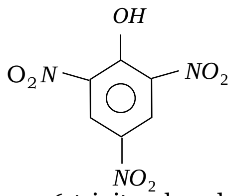
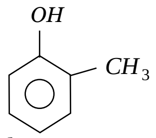
Answers and Solutions

General introduction of alcohol, Phenol & Ethers

2. (d) 

2, 4, 6-trinitrophenol or picric acid

4. (d) $\underset{OH}{CH_2} - \underset{OH}{CH} - \underset{OH}{CH_2}$ Glycerol is trihydric alcohols.

5. (a) 

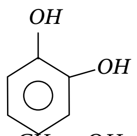
Hydroxy

6. (c) % of $C = \frac{\text{Mass of } C}{\text{Mass of substance}} \times 100$

$$CCl_4 = \frac{12}{154} \times 100 = 7.79\%$$

$$C_6H_6Cl_6 = \frac{72}{291} \times 100 = 24.74\%$$

$$CH_2OH - CH_2OH = \frac{24}{62} \times 100 = 38.70\%.$$

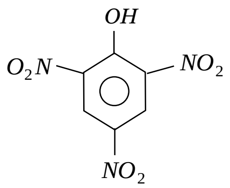
7. (c)  *o*-dihydroxy benzene or catechol.

8. (b) $CH_2 - OH$ | $CH - OH$ | $CH_2 - OH$

one secondary and two primary alcoholic groups.

11. (b) Carbinol is CH_3OH (Methanol).

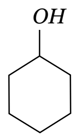
12. (c) $-OH$ group is attached to primary carbon.

13. (c) 

(Picric acid) or 2, 4, 6-trinitrophenol

Picric acid is phenolic while others are non phenolic.

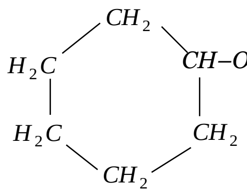
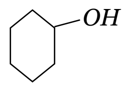
15. (c) Butanal $CH_3 - CH_2 - CH_2 - CHO$, an aliphatic aldehyde.

16. (b) 

Cyclohexanol is a secondary alcohol because $-OH$ group is linked to 2^o carbon.

18. (b) C_2H_5OH and $CH_3 - O - CH_3$ are isomers.

20. (b) 5-10 % methyl and remaining ethanol is called methylated spirit. It is also known as denatured alcohol because it is unfit for drinking.

21. (a)  or 

cyclohexanol

23. (a) 5% aqueous solution of phenol at room temperature is called as carbolic acid.

25. (b) Glycols are dihydric alcohols (having two hydroxyl groups). Ethylene glycol is the first member of this series.

CH_2OH | CH_2OH (Ethyleneglycol)

26. (a) Methanol is also referred as wood alcohol or wood spirit or wood naphtha as the earliest method for its preparation was by destructive distillation of wood.

34. (b) Ether is basic because lone pairs of electrons are present on oxygen atom, $R - \ddot{\underset{\cdot\cdot}{O}} - R$.

39. (a) Thio alcohol is known as mercaptans.

Preparation of alcohol, Phenol and Ethers

1. (c) Hydration of alkenes

$$CH_2 = CH_2 + \overset{+}{H}\overset{-}{HSO_4} \rightarrow CH_3 - CH_2 - HSO_4$$

$$CH_3 - CH_2HSO_4 \xrightarrow[Boil]{H_2O} CH_3 - CH_2 - OH + H_2SO_4$$

Fermentation of sugars:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose or Fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

2. (c) $CH_2 = CH_2 \xrightarrow{H_2SO_4} CH_3 - CH_2 - HSO_4 \xrightarrow{\text{Hydrolysis}}$

$$CH_3CH_2 - OH + H_2SO_4$$

3. (b) Hydroboration oxidation (Industrial preparation of alcohol)

$$3CH_3CH = CH_2 + \frac{1}{2}B_2H_6 \xrightarrow[\text{ether}]{\text{Dry}} (CH_3CH_2CH_3)_3B$$

$$(CH_3CH_2CH_3)_3B \xrightarrow{H_2O_2} 3CH_3CH_2CH_2 - OH$$

4. (c) $CH_2 - CH_2$ (with bridging O) $+ CH_3MgI \rightarrow \underset{CH_3}{CH_2} - \underset{OMgI}{CH_2} \rightarrow$

$$\underset{\text{Propyl alcohol}}{CH_3 - CH_2 - CH_2 - OH} + Mg\begin{matrix} I \\ OH \end{matrix}$$

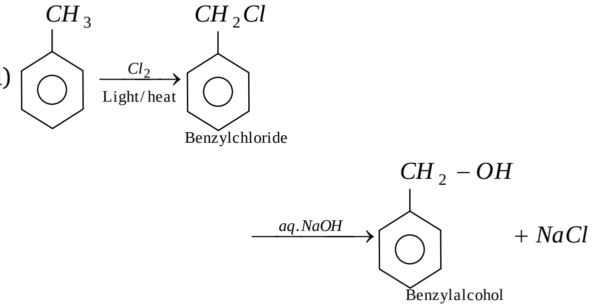
5. (d) Starch $\xrightarrow{\text{Enzymes}}$ Alcohol

6. (c) Coconut oil + Alkali $\rightarrow$ Soap + Glycerol

It is a saponification reaction.

7. (c) $\underset{\text{Glucose or Fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethylalcohol}}{2C_2H_5OH} + 2CO_2$

8. (d)



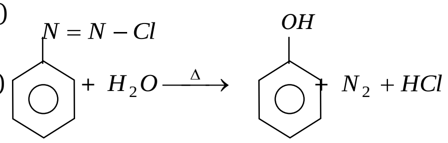
9. (a) $2(C_6H_{10}O_5)_n + nH_2O \xrightarrow[\text{(from germinated barley)}]{\text{Diastase}} n(C_{12}H_{22}O_{11})$ (Starch → Maltose)

$C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{(from yeast)}]{\text{Maltase}} 2C_6H_{12}O_6$ (Glucose)

$C_6H_{12}O_6 \xrightarrow[\text{(from yeast)}]{\text{Zymase}} 2C_2H_5OH + 2CO_2$

10. (b)

11. (c)

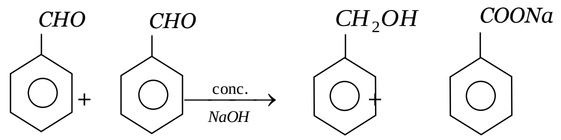


12. (c) $CH_3COOH + 4H \xrightarrow{LiAlH_4} CH_3CH_2OH + H_2O$

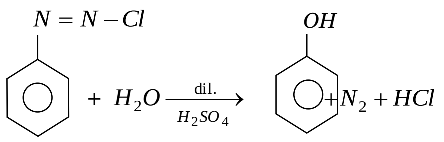
13. (b) $\begin{matrix}H\\H\end{matrix}\!\!>C=O \xrightarrow{CH_3MgI} \underset{\displaystyle CH_3}{\underset{|}{CH_2}} - O - MgI \xrightarrow{\text{Hydrolysis}}$

$CH_3 - CH_2 - OH + Mg\begin{matrix}I\\OH\end{matrix}$

14. (b)

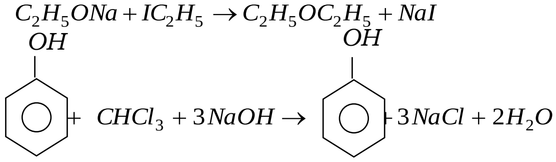


15. (d)



16. (c) $C_2H_5ONa + IC_2H_5 \rightarrow C_2H_5OC_2H_5 + NaI$

17. (b)



18. (c) $HCHO + HCHO \xrightarrow{\text{Conc. } KOH} \underset{\text{Methyl alcohol}}{CH_3OH} + \underset{\text{Potassium formate}}{HCOOK}$

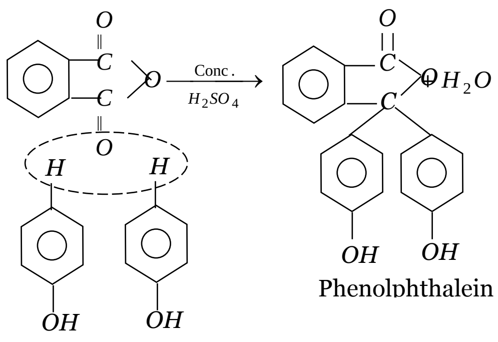
It is cannizzaro's reaction.

19. (d) Alcohol + Benzene $\rightarrow$ Soluble (dry)

(Alcohol) $R-OH + Na \rightarrow R-ONa + H_2$

21. (c) $\underbrace{CO + H_2}_{\text{water gas}} + H_2 \xrightarrow[672\,K,\ 200\ atm]{Cr_2O_2\ /\ ZnO} CH_3OH$

23. (c)



24. (c) $\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{(from yeast)}]{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$.

26. (d) Grignard reagent reacts with compounds containing multiple bonds like

$>C=O, \quad >C=S, \quad >C\equiv N$.

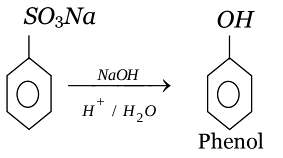
28. (d) Acetone reacts with Grignard's reagent to give tertiary alcohol.

$(CH_3)_2C=O + CH_3MgBr \xrightarrow{H_2O} \underset{\text{ter-butyl alcohol}}{(CH_3)_3C-OH}$

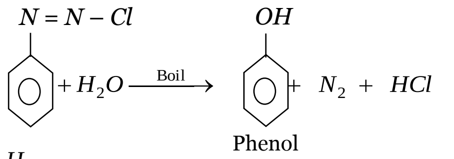
29. (b) $C_2H_5MgBr + H_2C - CH_2$ (with O bridging, epoxide) $\xrightarrow{H_2O}$

$\underset{\underset{n\text{-butyl alcohol}}{(A)}}{C_2H_5CH_2CH_2OH} + MgBr(OH)$

30. (a)



31. (b)



32. (b) $\begin{matrix}H\\H\end{matrix}\!\!>C=O + C_2H_5MgI \rightarrow \underset{\displaystyle C_2H_5}{\underset{|}{CH_2}} - O - MgI$

$\xrightarrow{\text{Hydrolysis}} C_2H_5 - CH_2 - OH$ or $C_3H_7OH + Mg\begin{matrix}I\\OH\end{matrix}$

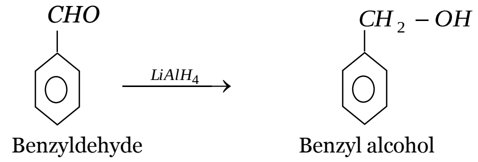
35. (d) $\underset{\text{Grignard reagent}}{RMgBr} + O_2 \rightarrow R-OMgBr \xrightarrow{\text{hydrolysis}} \underset{\text{Alcohol}}{R-OH} + Mg\begin{matrix}Br\\OH\end{matrix}$

39. (b) $\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$

During fermentation CO_2 gas is eliminated.

40. (c) $C_2H_5 - NH_2 + HNO_2 \rightarrow C_2H_5OH + N_2 + H_2O$

41. (b)



42. (a) $CO + H_2 \xrightarrow[573\,K,\ 200\ \text{atm}]{CuO-ZnO-Cr_2O_3} \underset{\text{Methanol}}{CH_3OH}$

43. (a) $\underset{\text{2 methyl 2 butene}}{CH_3 - CH = C\begin{matrix}CH_3\\CH_3\end{matrix}} + H_2O \xrightarrow[\text{Markownikoff rule}]{H_2SO_4}$

$$CH_3-CH_2-\underset{\underset{OH}{|}}{C}\langle{}^{CH_3}_{CH_3}$$

2 methyl butan-2-ol

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

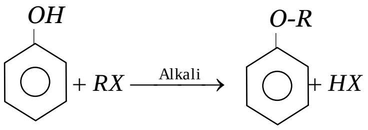
propene → propene-2-ol

44. (c) $CH_3CONa+Br-CH_3\rightarrow CH_3-O-CH_3+NaBr$
Dimethyl ether (symmetrical ether)

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O^-Na+CH_3Br\rightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OCH_3+NaBr$$

Methyl ter-butyl ether (unsymmetrical ether)

45. (c)



46. (b) $C_2H_5Br+C_2H_5ONa\xrightarrow[-NaBr]{}C_2H_5-O-C_2H_5$
Sod. ethaoxide; diethyl ether

47. (c) $RX+RONa\rightarrow R-O-R+NaX$
Ether

It is a Williamson's synthesis reaction.

48. (b) Williamson's synthesis –

$CH_3-CH_2-ONa+Cl-CH_2-CH_3\rightarrow$
$CH_3-CH_2-O-CH_2-CH_3$

49. (a) Dehydration of alcohols gives ethers.

50. (b) $2C_2H_5Br+\underset{\text{Dry}}{Ag_2O}\rightarrow C_2H_5-O-C_2H_5+2AgBr$

If we take moist Ag_2O then alcohol is formed

$Ag_2O+H_2O\rightarrow 2AgOH$

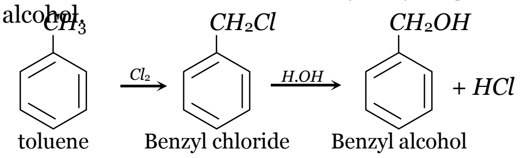
$C_2H_5Br+AgOH\rightarrow C_2H_5OH+AgBr$

51. (d) $CH_3OCH_3\xrightarrow{Cl_2/hv}CH_3OCH_2Cl$
Methoxymethane (Lower ether); α–Chlorodimethyl ether

$\xrightarrow[-MgBr(Cl)]{CH_3MgBr}CH_3OCH_2CH_3$
Methoxyethane (Higher ether)

52. (a) $CH_3-\overset{\overset{O}{\|}}{C}-Br\xrightarrow[\text{(ii)Saturated } NH_4Cl]{\text{(i)Excess-}CH_3MgI}CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$
Acetyl bromide; 2-methyl 2-propanol

53. (d) When chlorine is passed in boiling toluene, substitution inside chain takes place and benzyl chloride is obtained which on hydrolysis give benzyl alcohol.



54. (a) $2C_6H_5CHO+NaOH\rightarrow C_6H_5CH_2OH+C_6H_5COONa$
Benzaldehyde; (Benzyl alcohol)

55. (c) Ethanal with CH_3MgBr gives propanol-2 (after hydrolysis) and with C_2H_5OH, it gives acetal.

$$CH_3CHO+CH_3MgBr\rightarrow CH_3CH\langle{}^{OMgBr}_{CH_3}\xrightarrow{H^+}$$

Acetaldehyde

$$CH_3CH\langle{}^{OH}_{CH_3}$$

2 propanol

$$CH_3CHO+2C_2H_5OH\xrightarrow{\text{dry } HCl}CH_3CH\langle{}^{OC_2H_5}_{OC_2H_5}$$

Acetal

56. (a) $H_2C=CH_2+HOCl\rightarrow H_2\underset{\underset{Cl}{|}}{C}-CH_2OH$
Ethylene; (hypochlorous); Ethylene chlorohydrine

$\xrightarrow{[NaHCO_3]}H_2\underset{\underset{OH}{|}}{C}-\underset{\underset{OH}{|}}{CH_2}+NaCl+CO_2$
(Ethylene glycol)

57. (b) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-Na+Cl-CH_3\rightarrow$
2, 2 dimethyl sodium ethoxide

$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_3+NaCl$
Methyl-t butyl ether

58. (c) $CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5+CH_3MgI\rightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{O-MgI}{|}}{C}}-OC_2H_5$
Ethyl methyl ester

$\xrightarrow{\text{Hydrolysis}}CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-O\,C_2H_5\xrightarrow{+Mg\langle{}^{Br}_{OH}}$

$\begin{matrix}CH_3\\CH_3\end{matrix}\rangle C=O+C_2H_5OH$
Acetone; Ethyl alcohol

59. (b) $NaBH_4$ and $LiAlH_4$ attacks only carbonyl group and reduce it into alcohol group. They do not attack on double bond.

$C_6H_5-CH=CHCHO\xrightarrow{NaBH_4}$
cinnamic aldehyde

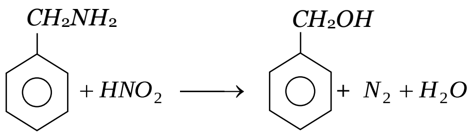
$C_6H_5-CH=CH.CH_2OH$
cinnamic alcohol

60. (b,c)
$CH_2=CH_2+H_2O+[O]\xrightarrow{\text{alk.}KMnO_4}\underset{\underset{OH}{|}}{CH_2}-\underset{\underset{OH}{|}}{CH_2}$
Glycol

$CH_2=CH_2+H_2O\xrightarrow{\text{Conc. }H_2SO_4}CH_3-CH_2-OH$
Ethene; Ethanol

61. (a) Wood $\xrightarrow[\text{distillation}]{\text{Destructive}}$ Wood gas + Tar + Charcoal
$+\ CH_3OH+CH_3COOH$
(wood alcohol) (vinegar)

62. (d)



64. (a) $C_6H_6O^-+CH_3I\rightarrow C_6Hl5OCH_3+I^-$

Properties of alcohol, Phenol and Ethers

1. (c) $CH_3-OH + CH_3Mg-X \rightarrow CH_4 + CH_3O-Mg-X$

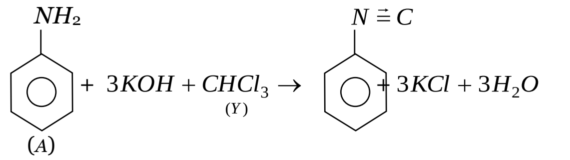
4. (c) $C_2H_5OH \xrightarrow[\text{Iodoform test}]{NaOH / I_2} CHI_3$ (yellowppt)

$CH_3OH \xrightarrow{NaOH / I_2}$ No *ppt*

5. (a) $\underset{X}{CH_3-CH_2-CH_2-OH} \xrightarrow{\text{Oxidation}} \underset{Y}{CH_3CH_2COOH}$

Since on oxidation same no. of carbon atoms are obtained in as therefore alcohol is primary

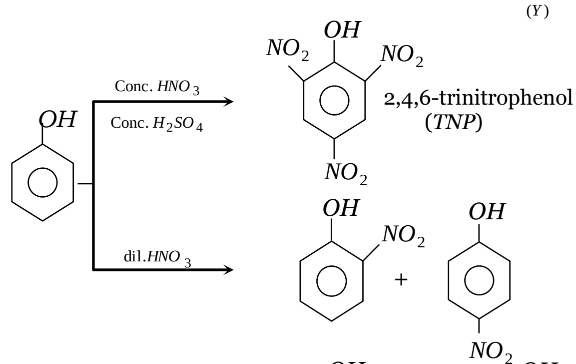
8. (b)



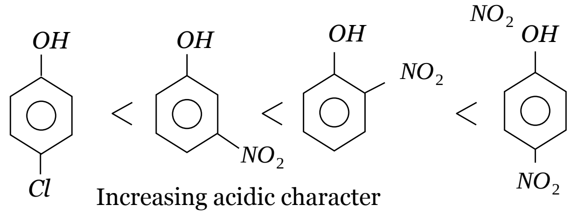
$\underset{(Z)}{C_2H_5OH + Cl_2} \xrightarrow{Ca(OH)_2} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{Cl_2}$

$\underset{\text{Chloral}}{CCl_3CHO} \xrightarrow{Ca(OH)_2} \underset{\text{chloroform } (Y)}{CHCl_3}$

12. (b)

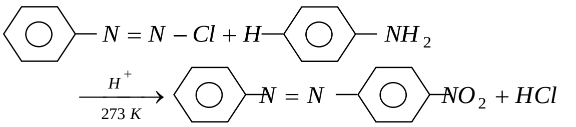


14. (c)



Increasing acidic character

15. (c)



16. (b) $\begin{matrix} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2OH \end{matrix} \xrightarrow[\text{Small amount}]{P_4+I_2} \underset{\text{Unstable}}{\begin{matrix} CH_2-I \\ | \\ CH-I \\ | \\ CH_2-I \end{matrix}} \xrightarrow{-I_2} \underset{\text{Allyl iodide}}{\begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CH_2-I \end{matrix}}$

18. (c) $\begin{matrix} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{matrix} \xrightarrow[-3H_2O]{3HI} \begin{matrix} CH_2-I \\ | \\ CH-I \\ | \\ CH_2-I \end{matrix} \xrightarrow{-I_2}$

$\begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CH_2-I \end{matrix} \xrightarrow{HI} \begin{matrix} CH_3 \\ | \\ CH-I \\ | \\ CH_2-I \end{matrix} \xrightarrow{-I_2} \begin{matrix} CH_3 \\ | \\ CH \\ \| \\ CH_2 \end{matrix}$

19. (d) $HOOC-COOH \xrightarrow[\text{Decarboxylation}]{\text{Glycerol}} HCOOH + CO_2$

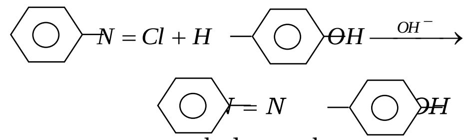
$HCOOH + \text{Fehlingsolution} \rightarrow \underset{\text{Red ppt.}}{Cu_2O} + CO_2 + H_2O$

21. (b) Glycerol undergoes extensive hydrogen bonding due to the presence of 3 $-OH$ groups. As a result the glycerol molecules are highly associated and thus it has high viscosity.

22. (b) $\begin{matrix} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{matrix} \xrightarrow[H_2SO_4]{\text{conc.}} \underset{\text{Acrolein}}{\begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CHO \end{matrix}} + 2H_2O$

23. (a) $\begin{matrix} CH_3-CH-CH_3 \\ | \\ OH \end{matrix} \xrightarrow[KMnO_4]{\text{Oxidation}} \underset{\text{Acetone}}{\begin{matrix} CH_3-C-CH_3 \\ \| \\ O \end{matrix}}$

24. (b)



p-hydroxyazobenzene

25. (c) $(CH_3)_3C-OH + HCl \xrightarrow{Anhyd.\ ZnCl_2 + HCl}$

$(CH_3)_3C-Cl + H_2O$ 3^o reacts immediately

$(CH_3)_3CH-OH + HCl \xrightarrow{Anhyd.\ ZnCl_2 + HCl}$

$(CH_3)_2CH-Cl + H_2O$ 2^o reacts after 5 min.

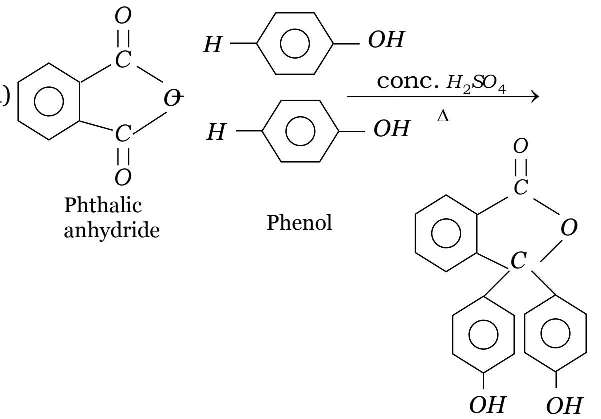
$CH_3CH_2CH_2-OH + HCl \xrightarrow{Anhyd.\ ZnCl_2 + HCl}$

$CH_3CH_2CH_2-Cl + H_2O$ 1^o reacts only on heating.

26. (b) $C_2H_5OH + R-Mg-X \rightarrow \underset{\text{Alkane}}{RH} + C_2H_5OMgX$

$C_3H_7OH + R-Mg-X \rightarrow RH + C_3H_7OMgX$

30. (d)



Phthalic anhydride

Phenol

Phenolphthalein

33. (c) $\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + HIO_4 \rightarrow 2HCHO + HIO_3 + H_2O$

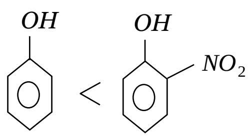
35. (b) $\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + PI_3 \rightarrow \begin{matrix} CH_2I \\ | \\ CH_2I \end{matrix} \xrightarrow{-I_2} CH_2=CH_2$

36. (a) $\underset{\text{alcohol}}{R-OH} + \underset{\text{Cerric amm. nitrate}}{(NH_4)_2Ce(NO_3)_6} \rightarrow \underset{\text{yellow } ppt.}{Ce(NO_3)_6(ROH)_9} + 2N + 14NO_3$

37. (d) $C_2H_5-O-C_2H_5 + O_2 \xrightarrow[25^oC]{hv} CH_3-CH(OOH)-O-C_2H_5$

38. (a) $H_2SO_4 \rightarrow H^+ + HSO_4^-$

$C_2H_5OH + H^+ \xrightarrow[\text{of alcohol}]{\text{Protonation}} \underset{\text{Protonated alcohol}}{C_2H_5-\overset{\oplus}{O}(\downarrow H)-H}$

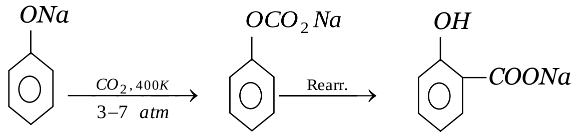


Nitro group is electron with-drawing. Hence, increases acidic nature.

39. (c)

43. (d) $CH_3CH_2OH \xrightarrow[350^oC]{Al_2CO_3 (X)} CH_2 = CH_2 + H_2O$

44. (a)



45. (c) $C_2H_5OH \xrightarrow{H_2SO_4}$
- $\xrightarrow{110^oC} C_2H_5HSO_4 + H_2O$ (Ethylhydrogen sulphate)
- $\xrightarrow{137^oC} C_2H_5 - O - C_2H_5 + H_2O$ (Diethyl Ether)
- $\xrightarrow{170^oC} C_2H_4 + H_2O$ (Ethene)

46. (b) $CH_3 - \overset{CH_3}{\underset{CH_3}{C^+}} > CH_3 - \overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$

3^o 2^o 1^o Methyl Carbonium ion

47. (c) Alcohols having less number of carbon atoms are more soluble in water.

48. (a) $C_2H_5OH + Na \rightarrow C_2H_5ONa$

$2C_2H_5OH \xrightarrow[H_2SO_4]{Conc.} C_2H_5 - O - C_2H_5 + H_2O$

50. (a) $C_2H_5O - C_2H_5 \xrightarrow{Cl_2}$
- $\xrightarrow{Dark} CH_3 - \overset{Cl}{C}H - O - \overset{Cl}{C}H - CH_3$ α-α'-dichlorodiethyl ether
- $\xrightarrow{Light} CCl_3 - CCl_2 - O - CCl_2 - CCl_3$ Perchlorodiethylether

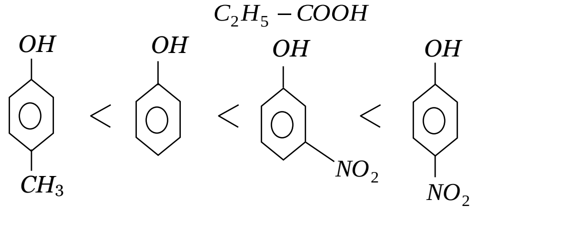
51. (d) $C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$
(A) (B)

$C_2H_5Cl + KCN \rightarrow C_2H_5CN + KCl$
(B)

$\downarrow$ Hydrolysi

$C_2H_5 - COOH$

52. (c)



53. (b) Higher alcohols are stronger and have bitter taste.

54. (c) Order of reactivity with alkali metal (*e.g.*-Sodium) follows the order $1^o > 2^o > 3^o$.

56. (c) $\underset{1\,mole}{CH_3OH} + \underset{\substack{1\,mole\\(23\,gms)}}{Na} \rightarrow CH_3ONa + \underset{1/2\,mole}{\frac{1}{2}H_2}$

57. (d) $3CH_3CH_2CH_2CH_2 - OH + PBr_3 \rightarrow$

$3CH_3CH_2CH_2CH_2 - Br + H_3PO_3$

58. (a) $CH_3OH + Cl_2 \rightarrow$ No reaction

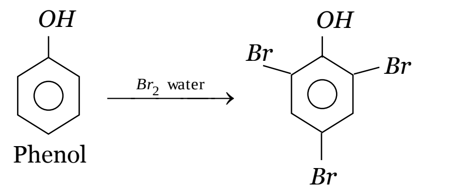
$CH_3OH + HCl \xrightarrow{ZnCl_2} CH_3Cl + H_2O$

$3CH_3OH + PCl_3 \rightarrow 3CH_3Cl + H_3PO_3$

$CH_3OH + PCl_5 \rightarrow CH_3Cl + POCl_3 + HCl$

59. (d) $CH_3 - \underset{OH}{CH} - CH_3 \xrightarrow{[O]} CH_3 - \underset{\parallel\\O}{C} - CH_3$

60. (c)



Phenol

2,4,6 tribromophenol or white *ppt*.

61. (d) Due to hydrogen bonding.

62. (a) $C_2H_5OH \xrightarrow[air]{Pt} CH_3CHO$

63. (c) $CH_3 - CH_2 - OH \xrightarrow[170^oC]{Conc.\ H_2SO_4} CH_2 = CH_2 + H_2O$

66. (b) Tertiary alcohol readily reacts with halogen acid

$CH_3 \rightarrow \overset{CH_3\downarrow}{\underset{\uparrow CH_3}{C}} - OH \rightarrow CH_3 - \overset{CH_3}{\underset{CH_3}{C^+}} + OH^-$

Presence of 3 alkyl group increases electron density on 3^o carbon atom. Hence $-OH$ group is easily removed. After the removal of $-OH$ group 3^o carbonium ion is formed which is most stable

67. (d) $CH_3CH_2CH_2OH \xrightarrow[160-180^oC]{conc.\ H_2SO_4} CH_3CH = CH_2$

$\xrightarrow{Br_2} CH_3 - \underset{Br}{CH} - \underset{Br}{CH_2} \xrightarrow{Alc.\ KOH} \underset{Propyne}{CH_3 - C \equiv CH}$

68. (b) Lower alcohols are soluble in all solvents.

69. (c) $CH_3 - \underset{OH}{CH} - CH_2 - CH_3 \xrightarrow{[O]} CH_3 - \overset{O}{\overset{\parallel}{C}} - CH_2CH_3$

70. (b) Due to the resonance stabilisation of phenoxide ion.

73. (a) $\underset{1^o\ alcohol}{R - CH_2 - CH_2 - OH} \xrightarrow[170^oC]{Conc.\ H_2SO_4}$

$\underset{Alkene}{R - CH = CH_2} + H_2O$

74. (a) $\underset{1^o\ alcohol}{R\text{-}CH_2OH} \xrightarrow{Cu} R - CHO + H_2$

$R - \underset{\substack{OH\\2^o\ alcohol}}{CH} - R \xrightarrow{Cu} R - \underset{\parallel\\O}{C} - R + H_2$

75. (c) $CH_3OH \xrightarrow[H_2SO_4]{K_2Cr_2O_7} HCOOH$

76. (a) $CH_3CH_2OH \xrightarrow{K_2Cr_2O_7} CH_3COOH$

77. (a) Lucas test is used for the distinction of primary secondary and tertiary alcohols.

78. (a) $+ NH_3 \xrightarrow[300^oC]{ZnCl_2} + H_2O$

80. (a) A compound that undergoes bromination easily is phenol. Due to presence of $-OH$ group the ring becomes much more active in substitution reactions. The bromination occurs due to availability of electrons on ortho and para position.

81. (c) *o*-Nitrophenol has intramolecular *H*-bonding.

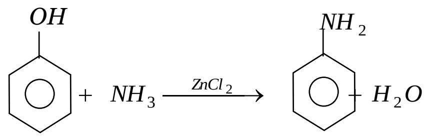
84. (b) C_2H_5OH gives iodoform test having α-hydrogen atom while CH_3OH does not give due to the absence of α-hydrogen atom.

85. (c) Phenol has higher boiling point than toluene because of hydrogen bonding.

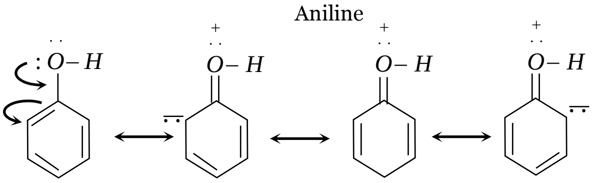
87. (b) $\underset{\text{Propene}-1}{CH_3-CH=CH_2} + aq.KOH \rightarrow \underset{\text{Propanol}-1}{CH_3-CH_2-CH_2OH}$

88. (d) $C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl \xrightarrow{KCN} C_2H_5CN \xrightarrow{HCl/H_2O} C_6H_5COOH$

89. (b) $LiAlH_4$ + ether, is reducing agent.

97. (b) 

Aniline

98. (a) 

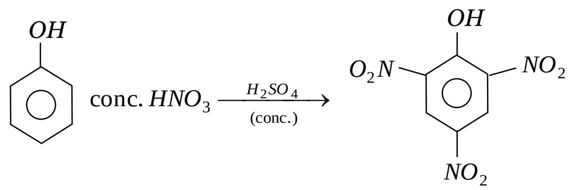
Oxygen atom of $-OH$ group acquires positive charge.

99. (c)

$$\underset{\text{Glycerol}}{\begin{matrix} H \\ | \\ H-C-OH \\ | \\ HO-C-H \\ | \\ H-C-H \\ | \\ OH \end{matrix}} \xrightarrow{KHSO_4} \underset{\text{Unstable}}{\begin{matrix} H \\ | \\ H-C \\ \| \\ C \\ \| \\ C-H \\ | \\ OH \end{matrix}} \longrightarrow \begin{matrix} H \\ | \\ H-C \\ \| \\ C-H \\ | \\ C-H \\ \| \\ O \end{matrix} \text{ or } \underset{\text{Acrolein}}{\begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CHO \end{matrix}}$$

100. (d) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

$\xrightarrow[I_2]{NaOH} \underset{\text{Yellow } ppt}{CHI_3} + CH_3COONa$

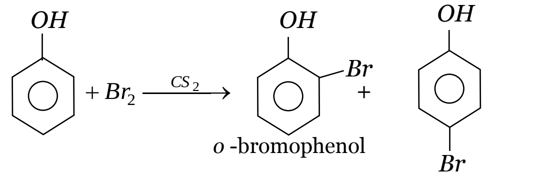
101. (d) 

Picric

102. (c) Phenol is weaker acid than carbonic acid

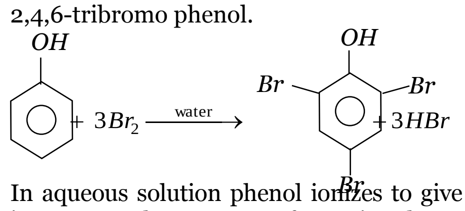
$$\underset{K_a = 10^{-8} - 10^{-10}}{C_6H_5OH}, \quad \underset{K_a = 10^{-7}}{H_2CO_3}, \quad \underset{K_a = 10^{-5}}{CH_3COOH}$$

103. (a)

104. (b) 

In presence of non-polar solvent (CS_2) the ionization of phenol is suppressed. The ring is slightly activated and hence mono substitution occurs.

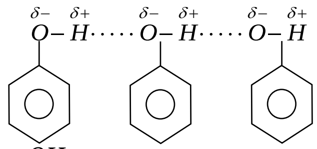
On the other hand with Br_2 water phenol forms 2,4,6-tribromo phenol.

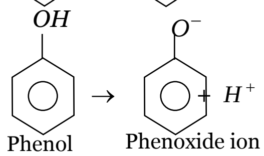


In aqueous solution phenol ionizes to give phenoxide ion. Due to the presence of negative charge on oxygen the benzene ring is highly activated and hence trisubstituted product is obtained.

105. (d) $\underset{\text{Ethylalcohol}}{C_2H_5OH} \xrightarrow{CrO_3} \underset{\text{Aceticacid}}{CH_3COOH}$

107. (d) $\underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow[170^oC]{Conc.H_2SO_4} \underset{\text{Ethane}}{C_2H_4} + H_2O$

108. (b) 

109. (a) 

Phenol Phenoxide ion

110. (c) (a) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{\text{Oxidation}} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

(b) $CH_3-CH_2-OH \xrightarrow[180^oC]{\text{Conc. }H_2SO_4} CH_2=CH_2+H_2O$

(d) $2CH_3CH_2OH + 2Na \rightarrow 2CH_3-CH_2-ONa + H_2$

112. (b) Carbylamine reaction

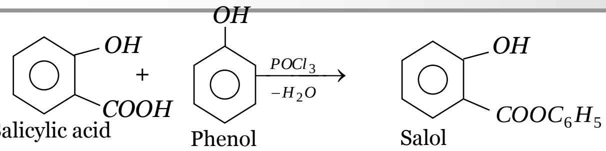
$CHCl_3 + CH_3NH_2 + 3\underset{\text{alc.}}{KOH} \rightarrow \underset{\text{Methyl isocyanide}}{CH_3N \equiv C} + 3KCl + 3H_2O$

113. (a) Secondary alcohol on dehydrogenation gives acetone

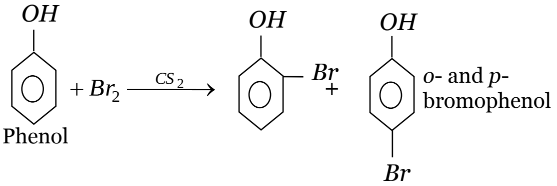
$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[300^oC]{Cu} CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + H_2$

114. (a) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{[O]} CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

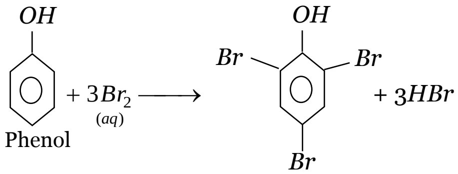
118. (d) $C_2H_5OH + [O] \rightarrow CH_3CHO \rightarrow CH_3COOH$.

119. (a) 

Salicylic acid + Phenol → Salol (Phenyl salicylate)

120. (c) (i) 

Phenol; *o*- and *p*- bromophenol

(ii) 

Phenol; 2, 4, 6-tribromophenol

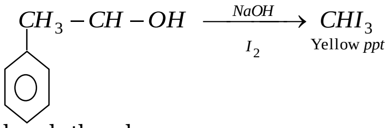
In *aq*. solution phenol ionize to give phenoxide in which highly activates benzene ring and give trisubstituted product while in presence of CS_2 an inert solvent phenol is unable to ionize due to which benzene ring is slightly activated. Hence, monosubstituted product is obtained.

122. (d) Traces of water from ethanol is removed by reacting with *Mg* metal.

123. (a) $\underset{\text{Glycerol}}{\begin{matrix} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{matrix}} + \begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow{260^oC} \underset{\text{Allylalcohol}}{CH_2=CH-CH_2-OH}$

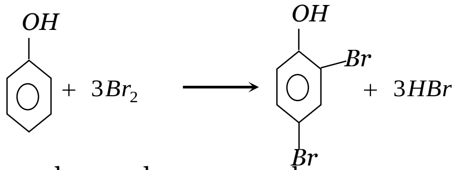
125. (c) $C_2H_5OH \xrightarrow[250^oC]{Al_2O_3} C_2H_5OC_2H_5 + H_2O$ (Diethyl ether)

$C_2H_5OH \xrightarrow[250^oC]{Al_2O_3} C_2H_4 + H_2O$ (Ethene)

126. (b) 

1-phenyl ethanol

Iodoform test is given by compounds in which $CH_3-\underset{OH}{\underset{|}{CH}}-$ or $CH_3-\underset{O}{\underset{||}{CH}}-$ group is present.

127. (c) 

1 mole 3 moles 1 mole

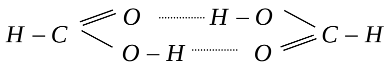
94 grams of phenol reacts with 480 *gms*. of Br_2.

2 *gm*. of phenol — $\frac{480}{94} \times 2 = 10.22 gms.$

128. (b) $2C_2H_5OH + 2Na \rightarrow 2C_2H_5ONa + H_2$

130. (a) $CH_3COOH + CH_3OH \xrightarrow[\text{Esterification}]{} CH_3COOCH_3 + H_2O$

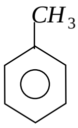
131. (b) CH_3OH has highest boiling point because of hydrogen bonding.

132. (b) 

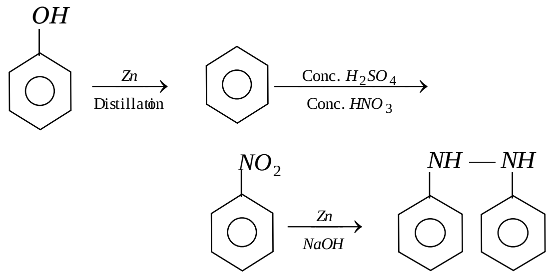
Formic acid forms dimer due to which strength of *H* – bond increases Hence, boiling point increases.

133. (c) Lower members are soluble in water and solubility decreases with increasing molecular mass because hydrophobic character increases.

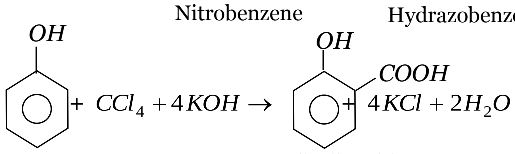
135. (d) Alcohols can not be dried using anhydrous $CaCl_2$ because it forms an addition compound $CaCl_2.4CH_3OH$.

137. (b) 

Presence of methyl group increases electron density at *o*- and *p*- positions. Hence, it undergoes nitration readily.

138. (d) 

Nitrobenzene; Hydrazobenzene

140. (b) 

Salicylic acid

141. (a) $\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethylalcohol}}{2C_2H_5OH} + 2CO_2$

144. (a) $C_2H_5OH + NH_3 \xrightarrow{Al_2O_3} C_2H_5NH_2 + H_2O$

145. (b) $CH_3OH + \frac{1}{2}O_2 \xrightarrow{Cu} HCHO + H_2O$

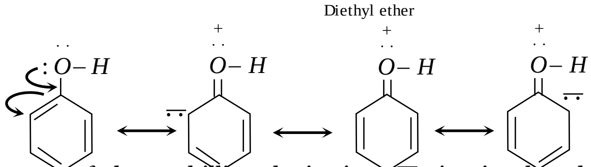
146. (a) $CH_3COOH + C_2H_5OH \rightarrow \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$

147. (a) $\underset{\underset{A}{1^o\text{alcohol}}}{CH_3CH_2OH} \xrightarrow{\text{Oxi.}} CH_3CHO \xrightarrow{\text{Oxi.}} CH_3COOH$

$CH_3CHO \xrightarrow{\text{Ammonical } AgNO_3}$ Silver Mirror

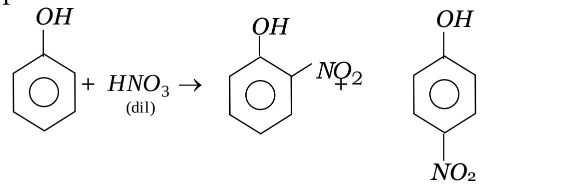
150. (b) $CH_3CH_2-OH + HO-CH_2-CH_3 \xrightarrow[140^oC]{\text{Conc. } H_2SO_4}$

$\underset{\text{Diethyl ether}}{CH_3CH_2-O-CH_2-CH_3} + H_2O$

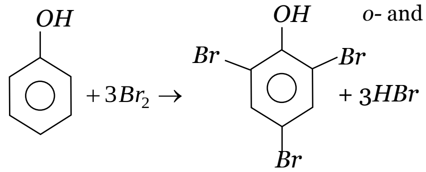
151. (b) 

Rate of electrophillic substitution reaction in phenol is faster than in benzene because presence of $-OH$

group increases electron density at *o*- and *p*-positions.

152. (b) 

o- and *p*- nitrophenol

153. (b) 

2,4,6 – tribromophenol

155. (b) Secondary alcohol on dehydrogenation gives acetone

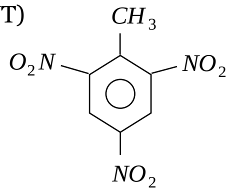
$$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[300^0C]{Cu} CH_3-\underset{\underset{O}{\|}}{C}-CH_3+H_2$$

156. (c) $C_2H_5OH \xrightarrow{NaOH\,/\,I_2} CHI_3$

$CH_3COCH_3 \xrightarrow{NaOH\,/\,I_2} CHI_3$

$CH_3OH \xrightarrow{NaOH\,/\,I_2}$ No reaction.

157. (d) 2,4,6 Trinitro toulene (TNT)



159. (c)

$$\begin{matrix}CH_2-OH\\|\\CH-OH\\|\\CH_2-OH\end{matrix} + 3HNO_3 \xrightarrow[H_2SO_4]{\text{Conc. } H_2SO_4} \begin{matrix}CH_2-ONO_2\\|\\CH-ONO_2\\|\\CH_2-ONO_2\end{matrix} + 3H_2O$$

Glycerol trinitrate

160. (a)

$$\begin{matrix}CH_2-OH\\|\\CH-OH\\|\\CH_2-OH\end{matrix} + \begin{matrix}COOH\\|\\COOH\end{matrix} \xrightarrow[-H_2O]{110^oC} \begin{matrix}CH_2-O-CO-COOH\\|\\CH-OH\\|\\CH_2-OH\end{matrix} \xrightarrow{-CO_2}$$

Glycerol mono-oxolate

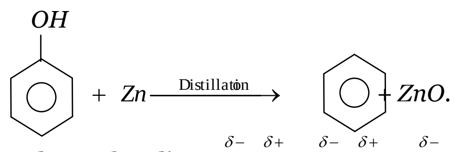
$$\begin{matrix}CH_2-O-CO-H\\|\\CH-OH\\|\\CH_2-OH\end{matrix} \xrightarrow{\text{Hydrolysis}} \begin{matrix}CH_2-OH\\|\\CH-OH\\|\\CH_2-OH\end{matrix} + HCOOH$$

Glycerol mono-formate   Formic acid

163. (b) $C_2H_5OH + CH_3COOH \xrightarrow[\text{Esterification}]{H_2SO_4}$

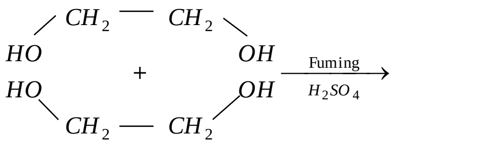
$CH_3COOC_2H_5 + H_2O$

Ethylacetate

165. (a) 

166. (b) Hydrogen bonding : $\overset{\delta-}{O}-\overset{\delta+}{H} \ldots\ldots \overset{\delta-}{O}-\overset{\delta+}{H} \ldots\ldots \overset{\delta-}{O}-\overset{\delta+}{H}$ (with R, H, R attached to the oxygens)

Alcohol   Water   Alcohol

167. (c) 

Ethyleneglycol

168. (b) Tertiary carbonium ion is the most stable and it will be given by dehydration of tertiary alcohol.

169. (d) $CH_3CH_2OH \xrightarrow[\text{bond fission}]{\text{Heterolytic}} CH_3CH_2O^- + H^+$

170. (b) C_2H_5OH is soluble in water due to H-bonding.

173. (b) When ethanol dissolves in water then emission of heat and contraction in volume.

175. (a) Azeotropic distillation method –

Rectified spirit + Benzene + water

↓ Fractional distillation

First fraction at 331.8 K is ternary azeotrope

(H_2O 7.4% + Benzene 74% + alcohol 18.5%)

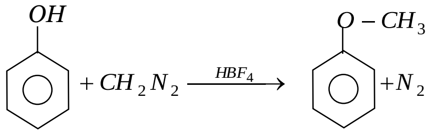
Second fraction 341.2 K is a binary azeotrope

(Benzene 67.7% + Alcohol 32.2%)

Last fraction at 351K is absolute alcohol.

176. (a) $CH_3-O-\boxed{H + C_2H_5}MgBr \rightarrow C_2H_6 + Mg\begin{matrix}Br\\OCH_3\end{matrix}$

Methyl alcohol   Ethylmagnesium bromide   Ethane

177. (c) 

Anisole

180. (c) Alcohol is soluble in water due to H-bonding

$\overset{\delta-}{O}-\overset{\delta+}{H}\cdots\cdot\overset{\delta-}{O}-\overset{\delta+}{H}\cdots\overset{\delta-}{O}-\overset{\delta+}{H}$ (with R, H, R attached to the oxygens)

Alcohol   Water

183. (c) $CH_3CH_2-OH + 2Cl_2 \rightarrow CCl_3-CHO$

Oxidation will occur with chlorination of methyl group.

185. (d) $CH_3CHO \xrightarrow{NaOH/I_2} CHI_3$

$CH_3CH_2OH \xrightarrow{NaOH\,/\,I_2} CHI_3$ Yellow *ppt.*

$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{NaOH\,/\,I_2} CHI_3$

$C_6H_5-CH_2-OH \xrightarrow{NaOH\,/\,I_2}$ No yellow *ppt.*

186. (c) Benzyl alcohol and cyclohexanol are not acidic while phenol and *m*-chlorophenol are acidic due to presence of electron withdrawing groups like $-NO_2$, $-Cl$, $-CN$ increases the acidic character of phenols. Hence, *m*-chlorophenol is more acidic than phenol.

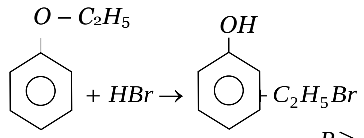
187. (b) Three, these are $CH_3CH_2OCH_2CH_3$ (I), $CH_3OCH_2CH_2CH_3$ (II) and $CH_3OCH(CH_3)_2$ (III). Here I and II, I and III are pairs of metamers.

189. (c) CH_3OCH_3 and $C_2H_5OCH_3$ are gases while $C_2H_5OC_2H_5$ (b.p. 308 K) is low boiling liquid.

190. (a) $C_2H_5OC_2H_5 \xrightarrow[\text{Cleavage of ethers}]{\text{Red } P/HI} 2C_2H_5I \xrightarrow[\text{Reduction}]{\text{Red } P/HI} \underset{\text{Ethane}}{2C_2H_6}$

191. (d) $C_2H_5OC_2H_5 + O_2 \rightarrow CH_3 - \underset{\underset{\text{Ether peroxide}}{O-OH}}{\underset{|}{CH}} - O - C_2H_5$

192. (a) $C_2H_5OC_2H_5 + HI \rightarrow C_2H_5OH + C_2H_5I$

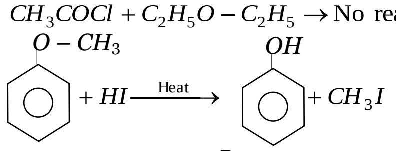
193. (a) 

196. (d) $R-\underset{\underset{H}{|}}{C}=O + R'OH \xrightarrow{\text{Dry } HCl} \frac{R}{H}\!>\!C\!<\!\frac{OH}{OR'} \underset{\text{Dry } HCl}{\overset{R'OH}{\rightleftharpoons}} \underset{\text{Acetal}}{\frac{R}{H}\!>\!C\!<\!\frac{OR'}{OR'}}$

198. (b) $CH_3 - O - CH_3 + 2HI \rightarrow 2CH_3I + H_2O$

199. (b) Only alkyl aryl ethers *e.g.*, $C_6H_5OCH_3$ undergoes electrophilic substitution reactions.

200. (a) $CH_3COCl + C_2H_5O - C_2H_5 \rightarrow$ No reaction

201. (b) 

202. (c) $R-O-R \xrightarrow{BF_3} \underset{\text{Etherate}}{\frac{R}{R}\!>\!\ddot{O}: \rightarrow BF_3}$

203. (d) Due to inter-molecular hydrogen bonding in alcohols boiling point of alcohols is much higher than ether.

205. (b) $CH_3 - OCH_3$ does not have replaceable H – atom.

206. (a) $CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - O - CH_3 + H_2 \rightarrow CH_3I + (CH_3)_3COH$

207. (b) $CH_3CH(OH)CH_2CH_3 \xrightarrow{\text{Conc. } H_2SO_4} \underset{(C_4H_8)}{CH_3CH = CHCH_3}$

$\underset{\text{2-Butanol}}{CH_3CHOHCH_2CH_3} \xrightarrow{[O]} \underset{\text{Butanone}}{CH_3COCH_2CH_3}$

Butanone gives both an oxime and positive iodoform test, therefore, the original compound is 2-butanol.

208. (b) $\underset{\text{Ethyleneglycol}}{\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}} + 2PCl_5 \rightarrow \underset{\text{1, 2 dichloroethane}}{\begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix}} + 2POCl_3 + 2HCl$

209. (b) C_2H_5OH (ethanol) is a very weak acid hence it does not react with $NaOH$. However it reacts with metallic sodium.

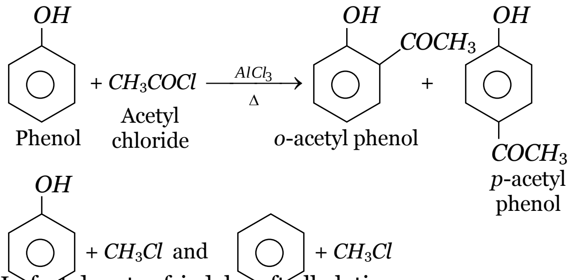
210. (b) Methanol has high boiling point than methyl thiol because there us intermolecular hydrogen bonding in methanol and no hydrogen bonding in methyl thiol.

211. (a) $\underset{\text{Glycerol}}{\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix}} + \underset{\text{oxalic acid}}{\begin{matrix} COOH \\ | \\ COOH \end{matrix}} \xrightarrow{110°C} \underset{\text{Glycerol acid oxalate}}{\begin{matrix} CH_2-O-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix}}$

$\xrightarrow{-CO_2} \underset{\text{Glycerol monoformate}}{\begin{matrix} CH_2-O-\overset{O}{\overset{\|}{C}}-H \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix}}$

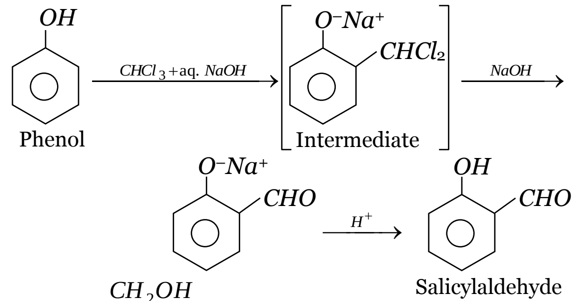
212. (a) Formation of a yellow precipitate on heating a compound with an alkaline solution of iodine is known as iodoform reaction. Methyl alcohol does not respond to this test. Iodoform test is exhibited by ethyl alcohol, acetaldehyde, acetone, methyl ketone and those alcohols which possess $CH_3CH(OH)-$ group.

213. (b) In friedal craft acylation, aromatic compounds such as benzene, phenol etc. undergo acylation with CH_3COCl in the presence of anhydrous $AlCl_3$ and gives ortho and para derivatives. Intermediate is $CH_3C^+ = O$ (acylium ion) of this reaction.



In fact denotes friedel craft alkylation.

214. (a) This reaction is known as Reimer Tiemann reaction.



215. (a) $\underset{\text{oxalic acid}}{\begin{matrix} COOH \\ | \\ COOH \end{matrix}} + \underset{\text{Glycerol}}{\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix}} \xrightarrow{380\ K} \underset{\text{Formic acid}}{HCOOH} + CO_2\uparrow$

$\underset{\text{oxalic acid}}{\begin{matrix} COOH \\ | \\ COOH \end{matrix}} + \underset{\text{Glycerol}}{\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix}} \rightarrow \underset{\text{Dioxalin}}{\begin{matrix} CH_2OCO \\ | \quad | \\ CHO\ CO \\ | \\ CH_2OH \end{matrix}} \xrightarrow{-2CO_2} \underset{\text{Allylalcohol}}{\begin{matrix} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{matrix}}$

Thus at 530 K allyl alcohol is formed.

216. (c) $\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} \xrightarrow[-H_2O]{\text{anh. } ZnCl_2} \underset{\text{Acetaldehyde}}{CH_3CHO}$

217. (d) Ethyl alcohol give positive iodoform test (*i.e.* yellow ppt. with I_2 and $NaOH$)

$$CH_3CH_2OH + 4I_2 + 6NaOH \rightarrow \underset{\text{yellow ppt.}}{CHI_3} + 5NaI + CH_3COONa + 3H_2O$$

218. (d) Tertiary alcohols react fastest with hydrogen halides 2 methyl propan-2-ol is a tertiary alcohol.

219. (a) When benzoic acid reacts with ethyl alcohol in the presence of sulphuric acid ethyl benzoate is formed. This is known as esterification.

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + \underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow{H_2SO_4} \underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5} + \underset{\text{water}}{H_2O}$$

220. (a) $\underset{\text{Phenyl magnesium bromide}}{\overset{\ominus\ \oplus}{PhMgBr}} + H - O - C(CH_3)_3 \rightarrow Ph - H + (CH_3)_3C - OMgBr$

221. (b) $Mg + CH_3I \xrightarrow{\text{Dry ether}} CH_3MgI$

222. (a) Ethyl alcohol on dehydration with conc. H_2SO_4 at $170°C$ gives ethylene.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow[\text{conc. } H_2SO_4]{170°C} \underset{\text{Ethylene}}{CH_2 = CH_2} + H_2O$$

223. (d) $\underset{\text{2 butanol}}{CH_3 - CH_2 - \underset{|}{\overset{OH}{CH}} - CH_3} \xrightarrow{\text{Dehydration}}$

$$\underset{\text{1 butene (Major product)}}{CH_3 - CH_2 - CH = CH_2} + \underset{\text{2 butene}}{CH_3 - CH = CH - CH_3}$$

224. (b) Fats are esters of higher fatty acids with glycerol, hence on alkaline hydrolysis they give back glycerol and sodium or potassium salt of acid (this is called soap).

$$\underset{\text{Fat}}{\begin{matrix} CH_2OCOR \\ | \\ CHOCOR \\ | \\ CH_2OCOR \end{matrix}} + 3NaOH \rightarrow \begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix} + \underset{\text{(Soap)}}{3RCOONa}$$

225. (c) $CH_3 - \overset{OH}{\underset{CH_3}{C}} - CH_3 \xrightarrow[300^0C]{Cu} CH_3 - \overset{CH_3}{C} = CH_2 + H_2O$

227. (c) $CH_3 - C(OH)_3 \rightarrow CH_3 - \overset{O}{\overset{\|}{C}} - OH + H_2O$

If two or more $-OH$ groups are present on carbon atom then it immediately looses water molecule and forms acid or aldehyde.

Two $-OH$ groups on the same carbon aldehyde is formed

$$\underset{\text{Unstable}}{R - CH(OH)_2} \xrightarrow{-H_2O} \underset{\text{Aldehyde}}{R - \underset{H}{\underset{|}{C}} = O}$$

Three $-OH$ groups on the same carbon acid is formed.

$$R - C(OH)_3 \xrightarrow{-H_2O} \underset{\text{acid}}{R - C \overset{OH}{\underset{O}{\lessgtr}}}$$

228. (d) H_2SO_4, Al_2O_3 and H_3PO_4 all can act as dehydrating agent.

229. (b) $\underset{\text{Glycerol}}{\begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix}} + 3HI \xrightarrow{-3H_2O} \left[\begin{matrix} CH_2-I \\ | \\ CH - I \\ | \\ CH_2-I \end{matrix}\right] \xrightarrow{-I_2} \underset{\text{Allyliodide}}{\begin{matrix} CH_2I \\ | \\ CH \\ \| \\ CH_2 \end{matrix}}$

230. (a) $\underset{\text{2 Methyl butanol}}{H_3C - CH_2 - \underset{CH_3}{\underset{|}{CH}} - CH_2 - OH} \xrightarrow[\text{dehydration}]{\text{Conc. } H_2SO_4}$

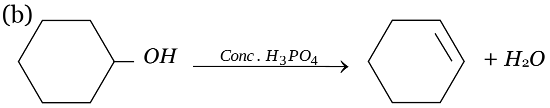
$$\underset{\text{2-Methyl butene Major product}}{H_3C - H_2C - \underset{CH_3}{\underset{|}{C}} = CH_2}$$

233. (c) $CH_3CHO \xleftarrow[\Delta]{Cu} CH_3CH_2OH \xrightarrow[\Delta]{Al_2O_3} CH_2 = CH_2$

234. (b) $\underset{\text{Acetophenone}}{C_6H_5 - \overset{O}{\overset{\|}{C}} - CH_3} \xrightarrow{LiAlH_4} \underset{2^o \text{ alcohol}}{C_6H_5 - \overset{O}{\overset{\|}{CH}} - CH_3}$

235. (d) $C_2H_5OH \xrightarrow[170^oC]{Conc\ H_2SO_4} C_2H_4 + H_2O$

236. (b)



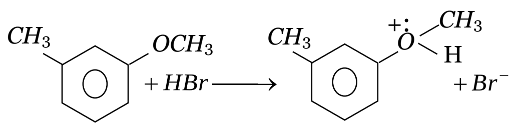
Because conc. H_3PO_4 acts as a dehydrating agent.

238. (c) $C_2H_5OH \xrightarrow[I_2]{NaOH} CHI_3$ yellow *ppt.*

$$CH_3OH \xrightarrow[I_2]{NaOH} \text{No reaction}$$

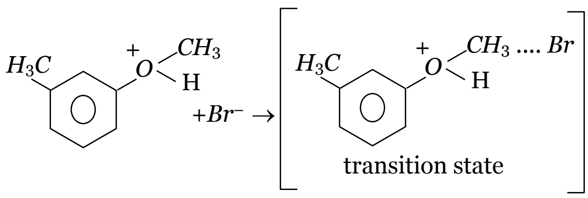
239. (d) It is not acetaldehyde or acetone as does not react with hydrazine. It is not CH_3OH as does not react with *Na*.

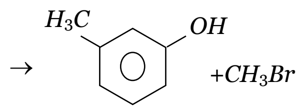
240. (a) The ether molecule gets protonated by the hydrogen of the acid to form protonated ether or oxonium salt.



Protonated ether

The protonated ether undergoes nucleophilic attack by halide ion (X^-) and forms alkyl alcohol and alkyl halide

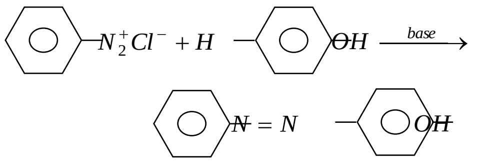




241. (a) $H_3C-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH \xrightarrow[ZnCl_2]{conc.HCl} H_3C-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-Cl$

t-butyl alcohol → t-butyl chloride

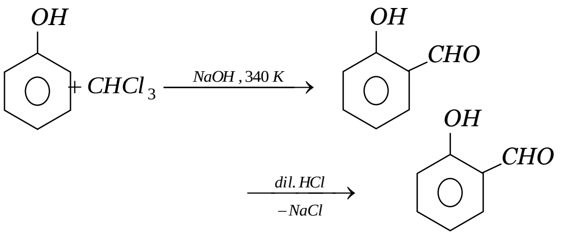
242. (a)



p-hydroxy azobenzene
(orange dye)

This is an example of coupling reaction

243. (b) Reimer-Tiemann reaction involves the carbon carbon bond formation.



salicylaldehyde

244. (a) This is Reimer-Tiemann reaction where the electrophile is dichlorocarbene $(:CCl_2)$ generated from chloroform by the action of a base.

$OH^- + CHCl_3 \rightleftharpoons HOH + :CCl_3^- \rightarrow Cl^- + :CCl_2$

245. (a) Phenols are much more acidic than alcohols but less so than carboxylic acids or even carbonic acid. This is indicated by the values of ionisation constants. The relative acidity follows the order:

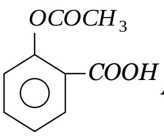
$K_a \;\; \underset{RCOOH}{10^{-5}} > \underset{H_2CO_3}{10^{-7}} > \underset{C_6H_5OH}{10^{-10}} > \underset{HOH}{10^{-14}} > \underset{ROH}{10^{-18}}$

Uses of alcohol, Phenol and Ethers

1. (a) $\text{Glycerol} \xrightarrow{HNO_3} \text{Glyceryl trinitrate} \xrightarrow[\text{Kieselguhr}]{\text{Absorbed on}} \text{Dynamite}$
+
Glyceryl dinitrate

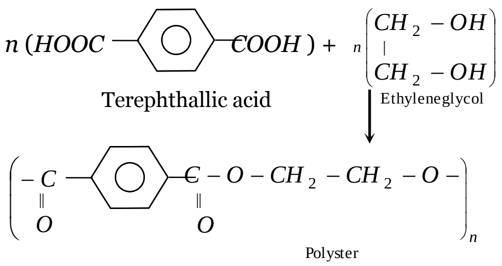
3. (d) $C_2H_5OH \xrightarrow[\text{Acetobacter aceti}]{\text{air}} CH_3COOH$

4. (b)



Aspirin or Acetyl salicylic acid.

6. (a)



9. (a) Ethylene glycol is added to lowering down the freezing point of water so that it does not freeze.

10. (b) Power alcohol 80% petrol and 20% ethyl alcohol

12. (d) $\text{Glucose} \xrightarrow[\text{(From yeast)}]{\text{Zymase}} 2C_2H_5OH + 2CO_2$

16. (d) Glycerol is not used as an antiseptic agent.

18. (c) Denaturing can also be done by adding 0.5% pyridine, petroleum naptha, $CuSO_4$ etc.

20. (b) A mixture of glyceryl trinitrate and glyceryl dinitrate when absorbed on kieselgurh is called dynamite.

22. (c) Tonics have generally contains ethyl alcohol.

23. (c) Due to presence of methyl alcohol in liquor.

24. (d) An anaesthetic.

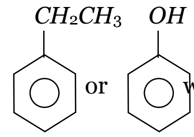
25. (c) Groundnut oil.

27. (a) $\underset{\text{Ethyl butyrate}}{C_3H_7COOC_2H_5} \xrightarrow{Na/C_2H_5OH} \underset{\text{Butyl alcohol}}{C_3H_7CH_2OH}$

28. (a) Glycol is used as an antifreeze for automobile radiators because it lowers down the melting point of water.

Critical Thinking Questions

1. (c)



will undergoes a Friedel Craft's alkylation on ortho or para position because of more electron density.

2. (c) $CH_2=CH_2 + RMgI \rightarrow \underset{OMgI}{\underset{|}{CH_2}}-CH_2-R \xrightarrow{HOH}$

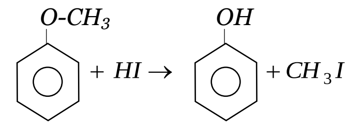
$MgI(OH) + R-CH_2-CH_2-OH$

3. (c) The liquids which decompose at its boiling point can be purified by vacuum distillation. Glycerol which decomposes at its boiling point (–563K) can be distilled without decomposition at 453K under 12mm Hg pressure.

4. (a) Liebermann's reaction.

5. (a) 1^o alcohol > 2^o alcohol > 3^o alcohol
Boiling point of alcohols decreases as the number of branches increases.

6. (c)



7. (c) $3CH_2=CH_2 + 2KMnO_4 + 4H_2O \rightarrow$

$3\underset{\text{Glycol}}{\begin{matrix} CH_2-OH \\ | \\ CH_2-OH \end{matrix}} + 2KMnO_2 + 2KOH$

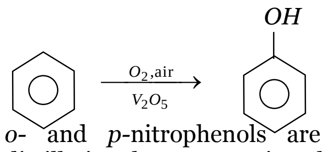
8. (c) Correct order of dehydration in alcohols 3° > 2° > 1°.

9. (a) Oxiran is ethylene oxide, CH_2-CH_2 (bridged by O)

10. (c) $6CH_3-CH=CH_2 + B_2H_6 \xrightarrow{H_2O_2}$

$CH_3-CH_2-CH_2OH$

11. (d) Distinction between primary, secondary and tertiary alcohol is done by all three methods : oxidation, Victormeyer and Lucas test.

12. (b) 

13. (a) *o*- and *p*-nitrophenols are separated by steam distillation because *o*-nitrophenol is steam volatile while *p*-isomer is not.

14. (b) Benzoic acid.

15. (a) $R-O-R' \xrightarrow{O_2\,/\,\text{light}}$

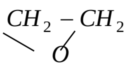
$$C_2H_5-O-CH(CH_3)-O-OH$$

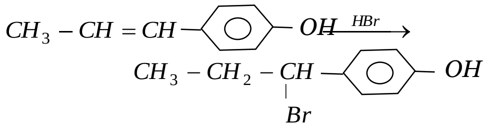
16. (d) $CH_3OH + CH_3OH \xrightarrow{H_2SO_4(Conc)} CH_3OCH_3$

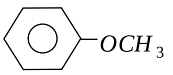
$CH_3OH + C_2H_5OH \xrightarrow{H_2SO_4(Conc)} CH_3OC_2H_5$

$C_2H_5OH + C_2H_5OH \xrightarrow{H_2SO_4(Conc)} C_2H_5OC_2H_5$

17. (b) IV > III > I > II.

18. (a) Cyclic ethers are called epoxides. 

19. (b) 

20. (c)  on $KMnO_4$ oxidation does not give benzoic acid.

21. (c) Chromic anhydride in glacial acetic acid is the best reagent to convert pen-3-en-2-ol into pent-3-in-2-one.

22. (a) $-\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- \underset{}{\overset{H^+}{\rightleftharpoons}} -\underset{H}{\overset{|}{C}}-\underset{^+OH_2}{\overset{|}{C}}- \overset{-H_2O}{\rightleftharpoons}$
Protonated alcohol

$-\underset{H}{\overset{|}{C}}-\overset{|}{C}^{+}- \overset{-H^+}{\rightleftharpoons} \overset{|}{C}=\overset{|}{C}-$
carbonium ion

In all cases intermediate is carbonium ion, and there may be 1, 2-hydride or 1, 2-methyl shift to form more stable carbonium ion.

Assertion & Reason

3. (a) It is correct that phenol is more reactive than benzene.

4. (c) It is correct that sodium phenoxide (sodium salt of phenol) and CO_2 on heating from sodium salicylate. This is known as Kolbe's reaction. Ethanol does not respond to this reaction. Therefore, assertion is true. But the reason that phenoxide ion is more basic than ethoxide ion is not correct.

5. (c) Lucas reagent is a mixture of anhydrous $ZnCl_2$ and coc. HCl is used for the distinction of monohydric alcohol. Tertiary alcohols on addition produce a precipitate immediately while secondary alcohols produce ppt. after 5 minutes. Primary alcohols do not produce any precipitate. Therefore, assertion is true but reason is false.

6. (a) Phenols on treatment with neutral $FeCl_3$ solution produce purple colour, resorcinol contains phenolic group hence in treatment with $FeCl_3$ solution it gives purple colour. Here both assertion and reason are correct and reason is a correct explanation of assertion.

7. (b) Glycerol is purified by distillation under reduced pressure because it decomposes on heating below its melting point. It is a trihydric alcohol. Here, both assertion and reason are true but reason is not a correct explanation of assertion.

8. (a) Alcohols and phenols can be distinguished by treating with *NaOH*. Phenols react with *NaOH* to produce sodium phenoxide because phenols are acidic and alcohols are neutral. Both assertion and reason are true and reason is correct explanation.

9. (b) Zeolites are shape-selective porous solid acid catalysts, their catalytic activity originates from the presence of highly acidic $Al-O(H)-Si$ hydroxyl in the framework.

10. (a) $C_6H_5CH_2OCH_3 \xrightarrow{H^+} C_6H_5CH_2^+ + CH_3OH$

$$\xrightarrow{I^-} C_6H_7CH_2I$$

This can be explained on the basis of S_N1 mechanism. The carbonium ion produced being benzylium ion. Since this type is more stable than alkylium ion.

11. (c) Lower the value of *pKa*, more acidic will be the compound. Acetic acid is more acidic than phenol. This indicates that carboxylate ion should be more stable than the phenoxide ion and it is clear that carboxylate ion has more equivalent resonating structures than the phenoxide ion.

12. (a) The conversion of sugar into ethyl alcohol by yeast is called alcoholic fermentation.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

13. (b) The tendency to show *H*-bonding decreases with increasing hydrophobic character of carbon chain. The hydrophobic character of carbon chain increases with he length of carbon chain.

14. (e) Ethyl alcohol forms azeotropic mixture with water which distils with unchanged composition (about 75% ethanol) and thus absolute alcohol cannot be obtained by simple distillation.

15. (e) The dehydration of *t*-butanol involves the formation of 3° carbocation which is more stable than 1° carbocation in *n*-butanol. Thus, tendency to lose water becomes more in *t*-butanol.

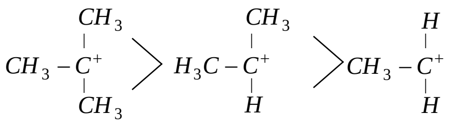
16. (c) A mixture of conc. HCl + anhyd. $ZnCl_2$ is called Lucas reagent.

17. (e) Electron withdrawing groups such as $-NO_2$, – CN, – X, increase the acidity. Greater the number of electron withdrawing groups more is the acidic character *i.e.* 2, 4, 6-trinitrophenol is more acidic than 4-nitrophenol.

18. (b) Phenols cannot be converted into esters by direct reaction with carboxylic acids since phenols are less nucleophilic than alcohols.

19. (b) Alcohol which forms the more stable carbocation undergoes dehydration more readily. Since tert-butyl alcohol forms more stable tert-butyl cation, therefore, it undergoes dehydration most readily than propanol.

20. (e) The ease of dehydration of alcohols can be explained on the basis of stability of the intermediate carbocation. Greater the stability of the carbonation formed, greater will be the rate of reaction. The order of stability of carbocation formed is



This is due to the electron releasing (+*I*) effect of the alkyl group. Therefore the ease of dehydration of alcohols follows the order.

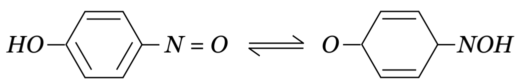
Tertiary > secondary > primary alcohol.

21. (c) Benzoylation in phenols is usually carried out in the presence of aqueous $NaOH$ because benzoyl chloride is not readily hydrolysed by alkalies.

22. (b) In phenols, the lone pairs of electrons on the oxygen atom are delocalised over the benzene ring due to resonance and hence are not easily available for protonation. On the other hand, in alcohols, the lone pairs of electrons on oxygen atom are localized due to the absence of resonance and hence are easily available for ptotonation.

23. (c) *p*-Nitrophenolate ion is more stable than phenolate ion.

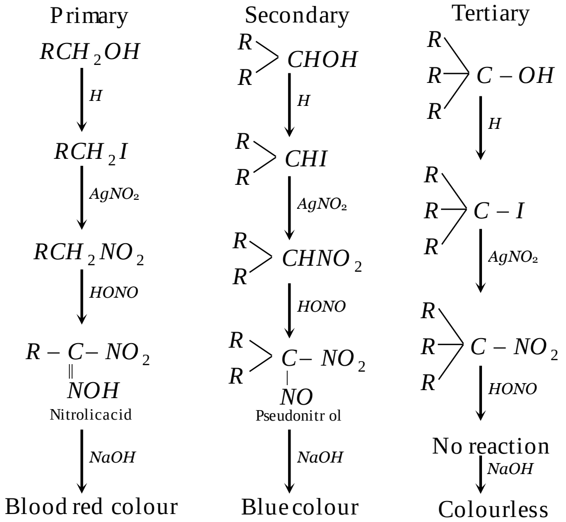
24. (b) Nitrous acid gives nitrosomine ion (NO^+) which attacks phenol at less hindered *p*-position of form *p*-nitrosophenol which is a tautomer of *p*-benzoquinone monoxide.



p-Nitrosophenol *p*-Benzoquinone monoxime

25. (c) Nucleophilic attack of phenolate ion through the ortho-carbon atom occurs on CCl_4 to form an intermediate which on hydrolysis gives salicylic acid.

26. (a) Victor-Meyer's test is used to distinguish primary, secondary and tertiary alcohols.



28. (b) Removal of two molecules of water gives a product which tautomerises to yield acrolein-an α, β-unsaturated aldehyde.

29. (b) Depending upon whether the alkyl halide and the alkoxide ion carry the same or different alkyl groups both symmetrical and unsymmetrical ethers can be prepared by Williamsons synthesis.

30. (c) Ethers being Lewis bases form etherates with Lewis acids.

31. (d) $(CH_3)_3CONa$ and CH_3CH_2Br react to form $(CH_3)_3C-O-CH_2CH_3$. Good yields of ethers are obtained when primary alkyl halides are treated with alkoxides derived from any alcohol. 1°, 2° or 3°.