Alcohols, Phenols and Ethers

Case Study Based Questions

Case Study 1

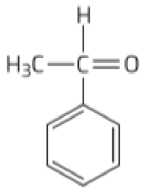
A phenol contains-OH group(s) directly attached to carbon atom(s) of an aromatic system (CH_2OH). In phenols, the OH group is attached to sp^2-hybridised carbon of an aromatic ring. The carbon-oxygen bond length (136 pm) in phenol is slightly less than that in methanol. This is due to

(i) partial double bond character on account of the conjugation of unshared electron pair of oxygen with the aromatic ring and (ii) sp^3-hybridised state of carbon to which oxygen is attached. It can be prepared by various means or methods. Some important methods are alkali fusion of sulphonates, hydrolysis of diazonium salts, decarboxylation of salicyclic acid and from Grignard reagent. Commercially, it is prepared from Dow's process and from cumene. In Dow's process, phenol is obtained when chlorobenzene is heated with 6-8% NaOH at 623 K under 320 atm pressure. Aerial oxidation of cumene produces cumene hydroperoxide which upon subsequent hydrolysis with an aqueous acid gives phenol and propanone. Benzene is sulphonated with oleum and benzene sulphonic acid so formed is converted to sodium
phenoxide on heating with molten sodium hydroxide. Acidification of the sodium salt gives phenol. Diazonium salts are hydrolysed to phenols by warming with water by treating with dilute acids.

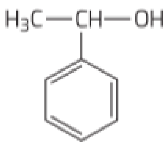
Read the given passage carefully and give the answer of the following questions:

Q1. The structural formula of cumene is:

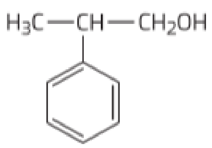
a.



b.



c.



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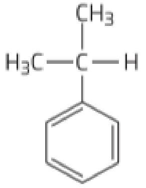


Q2. Which of the following hydrocarbon is used for the world wide production of phenol?

a. Iso-butylbenzene

b. Iso-propylbenzene

c. Iso-pentylbenzene

d. None of the above

Q3. The name of product which is obtained by the decarboxylation of sodium salt of salicylic acid with soda-lime is:

a. phenol

b. toluene

c. benzene

d. benzoic acid

Q4. Which of the following reagents is used for the conversion of benzene sulphonic acid to phenol?

a. CaCO3

b. NaOH, HCL

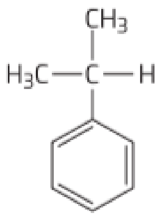
c. Ca(OH)2

d. None of these

Answers

1.

(d)



2. (b) Iso-propylbenzene

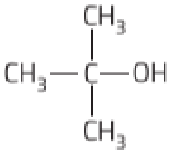
3. (a) Phenol

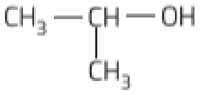
4. (b) NaOH, HCL

Case Study 2

Alcohols and Phenols are acidic in nature. Electron withdrawing groups in phenol increase its acidic strength and electron donating groups decrease it. Alcohols undergo nucleophilic substitution with hydrogen halides to give alkyl halides. On oxidation primary alcohols yield aldehydes with mild oxidising agents and carboxylic acids with strong oxidising agents while secondary alcohols yield ketones. The presence of -OH groups in phenols activates the ring towards electrophilic substitution. Various important products are obtained from phenol like salicylaldehyde, salicylic acid, picric acid etc. Read the given passage carefully and give the answer of the following questions: (CBSE 2021 Term-1)

Q1. Which of the following alcohols is resistant to oxidation?

a. 
$(CH_3)_3C-OH$

b. 
$CH_3-CH(CH_3)-OH$

c. CH_3CH_2OH

d. CH_3-OH

Q2. Which of the following group increases the acidic character of phenol?

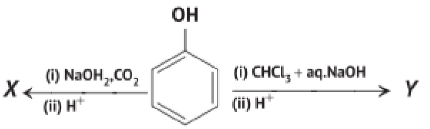
a. CH_2O

b. CH_3

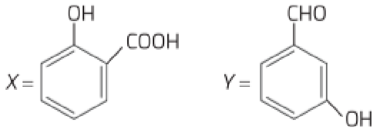
c. NO_2

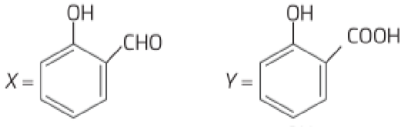
d. All of these

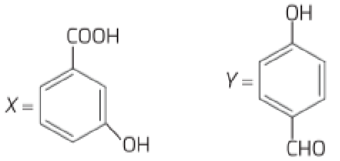
Q3. Consider the following reaction:

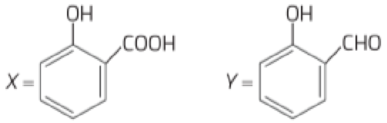


The products *X* and *Y* are

a. 

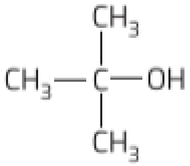
b. 

c. 

d. 

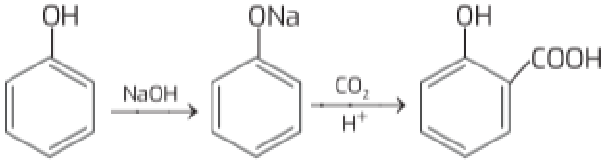
Answers

1. (a) Tertiary alcohols do not undergo oxidation.

Thus, 
$CH_3-C(CH_3)_2-OH$ being a tertiary alcohol is resistant to oxidation.

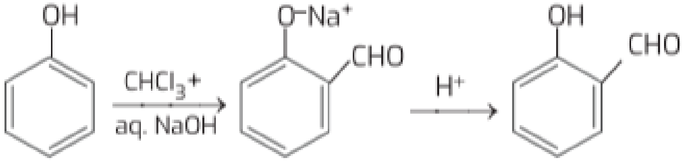
2. (c) -NO_2, - CN, -X (halogens), etc., groups will increase the acidic character of phenol.

3. (d) Kolbe's reaction:



(X)

Reimer-Tiemann Reaction:



Salicylaldehyde (Y)

Case Study 3

Alkene hydration is a catalytic process that involves the addition of water across the double bond of an alkene to produce an alcohol. This is most direct and atom-economical approach to the synthesis of alcohols. Acid-catalysed alkene hydration is the most well-known hydration process. This process is used industrially with several different acidic species as the catalyst, including zeolites, oxides, phosphoric acid and sulphuric acid. There are several major drawbacks with this catalytic process. The first drawback is the acidic environment which is very corrosive and can lead to degradation of reactors or the need to use specially engineered and expensive reactors to resist the acidic conditions. Another drawback is the acidic environment required for hydration which is not suitable for alkenes with acid- sensitive functional groups. Thus, this process is typically only used with simple alkenes such as ethylene, propylene and butene. The final and biggest drawback is the selectivity of the reaction. Acid catalysed hydration follows Markovnikov's rule which states that the proton will add to the carbon with the most hydrogens attached to it. Therefore, starting with propylene, acid-catalysed hydration will always be selective for internal alcohols (secondary or tertiary). Except for ethanol, primary alcohol cannot be synthesized by acid- catalysed hydration. Generally, primary alcohols are the more valuable commodity industrially. Therefore, different synthetic strategies have to be invented for the synthesis of primary alcohols.

$$CH_2 = CH_2 + H_2O \xrightarrow[\text{Hydration}]{\text{Catalyst}} CH_3CH_2OH$$

Hydration of ethylene

Read the given passage carefully and give the answer of the following questions:

Q1. When propene reacts with water under acidic condition, what is the product formed?

Q2. What is the product formed when propyne in the presence of HgSO, and sulphuric acid is hydrated?

Q3. Methylpropene when undergoes hydration in presence of acid catalyst, what is the product obtained? Also give its structure.

OR

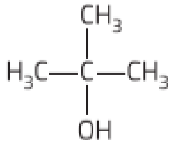
But-1-ene (P) on acidic condition hydration will produce 'X' compound, which on dehydration produce 'Y', acidic condition hydration of 'Y' will produce 'Z'. What happens when X reacts with Na?

Answers

1. Propan-2-ol

2. Propanone

3. 2-methylpropan-2-ol is obtained and its structure is



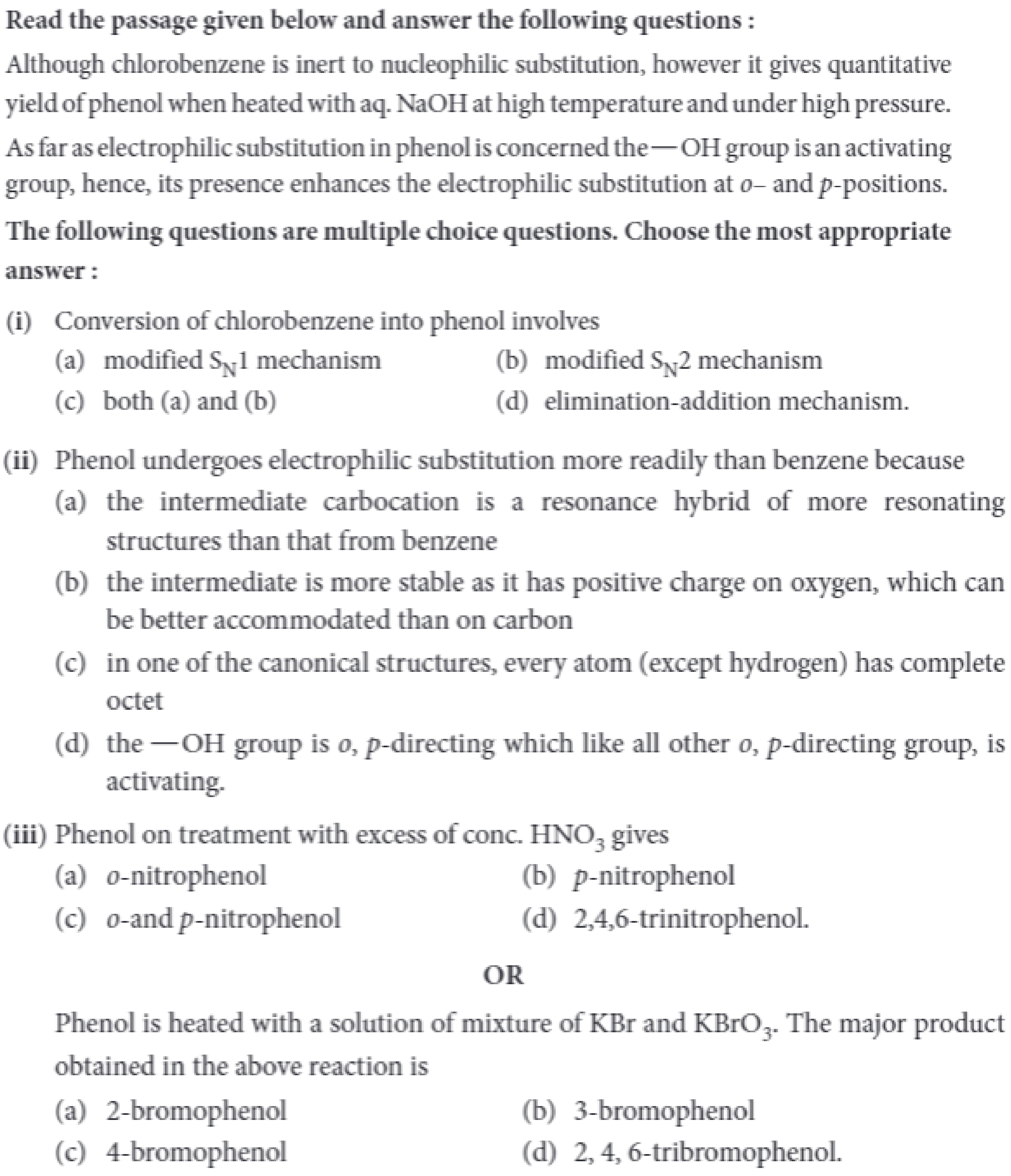
$$H_3C-\underset{\displaystyle OH}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$$

OR

X on reaction with Na, does not produce H_2 gas.

Solutions for Questions 4 to 13 are Given Below

Case Study 4



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

(a) the intermediate carbocation is a resonance hybrid of more resonating structures than that from benzene

(b) the intermediate is more stable as it has positive charge on oxygen, which can be better accommodated than on carbon

(c) in one of the canonical structures, every atom (except hydrogen) has complete octet

(d) 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) *o*-nitrophenol (b) *p*-nitrophenol

(c) *o*-and *p*-nitrophenol (d) 2,4,6-trinitrophenol.

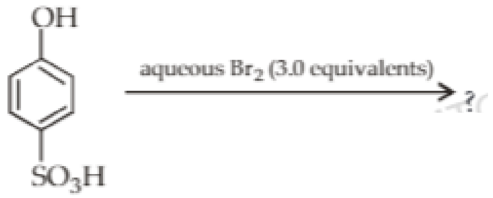
OR

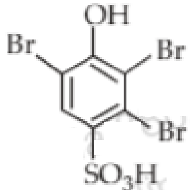
Phenol is heated with a solution of mixture of KBr and $KBrO_3$. The major product obtained in the above reaction is

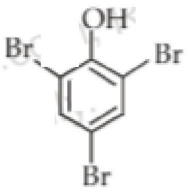
(a) 2-bromophenol (b) 3-bromophenol

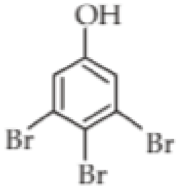
(c) 4-bromophenol (d) 2, 4, 6-tribromophenol.

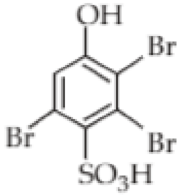
(iv) The major product of the following reaction is



(a) 

(b) 

(c) 

(d) 

Case Study 5

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 Cl_2 in presence of light gives

(a) α-chlorodiethyl ether (b) α, α′-dichlorodiethyl ether

(c) perchlorodiethyl ether (d) none of these.

Case Study 6

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 :

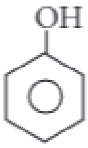
(i) Phenols are highly acidic as compare to alcohols due to

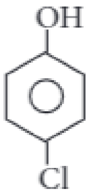
(a) the higher molecular mass of phenols
(b) the stronger hydrogen bonds in phenols
(c) alkoxide ion is a strong conjugate base
(d) phenoxide ion is resonance stabilised.

(ii) The correct order of acidic strength among the following is

(I) H_2O

(II) CH_3CH_2OH

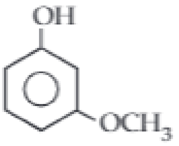
(III) 

(IV) 

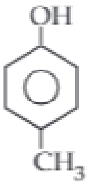
(a) (III) > (IV) > (II) > (I)
(b) (IV) > (III) > (I) > (II)
(c) (IV) > (III) > (II) > (I)
(d) (I) > (II) > (IV) > (III)

OR

The correct decreasing order of pK_a value is

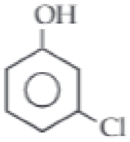


(I)



(II)

(III)



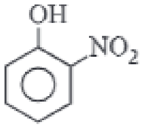
(IV)

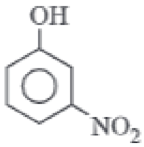
(a) II > IV > I > III
(b) IV > II > III > I
(c) III > II > IV > I
(d) IV > I > II > III

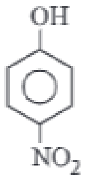
(iii) The compound that does not liberate CO_2, on treatment with aqueous sodium bicarbonate solution is

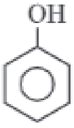
(a) benzoic acid
(b) benzenesulphonic acid
(c) salicylic acid
(d) carbolic acid.

(iv) Most acidic amongst the following is

(a) 

(b) 

(c) 

(d) 

Case Study 7

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.

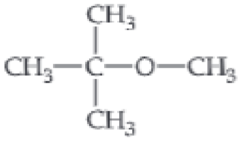
$$R-O-R+HX\xrightarrow{373\text{ K}}R-X+R-OH$$

$$R-OH+HX\xrightarrow{373\text{ K}}R-X+H_2O$$

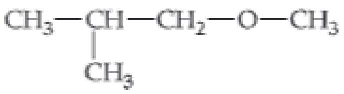
Mixed ether, containing primary or secondary alkyl group, when heated with hydrogen halide, the lower alkyl group forms halide and higher will form an alcohol. Tertiary alkyl ether when heated with hydrogen halide gives tertiary alkyl halide.

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?

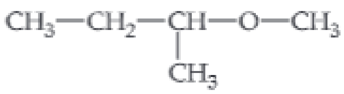
(a) 

$CH_3-C(CH_3)_2-O-CH_3$

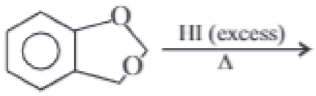
(b) 

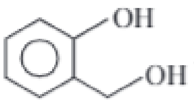
$CH_3-CH(CH_3)-CH_2-O-CH_3$

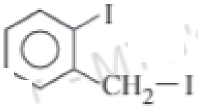
(c) $CH_3-CH_2-CH_2-CH_2-O-CH_3$

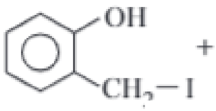
(d) 

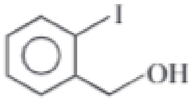
$CH_3-CH_2-CH(CH_3)-O-CH_3$

(ii) 

(a)  + CH_2I_2

(b)  + HCHO

(c)  + $I-CH_2-OH$

(d)  + $I_2 + CH_3OH$

OR

When $CH_2{=}CH-O-CH_2-CH_3$ reacts with one mole of HI, one of the products formed is

(a) ethane (b) ethanol

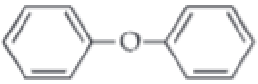
(c) iodoethene (d) ethanal.

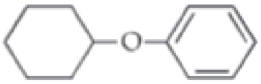
(iii) $(CH_3)_3COCH_3$ and $CH_3OC_2H_5$ are treated with hydroiodic acid. The fragments obtained after reactions are respectively

(a) $(CH_3)_3CI + CH_3OH; CH_3I + C_2H_5OH$ (b) $(CH_3)_3CI + CH_3OH; CH_3OH + C_2H_5I$

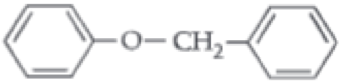
(c) $(CH_3)_3COH + CH_3I; CH_3OH + C_2H_5I$ (d) $CH_3I + (CH_3)_3COH; CH_3I + C_2H_5OH$

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

(a) 

(b) 

(c) 

(d) 

Case Study 8

Read the passage given below and answer the following questions :

An organic compound (*A*) having molecular formula C_6H_6O gives a characteristic colour with aqueous $FeCl_3$ solution. (*A*) on treatment with CO_2 and 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) salicyladehyde (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 $POCl_3$ gives a compound (*D*) which is used

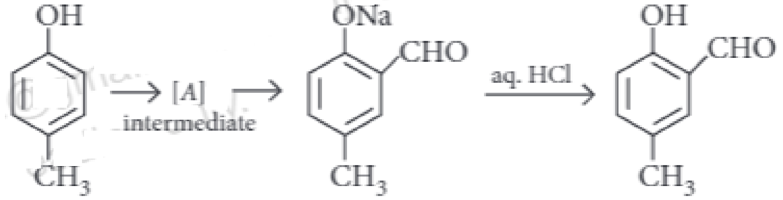
(a) in perfumery as a flavouring agent (b) as an antipyretic

(c) as an analgesic (d) as an intestinal antiseptic.

Case Study 9

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_3Cl (b) aq. NaOH + CH_2Cl_2 (c) aq. NaOH + $CHCl_3$ (d) aq. NaOH + CCl_4

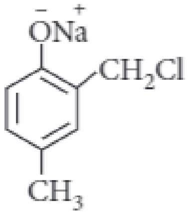
OR

The electrophile in this reaction [*A*] is

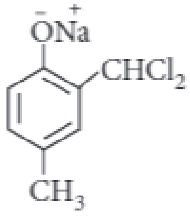
(a) $:CHCl$ (b) $^+CHCl_2$ (c) $:CCl_2$ (d) $\cdot CCl_3$

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

(a)



(b)



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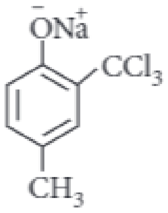
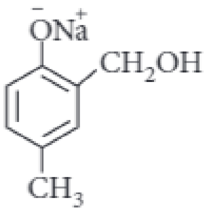


(d)



(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.

Case Study 10

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_2SO_4, H_3PO_4 or catalysts such as anhydrous $ZnCl_2$ or Al_2O_3. When primary alcohols are heated with conc. H_2SO_4 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.

$$CH_3CH_2OH \xrightarrow[433\text{-}443\ K]{conc.\ H_2SO_4} CH_2{=}CH_2 + H_2O$$

$$2CH_3CH_2OH \xrightarrow[413\ K]{conc.\ H_2SO_4} CH_3CH_2{-}O{-}CH_2CH_3 + H_2O$$

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) $(CH_3)_2CHCH_2OH$ (b) $(CH_3)_3COH$ (c) $CH_3CHOHCH_3$ (d) $CH_3CH_2CH_2OH$

(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.

(iv) 

$\xrightarrow{\text{conc.}H_2SO_4}$ products.

The most stable product(s) is/are

(a) 

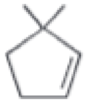
(b) 

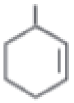
(c) both (a) and (b) (d) none of these.

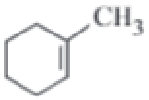
OR

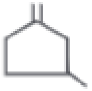
The product of the reaction 

$\xrightarrow[\Delta]{H^+}$ *X*, is

(a) 

(b) 

(c) 

(d) 

Case Study 11

Read the passage given below and answer the following questions :

Williamson's synthesis is used for the preparation of symmetrical as well as unsymmerical ether. It is S_N2 reaction mechanism. In Williamson's synthesis, 1° alkyl halide are used for preparation of ethers because 2° and 3°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 $1°RX > 2°RX > 3°RX$.
Reason : It is a type of bimolecular substitution reaction (S_N2).

(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.

Case Study 12

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.

Case Study 13

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 $ZnCl_2$ 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° alcohol.

OR

Assertion : Tertiary alcohols react fastest with Lucas' reagent by S_N1 mechanism.
Reason : 3° carbocation is most stable.

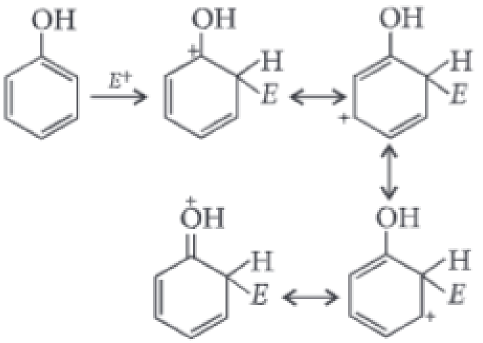
(iii) **Assertion :** Amongst the compounds, $H_2C=CHCH_2OH$ (I), C_6H_5OH (II), $CH_3CH_2CH_2OH$ (III) and $(CH_3)_3COH$ (IV), only (IV) reacts with Lucas' reagent at room temperature.
Reason : Tertiary alcohol gives turbidity immediately with Lucas' reagent.

(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. $ZnCl_2$.

HINTS & EXPLANATIONS

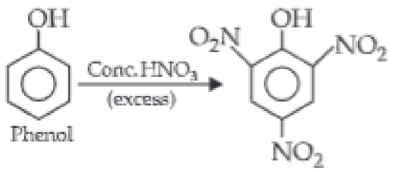
4. (i) (d)

(ii) (c) :



Oxonium cation
(Every atom has complete octet)

(iii) (d) :

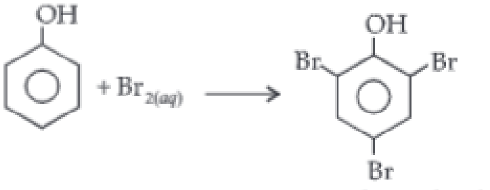


2, 4, 6-Trinitrophenol
(Picric acid)

OR

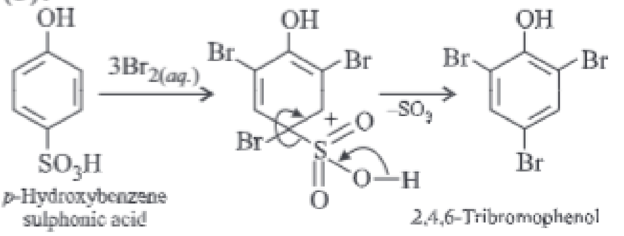
(d) : $KBr_{(aq)} + KBrO_{3(aq)} \longrightarrow Br_{2(aq)}$

This bromine reacts with phenol and gives 2,4,6-tribromophenol.



2,4,6-tribromophenol

(iv) (b):

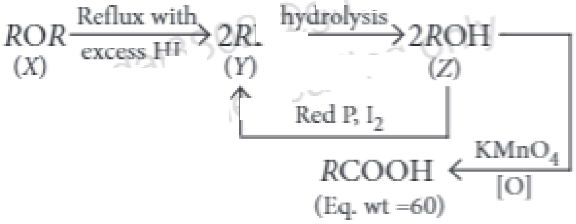


p-Hydroxybenzene sulphonic acid

2,4,6-Tribromophenol

5. **(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 :

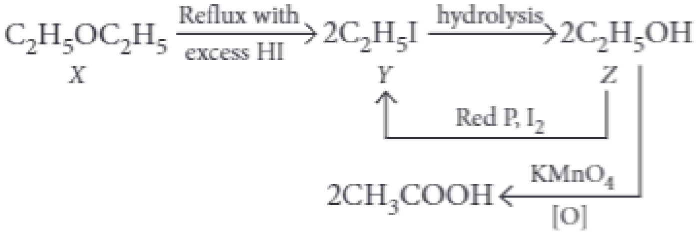


$$\underset{(X)}{ROR} \xrightarrow[\text{excess HI}]{\text{Reflux with}} \underset{(Y)}{2RI} \xrightarrow{\text{hydrolysis}} \underset{(Z)}{2ROH}$$

$$2ROH \xrightarrow[{[O]}]{KMnO_4} \underset{\text{(Eq. wt = 60)}}{RCOOH}; \quad 2ROH \xrightarrow{\text{Red P, } I_2} 2RI$$

Since the equivalent weight of carboxylic acid is 60. So, it must be CH_3COOH *i.e.*, ethanoic acid.

(iii) (a) : The alcohol *Z* in that case should be C_2H_5OH and the compound *Y* should be ethyl iodide.
X is therefore diethyl ether ($C_2H_5—O—C_2H_5$)



$$\underset{X}{C_2H_5OC_2H_5} \xrightarrow[\text{excess HI}]{\text{Reflux with}} \underset{Y}{2C_2H_5I} \xrightarrow{\text{hydrolysis}} \underset{Z}{2C_2H_5OH}$$

$$2C_2H_5OH \xrightarrow[{[O]}]{KMnO_4} 2CH_3COOH; \quad 2C_2H_5OH \xrightarrow{\text{Red P, } I_2} 2C_2H_5I$$

OR

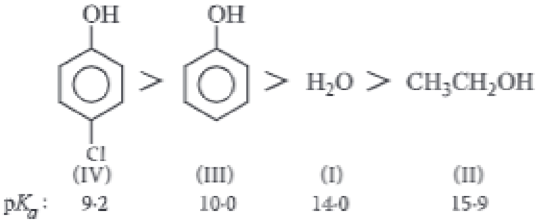
(b)

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

$$CH_3CH_2—O—CH_2CH_3 + \underset{\text{(excess)}}{10Cl_2} \xrightarrow{h\nu} \underset{\text{Perchlorodiethyl ether}}{CCl_3CCl_2—O—CCl_2—CCl_3} + 10HCl$$

6. **(i) (d)**

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



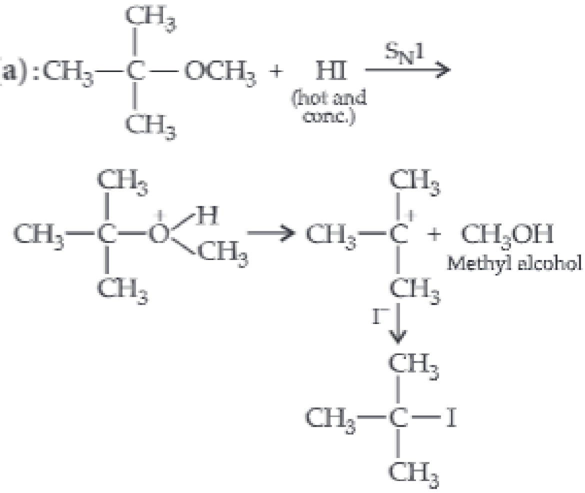
OR

(a) : Weaker acids have higher pK_a.
– OCH_3 at *meta*-position exerts only –*I* effect, hence increases the acidity.
–*I* effect order : – NO_2 > – OCH_3 > – Cl.
– CH_3 has +*I* effect. So, order is (a).

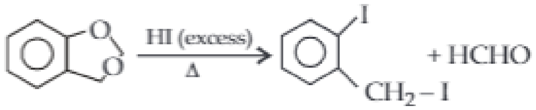
(iii) (d): Phenol (Carbolic acid) is a weaker acid than carbonic acid (H_2CO_3) and does not liberate CO_2 on treatment with aqueous sodium bicarbonate solution.

(iv) (c) : –NO_2 exhibits both –*I* and –*R* influence to stabilise the corresponding phenoxide. In ortho derivative, intermolecular H-bonding lowers the acidity.

7. **(i) (a) :**

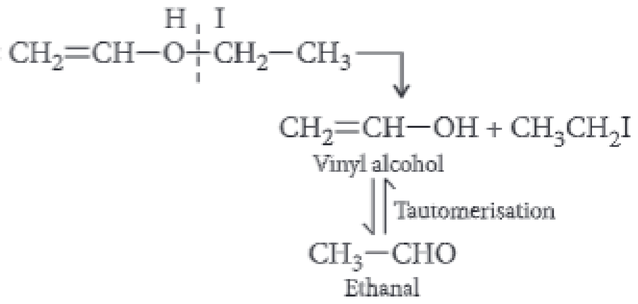


(ii) (b):



OR

(d) :



$$CH_2=CH—O—CH_2—CH_3 \xrightarrow{HI} \underset{\text{Vinyl alcohol}}{CH_2=CH—OH} + CH_3CH_2I$$

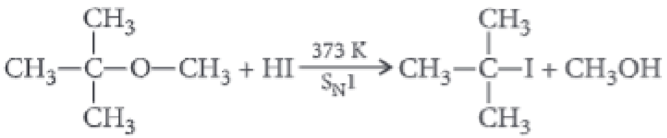
$$\underset{\text{Vinyl alcohol}}{CH_2=CH—OH} \xrightleftharpoons{\text{Tautomerisation}} \underset{\text{Ethanal}}{CH_3—CHO}$$

(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 S_N2 mechanism and because of the steric effect of the larger group, I^- attacks the smaller (Me) group.

$$CH_3OC_2H_5 + HI \longrightarrow CH_3I + C_2H_5OH$$

When the substrate is a methyl *t*-alkylether, the products are *t*-*RI* and MeOH. Here, reaction follows S_N1 mechanism and formation of products is controlled by the stability of carbocation. Since, carbocation stability order is :

3° > 2° > 1° > $\overset{+}{C}H_3$, therefore alkyl halide is always derived from *tert*-alkyl group.

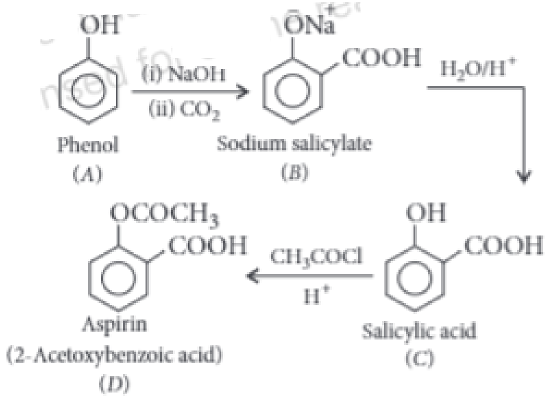


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O-CH_3 + HI \xrightarrow[S_N1]{373\ K} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-I + CH_3OH$$

tert-Butyl methyl ether *tert*-Butyl iodide

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

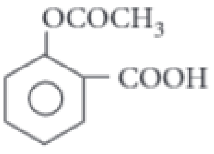
8. **(i) (c):**



OR

(a)

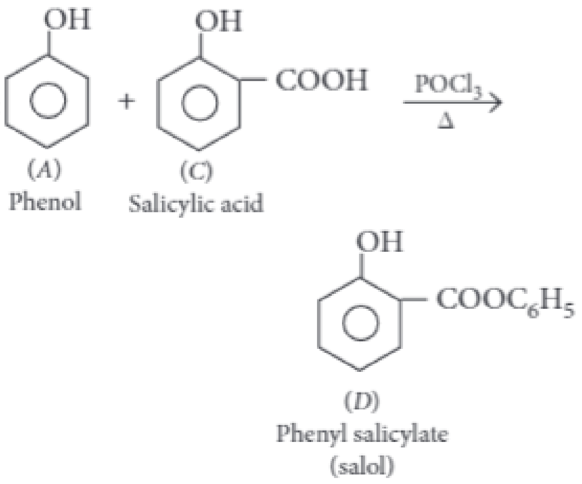
(ii) (d):



It has 9 C-atoms.

(iii) (b): Sodium phenoxide when heated with 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.

(iv) (d):



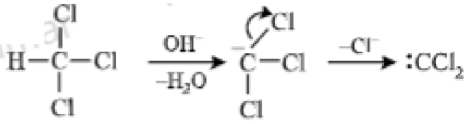
Salol is used as an intestinal antiseptic.

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

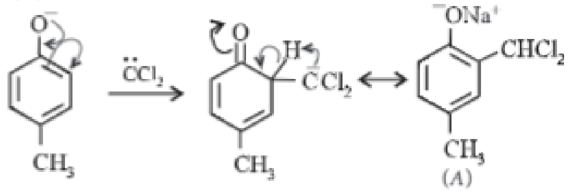
(ii) (c)

OR

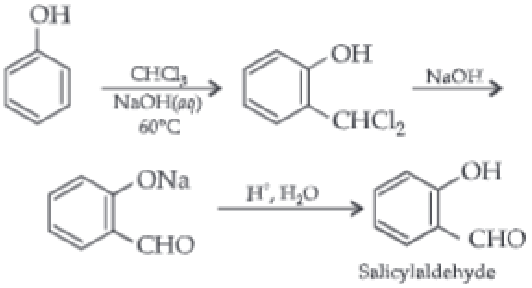
(c):



(iii) (b):



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



10. **(i) (b):** The order of dehydration of alcohols is 3° > 2° > 1°.

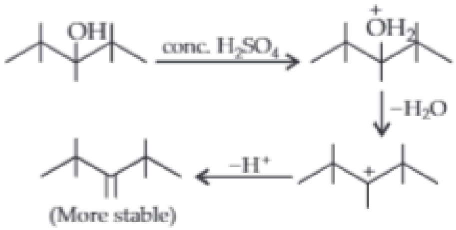
(ii) (b): The dehydration of alcohol is an example of elimination reaction.

(iii) (b): Dehydration of CH_3OH will give methylene (a carbene) which is unstable.

$$CH_3OH \xrightarrow{H_2SO_4} :CH_2 + H_2O$$

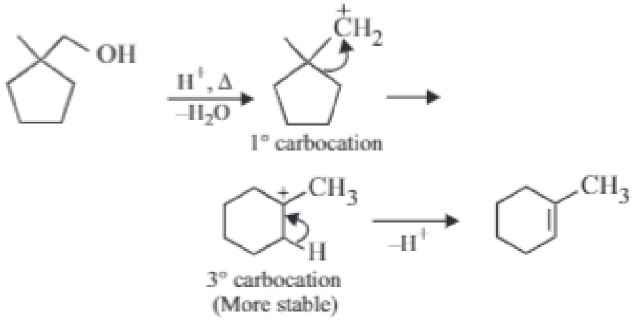
(unstable)

(iv) (a):



OR

(c):



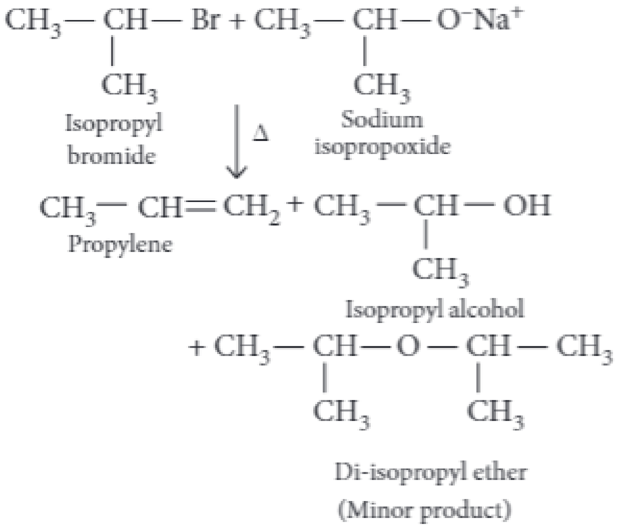
11. **(i) (a):** Williamson's synthesis occurs by S_N2 mechanism and primary alkyl halides are most reactive in S_N2 reactions.

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



$$CH_3-\underset{CH_3}{\underset{|}{CH}}-Br + CH_3-\underset{CH_3}{\underset{|}{CH}}-O^-Na^+ \xrightarrow{\Delta} CH_3-CH=CH_2 + CH_3-\underset{CH_3}{\underset{|}{CH}}-OH + CH_3-\underset{CH_3}{\underset{|}{CH}}-O-\underset{CH_3}{\underset{|}{CH}}-CH_3$$

Isopropyl bromide

Sodium isopropoxide

Propylene

Isopropyl alcohol

Di-isopropyl ether (Minor product)

(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 Williamsons synthesis.

12. **(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.

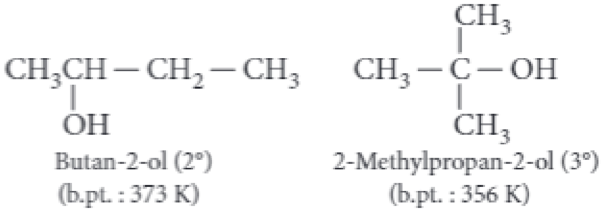
(iii) (d): Boiling point increases with increase in molecular mass so, 1-butanol has higher boiling point than 1-propanol. Ethers do not form hydrogen bonds thus, they have lower boiling points than the corresponding alcohols. Due to weak dipole-dipole interactions, the boiling points of lower ethers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

(a) :



$$CH_3\underset{OH}{\underset{|}{CH}}-CH_2-CH_3 \qquad CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH$$

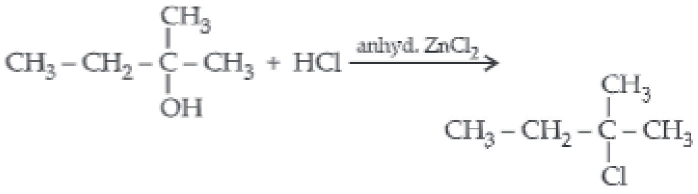
Butan-2-ol (2°)
(b.pt. : 373 K)

2-Methylpropan-2-ol (3°)
(b.pt. : 356 K)

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

13. **(i) (c):** Both methanol and ethanol are 1° alcohols and hence, cannot be distinguished by Lucas' reagent.

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



$$CH_3-CH_2-\overset{CH_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CH_3 + HCl \xrightarrow{\text{anhyd. } ZnCl_2} CH_3-CH_2-\overset{CH_3}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-CH_3$$

OR

(a)

(iii) (d): The order of reactivity of alcohols towards Lucas' reagent is 3° alcohol > 2° alcohol > 1° alcohol. 1° alcohols do not react with Lucas' reagent at room temperature. It requires high temperature.
The benzyl and allyl alcohols react as rapidly as 3° alcohols with Lucas' reagent because their cations are resonance stabilised.

(iv) (b) : When Lucas' reagent (conc. HCl + $ZnCl_2$) is added to 2-propanol (2° alcohol) turibitity appears within five minutes whereas with 1-propanol no turbidity appears and solution remains clear at room temperature.