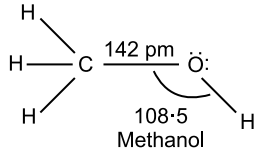
Alcohols, Phenols and Ethers

Chapter at a Glance

1. **Alcohols:** Alcohols are compounds in which a hydroxyl (—OH) group is attached to saturated carbon atom.

2. **Classification of Alcohols:**
   - **(a) Monohydric alcohols:** Alcohols containing one —OH group.
     - (i) Primary alcohols: *e.g.*, CH_3OH
     - (ii) Secondary alcohols: *e.g.*, CH_3-CH_2OH
     - (iii) Tertiary alcohols: *e.g.*, $CH_3-C(CH_3)_2-OH$
   - **(b) Polyhydric alcohols:** Alcohols containing more than one —OH group.
     - (i) Dihydric alcohols: *e.g.*, $CH_2(OH)-CH_2OH$ (1, 2 Ethanediol)
     - (ii) Trihydric-alcohols: *e.g.*, $CH_2(OH)-CH(OH)-CH_2OH$ (1, 2, 3 propane triol)

Structure of alcohol:



3. **Preparation of alcohols:**
   - (a) Hydration of Alkenes
   - (b) By hydroboration: Oxidation reaction
   - (c) By Grignards reagent
   - (d) Hydrolysis of alkyl halide
   - (e) Reduction of carboxylic acids
   - (f) Oxidation of alcohols:
   - (i) **Primary alcohols:** On oxidation with acidified potassium dichromate, first give an aldehyde which on further oxidation gives an acid with the same number of carbon atoms as the original alcohol.

(ii) **Secondary alcohols:** On oxidation, gives a ketone with the same number of carbon atoms as the original alcohol.

(iii) **Tertiary alcohols:** Oxidation is carried out under acidic conditions, tertiary alcohols first undergo dehydration to form alkene. The alkene formed is then oxidized to ketone which is finally oxidised to carboxylic acid with lesser number of carbon atoms than the starting alcohol.

Phenols:

4. Methods of preparation:

(a) From Aryl sulphonic Acids

(b) From Aryl Halides (Dow's Process)

(c) From Diazonium Salts

5. Reactions of OH group:

(a) Acidic nature of phenols:

(i) Reaction with Sodium

(ii) Reaction with Alkali

(iii) Phenol behaves as stronger acids than alcohols because phenols on ionisation gives phenoxideion.

$$C_6H_5OH \rightleftharpoons C_6H_5O^- + H^+$$

Phenoxide is more stable than phenol itself and liberating H^+. Both the stabilised by resonance.

$$R-\ddot{O}-H \rightleftharpoons R-\ddot{O}^{\ominus}: + H^+$$

Neither alcohol nor alkoxide ion is stabilised by resonance.

(b) Reaction of Benzene Ring:

In phenols, —OH group activates the benzene ring towards electrophilic substitution reactions with directs the substitution at *ortho* and *para* positions.

(i) Halogenation: Phenols readily react with hologens to form polyhalogen substituted compounds. For example, phenol gives **white precipitate** of 2, 4, 6-tribromophenol when treated with bromine water.

Monobromophenol is obtained by reacting phenol with bromine in the presence of less polar solvent such as a carbon disulphide or carbon tetrachloride at low temperature.

(ii) Nitrosation: Phenol reacts with ice cold solution of nitrous acid (HNO_2) to form *p*-nitrosophenol. The *p*-nitrosophenol. Can be further oxidised with dilute HNO_3 to *p*-nitrophenol.

This reaction can be suitably employed to obtain more yield of nitro product.

(iii) Sulphonation: Phenols are sulphonated with conc. H_2SO_4. Sulphonation takes places mainly at *ortho* position at low temperature and at *para* position at high temperature.

(iv) Friedel-Crafts Alkylation: Phenol reacts with alkyl halides in the preseence of anhydrous $AlCl_3$ to form mainly *para*-derivative with a small quantity of the *ortho*-isomer.

The yield to alkyl phenols is low because $AlCl_3$ reacts with phenol to produce a coordination compound.

6. Chemical Tests:

(a) Ferric Chloride Test:

Phenol gives a violet-coloured water soluble complex with ferric-chloride.

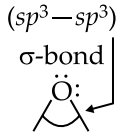
(b) Azodye test:

Most of the phenols gives this test. Red or brown colouration is produced when a nitrite, is added to a phenol dissolved in conc. sulphuric acid. The colour changes to blue or green by the addition of a strong alkali.

7. Ethers: Ethers are a class of compound characterised by a functional group, —O—, bonded to, two alkyl groups, —O— is referred to as ethereal group. Ethers are termed as simple ethers or mixed ethers according as the two alkyl groups are same or different.

$R-O-R$	$R-O-R'$
Simple ether or Symmetrical ether	Mixed ethers or Unsymmetrical ether

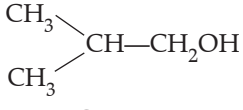
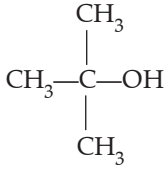
8. Structure of Ethers: In ethers, O-atom is sp^3-hybridized. Two sp^3 hybrid orbitals contain one lone pair of electrons. Each of the two C—C σ-bonds (C-atom is from alkyl group, R) is formed by sp^3-sp^3 overlap. C—O—C bond angle is equal to 110°.



General molecular formula of ethers is $C_nH_{2n+2}O$.

9. **General Methods of Preparation:**
   (a) By heating excess of ethyl alcohol with concentrated sulphuric acid at 140°C.
   (b) By passing vapours of alcohol over alumina heated to 250°–260°C.
   (c) **Williamson's Synthesis:** By the reaction of an alkylhalide with a sodium alkoxide. It is useful for the preparation of both mixed and simple ethers.
   (d) By heating an alkyl halide with dry silver oxide.
10. **Properties:**
   (a) Physical Properties:
      (i) Dimethyl ether and ethyl methyl ether are gases, all others are colourless liquids with pleasant odour.
      (ii) Highly volatile and very inflammable.
      (iii) Slightly soluble in water.
      (iv) Lighter than water.
   (b) Chemical Properties: Ethers are relatively, chemically inert owing to the absence of active groups in their molecules. A molecule of ether consists of two alkyl groups attached to oxygen atom.
11. **Uses:**
   (a) In ether extraction's for the purification of organic substances.
   (b) As a refrigerant and anesthetic.
   (c) As a substitute for petrol with ethanol.
   (d) For the preparation of Grignard reagent.
   (e) As a solvent for fats, waxes, oils, plastics, lacquers etc.

Multiple choice questions

1. When acetaldehyde is treated with grignard reagent, followed by hydrolysis the product formed is:
   (a) Primary alcohol
   (b) Secondary alcohol
   (c) Carboxylic acid
   (d) Tertiary alcohol
2. When oxalic acid is heated with glycerol we get:
   (a) Formic acid (b) Acetic acid
   (c) Lactic acid (d) Tartaric acid
3. Ethanol on heating with conc. H_2SO_4 at 445 K gives:
   (a) Diethyl sulphate
   (b) Ethylene, C_2H_4
   (c) Diethyl ether, $(C_2H_5)_2O$
   (d) Ethyl hydrogensulphate, $C_2H_5HSO_4$
4. Which of the following is most acidic?
   (a) H_2O (b) CH_3OH
   (c) C_2H_5OH (d) $CH_3CH_2CH_2OH$
5. Which one of the following will produce a primary alcohol by reacting with CH_3MgI?
   (a) Acetone (b) Methyl cyanide
   (c) Ethylene oxide (d) Ethyl acetate
6. Which of the following has highest boiling point?
   (a) $CH_3CH_2CH_2OH$ (c) 
   (b) $CH_3CH_2CH_2CH_2OH$ (d) 
7. Chlorine reacts with ethanol to give:
   (a) Diethyl chloride
   (b) Chloroform
   (c) Acetaldehyde
   (d) Chloral
8. Which of the following alcohol is least soluble in water?
   (a) N-Butyl alcohol (b) Iso-Butyl alcohol
   (c) Tert-Butyl alcohol (d) Sec-Butyl alcohol

9. Glycerol on heating with potassium bisulphate yields:

(a) Acetone (b) Glyceraldehyde

(c) Acrolein (d) Propanol

10. The reaction of Lucas reagent is fastest with:

(a) $(CH_3)_3COH$ (b) $(CH_3)_2CHOH$

(c) $CH_3(CH_2)_2OH$ (d) CH_3CH_2OH

11. The ionization constant of phenol is higher than that of ethanol because**:**

(a) Phenoxide ion is a stronger base than ethoxide ion

(b) Phenoxide ion is stabilized through delocalization

(c) Phenoxide ion is less stable than ethoxide ion

(d) Phenoxide ion is bulkier than ethoxide ion

12. The correct order of boiling points for primary (1°), secondary (2°) and tertiary alcohol (3°) is:

(a) 1° > 2° > 3° (b) 3° > 2° > 1°

(c) 2° > 1° > 3° (d) 2° > 3° > 1°

13. Which of the following is the most suitable method for removing the traces of water from ethanol?

(a) Heating with Na metal

(b) Passing dry HCl gas through it

(c) Distilling Cl^-

(d) Reacting with Mg

14. Phenol is heated with $CHCl_3$ and alcoholic KOH when salicylaldehyde is produced. This reaction is known as:

(a) Rosenmund's reaction

(b) Reimer-Tiemann reaction

(c) Friedel-Crafts reaction

(d) Sommelet reaction

15. Lucas test is used for distinction of:

(a) Alcohols (b) Phenols

(c) Alkyl halides (d) Aldehydes

16. Which of the following is simple ether?

(a) $C_2H_5OCH_3$

(b) CH_3OCH_3

(c) $C_6H_5OCH_3$

(d) All are simple ethers.

17. Alcohols of low molecular weight are:

(a) Insoluble in water

(b) Soluble in water

(c) Insoluble in all solvents

(d) Soluble in water on heating

18. The boiling point of methanol is greater than that of methyl thiol because:

(a) There is intermolecular hydrogen bonding in methanol and no hydrogen bonding in methyl thiol.

(b) There is intramolecular hydrogen bonding in methanol and no hydrogen bonding in methyl thiol.

(c) There is intramolecular hydrogen bonding in methanol and intermolecular hydrogen bonding in methyl thiol.

(d) There is no hydrogen bonding in methanol and intermolecular hydrogen bonding in methyl thiol

19. In the reaction of phenol with $CHCl_3$ and aqueous NaOH at 70°C, the electrophile attacking the ring is:

(a) $CHCl_3$ (b) $CHCl_2$

(c) CCl_2 (d) $COCl_2$

20. Which of the following statements about phenol are incorrect?

(i) It is insoluble in water.

(ii) It has lower melting point as compared to aromatic hydrocarbons of comparable molecular weight.

(iii) It does not show acidic property.

(iv) It has higher boiling point than toluene.

(a) (i) and (ii) are correct

(b) (i) and (iii) are correct

(c) (ii) and (iv) are correct

(d) (i), (ii) and (iii) are correct.

21. Alcohols can be obtained from all methods except:

(a) Hydroboration-oxidation

(b) Oxymercuration-demercuration

(c) Reduction of aldehyde/ketones with Zn-Hg/HCl

(d) By fermentation of starch

22. When phenol is treated with excess of bromine water, it gives:

(a) *m*-bromophenol

(b) *o*-and *p*-bromophenol

(c) 2, 4-dibromophenol

(d) 2, 4, 6-tribromophenol

23. Which of the following statements are correct?

(i) A secondary alcohol on oxidation gives a ketone.

(ii) Ethanol reacts with conc. H_2SO_4 at 180°C to yield ethylene.

(iii) Hydrogen gas is liberated when sodium is added to alcohol.

(iv) Methanol reacts with iodine and sodium hydroxide to give a yellow precipitate of iodoform.

(a) (i) and (ii) are correct

(b) (i) and (iii) are correct

(c) (ii) and (iv) are correct

(d) (i), (ii), and (iii) are correct

24. Which of the following is not true in case of reaction with heated copper at 300°C?

(a) Primary alcohol → Aldehyde

(b) Secondary alcohol → Ketone

(c) Tertiary alcohol → Olefin

(d) Phenol → Benzyl alcohol

25. In cold countries, ethylene glycol is added to water in the radiators to:

(a) Lower the viscosity

(b) Reduce the viscosity

(c) Make water a better lubricant

(d) Bring down the specific heat of water

26. Boiling point of ethyl alcohol is greater than diethyl ether due to:

(a) Vander Waals forces

(b) London forces

(c) Polarity

(d) Hydrogen bonding

27. Reaction between acetone and methyl magnesium chloride, followed by hydrolysis will give:

(a) tert-butyl alcohol

(b) iso-butyl alcohol

(c) iso-propyl alcohol

(d) sec-butyl alcohol

28. The optically active compound is:

(a) Butan-1-ol

(b) Butan-2-ol

(c) Propan-1-ol

(d) 2-methyl-propan-1-ol

29. The reaction: Sodium alkoxide + alkyl halide → Ether + Sodium halide is called:

(a) Wurtz reaction

(b) Kolbe's reaction

(c) Perkin's reaction

(d) Williamson's synthesis

30. Benzene diazonium chloride on hydrolysis gives:

(a) Benzene (b) Phenol

(c) Chlorobenzene (d) Benzyl alcohol

31. A liquid is mixed with ethanol and few drops of conc. H_2SO_4 is added. A compound with a fruity smell is formed. The liquid is:

(a) HCHO (b) CH_3CHO

(c) CH_3COOH (d) CH_3COCH_3

32. The gas evolved when sodium metal reacts with ethanol:

(a) Carbon dioxide

(b) Hydrogen

(c) Phosgene

(d) Hydrogen sulphide

Fill in the blanks

33. During acid catalysed dehydration of alcohols, the intermediate species involved are ..... In case of ..... alcohols, the cloudiness appears immediately while performing Lucas test.

(a) Carboanion, primary

(b) Carbocation, tertiary

(c) Radical anion, secondary

(d) Radical cation, tertiary

34. ..... is an example of trihydric alcohol and ..... is an example of dihydric alcohol. Ethyl bromide on reaction with moist silver oxide gives ..... as the main product.

(a) iso-propanol, methanol, ethanol

(b) Glycol, ethanol, methanol

(c) Ethanol, glycol, propanol

(d) Glycerol, glycol, ethanol

35. The common name of 1, 2, 3-trihydroxy-benzene is ..... Phenol reacts with sodium liberating ..... gas.

(a) TNT, nitrogen

(b) Butyrophenone, Oxygen

(c) Pyrogallol, hydrogen

(d) Benzophenone, carbon dioxide

36. Phenol is ..... reactive than chlorobenzene towards electrophilic substitution reactions. IUPAC name of picric acid is ..... .

(a) More, 2,3-dihydroxybutanedioic acid

(b) More, 2, 4, 6-Trinitrophenol

(c) Less, 2-hydroxypropane-1,2,3-tricarboxylic acid

(d) Less, 2-hydroxypropanoic acid

37. A mixture of conc. HCl and anhydrous $ZnCl_2$ is called ..... which shows maximum reactivity with ..... alcohol.

(a) Lucas reagent, tertiary

(b) Grignard reagent, primary

(c) Fehling's reagent, secondary

(d) Tollen's reagent, primary

38. Ethers behave as weakly ..... substances because of the presence of ..... electrons on the oxygen atom. IUPAC name of cumene is .....

(a) Basic, unpaired, 4-oxopentanal

(b) Acidic, unpaired, 3-hydroxybutan-2-one

(c) Acidic, extra electrons in valence shell, 3-methylphenol

(d) Basic, lone pair, 2-Phenylpropane

39. Alcohols act as …… due to the presence of unshared electron pairs on oxygen atom. Ethers are…… in nature.

(a) Bronsted bases, basic

(b) Bronsted acids, acidic

(c) Bronsted acid, neutral

(d) Bronsted bases, amphoteric

40. Acetone reacts with Grignard reagent to form……When Phenol is distilled with zinc dust, it gives…….

(a) Ether, benzoic acid

(b) 3° alcohol, Benzene

(c) 2° alcohol, toluene

(d) No reaction, benzaldehyde

Match the following

41. Match column I and column II and choose the correct combination from the given options.

	Column I		Column II
1	Antifreeze used in car engine	(p)	Methanol
2	Solvent used in perfumes	(q)	Phenol
3	Starting material for picric acid	(r)	Ethylene glycol
4	Wood spirit	(s)	Ethanol

(a) 1-(s), 2-(q), 3-(r), 4-(p)

(b) 1-(s), 2-(q), 3-(p), 4-(r)

(c) 1-(p), 2-(r), 3-(q), 4-(s)

(d) 1-(r), 2-(s), 3-(q), 4-(p)

42. Match column I and column II and choose the correct combination from the given options.

	Column I		Column II
1	Anhydrous $ZnCl_2$ + conc.HCl	(p)	Ethyl alcohol
2	Phenol	(q)	Invertase
3	Fermentation	(r)	Tertiary alcohol
4	Dynamite	(s)	Lucas reagent
5	Enzyme	(t)	Reimer-Tiemann reaction
6	Lucas test	(u)	Nitro glycerine

(a) 1-(s), 2-(t), 3-(p), 4-(u), 5-(q), 6-(r)

(b) 1-(r), 2-(u), 3-(q), 4-(t), 5-(p), 6-(s)

(c) 1-(t), 2-(s), 3-(q), 4-(r), 5-(p), 6-(u)

(d) 1-(p), 2-(q), 3-(s), 4-(r), 5-(t), 6-(u)

43. Please put coupling reaction instead of test in the column below at number 1

	Column I		Column II
1	Coupling test	(p)	100 % Ethyl alcohol
2	Methylated spirit	(q)	Polar
3	Power alcohol	(r)	propane-1,2,3-triol
4	Glycerine	(s)	Mixture of petrol and ethyl alcohol
5	O–H Bond	(t)	Methyl alcohol
6	Absolute alcohol	(u)	Phenol

(a) 1-(s), 2-(t), 3-(p), 4-(u), 5-(q), 6-(r)

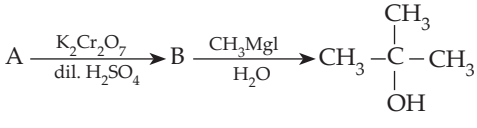
(b) 1-(r), 2-(u), 3-(q), 4-(t), 5-(p), 6-(s)

(c) 1-(t), 2-(s), 3-(q), 4-(r), 5-(p), 6-(u)

(d) 1-(u), 2-(t), 3-(s), 4-(r), 5-(q), 6-(p)

Reaction based questions

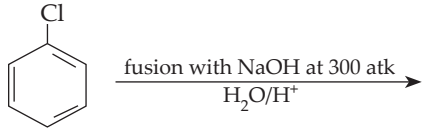
44. In the following reaction, reactant A is:

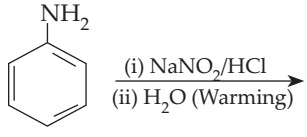


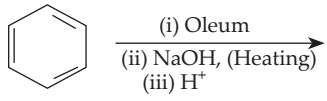
(a) C_2H_5OH (b) CH_3COOH

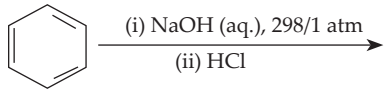
(c) CH_3COCH_3 (d) $CH_3CHOHCH_3$

45. Which of the following reactions will yield phenol?

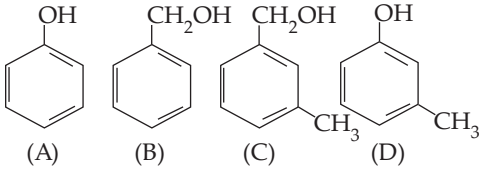
(a) 

(b) 

(c) 

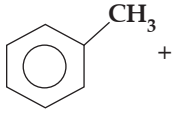
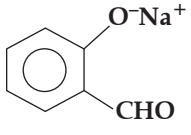
(d) 

46. Which of the following compounds is aromatic alcohol?



(a) A, B, C, D (b) A, D

(c) B, C (d) A

47.  + $CHCl_3$ + NaOH $\longrightarrow$ 

The electrophile involved in the above reaction is:

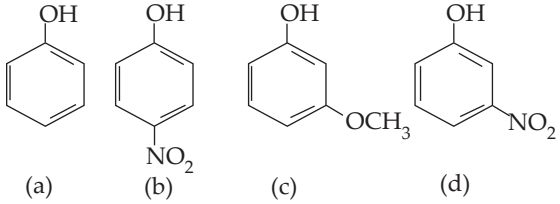
(a) Dichloromethyl cation ($CHCl_2$)

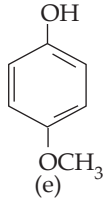
(b) Dichlorocarbene (: CCl_2)

(c) Trichloromethyl anion (CCl_3)

(d) Formylcation (CHO)

48. Mark the correct order of decreasing acid strength of the following compounds.





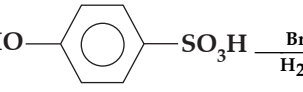
(a) e > d > b > a > c (b) b > d > a > c > e

(c) d > e > c > b > a (d) e > d > c > b > a

49. $C_6H_5Cl \xrightarrow[624K,300atm]{NaOH(aq)}$ A. Here, A is:

(a) Phenol (b) Sodium phenoxide

(c) Benzene (d) Cyclohexyl chloride

50. In the sequence 

is:

(a) 2-Bromo-4-hydroxybenzene sulphonic acid

(b) 3, 5-Dibromo-4-hydroxybenzene sulphonic acid

(c) 2-Bromophenol

(d) 2, 4, 6-Tribromophenol

51. Phenol is heated with alcoholic KOH and chloroform:

(i) What is the name of the reaction?

(a) Cannizzaro reaction

(b) Gattermann reaction

(c) Reimer –Tiemann reaction

(d) Kolbe reaction

(ii) What is the main product formed in this reaction?

(a) Salicylaldehyde (b) Salicylic acid

(c) Aniline (d) Phenyl isocyanide

52. Conversion of Chlorobenzene into phenol.

(i) Which of the following statements is correct for the above conversion?

(a) Heating it with alc. KOH at room temperature

(b) Heating it with aqueous NaOH at 623 K under pressure followed by acidification with dilute HCl

(c) Heating it with CuCN followed by acidification with dilute HCl

(d) Heating it with sodium metal in the presence of dry ether

(ii) What is the name of the above reaction?

(a) Dow process

(b) Wurtz reaction

(c) Sandmeyer's reaction

(d) Kolbe's reaction

53. An unknown alcohol is treated with Lucas reagent to determine whether the alchol is primary, secondary or tertiary.

(a) Tertiary alcohol by S_N2

(b) Secondary alcohol by S_N1

(c) Tertiary alcohol by S_N1

(d) Secondary alcohol by S_N2

Assertion and Reason based questions

Directions: In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as:

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

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

(c) If assertion is true, but reason is false.

(d) If both assertion and reason are false

54. Assertion: $(CH_3)_3$–CONa and CH_3CH_2Br 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.

55. Assertion: Ortho and para-nitro phenols can be separated by steam distillation.

Reason: Ortho isomer associates through intermolecular hydrogen bonding while Para isomer associates through intramolecular hydrogen bonding.

56. Assertion: In Lucas test, 3° alcohols react immediately.

Reason: An equimolar mixture of anhyd. $ZnCl_2$ and conc. HCl is called Lucas reagent.

57. Assertion: The water solubility of the alcohols follow the order: *tert*-butyl alcohol > *sec*-butyl alcohol > *n*-butyl alcohol.

Reason: Alcohols form H-bonding with water to show soluble nature.

58. Assertion: *Tert*-butyl alcohol undergoes acid catalysed dehydration readily than propanol.

Reason: 3°Alcohols do not give Victor-Meyer's test.

59. Assertion: Phenol is less acidic than *p*-nitrophenol.

Reason: Phenolate ion is more stable than *p*-nitrophenolate ion.

60. Assertion: Reimer-Tiemann reaction of phenol with CCl_4 in NaOH at 340 K gives salicylic acid as the major product.

Reason: The reaction occurs through intermediate formation of dichlorocarbene.

61. Assertion: The C—O—C bond angle in ethers is slightly less than tetrahedral angle.

Reason: Due to the repulsive interaction between the two alkyl groups in ethers.

62. Assertion: Phenol undergo Kolbe reaction, ethanol does not.

Reason: Phenoxide ion is more basic than ethoxide ion.

63. Assertion: Etherates are coordination complexes of ethers with Lewis acids.

Reason: Ethers are easily cleaved by mineral acids such as HCl and H_2SO_4 at 373 K.

64. Assertion: Boiling points of alcohols are higher than that of ethers of comparable molecular mass.

Reason: Alcohols can form intermolecular hydrogen bonding while ethers can not.

Source based questions

Read the passages given below and answer the following questions:

65. Ether protecting groups are in many respects complimentary to the acetals. Like the acetals they are stable to basic condition and most ethers are also much more acid stable. The most commonly used ethers for protecting purposes, the benzyl ethers, are in addition removable by catalytic hydrogenolysis under very mild, pH neutral, conditions. However, the strongly basic conditions most commonly used for the introduction of an ether protecting group and the lack of regioselectivity put certain restrictions on their use. The triphenylmethyl (trityl) ether group has also found use, especially in carbohydrate chemistry. The bulk of this group gives it a strong preference for the primary hydroxyl group.

Mark the correct choice as

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Both assertion and reason are wrong.

(i) Assertion: The formation of ether from alcohol in acidic medium is a bimolecular reaction.

Reason: A protonated alcohol molecule is attacked by another alcohol molecule while ether formation in acidic medium.

(ii) Assertion: Dehydration of secondary and tertiary alcohols to give corresponding ethers is not a productive reaction.

Reason: Elimination does not compete with ether formation reaction.

(iii) Assertion: Alkyl aryl ethers are cleaved at the alkyl-oxygen bond when reacted with hydrogen halides.

Reason: Aryl oxygen bond are more stable.

(iv) Assertion: Anisole undergoes bromination with bromine in absence of iron (III) bromide.

Reason: Iron (III) bromide is used to catalyse halogenation reaction of phenylalkyl ethers.

Answers

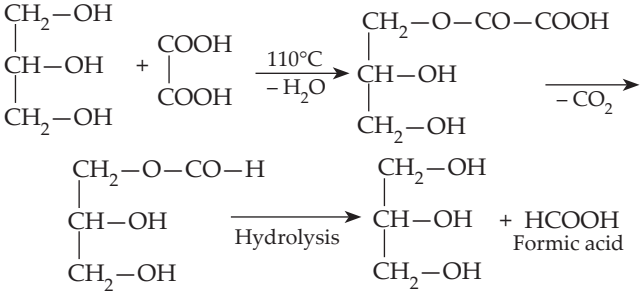
Multiple choice questions

1. (b) Secondary alcohol

Explanation: The product formed is secondary alcohol (R-OH) and magnesium hydroxy halide (R-Mg-X). In this reaction in the presence of ether, Grignard reagent and acetaldehyde reacts with each other and produced compound is further proceeded in the presence of H_3O^+ and as a result 2-butanol (secondary alcohol) and magnesium hydroxyl halide is formed.

2. (a) Formic acid

Explanation: When oxalic acid is heated with glycerol we get Formic acid.



3. (b) Ethylene, C_2H_4

Explanation: When ethanol is heated with conc. H_2SO_4 at 445K, by the process of dehydration ethylene is formed. In this reaction conc. H_2SO_4 acts as a dehydrating agent.

4. (a) H_2O

Explanation: *pKa* values of the given compounds are as follows:

H—OH = 14

CH_3—OH = 15.5

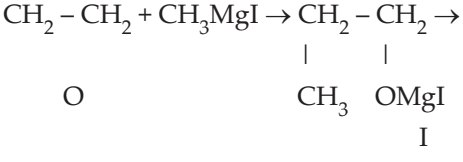
CH_3CH_2—OH = 16.0

CH_3-CH_2—CH_2—OH = 16.85

One can observe that pKa value increases as the alkyl chain length attached to the –OH group increases. This is due to the electron donating properties of alkyl groups which, in turn, destabilizes the -ve charge on oxygen when the H on the OH ionizes: $R—OH = RO^- + H^+$.

5. (c) Ethylene oxide

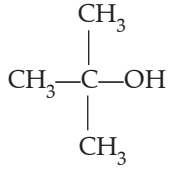
Explanation: Ethylene oxide will produce a primary alcohol by reacting with grignard reagent (CH_3MgI). The primary alcohol formed will be propyl alcohol. The reaction can be represented as follows:



$CH_3 – CH_2 – CH_2 – OH + Mg$

Propyl alcohol

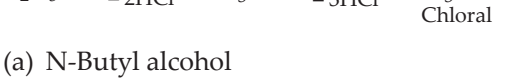
6. (d)



Explanation: Among the given compound 4th one has highest intermolecular force, thus it has highest boiling point.

7. (d) Chloral

Explanation: When chlorine reacts with ethanol, Chloral is formed. The reaction can be represented as follows:



8. (a) N-Butyl alcohol

Explanation: Amongst isomeric alcohols, as branching increases, the surface area of the non-polar hydrocarbon increases, consequently the solubility increases. So, the solubility of Tertiary alcohol will be more compared to other available options.

9. (c) Acrolein

Explanation: When glycerol is heated with potassium bisulphate, due to dehydration unsaturated aldehyde *i.e.* acrylic aldehyde is formed. Hence the product formed is acrylic aldehyde, also called acrolein.

10. (a) $(CH_3)_3COH$

Explanation: Lucas reagent is a mixture of conc. HCl and anhydrous zinc chloride. We know that the order of reactivity of alcohols towards Lucas reagent is: tertiary > secondary > primary. So among the given options, $(CH_3)_3COH$, a tertiary alcohol, will react most readily with Lucas reagent.

11. (b) Phenoxide ion is stabilized through delocalization

Explanation: As phenoxide ion is stabilized through delocalization, thus the ionization constant of phenol is higher than that of ethanol.

12. (a) 1° > 2° > 3°

Explanation: For alcohols boiling points depends upon 3 factors, viz. molecular weight, number of available H-bonds and the surface area of the molecule. If the molecular weight of all the alcohols are more or less same, then the boiling point will also be nearly same. Now, both the number of available H-bonds and the surface area of the molecule are least In 3° alcohols and maximum in 1° alcohols. Hence, 3° alcohols have a least boiling point while 1° alcohols have a maximum boiling point. Hence the correct sequence will be, 1° > 2° > 3°.

13. (d) Reacting with Mg

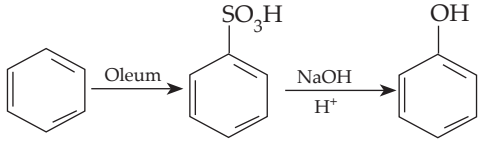
Explanation: The traces of water can be removed from ethanol by reacting it with Mg. The reaction can be represented as follows:

$Mg + C_2H_5OH \rightarrow Mg(OC_2H_5)_2 + H_2$

$Mg(OC_2H_5)_2 + H_2O \rightarrow MgO + 2C_2H_5OH$

14. (b) Riemer - Tiemann reaction

Explanation: When Phenol is heated with chloroform and alcoholic KOH, it gives salicylaldehyde. The reaction is called Reimer-Tiemann reaction and can be represented as follows:



Phenol Salicylaldehyde

15. (a) Alcohols

Explanation: Lucas test in alcohols is conducted to distinguish between primary, secondary, and tertiary alcohols. It is based on the difference in reactivity of the three classes of alcohols with hydrogen halides through a substitution reaction:

$$ROH + HCl \rightarrow RCl + H_2O$$

16. (b) CH_3OCH_3

Explanation: In general, simple Ether is R–O–R where R is an alkyl group. Hence, here CH_3OCH_3 is the simple ether.

17. (b) soluble in water

Explanation: The lower alcohols are readily soluble in water and the solubility decreases with the increase in molecular weight. The solubility of alcohols in water can be explained due to the formation of hydrogen bond between the highly polarised —OH groups present both in alcohol and water.

18. (a) There is intermolecular hydrogen bonding in methanol and no hydrogen bonding in methyl thiol.

Explanation: Methanol has high boiling point than methyl thiol because there is intermolecular hydrogen bonding in methanol and no hydrogen bonding in methyl thiol.

19. (b) $CHCl_2$

Explanation: When phenol is reacted with $CHCl_3$ and aqueous NaOH at 70°C, the electrophile attacking the ring is CCl_2 (Reimer Tiemann Reaction and Carbene formation).

20. (d) (i), (ii) and (iii) are correct

Explanation: Phenol has higher boiling point than toluene because of hydrogen bonding.

21. (c) Reduction of aldehyde/ketones with Zn-Hg/ HCl

Explanation: As per the Clemmensen reduction, reduction of aldehydes and ketones with Zn(Hg)/ HCl yields alkanes.

22. In the reaction of phenol with $CHCl_3$ and aqueous NaOH at 70°C, the electrophile attacking the ring is: (d) 2, 4, 6-tribromophenol

Explanation: When phenol is treated with excess bromine water, it gives 2, 4, 6-tribromophenol

23. (d) (i), (ii), and (iii) are correct

Explanation:

(i) $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{\text{Oxidation}} CH_3-\underset{\underset{O}{||}}{C}-CH_3$

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

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

(iv) Methanol does not undergo iodoform reaction.

24. (d) Phenol → Benzyl alcohol

Explanation: When primary (1°) alcohols are treated with copper at 300°C, then aldehydes are obtained by dehydrogenation of alcohols. Similarly secondary (2°) alcohols form ketone and alkene is obtained by dehydration of tertiary (3°)-alcohols. But phenol does not respond to this test.

25. (d) Bring down the specific heat of water

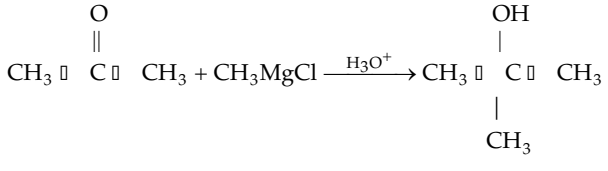
Explanation: Ethylene glycol is added to lowering down the freezing point of water so that it does not freeze.

26. (d) Hydrogen bonding

Explanation: The boiling point of ethanol is higher than ether due to extensive intermolecular hydrogen bonding in the molecule of ethyl alcohol.

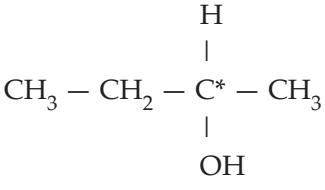
27. (a) tert-butyl alcohol

Explanation: Reaction between acetone and methyl magnesium chloride, followed by hydrolysis will give tert-butyl alcohol. The reaction is as follows:



28. (b) Butan-2-ol

Explanation: Only chiral or asymmetric (the carbon, four valencies of which are satisfied by four different groups) containing compounds optically active.



butan-2-ol

(C* = chiral carbon atoms)

So, butan-2-ol is optically active.

29. (d) Williamson's synthesis

Explanation: The reaction of metal alkoxide (such as Na) with alkyl halide to form ether is called as Williamson's synthesis. It is the industrial method to prepare ethers.

$$R - X + R'ONa \longrightarrow R - O - R' + NaX$$

Alkyl halide Sod. alkoxide Ether

$$CH_3I + CH_3CH_2ONa \longrightarrow$$

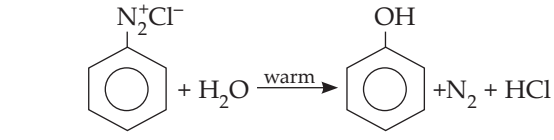
Methyl iodide Sod. ethoxide

$$CH_3 - O - CH_2CH_3 + NaI$$

Ethyl methyl ether

30. (b) Phenol

Explanation:



Benzene diazonium chloride Phenol

31. (c) CH_3COOH

Explanation: A fruity smell compound called ester is formed when CH_3COOH is mixed with ethanol and few drops of conc. H_2SO_4. The reaction is as follows:

$$CH_3COOH + CH_3CH_2OH \rightarrow CH_3COOC_2H_5$$

Acetic acid Ethyl alcohol Ethyl ethanoate

32. (b) Hydrogen

Explanation: The gas evolved when sodium metal reacts with ethanol is hydrogen. The reaction is as follows:

$$2Na + 2CH_3CH_2OH \rightarrow 2CH_3CH_2ONa + H_2$$

Fill in the blanks

33. (b) Carbocation, tertiary

Explanation: During acid catalysed dehydration of alcohols, the intermediate species involved are carbocation. In case of tertiary alcohols, the cloudiness appears immediately while performing Lucas test.

34. (d) Glycerol, glycol, ethanol

Explanation: Glycerol is an example of trihydric alcohol and glycol is an example of dihydric alcohol. Ethyl bromide on reaction with moist silver oxide gives ethanol. as the main product.

35. (c) Pyrogallol, hydrogen

Explanation: The common name of 1, 2, 3-trihydroxy-benzene is Pyrogallol. Phenol reacts with sodium liberating hydrogen gas.

36. (b) More, 2, 4, 6-Trinitrophenol

Explanation: Phenol is more reactive than chlorobenzene towards electrophilic substitution reactions. IUPAC name of picric acid is 2, 4, 6-Trinitrophenol.

37. (a) Luca's reagent, tertiary

Explanation: A mixture of conc. HCl and anhydrous $ZnCl_2$ is called Lucas reagent which shows maximum reactivity with tertiary alcohol.

38. (d) Basic, lone pair,2-Phenylpropane

Explanation: Ethers behave as weakly basic substances because of the presence of lone pair of electrons on the oxygen atom. IUPAC name of cumene is 2-Phenylpropane.

39. (a) Bronsted bases, basic

Explanation: Alcohols act as bronsted bases due to the presence of unshared electron pairs on oxygen atom. Ethers are basic in nature.

40. (b) 3° alcohol, Benzene

Explanation: Acetone reacts with Grignard reagent to form 3° alcohol. When Phenol is distilled with zinc dust, it gives benzene.

Match the following

41. (d) 1-(r), 2-(s), 3-(q), 4-(p)

Explanation: Ethylene glycol is used as Antifreeze in car engines. Ethanol is used as solvent in perfumes. Phenol is used as starting material for picric acid. Methanol is also known as wood spirit.

42. (a) 1-(s), 2-(t), 3-(p), 4-(u), 5-(q), 6-(r)

Explanation: Anhydrous $ZnCl_2$ + Conc. HCl is Lucas reagent. In Reimer Tiemann reaction, phenol is converted into an ortho hydroxy benzaldehyde using chloroform. Ethyl alcohol is obtained by the fermentation of sugar or starch from agricultural crops by yeasts or bacteria. Nitroglycerin is a powerful and unstable explosive that Alfred Nobel used in his invention of dynamite. Invertase is an enzyme. Tertiary alchols can be tested by Lucas test.

43. (d) 1-(u), 2-(t), 3-(s), 4-(r), 5-(q), 6-(p)

Explanation: When benzene diazonium chloride reacts with phenol in which the phenol molecules at its para position is coupled with the diazonium salt to form p-hydroxyazobenzene. This reaction is known as coupling reaction. Methylated spirit is methyl alcohol. Power alcohol is a mixture of petrol and ethyl alcohol. The IUPAC name of glycerine is propane-1,2,3-triol. –OH bond is polar in nature. Absolute alcohol is 100% ethyl alcohol.

Reaction based questions

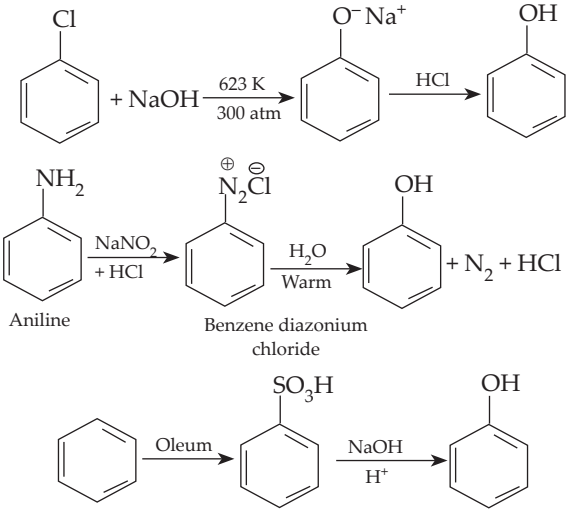
44. (d) $CH_3CHOHCH_3$

Explanation: Complete reaction,

$$\underset{A}{CH_3CHOHCH_3} \xrightarrow[dil.\ H_2SO_4]{K_2Cr_2O_2} \underset{B}{CH_3COCH_3} \xrightarrow[H_2O]{CH_3MgI} (CH_3)_3COH$$

45. (a,b,c)

Explanation:



46. (c) B, C

Explanation: Compound (A) *i.e.*, phenol and compound (D) i.e., a derivative of phenol cannot be considered as aromatic alcohol. As phenol is also known as, carbolic acid cannot be considered as aromatic alcohol.

47. (b) Dichlorocarbene (: CCl_2)

Explanation: $NaOH + CCl_3^- \rightarrow :CCl_2 + NaCl + H_2O$

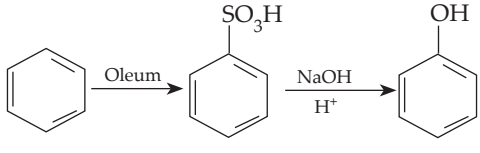
Here, the electrophile is dichlorocarbene (:CCl_2).

48. (b) b > d > a > c > e

Explanation: The most acidic is p-nitrophenol, whereas the least acidic is p-methoxyphenol. The acidity is greatest when an electron withdrawing group is parallel to the OH group. The acidity is lowest when an electron releasing group is opposite the OH group.

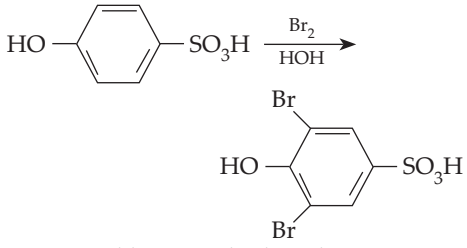
49. (b) Sodium phenoxide

Explanation: When C_6H_5Cl is put into aqueous solution of NaOH, under the condition of 624K and 300 atm it produces Sodium Phenoxide. The reaction can be represented as:



50. (b) 3, 5-Dibromo-4-hydroxybenzene sulphonic acid

Explanation: The compound 'X' will be 3, 5-Dibromo-4-hydroxybenzene sulphonic acid. The reaction can be represented as:

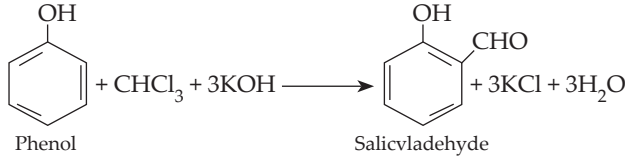


3, 5-dibromo-4-hydroxybenzene sulphonic acid
(X)

51. (i) (c) Reimer –Tiemann reaction

(ii) Salicylaldehyde

Explanation (i) and (ii): When phenol is heated with alcoholic KOH and chloroform, an aldehyde group (–CHO) gets introduced in the ring at a position ortho to the phenolic group and salicylaldehyde is formed. The reaction is known as Reimer –Tiemann reaction and the reactions is as follows:



Phenol Salicvladehyde

52. (i) (b) Heating it with aqueous NaOH at 623 K under pressure followed by acidification with dilute HCl

(ii) (a) Dow process

Explanation (i) and (ii): Dow's process is a method to prepare phenol. The reactant chlorobenzene is heated with aqueous sodium hydroxide at temperature 623K and 300atm to get sodium phenoxide ion. Then in the next step sodium phenoxide ion is treated with dilute HCl which gives the final product as phenol.

53. (i) (c) Tertiary alcohol by S_N1

Explanation: Lucas test in alcohol is a test to differentiate between primary, secondary and tertiary alcohols. It is based on the difference in reactivity of three classes of alcohols with hydrogen halides. Reaction proceeds through carbocation formation as 3^0 carbocation is highly stable. Hence, the reaction proceeds through S_N1 with 3^0 alcohol.

(ii) (a) Anhydrous zinc chloride in concentrated HCl

Explanation: Lucas reagent it anhydrous zinc chloride in concentrated HCl

Assertion and Reason based questions

54. (c) $(CH_3)_3CONa$ and CH_3CH_2Br react to form $(CH_3)_3C—O—CH_2CH_3$. Good yields of ether are obtained when primary alkyl halides are treated with alkoxides derived from any alcohol, 1°, 2°, or 3°. Thus, assertion is true but reason is false.

55. (c) Ortho and para isomers of nitro phenol can be separated by steam distillation because of nearly same boiling point of both. Ortho isomers associate by intramolecular hydrogen bonding and para isomers associate by hydrogen bonding. Thus, assertion is true but reason is false.

56. (b) Lucas reagent is an equimolar mixture of anhyd. $ZnCl_2$ and conc. HCl. In Lucas test, tertiary alcohols react immediately because of the formation of the more stable tertiary carbocations. Thus, both assertion and reason are true, but reason is not the correct explanation of assertion.

57. (b) The water solubility of the alcohols follow the order: tert-butyl alcohol > sec-butyl alcohol > *n*-butyl alcohol. The tendency to show H-bonding decreases with increasing hydrophobic character of carbon chain. The hydrophobic character of carbon chain increases with the length of carbon chain. Thus, both assertion and reason are true, but reason is not the correct explanation of assertion.

58. (b) Alcohols which form the more stable carbocations undergo dehydration more readily. Since *tert*-butyl alcohol forms more stable *tert*-butyl cation, therefore, it undergoes dehydration more readily than propanol. 3°Alcohols do not give Victor-Meyer's test. Thus, both assertion and reason are true, but reason is not the correct explanation of assertion.

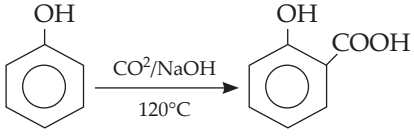
59. (c) Phenol is less acidic than *p*-nitrophenol. Nitrophenolate ion is more stable than phenolate ion. Thus, assertion is true, but reason is false.

60. (c) Nucleophilic attack of phenolate ion through the *ortho*-carbon atom occurs on CCl_4 (a neutral electrophile) to form an intermediate which on hydrolysis gives salicylic acid (ArSE reaction). Thus, assertion is true, but reason is false.

61. (d) In ethers, bond angle around oxygen is not exactly 109° 28′. There is deviation in angle caused due to repulsive interactions between bulkier alkyl groups. Thus, assertion is false but reason is true.

62. (c) On using *tert*-butyl bromide and sodium ethoxide as reactants, the major product would be 2-methylpropene and ethanol (elimination reaction).

Phenol undergoes Kolbe reaction in the presence of CO_2/NaOH at 120C and 6-7atm to form salicylic acid. Whereas, ethanol does not undergo this reaction.



6-7 atc Solicylic acid

The conjugate base phenoxide ion is more resonance stabilised than ethoxide ion and can participate in the electrophilic substitution more readily than ethoxide ion. Thus, assertion is true, but reason is false.

63. (c) Ethers being Lewis bases form etherates with Lewis acids. Ethers are not easily cleaved by H_2SO_4. Thus assertion is true but reason is false.

64. (a) Alcohols have high boiling point than ethers of comaparable molecular mass. This is because intermolecular H-bonding is found in alcohols. Thus, both assertion and reason are true and reason is the correct explanation of assertion.

Source based questions

65. (i) (a) The formation of ether from alcohol in acidic medium is a bimolecular reaction. A protonated alcohol molecule is attacked by another alcohol molecule while ether formation in acidic medium. Thus, Assertion and reason both are correct statements and reason is correct explanation for assertion.

(ii) (c) Dehydration of secondary and tertiary alcohols to give corresponding ethers is not a productive reaction. Elimination does compete with ether formation reaction. Thus, Assertion is correct statement but reason is wrong statement.

(iii)(a) Alkyl aryl ethers are cleaved at the alkyl-oxygen bond when reacted with hydrogen halides and aryl oxygen bond are more stable. Thus, Assertion and reason both are correct statements and reason is correct explanation for assertion.

(iv)(b) Anisole undergoes bromination with bromine in absence of iron (III) bromide. Iron (III) bromide is used to catalyse halogenation reaction of phenylalkyl ethers. Thus, Assertion and reason both are correct statements but reason is not correct explanation for assertion.

Word of Advice

1. Most of the students wrote the correct product i.e., p-hydroxyazobenzene for the given chemical equation but they did not mentioned the formation of the by-product, i.e., HCl when phenol is treated with ice cold alkaline solution of benzene diazonium chloride.
2. Majority of the students wrote the correct balanced chemical equation for the reaction of diethyl ether with phosphorous pentachloride but some of the students missed writing the by-product $POCl_3$.
3. A few students did not mentioned the formation of by-product when ethyl alcohol is treated with thionyl chloride .
4. Most of the students used correct test i.e., Lucas test to distinguish between propan-1-ol and propan-2-ol but some of them did not gave the correct observation like the heating time and appearance of turbidity.
5. For Williamson's synthesis, some of the students wrote the reactant sodium alkoxide as C_2H_5OH instead of C_2H_5ONa. During this synthesis, ether is obtained as the main product but the by-product NaBr was not mentioned by few students.
6. Most of the students were not able to write the Reimer-Tiemann reaction correctly, either the main product was incorrect or in some cases by-product was missing

7. Most of the students identified compound A correctly as acetaldehyde (CH_3CHO) which is formed when ethyl alcohol is passed over red hot copper at 300°C, it forms acetaldehyde . However, they went wrong by writing only 'aldol' as compound 'B', instead of writing the complete formula of aldol which is β hydroxy butyraldehyde ($CH_3CHOHCH_2CHO$).
8. Most of the students did not write ZnO as a by-product during the preparation of benzene from phenol.
9. Most of the students did not write the complete reaction including the by-product for the preparation of iodoform from ethanol. In some answer scripts, a few students wrote incorrect formula for iodoform.
10. Most of the students wrote the formula for salicylaldehyde as 4-hydroxybenzaldehyde instead of 2-hydroxybenzaldehyde which is formed during the preparation of salicylaldehyde from phenol.
11. Majority of the students did not write the by-product Mg(OH)Br and H_2O for hydrolysis for the formation of Propan-2-ol from grignard reagent.
12. Most of the students did not write that phenol reacts with concentrated HNO_3 in the presence of concentrated H_2SO_4 to form picric acid. Also, a few students did not write that water molecule are released as the by-product during the reaction.
13. Some of the students wrote the incorrect reactants used in the preparation of ethyl chloride from diethyl ether. They wrote Cl_2 instead of PCl_5 or $SOCl_2$.
14. Most of the students directly converted phenol to anisole instead of writing that phenol first reacts with NaOH to form sodium phenoxide which further reacts with CH_3Br to form anisole.
15. Most of the students could not identify an esterification reaction. They did not write that the reaction takes place in the presence of a few drops of concentrated sulphuric acid which acts as a catalyst and they provided the incorrect structure of the product ethyl acetate.
16. Most of the students were able to identify compounds A and B they were not able to identify the but compound C *i.e.,* benzoin.
17. Most of the students were able to identify compound C but they did not indentify the compound A and B *i.e.,* CH_3CHO and C_2H_5OH correctly.
18. Some of the students did not read the question correctly and they wrote the chemical equation for Friedel Crafts acylation instead of Friedel-Crafts alkylation. Also, some of the students who gave the correct chemical equation did not mention the name of the catalyst used in the reaction.
19. Most of the students gave correct observations for the distinction between ethyl alcohol and secondary propyl alcohol using Lucas test or Victor Meyer's test but there were few students who wrote the iodoform test which cannot be used for the distinction between ethyl alcohol and secodary propyl alcohol.
20. Some of the students mentioned that dimethyl ether will not react with PCl_5.
21. Some of the students wrote the positive test for ethyl alcohol but did not write anything about dimethyl ether.
22. Most of the students were able to write the structure of at least two ethers. However, a number of students were not able to write the structure of branched chain ether.
23. Most of the students wrote wrong products for the reaction of diethyl ether with phosphorous pentachloride. Instead of writing C_2H_5Cl and $POCl_3$,they wrote C_2H_5COCl or C_2Cl_5-O-C_2Cl_5.
24. Most of the students failed to write the correct names of the products formed when phenol and nitrobenzene are treated separately with a mixture of concentrated sulphuric acid and concentrated nitric acid.