanal and *iso*-propyl magnesium iodide *(Term I, 2021-22)*

9. *o*-Hydroxybenzyl alcohol when reacted with PCl_3 gives the product as (IUPAC name)
   (a) *o*-hydroxybenzyl chloride
   (b) 2-(chloromethyl) phenol
   (c) *o*-chloromethylchlorobenzene
   (d) 4-hydroxymethyl phenol. *(Term I, 2021-22)*

SA I (2 marks)

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



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \xrightarrow{HBr} CH_3-\overset{\displaystyle Br}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2-CH_3$$

Give a mechanism for this reaction. *(2020-21)*

7.6 Ethers

MCQ

11. What would be the major product of the following reaction?
$C_6H_5-CH_2-OC_6H_5+HBr \rightarrow A+B$
(a) $A=C_6H_5CH_2OH$, $B=C_6H_6$
(b) $A=C_6H_5CH_2OH$, $B=C_6H_5Br$
(c) $A=C_6H_5CH_3$, $B=C_6H_5Br$
(d) $A=C_6H_5CH_2Br$, $B=C_6H_5OH$ *(2022-23)*

12. Given below are two statements labelled as Assertion (A) and Reason (R).
Assertion (A) : An ether is more volatile than an alcohol of comparable molecular mass.
Reason (R) : Ethers are polar in nature.
Select the most appropriate answer from the options given below:
(a) Both A and R are true and R is the correct explanation of A.
(b) Both A and R are true but R is not the correct explanation of A.
(c) A is true but R is false.
(d) A is false but R is true. *(2022-23)*

13. Williamson's synthesis of preparing dimethyl ether is a/an
(a) S_N1 reaction
(b) elimination reaction
(c) S_N2 reaction
(d) nucleophilic addition reaction.
(Term I, 2021-22)

14. **Assertion :** Methoxyethane reacts with HI to give ethanol and iodomethane.
Reason : Reaction of ether with HI follows S_N2 mechanism.
(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement. *(2020-21)*

SA II (3 marks)

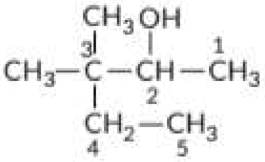
15. Write the equations for the following reactions:
(a) Salicylic acid is treated with acetic anhydride in the presence of conc. H_2SO_4.
(b) *tert*-Butyl chloride is treated with sodium ethoxide.
(c) Phenol is treated with chloroform in the presence of NaOH. *(2022-23)*

Detailed SOLUTIONS

Previous Years' CBSE Board Questions

1. (c) : 2-Methylbutan-2-ol

2.



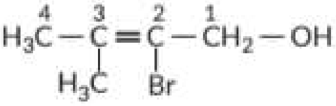
$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle \overset{4}{C}H_2-\overset{5}{C}H_3}{\overset{3}{C}}}-\overset{\displaystyle OH}{\overset{2}{C}H}-\overset{1}{C}H_3$$

3,3 - Dimethylpentan-2-ol

Commonly Made Mistake

- Always identify longest carbon chain.

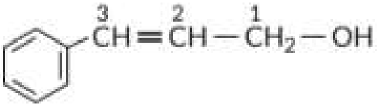
3.



$$H_3\overset{4}{C}-\underset{\displaystyle H_3C}{\overset{3}{C}}=\underset{\displaystyle Br}{\overset{2}{C}}-\overset{1}{C}H_2-OH$$

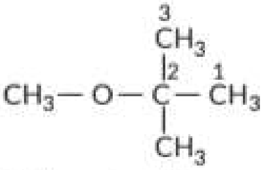
2-Bromo-3-methylbut-2-en-1-ol

4.



3-Phenylprop-2-en-1-ol

5.



$$CH_3-O-\overset{\displaystyle \overset{3}{C}H_3}{\underset{\displaystyle CH_3}{\overset{2}{C}}}-\overset{1}{C}H_3$$

2-Methoxy-2-methylpropane

6. 2-Phenylethan-1-ol

7. 2,5-Dinitrophenol

Answer Tips

- Take phenol as a parent compound.

8. 2-Methylprop-2-en-1-ol

9. 3-Methylbut-2-en-1-ol

10. Butan-2-ol

11. Propane-1,2,3-triol

12. (b): C — O — H bond angle in alcohol is 108°9′ which is slightly less than 109°28′.

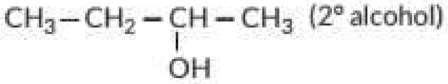
13. (a): The C—O—H bond angle in alcohols is slightly less than the tetrahedral angle due to greater lone pair-lone pair repulsions than lone pair-bond pair repulsions.

Answer Tips

- Apply VSEPR theory.

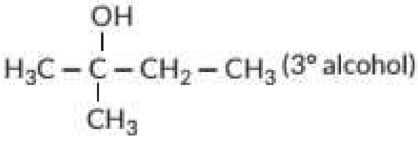
14. (c): Butanol : $CH_3-CH_2-CH_2-CH_2-OH$ (1° alcohol)

Butan-2-ol :



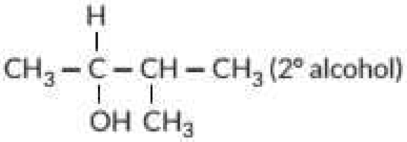
$CH_3-CH_2-\underset{OH}{CH}-CH_3$ (2° alcohol)

2-Methylbutan-2-ol :



$H_3C-\overset{OH}{\underset{CH_3}{C}}-CH_2-CH_3$ (3° alcohol)

3-Methylbutan-2-ol :



$CH_3-\overset{H}{\underset{OH}{C}}-\underset{CH_3}{CH}-CH_3$ (2° alcohol)

3° alcohol does not undergo oxidation, hence in 2-methylbutan-2-ol, oxidation is not possible.

15. (a): $ROH + HX \xrightarrow[\Delta]{\text{Anhyd. } ZnCl_2} RX + H_2O$

This is a nucleophilic substitution reaction in which -OH group gets replaced by -X group. It involves formation of carbocation. As we know, with Lucas reagent,

Primary alcohols - No cloudiness

Secondary alcohols - Cloudiness appears in 5 minutes

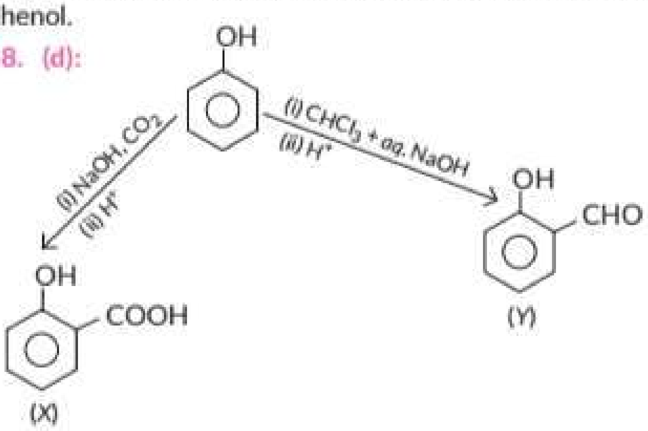
Tertiary alcohols - Cloudiness appears immediately

Thus, the reactivity order is 3° > 2° > 1°.

16. (a): Tertiary alcohols do not undergo oxidation.

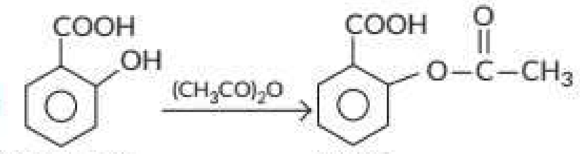
17. (c): —NO_2 acts as EWG and increases the polarity of O — H bond resulting in increased acidic character of phenol.

18. (d):



19. (c): $CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3-CH=CH-CHO$

20. (b):



Salicyclic acid Aspirin

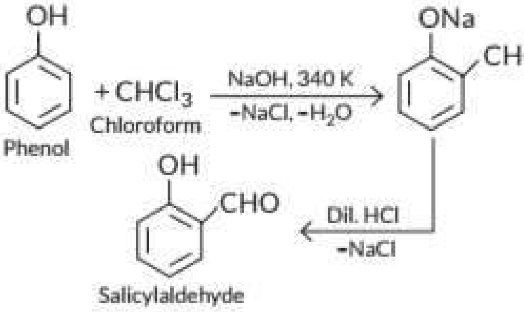
21. (a): Intramolecular H-bonding present in *o*-nitrophenol makes it weaker acid than *p*-nitrophenol.

22 (b): $RX + NaOH \rightarrow ROH + NaX$

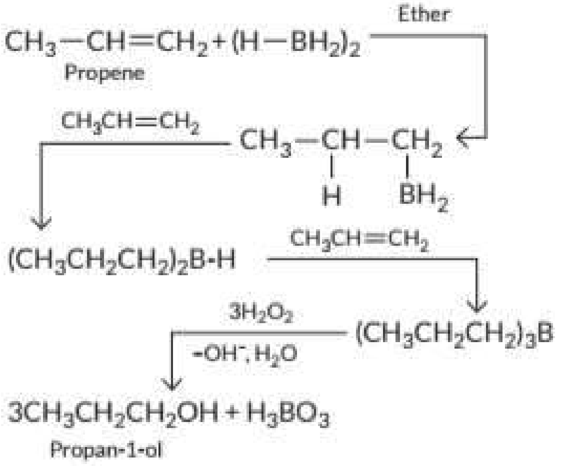
This is a substitution reaction.

23. (a): In alcohols, intramolecular hydrogen bonding is present, resulting in higher boiling point than alkanes of comparable molecular mass.

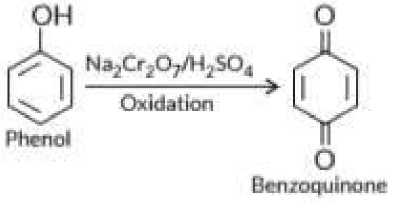
24.



25.



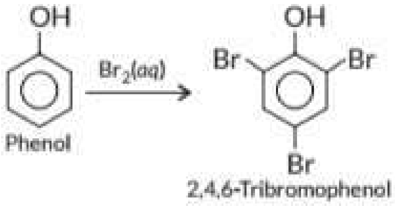
26.



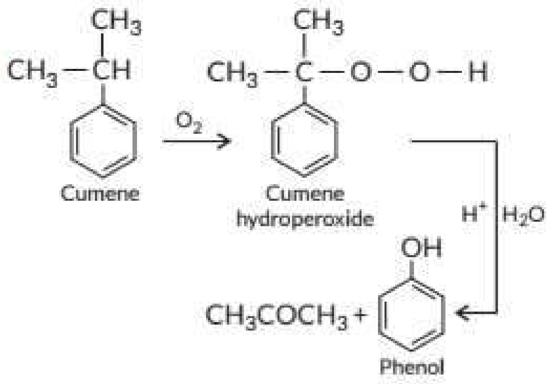
Answer Tips

- $Na_2Cr_2O_7/H_2SO_4$ is an oxidising agent.

27.



28.

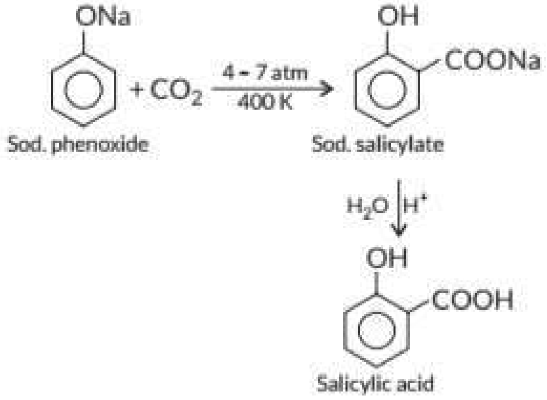


29.

Key Points

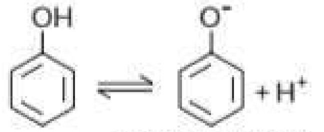
- Benzene undergoes electrophilic substitution reaction with Cl_2/anhy. $FeCl_3$.

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



31. $\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[Br_2]{\text{Red P}} \underset{\text{Ethyl bromide}}{CH_3CH_2Br} \xrightarrow{NaCN} \underset{\text{Propanenitrile}}{CH_3CH_2CN}$

32. Phenol is more acidic than alcohol. It can be explained on the basis of that alcohol on losing H^+ ions forms alkoxide ion and phenol forms phenoxide ion. The greater acidity of phenol is due to the stability of the phenoxide ion which is resonance stabilised.



Resonance stabilised

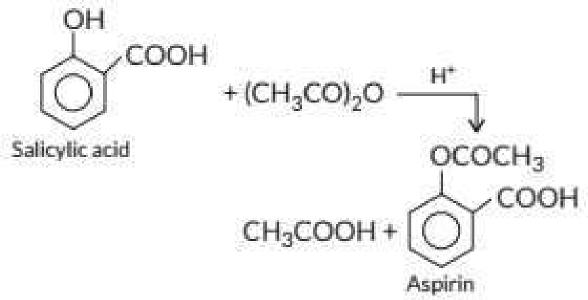
On the other hand, alkoxide ion shows no such resonance stabilisation.

$$\underset{\text{Alcohol}}{R-\ddot{\underset{..}{O}}-H} \rightleftharpoons \underset{\text{Alkoxide ion}}{R-\ddot{\underset{..}{O}}{:}^{-}} + H^+$$

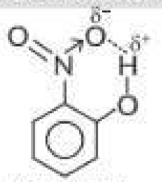
Commonly Made Mistake

- More stable the conjugate base, higher is the acidity.

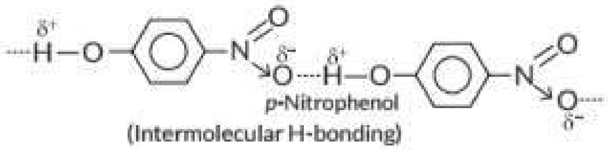
33.



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



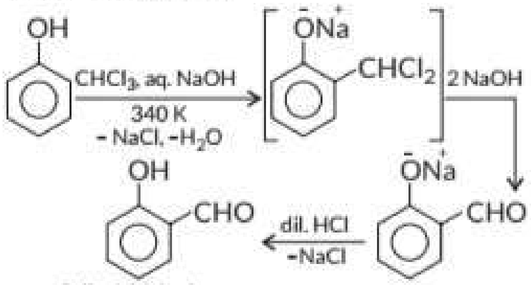
o-Nitrophenol
(Intramolecular H-bonding)



p-Nitrophenol
(Intermolecular H-bonding)

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

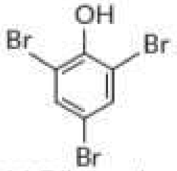
35. **Reimer-Tiemann reaction :**



Salicylaldehyde

36. (i) $CH_3CH_2OH \xrightarrow{Cu/573K} CH_3CHO$

(ii) $C_6H_5OH \xrightarrow{Br_2(aq)}$



2,4,6-Tribromophenol

37. (a) Phenol is more acidic than cyclohexanol due to resonance effect or delocalisation of π-electrons in benzene which stabilises the negative charge present on O-atom while in cyclohexanol, alkyl group is present which shows $+I$ effect that destabilises the negative charge and hence, removal of H-atom becomes difficult.

(b) Phenol gives violet colour with neutral $FeCl_3$ solution while cyclohexanol does not.

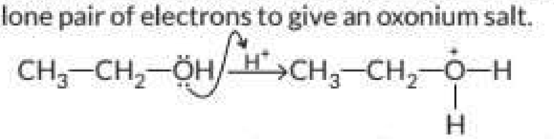
38. (i) Phenol is a stronger acid than an alcohol due to the stabilisation of phenoxide ion through resonance. Due to higher electronegativity of sp^2 hybridised carbon of phenol to which -OH is attached, electron density decreases on oxygen. This increases the polarity of O-H

bond and results in an increase in ionisation of phenol than that of alcohol. Thus, removal of proton is easier in case of phenol as compared to alcohol.

(ii) The boiling point of alcohol decreases with increase in branching of alkyl chain due to a decrease in surface area. The decrease in surface area decreases the van der Waals forces of attraction causing a decrease in the boiling point.

OR

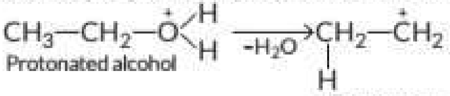
(i) **Mechanism of dehydration :** The H^+ ion of acid acts as electrophile and attacks at the oxygen atom of alcohol having lone pair of electrons to give an oxonium salt.



$$CH_3-CH_2-\ddot{O}H \xrightarrow{H^+} CH_3-CH_2-\underset{\underset{H}{|}}{\overset{+}{O}}-H$$

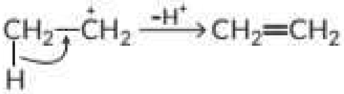
Oxonium salt (Protonated alcohol)

Water is removed from protonated salt to give carbocation (ethylium ion). As formation of intermediate is a slow step, hence this step is rate determining step.



$$CH_3-CH_2-\overset{+}{O}\begin{smallmatrix}H\\H\end{smallmatrix} \xrightarrow{-H_2O} \underset{\underset{H}{|}}{CH_2}-\overset{+}{C}H_2$$

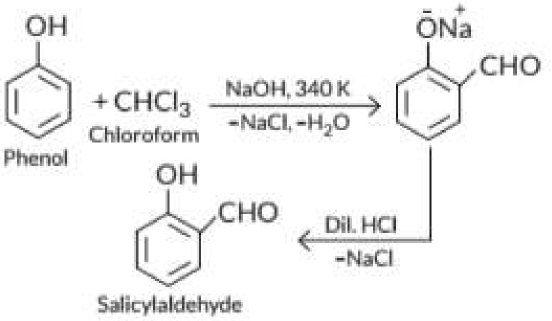
As ethylium ion (carbocation) is highly reactive species, it will try to be stabilized as soon as possible by the removal of proton to give alkene. This is a fast step.



$$\underset{\underset{H}{|}}{CH_2}-\overset{+}{C}H_2 \xrightarrow{-H^+} CH_2=CH_2$$

The carbocation is formed as intermediate, so rearrangement of carbocation is also possible which gives rise to more than one products. The major product will be according to Saytzeff rule.

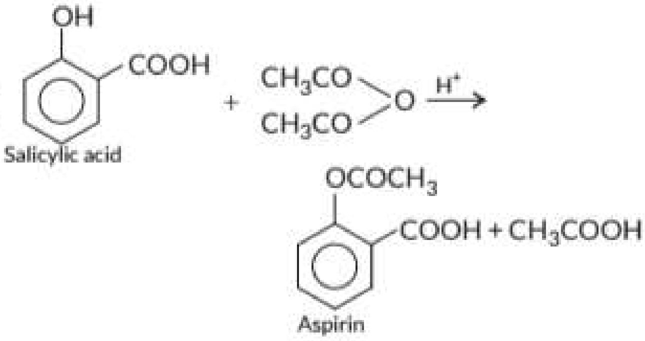
(ii)



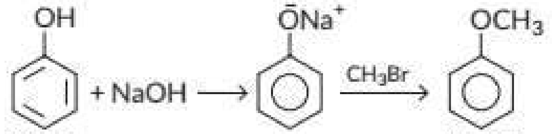
39. (i)

$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{Cu/573\,K} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

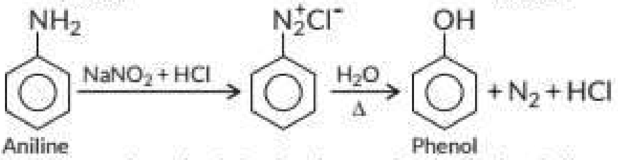
(ii)



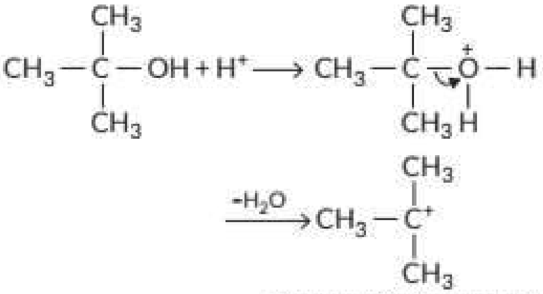
40. (i)



(ii)



41. Acid catalysed dehydration of alcohols follows carbocation mechanism.



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH+H^+\longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{H}{|}}{\overset{+}{O}}-H \xrightarrow{-H_2O} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}}$$

3° carbocation (more stable)

$$CH_3CH_2CH_2CH_2OH+H^+\longrightarrow$$
$$CH_3CH_2CH_2CH_2\overset{+}{O}H_2 \xrightarrow{-H_2O} CH_3CH_2CH_2\overset{+}{C}H_2$$

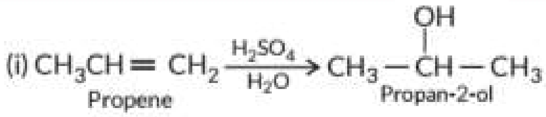
1° carbocation (less stable)

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

Answer Tips

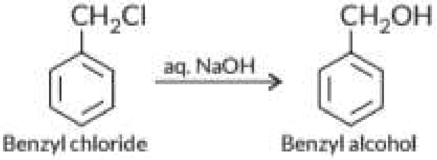
- The relative ease of dehydration of alcohols follows the order : 3° > 2° > 1°.

42. (i)

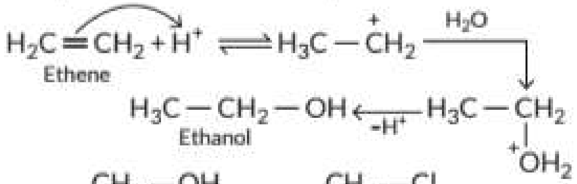


$$CH_3CH=CH_2 \xrightarrow[H_2O]{H_2SO_4} CH_3-\overset{\overset{OH}{|}}{CH}-CH_3$$

(ii)

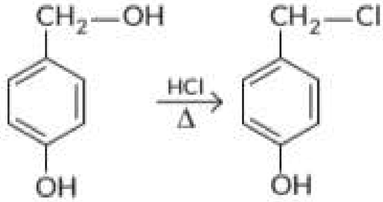


43.

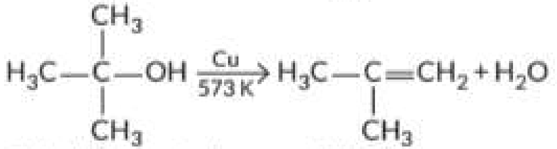


$$H_2C=CH_2+H^+ \rightleftharpoons H_3C-\overset{+}{C}H_2 \xrightarrow{H_2O} H_3C-CH_2-\overset{+}{O}H_2 \xrightarrow{-H^+} H_3C-CH_2-OH$$

44. (i)



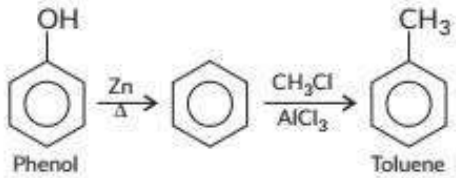
(ii)



$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \xrightarrow[573\,K]{Cu} H_3C-\underset{\underset{CH_3}{|}}{C}=CH_2+H_2O$$

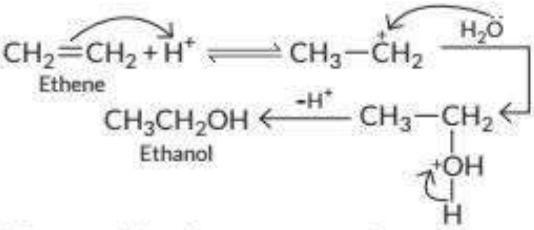
2-Methylpropan-2-ol 2-Methylpropene

45. (a)



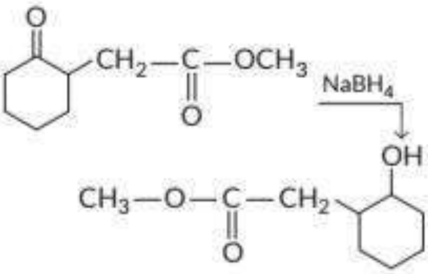
(b) $\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{or PCC}]{CrO_3} \underset{\text{Ethanal}}{CH_3CHO}$

46. (a)

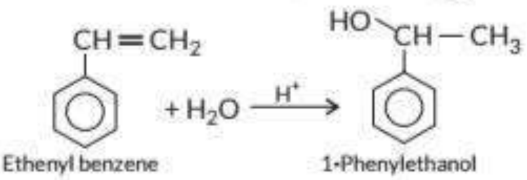


(b) IUPAC name of the given compound:
2, 6-dimethyl phenol

47. (i)



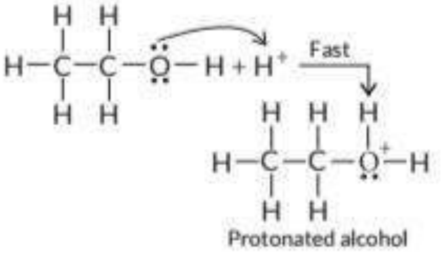
(ii)



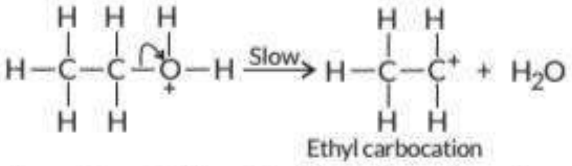
48. Acid catalysed dehydration of alcohols at high temperature takes place with formation of a carbocation.

Mechanism : The dehydration of ethanol involves the following steps :

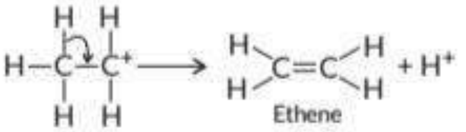
I. Formation of protonated alcohol.



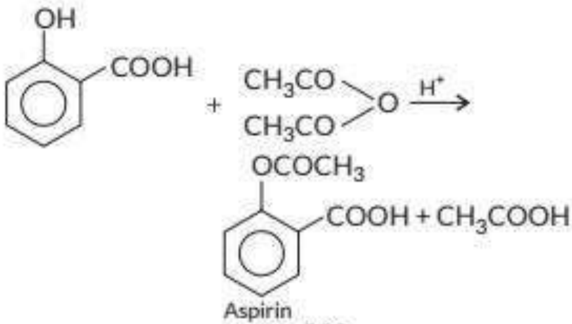
II. Formation of carbocation.



III. Formation of ethene by elimination of a proton.



49. (i)



(ii) $\underset{\text{But-2-en-1-ol}}{CH_3-CH=CH-CH_2OH} \xrightarrow{PCC} \underset{\text{But-2-enal}}{CH_3-CH=CH-CHO}$

Answer Tips

- PCC is an oxidising agent, oxidises 1° and 2° alcohols to aldehyde and ketone respectively.

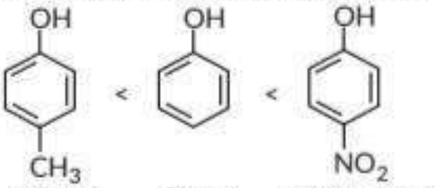
50. (i) Distinction between ethanol and phenol can be done by $FeCl_3$ test. Phenol gives a violet colouration with $FeCl_3$ solution while ethanol does not.

$\underset{\text{Phenol}}{6C_6H_5OH} + FeCl_3 \longrightarrow \underset{\text{Violet colouration}}{[Fe(C_6H_5O)_6]^{3-}} + 3H^+ + 3HCl$

$C_2H_5OH + FeCl_3 \longrightarrow$ No violet colouration

(ii) Propanol (1° alcohol) and 2-methylpropan-2-ol (3° alcohol) can be distinguished by Lucas test. With Lucas reagent (conc. HCl and anhyd. $ZnCl_2$), 1° alcohols show no cloudiness while 3° alcohols show cloudiness immediately.

51. (a)

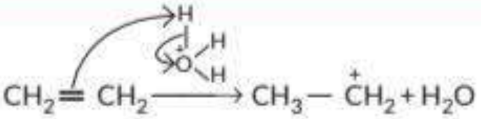


p-Cresol Phenol *p*-Nitrophenol

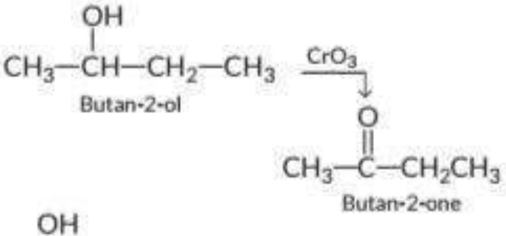
Answer Tips

- Electron donating groups at *p*-position decrease acidity while electron withdrawing groups increase acidity.

(b)

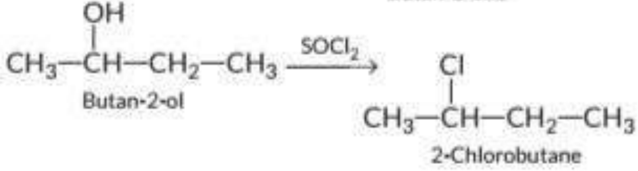


52. (a)



$\underset{\text{Butan-2-ol}}{CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CH_3} \xrightarrow{CrO_3} \underset{\text{Butan-2-one}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2CH_3}$

(b)



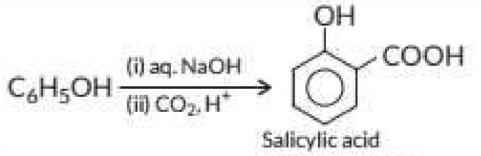
$\underset{\text{Butan-2-ol}}{CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CH_3} \xrightarrow{SOCl_2} \underset{\text{2-Chlorobutane}}{CH_3-\overset{Cl}{\overset{|}{C}H}-CH_2-CH_3}$

53. (i) $CH_3-CH=CH_2 \xrightarrow[\text{(ii) } 3H_2O_2/OH^-]{\text{(i) } B_2H_6} \underset{\text{Propanol}}{CH_3CH_2CH_2OH}$

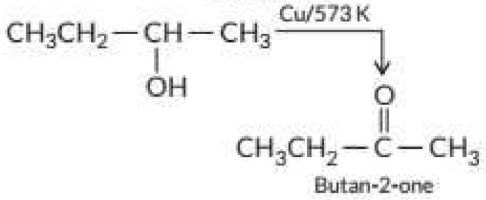
Answer Tips

- Hydroboration-oxidation of alkene takes place as addition of water to alkene in anti-Markovnikov's manner.

(ii)

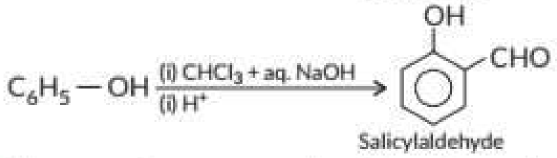


54. (i)

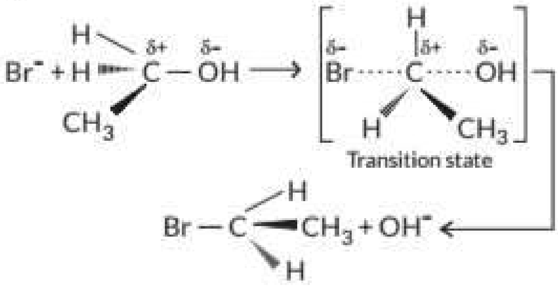


$CH_3CH_2-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow{Cu/573\,K} CH_3CH_2-\overset{O}{\overset{||}{C}}-CH_3$

(ii)



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, ($LiAlH_4$) or H_2/Ni

(iii) Alkyl halide in the presence of anhydrous aluminium chloride, CH_3Cl and $AlCl_{3(anhy.)}$

(iv) Acidified potassium permangante, $KMnO_4$ and H_3O^+

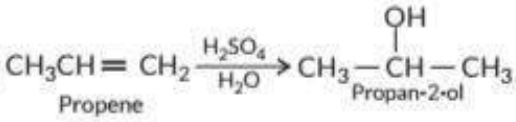
57. (i) Zinc dust

(ii) Concentrated H_2SO_4

(iii) Alkyl halide in the presence of anhydrous aluminium chloride, CH_3Cl and $AlCl_3$ (anhy.)

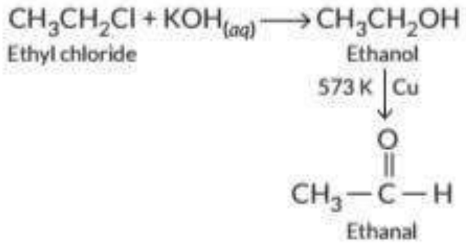
(iv) Cu at 573 K

58. (i)



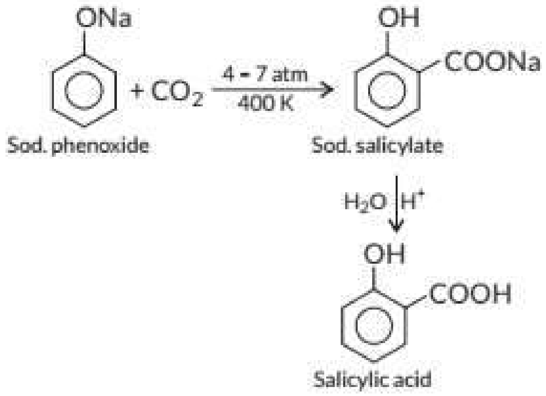
$CH_3CH=CH_2 \xrightarrow[H_2O]{H_2SO_4} CH_3-\overset{OH}{\overset{|}{CH}}-CH_3$

(ii)

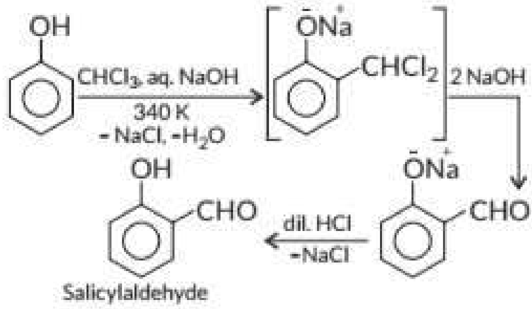


$CH_3CH_2Cl + KOH_{(aq)} \longrightarrow CH_3CH_2OH \xrightarrow{573\,K,\ Cu} CH_3-\overset{O}{\overset{||}{C}}-H$

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



(ii) **Reimer-Tiemann reaction :**



60. (i) Due to resonance, C—O bond acquires some partial double bond character. So, in phenol, C—O bond length is smaller than methanol.

(ii) Butanol > Butanal > Ethoxyethane > *n*-Butane

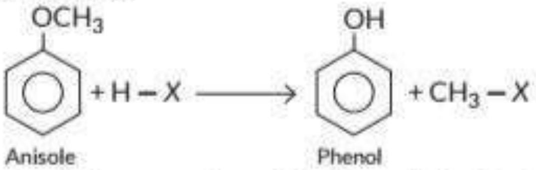
(117.7°C) (74.8°C) (34.6°C) (-1°C)

The boiling point of alcohol is higher in comparison to hydrocarbons and ethers of comparable molecular masses due to intermolecular hydrogen bonding.

The boiling points of aldehydes and ketones are higher than hydrocarbons and ethers of comparable molecular masses.

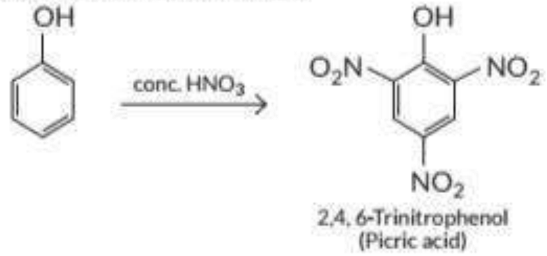
The boiling point of ether is higher than alkanes of comparable molecular masses but is much lower than that of alcohols.

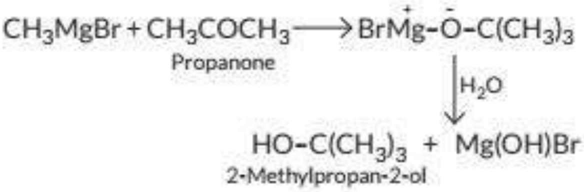
(iii)



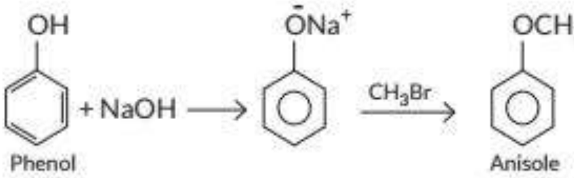
Alkyl aryl ethers reaction with HX results in the cleavage of R—O bond instead of Ar—O bond as Ar—O bond is more stable due to double bond character.

61. (a) Phenol when treated with concentrated nitric acid gives 2, 4, 6-trinitrophenol.



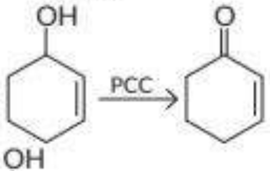
(b) 

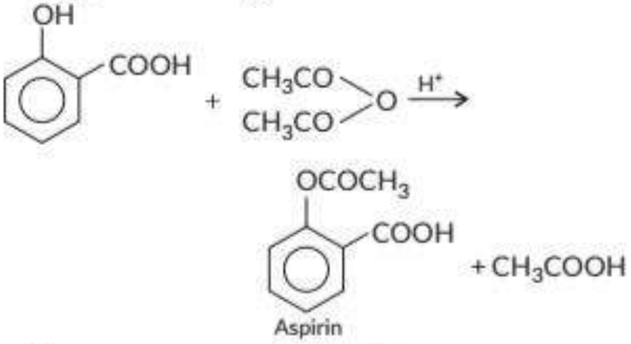
$$CH_3MgBr + \underset{\text{Propanone}}{CH_3COCH_3} \longrightarrow Br\overset{+}{Mg}-\bar{O}-C(CH_3)_3 \xrightarrow{H_2O} \underset{\text{2-Methylpropan-2-ol}}{HO-C(CH_3)_3} + Mg(OH)Br$$

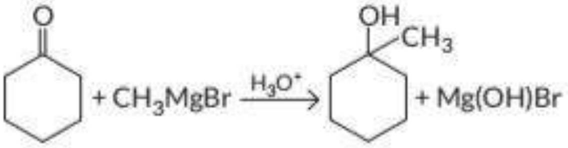
(c) 

(d) $CH_3-CH{=}CH_2 \xrightarrow[\text{(ii) }3H_2O_2/OH^-]{\text{(i) }B_2H_6} CH_3CH_2CH_2OH$

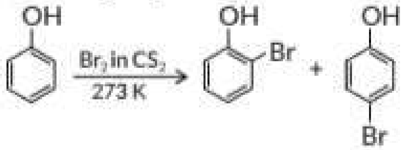
Propene — Propan-1-ol

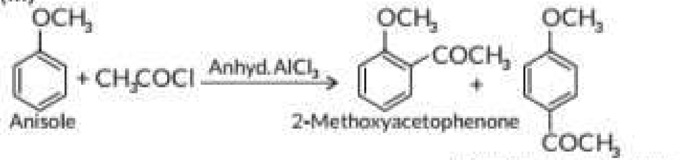
62. (i) 

(ii) 

(iii) 

63. (i) $CH_3CH_2OCH_3 + HI \rightarrow CH_3CH_2OH + CH_3I$

(ii) 

(iii) 

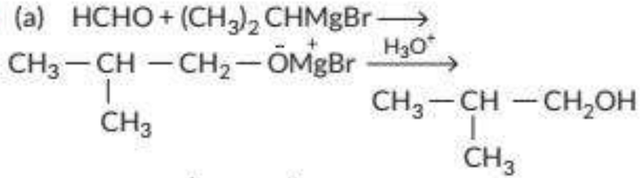
64. Test to distinguish between:

(a) **Phenol and 1-propanol :** Phenols react with neutral $FeCl_3$ solution to give blue, violet or green colouration whereas alcohols do not react with neutral $FeCl_3$ solution.

(b) **Ethanol and dimethyl ether :** When ethanol is heated with iodine and aqueous NaOH solution at 333-343 K, a yellow ppt. of iodoform is produced. Dimethyl ether do not undergo this test

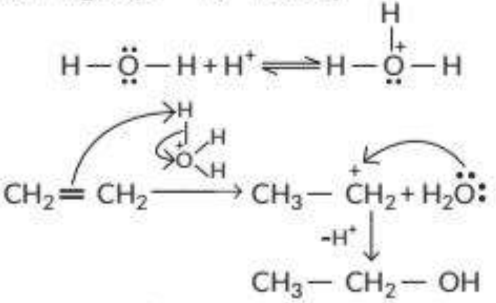
$$CH_3CH_2OH + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3 + HCOONa + 5NaI + 5H_2O$$

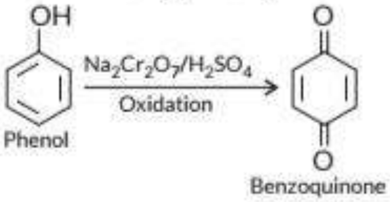
(c) **1-propanol and 2-methyl-2-propanol :** When 2-methyl-2-propanol (3° alcohol) is treated with Lucas reagent at room temperature, turbidity appears immediately. 1-propanol (1° alcohol) does not react with Lucas reagent at room temperature, hence no turbidity is formed.

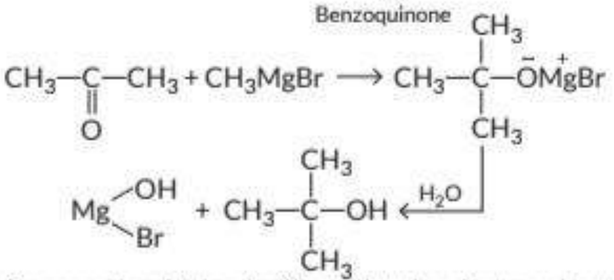
65. (a) 

$$HCHO + (CH_3)_2CHMgBr \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\bar{O}\overset{+}{Mg}Br \xrightarrow{H_3O^+} CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$$

(b) $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$



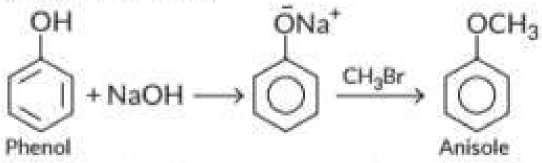
66. (a) (i) 

(ii) 

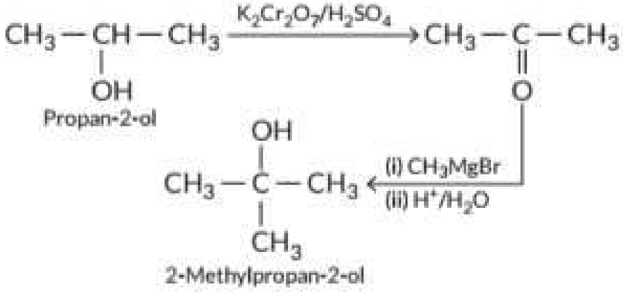
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + CH_3MgBr \longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\bar{O}\overset{+}{Mg}Br \xrightarrow{H_2O} Mg\begin{smallmatrix}OH\\Br\end{smallmatrix} + CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$$

(b) Propanol has higher boiling point than butane due to presence of intramolecular H-bonding.

67. (i) Phenol to anisole

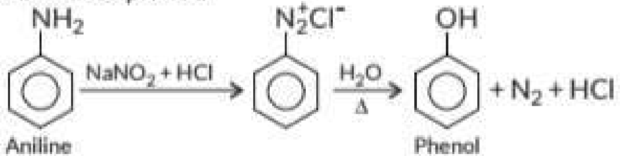


(ii) Propan-2-ol to 2-methylpropan-2-ol

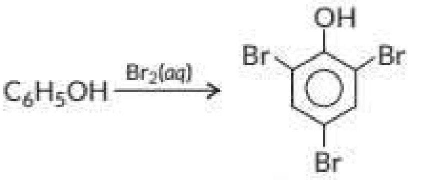


$$\underset{\text{Propan-2-ol}}{CH_3-\underset{\underset{OH}{|}}{CH}-CH_3} \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow[\text{(ii) }H^+/H_2O]{\text{(i) }CH_3MgBr} \underset{\text{2-Methylpropan-2-ol}}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}$$

(iii) Aniline to phenol

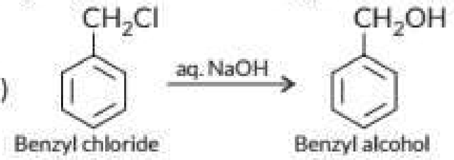


68. (i) $CH_3-CH{=}CH_2 \xrightarrow[\text{(ii) }3H_2O_2/OH^-]{\text{(i) }B_2H_6} CH_3CH_2CH_2OH$

(ii) 

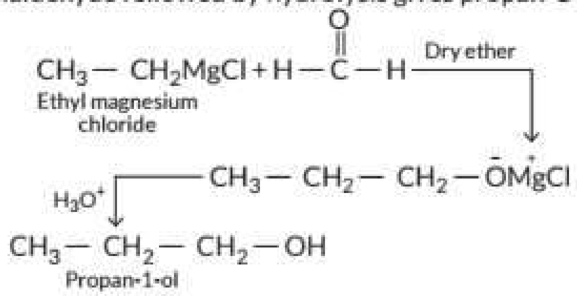
2,4,6-Tribromophenol

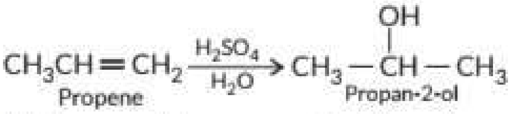
(iii) $CH_3CH_2OH \xrightarrow{Cu/573\,K} CH_3CHO$

69. (i) 

Benzyl chloride Benzyl alcohol

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

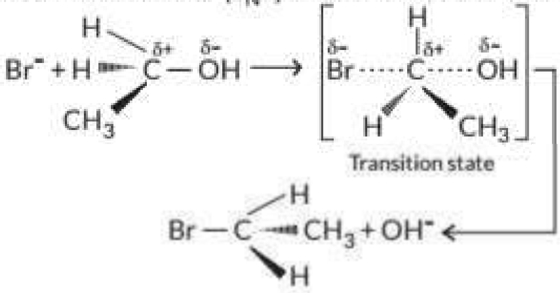


(iii) 

$CH_3CH{=}CH_2 \xrightarrow[H_2O]{H_2SO_4} CH_3-\overset{OH}{\overset{|}{C}H}-CH_3$

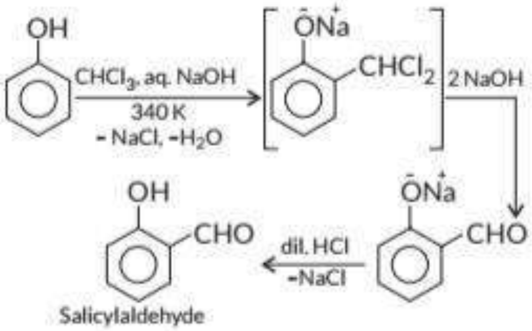
Propene Propan-2-ol

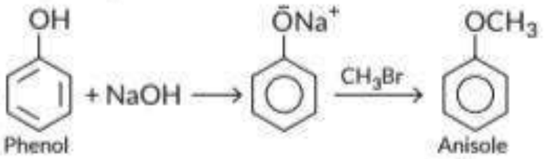
70. (a) The reaction proceeds through nucleophilic substitution bimolecular (S_N2) mechanism as shown below :

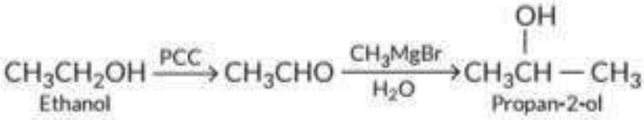


Inversion of configuration takes place during this reaction.

(b) Reimer–Tiemann reaction :



71. (a) (i) 

(ii) 

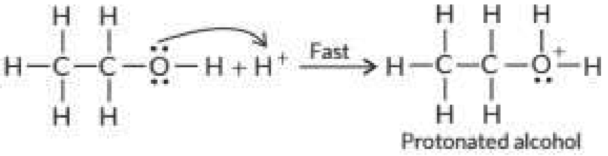
$CH_3CH_2OH \xrightarrow{PCC} CH_3CHO \xrightarrow[H_2O]{CH_3MgBr} CH_3\overset{OH}{\overset{|}{C}H}-CH_3$

Ethanol Propan-2-ol

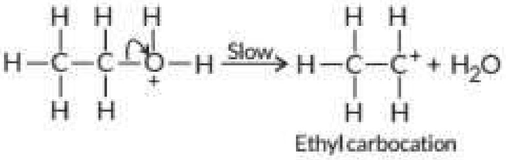
(b) Acid catalysed dehydration of alcohols at high temperature takes place with formation of a carbocation.

Mechanism : The dehydration of ethanol involves the following steps :

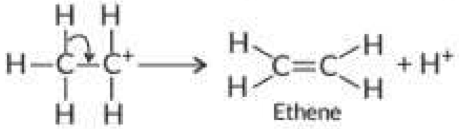
Step I : Formation of protonated alcohol.



Step II : Formation of carbocation.

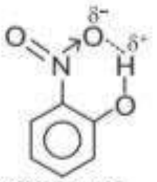


Step III : Formation of ethene by elimination of a proton.



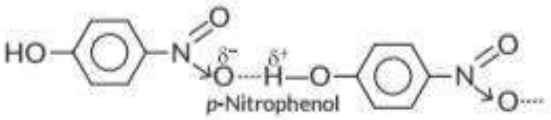
(c) Phenol undergoes electrophilic substitution reaction more easily than benzene due to strong ring activating effect of –OH group attached to benzene ring.

72. (a) (i) *o*-Nitrophenol is more volatile than *p*-nitrophenol due to the presence of intramolecular H-bonding. *p*-Nitrophenol shows intermolecular H-bonding.



o-Nitrophenol

(Intramolecular H-bonding)

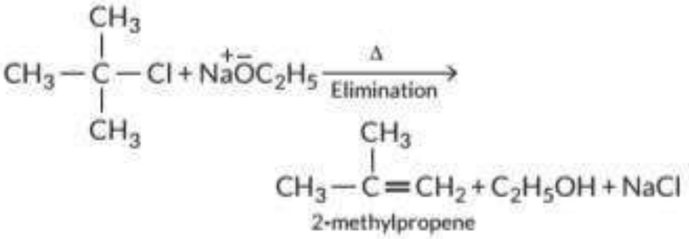


p-Nitrophenol

(Intermolecular H-bonding)

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

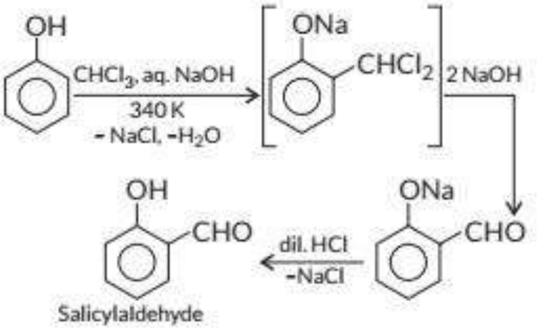
(ii) This is because *tert*-alkyl halides undergo elimination instead of substitution.



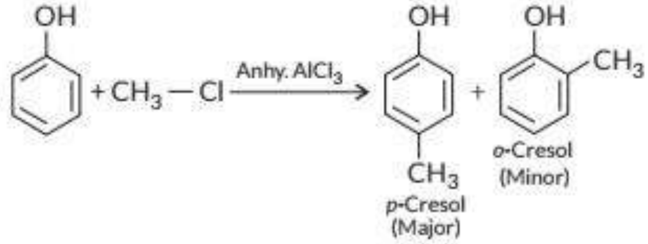
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl + \overset{+}{N}a\overset{-}{O}C_2H_5 \xrightarrow[\text{Elimination}]{\Delta} CH_3-\overset{CH_3}{C}{=}CH_2 + C_2H_5OH + NaCl$

2-methylpropene

(b) (i) Reimer–Tiemann reaction :



(ii)



(c) Distinction between ethanol and phenol can be done by $FeCl_3$ test. Phenol gives a violet colouration with $FeCl_3$ solution while ethanol does not.

$$\underset{\text{Phenol}}{6C_6H_5OH} + FeCl_3 \longrightarrow \underset{\text{Violet colouration}}{[Fe(C_6H_5O)_6]^{3-}} + 3H^+ + 3HCl$$

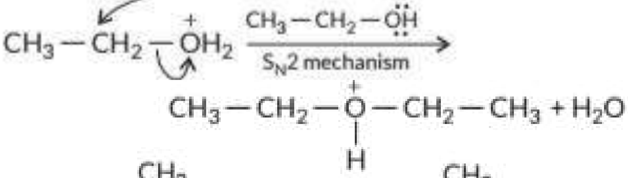
$C_2H_5OH + FeCl_3 \longrightarrow$ No violet colouration

73. (a) (i) Br_2/H_2O (ii) BH_3 in THF/H_2O_2, OH^-

(b) (i) Ethanol < phenol < *p*-nitrophenol

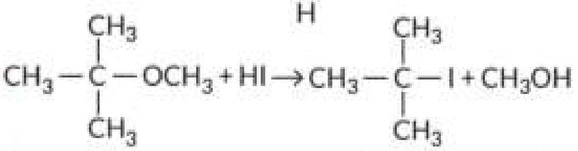
(ii) Propane < propanal < propanol

(c)



$$CH_3-CH_2-\overset{+}{O}H_2 \xrightarrow[S_N2\text{ mechanism}]{CH_3-CH_2-\ddot{O}H} CH_3-CH_2-\underset{H}{\overset{+}{O}}-CH_2-CH_3+H_2O$$

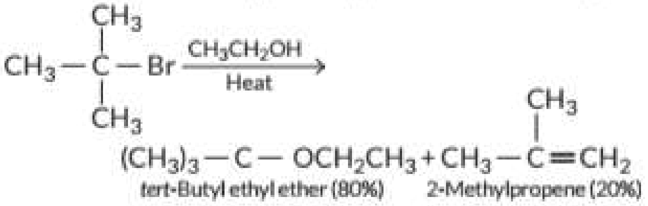
74. (a) :



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OCH_3+HI\rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I+CH_3OH$$

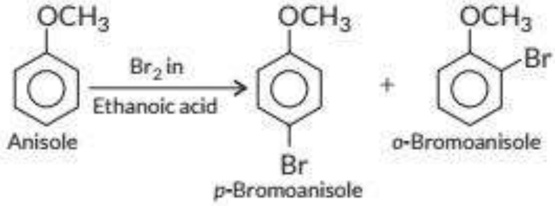
75. (d): In ether, the C—O—C bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky(-*R*) groups.

76. 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) will be 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,



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br \xrightarrow[\text{Heat}]{CH_3CH_2OH} \underset{\textit{tert}\text{-Butyl ethyl ether (80\%)}}{(CH_3)_3-C-OCH_2CH_3} + \underset{\text{2-Methylpropene (20\%)}}{CH_3-\overset{CH_3}{C}=CH_2}$$

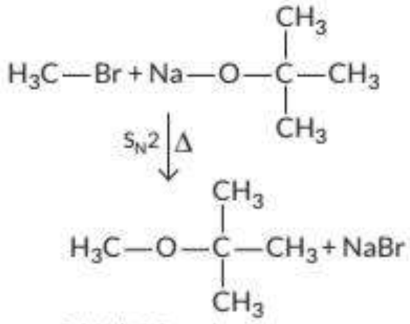
77.



Concept Applied

- –OCH_3 group is *o/p* directing group.

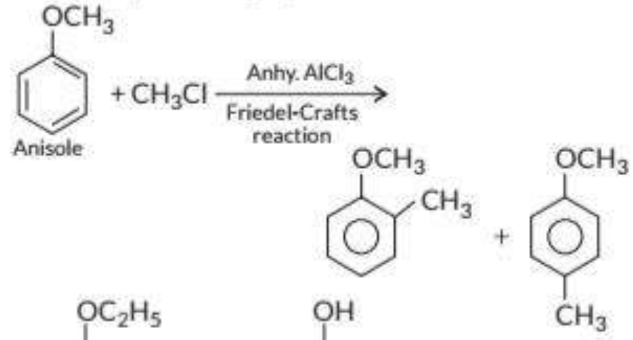
78.



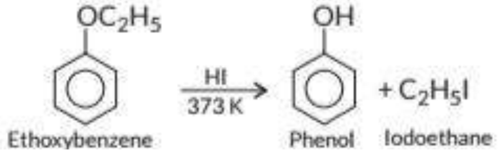
$$H_3C-Br+Na-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{S_N2,\ \Delta} H_3C-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3+NaBr$$

2-Methyl-2-methoxypropane

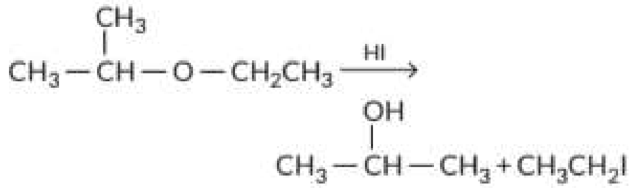
79.



80.

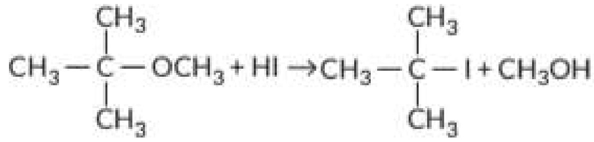


81.



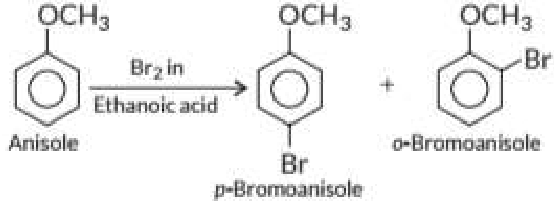
$$CH_3-\overset{CH_3}{CH}-O-CH_2CH_3 \xrightarrow{HI} CH_3-\overset{OH}{CH}-CH_3+CH_3CH_2I$$

82.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OCH_3+HI\rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I+CH_3OH$$

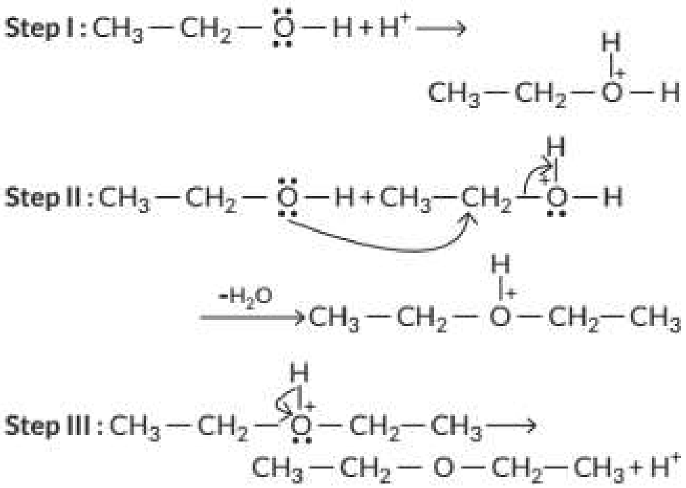
83.



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

$C_2H_5ONa + C_2H_5Cl \longrightarrow C_2H_5 - O - C_2H_5 + NaCl$

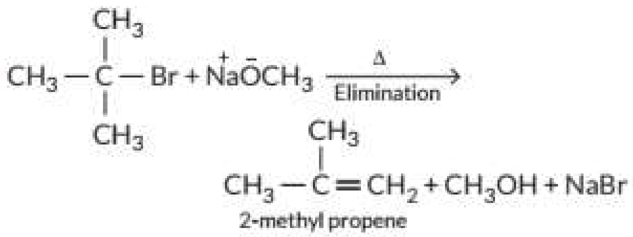
85. **Mechanism** : The formation of ether is nucleophilic bimolecular reaction.



Step I : $CH_3-CH_2-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H+H^+\longrightarrow CH_3-CH_2-\overset{H}{\overset{|}{O^+}}-H$

Step II : $CH_3-CH_2-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H+CH_3-CH_2-\overset{H}{\overset{|}{\underset{\cdot\cdot}{O^+}}}-H\xrightarrow{-H_2O}CH_3-CH_2-\overset{H}{\overset{|}{O^+}}-CH_2-CH_3$

Step III : $CH_3-CH_2-\overset{H}{\overset{|}{O^+}}-CH_2-CH_3\longrightarrow CH_3-CH_2-O-CH_2-CH_3+H^+$

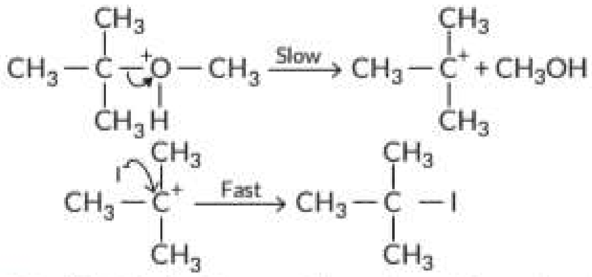
86. 

$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-Br+\overset{+}{Na}\overset{-}{O}CH_3\xrightarrow[\text{Elimination}]{\Delta}CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2+CH_3OH+NaBr$$

2-methyl propene

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

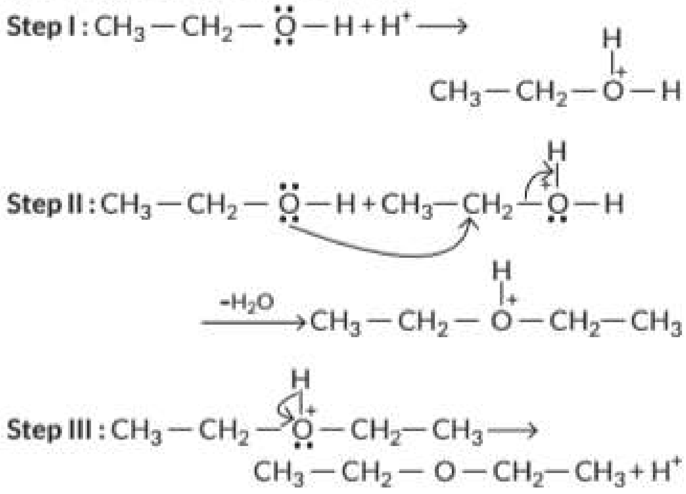
(ii) When the alkyl group is a tertiary group, the halide formed is tertiary halide. The departure of leaving group $-\underset{H}{\underset{|}{\overset{+}{O}}}-CH_3$ creates a more stable carbocation (3°) and the reaction follows S_N1 mechanism.



$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{+}{O}}}-CH_3\xrightarrow{\text{Slow}}CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C^+}}}}+CH_3OH$$

$$CH_3-\underset{CH_3}{\underset{|}{\overset{I\ \ CH_3}{\overset{|}{C^+}}}}\xrightarrow{\text{Fast}}CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-I$$

88. (i) **Mechanism** : The formation of ether is nucleophilic bimolecular reaction.

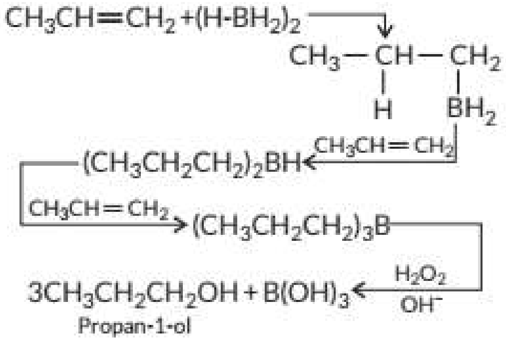


Step I : $CH_3-CH_2-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H+H^+\longrightarrow CH_3-CH_2-\overset{H}{\overset{|}{O^+}}-H$

Step II : $CH_3-CH_2-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-H+CH_3-CH_2-\overset{H}{\overset{|}{\underset{\cdot\cdot}{O^+}}}-H\xrightarrow{-H_2O}CH_3-CH_2-\overset{H}{\overset{|}{O^+}}-CH_2-CH_3$

Step III : $CH_3-CH_2-\overset{H}{\overset{|}{O^+}}-CH_2-CH_3\longrightarrow CH_3-CH_2-O-CH_2-CH_3+H^+$

(ii) **Hydroboration-oxidation reaction :** Diborane (B_2H_6) adds on alkane to give trialkyl boranes which on oxidation with hydrogen peroxide in presence of alkali give alcohols.

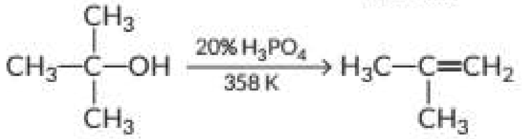


$$CH_3CH=CH_2+(H\text{-}BH_2)_2\longrightarrow CH_3-\underset{H}{\underset{|}{CH}}-\underset{BH_2}{\underset{|}{CH_2}}\xrightarrow{CH_3CH=CH_2}(CH_3CH_2CH_2)_2BH\xrightarrow{CH_3CH=CH_2}(CH_3CH_2CH_2)_3B\xrightarrow[OH^-]{H_2O_2}3CH_3CH_2CH_2OH+B(OH)_3$$

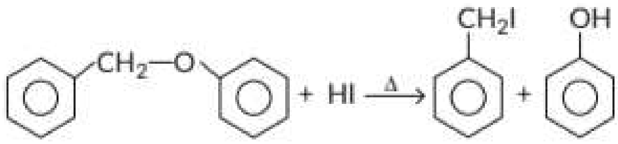
Propan-1-ol

89. (i) $3CH_3-CH=CH_2\xrightarrow[H_2O_2/OH^-]{(BH_3)_2}3CH_3-CH_2-CH_2-OH$

Propanol

(ii) 

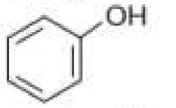
$$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH\xrightarrow[358\text{ K}]{20\%\ H_3PO_4}H_3C-\underset{CH_3}{\underset{|}{C}}=CH_2$$

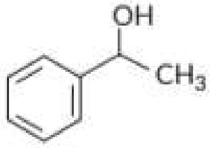
(iii) 

CBSE Sample Questions

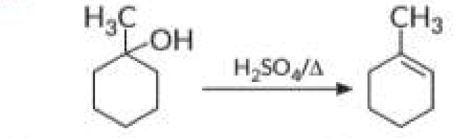
1. (a) : (i) $CH_3CH_2CH(OH)CH_3$ (secondary alcohol)

(ii) $(C_2H_5)_3COH$ (tertiary alcohol)

(iii)  (phenol, not an alcohol)

(iv)  (secondary alcohol) **(0.77)**

2. (b):



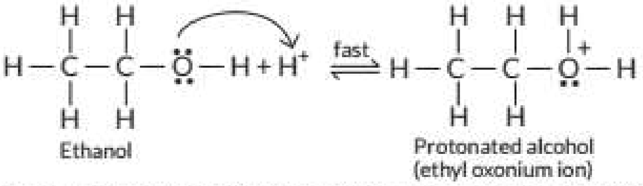
1-Methylcyclohexanol 1-Methylcyclohexene

According to Saytzeff rule, highly substituted alkene is major product. Here, dehydration reaction takes place, alkene is formed due to the removal of a water molecule. **(1)**

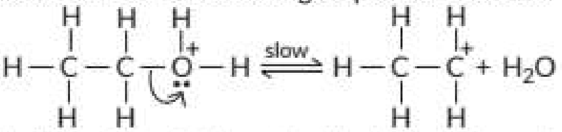
3. (a): Alcohols form intermolecular hydrogen bonds. So, alcohols have higher boiling points than hydrocarbons of comparable masses. **(0.77)**

4. (a): Protonation of alcohol molecule is initial step in dehydration of alcohols to alkenes.

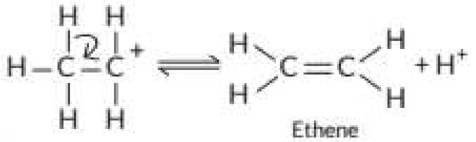
Step 1 : Formation of protonated alcohol



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

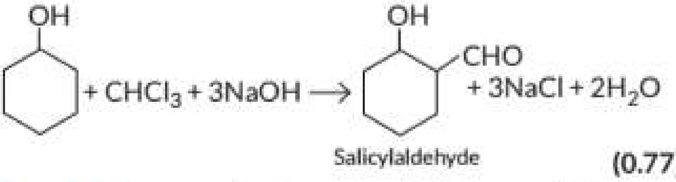


Step 3 : Formation of ethene by elimination of a proton.



(0.77)

5. (c) : Reimer-Tiemann reaction is used to prepare salicylaldehyde, Kolbe's reaction to prepare salicylic acid, Etard reaction for benzaldehyde and Stephen's reduction for aldehyde.

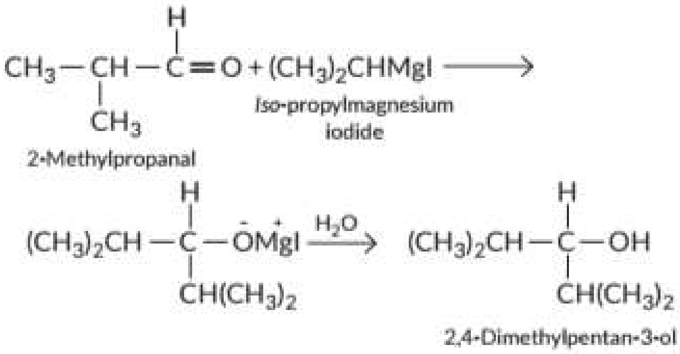


(0.77)

6. (c) : Lower molecular mass alcohols are able to form hydrogen bonds with water. Hence, they are miscible in water in all proportions. (0.77)

7. (b): Phenol does not undergo nucleophilic substituiton reaction easily due to partial double bond character of C – OH bond. (0.77)

8. (d): 2-Methylpropanal and *iso*-propyl magnesium iodide react to form 2,4-dimethylpentane 3-ol.

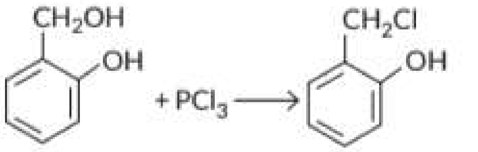


$$CH_3-\underset{CH_3}{CH}-\overset{H}{C}{=}O+(CH_3)_2CHMgI \longrightarrow$$

$$(CH_3)_2CH-\underset{CH(CH_3)_2}{\overset{H}{C}}-\bar{O}\overset{+}{M}gI \xrightarrow{H_2O} (CH_3)_2CH-\underset{CH(CH_3)_2}{\overset{H}{C}}-OH$$

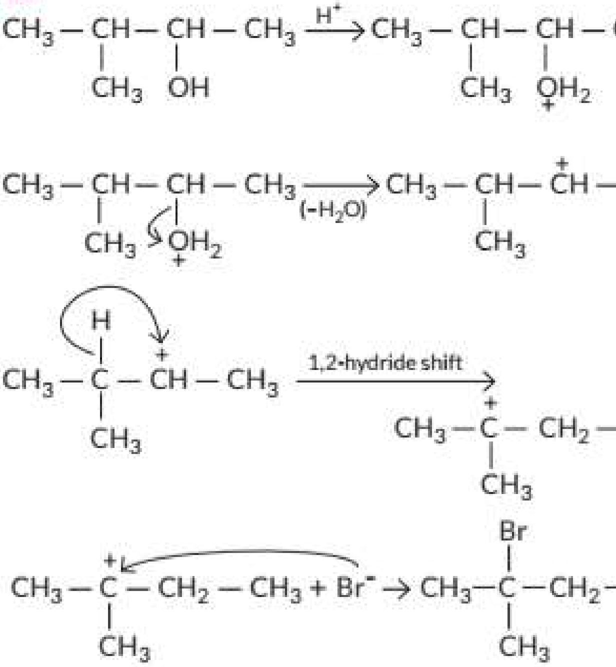
(0.77)

9. (b): 2-(Chloromethyl) phenol is formed.



(0.77)

10.



$$CH_3-\underset{CH_3}{CH}-\underset{OH}{CH}-CH_3 \xrightarrow{H^+} CH_3-\underset{CH_3}{CH}-\underset{\overset{+}{O}H_2}{CH}-CH_3$$

(1/2)

$$CH_3-\underset{CH_3}{CH}-\underset{\overset{+}{O}H_2}{CH}-CH_3 \xrightarrow[(-H_2O)]{} CH_3-\underset{CH_3}{CH}-\overset{+}{C}H-CH_3$$

(1/2)

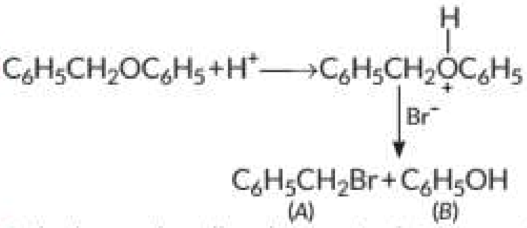
$$CH_3-\underset{CH_3}{\overset{H}{C}}-\overset{+}{C}H-CH_3 \xrightarrow{\text{1,2-hydride shift}} CH_3-\underset{CH_3}{\overset{+}{C}}-CH_2-CH_3$$

(1/2)

$$CH_3-\underset{CH_3}{\overset{+}{C}}-CH_2-CH_3+Br^- \rightarrow CH_3-\underset{CH_3}{\overset{Br}{C}}-CH_2-CH_3$$

(1/2)

11. (d):



$$C_6H_5CH_2OC_6H_5+H^+ \longrightarrow C_6H_5CH_2\overset{H}{\underset{+}{O}}C_6H_5 \xrightarrow{Br^-} \underset{(A)}{C_6H_5CH_2Br}+\underset{(B)}{C_6H_5OH}$$

(1)

12. (b): As hydrogen bonding does not exist among ether molecule, it is more volatile than alcohol. (1)

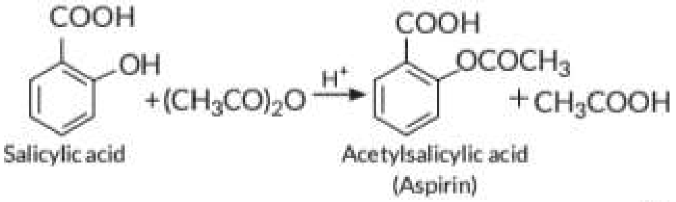
13. (c) : It is S_N2 reaction.

In this, alkoxide ion reacts with primary alkyl halide in a single step to form ether.)

$CH_3Br \xrightarrow{CH_3\bar{O}\overset{+}{N}a} CH_3OCH_3 + NaBr$ (0.77)

14. (a): $CH_3CH_2OCH_3 + HI \rightarrow CH_3CH_2OH + CH_3I$ (1)

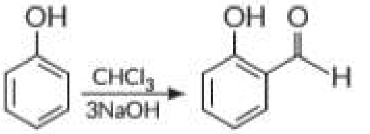
15. (a) : Aspirin is formed.



(1)

(b) $(CH_3)_3CCl \xrightarrow{\text{Sodium ethoxide}} \underset{\text{2-Methylpropene}}{(CH_3)_2C{=}CH_2}$ (1)

(c) *o*-hydroxybenzaldehyde will be formed.



(1)