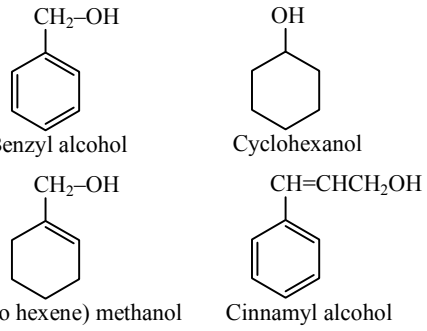
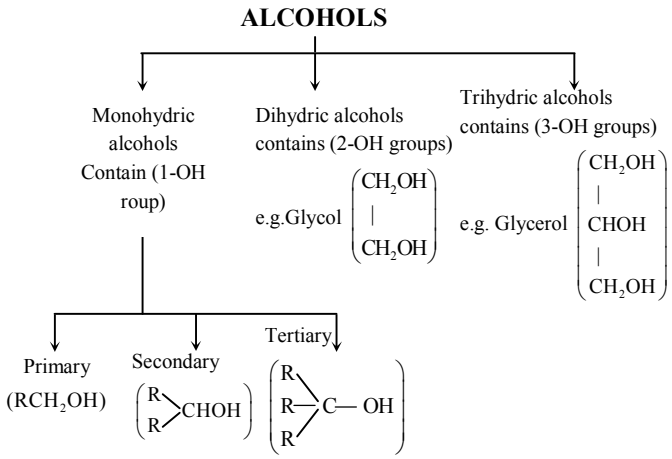
19 Alcohols, Phenols and Ethers

QUICK LOOK

Alcohols: Alcohols are compounds of the general formula ROH, where R is alkyl or substituted alkyl group. The group may be open chain or cyclic, it may contains double bond, a halogen atom, an aromatic ring or additional hydroxyl groups, *e.g.* $\underset{\text{Butanol-1}}{CH_3CH_2CH_2CH_2OH}$



Alcohols can be classified as,



Monohydric Alcohols: Preparation

- **By oxymercuration - demercuration reaction of alkene:**

$$CH_3-CH=CH_2+(CH_3COO)_2Hg+H_2O\xrightarrow[CH_3COOH]{THF}$$

$$\left[CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle HgOCOCH_3}{\underset{|}{CH_2}}\right]\xrightarrow[-1/2B_2H_6]{NaBH_4/OH^-}$$

$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3+Hg+CH_3COO^-$$

2–propanol

Note: It is fast and convenient. The addition of water to an alkene is anti-Markownikoff and free from rearrangement.

- **Hydroboration of Alkene**

$$\underset{\text{Propene}}{3CH_3-CH=CH_2}+\underset{\text{Diborane}}{\frac{1}{2}B_2H_6}\longrightarrow\underset{\text{Tripropyl boron}}{(CH_3-CH_2-CH_2)_3B}\xrightarrow[OH^-/H_2O]{3H_2O_2}$$

$$3CH_3-CH_2-\underset{\text{1–propanol}}{CH_2}-OH+H_3BO_3$$

Note: In this reaction addition of water to an alkene is syn, anti-Markownikoff and free from rearrangement.

- **Hydrolysis of ethers:** $C_2H_5-O-C_2H_5+H_2O\xrightarrow[\Delta]{dil.H_2SO_4}2C_2H_5OH$
- By reaction of Grignard reagent with formaldehyde/ other aldehydes/ ketones

(a) When Grignard reagent reacts with HCHO, it forms primary alcohol.

$$H-\underset{\displaystyle H}{\underset{|}{C}}=O+RMgX\longrightarrow H-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle R}{\overset{|}{C}}}}-OMgX$$

$$\longrightarrow H-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle R}{\overset{|}{C}}}}-OH+Mg\begin{matrix}X\\OH\end{matrix}$$

(b) **Oxirane** on reaction with Grignard reagent also forms primary alcohol.

$$\triangle O + RMgX\longrightarrow RCH_2CH_2OMgX$$

$$\longrightarrow RCH_2CH_2OH+Mg\begin{matrix}X\\OH\end{matrix}$$

(c) Any aldehyde except formaldehyde when treated with Grignard reagent forms secondary alcohol.

$$R'-\underset{\displaystyle H}{\underset{|}{C}}=O+RMgX\longrightarrow R'-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle R}{\overset{|}{C}}}}-OMgX$$

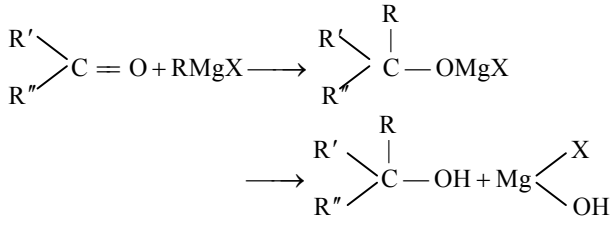
$$\longrightarrow R'-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle R}{\overset{|}{C}}}}-OH+Mg\begin{matrix}X\\OH\end{matrix}$$

(d) When 2-alkyl oxirane reacts with Grignard reagent, secondary alcohol is formed. The ring is opened from least hindered site.

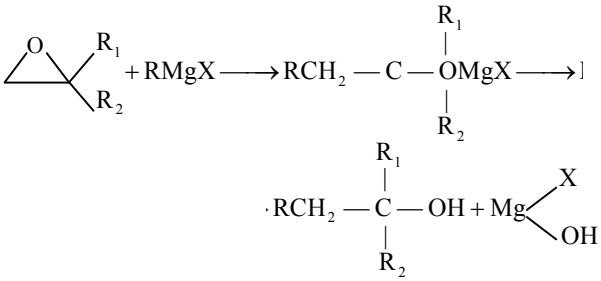
$$\overset{3}{\underset{2}{\triangle}}\overset{1}{O}+RMgX\longrightarrow\overset{\displaystyle CH_3}{\overset{|}{}}RCH_2CH_2OMgX$$

$$\longrightarrow RCH_2-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-OH+Mg\begin{matrix}X\\OH\end{matrix}$$

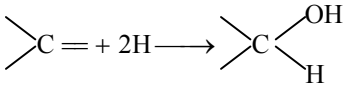
(e) When ketone reacts with Grignard reagent, it forms tertiary alcohol.



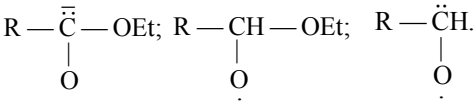
(f) When 2, 2-dialkyl oxirane reacts with Grignard reagent, it forms tertiary alcohol.

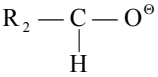


- **By reduction of carbonyl compounds**

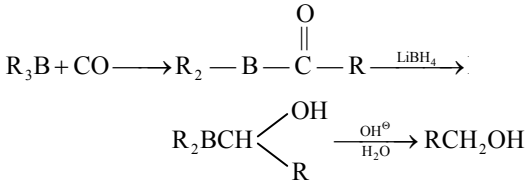


The reduction can be carried out by using H_2 /catalyst like Ni, Pt, Pd, $LiAlH_4$, $NaBH_4$, NaH, LiH. When the reduction is carried out by using metal/solvent combination it is known as Bouveault blanc recduction. The intermediates are:



In case of metal hydride the reaction intermediate is 

- **By hydrolysis of ester :** $R_1COOR_2+KOH \longrightarrow R_1COOK + R_2OH$
- **By reaction of alkyl boride with CO**



- **By reaction of primary amines with nitrous acid**

$RNH_2 + HNO_2 \longrightarrow ROH + N_2 + H_2O$

- **From glucose**: $C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2CH_3CH_2OH + 2CO_2$

- **Industrial method for methanol and ethanol are** as follows:

$CH_4 + H_2O \xrightarrow{\text{Heat}} CO + 3H_2; CO + 2H_2 \xrightarrow[400°C, 200atm]{ZnO+CrO_3} CH_3OH$

for ethanol we take ethylene obtained from petroleum :

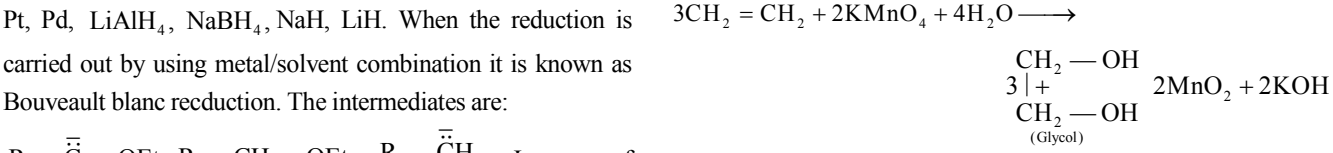
$CH_2 = CH_2 + H_2O(\text{steam}) \xrightarrow[300-350°C]{H_3PO_4} CH_3CH_2OH$

It is an Oxo process.

- Primary, Secondary and Tertiary alcohols can be distinguished by Victor Meyer's Method:

Dihydric Alcohol /Glycol (Ethane – 1, 2- Di-Ol)

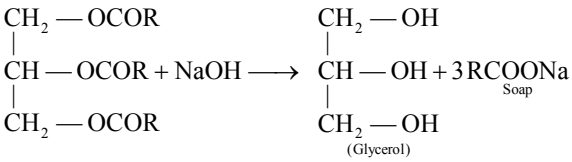
Preparation



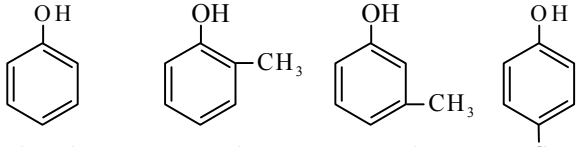
Trihydric Alcohol Glycerol (Propan - 1, 2, 3 - Triol)

Preparation

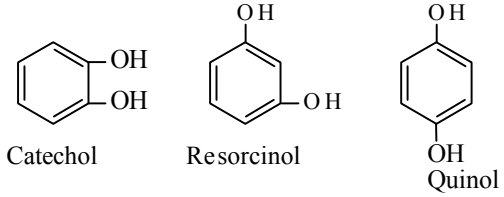
By saponification of oils and fats



Phenols: Phenols are the organic compounds in which –OH group is directly linked to aromatic ring system. The simplest formula of such compound is phenol (C_6H_5OH). Structure of some common phenols is as follows:

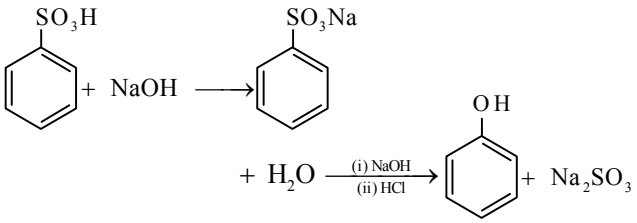


Phenol o-Cresol m-Cresol p-Cresol

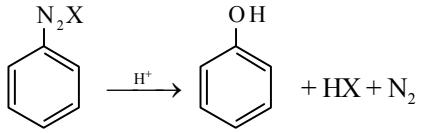


Catechol Resorcinol Quinol

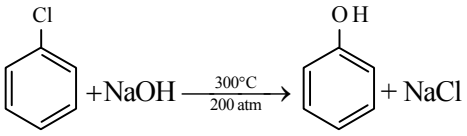
Preparation: (1) Phenols can be prepared by reaction of benzene sulphonic acid with NaOH.



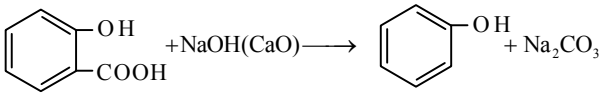
(2) Phenols can also be obtained by warming diazonium salt solution with hot dilute acid solution.



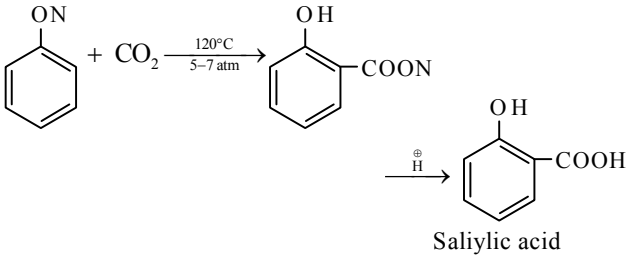
(3) Phenols can be prepared from aryl halides,



(4) By reaction of phenolic acid with soda lime.

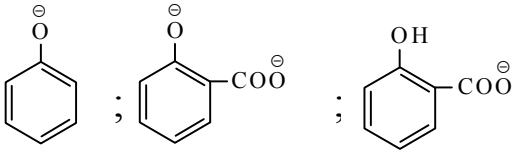


Kolbe Reaction or Kolbe-schmidt Reaction: When sodium phenoxide reacts with CO_2 at 120°C under 5-7 atmosphere followed by acidification with $\overset{\oplus}{H}$, it forms salicylic acid.

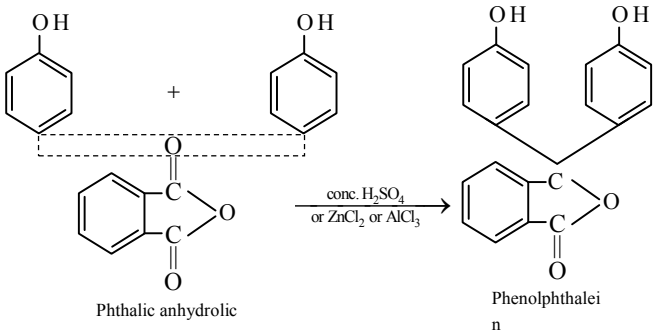


Saliylic acid

The reaction intermediate (s) are:

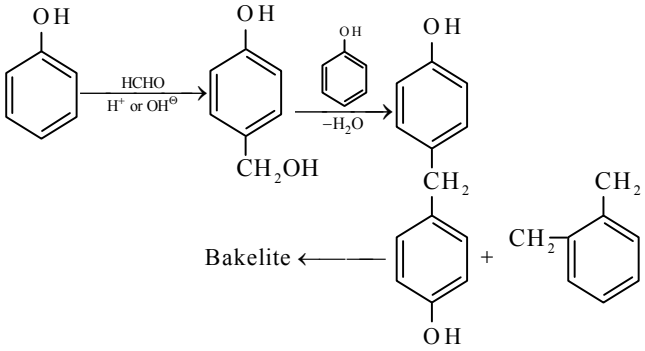


Phthalein Reaction



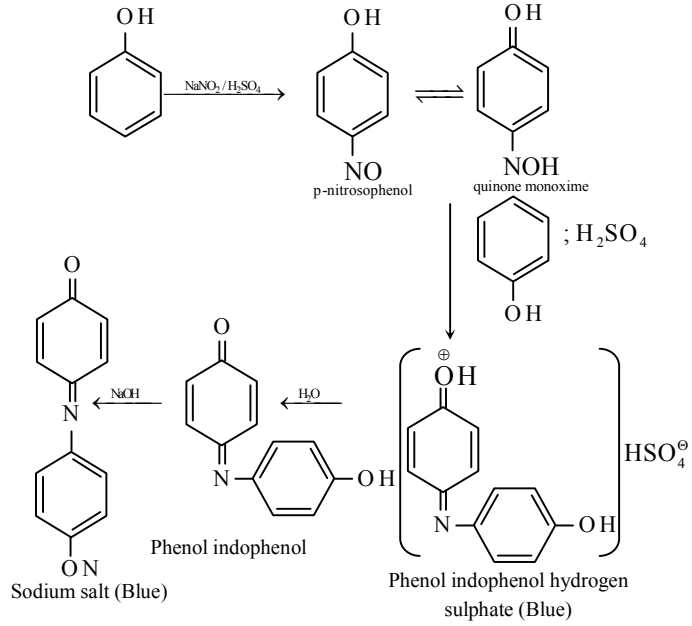
note that H para to OH is removed.

Ledrer-manasse Reaction: When phenol reacts with formaldehyde in the presence of acid or alkali, it forms bakelite, a thermostat polymer.

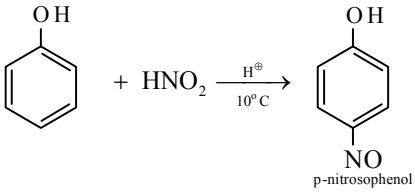


Liebermann's Nitroso Reaction

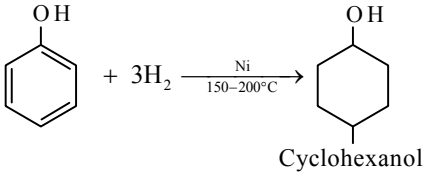
Phenol $\xrightarrow{NaNO_2/\text{conc. } H_2SO_4}$ deep green or blue colour $\xrightarrow{H_2O}$ Red $\xrightarrow{NaOH}$ green or blue colour. The reactions are as follows:



Nitrosation:

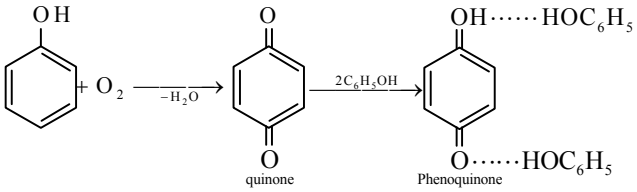


Hydrogenation:

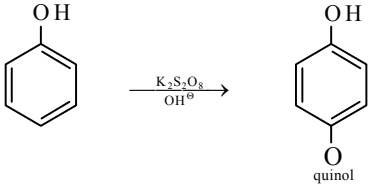


Oxidation

Phenols turn pink or red or brown when exposed to air and light due to slow oxidation. The exact nature of these oxidation products is not known; but probable products are quinones and phenoquinones.



When phenols is oxidised with potassium persulphate in alkaline solution, it forms quinol and the reaction is known as Elbs persulphate oxidation.

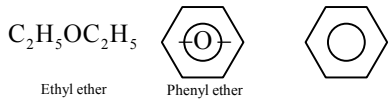


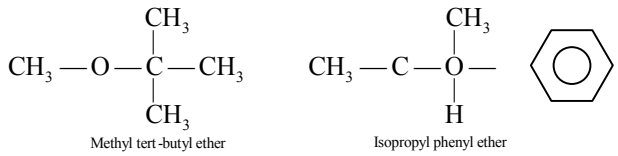
Structure and Nomenclature of Ethers

Ethers are compounds of the general formula

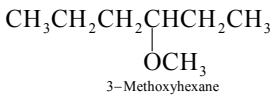
R–O–R, Ar–O–R, or Ar – O –Ar.

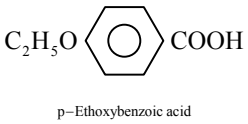
To commonly name ethers we usually name the two groups that are attached to oxygen, and follow these names by the word ether:

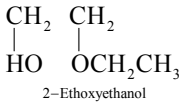




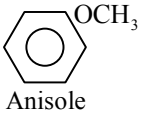
If one group has no simple name, the compound may be named as an alkoxy derivative:







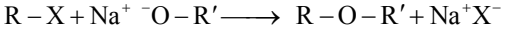
The simplest aryl alkyl ether has the special name of anisole.



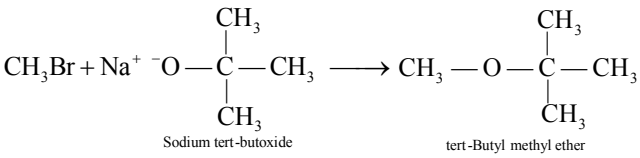
If the two groups are identical, the ether is said to be symmetrical (*e.g.,* diethyl ether, diphenyl ether), if different, unsymmetrical (e.g., methyl tert-butyl ether, anisole).

Preparation of Ethers

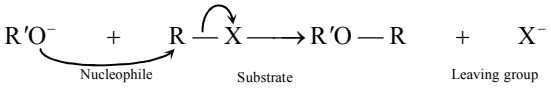
In the laboratory, the Williamson synthesis of ethers can be used to make unsymmetrical ethers as well as symmetrical ethers. In the Williamson synthesis an alkyl halide (or substituted alkyl halide) is allowed to react with a sodium alkoxide.



Example

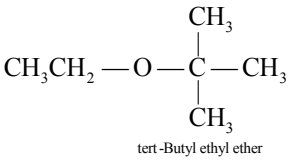


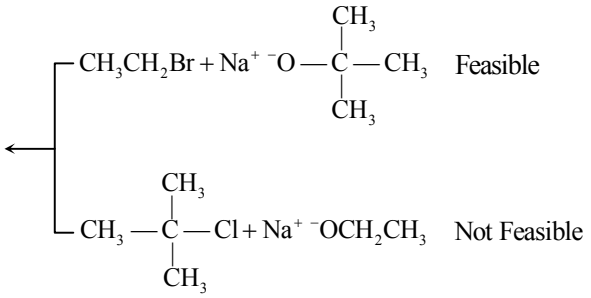
Reaction involves nucleophilic substitution of alkoxide ion for halide ion; it is strictly analogous to the formation of alcohols by treatment of alkyl halides with aqueous hydroxide.



Since alkoxides and alkyl halides are both prepared from alcohols, the Williamson method ultimately involves the synthesis of ether from two alcohols.

If we wish to make unsymmetrical dialkyl ether, we have a choice of two combinations of reagents; one of these is nearly always better than the other. In the preparation of tert-butyl ethyl ether, for example, the following combinations are conceivable:



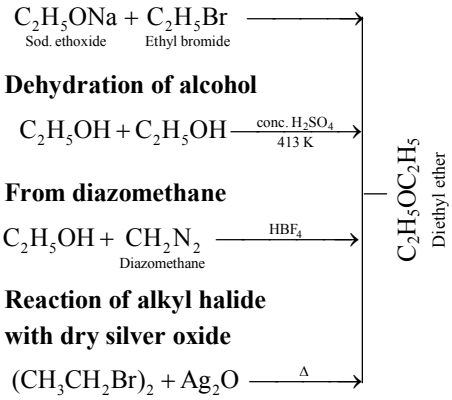


Which do we choose? Alkoxides are not only nucleophiles, but also strong bases which tend to react with alkyl halides by elimination, to yield alkenes. Whenever we are trying to carry out nucleophilic substitution, one must be aware of the danger of a competing elimination reaction. The tendency of alkyl halides to undergo elimination is $3° > 2° > 1°$.

In the above example, the use of the tertiary halide is rejected as it would be expected to yield mostly or all elimination product; hence the other combination is used. Ethers are the alkoxy derivatives of alkanes with general formula $R\,OR'$. If R and R' are same they are simple ethers while If R and R' are different they are mixed ethers.

Preparation of Ethers

Willlamson's synthesis



Dehydration of alcohol

$$C_2H_5OH + C_2H_5OH \xrightarrow[413\ K]{conc.\ H_2SO_4} C_2H_5OC_2H_5$$

Diethyl ether

From diazomethane

$$C_2H_5OH + CH_2N_2 \xrightarrow{HBF_4} C_2H_5OC_2H_5$$

Diazomethane — Diethyl ether

Reaction of alkyl halide with dry silver oxide

$$(CH_3CH_2Br)_2 + Ag_2O \xrightarrow{\Delta} C_2H_5OC_2H_5$$

Diethyl ether

Reactions of Ethers Cleavage by Acids

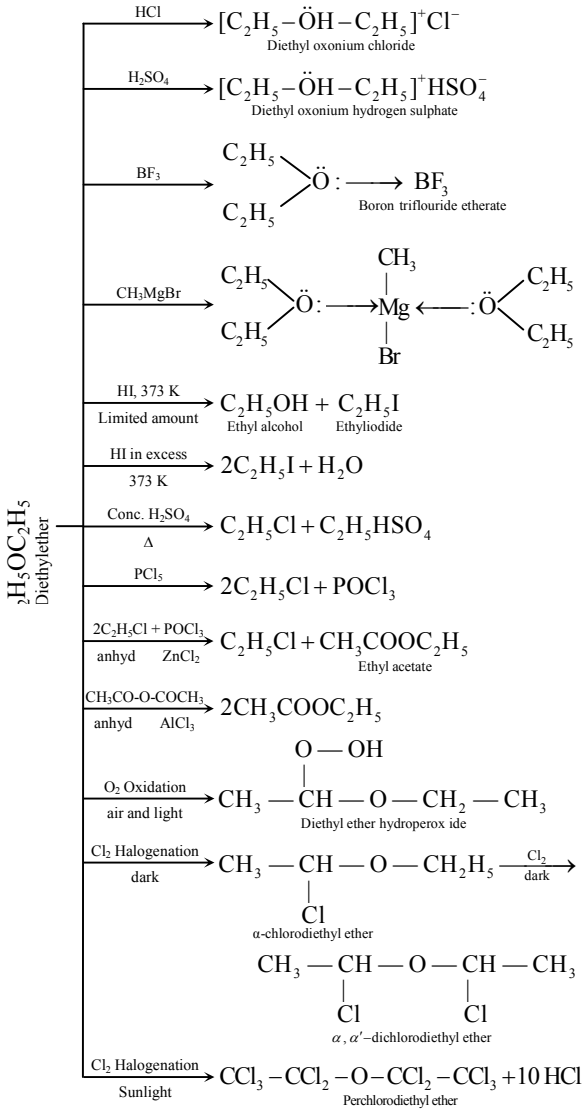
Ethers are comparatively unreactive compounds. The ether linkage is quite stable toward bases, oxidizing agents, and reducing agents. In so far as the ether linkage itself is concerned, ethers undergo just one kind of reaction, cleavage by acids:

$$R-O-R'HX \longrightarrow R-X+R'-OH \xrightarrow{HX} R'-X$$

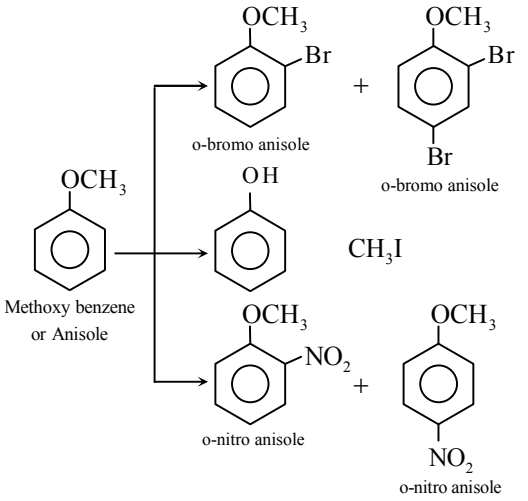
Reactivity of HX: HI > HBr > HCl

Cleavage takes place only under quite vigorous conditions: concentrated acids (usually HI or HBr) and high temperatures.

Chemical Properties



Reactions of Aromatic Ethers



MULTIPLE CHOICE QUESTIONS

Structure and Nomenclature of Ethers

1. The reaction of ethylene glycol with PI_3 gives:

a. ICH_2CH_2I **b.** $CH_2 = CH_2$

c. $CH_2 = CHI$ **d.** $ICH = CHI$

2. The compound 'A' when treated with ceric ammonium nitrate solution gives yellow ppt. The compound 'A' is?

a. Alcohol **b.** Aldehyde **c.** Acid **d.** Alkane

3. Which of the following product is formed, when ether is exposed to air?

a. Oxide **b.** Alkanes

c. Alkenes **d.** Peroxide of diethyl ether

4. During dehydration of alcohols to alkenes by heating with conc. 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

5. Phenol is less acidic than:

a. Ethanol **b.** Methanol

c. o-nitrophenol **d.** p-methylphenol

6. Primary alcohols on dehydration give:

a. Alkenes **b.** Alkanes

c. Both a. and b. **d.** None of these

7. Primary and secondary alcohols on action of reduced copper give:

a. Aldehydes and ketones respectively

b. Ketones and aldehydes respectively

c. Only aldehydes

d. Only ketones

8. Methyl alcohol on oxidation with acidified $K_2Cr_2O_7$ gives:

a. CH_3COCH_3 **b.** CH_3CHO

c. $HCOOH$ **d.** CH_3COOH

9. Ethyl alcohol on oxidation with $K_2Cr_2O_7$ gives:

a. Acetic acid **b.** Acetaldehyde

c. Formaldehyde **d.** Formic acid

10. Lucas test is used for:

a. Alcohols **b.** Amines

c. Diethyl ether **d.** Glacial acetic acid

11. When phenol reacts with ammonia in presence of $ZnCl_2$ at 300°C, it gives?

a. Primary amine **b.** Secondary amine

c. Tertiary amine **d.** Both (b) and (c)

12. An organic compound X on treatment with acidified $K_2Cr_2O_7$ gives a compound Y which reacts with I_2 and sodium carbonate to form tri-odomethane. The compound X is?

a. CH_3OH **b.** $CH_3 - CO - CH_3$

c. CH_3CHO **d.** $CH_3CH(OH)CH_3$

13. The reaction of conc. HNO_3 and phenol forms:

a. Benzoic acid **b.** Salicylic acid

c. o-and p-nitrophenol **d.** Picric acid

14. Phenol is:

a. A weaker base than NH_3

b. Stronger than carbonic acid

c. Weaker than carbonic acid

d. A neutral compound

15. Phenol at 25ºC is:

a. A white crystalline solid

b. A transparent liquid

c. A gas

d. Yellow solution

16. At low temperature phenol reacts with Br_2 in CS_2 to form:

a. m-bromophenol **b.** o-and p-bromophenol

c. p-bromophenol **d.** 2, 4, 6-tribromophenol

17. Oxidation of ethanol by chromic acid forms:

a. Ethanol **b.** Methanol

c. 2-propanone **d.** Ethanoic acid

18. Methanol and ethanol are miscible in water due to:

a. Covalent character

b. Hydrogen bonding character

c. Oxygen bonding character

d. None of these

19. By distilling glycol with fuming sulphuric acid, which of following is obtained?

a. Glycerol **b.** Pinacol

c. Dioxan **d.** Ethylene oxide

20. The compound which gives the most stable carbonium ion on dehydration is?

a. $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2OH$ **b.** $CH_3 - \overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}} - OH$

c. $CH_3 - CH_2 - CH_2 - CH_2OH$

d. $CH_3 - \overset{\displaystyle CH_3}{\overset{|}{CH}} - CH_2 - CH_3$

General Introduction of Alcohol, Phenol and Ethers

21. Butanal is an example of:
a. Primary alcohol **b.** Secondary alcohol
c. Aliphatic aldehyde **d.** Aliphatic ketone

22. Methylated spirit is:
a. Methanol **b.** Methanol + ethanol
c. Methanoic acid **d.** Methanamide

23. Which of the following is dihydric alcohol?
a. Glycerol **b.** Ethylene glycol
c. Catechol **d.** Resorcinol

24. According to Lewis concept of acids and bases, ether is:
a. Acidic **b.** Basic
c. Neutral **d.** Amphoteric

Preparation of Alcohol, Phenol and Ethers

25. Ethanol is prepared industrially by:
a. Hydration of ethylene **b.** Fermentation of sugars
c. Both the above **d.** None of these

26. Ethyl alcohol is industrially prepared from ethylene by:
a. Permanganate oxidation
b. Catalytic reduction
c. Absorbing in H_2SO_4 followed by hydrolysis
d. Fermentation

27. Propene, $CH_3 - CH = CH_2$ can be converted to 1-propanol by oxidation. Which set of reagents among the following is ideal to effect the conversion?
a. Alkaline $KMnO_4$
b. B_2H_6 and alkaline H_2O_2
c. O_3 / Zn dust
d. $OsO_4 / CH_4, Cl_2$

28. Coconut oil upon alkaline hydrolysis gives:
a. Glycol **b.** Alcohol
c. Glycerol **d.** Ethylene oxide

29. In the commercial manufacture of ethyl alcohol from starchy substances by fermentation method, which enzymes stepwise complete the fermentation reaction?
a. Diastase, maltase and zymase
b. Maltase, zymase and invertase
c. Diastase, zymase and lactase
d. Diastase, invertase and zymase

30. If formaldehyde and potassium hydroxide are heated, then we get:
a. Acetylene **b.** Methane
c. Methyl alcohol **d.** Ethyl formate

31. Acetone on treatment with $CH_3 - Mg - I$ and on further hydrolysis gives:
a. Isopropyl alcohol **b.** Primary alcohol
c. Acetic acid **d.** 2-methyl 2-propanol

32. Which gas is eliminated in fermentation?
a. O_2 **b.** CO_2
c. N_2 **d.** H_2

33. Commercially methanol is prepared by:
a. Reduction of CO in presence of $ZnO.Cr_2O_3$
b. Methane reacts with water vapours at 900°C in presence of Ni catalyst
c. Reduction of HCHO by $LiAlH_4$
d. Reduction of HCHO by aqueous NaOH

34. From Williamson's synthesis preparation of which of following is possible?
a. Only symmetrical ethers **b.** Only symmetrical ethers
c. Both types **d.** None of these

35. In the reaction $Ar - OH + Rx \xrightarrow{\text{alkali}} A$, A is:
a. An aldehyde **b.** An aryl chloride
c. An ether **d.** A ketone

36. The compound formed when ethyl bromide is heated with dry silver oxide is:
a. Dimethyl ether **b.** Diethyl ether
c. Methyl alcohol **d.** Ethyl alcohol

37. The reagent used for the preparation of higher ether from halogenated ethers is:
a. conc. H_2SO_4 **b.** Sodium alkoxide
c. Dry silver oxide **d.** Grignard reagent

38. Acetyl bromide reacts with excess of CH_3MgI followed by treatment with a saturated solution of NH_4Cl gives:
a. 2-methyl-2-propanol **b.** Acetamide
c. Acetone **d.** Acetyl iodide

39. What is obtained when chlorine is passed in boiling toluene and product is hydrolysed?
a. *o*-Cresol **b.** *p*-Cresol
c. 2, 4-Dihydroxytoluene **d.** Benzyl alcohol

40. In which case methyl-*t*-butyl ether is formed?
a. $(C_2H_5)_3CONa + CH_3Cl$
b. $(CH_3)_3CONa + CH_3Cl$
c. $(CH_3)_3CONa + C_2H_5Cl$
d. $(CH_3)_3CONa + CH_3Cl$

41. $C_6H_5-CH=CHCHO \xrightarrow{X} C_6H_5CH=CHCH_2OH$. In the above sequence *X* can be:

a. H_2/Ni **b.** $NaBH_4$

c. $K_2Cr_2O_7/H^+$ **d.** Both a.and b.

42. Methylphenyl ether can be obtained by reacting:

a. Phenolate ions and methyl iodide

b. Methoxide ions and bromobenzene

c. Methanol and phenol

d. Bromo benzene and methyl bromide

Properties of alcohol, Phenol and Ethers

43. Methyl alcohol can be distinguished from ethyl alcohol using:

a. Fehling solution

b. Schiff's reagent

c. Sodium hydroxide and iodine

d. Phthalein fusion test

44. For phenol, which of the following statements is correct?

a. It is insoluble in water?

b. It has lower melting point compared to aromatic hydrocarbons of comparable molecular weight

c. It has higher boiling point than toluene

d. It does not show acidic property

45. Final product formed on reduction of glycerol by hydroiodic acid is:

a. Propane **b.** Propanoic acid

c. Propene **d.** Propyne

46. Which of the following explains the viscous nature of glycerol?

a. Covalent bonds **b.** Hydrogen bonds

c. Vander Wall's forces **d.** Ionic forces

47. The alcohol that produces turbidity immediately with $ZnCl_2$ + conc. HCl at room temperature:

a. 1-hydroxybutane

b. 2-hydroxybutane

c. 2-hydroxy-2-methylpropane

d. 1-hydroxy-2-methylpropane

48. The alcohol which easily reacts with conc. HCl is?

a. $CH_3-CHOH-CH_2-CH_3$

b. $(CH_3)_3-C-OH$

c. $CH_3-CH_2-CH_2-CH_2-OH$

d. $(CH_3)_3-CH-CH_2OH$

49. A compound that easily undergoes bromination is:

a. Phenol **b.** Toluene

c. Benzene **d.** Benzoic acid

50. Read the following statements carefully:

a. A secondary alcohol on oxidation gives a ketone

b. Ethanol reacts with conc. H_2SO_4 at 180°C to yield ethylene

c. Methanol reacts with iodine and sodium hydroxide to give a yellow precipitate of iodoform

d. Hydrogen gas is liberated when sodium is added to alcohol. Select the correct statements from the above set:

a. A, B **b.** C, D **c.** A, B, D **d.** A, C, D

51. The reagent used for the dehydration of an alcohol is:

a. Phosphorus pentachloride

b. Calcium chloride

c. Aluminium oxide

d. Sodium chloride

52. When rectified spirit and benzene are distilled together, the first fraction obtained is?

a. A ternary azeotrope **b.** Absolute alcohol

c. A binary azeotrope **d.** Denatured spirit

53. Which of the following is most acidic?

a. Phenol **b.** Benzyl alcohol

c. *m*-chlorophenol **d.** Cyclohexanol

54. Which is not correct?

a. Phenol is more acidic than acetic acid

b. Ethanol is less acidic than phenol

c. Ethanol has lower boiling point than ethane

d. Ethyne is a non-linear molecule

Uses of alcohol, Phenol and Ethers

55. Glycerol is used in the manufacture of:

a. Dynamite **b.** Varnish

c. Paints **d.** Soft drinks

56. Alcoholic fermentation is brought about by the action of:

a. CO_2 **b.** O_2 **c.** Invertase **d.** Yeast

57. In order to make alcohol undrinkable pyridine and methanol are added to it. The resulting alcohol is called:

a. Power alcohol **b.** Proof spirit

c. Denatured spirit **d.** Poison alcohol

58. Main constituent of dynamite is:

a. Nitrobenzene **b.** Nitroglycerine

c. Picric acid **d.** TNT

59. The Bouveault-Blanc reduction involves:

a. C_2H_5OH/Na **b.** $LiAlH_4$

c. $C_2H_5MgX^-$ **d.** Zn/HCl

60. Which is used as antifreeze?

a. Glycol **b.** Ethyl alcohol

c. Water **d.** Methanol

NCERT EXEMPLAR PROBLEMS

More than One Answer

61. Alkenes convert into alcohols by:

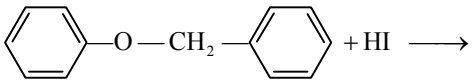
a. Hydrolysis by dil. H_2SO_4

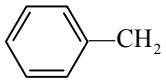
b. Hydration of alkene by alkaline $KMnO_4$

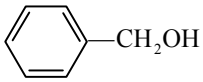
c. Hydrolysis by water vapours and conc. H_2SO_4

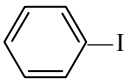
d. Hydration of alkene by aqueous KOH

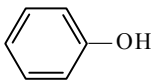
62. The following ether, when treated with HI produces:



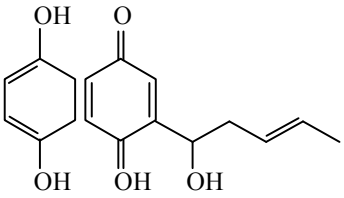
a. 

b. 

c. 

d. 

63. Structure of compound X is:



Than which of the following statements are correct?

a. X have two stereoisomers

b. All stereomers of X have the same melting point

c. X reaction with $SOCl_2$ followed by alcoholic KOH product E which containing 8π bonds

d. None of these

64. An organic compound X of molecular formula $C_4H_{10}O$ undergoes oxidation to give a compound Y of molecular formula $C_4H_8O_2$. X could be:

a. $CH_3CH_2CH_2CH_2OH$ **b.** $CH_3CH_2CH(OH)CH_3$

c. $(CH_3)_2CHCH_2OH$ **d.** $(CH_3)_3COH$

65. Which of the following methods is/are not the industrial methods to prepare methanol?

a. catalytic reduction of carbon monoxide in presence of $ZnO - Cr_2O_3$

b. reacting methane with steam at 900°C with a Ni catalyst

c. reducing formaldehyde with lithium aluminium hydride

d. reacting formaldehyde with aqueous sodium hydroxide solution

66. Which of the following reagent (s) or test (s), can be used to distinguish 2 methyl propanol and 2-methyl propanol – 2?

a. I_2 / NaOH **b.** HCl/anhyd. $ZnCl_2$

c. Victor-Meyer test **d.** oxidation with Cu at 573 K

67. Phenol has higher pk_a value than:

a. acetic acid

b. p-methoxy phenol

c. p-nitrophenol

d. ethanol

68. Which of the following reactions can be used to prepare methyl phenyl ether?

a. reacting sodium phenoxide with methyl chloride

b. reacting phenol with diazomethane (CH_2N_2)

c. reacting sodium methoxide with chlorobenzene

d. reacting C_6H_5OMgCl with chloromethane

69. Carbinol is:

a. C_2H_5OH **b.** CH_3OH

c. $(CH_3)_2CHOH$ **d.** $CH_3CH_2CH(OH)CH_3$

70. Wood spirit is known as:

a. Methanol **b.** Ethanol

c. Acetone **d.** Benzene

Assertion and Reason

Note: Read the Assertion (A) and Reason (R) carefully to mark the correct option out of the options given below:

a. If both assertion and reason are true and the reason is the correct explanation of the assertion.

b. If both assertion and reason are true but reason is not the correct explanation of the assertion.

c. If assertion is true but reason is false.

d. If the assertion and reason both are false.

e. If assertion is false but reason is true.

71. **Assertion:** Phenol is more reactive than benzene towards electrophilic substitution reaction.

Reason: In the case of phenol, the intermediate carbocation is more resonance stabilized.

72. **Assertion:** Phenol undergo Kolbe reaction, ethanol does not.

Reason: Phenoxide ion is more basic than ethoxide ion.

73. **Assertion:** Lucas reagent is a mixture of anhydrous $ZnCl_2$ and concentrate HCl.

Reason: Primary alcohol produce ppt. with Lucas reagents.

74. **Assertion:** Resorcinol turns $FeCl_2$ solution purple.

Reason: Resorcinol have phenolic group.

75. **Assertion:** The major products formed by heating $C_6H_5CH_2OCH_3$ with HI are C_6H_5CH,I and CH_3OH.

Reason: Benzyl cation is more stable than methyl cation.

76. **Assertion:** The pka of acetic acid is lower than that of phenol.
Reason: Phenoxide ion is more resonance stabilized.

77. **Assertion:** Alcoholic fermentation involves conversion of sugar into ethyl alcohol by yeast.
Reason: Fermentation involves the slow decomposition of complex organic.

78. **Assertion:** Acid catalysed dehydration of t-butanol is slower than n-butanol.
Reason: Dehydration involves formation of the protonated alcohol, ROH_2^+.

79. **Assertion:** Tertiary alcohols give turbidity immediately with Lucas reagent.
Reason: A mixture of conc. HI + anhydrous $ZnCl_2$ is called Lucas reagent.

80. **Assertion:** The ease of dehydration of alcohols follows the order. Primary > Secondary > Tertiary.
Reason: Dehydration proceeds through the formation of oxonium ions.

81. **Assertion:** Phenol reacts with acyl halides in presence of pyridine to form phenyl acetate.
Reason: Benzoylation of phenol is carried out in the presence of NH_4OH.

82. **Assertion:** Treatment of phenol with nitrous acid yields p-benzoquinone monoxime.
Reason: p-nitrosophenol and p-benzoquinone monoxime are tautomers.

83. **Assertion:** Reimer-Tiemann reaction of phenol with CCl_4 in NaOH at 340 K gives salicylic acis as the major product.
Reason: The reaction occurs through intermediate formation of dichlorocarbene.

84. **Assertion:** Both symmetrical and unsymmetrical ethers can be prepared by Williamson's synthesis.
Reason: Williamson's synthesis is an example of nucleophilic substitution reaction.

85. **Assertion:** $(CH_3)_3 - Br$ and CH_3CH_2ONa react to form $(CH_3)_3C-O-CH_2CH_3$.
Reason: Good yields of ethers are obtained when tert-alkyl halides are treated with alkoxides.

Comprehension Based

Paragraph –I

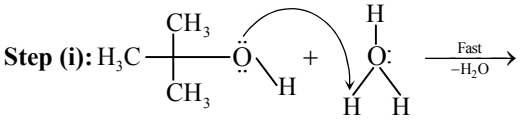
The dehydration of alcohols and the conversion of alcohols to alkyl halides by treatment of hydrogen halides are similar in two important ways suggesting the formation of carbocation as key intermediate.

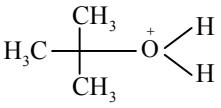
(a) Both reactions are protonated by acids.

(b) The reactivity of alcohols decrease in the order, tertiary > secondary>primary due to the formation of stable carbocations, which is stabilized by hyperconjugation and +I effect. The dehydration of alcohol follows three steps mechanism for acid-base catalysed dehydration of least stable tertiary butyl alcohol, *i.e.,* $(CH_3)_3COH \xrightarrow[\Delta]{H_2SO_4} (CH_3)_2C=CH_2 + H_2O$

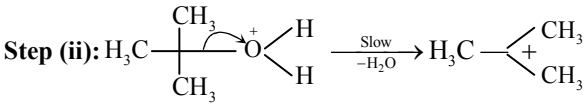
In step I, protonation (acid catalysed) of tert-butyl alcohol takes place. In step II, dissociation of tert-butyloxenium ion takes place followed by formation of carbocation. Alkene is formed in step III by deprotonation (base catalysed) of tert-butyl cation.

Step (i):

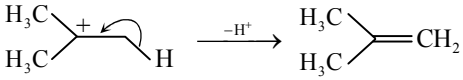




Step (ii):



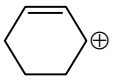
Step (iii):



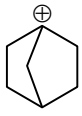
Another important reaction of alcohols is iodoform reaction given by ethanol (in primary alcohols) and are secondary alcohols having 2-ol nature. Such alcohols give yellow ppt. of CHI_3 with NaOH and I_2 solution.

86. Why dehydration of vinyl alcohol is not difficult?
a. Due to high enthalpy of vinylic $-C-OH$ bond
b. Due to unstable nature of $=C-OH$ bond by tautomerism
c. Carbocation never forms in case of vinyl alcohol
d. Both (a) and (b) are correct

87. Which carbocation will not form an intermediate?
a. $(C_6H_5)_3\overset{+}{C}$ **b.**



c.



d. $CH_3=\overset{+}{C}H$

88. Which will give iodoform test?
a. 2-methylpropan-2-ol
b. Ethyl acetoacetate
c. 2-methylbutan-2-ol
d. 3-methylpentant-2-ol

89. Iodoform reaction is given by molecules having $CH_3—\underset{\underset{O}{\|}}{C}—$ unit or $CH_3—\underset{|}{CHOH}$ unit attached to carbon or H-atom.

However $H_2C\begin{matrix}COR\\COR\end{matrix}$ and $CH_3 \cdot CO \cdot CH_2COOC_2H_5$ does not give iodoform reaction because:

a. I_2 reacts at active H-atom

b. I_2 reacts at α-methyl group

c. I_2 does not react with these molecule

d. Hydrolysis of iodide substituted molecule does not occur

90. The reagent used to distinguish 1-cycloethanol and 2-cyclohexanol is:

a. soda lime **b.** $NaOH + H_2O$

c. acidified $KMnO_4$ **d.** $(aq.)FeCl_3$

91. An alcohol on iodoform reaction give iodoform and sodium salt of unsaturated acid containing 3 carbon atoms. The alcohol is:

a. but-3-en-2-ol **b.** prop-2-en-2-ol

c. pent-3-en-2-ol **d.** 3-methyl-but-3-en-2-ol

Match the Column

92. Match the column.

Column I	Column II
(A) Absolute alcohol	**1.** Isopropyl alcohol
(B) Denaturated spirit	**2.** Anhydrous alcohol
(C) 80° proof alcoholic liquor	**3.** 20% absolute alcohol + 80% gasoline
(D) Power alcohol	**4.** alcoholic liquors containing 40% ethanol
(E) Power alcohol	**5.** Ethanol containing CH_3OH and pyridine.

a. A→1; B→2; C→3; D→4; E→5

b. A→2; B→5; C→4; D→1; E→3

c. A→3; B→2; C→1; D→5; E→4

d. A→2; B→1; C→4; D→3; E→5

93. Match the column.

Column I	Column II
(A) $CH_3CH_2CH_2MgBr + H_2O$	**1.** $CH_3(CH_2)_2CH_2OH$
(B) $CH_3CH_2CH_2COCH_3 + CH_3MgI$	**2.** $(CH_3)_2C(OH)CH_2CH_2CH_3$
(C) $CH_3MgI + \underset{\diagdown\ \diagup}{\overset{O}{}}CH_2 — CH_2$	**3.** $CH_3CH(Ph)OH$
(D) $PhCH_2CHO + CH_3MgI$	**4.** $CH_3CH_2CH_2OH$
(E) $CH_3CHO + PhMgBr$	**5.** $PhCH_2CH(OH)CH_3$

a. A→1; B→2; C→3; D→4; E→5

b. A→1; B→2; C→4; D→5; E→3

c. A→3; B→2; C→5; D→4; E→1

d. A→5; B→1; C→4; D→3; E→2

94. Match the column.

Column I	Column II
(A) Wood spirit	**1.** Trinitroglycerine and dinitroglycerine
(B) Fermentation	**2.** Methyl alcohol
(C) Glycerine	**3.** ethyl alcohol
(D) Lucas test	**4.** Propane-1, 2, 3-triol
(E) Dynamite	**5.** Tertiary alcohol

a. A→1; B→2; C→3; D→5; E→4

b. A→4; B→3; C→2; D→1; E→5

c. A→3; B→2; C→1; D→4; E→5

d. A→2; B→3; C→4; D→5; E→1

95. Match the column.

Column I	Column II
(A) Etherates	**1.** Estimation of methoxy or ethoxy groups
(B) Williamson's synthesis	**2.** Ether + BF_3
(C) Zeisel method	**3.** Ether + mineral acid
(D) Oxonium salts	**4.** $RX + R'ONa$
(E) Phenetol	**5.** $C_6H_5OH + (C_2H_5)_2SO_4$ presence of NaOH

a. A→1; B→2; C→3; D→4; E→5

b. A→4; B→3; C→5; D→1; E→2

c. A→2; B→4; C→1; D→3; E→5

d. A→2; B→1; C→4; D→3; E→5

Integer

96. The vapour density of C_2H_5OH is?

97. 10 gm of a mixture of hexane and ethanol reacts with sodium to give 200 ml. of H_2 at 27°C and 760 mm pressure. The percentage of ethanol is?

98. Number of metamers represented by molecular formula $C_4H_{10}O$ is:

99. What amount of bromine will be required to convert 2 g of phenol into 2, 4, 6-tribromophenol?

100. One mole of phenol reacts with bromine to form tribromophenol. How much bromine is used?

ANSWER

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
b	a	d	a	c	a	a	c	a	a
11.	**12.**	**13.**	**14.**	**15.**	**16.**	**17.**	**18.**	**19.**	**20.**
a	d	d	c	a	b	d	b	c	b
21.	**22.**	**23.**	**24.**	**25.**	**26.**	**27.**	**28.**	**29.**	**30.**
c	b	b	b	c	c	b	c	a	c
31.	**32.**	**33.**	**34.**	**35.**	**36.**	**37.**	**38.**	**39.**	**40.**
d	b	a	c	c	b	d	a	d	b
41.	**42.**	**43.**	**44.**	**45.**	**46.**	**47.**	**48.**	**49.**	**50.**
b	a	c	c	c	b	c	b	a	c
51.	**52.**	**53.**	**54.**	**55.**	**56.**	**57.**	**58.**	**59.**	**60.**
c	a	c	a	a	d	c	b	a	a
61.	**62.**	**63.**	**64.**	**65.**	**66.**	**67.**	**68.**	**69.**	**70.**
b,c	a,d	a,b,c	a,c	b,c,d	b,c,d	a,c	a,b	b	a
71.	**72.**	**73.**	**74.**	**75.**	**76.**	**77.**	**78.**	**79.**	**80.**
a	c	c	a	a	c	a	e	c	e
81.	**82.**	**83.**	**84.**	**85.**	**86.**	**87.**	**88.**	**89.**	**90.**
c	b	c	b	d	d	c	d	a	b
91.	**92.**	**93.**	**94.**	**95.**	**96.**	**97.**	**98.**	**99.**	**100.**
a	b	b	d	c	23	10	3	10.22	3

SOLUTION

Multiple Choice Questions

1. **(b)** $\underset{CH_2OH}{\overset{CH_2OH}{|}} + PI_3 \longrightarrow \underset{CH_2I}{\overset{CH_2I}{|}} \xrightarrow{-I_2} CH_2 = CH_2$

2. **(a)** $\underset{\text{alcohol}}{R-OH} + \underset{\text{Cerric amm. nitrate}}{(NH_4)_2Ce(NO_3)_6} \longrightarrow$

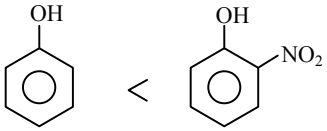
$$\underset{\text{yellow ppt.}}{Ce(NO_3)_6(ROH)_9} + 2N + 14NO_3$$

3. **(d)** $C_2H_5-O-C_2H_5 + O_2 \xrightarrow[25°C]{hv}$

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

4. **(a)** $H_2SO_4 \longrightarrow H^+ + HSO_4^-$

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

5. **(c)**  Nitro group is electron with-drawing. Hence, increases acidic nature.

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

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

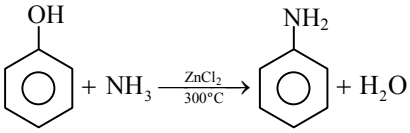
7. **(a)** $\underset{1^o\text{ alcohol}}{R-CH_2OH} \xrightarrow{Cu} R-CHO + H_2$

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

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

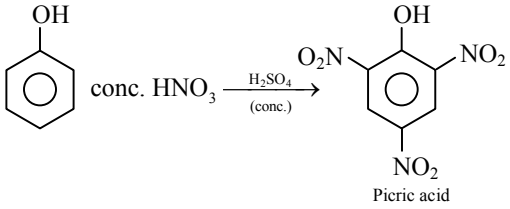
9. **(a)** $CH_3CH_2OH \xrightarrow{K_2Cr_2O_7} CH_3COOH$

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

11. **(a)** 

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

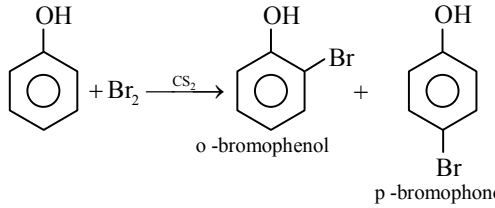
$$\xrightarrow[I_2]{NaOH} \underset{\text{Yellow ppt}}{CHI_3} + CH_3COONa$$

13. **(d)** 

14. **(c)** Phenol is weaker acid than carbonic acid

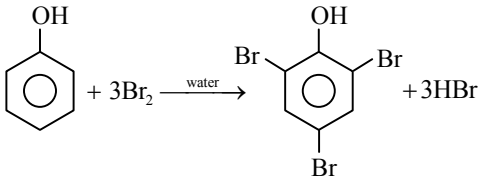
15. **(a)** $C_6H_5OH \qquad H_2CO_3 \qquad CH_3COOH$

$K_a = 10^{-8} - 10^{-10}, \quad K_a = 10^{-7} \qquad K_a = 10^{-5}$

16. **(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.

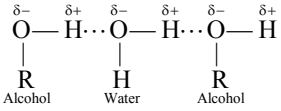


In aqueous solution phenol ionizes to give phenoxide ion.

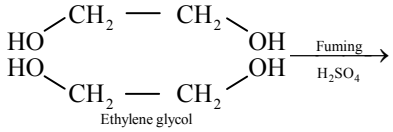
Due to the presence of negative charge on oxygen the benzene ring is highly activated and hence trisubstituted product is obtained.

17. **(d)** $\underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow{CrO_3} \underset{\text{Acetic acid}}{CH_3COOH}$

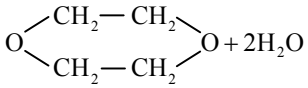
18. **(b)** Hydrogen bonding:



19. **(c)**



Ethylene glycol



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

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

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

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

$\underset{\text{(Ethylene glycol)}}{\begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}}$

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

25. **(c)** Hydration of alkenes

$$CH_2=CH_2+\overset{+}{H}\overset{-}{H}SO_4 \longrightarrow CH_3-CH_2-HSO_4$$

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

Fermentation of sugars:

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

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

26. **(c)** $CH_2=CH_2 \xrightarrow{H_2SO_4} CH_3-CH_2-HSO_4$

$$\xrightarrow{\text{Hydrolysis}} CH_3CH_2-OH+H_2SO_4$$

27. **(b)** Hydroboration oxidation (Industrial preparation of alcohol)

$$3CH_3CH=CH_2+\frac{1}{2}B_2H_6 \xrightarrow[\text{ether}]{\text{Dry}} (CH_3CH_2CH_2)_3B$$

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

28. **(c)** Coconut oil + Alkali → Soap + Glycerol

It is a saponification reaction.

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

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

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

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

It is cannizzaro's reaction.

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

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

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

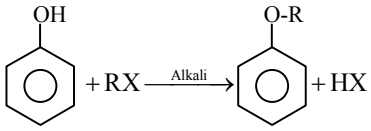
During fermentation CO_2 gas is eliminated.

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

34. **(c)** $CH_3CONa+Br-CH_3 \longrightarrow \underset{\substack{\text{Dimethyl ether}\\ \text{(symmetrical ether)}}}{CH_3-O-CH_3}+NaBr$

$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-O^-Na+CH_3Br \longrightarrow \underset{\substack{\text{Methyl ter-butyl ether}\\ \text{(unsymmetrical ether)}}}{CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OCH_3}+NaBr$$

35. **(c)**



36. **(b)** $2C_2H_5Br+\underset{\text{Dry}}{Ag_2O} \longrightarrow C_2H_5-O-C_2H_5+2AgBr$

If we take moist Ag_2O then alcohol is formed

$$Ag_2O+H_2O \longrightarrow 2AgOH$$

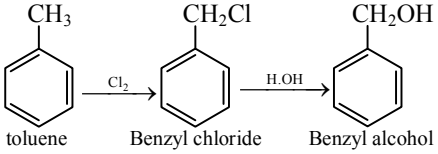
$$C_2H_5Br+AgOH \longrightarrow C_2H_5OH+AgBr$$

37. **(d)** $\underset{\substack{\text{Methoxymethane}\\ \text{(Lower ether)}}}{CH_3OCH_3} \xrightarrow{Cl_2/hv} \underset{\alpha-\text{Chlorodimethyl ether}}{CH_3OCH_2Cl}$

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

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

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



40. **(b)** $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-Na+Cl-CH_3\longrightarrow$

2, 2 dimethyl sodium ethoxide

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

Methyl-t butyl ether

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

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

$$\underset{\text{cinnamic alcohol}}{C_6H_5-CH=CH.CH_2OH}$$

42. **(a)** $C_6H_6O^-+CH_3I\longrightarrow C_6Hl5OCH_3+I^-$

43. **(c)** $C_2H_5OH\xrightarrow[\text{Iodoform test}]{NaOH/I_2}CHI_3\,(\text{yellow ppt})$

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

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

45. **(c)** $CH_3OH\xrightarrow[I_2]{NaOH}\underset{\underset{CH_2-I}{|}}{\overset{\overset{CH_2}{\|}}{CH}}\xrightarrow{HI}\underset{\underset{CH_2-I}{|}}{\overset{\overset{CH_3}{\|}}{CH}}-I\xrightarrow{-I_2}\underset{\underset{CH_2}{\|}}{\overset{\overset{CH_3}{|}}{CH}}$

46. **(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.

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

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

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

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

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

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

48. **(b)** Tertiary alcohol readily reacts with halogen acid

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

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

49. **(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.

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

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

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

51. **(c)**

$$C_2H_5OH\begin{cases}\xrightarrow[250^\circ C]{Al_2O_3}C_2H_5OC_2H_5+H_2O & \text{Diethyl ether}\\ \xrightarrow[250^\circ C]{Al_2O_3}C_2H_4+H_2O & \text{Ethene}\end{cases}$$

52. **(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 351*K* is absolute alcohol.

53. **(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.

54. **(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:

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

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

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

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

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

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

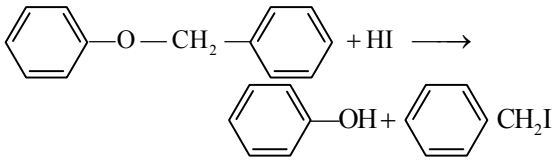
60. **(a)** Glycol is used as an antifreeze for automobile radiators because it lowers down the melting point of water.

NCERT Exemplar Problems

More than One Answer

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

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

62. **(a,d)** 

Phenol does not react further with HI.

63. **(a, b, c)** X have two stereoisomers, All stereomers of X have the same melting point, X reaction with $SOCl_2$ followed by alcoholic KOH product E which containing 8π bonds

64. **(a, c)** $CH_3CH_2CH_2CH_2OH$, $(CH_3)_2CHCH_2OH$

65. **(b, c, d)** Reacting methane with steam at 900°C with a Ni catalyst, Reducing formaldehyde with lithium aluminium hydride,Reacting formaldehyde with aqueous sodium hydroxide solution

66. **(b, c, d)** HCl/anhyd. $ZnCl_2$,Victor-Meyer test,oxidation with Cu at 573 K

67. **(a, c)** acetic acid,p-nitrophenol

68. **(a, b)** Reacting sodium phenoxide with methyl chloride, Reacting phenol with diazomethane (CH_2N_2)

69. **(b)** Carbinol is CH_3OH (Methanol).

70. **(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.

Assertion and Reason

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

72. **(c)** It is correct that sodium phenoxide (sodium salt of phenol) and CO_2on 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.

73. **(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.

74. **(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.

75. **(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.

76. **(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.

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

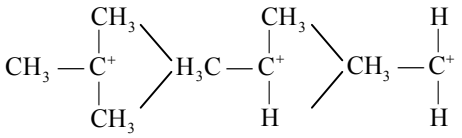
$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$

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

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

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

80. **(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

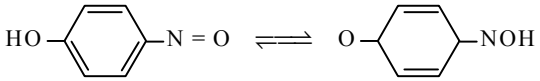


This is due to the electron releasing (+I) effect of the alkyl group. Therefore the ease of dehydration of alcohols follows the order.

Tertiary > secondary > primary alcohol.

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

82. **(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

83. **(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.

84. **(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.

85. **(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. 1º, 2º or 3º.

Comprehension Based

86. **(d)** These are facts.

87. **(c)** Rest all will form carbocation

88. **(d)** $CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3$ has $CH_3-\underset{|}{CHOH}$

Unit responsible for iodoform reaction.

89. **(a)** Both have $H_2C <$ group attached to electron with drawing groups and thus H-atom of $> CH_2$ ecome reactive and such a $H_2C <$ group is called reactive methylene gp.

$$>CH_2 + I_2 \longrightarrow >Cl_2 \xrightarrow{OH^-} >C(OH)_2 \longrightarrow >C=O$$

90. **(b)** 1-cycloethanol will give iodoform reaction.

91. **(a)** $CH_2=\underset{\underset{OH}{|}}{CH}\cdot CH\cdot CH_3 \xrightarrow[[O]]{I_2} CH_2=CH\cdot CO\cdot CH_3$

But-3-en-2-ol

$$CH_2=CHCOCH_3 \xrightarrow{I_2} CH_2=CH\cdot CO\cdot CI_3$$

$$CH_3=CHCOCI_3 \xrightarrow{NaOH} CH_2=CHCOONa + CHI_3$$

Match the Column

92. **(b)** A→2; B→5; C→4; D→1; E→3

93. **(b)** A→1; B→2; C→4; D→5; E→3

94. **(d)** A→2; B→3; C→4; D→5; E→1

95. **(c)** A→2; B→4; C→1; D→3; E→5

Integer

96. **(23)** Vapour density $= \dfrac{\text{Molecular mass}}{2} = \dfrac{46}{2} = 23$

97. **(10)** 22400 ml of H_2 is produced by 46 gms of ethanol.

200 ml of H_2 is produced by $\dfrac{46\times 200}{22400} = \dfrac{23}{56}$

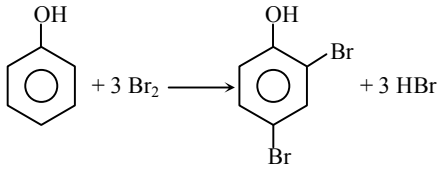
Percentage of $C_2H_5OH = \dfrac{23}{56\times 10}\times 100 = 9.6\% \simeq 10\%$

98. **(3)** 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.

99. **(10.22)**

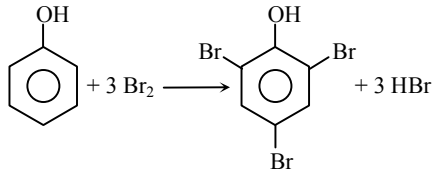


1 mole 3 moles 1 mole

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

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

100. **(3)**



2,4,6-tribromophenol

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