

# Alcohols, Phenols and Ethers

## CASE STUDY / PASSAGE BASED QUESTIONS

1

### Syllabus

#### Alcohols :

Nomenclature, methods of preparation, physical and chemical properties (of primary alcohols only), identification of primary, secondary and tertiary alcohols, mechanism of dehydration.

#### Phenols :

Nomenclature, methods of preparation, physical and chemical properties, acidic nature of phenol, electrophilic substitution reactions, uses of phenols.

#### Ethers :

Nomenclature, methods of preparation, physical and chemical properties, uses.

Read the passage given below and answer the following questions :

Although chlorobenzene is inert to nucleophilic substitution, however it gives quantitative yield of phenol when heated with aq. NaOH at high temperature and under high pressure.

As far as electrophilic substitution in phenol is concerned the —OH group is an activating group, hence, its presence enhances the electrophilic substitution at *o*- and *p*-positions.

The following questions are multiple choice questions. Choose the most appropriate answer :

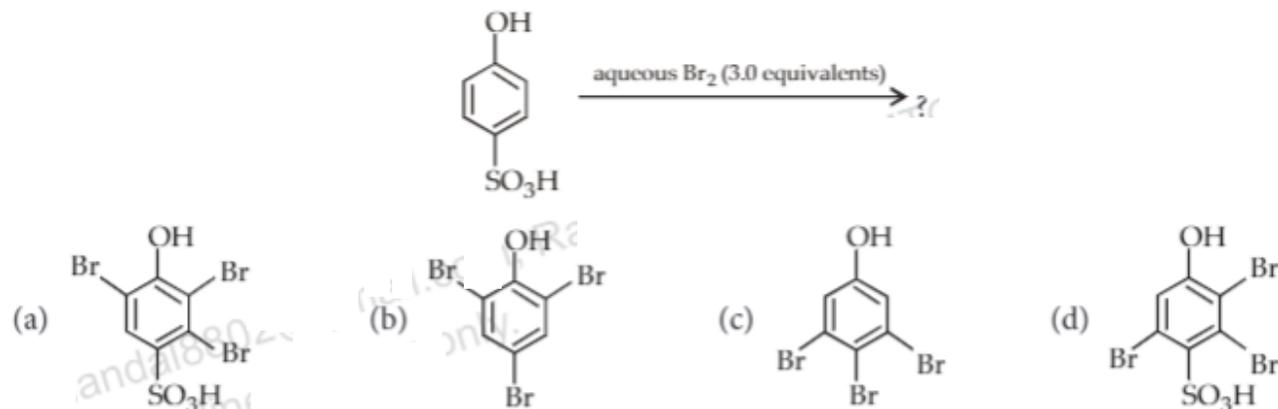
- (i) Conversion of chlorobenzene into phenol involves
- |                               |                                     |
|-------------------------------|-------------------------------------|
| (a) modified $S_N1$ mechanism | (b) modified $S_N2$ mechanism       |
| (c) both (a) and (b)          | (d) elimination-addition mechanism. |
- (ii) Phenol undergoes electrophilic substitution more readily than benzene because
- the intermediate carbocation is a resonance hybrid of more resonating structures than that from benzene
  - the intermediate is more stable as it has positive charge on oxygen, which can be better accommodated than on carbon
  - in one of the canonical structures, every atom (except hydrogen) has complete octet
  - the —OH group is *o*, *p*-directing which like all other *o*, *p*-directing group, is activating.
- (iii) Phenol on treatment with excess of conc.  $HNO_3$  gives
- |  |                           |
|--|---------------------------|
| (a) <i>o</i> -nitrophenol                | (b) <i>p</i> -nitrophenol |
| (c) <i>o</i> - and <i>p</i> -nitrophenol | (d) 2,4,6-trinitrophenol. |

OR

Phenol is heated with a solution of mixture of KBr and  $KBrO_3$ . The major product obtained in the above reaction is

- |                   |                             |
|-------------------|-----------------------------|
| (a) 2-bromophenol | (b) 3-bromophenol           |
| (c) 4-bromophenol | (d) 2, 4, 6-tribromophenol. |

(iv) The major product of the following reaction is



2

Read the passage given below and answer the following questions :

A compound (X) containing C, H and O is unreactive towards sodium. It also does not react with Schiff's reagent. On refluxing with an excess of hydroiodic acid, (X) yields only one organic product (Y). On hydrolysis, (Y) yields a new compound (Z) which can be converted into (Y) by reaction with red phosphorus and iodine. The compound (Z) on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60.

The following questions are multiple choice questions. Choose the most appropriate answer :

- (i) The compound (X) is an  
(a) acid                                      (b) aldehyde                                      (c) alcohol                                      (d) ether.
- (ii) The IUPAC name of the acid formed is  
(a) methanoic acid                                      (b) ethanoic acid                                      (c) propanoic acid                                      (d) butanoic acid.
- (iii) Compound (Y) is  
(a) ethyl iodide                                      (b) methyl iodide  
(c) propyl iodide                                      (d) mixture of (a) and (b).

OR

Compound (Z) is

- (a) methanol                                      (b) ethanol                                      (c) propanol                                      (d) butanol.
- (iv) Compound (X) on treatment with excess of  $\text{Cl}_2$  in presence of light gives  
(a)  $\alpha$ -chlorodiethyl ether                                      (b)  $\alpha, \alpha'$ -dichlorodiethyl ether  
(c) perchlorodiethyl ether                                      (d) none of these.

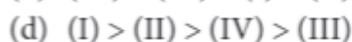
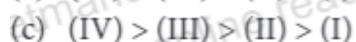
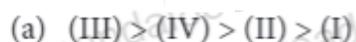
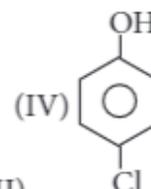
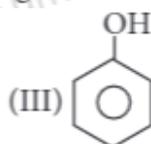
3

Read the passage given below and answer the following questions :

Both alcohols and phenols are acidic in nature, but phenols are more acidic than alcohols. Acidic strength of alcohols mainly depends upon the inductive effect. Acidic strength of phenols depends upon a combination of both inductive effect and resonance effects of the substituent and its position on the benzene ring. Electron withdrawing groups increases the acidic strength of phenols whereas electron donating groups decreases the acidic strength of phenols. Phenol is a weaker acid than carboxylic acid.

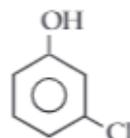
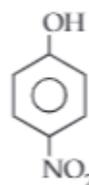
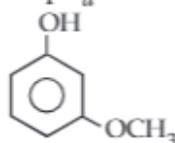
The following questions are multiple choice questions. Choose the most appropriate answer :

- (i) Phenols are highly acidic as compare to alcohols due to  
 (a) the higher molecular mass of phenols (b) the stronger hydrogen bonds in phenols  
 (c) alkoxide ion is a strong conjugate base (d) phenoxide ion is resonance stabilised.
- (ii) The correct order of acidic strength among the following is -



OR

The correct decreasing order of  $\text{p}K_a$  value is



(I)

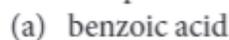
(II)

(III)

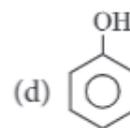
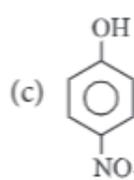
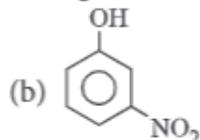
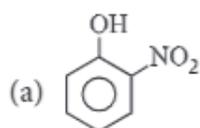
(IV)



(iii) The compound that does not liberate  $\text{CO}_2$ , on treatment with aqueous sodium bicarbonate solution is



(iv) Most acidic amongst the following is



4

Read the passage given below and answer the following questions :

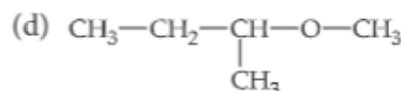
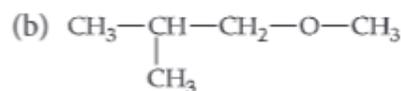
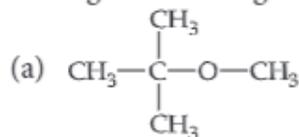
Ethers are readily cleaved by HI or HBr at 373 K to form an alcohol and an alkyl halide.

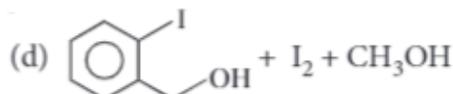
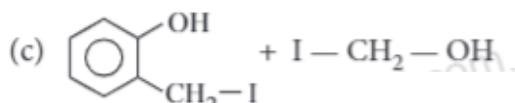
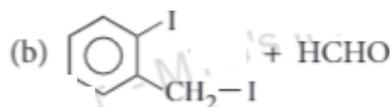
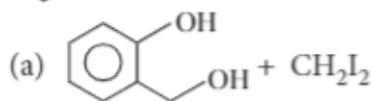
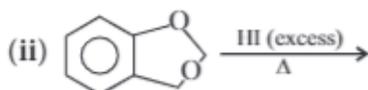


Mixed ether, containing primary or secondary alkyl group, when heated with hydrogen halide, the lower alkyl group forms halide and higher will form an alcohol. Tertiary alkyl ether when heated with hydrogen halide gives tertiary alkyl halide.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Among the following ethers, which one will produce methyl alcohol on treatment with hot concentrated HI?





OR

When  $\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2-\text{CH}_3$  reacts with one mole of HI, one of the products formed is

(a) ethane

(b) ethanol

(c) iodoethene

(d) ethanal.

(iii)  $(\text{CH}_3)_3\text{COCH}_3$  and  $\text{CH}_3\text{OC}_2\text{H}_5$  are treated with hydroiodic acid. The fragments obtained after reactions are respectively

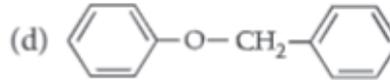
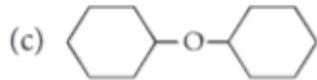
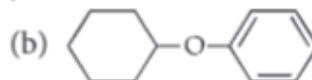
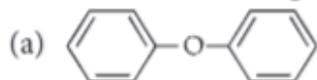
(a)  $(\text{CH}_3)_3\text{CI} + \text{CH}_3\text{OH}; \text{CH}_3\text{I} + \text{C}_2\text{H}_5\text{OH}$

(b)  $(\text{CH}_3)_3\text{CI} + \text{CH}_3\text{OH}; \text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{I}$

(c)  $(\text{CH}_3)_3\text{COH} + \text{CH}_3\text{I}; \text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{I}$

(d)  $\text{CH}_3\text{I} + (\text{CH}_3)_3\text{COH}; \text{CH}_3\text{I} + \text{C}_2\text{H}_5\text{OH}$

(iv) Which of the following ether is unlikely to be cleaved by hot conc. HBr?



5

Read the passage given below and answer the following questions :

An organic compound (A) having molecular formula  $\text{C}_6\text{H}_6\text{O}$  gives a characteristic colour with aqueous  $\text{FeCl}_3$  solution. (A) on treatment with  $\text{CO}_2$  and  $\text{NaOH}$  at 400 K under pressure gives (B), which on acidification gives a compound (C). The compound (C) reacts with acetyl chloride to give (D) which is a popular pain killer.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Compound (A) is

(a) 2-hexanol

(b) dimethyl ether

(c) phenol

(d) 2-methyl pentanol.

OR

Compound (C) is

(a) salicylic acid

(b) salicylaldehyde

(c) benzoic acid

(d) benzaldehyde

(ii) Number of carbon atoms in compound (D) is

(a) 7

(b) 6

(c) 8

(d) 9

(iii) The conversion of compound (A) to (C) is known as

(a) Reimer-Tiemann reaction

(b) Kolbe's reaction

(c) Schimdt reaction

(d) Swarts reaction.

(iv) Compound (A) on heating with compound (C) in presence of  $\text{POCl}_3$  gives a compound (D) which is used

(a) in perfumery as a flavouring agent

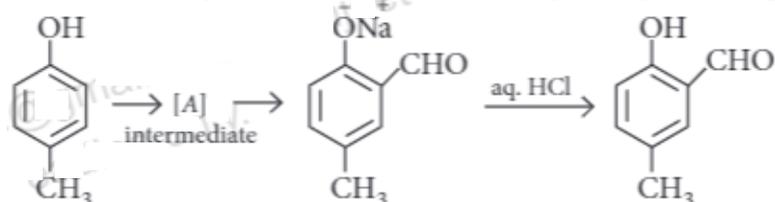
(b) as an antipyretic

(c) as an analgesic

(d) as an intestinal antiseptic.

Read the passage given below and answer the following questions :

Reimer-Tiemann reaction introduces an aldehyde group, on aromatic ring of phenol, *ortho* to the hydroxyl group. This is a general method for the synthesis of substituted salicylaldehydes as depicted below.



The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Reimer-Tiemann reaction is an example of

- (a) nucleophilic substitution reaction (b) electrophilic substitution reaction  
(c) nucleophilic addition reaction (d) electrophilic addition reaction.

(ii) Which of the following reagents is used in the given reaction in steps I?

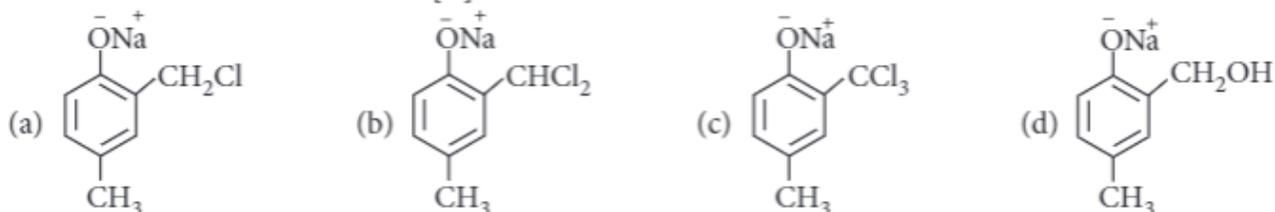
- (a) aq. NaOH + CH<sub>3</sub>Cl (b) aq. NaOH + CH<sub>2</sub>Cl<sub>2</sub> (c) aq. NaOH + CHCl<sub>3</sub> (d) aq. NaOH + CCl<sub>4</sub>

OR

The electrophile in this reaction [A] is

- (a) :CHCl (b) <sup>+</sup>CHCl<sub>2</sub> (c) :CCl<sub>2</sub> (d) ·CCl<sub>3</sub>

(iii) The structure of the intermediate [A] is



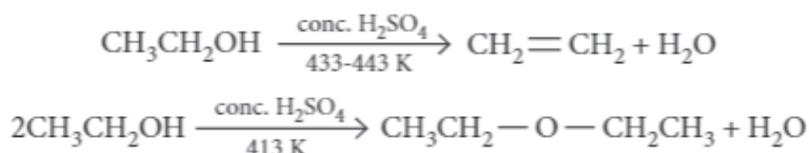
(iv) When phenol reacts with chloroform in presence of KOH, the product formed is

- (a) salicylic acid (b) salicylaldehyde (c) both (a) and (b) (d) none of these.

Read the passage given below and answer the following questions :

Dehydration of alcohols can lead to the formation of either alkenes or ethers. This dehydration can be carried out either with protonic acids such as conc. H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub> or catalysts such as anhydrous ZnCl<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>. When primary alcohols are heated with conc. H<sub>2</sub>SO<sub>4</sub> at 433-443 K, they undergo intramolecular dehydration to form alkenes. Secondary and tertiary alcohols undergo dehydration under milder conditions. The ease of dehydration of alcohols follows the order : 3° > 2° > 1°.

The dehydration of alcohols always occurs in accordance with the Saytzeff's rule. Primary alcohols when heated with protic acid at 413 K, gives dialkyl ether.

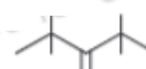
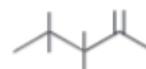


The following questions are multiple choice questions. Choose the most appropriate answer :

- (i) Which one of the following alcohols undergoes acid-catalysed dehydration to alkenes most readily?  
 (a)  $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$     (b)  $(\text{CH}_3)_3\text{COH}$     (c)  $\text{CH}_3\text{CHOHCH}_3$     (d)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- (ii) Dehydration of alcohol is an example of which type of reaction?  
 (a) Substitution    (b) Elimination    (c) Addition    (d) Rearrangement
- (iii) The alcohol which does not give a stable compound on dehydration is  
 (a) ethyl alcohol    (b) methyl alcohol    (c) *n*-propyl alcohol    (d) *n*-butyl alcohol.

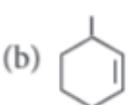
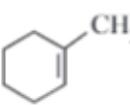


The most stable product(s) is/are

- (a)     (b)     (c) both (a) and (b)    (d) none of these.

OR



- (a)     (b)     (c)     (d) 

8

Read the passage given below and answer the following questions :

Williamson's synthesis is used for the preparation of symmetrical as well as unsymmetrical ether. It is  $\text{S}_{\text{N}}2$  reaction mechanism. In Williamson's synthesis,  $1^\circ$  alkyl halide are used for preparation of ethers because  $2^\circ$  and  $3^\circ$  alkyl halide give alkene. Ethers are cleaved by hydrogen halides to alcohol and alkyl halide where alkyl halide is corresponding to that alkyl which has less number of carbon atom (it is because of less steric hindrance). In polar media unsymmetrical ether like tertiary butyl ethyl ether gives ethyl alcohol and tertiary butyl halide as reaction proceeds via carbocation.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.  
 (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.  
 (c) Assertion is correct statement but reason is wrong statement.  
 (d) Assertion is wrong statement but reason is correct statement.
- (i) **Assertion :** Rate of reaction of alkyl halide in Williamson's synthesis reaction is  $1^\circ\text{RX} > 2^\circ\text{RX} > 3^\circ\text{RX}$ .  
**Reason :** It is a type of bimolecular substitution reaction ( $\text{S}_{\text{N}}2$ ).
- (ii) **Assertion :** *t*-Butyl methyl ether is not prepared by the reaction of *t*-butyl bromide with sodium methoxide.  
**Reason :** Sodium methoxide is a weak nucleophile.

OR

**Assertion :** Williamson's synthesis method cannot be used for preparing diphenyl ether.

**Reason :** Aryl halides do not undergo nucleophilic substitution easily.

(iii) **Assertion :** When isopropyl bromide is treated with sodium isopropoxide, di-isopropyl ether is obtained as a major product.

**Reason :** With secondary alkyl halides, both substitution and elimination occur.

(iv) **Assertion :** Both symmetrical and unsymmetrical ethers can be prepared by Williamson's synthesis.

**Reason :** Williamson's synthesis is an example of nucleophilic substitution reaction.

9

Read the passage given below and answer the following questions :

Due to intermolecular hydrogen bonding, the boiling points of alcohols and phenols are much higher than those of corresponding haloalkanes, haloarenes, aliphatic and aromatic hydrocarbons. Among isomeric alcohols, the boiling points follow the order : primary > secondary > tertiary. Boiling points of ethers are much lower than those of isomeric alcohols. The solubility of alcohols in water decreases as the molecular mass of alcohols increases. Amongst isomeric alcohols solubility increases with branching. The solubility of phenols in water is much lower than that of alcohols. Lower ethers such as dimethyl ether and ethylmethyl ether are soluble in water, but the solubility decreases as the molecular mass increases.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

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

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

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

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

(i) **Assertion :** Alcohols have higher boiling points than ethers of comparable molecular masses.

**Reason :** Alcohols and ethers are isomeric in nature.

(ii) **Assertion :** The solubility of phenols in water is much lower than that of alcohols.

**Reason :** Phenols do not form H-bonds with water.

(iii) **Assertion :** Among *n*-butane, ethoxyethane, 1-propanol and 2-propanol, the increasing order of boiling points is, 1-butanol < 1-propanol < ethoxyethane < *n*-butane.

**Reason :** Boiling point increases with increase in molecular mass.

(iv) **Assertion :** Dimethyl ether and diethylether are soluble in water.

**Reason :** As the molecular mass increases, solubility of ethers in water decreases.

OR

**Assertion :** Butan-2-ol has higher boiling point than 2-methylpropan-2-ol.

**Reason :** Amongst isomeric alcohols, the boiling points decreases with branching.

10

Read the passage given below and answer the following questions :

Lucas test is a test to differentiate between primary, secondary and tertiary alcohols. This test consists of treating an alcohol with Lucas' reagent, and turbidity, due to the formation of insoluble alkyl chloride, is observed. Lucas test is based on the difference in reacting of three classes of alcohols with hydrogen chloride via  $S_N1$  reaction. The different reactivity reflects the differing ease of formation of the corresponding carbocations.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
- (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion** : Equimolar mixture of conc. HCl and anhydrous  $\text{ZnCl}_2$  is called Lucas' reagent.

**Reason** : Lucas' reagent can be used to distinguish between methanol and ethanol.

(ii) **Assertion** : 2-Methyl-2-butanol gives no turbidity with Lucas' reagent at room temperature.

**Reason** : It is a  $3^\circ$  alcohol.

OR

**Assertion** : Tertiary alcohols react fastest with Lucas' reagent by  $\text{S}_{\text{N}}1$  mechanism.

**Reason** :  $3^\circ$  carbocation is most stable.

(iii) **Assertion** : Amongst the compounds,  $\text{H}_2\text{C}=\text{CHCH}_2\text{OH}$  (I),  $\text{C}_6\text{H}_5\text{OH}$  (II),  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  (III) and  $(\text{CH}_3)_3\text{COH}$  (IV), only (IV) reacts with Lucas' reagent at room temperature.

**Reason** : Tertiary alcohol gives turbidity immediately with Lucas' reagent.

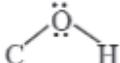
(iv) **Assertion** : Lucas test can be used to distinguish between 1-propanol and 2-propanol.

**Reason** : Lucas test is based upon the difference in reactivity of primary, secondary and tertiary alcohols with conc. HCl and anhyd.  $\text{ZnCl}_2$ .

## ASSERTION & REASON

In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

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- (b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
- (c) Assertion is correct statement but reason is wrong statement.
- (d) Assertion is wrong statement but reason is correct statement.

11. **Assertion** :  bond angle is less than the normal tetrahedral bond angle.

**Reason** : Lone pair-lone pair repulsion decreases bond angle.

12. **Assertion** : Boiling points of alcohols are lower than hydrocarbons.

**Reason** : Among isomeric alcohols, boiling point decreases in the order :  $1^\circ > 2^\circ > 3^\circ$ .

13. **Assertion** : The ease of dehydration of alcohols follows the order : Primary > Secondary > Tertiary.

**Reason** : Dehydration proceeds through the formation of carbocations.

14. **Assertion** : 2-Butanol on heating with  $\text{H}_2\text{SO}_4$  gives 1-butene and 2-butene.

**Reason** : Dehydration of 2-butanol follows Saytzeff's rule.

15. **Assertion** : *o*-Nitrophenol is more volatile than *p*-nitrophenol.

**Reason** : Intramolecular hydrogen bonding is present in *o*-nitrophenol while intermolecular H-bonding is in *p*-nitrophenol.

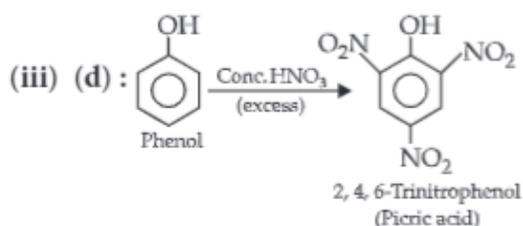
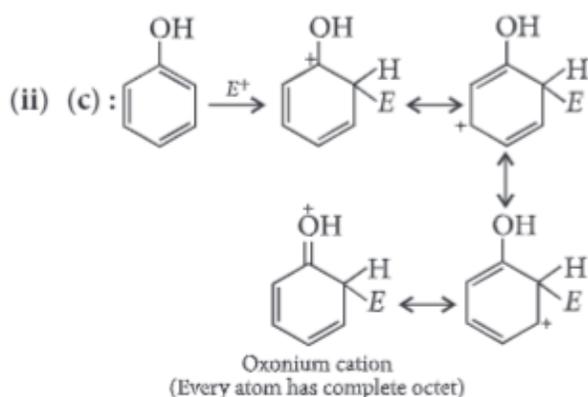
16. **Assertion** :  $\text{CH}_3\text{OCH}_3$  and  $\text{C}_2\text{H}_5\text{OH}$  has comparable molecular weight but boiling point of  $\text{C}_2\text{H}_5\text{OH}$  is more than dimethyl ether.

**Reason** :  $\text{C}_2\text{H}_5\text{OH}$  forms intermolecular H-bonding while  $\text{CH}_3\text{OCH}_3$  forms intramolecular H-bonding.

17. **Assertion** : Phenol is less acidic than *p*-nitrophenol.  
**Reason** : Phenolate ion is more stable than *p*-nitrophenolate ion.
18. **Assertion** : *p*-Nitrophenol gives more electrophilic substituted compound than *m*-methoxyphenol.  
**Reason** : Methoxy group shows both +*R* and -*I*-effect.
19. **Assertion** : With  $\text{Br}_2\text{-H}_2\text{O}$ , phenol gives 2,4,6-tribromophenol but with  $\text{Br}_2\text{-CS}_2$ , it gives 4-bromophenol as the major product.  
**Reason** : In water, ionisation of phenol is enhanced but in  $\text{CS}_2$ , it is greatly suppressed.
20. **Assertion** : Phenol is more acidic than ethanol.  
**Reason** : Phenoxide ion is resonance stabilised.
21. **Assertion** : Solubility of alcohols decreases with increase in size of alkyl/aryl groups.  
**Reason** : Alcohols form H-bonding with water to show soluble nature.
22. **Assertion** : *tert*-Butyl alcohol undergoes acid catalysed dehydration readily than propanol.  
**Reason** : 3° Alcohols do not give Victor-Meyer's test.
23. **Assertion** : Phenol decomposes  $\text{NaHCO}_3$  solution to evolve  $\text{CO}_2$  gas.  
**Reason** : Picric acid is 2, 4, 6-trinitrophenol.
24. **Assertion** : Reimer-Tiemann reaction of phenol with  $\text{CHCl}_3$  in  $\text{NaOH}$  at 340 K gives salicylic acid as the major product.  
**Reason** : The reaction occurs through intermediate formation of  $^+\text{CHCl}_2$ .
25. **Assertion** : Primary and secondary alcohols can be distinguished by Victor-Meyer's test.  
**Reason** : Primary alcohols form nitrolic acid which dissolves in  $\text{NaOH}$  to form blood red colouration but secondary alcohols form pseudonitrols which give blue colouration with  $\text{NaOH}$ .

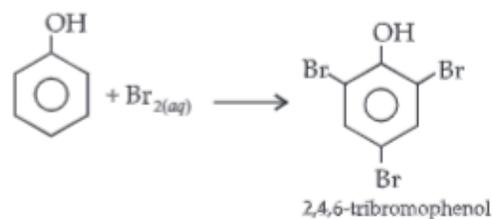
## HINTS & EXPLANATIONS

1. (i) (d)

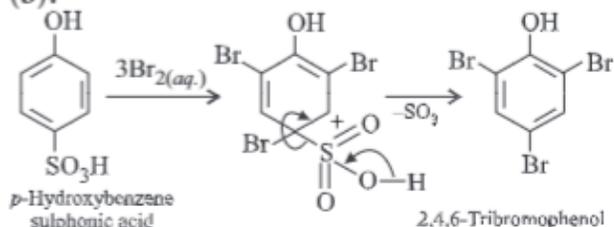


OR

(d) :  $\text{KBr}_{(aq)} + \text{KBrO}_{3(aq)} \longrightarrow \text{Br}_{2(aq)}$   
 This bromine reacts with phenol and gives 2,4,6-tribromophenol.



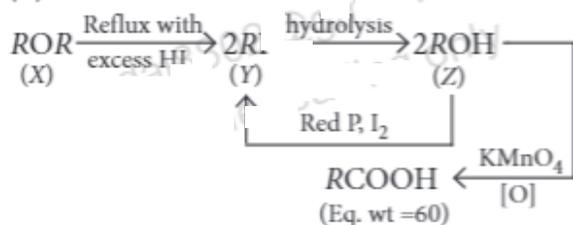
(iv) (b) :



2. (i) (d): Since the compound X is unreactive towards sodium so it is neither an acid nor an alcohol. Since the compound X is unreactive towards Schiff's base so it is not an aldehyde.

The compound X forms only one product on reaction with excess HI, indicates that the compound X may be ether.

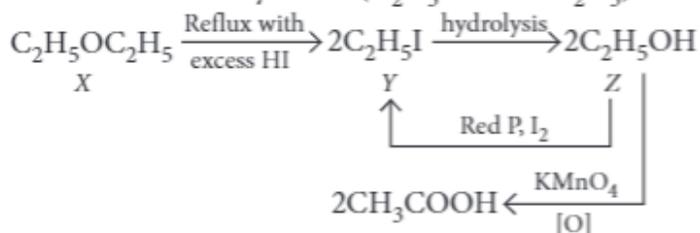
(ii) (b): The reactions can be written as:



Since the equivalent weight of carboxylic acid is 60. So, it must be  $\text{CH}_3\text{COOH}$  i.e., ethanoic acid.

(iii) (a): The alcohol Z in that case should be  $\text{C}_2\text{H}_5\text{OH}$  and the compound Y should be ethyl iodide.

X is therefore diethyl ether ( $\text{C}_2\text{H}_5 - \text{O} - \text{C}_2\text{H}_5$ )

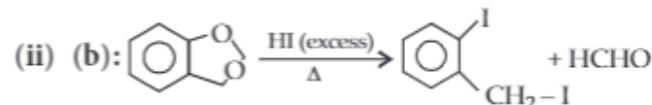
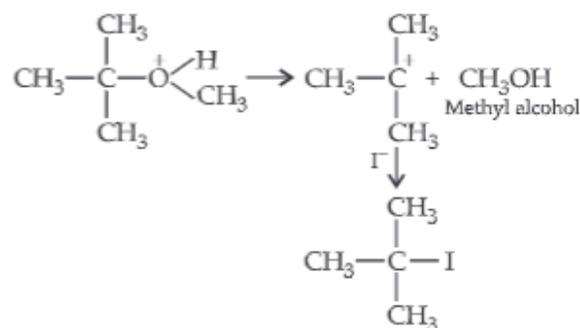
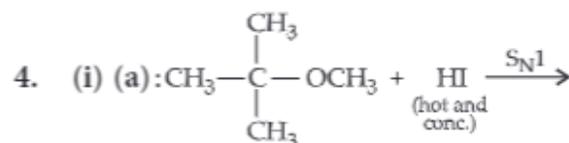


OR

-I effect order:  $-\text{NO}_2 > -\text{OCH}_3 > -\text{Cl}$ .  
 $-\text{CH}_3$  has +I effect. So, order is (a).

(iii) (d): Phenol (Carbolic acid) is a weaker acid than carbonic acid ( $\text{H}_2\text{CO}_3$ ) and does not liberate  $\text{CO}_2$  on treatment with aqueous sodium bicarbonate solution.

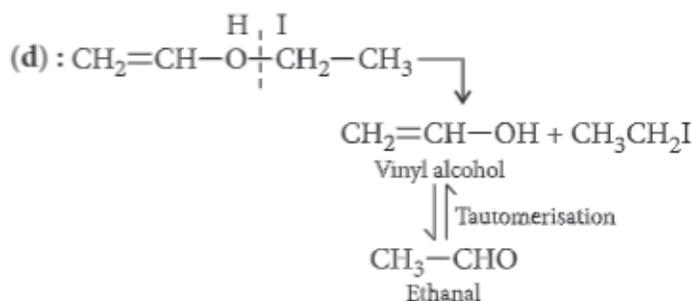
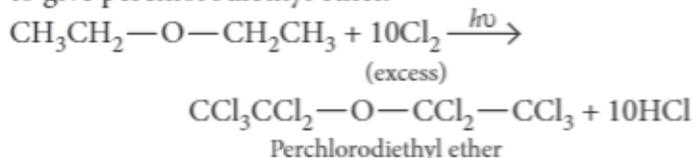
(iv) (c):  $-\text{NO}_2$  exhibits both -I and -R influence to stabilise the corresponding phenoxide. In ortho derivative, intermolecular H-bonding lowers the acidity.



OR

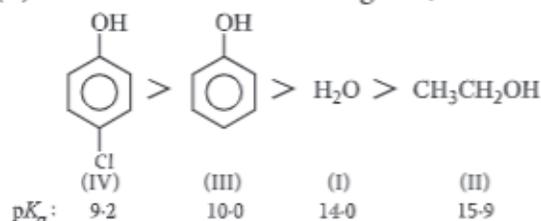
(b)

(iv) (c): In the presence of light and excess of chlorine, all the hydrogen atoms of diethyl ether are substituted to give perchlorodiethyl ether.



3. (i) (d)

(ii) (b): The order of acidic strength is,



OR

(a): Weaker acids have higher  $\text{p}K_a$ .

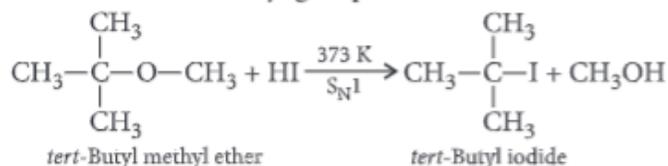
$-\text{OCH}_3$  at meta-position exerts only -I effect, hence increases the acidity.

(iii) (a): When mixed ethers are used, the formation of alkyl iodide depends on the nature of alkyl groups. Methyl iodide is formed when one group is methyl and the other a primary or secondary alkyl group. Here reaction follows  $\text{S}_\text{N}2$  mechanism and because of the steric effect of the larger group,  $\text{I}^-$  attacks the smaller (Me) group.



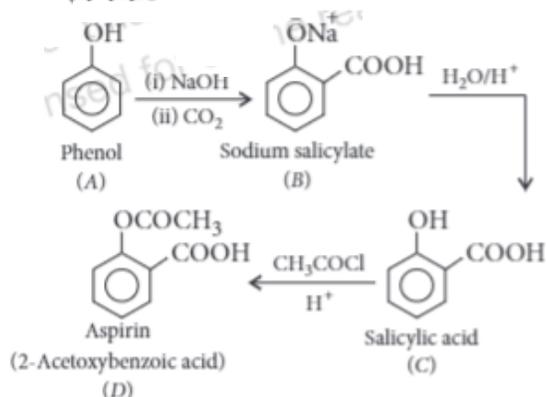
When the substrate is a methyl t-alkylether, the products are t-RI and MeOH. Here, reaction follows  $\text{S}_\text{N}1$  mechanism and formation of products is controlled by the stability of carbocation. Since, carbocation stability order is:

$3^\circ > 2^\circ > 1^\circ > \overset{+}{\text{C}}\text{H}_3$ , therefore alkyl halide is always derived from *tert*-alkyl group.



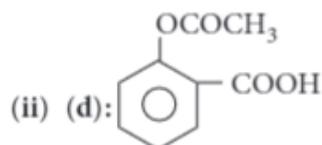
(iv) (a): Diphenyl ethers are not cleaved by HBr or HI.

5. (i) (c):



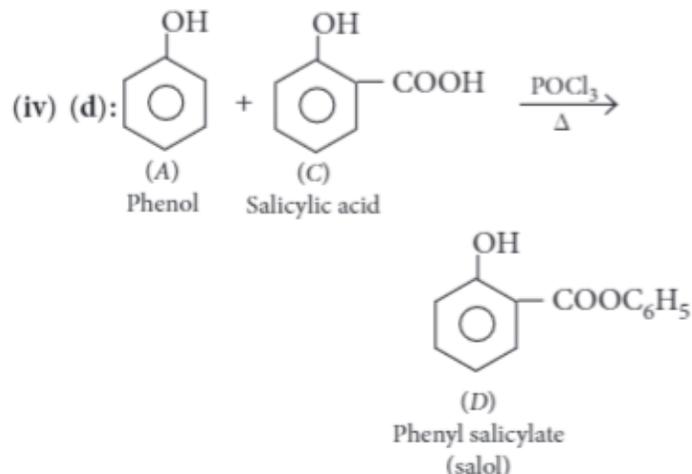
OR

(a)



It has 9 C-atoms.

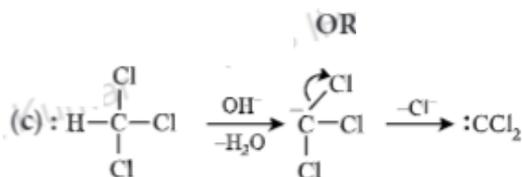
(iii) (b): Sodium phenoxide when heated with  $\text{CO}_2$  at 400 K under a pressure of 4-7 atm followed by acidification gives 2-hydroxybenzoic acid (salicylic acid) as the main product along with a small amount of 4-hydroxybenzoic acid. This reaction is called Kolbe's reaction.



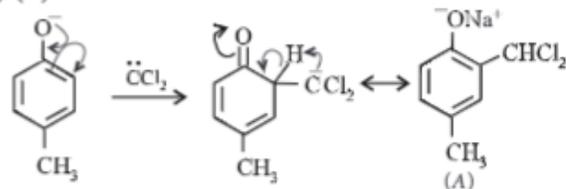
Salol is used as an intestinal antiseptic.

6. (i) (b): It is an electrophilic substitution reaction.

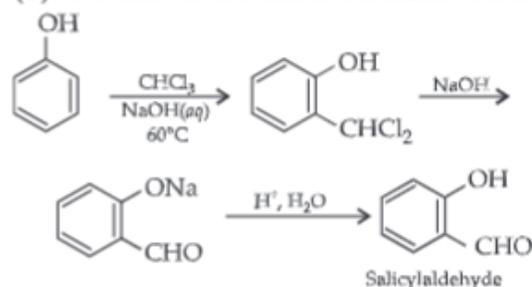
(ii) (c)



(iii) (b):



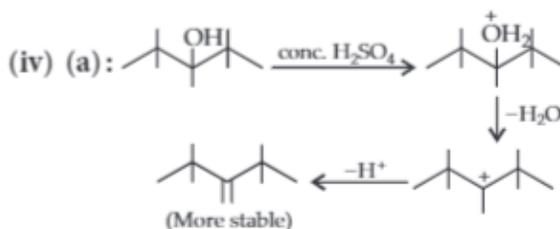
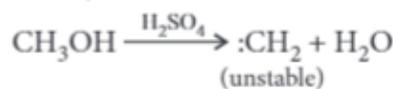
(iv) (b): It is known as Reimer-Tiemann reaction.



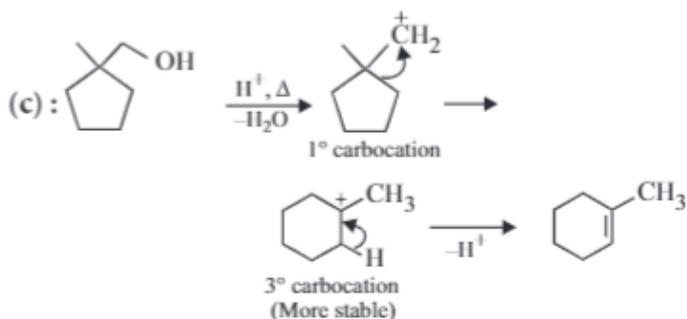
7. (i) (b): The order of dehydration of alcohols is  $3^\circ > 2^\circ > 1^\circ$ .

(ii) (b): The dehydration of alcohol is an example of elimination reaction.

(iii) (b): Dehydration of  $\text{CH}_3\text{OH}$  will give methylene (a carbene) which is unstable.



OR



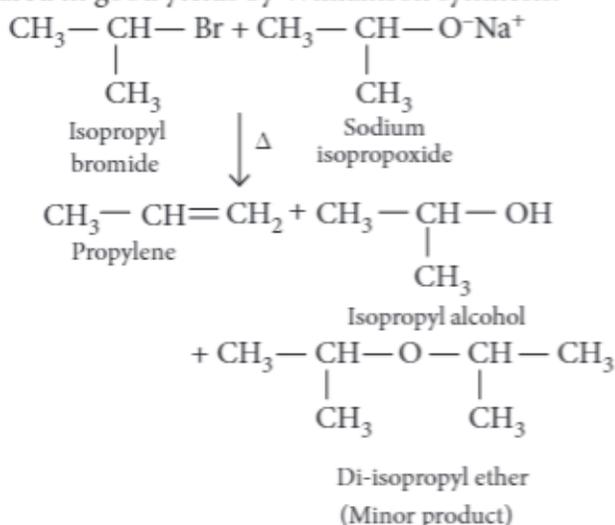
8 (i) (a): Williamson's synthesis occurs by  $S_N2$  mechanism and primary alkyl halides are most reactive in  $S_N2$  reactions.

(ii) (c): Sodium methoxide is a strong nucleophile. In presence of a strong base, *i.e.*, sodium methoxide, *t*-butyl bromide undergoes dehydrohalogenation to form isobutylene.

OR

(a): Diaryl ethers cannot be prepared by Williamson's synthesis since, aryl halides do not undergo nucleophilic substitution easily.

(iii) (d): Since secondary and tertiary alkyl halides prefer to undergo elimination rather than substitution, therefore, even symmetrical ethers containing secondary and tertiary alkyl groups cannot be prepared in good yields by Williamson synthesis.



(iv) (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 Williamson's synthesis.

9. (i) (b): Due to the presence of intermolecular H-bonding in alcohols, they have higher boiling points than isomeric ethers.

(ii) (c): Like alcohols, phenols also form H-bond with water. But the solubility of phenols in water is much lower than that of alcohols because of the larger non-polar hydrocarbon part (benzene ring) present in their molecules.

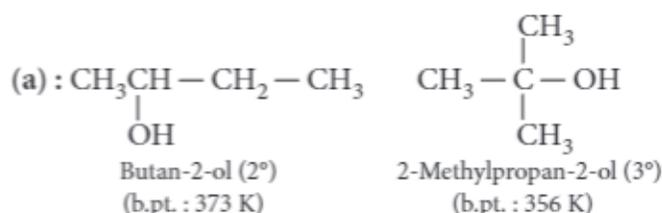
(iii) (d): Boiling point increases with increase in molecular mass so, 1-butanol has higher boiling point than 1-propanol. Ethers do not form hydrogen bonds thus, they have lower boiling points than the corresponding alcohols.

Due to weak dipole-dipole interactions, the boiling points of lower ethers are only slightly higher than those of the *n*-alkanes having comparable molecular masses.

Thus, the increasing order of boiling points is *n*-butane < ethoxyethane < 1-propanol < 1-butanol.

(iv) (b): The solubility of lower ethers in water is due to the formation of H-bonds between water and ether molecules. As the molecular mass increases, the solubility of ethers in water decreases due to corresponding increase in the hydrocarbon portion of the molecule.

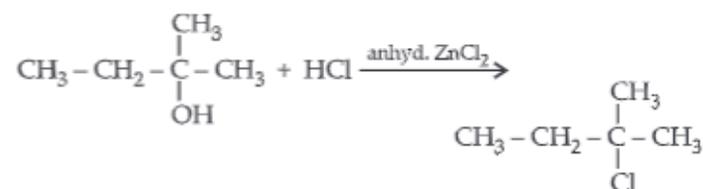
OR



Amongst isomeric alcohols, the boiling points decrease with branching due to a corresponding decrease in surface area.

10. (i) (c): Both methanol and ethanol are  $1^\circ$  alcohols and hence, cannot be distinguished by Lucas' reagent.

(ii) (d): Tertiary alcohols immediately react with Lucas' reagent.



OR

(a)

(iii) (d): The order of reactivity of alcohols towards Lucas' reagent is  $3^\circ$  alcohol >  $2^\circ$  alcohol >  $1^\circ$  alcohol.

$1^\circ$  alcohols do not react with Lucas' reagent at room temperature. It requires high temperature.

The benzyl and allyl alcohols react as rapidly as  $3^\circ$  alcohols with Lucas' reagent because their cations are resonance stabilised.

(iv) (b): When Lucas' reagent (conc. HCl +  $\text{ZnCl}_2$ ) is added to 2-propanol ( $2^\circ$  alcohol) turbidity appears within five minutes whereas with 1-propanol no turbidity appears and solution remains clear at room temperature.

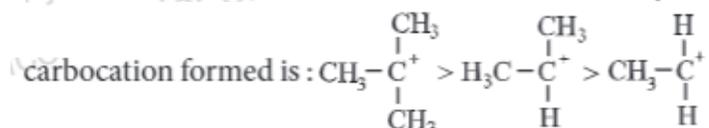
11. (a)

12. (d): Alcohols undergo intermolecular H-bonding and hence, their boiling points are higher than those of hydrocarbons.

Among isomeric alcohols, boiling point decreases in the order :  $1^\circ > 2^\circ > 3^\circ$ .

13. (d): The ease of dehydration of alcohols can be explained on the basis of stability of the intermediate carbocation.

Greater the stability of the carbocation formed, greater will be the rate of reaction. The order of stability of

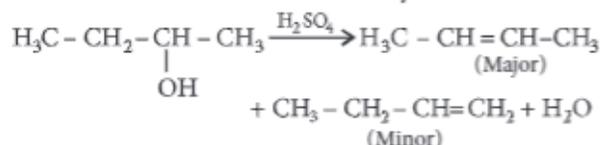


This is due to the electron releasing (+I) effect of the alkyl groups. Therefore, the ease of dehydration of alcohols follows the order : Tertiary > Secondary > Primary

Dehydration of alcohols proceed through carbocation formation.

14. (a): Saytzeff's rule : The alkene formed in greatest amount is the one that corresponds to removal of the hydrogen from the  $\beta$ -carbon having the fewest hydrogen substituent.

In case of  $2^\circ$  and  $3^\circ$  alcohols Saytzeff's rule is followed.



15. (a)

16. (c) : Due to the presence of hydroxyl group (-OH), there is extensive hydrogen bonding between the

ethanol molecules ( $\text{C}_2\text{H}_5\text{OH}$ ). But there is no such hydrogen bonding in dimethyl ether (due to absence of -OH group). So, boiling point of dimethyl ether is much lower than ethanol.

17. (c) : Phenol is less acidic than *p*-nitrophenol because  $-\text{NO}_2$  is strongly electron withdrawing. *p*-Nitrophenolate ion is more stable than phenolate ion.

18. (d) : In *p*-nitrophenol,  $-\text{NO}_2$  group has  $-I$  effect, as a result of which electron density decreases on the benzene ring, hence reactivity towards electrophilic substitution decreases. Methoxy group shows both  $+R$  (due to lone pair of electrons on O) and  $-I$  effect (due to greater electronegativity of O).

$-\text{OCH}_3$  at *meta*-position shows only  $-I$  effect but lesser than  $-I$  effect of  $-\text{NO}_2$  group.

19. (a)

20. (a)

21. (b): The tendency to show H-bonding decreases with increasing hydrophobic character of carbon chain.

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

23. (d): Phenol is a weaker acid than carbonic acid and hence, does not decompose  $\text{NaHCO}_3$  solution to evolve  $\text{CO}_2$  gas. Picric acid is 2, 4, 6-trinitrophenol.

24 (c) : Intermediate formed is dichlorocarbene.

25. (a)