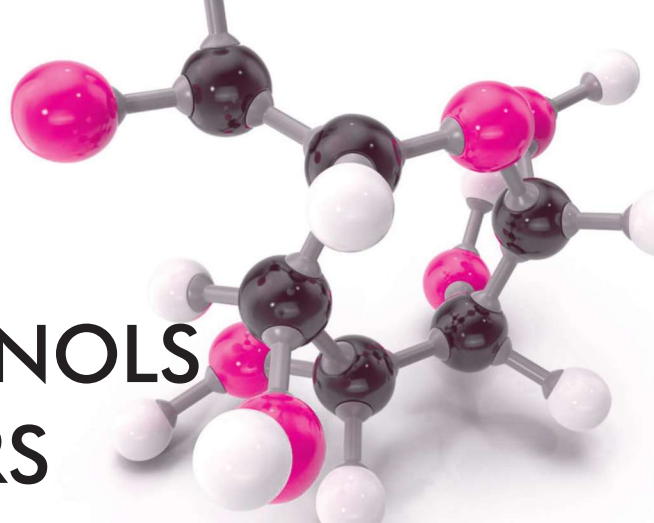
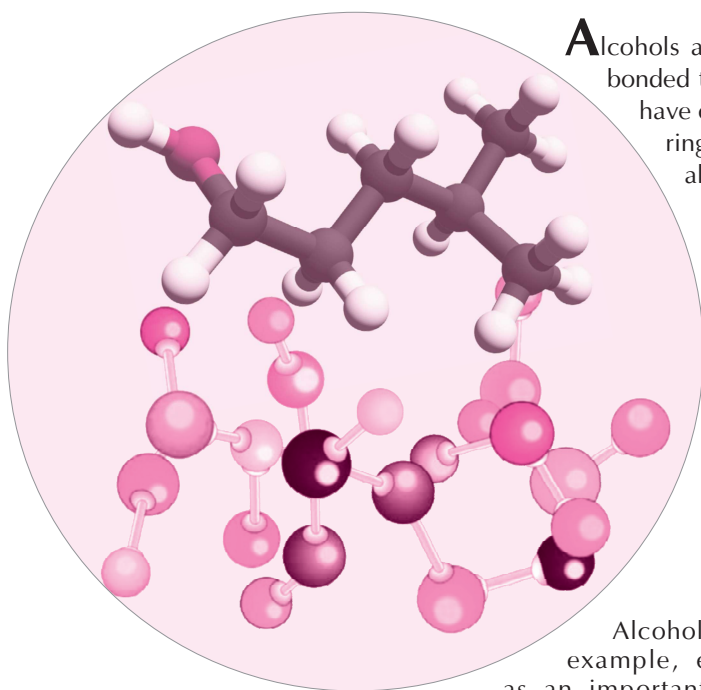




ALCOHOLS, PHENOLS AND ETHERS

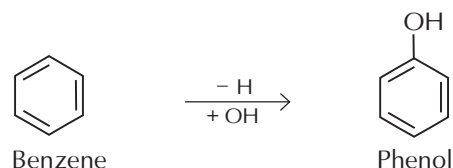
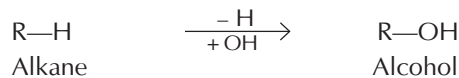


OBJECTIVES		
Building on.....	Assessing.....	Preparing for Competition.....
- Understanding Text - Conceptual Questions 56, 7	- Quick Memory Test with Answers 99 - HOTS & Advanced Level Questions with Answers 101	- Additional Useful Information 112 - Topicwise MCQs 113 - Competitive Examination Qs
CHAPTER SUMMARY & QUICK CHAPTER ROUND UP 78	REVISION EXERCISES (with Previous Years' CBSE Qs & Other State Boards Qs) 105	> AIPMT & Other State Boards' Medical Entrance 116 > JEE (Main) & Other State Boards' Engineering Entrance 119 > JEE (Advance) for IIT Entrance 123
NCERT FILE - In-text Qs & Exercises with Solutions 8 - NCERT Exemplar Problems with Answers & Solutions (Subjective) 96	Hints & Answers for Revision Exercises 1	- NCERT Exemplar Problems (Objective Questions) 13 - Hints & Explanations for Difficult Questions 1
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Alcohols are the compounds that have one or more hydroxyl (–OH) groups bonded to aliphatic carbon atoms while phenols are the compounds which have one or more –OH groups bonded to the aryl carbon atoms (aromatic rings). These are obtained by replacing one or more hydrogen atoms of aliphatic or aromatic hydrocarbons by hydroxyl (–OH) group.

The compounds obtained by replacing one hydrogen atom from aliphatic hydrocarbons by hydroxyl group are alcohols whereas those obtained by replacing hydrogen atom of aromatic hydrocarbons are phenols.



Alcohols have many important applications in day-to-day life. For example, ethanol (C₂H₅OH), simply called alcohol is widely used as an important component of all alcoholic beverages, as a solvent for many medicines, lacquers and varnishes. It is also used in the form of rectified spirit for polishing wooden furniture and as an antiseptic. Phenols are also used for the manufacture of dyes, resins (bakelite), etc. In fact, alcohols are very popularly used for the synthesis of other classes of organic compounds such as alkanes, haloalkanes, ethers, aldehydes, ketones, acids, etc.

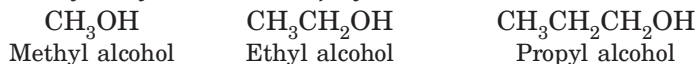
The substitution of a hydrogen atom in a hydrocarbon by an alkoxy (RO) or aryloxy group (ArO) gives another class of compounds known as **ethers**. These are also an important class of compounds. For example, diethyl ether has been extensively used as an industrial solvent.

PART A

ALCOHOLS AND PHENOLS

CLASSIFICATION OF ALCOHOLS AND PHENOLS

Alcohols are the compounds containing hydroxyl group ($-OH$) attached to the alkyl group. Therefore, these are regarded as *hydroxy derivatives of hydrocarbons* and are also called **aliphatic alcohols**. For example,

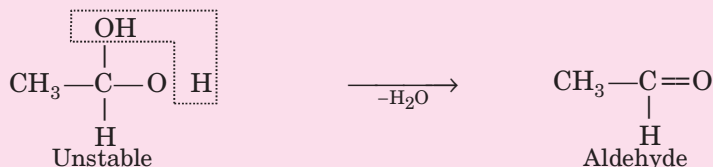


The alcohols are represented by the general formula ROH .

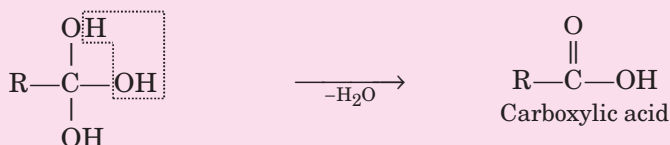
The alcohols are further classified as *monohydric*, *dihydric*, *trihydric* or *polyhydric* alcohols depending upon one, two, three or more hydroxyl groups present in their molecules. For example,



It may be noted that more than one OH groups cannot be present on the same carbon atom. In such a case, the compound will be extremely unstable and will readily lose a water molecule to form more stable aldehyde, ketone or carboxylic acid.

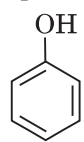


Similarly, if three OH groups are present on the same carbon atom, the molecule loses a molecule of water to form carboxylic acid.

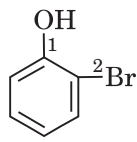
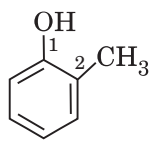
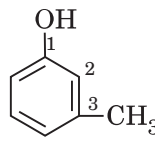
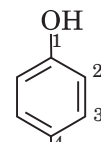


Phenols are hydroxyl derivatives of aromatic hydrocarbons in which the hydroxyl group ($-OH$) is directly attached to the carbon atom of the aromatic ring.

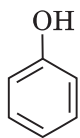
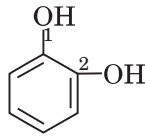
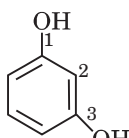
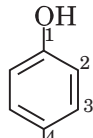
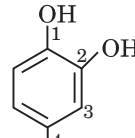
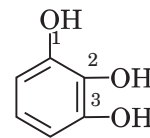
For example,



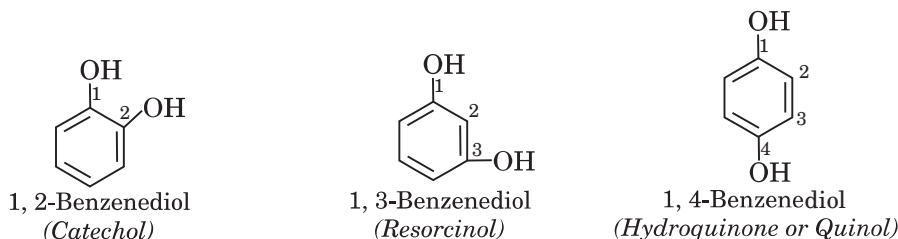
Phenol

2-Bromophenol
(*o*-Bromophenol)2-Methylphenol
(or *o*-Methyl phenol or
o-Cresol)3-Methylphenol
(or *m*-Methylphenol or
m-Cresol)4-Methylphenol
(*p*-Methylphenol or
p-Cresol)

Like alcohols, phenols may also be classified as *monohydric*, *dihydric*, *trihydric* or *polyhydric* according as their molecules contain *one*, *two*, *three* or more hydroxyl groups respectively. These compounds are popularly known by their common names. For example,

Phenol
(*Monohydric*)1, 2-Benzenediol
(Catechol)
(*Dihydric*)1, 3-Benzenediol
(Resorcinol)
(*Dihydric*)1, 4-Benzenediol
(Hydroquinone or quinol)
(*Dihydric*)1, 2, 4-Benzenetriol
(Hydroxyquinol)
(*Trihydric*)1, 2, 3-Benzenetriol
(Pyrogallol)
(*Trihydric*)

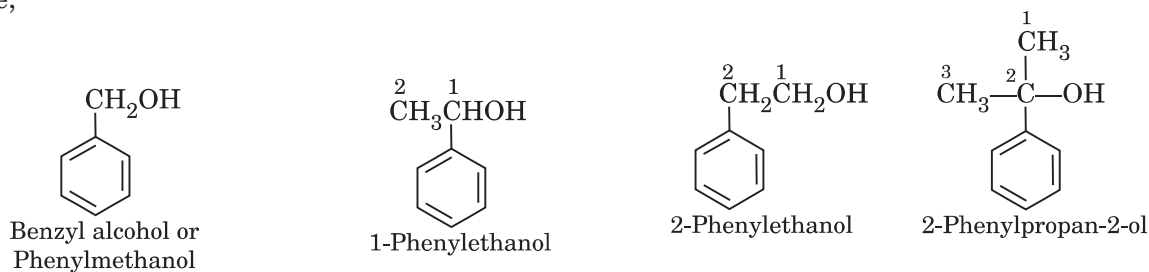
Dihydroxy derivatives of benzene are known as 1,2-, 1,3- and 1,4-benzenediol.



Aromatic alcohols

It may be noted that if the hydroxy group ($-\text{OH}$) is not directly linked with benzene ring and is present in the alkyl side chain, then the compound is not a phenol. It is called **aromatic alcohol** because it resembles aliphatic alcohols in its characteristics. Thus, the **aromatic alcohols** are those in which the hydroxyl group is present in the side chain of an aromatic hydrocarbon.

For example,



Classification of alcohols.

Monohydric alcohols may be classified on the basis of hybridisation of the carbon atom to which the hydroxyl group ($-\text{OH}$) is attached.

1. Compounds containing $\text{C}_{sp^3}-\text{OH}$ bond

In this type of alcohols, the hydroxyl group ($-\text{OH}$) is attached to an sp^3 hybridised carbon atom of an alkyl group. They are further classified as follows :

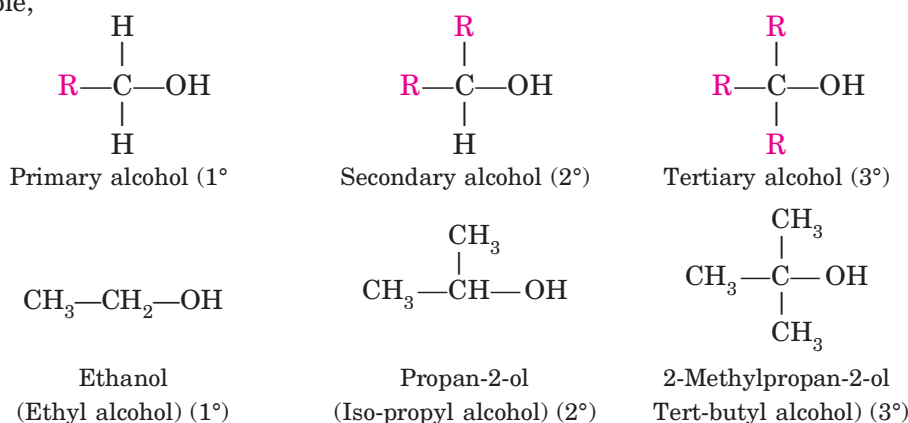
(a) **Primary, secondary and tertiary alcohols.** The alcohols are classified as *primary*, *secondary* and *tertiary alcohols* depending upon the hydroxyl group attached to a primary, secondary or a tertiary carbon atom.

(i) **Primary alcohols (1°)** which have one or none alkyl group on the carbon bonded to $-\text{OH}$ group.

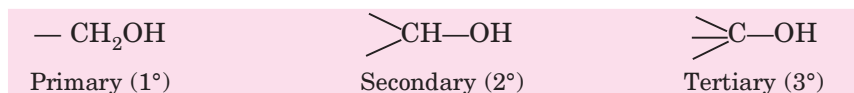
(ii) **Secondary alcohols (2°)** which have two alkyl groups on the carbon bonded to $-\text{OH}$ group.

(iii) **Tertiary alcohols (3°)** which have three alkyl groups on the carbon bonded to $-\text{OH}$ group.

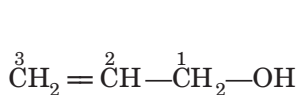
For example,



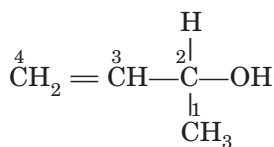
Thus, it is clear from the above structures that the characteristic functional groups of primary, secondary and tertiary alcohols are:



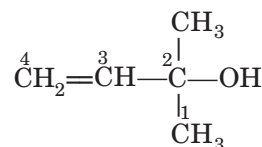
(b) **Allylic alcohols.** In these alcohols, the hydroxyl group is attached to a sp^3 hybridised carbon next to a carbon-carbon double bond (known as allylic carbon). These alcohols can also be classified as primary, secondary or tertiary allylic alcohols. For example,



Prop-2-en-1-ol
(1° allyl alcohol)

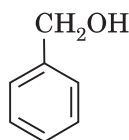


But-3-en-2-ol
(2° allyl alcohol)

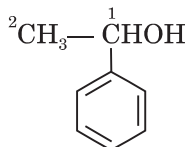


2-Methylbut-3-en-2-ol
(3° allyl alcohol)

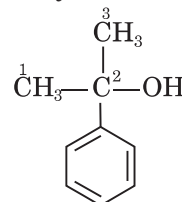
(c) **Benzylic alcohols.** In these alcohols, the hydroxyl group (—OH) is attached to a sp^3 hybridised carbon atom next to an aromatic ring. These alcohols may also be classified as 1°, 2° and 3° benzylic alcohols.



Benzyl alcohol (1°)



1-Phenylethanol (2°)



2-Phenylpropan-2-ol (3°)

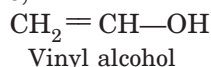
These are also called **aromatic alcohols**.

2. Compounds containing $\text{C}_{sp^2} - \text{OH}$ bond

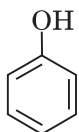
In this type of alcohols, the hydroxyl group (—OH) is attached to a carbon-carbon double bond.

These are of two types :

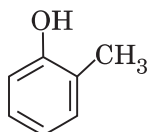
(a) **Vinylic alcohols.** These contain —OH group attached to a carbon atom of a carbon-carbon double bond. These alcohols are called vinyl alcohols. For example,



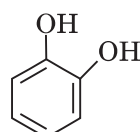
(b) **Phenols.** These contain —OH group attached to a carbon atom of benzene ring. For example,



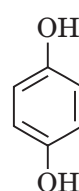
Phenol



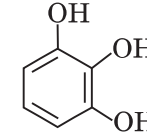
Cresol



Catechol



Hydroquinone or Quinol



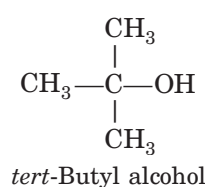
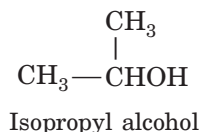
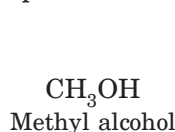
Pyrogallol

NOMENCLATURE

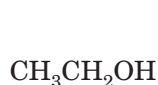
Nomenclature of Alcohols

(a) Monohydric alcohols.

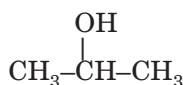
(i) **Common names.** According to **common system** of nomenclature, alcohols are named as *alkyl alcohols* in which the alkyl group attached to the —OH group is named and the **word alcohol is added to it**. For example,



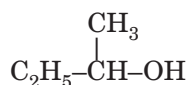
(ii) **Carbinol system.** In this system, the simplest monohydric alcohol, CH_3OH is called carbinol while other alcohols are named as alkyl derivatives of carbinol. For example,



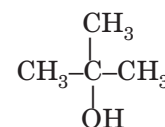
Methylcarbinol



Dimethylcarbinol



Ethylmethylcarbinol



Trimethylcarbinol

(iii) **IUPAC system.** According to **IUPAC nomenclature**, alcohols are named by *replacing 'e' in the name of parent alkane by 'ol'*.

Alkane — e + ol = **Alkanol**

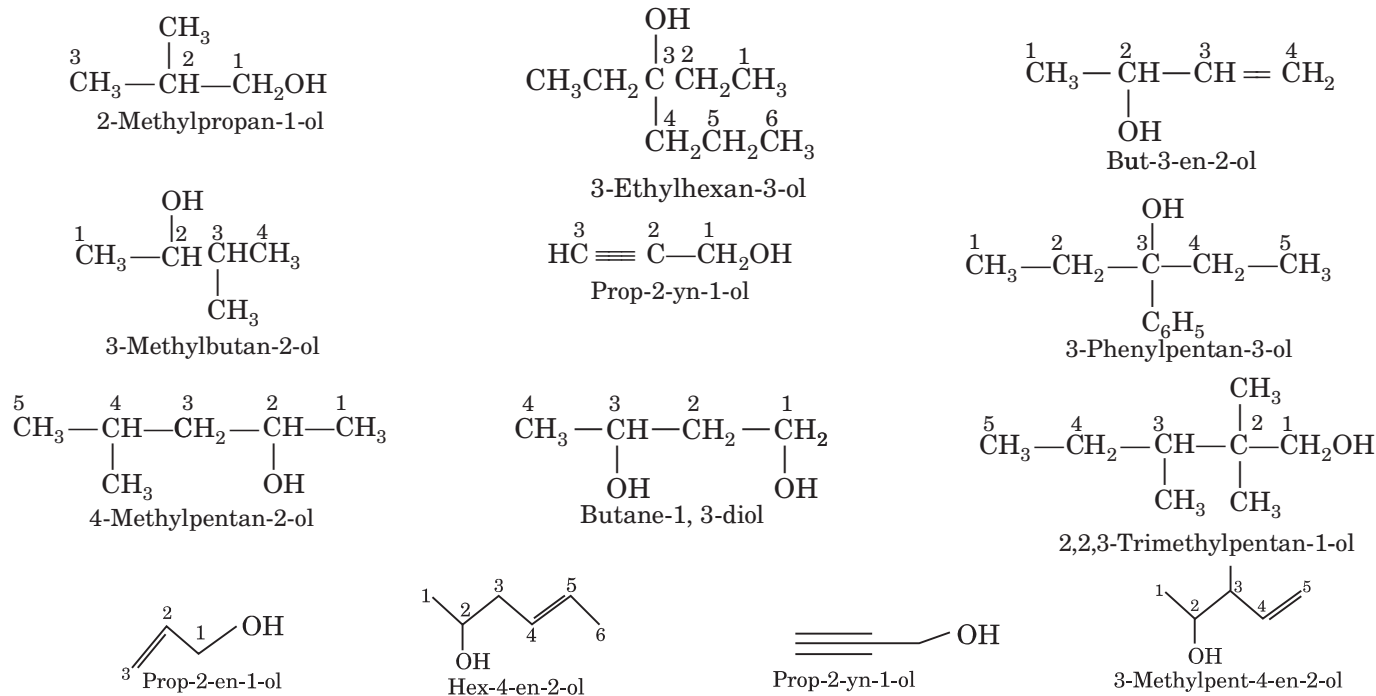
In this system, the following rules are followed :

- (i) The longest continuous chain containing the carbon bonded to OH group is selected as the parent chain.
- (ii) The carbon atoms in the chain are numbered in such a way that the carbon atom carrying the hydroxyl group (—OH) gets the lowest number.
- (iii) The position of the substituents is indicated by suitable numbers.

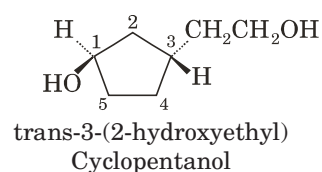
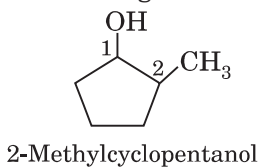
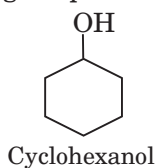
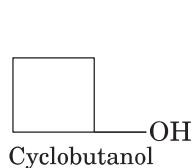
The common and IUPAC names of a few monohydric alcohols are given below :

Formula	Common name	IUPAC name
CH_3OH	Methyl alcohol	Methanol
$\text{CH}_3\text{CH}_2\text{OH}$	Ethyl alcohol	Ethanol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	<i>n</i> -Propyl alcohol	Propan-1-ol
$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$	Isopropyl alcohol	Propan-2-ol
$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3\text{CHCH}_2\text{CH}_3 \\ \\ \text{OH} \end{array}$	<i>sec</i> -Butyl alcohol	Butan-2-ol
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	<i>n</i> -Butyl alcohol	Butan-1-ol
$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$	Isobutyl alcohol	2-Methylpropan-1-ol
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$	<i>tert</i> -Butyl alcohol	2-Methylpropan-2-ol
$\begin{array}{ccccccc} 5 & 4 & 3 & 2 & 1 \\ \text{CH}_3 & -\text{CH}_2 & -\text{CH}_2 & -\text{CH}_2 & -\text{CH}_2 & -\text{OH} \end{array}$	<i>n</i> -Amyl alcohol	Pentan-1-ol
$\begin{array}{ccccccc} 4 & 3 & 2 & 1 \\ \text{CH}_3 & -\text{CH} & -\text{CH}_2 & -\text{CH}_2 & -\text{OH} \\ \\ \text{CH}_3 \end{array}$	Isoamyl alcohol	3-Methylbutan-1-ol

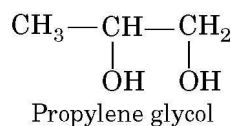
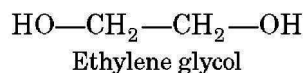
The IUPAC names of a few other substituted alcohols are given below :



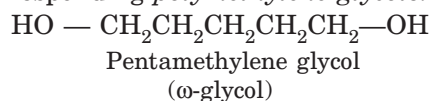
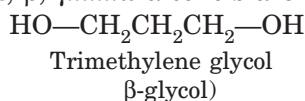
Cyclic alcohols are named by using the prefix cyclo and considering the—OH group attached to C—1. For example,



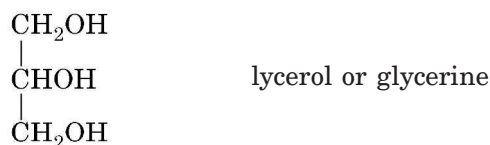
(b) Polyhydric alcohols. These contain two or more —OH groups in their molecules. The dihydric alcohols (containing two —OH groups) are called **glycols**. These are defined as, α , β , γ . . . ω glycols depending upon the relative positions of the two hydroxyl groups. For example, α -glycol is 1, 2-glycol, β -glycol is 1, 3 and ω -glycol has two OH groups attached to the terminal carbon atoms. In common system, α -glycols are named by adding the word glycol to the name of the alkene from which they can be obtained by direct hydroxylation. For example,



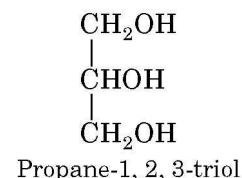
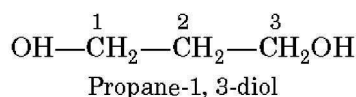
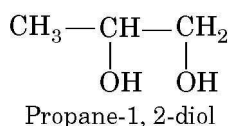
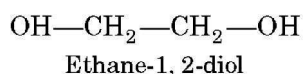
On the other hand, β , γ ω alcohols are named as the corresponding *polymethylene glycols*. For example,



The trihydric alcohols do not have any general rules for naming. The common example is

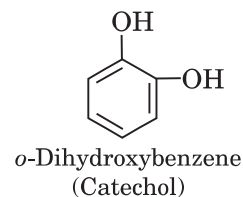
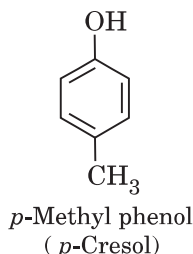
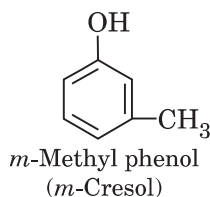
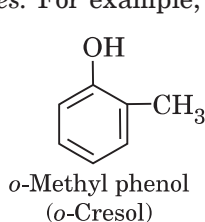


In **IUPAC system**, polyhydric alcohols are easily named as *diols*, *triols*,.....etc. indicating the position of hydroxyl groups. For example,

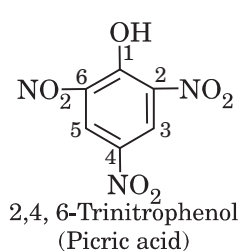
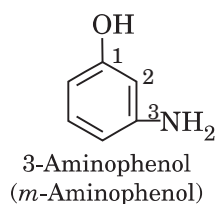
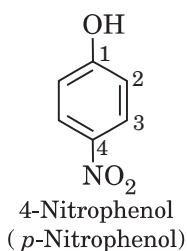
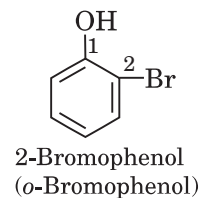
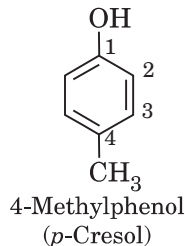
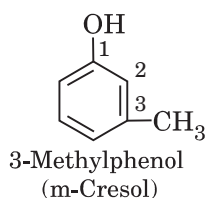
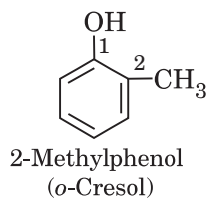


Nomenclature of Phenols

According to **common system** of nomenclature, the parent member of the family is **phenol**. The other members are named as *derivatives of phenol*. The position of the substituents is indicated by the prefixes *ortho* (o-) for 1, 2; *meta* (m-) for 1, 3 and *para* (p-) for 1, 4. However, some substituted phenols are still popularly known by their *trivial names*. For example,



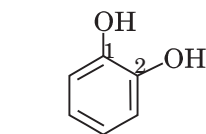
According to **IUPAC system** also, all the substituted phenols are named as derivatives of phenols. The position of the substituents w.r.t. —OH group is indicated by *Arabic* numerals (with the carbon carrying —OH group being numbered 1). For example,



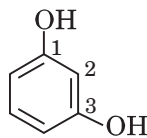
REMEMBER

2, 4, 6-Trinitrophenol is popularly known as **picric acid**.

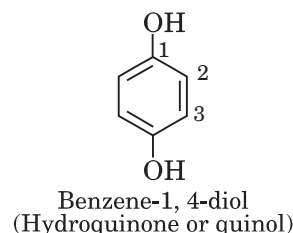
In IUPAC system, di, tri or polyhydric phenols are named as hydroxy derivatives of benzene. However, they are popularly known by their common names. For example,



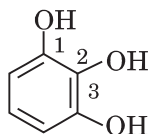
Benzene-1, 2-diol
(Catechol)



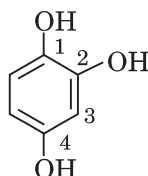
Benzene-1, 3-diol
(Resorcinol)



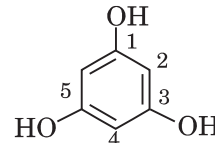
Benzene-1, 4-diol
(Hydroquinone or quinol)



Benzene-1, 2, 3-triol
(Pyrogallol)

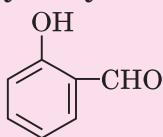


Benzene-1, 2, 4-triol
(Hydroxyquinol)

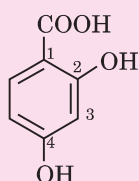


Benzene-1, 3, 5-triol
(Phloroglucinol)

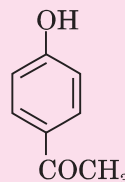
It may be noted that certain groups such as **carbonyl** (aldehydic, ketonic or acidic) or **acyl group** (esters) take preference over the phenolic —OH group in determining the parent name. In these cases, the phenolic group is named as **hydroxy** and is treated as a substituent.



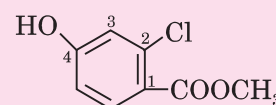
2-Hydroxybenzaldehyde
(o-Hydroxy benzaldehyde
or salicylaldehyde)



2, 4-Dihydroxybenzoic acid



4-Hydroxyacetophenone
(p-Hydroxyacetophenone)



Methyl 2-chloro-
4-hydroxybenzoate

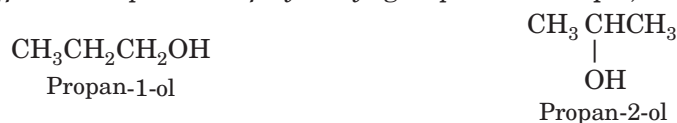
ISOMERISM IN ALCOHOLS

Alcohols exhibit four types of structural isomers :

(i) **Chain isomers.** Alcohols containing four or more carbon atoms exhibit chain isomerism in which the isomers differ in the chain of carbon atoms attached to the hydroxyl group. For example,



(ii) **Position isomerism.** The alcohols containing three or more carbon atoms exhibit position isomerism in which the isomers differ in the position of hydroxyl group. For example,

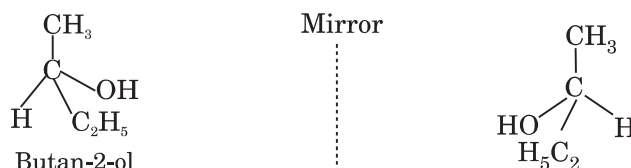


(iii) **Functional isomerism.** Monohydric alcohols containing two or more carbon atoms exhibit functional isomerism in which the isomers differ in the functional group. For example,



(iv) **Optical isomerism.** Monohydric alcohols containing chiral carbon atoms exhibit optical isomerism.

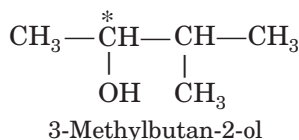
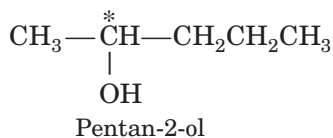
For example,



REMEMBER

Alcohols and ethers are functional isomers.

Other monohydric alcohols showing optical isomerism are :

**HELP**

Check if the compound has chiral carbon atom.

SOLVED EXAMPLES**Example 1.**

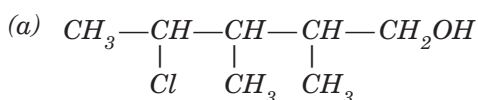
Draw the structures of all isomeric alcohols of molecular formula $\text{C}_5\text{H}_{12}\text{O}$ and give their IUPAC names. Classify them as primary, secondary and tertiary alcohols. **N.C.E.R.T.**

Solution: The isomeric alcohols of molecular formula $\text{C}_5\text{H}_{12}\text{O}$ are :

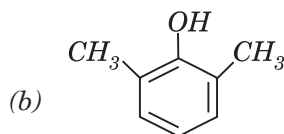
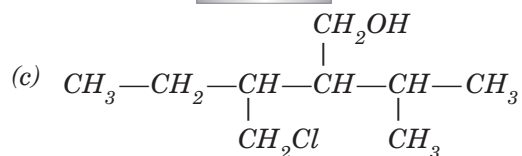
- | | | |
|---|----------------------------|-----------|
| (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ | : Pentan-1-ol | Primary |
| (ii) $\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCH}_2\text{OH} \\ \\ \text{CH}_3 \end{array}$ | : 2-Methylbutan-1-ol | Primary |
| (iii) $\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{CH}_2\text{OH} \\ \\ \text{CH}_3 \end{array}$ | : 3-Methylbutan-1-ol | Primary |
| (iv) $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2\text{OH} \\ \\ \text{CH}_3 \end{array}$ | : 2, 2-Dimethylpropan-1-ol | Primary |
| (v) $\begin{array}{c} \text{CH}_3\text{CH}_2\text{CH}_2\text{CHCH}_3 \\ \\ \text{OH} \end{array}$ | : Pentan-2-ol | Secondary |
| (vi) $\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3 \\ \\ \text{OH} \end{array}$ | : Pentan-3-ol | Secondary |
| (vii) $\begin{array}{c} \text{CH}_3\text{CH}-\text{CHCH}_3 \\ \quad \\ \text{CH}_3 \quad \text{OH} \end{array}$ | : 3-Methylbutan-2-ol | Secondary |
| (viii) $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$ | : 2-Methylbutan-2-ol | Tertiary |

Example 2.

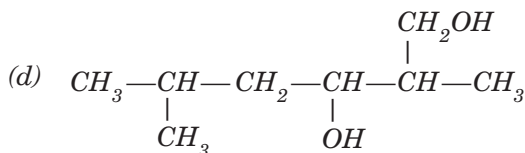
Name the following compounds according to IUPAC system :

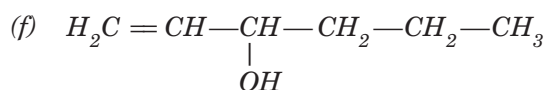
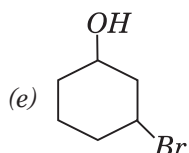


N.C.E.R.T. (Mizoram S.B. 2017)

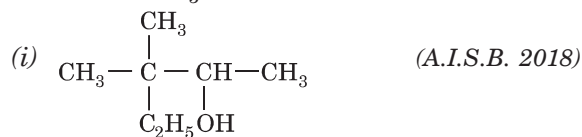
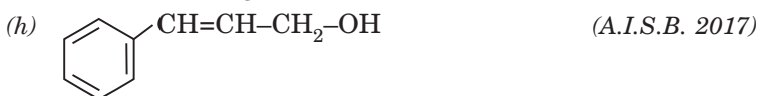
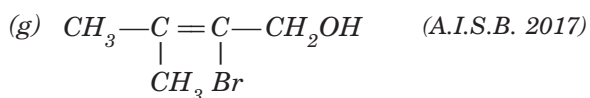


N.C.E.R.T.

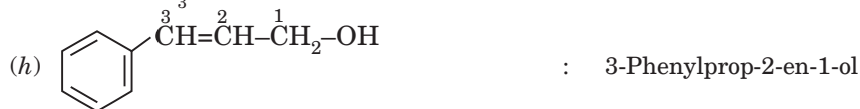
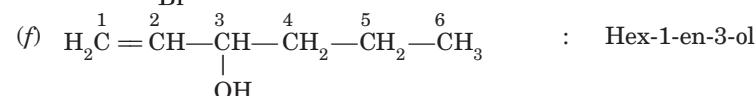
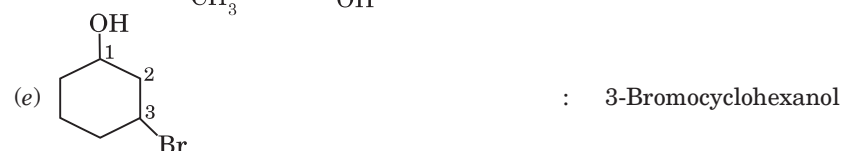
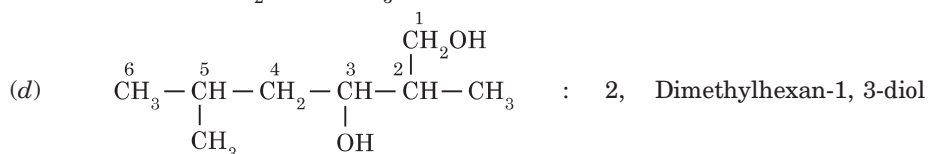
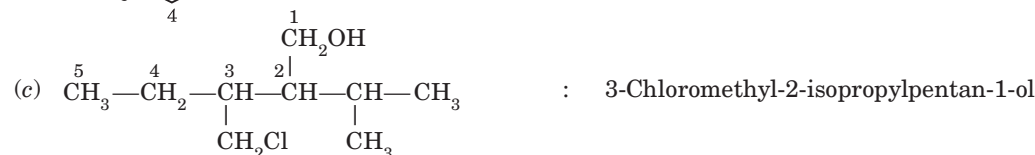




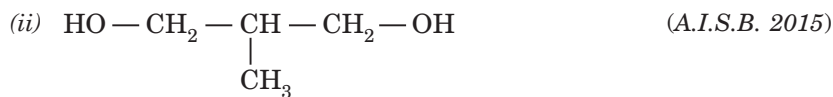
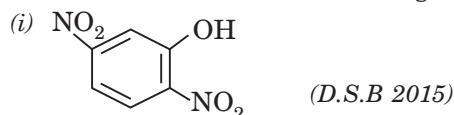
N.C.E.R.T.

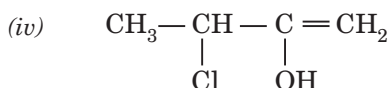
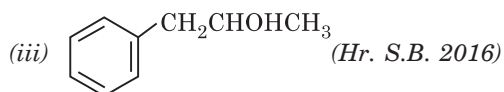
**HELP**

The functional group —OH gets lowest number.

Solution:**Practice Problems**

1. Write the IUPAC name of the following compounds:

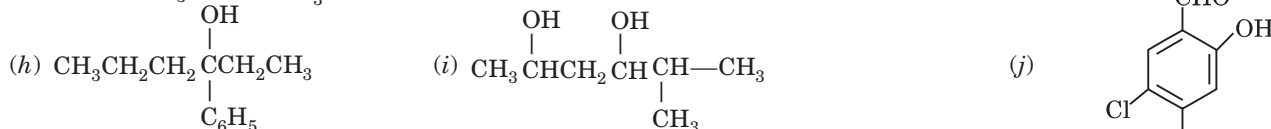
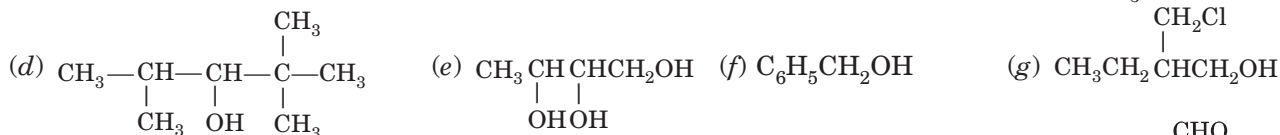
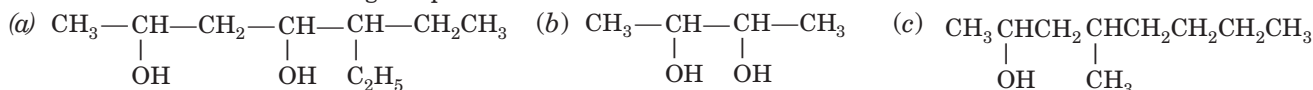




- Ans. (i) 2, 5-Dinitrophenol
(iii) 1-Phenylpropan-2-ol

- (ii) 2-Methylpropan-1, 3-diol
(iv) 3-Chlorobut-1-en-2-ol

2. Give IUPAC names of the following compounds :

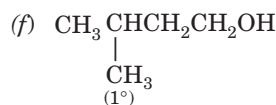
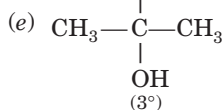
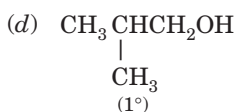
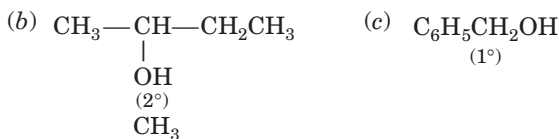
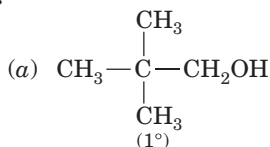


- Ans. (a) 5 Ethylheptane-2, 4-diol (b) Butan-2, 3-diol (c) 4-Methyloctan-2-ol
(d) 2, 2, 4 Trimethylpentan-3-ol (e) Butan-1, 2, 3-triol (f) Phenylmethanol
(g) 2-Chloromethyl butan-1-ol (h) 3-Phenylhexan-3-ol (i) Methylhexane-2, 4-diol
(j) 5-Chloro-2, 4-dihydroxybenzaldehyde.

3. Write the formula of the following alcohols and classify them as 1°, 2° or 3° :

- (a) *neo*-pentyl alcohol (b) *sec*-butyl alcohol (c) benzyl alcohol
(d) isobutyl alcohol (e) *tert*-butyl alcohol (f) isoamyl alcohol.

• Ans.

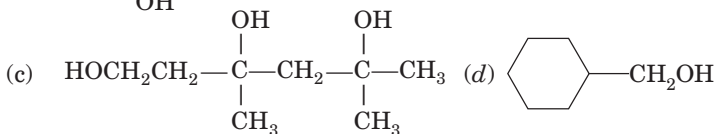
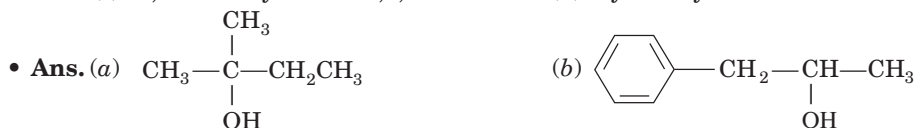


4. Write all the isomeric alcohols with molecular formula $\text{C}_4\text{H}_{10}\text{O}$ and give their IUPAC names.

- Ans. (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ Butan-1-ol (ii) $\text{CH}_3\text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_3$ Butan-2-ol (iii) $\text{CH}_3\underset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{OH}$ 2-Methylpropan-1-ol (iv) $\text{CH}_3-\underset{\text{CH}_3}{\overset{\text{OH}}{\text{C}}}-\text{CH}_3$ 2-Methylpropan-2-ol

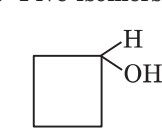
5. Write structures of the compounds whose IUPAC names are given below :

- (a) 2-Methylbutan-2-ol (b) 1-Phenylpropan-2-ol
(c) 3,5-Dimethylhexane-1,3,5-triol (d) Cyclohexyl methanol

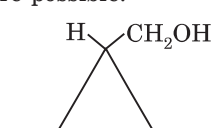


6. Give structures of all the cyclic isomers (alcohols) with molecular formula $\text{C}_4\text{H}_7\text{OH}$. Write their IUPAC names.

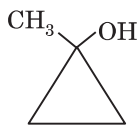
• Ans. Five isomers are possible.



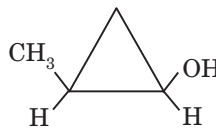
Cyclobutanol



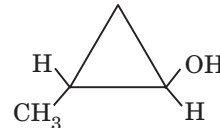
Cyclopropylmethanol



1-Methylcyclopropanol



Cis-2-Methylcyclopropanol



Trans-2-Methylcyclopropanol

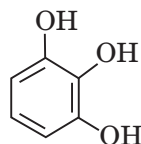
7. Write the IUPAC names and draw structures of the following compounds whose common names are given:

(i) Pyrogallol

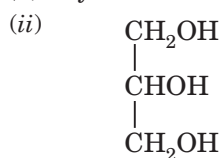
(ii) Glycerol

(iii) Resorcinol

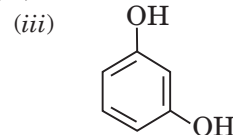
• Ans. (i)



Benzene-1, 2, 3-triol



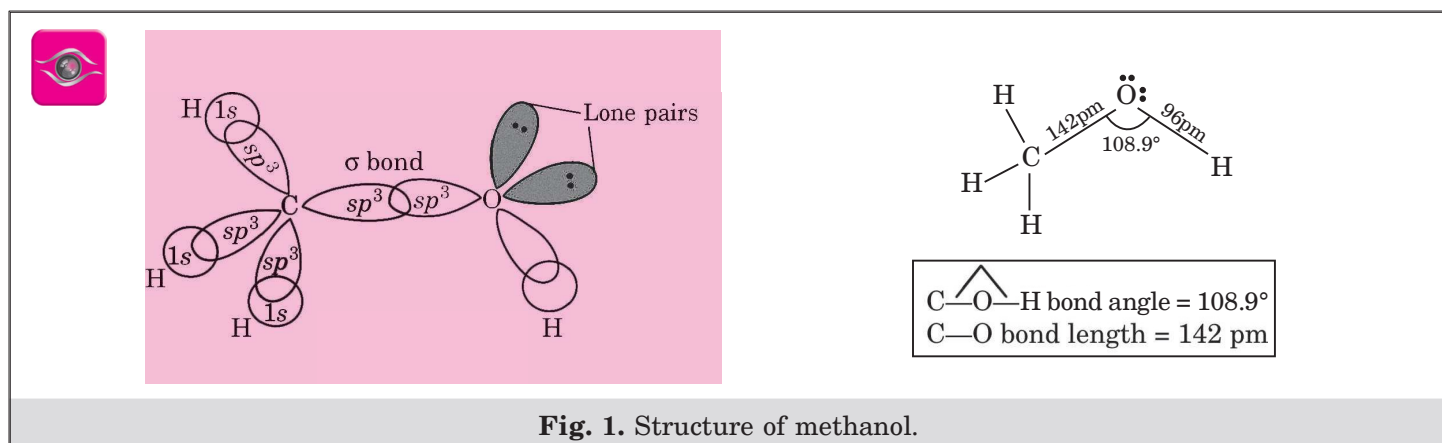
Propane-1, 2, 3-triol



Benzene-1, 3-diol

STRUCTURE OF COMPOUNDS CONTAINING —OH GROUP

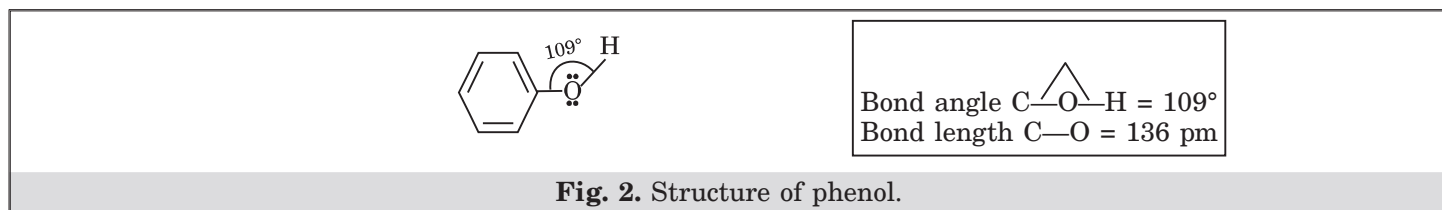
In alcohols, the oxygen of —OH group is bonded to the sp^3 hybridised carbon by a sigma bond. This bond is formed by the overlap of sp^3 hybrid orbital of carbon with one sp^3 hybrid orbital of oxygen. The remaining three sp^3 hybrid orbitals of carbon overlap with $1s$ orbitals of hydrogen. In the case of oxygen, one sp^3 hybrid orbital overlaps with $1s$ orbital of hydrogen and the remaining two sp^3 hybrid orbitals contain lone pairs of electrons as shown below for methanol.



The bond angle C—O—H in methanol is slightly less than the tetrahedral angle ($109^\circ 28'$). This is due to larger repulsions between the lone pairs of oxygen.

In contrast to methanol, the —OH group in phenols is attached to sp^2 hybridised carbon of an aromatic ring.

The bond angle C—O—H in phenol is 109° . The C—O bond length (136 pm) in phenol is slightly less than that in methanol. This is due to partial double bond character of C—O bond because of the conjugation of lone pair of electrons of oxygen with the aromatic ring.



It may be noted that since the oxygen atom is more electronegative than both carbon and hydrogen, the electrons of C—O and O—H bonds are more displaced towards the O atom. As a result, the electron density near the O atom is slightly more than that near carbon and hydrogen atoms. Consequently, an alcohol molecule is dipolar in nature with oxygen carrying a partial negative charge (δ^-) and carbon and hydrogen each carrying a partial positive charge (δ^+). This is supported by the fact that alcohols have high dipole moments. For example, methanol has a dipole moment of 1.71 D.



Phenol on the other hand, has smaller dipole moment (1.54 D) than methanol. This is due to the reason that C—O bond in phenol is *less polar* due to *electron withdrawing effect* of the benzene ring. On the other hand, C—O bond in methanol is more polar due to electron donating effect of the CH_3 group.

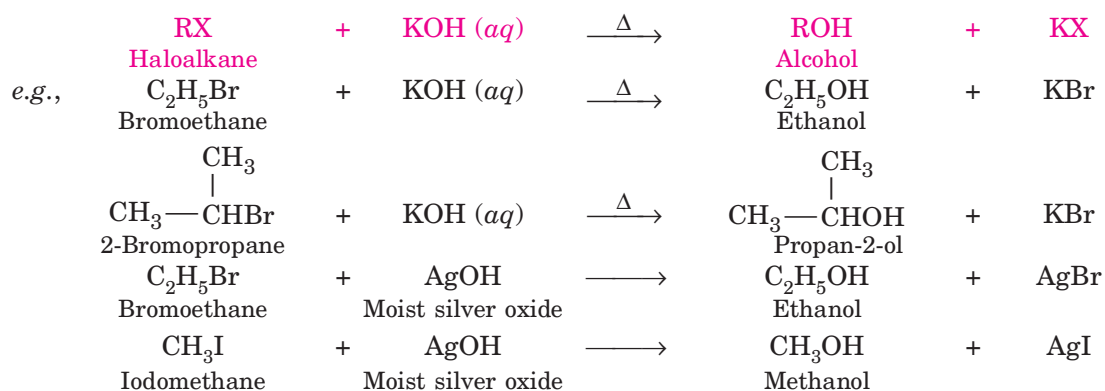
Due to dipolar nature, alcohols and phenols form intermolecular hydrogen bonds.

METHODS OF PREPARATION OF ALCOHOLS

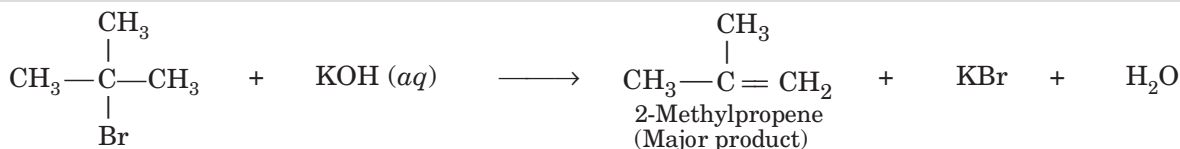
The important methods of preparation of alcohols are :

1. Preparation from haloalkanes.

Haloalkanes, when boiled with aqueous NaOH or KOH or moist silver oxide (AgOH), give alcohols.



Primary haloalkanes give good yield of alcohols. However, tertiary haloalkanes in this reaction give mainly alkenes due to dehydrohalogenation. Secondary haloalkanes give a mixture of alcohol and alkene.

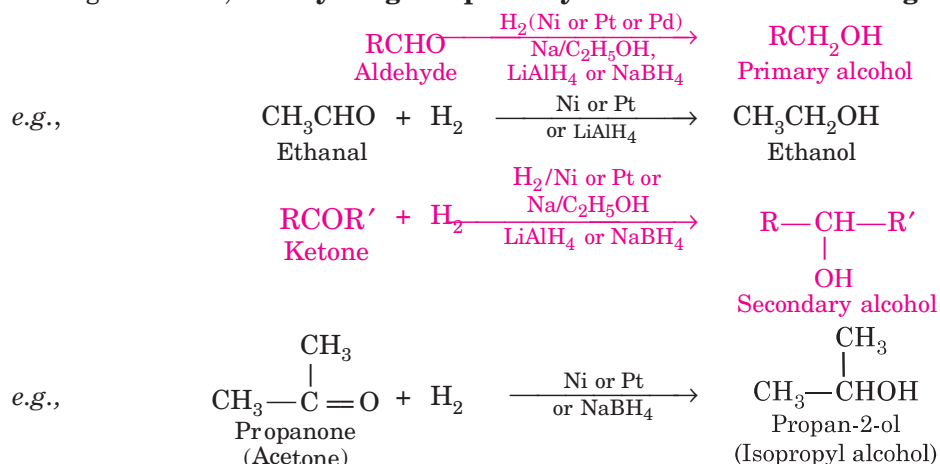


2. By reduction of aldehydes and ketones.

Alcohols are easily prepared by the reduction of aldehydes and ketones.

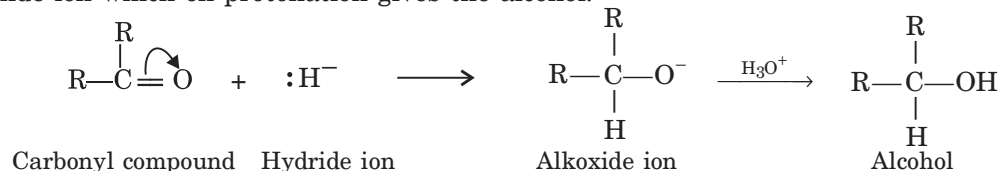
The reduction is carried out by common reducing agents such as (i) hydrogen in the presence of a catalyst (*catalytic hydrogenation*) such as finely divided platinum, palladium, nickel and ruthenium (ii) sodium in the presence of ethyl alcohol (iii) lithium aluminium hydride (lithium tetrahydridoaluminate (III), LiAlH_4) or sodium borohydride (sodium tetrahydridoborate (III), NaBH_4).

During reduction, **aldehydes gives primary alcohols while ketones give secondary alcohols.** For example,

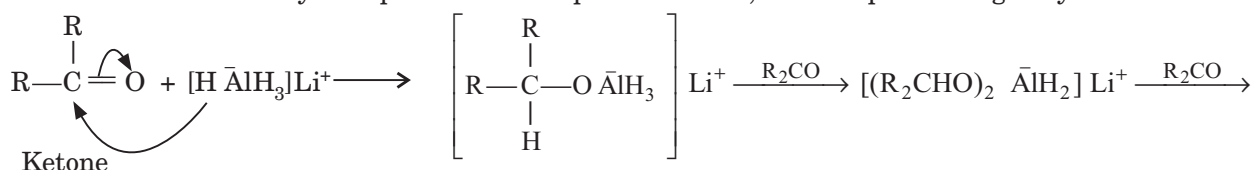


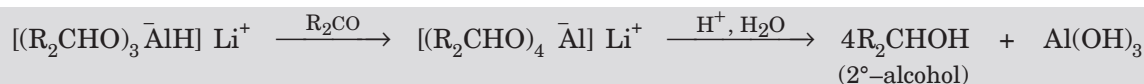
Tertiary alcohols cannot be obtained by reduction of carbonyl compounds.

Reduction of carbonyl compound involves the addition of hydride ion (H^-) reducing the carbonyl group to alkoxide ion which on protonation gives the alcohol.



The complex hydrides ; LiAlH_4 and NaBH_4 also reduce carbonyl compounds in excellent yields. They also reduce the carbonyl compounds in a stepwise manner, each step involving a hydride ion transfer as :



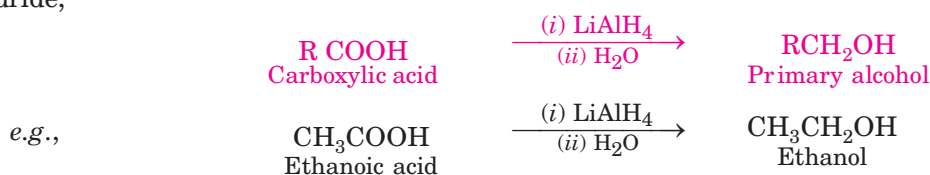


Sodium borohydride ($Na^+ BH_4^-$) also reacts in a similar manner.

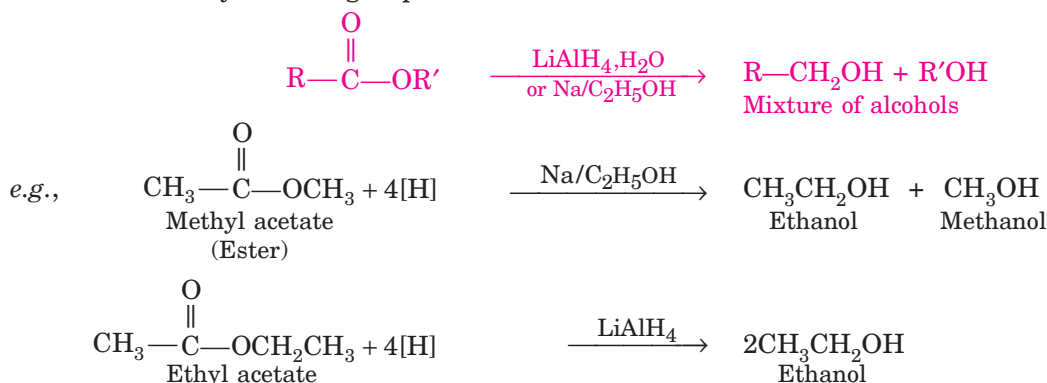
It may be noted that $LiAlH_4$ reacts **violently with water** and therefore, the reaction with $LiAlH_4$ must be carried out in anhydrous conditions generally in anhydrous ether. Usually ethyl acetate is added cautiously after the reaction is over to decompose excess $LiAlH_4$ and then water is added to decompose aluminium complex.

3. By reduction of carboxylic acids and esters

Carboxylic acids are reduced to primary alcohols in the presence of strong reducing agent, lithium aluminium hydride,

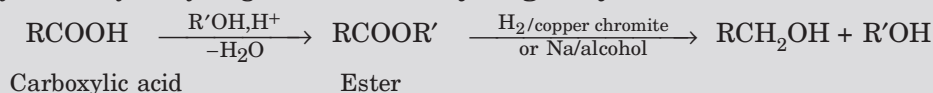


Esters are also reduced to alcohols and give a mixture of two alcohols; one from the acyl group ($RCO-$) and the other from the alkoxy ($-OR'$) group.



Reduction of aldehydes, ketones and esters with sodium and alcohol is commonly known as **Bouveault Blanc reduction**.

Note. It may be noted that reduction of carboxylic acids by $LiAlH_4$ gives excellent yield of alcohols. However, $LiAlH_4$ being an expensive reagent, is used only for preparing special chemicals. Therefore, commercially acids are reduced to alcohols by first converting them to the esters followed by their reduction using (i) hydrogen in the presence of a catalyst (catalytic hydrogenation called **hydrogenolysis**) and (ii) sodium and alcohol.



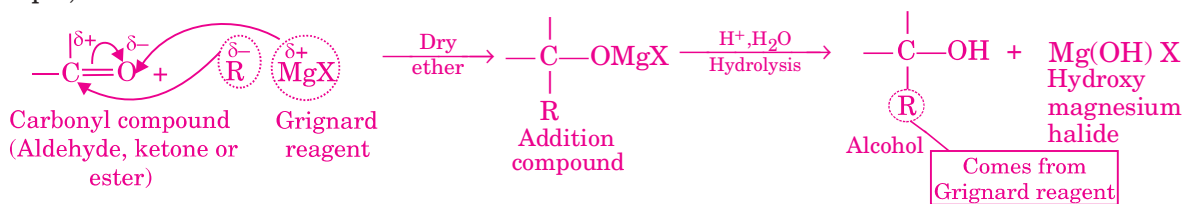
4. From Grignard's reagent

(a) By reaction with aldehydes, ketones and esters

Grignard's reagent ($RMgX$) are alkyl or aryl magnesium halides. The $C-Mg$ bond in Grignard's reagent $R-\overset{\delta-}{Mg}-\overset{\delta+}{X}$ is highly polar because carbon is electronegative (electronegativity = 2.5) relative to electropositive magnesium (electronegativity = 1.2). Due to the polar nature of $C-Mg$ bond, Grignard's reagents are very versatile reagents in organic synthesis. Grignard's reagent ($RMgX$) reacts with aldehydes, ketones and esters to form addition products which decompose with dil. HCl or dil. H_2SO_4 to give alcohols.

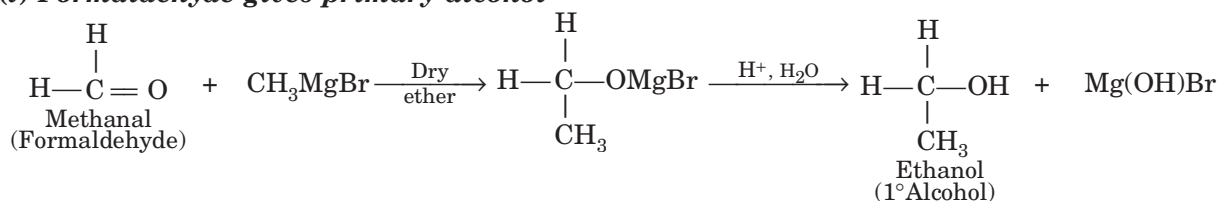
The reaction mechanism involves the simultaneous attack of the nucleophile alkyl carbanion (R^-) of the Grignard reagent on the carbonyl carbon atom and the remaining portion gets attached to the oxygen atom of carbonyl group forming addition product. This is then decomposed by water to give alcohol.

For example,

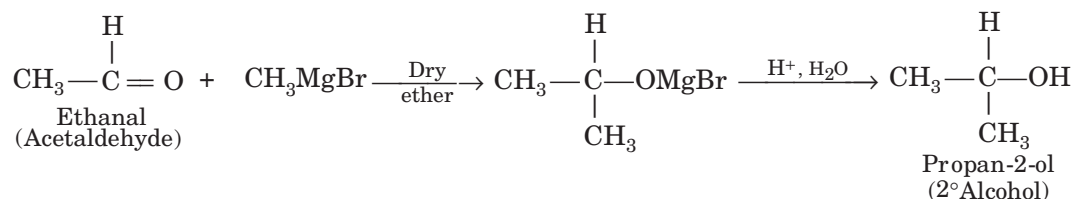


Different types of alcohols are obtained by this reaction.

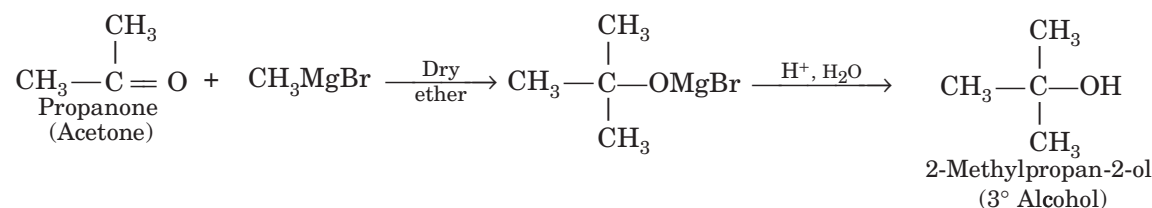
(i) Formaldehyde gives primary alcohol



(ii) All aldehydes (other than formaldehyde) give secondary alcohols

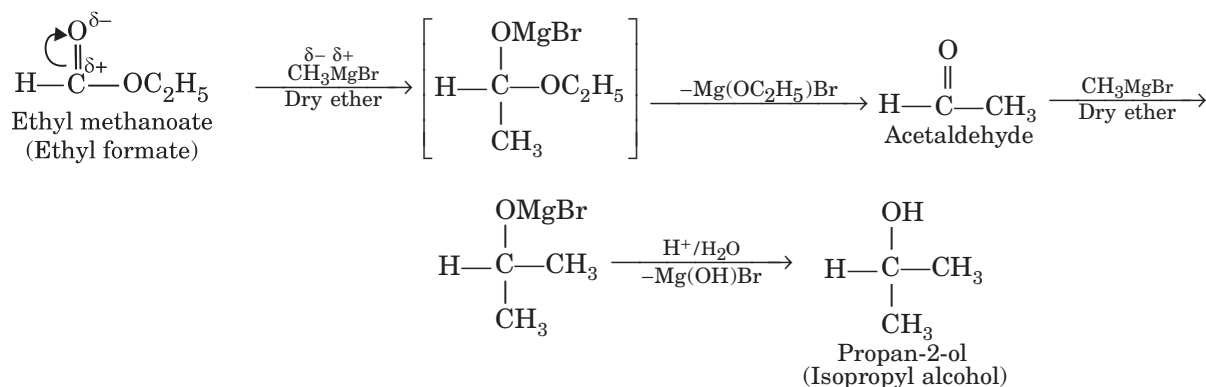


(iii) Ketones give tertiary alcohols

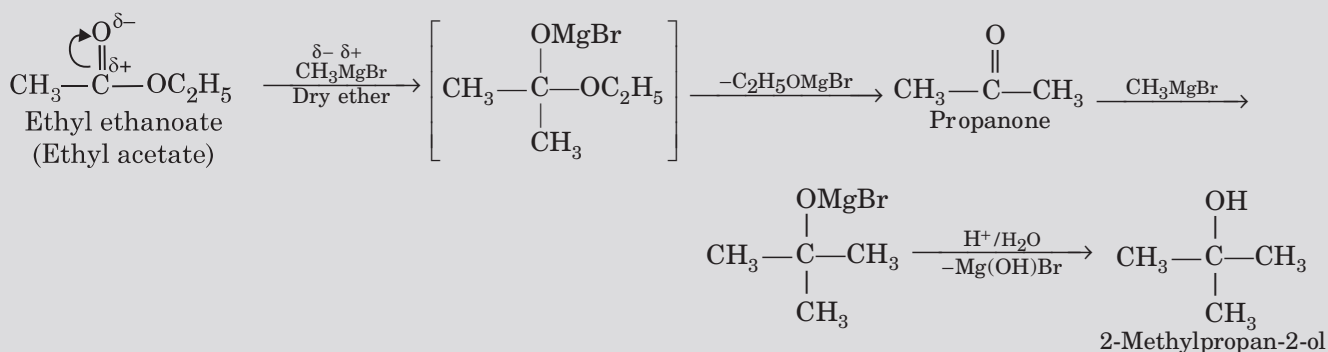


(iv) Esters give secondary and tertiary alcohols

Esters can also be converted into alcohols by treating with suitable Grignard reagent. Secondary alcohols can be prepared by the addition of suitable Grignard reagent to esters of formic acid followed by acid hydrolysis. For example,

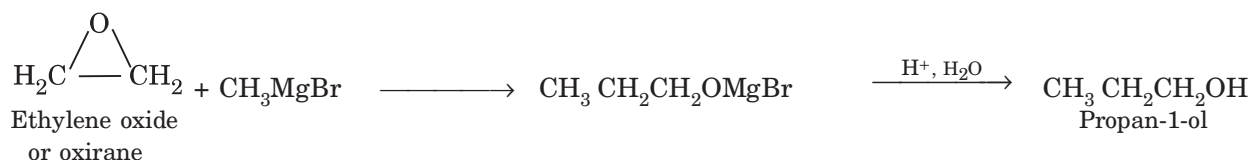


Tertiary alcohols containing at least two identical groups can be easily prepared by the addition of Grignard reagent to an ester other than formic ester followed by acid hydrolysis. For example,

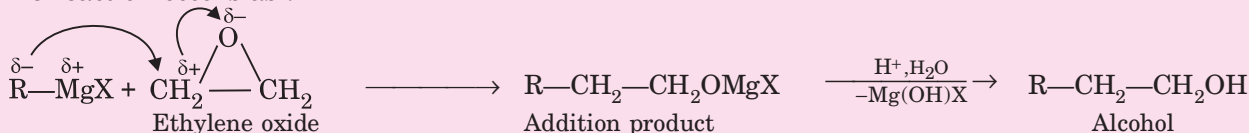


(b) By reaction with ethylene oxide or oxirane

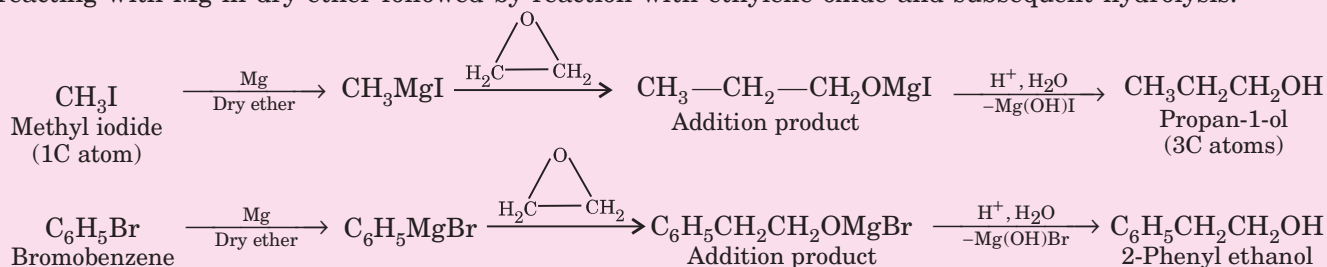
Epoxyalkanes such as oxiranes or ethylene oxide react with Grignard reagent in the presence of anhydrous ether to form addition products which are hydrolysed by water in the presence of acid to form alcohols. For example,



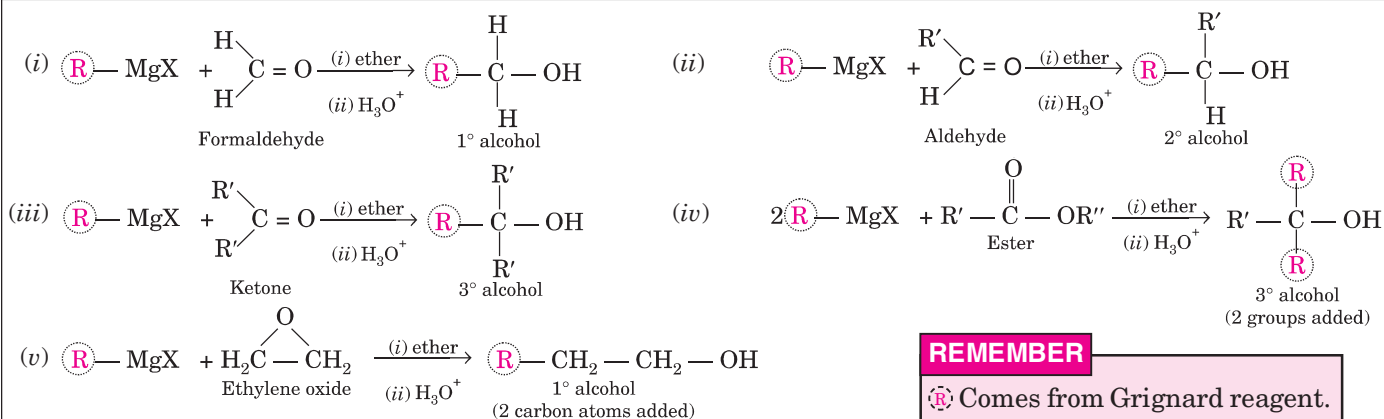
The reaction occurs as :



This is an excellent method for converting an alkyl halide into a **primary alcohol containing two carbon atoms more than the alkyl halide**. The alkyl halide is first converted into the corresponding Grignard reagent by reacting with Mg in dry ether followed by reaction with ethylene oxide and subsequent hydrolysis.



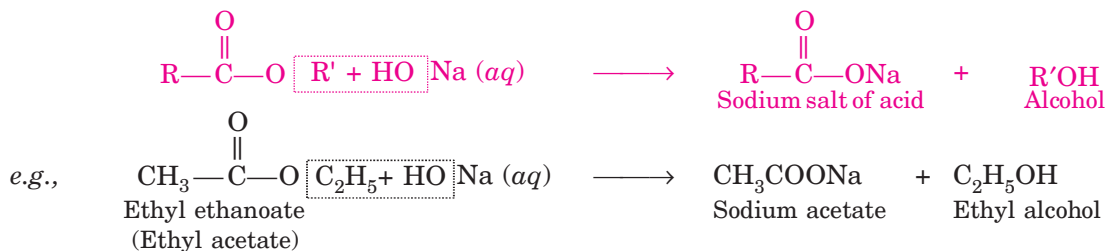
Summary : Grignard Reagent for Preparing Alcohols



REMEMBER

R Comes from Grignard reagent.

5. By hydrolysis of esters. Alcohols are generally prepared by hydrolysis of esters with aqueous alkalis.



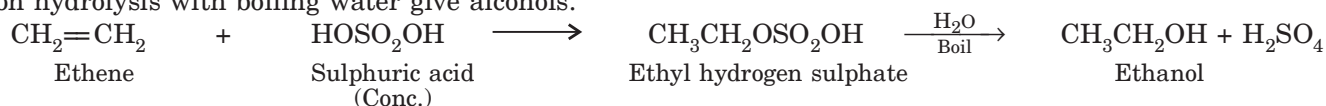
6. From alkenes.

Alkenes can be converted into alcohols by the following methods :

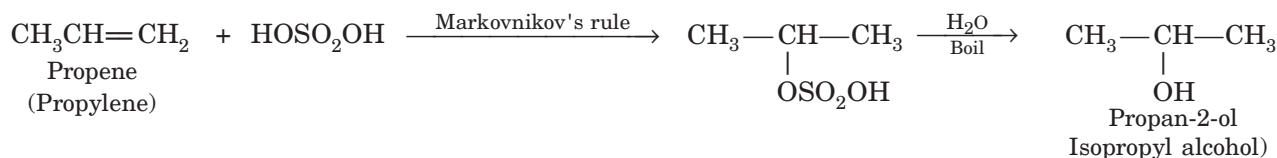
(a) By acid catalysed hydration of alkenes

The hydration of alkenes can be carried out directly or indirectly.

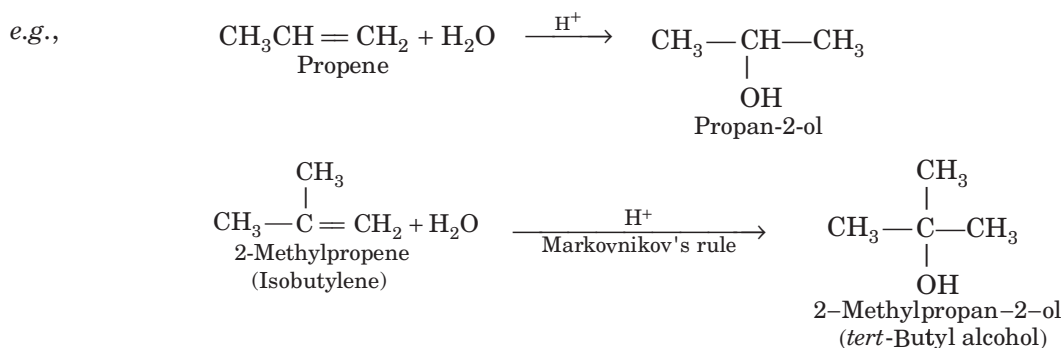
(i) In the **indirect process**, alkenes are passed through conc. H_2SO_4 to form alkyl hydrogen sulphates, which upon hydrolysis with boiling water give alcohols.



In case of unsymmetrical alkenes, the addition of H_2SO_4 takes place in accordance with **Markovnikov's rule** i.e., hydrogen goes to that carbon atom which contains large number of hydrogen atoms.



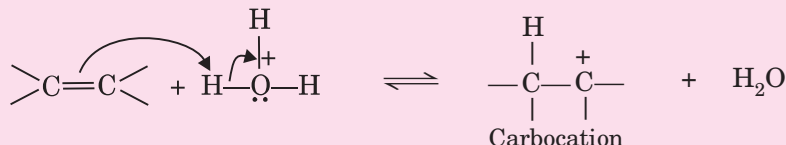
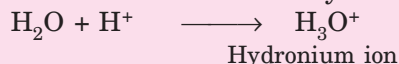
(ii) Reactive alkenes directly add a molecule of water in the presence of mineral acids as catalyst to form alcohol.



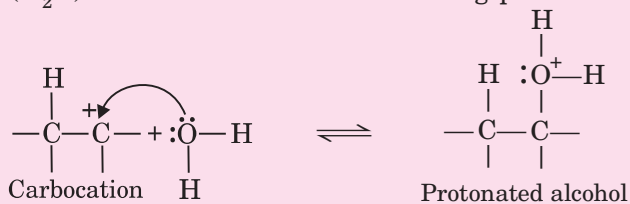
Mechanism : Hydration of alkenes

The mechanism of the reaction involves the following steps:

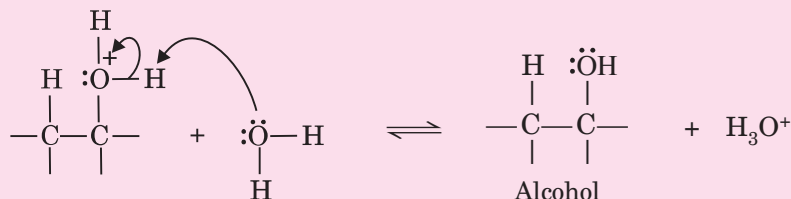
Step 1. Alkene gets protonated to form a carbocation by the electrophilic attack of H_3O^+ :



Step 2. Nucleophile (H_2O) attacks the carbocation forming protonated alcohol.



Step 3. Loss of H^+ from oxygen (deprotonation) to form alcohol



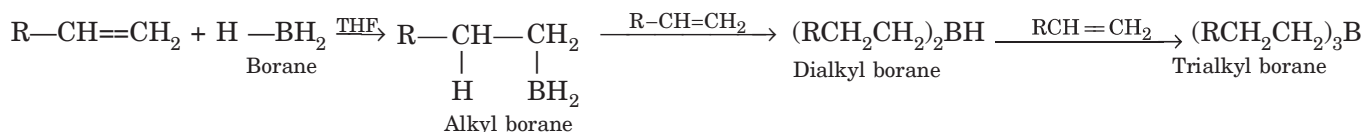
NOTE

It may be noted that during step 1, addition of a proton occurs on that carbon atom of the double bond which gives a more stable carbocation.

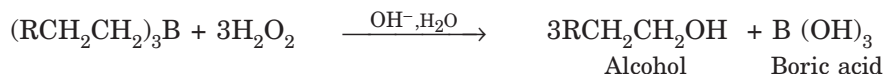
(b)Hydroboration oxidation reduction. Alkenes react with diborane (B_2H_6) to form trialkylboranes which upon subsequent treatment with alkaline H_2O_2 give alcohols. This reaction involves the addition of water to a double bond opposite to that of Markovnikov's rule *i.e.*, **anti-Markovnikov's rule**. This involves two reactions, addition of borane (BH_3) to double bond called **hydroboration-oxidation** and **hydrolysis** to give an alcohol.



Diborane is an electron deficient molecule. Therefore, it acts as an electrophile reacting with alkene to form alkyl boranes R_3B as



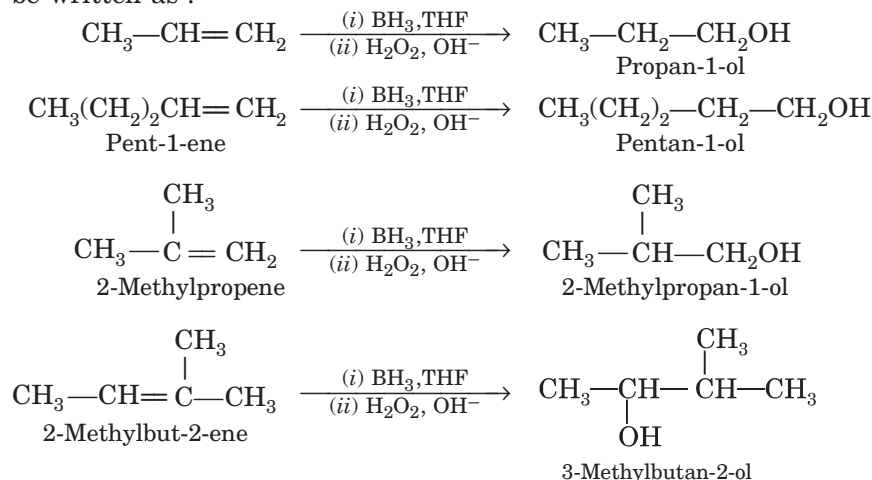
In each addition step, the boron atom is attached to carbon atom of the double bond that is bonded to larger number of hydrogen atoms. The hydrogen atom is transferred from boron atom to the other carbon atom of the double bond. Thus, the addition occurs according to **anti-Markovnikov's rule**. During oxidation of trialkyl borane, boron is replaced by —OH group. The yield of alcohol is excellent and the product can be easily isolated.



e.g.,



or the reaction may be written as :



(c) Oxymercuration-demercuration reaction

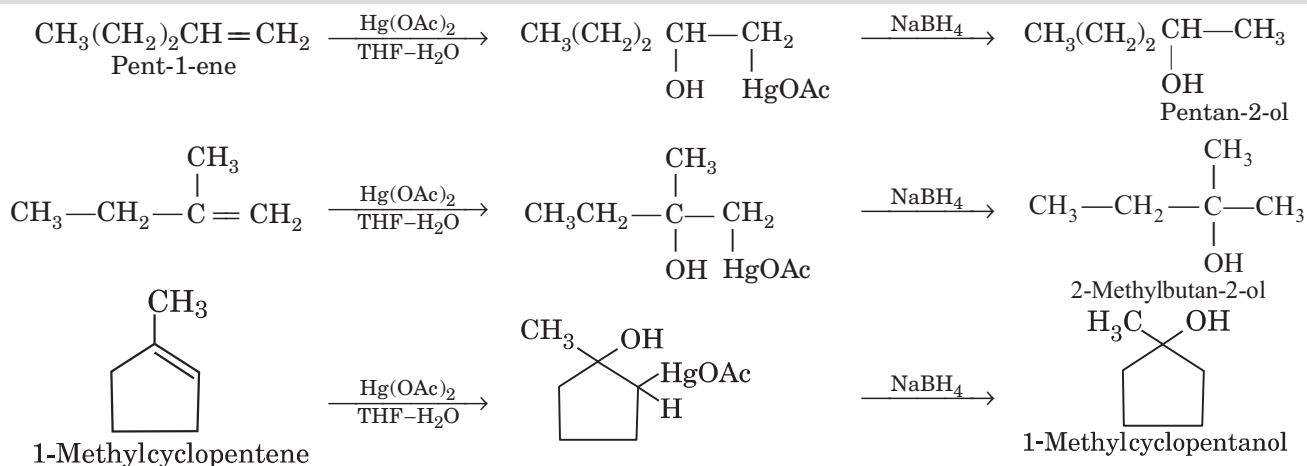
Alkenes react with mercuric acetate $(\text{CH}_3\text{COO})_2\text{Hg}$ or $\text{Hg}(\text{OAc})_2$ in the presence of water to form oxymercuration adducts which upon reduction with NaBH_4 in alkaline medium give alcohols.

Alkenes react with mercuric acetate in a mixture of tetrahydrofuran (THF) and water to give (hydroxyalkyl) mercury compound, involving addition of —OH and —HgOAc to the double bond. This is called **oxymercuration**. In the second step, sodium borohydride reduces —HgOAc and replaces it with hydrogen. This is called **demercuration**.



The net reaction involves addition of —H and —OH in accordance with **Markovnikov's rule**.

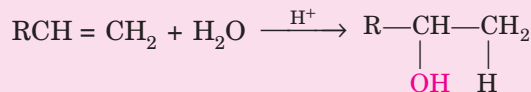
This reaction is very fast and produces the alcohol in high yield. The alcohol obtained corresponds to Markovnikov's addition of water to alkene.



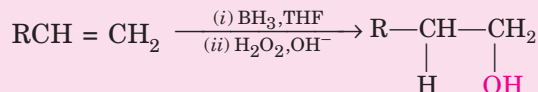
REMEMBER

Alkenes can be converted to alcohols :

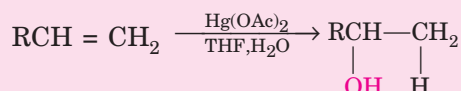
- Acid catalysed hydration proceeds according to **Markovnikov rule**.



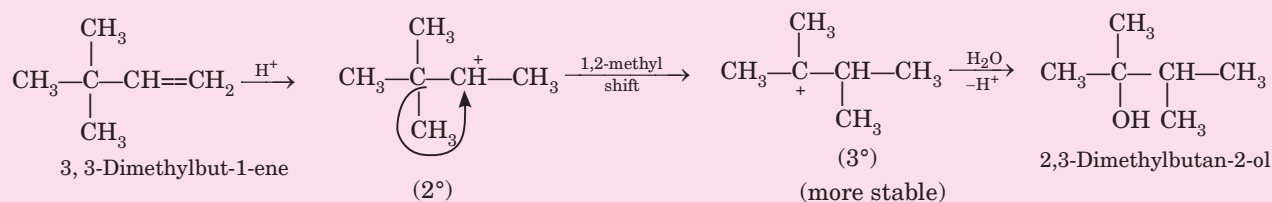
- Hydroboration oxidation reduction proceeds according to **anti-Markovnikov rule**.



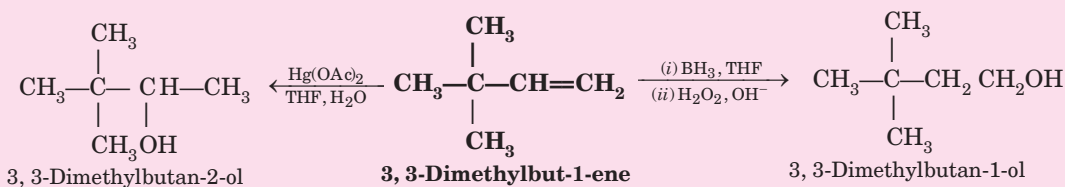
- Oxymercuration-demercuration proceeds according to **Markovnikov rule**.



- Hydration of alkene occurs through carbocation intermediates. Since carbocations have a tendency to undergo rearrangement to form stable carbocations (by 1, 2-hydride shift or 1, 2-methyl shift), the products are rearranged alcohols.

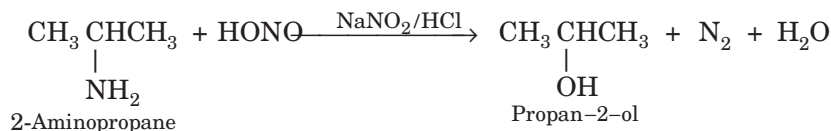
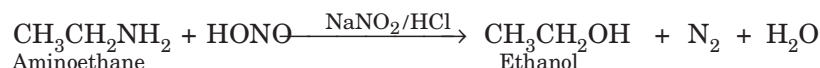
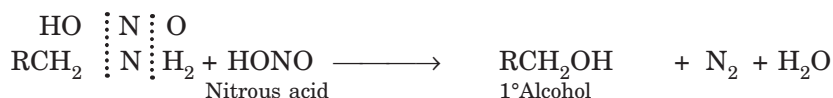


- Hydroboration oxidation or oxymercuration-reduction do not involve carbocation intermediates and hence always form expected (unrearranged) alcohols.



8. From aliphatic primary amines

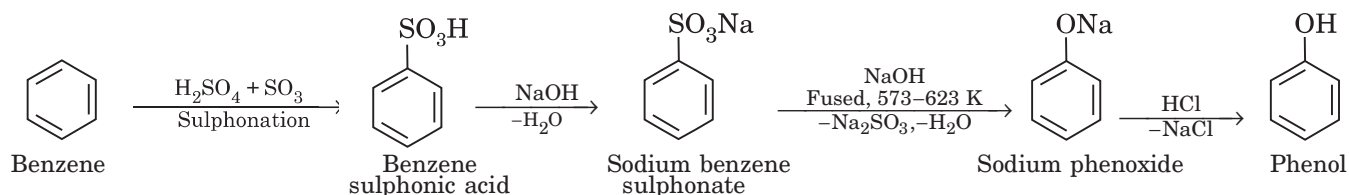
Primary amines react with nitrous acid ($\text{NaNO}_2 + \text{HCl}$) to form alcohols along with the evolution of nitrogen gas.



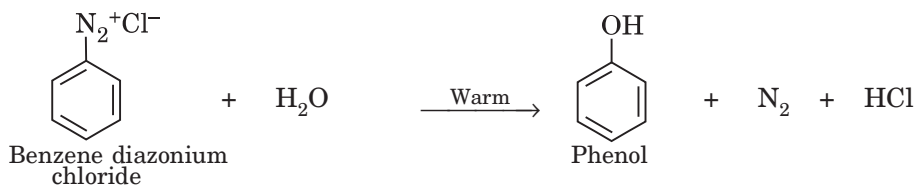
METHODS OF PREPARATION OF PHENOLS

Phenol is also called **carbolic acid**. It was first isolated in the early 19th century from coal tar. Nowadays, phenol is manufactured synthetically. In the laboratory, phenols are prepared from benzene derivatives by the following methods:

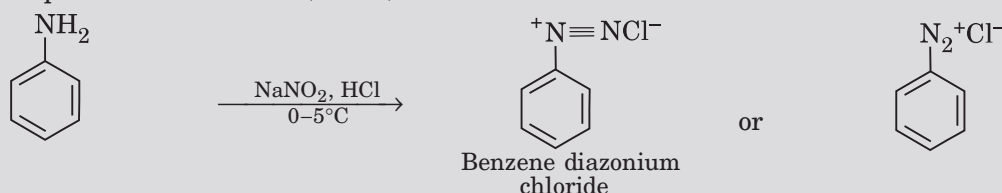
1. From benzene sulphonic acid. Benzene is sulphonated with oleum (mixture of H_2SO_4 and SO_3 i.e., $\text{H}_2\text{S}_2\text{O}_7$) and benzene sulphonic acid so formed is converted to sodium phenoxide by heating with molten sodium hydroxide. This on acidification gives phenol.



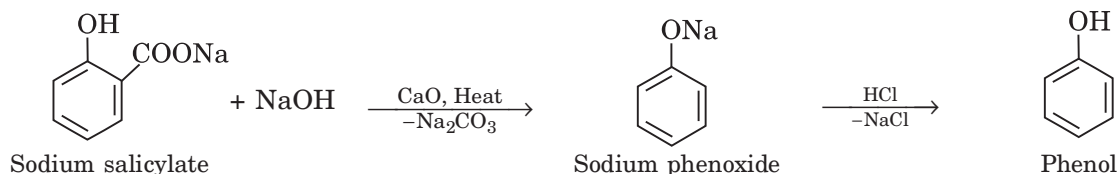
2. From diazonium salts. An aqueous solution of benzene diazonium salt on warming gives phenol.



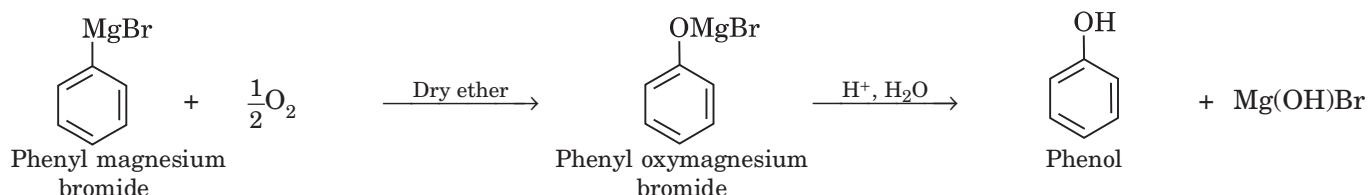
Benzene diazonium chloride required for the reaction is obtained by treating aniline with nitrous acid ($\text{NaNO}_2 + \text{HCl}$) at low temperature 273–278 K (0–5°C). This reaction is called **diazotisation reaction**.



3. By decarboxylation of sodium salt of salicylic acid. Phenol can be prepared by fusing sodium salicylate with soda lime (NaOH and CaO mixture) followed by acidification with dil. HCl .



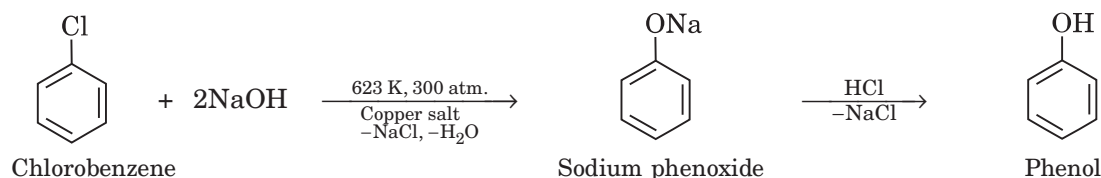
4. From Grignard reagent. When oxygen gas is bubbled through an ethereal solution of phenyl magnesium bromide (Grignard reagent), it forms an oxy compound which upon hydrolysis with dilute mineral acid gives phenol.



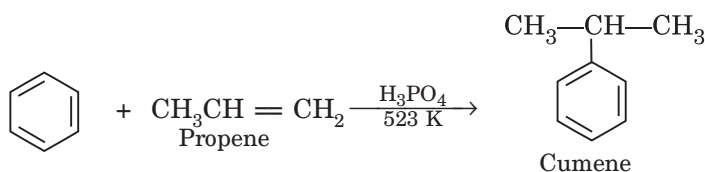
Commercial Preparation of Phenols

On a large scale, phenol is obtained by the following methods :

1. From chlorobenzene (Dow's process). Phenol is manufactured by heating chlorobenzene with 10% aqueous sodium hydroxide solution at about 623 K under 300 atmospheres and in the presence of copper salt acting as catalyst to form sodium phenoxide. The sodium salt when treated with dilute HCl , gives phenol. This method is called **Dow's process**.

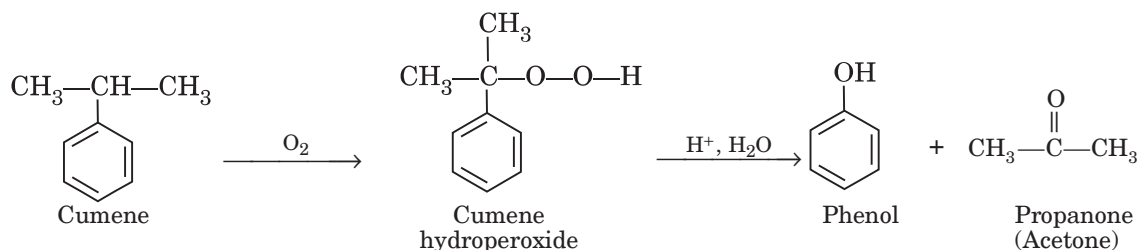


2. From cumene. Phenol is prepared commercially from cumene (isopropyl benzene). Cumene is prepared by Friedel Craft alkylation of benzene with propene in the presence of phosphoric acid at 523 K.

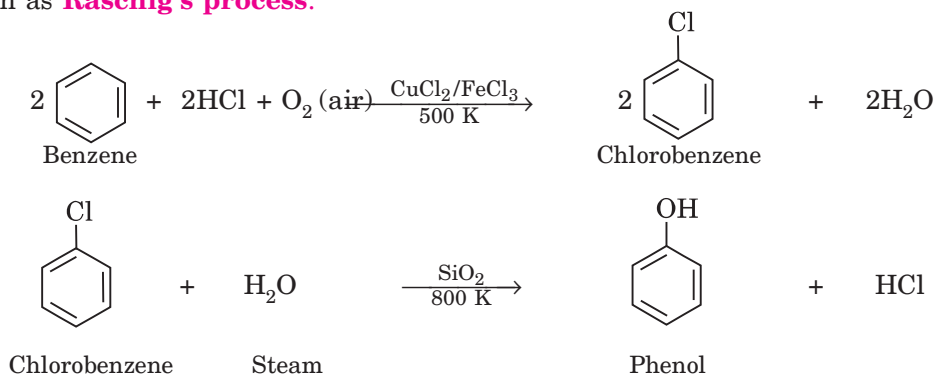


This reaction is Friedel Crafts alkylation reaction.

Cumene is oxidised in the presence of air to cumene hydroperoxide which upon subsequent hydrolysis with dil. H_2SO_4 gives phenol and propanone (acetone).



3. From benzene (Raschig's method). Vapours of hydrochloric acid are passed over benzene at 500 K in the presence of copper (II) chloride catalyst and ferric chloride catalyst and excess of air to form chlorobenzene. Steam is then passed through chlorobenzene at 800 K in the presence of silica as catalyst to give phenol. This method is known as **Raschig's process**.



SOLVED EXAMPLES

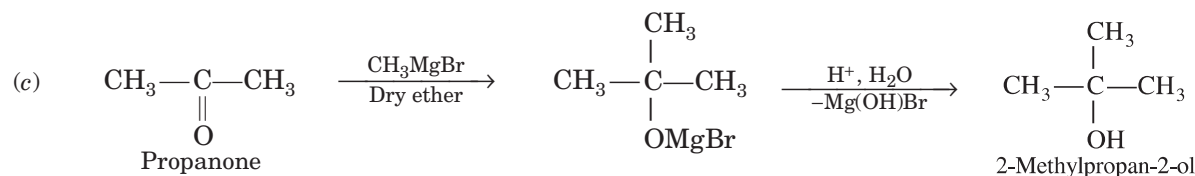
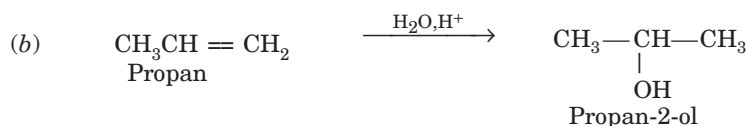
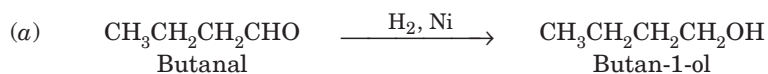
□ **Example 3.**

Give the structures and IUPAC names of products expected from the following reactions :

- Catalytic reduction of butanal
- Hydration of propene in the presence of dilute sulphuric acid.
- Reaction of propanone with methyl magnesium bromide followed by hydrolysis.

N.C.E.R.T.

Solution :



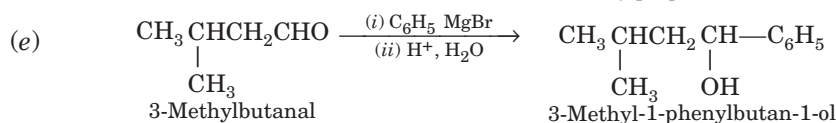
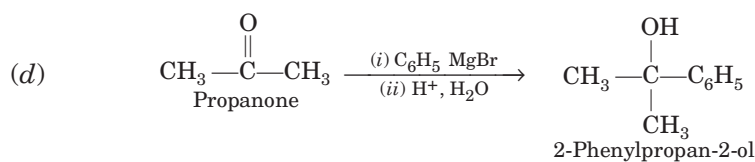
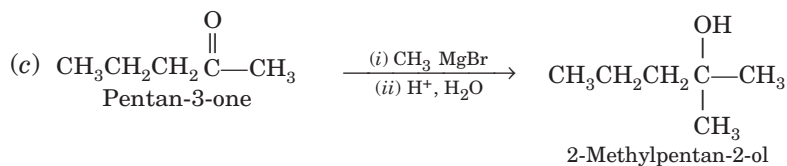
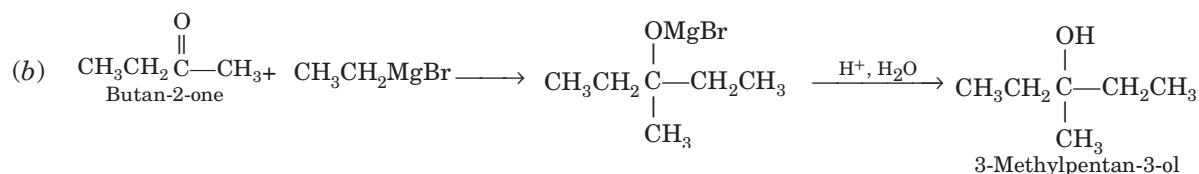
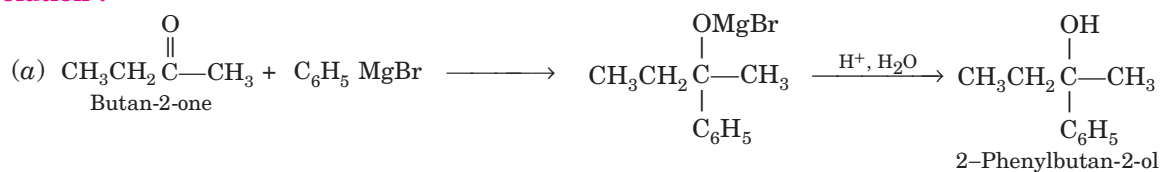
□ **Example 4.**

Use a Grignard's reagent to prepare the following alcohols :

- 2-Phenylbutan-2-ol
- 3-Methylpentan-3-ol
- 2-Methylpentan-2-ol
- 2-Phenylpropan-2-ol

(e) *3-Methyl-1-phenylbutan-1-ol*.

Solution :



PHYSICAL PROPERTIES OF ALCOHOLS

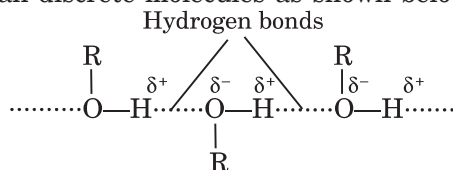
The important physical properties of alcohols are :

(i) Physical state. At ordinary temperature, the lower members are colourless liquids having a characteristic smell and burning taste. The higher members (having more than 12 carbon atoms) are colourless, odourless, wax-like solids.

(ii) Boiling points. The boiling points of alcohols are much higher than the corresponding aliphatic hydrocarbons and haloalkanes. For example,

Compound	CH ₄	CH ₃ Cl	CH ₃ Br	CH ₃ OH
Boiling point	90 K	249 K	278 K	337.5 K

This is because there is large difference in electronegativities of oxygen and hydrogen atoms. As a result, the O—H bond is strongly polar and forms hydrogen bonds in alcohols. Because of hydrogen bonds in alcohols, these exist as associated molecules rather than discrete molecules as shown below :



Therefore, a large amount of energy is needed to break these extensive hydrogen bonds and hence their boiling points are high.

It may be noted that alcohols have generally higher boiling points as compared to their isomeric ethers of same molecular masses. For example, the boiling point of ethyl alcohol (mol. mass = 46), dimethyl ether (mol. mass = 46) and propane (mol. mass = 44) are :

Ethyl alcohol	Dimethyl ether	Propane
351 K	248 K	23 K

This is *due to the presence of intermolecular hydrogen bonds in alcohols and their absence in ethers and hydrocarbons.*

The lower members have low boiling points but with the increase in number of carbon atoms (molecular mass), the boiling points keep on increasing gradually. This is because of increase in van der Waals forces. For isomeric alcohols having the same number of carbon atoms, the boiling points are in the order :

primary > secondary > tertiary.

Compound	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ Butan-1-ol (1°)	$(\text{CH}_3)_2\text{CHCH}_2\text{OH}$ 2 Methylpropan-1-ol (1°)	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ Butan-2-ol (2°)	$(\text{CH}_3)_3\text{COH}$ 2-Methylpropan-2-ol (3°)
Boiling point	391 K.	3 K	373 K	356 K

This is due to the fact that *with branching, the surface area decreases and therefore, van der Waals forces decrease. Consequently, boiling point also decreases.*

(iii) Solubility. The lower members of alcohols are highly soluble in water but the solubility decreases with increase in molecular weight. *The solubility of lower alcohols in water is due to the formation of hydrogen bonds between alcohols and water molecules.*

However, as the size of alcohol molecule increases, the alkyl group becomes larger and prevents the formation of hydrogen bonds with water molecules and hence the solubility goes on decreasing with increase in length of carbon chain (or molecular mass of alcohol).

For example,

Alcohol Solubility (in g/100g H_2O)	<i>n</i> -Butyl alcohol	<i>n</i> -Pentyl alcohol	<i>n</i> -Hexyl alcohol	<i>n</i> -Heptyl alcohol
	7.9	2.3	0.65	

However, amongst **isomeric alcohols**, the solubility increases with branching. This is due to the reason that as the branching increases, the surface area of non-polar hydrocarbon part decreases and the solubility increases.

Alcohol Solubility (in g/100g H_2O)	<i>n</i> -Butyl alcohol	Isobutyl alcohol	Sec-butyl alcohol	tert-Butyl alcohol
	7.9	10.0	12.5	very large

(iv) Density. Generally, alcohols are lighter than water although the density increases with increase in molecular mass.

(v) Intoxicating effects. Alcohols have intoxicating effects. Methanol is poisonous and is not good for drinking purposes. It may cause blindness and even death. Ethanol is used for drinking purposes.

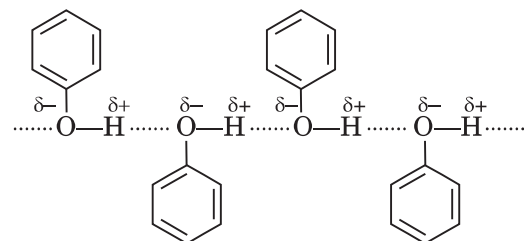
PHYSICAL PROPERTIES OF PHENOLS

The important physical properties of phenol are :

1. State and smell. Phenols are colourless crystalline solids or liquids. They have characteristic phenolic odours.

2. Solubility. Unlike alcohols, phenols are sparingly soluble in water. The non-polar aryl group is very large in size and it almost completely masks the polar character of the —OH group. However, phenols are soluble in alcohols, ethers and also in NaOH.

3. Boiling points. The boiling points of phenols are higher than the boiling points of the aromatic hydrocarbons and haloarenes of comparable molecular masses. For example, boiling point of phenol (molecular mass = 94) is 455 K while that of toluene (molecular mass = 92) is 384 K.



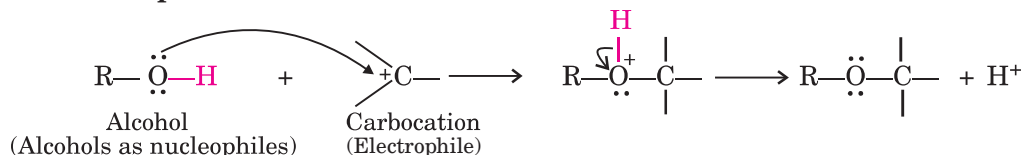
Compound	$\text{C}_6\text{H}_5\text{OH}$ Phenol	$\text{C}_6\text{H}_5\text{CH}_3$ Toluene	$\text{C}_6\text{H}_5\text{Cl}$ Chlorobenzene
Boiling point	455 K	384 K	405

The higher boiling point is due to the presence of intermolecular hydrogen bonding in phenols. Therefore, they exist as associated molecules.

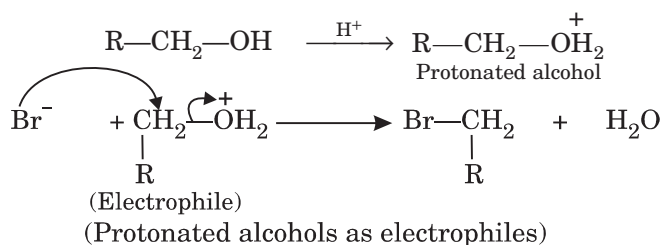
CHEMICAL PROPERTIES OF ALCOHOLS

Alcohols are versatile compounds. They behave both as nucleophiles as well as electrophiles.

(a) They behave as **nucleophiles** in the reactions in which the bond between O—H is broken as shown below :



(b) They behave as **electrophiles** in which the bond between C—O is broken. These reactions are carried out in the presence of acids to form protonated alcohols. Protonated alcohols react as electrophiles.



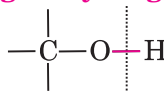
On the basis of cleavage of different bonds, the reactions of alcohols may be divided into the following types :

A. Reactions involving cleavage of oxygen-hydrogen bond.

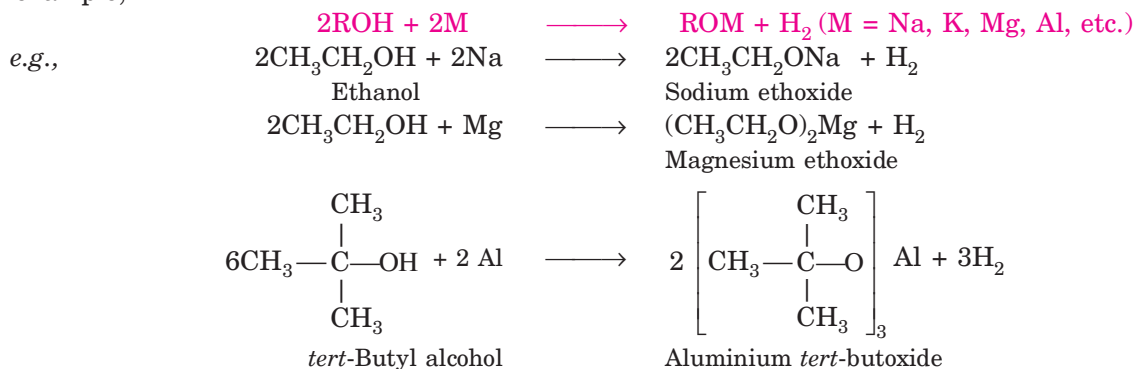
B. Reactions involving cleavage of carbon-oxygen bond.

C. Reactions involving both the alkyl and hydroxyl groups.

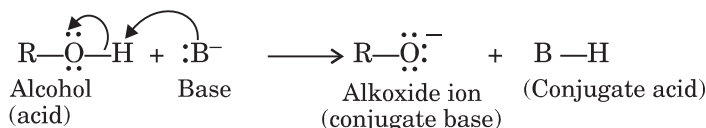
A. Reactions Involving the Cleavage of Oxygen-Hydrogen Bond



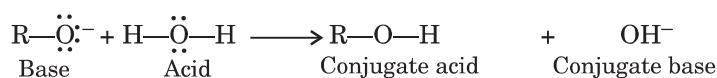
1. Reaction with active metals—acidic character. Alcohols are weakly acidic in nature and react with active metals such as sodium, potassium, magnesium, aluminium, etc. to liberate hydrogen gas and form metal alkoxide. For example,



The above reaction shows that alcohols are **acidic** in nature. The alcohols act as Bronsted acids because they donate a proton to a strong base (:B⁻). For example,



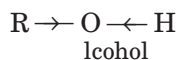
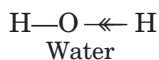
On reacting an alkoxide with water, the starting alcohol is obtained.



This reaction shows that **water is a better proton donor than alcohol. In other words, water is stronger acid than alcohols.** We can also note that alkoxide is a better proton acceptor than hydroxide ion. This means **alkoxides are stronger bases than hydroxide ion.** For example, sodium ethoxide is a stronger base than sodium hydroxide.

The acidic nature of alcohols is due to the presence of polar O—H bond. Oxygen is more electronegative than hydrogen and therefore, it withdraws the shared electron pair between O and H atoms towards itself. As a result,

O—H bond becomes weak and loses a proton (H^+). Therefore, alcohols behave as acids. However, alcohols are weak acids ($K_a = 10^{-16}$ to 10^{-18}) even weaker than water ($K_a = 1 \times 10^{-14}$). This is quite expected because of the *electron releasing inductive effect* (+I effect) of the *alkyl group* (CH_3). The alkyl group releases electrons towards oxygen atom and increases electron density over the oxygen atom tending to decrease the polarity of O—H bond. As a result, the tendency of oxygen to withdraw electrons in O—H bond towards itself decreases and therefore, the release of proton (H^+) becomes difficult. On the other hand, there is no electron releasing alkyl group in water and the electron pair of O—H bond gets more attracted towards oxygen atom than in alcohol. Thus, the release of H^+ from water is easier but it is slightly less in alcohol. Thus, **alcohols are weaker acids than water**.



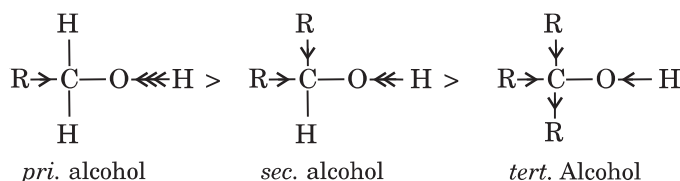
Comparison of acidic strength of different types of alcohols

The order of acidic strength among various types of alcohols is :

primary > secondary > tertiary

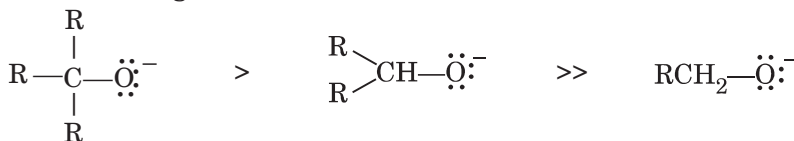
This order can be easily explained in terms of *electron releasing inductive effect of alkyl groups*. The acidic character of alcohols is due to the cleavage of O—H bond giving H^+ .

The alkyl groups are electron releasing groups (+I effect) and they increase the electron density around the oxygen. As a result, the electrons of O—H bond cannot be withdrawn strongly towards oxygen and O—H remains strong. Therefore, greater is the number of alkyl groups present, smaller will be its tendency to release proton (H^+) and consequently weaker will be its acidic strength. Now, electron releasing effect would be maximum in tertiary alcohols and least in primary alcohols. Thus, the acidic character decreases as :

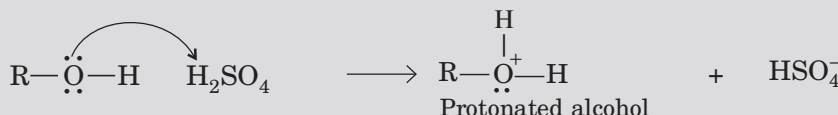


Acidic character decreases

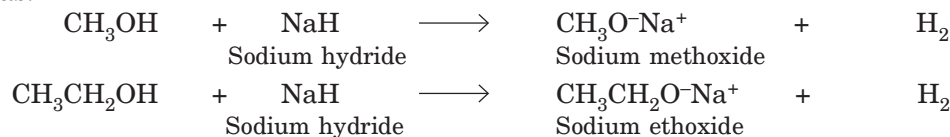
Obviously, the basic strength of their alkoxides follows the reverse order :



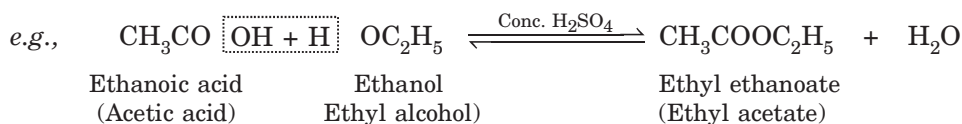
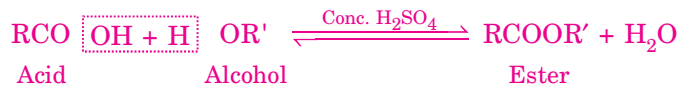
It may be noted that alcohols act as Lewis bases also. This is due to the presence of lone pairs on oxygen which makes alcohols proton acceptors :



2. Reaction with metal hydrides. Alcohols react with metal hydrides to form alkoxides with the evolution of hydrogen gas.

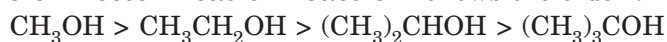


3. Reaction with carboxylic acids (esterification). Alcohols react with monocarboxylic acids, in the presence of conc. H_2SO_4 or dry HCl gas as catalyst, to form esters. The reaction is known as **esterification**. The function of conc. H_2SO_4 is to act as protonating agent as well as a dehydrating agent.

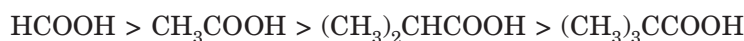


The reaction is *reversible* in nature and the equilibrium can be shifted towards the forward direction by removing water as soon as it is formed. When HCl gas is used as a catalyst, the reaction is called **Fischer-Speier esterification**.

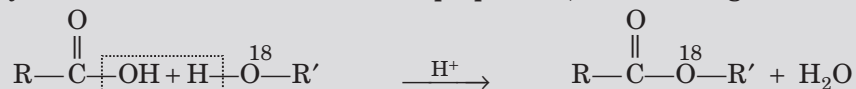
It may be noted that the presence of bulky groups in the alcohol or in the acid decreases the rate of esterification. This is due to *steric hindrance* of bulky groups. As a result, it is difficult to prepare esters of tertiary alcohol. Thus, the order of **reactivity of alcohols in esterification reaction** follows the order :



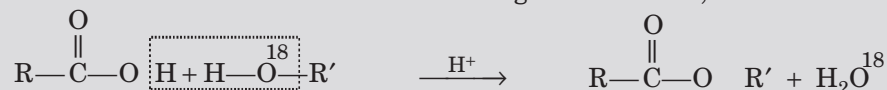
The **order of carboxylic acids** follows the sequence :



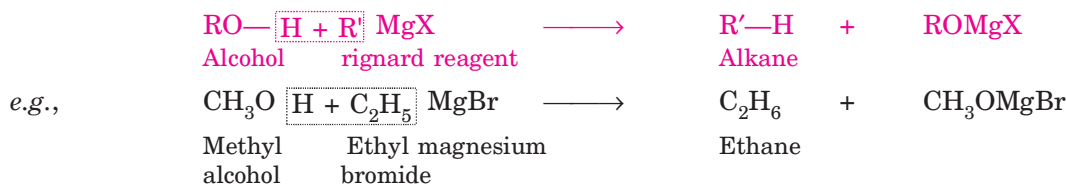
Note : It is important to note that esterification involves the cleavage of the O—H bond of alcohol. This has been established by isotopic tracer techniques. If the reaction is carried out with alcohol having isotopic oxygen O^{18} (which can be easily traced because of its radioactive properties), the resulting ester contains this isotope of oxygen.



If the C—O bond of alcohol would have cleaved during esterification, O^{18} would have gone to resulting water.



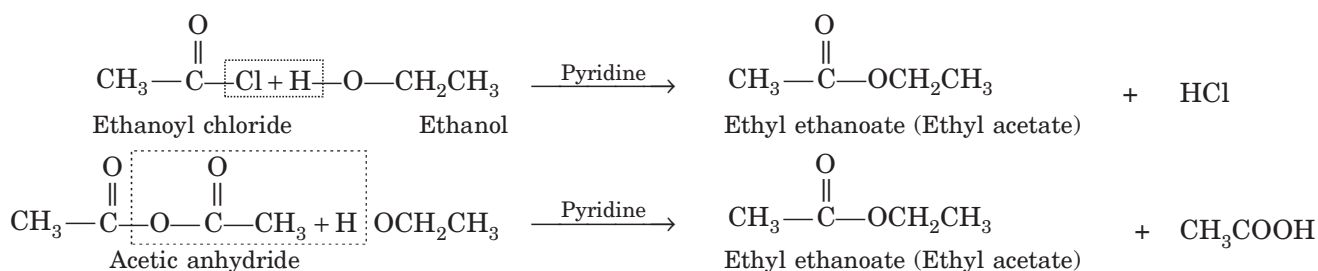
4. Reaction with Grignard reagents. Alcohols react with Grignard reagents (which are alkyl magnesium halides, RMgX) to form hydrocarbons.



NOTE

It may be noted that alkane formed corresponds to the alkyl group of the Grignard reagent.

5. Reaction with acyl chloride or acid anhydride (acylation). When alcohols are treated with acid chloride or acid anhydride in the presence of bases like pyridine or dimethyl aniline (as catalyst), the hydrogen atom of —OH group is replaced by acyl ($\text{RCO}-$) group forming esters.



This reaction is called **acylation reaction**. If the acid halide or anhydride used are acetyl chloride and acetic anhydride, the reaction is usually called **acetylation** which means the introduction of acetyl (CH_3CO) group in alcohols. It may be noted that the reaction with acetyl chloride is carried out in the presence of a base (pyridine) to neutralise HCl which is formed during the reaction. It shifts the equilibrium to the forward direction.

B. Reactions Involving Cleavage of Carbon-Oxygen Bond : $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—OH}$

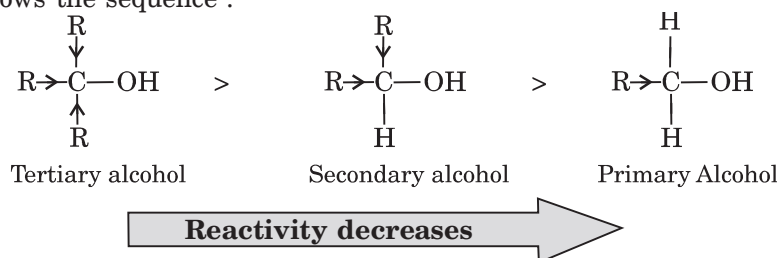
Alcohols undergo a number of reactions involving the cleavage of carbon-oxygen (C—OH) bond. In these reactions, the order of reactivity of alcohols is :

tertiary > secondary > primary

This can be explained in terms of *electron releasing inductive effect of alkyl groups*. The alkyl groups release electrons and, therefore, they increase the electron density towards oxygen. As a result, the polarity of C—O bond increases and this makes the cleavage of the bond between carbon and oxygen easier. Therefore, *the greater the*

number of alkyl groups attached to the carbon, the more easy would be the cleavage of C—O bond and consequently, the greater would be the reactivity of alcohol.

Thus, the reactivity follows the sequence :



1. Reaction with hydrogen halides. Alcohols react with hydrogen halides to form haloalkanes (alkyl halides). The order of **reactivity of hydrogen halides** is :

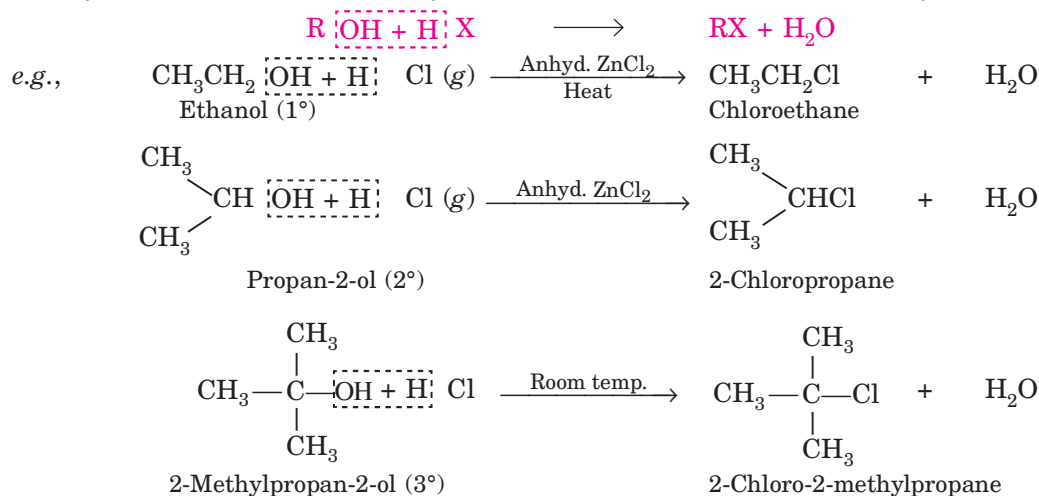


This is because I^- ion is a better nucleophile than Br^- ion, which in turn, is better than Cl^- ion.

The order of **reactivity of alcohols** is :

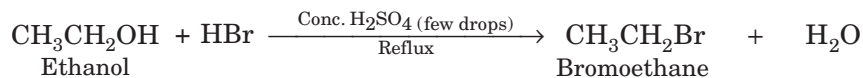


These trends have already been explained. Due to the low reactivity of primary and secondary alcohols with HCl, they require some Lewis acid catalyst for the reaction. In these reactions, anhydrous ZnCl_2 is used as a Lewis acid catalyst. However, no such catalyst is needed for the reaction of tertiary alcohols with HCl.



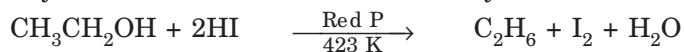
The reaction of primary and secondary alcohols with HCl gas in the presence of anhydrous ZnCl_2 is called **Groove's method**.

In the case of HBr, a small amount of conc. H_2SO_4 is also added as a catalyst for the reaction with primary alcohols. But no catalyst is added for the reaction with secondary and tertiary alcohols which get dehydrated in the presence of conc. H_2SO_4 .



In the case of HI, alkyl iodides are formed by heating the alcohol with HI.

However, if reaction between hydrogen iodide and alcohol is carried out in the presence of red phosphorus, alcohol gets reduced to hydrocarbon rather than to form alkyl halide. For example,

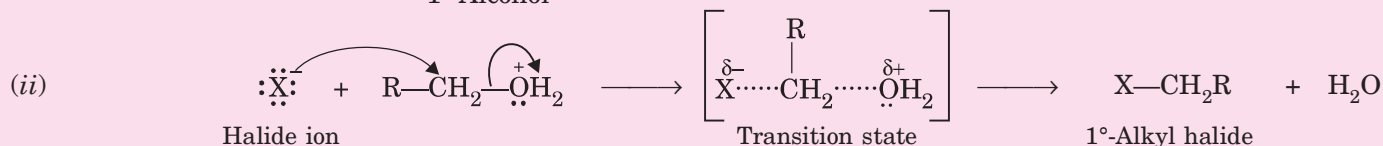
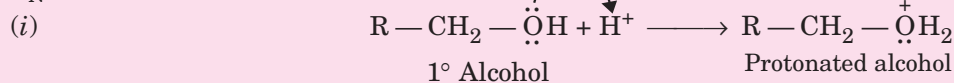


Mechanism : Reaction of alcohols with hydrogen halides.

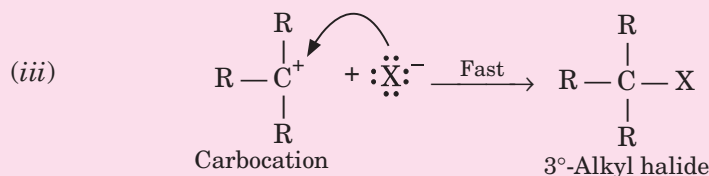
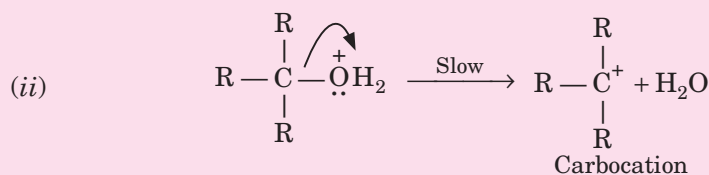
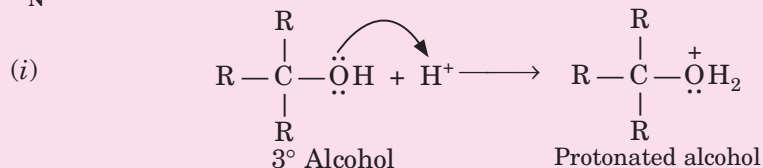
The **reactivity** of the above reaction can be easily understood in terms of its **mechanism**. Primary alcohols react by $\text{S}_\text{N}2$ mechanism whereas secondary and tertiary alcohols react by $\text{S}_\text{N}1$ mechanism as :



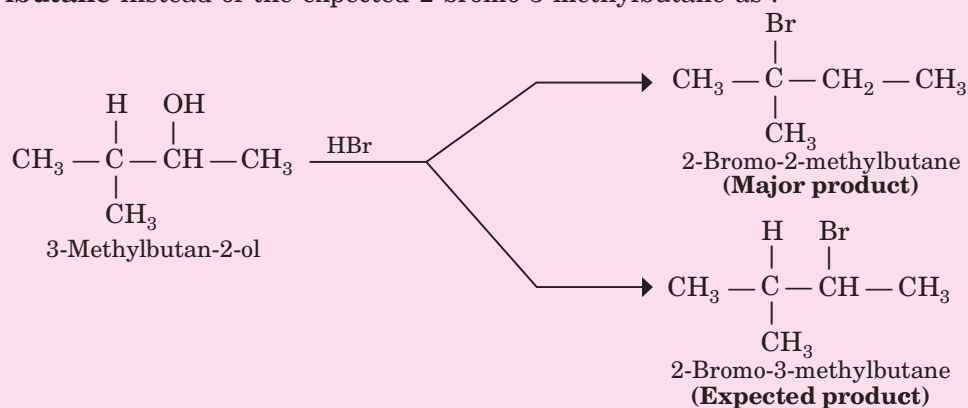
S_N2 mechanism



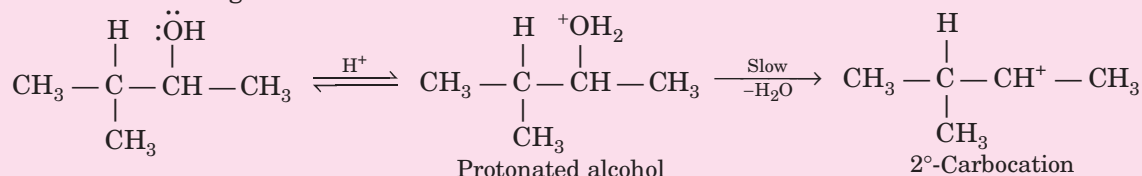
S_N1 mechanism



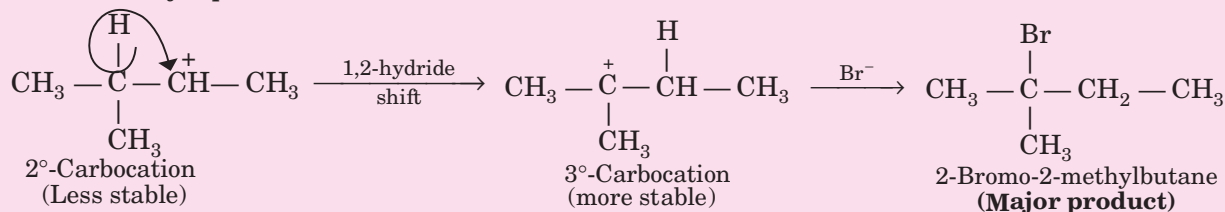
The reaction of 2° or 3° alcohols by S_N1 mechanism, quite often gives rearranged products which are different from the expected products. As already learnt in Unit 10, (S_N1 reactions of alkyl halides), this is due to 1,2-hydride or 1,2-methyl shift. For example, when 3-methylbutan-2-ol is treated with concentrated HBr the major product is **2-bromo-2-methylbutane** instead of the expected 2-bromo-3-methylbutane as :



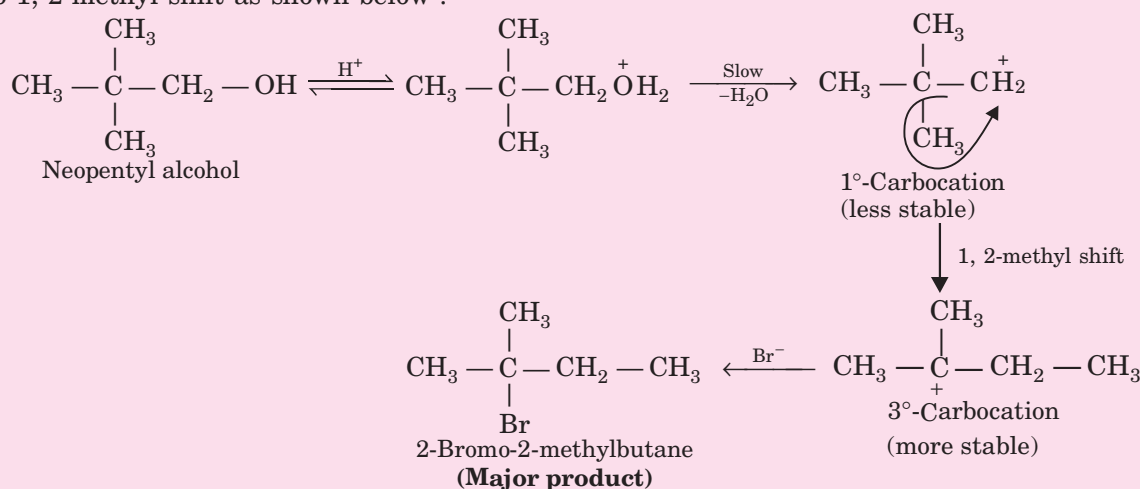
This is because of rearrangement of the carbocation as shown below :



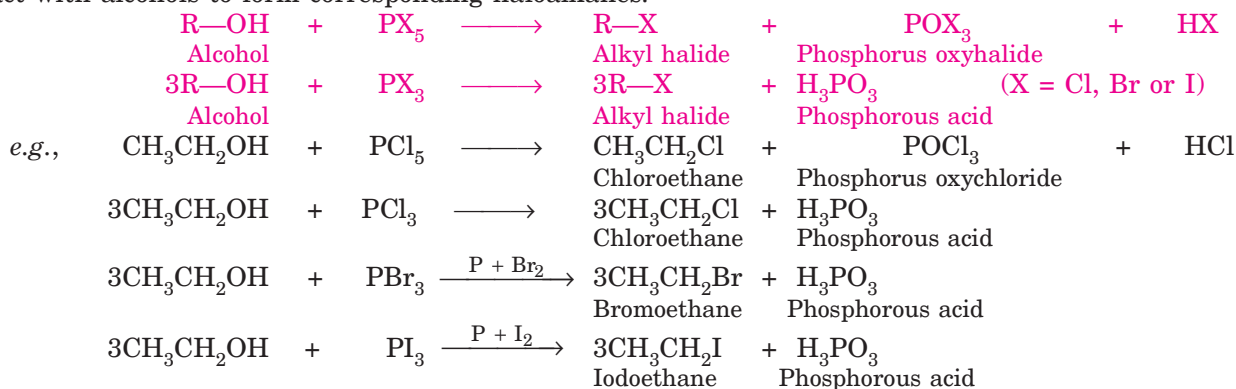
A hydride shift transforms the 2° carbocation into a more stable 3° carbocation and attack by bromide ion gives the observed major product.



Similarly, neopentyl alcohol, $(\text{CH}_3)_3\text{CCH}_2\text{OH}$ reacts with HBr to give **2-bromo-2-methylbutane** as rearranged product. This is due to 1, 2-methyl shift as shown below :

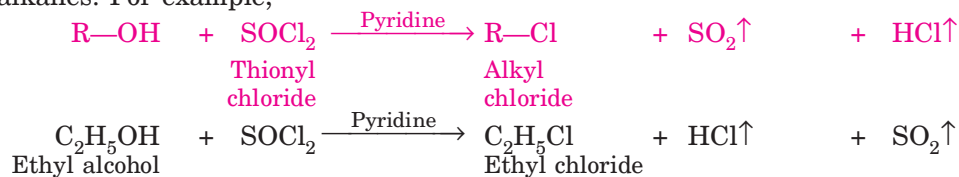


2. Reaction with phosphorus halides. Phosphorus halides such as PCl_5 , PCl_3 , PBr_3 ($\text{P} + \text{Br}_2$) or PI_3 ($\text{P} + \text{I}_2$) react with alcohols to form corresponding haloalkanes.



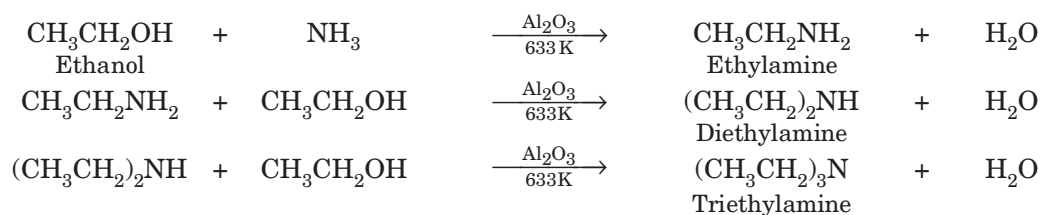
PBr_3 and PI_3 are generally prepared *in situ* by the reaction between phosphorus and bromine or iodine.

3. Reaction with thionyl chloride. On treatment with thionyl chloride in the presence of pyridine, alcohols form chloroalkanes. For example,



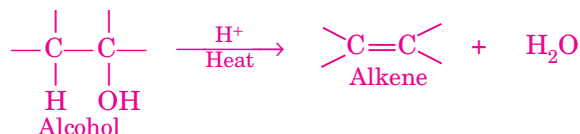
The reaction with thionyl chloride is preferred because the by products (SO_2 and Cl_2) formed are gases and can be easily removed from the reaction mixture.

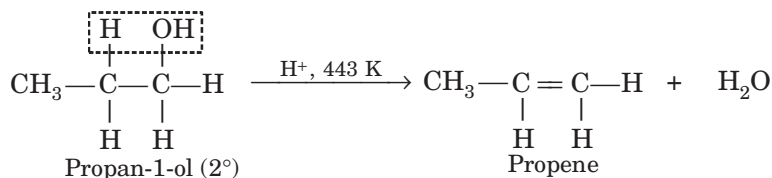
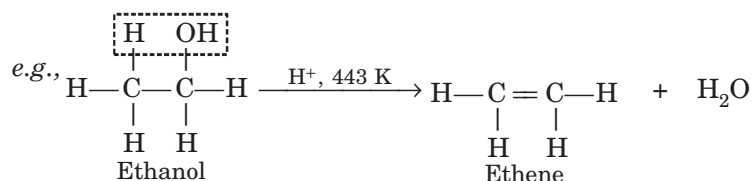
4. Reaction with ammonia. When vapours of an alcohol and ammonia are passed over heated alumina (Al_2O_3) at 633K, a mixture of primary, secondary and tertiary amines is produced. For example,



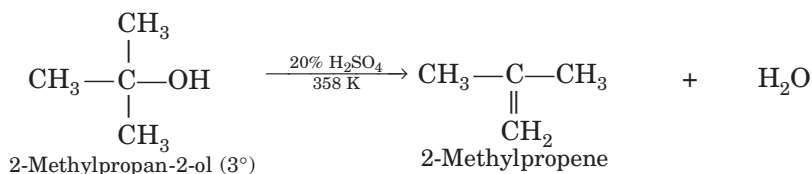
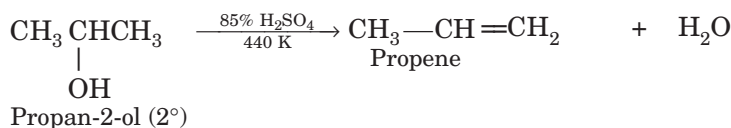
C. Reactions involving both the Cleavage of Alkyl and Hydroxyl Groups

1. Acidic dehydration. When alcohols are heated with a protonic acid such as conc. H_2SO_4 or H_3PO_4 at 443 K, they get dehydrated to form alkenes.





Secondary and tertiary alcohols are dehydrated under mild conditions. For example,



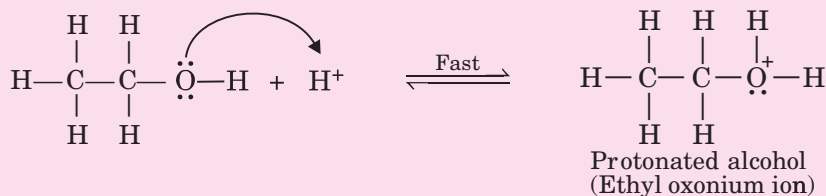
Thus, the relative ease of dehydration of alcohols follows the following order :

Tertiary alcohol > Secondary alcohol > Primary alcohol

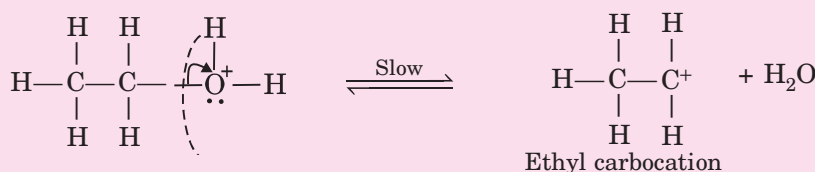
Mechanism : Acidic dehydration of alcohols

The reaction is believed to occur as follows :

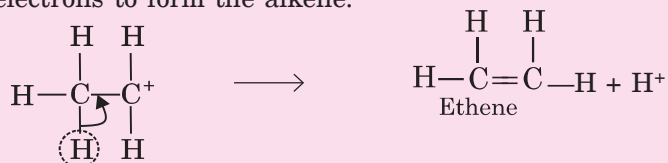
(i) **Formation of protonated alcohol.** Alcohol combines with a proton to form a protonated alcohol.



(ii) **Formation of carbocation.** The protonated alcohol loses a water molecule to form a carbocation.



(iii) **Elimination of a proton to form alkene.** The carbocation then eliminates a proton and undergoes rearrangement of electrons to form the alkene.



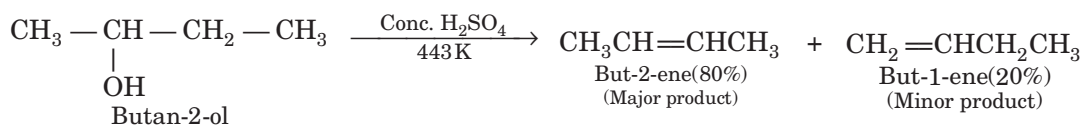
The acid used in step (i) is released in step (iii). To drive the equilibrium reaction in the forward direction, ethene is removed as soon as it is formed.

Some Important Facts about Dehydration of Alcohols Reaction

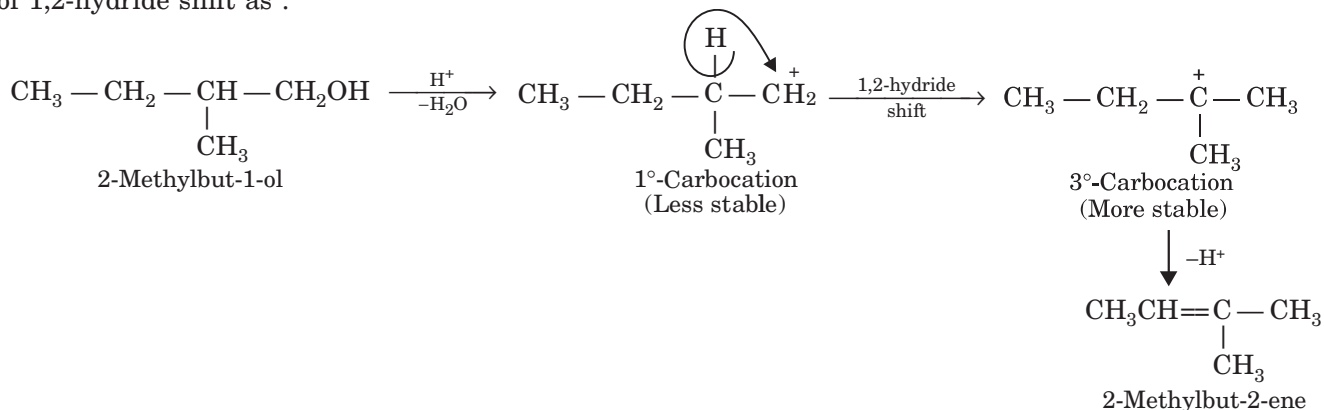
● The acidic dehydration of alcohols to alkenes occurs through the formation of intermediate carbocations and the stability of carbocation follows the order : $3^\circ > 2^\circ > 1^\circ$. Therefore, the relative ease of dehydration of alcohols follows the same order :

Tertiary alcohol > Secondary alcohol > Primary alcohol

● The dehydration of 2° and 3° alcohols always occurs in accordance with **Saytzeff's rule**. According to this rule, the more highly substituted alkene is always the major product. For example,

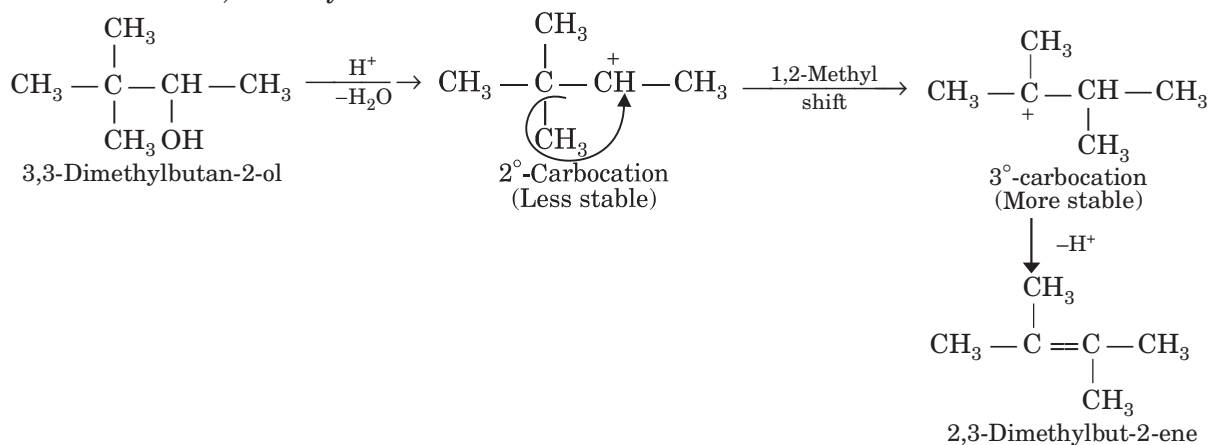


● Since, the dehydration of alcohols involves the formation of intermediate carbocations which are always prone to rearrangements, therefore, the alkenes formed are always those obtained from rearranged carbocations. In the dehydration of 2-methylbutan-1-ol, the major product is 2-methylbut-2-ene instead of expected 2-methylbut-1-ene because of 1,2-hydride shift as :



It may be noted that from 3°-carbocation, the H⁺ can be abstracted either from C-1 or from C-3. But it is preferably abstracted from C-3 to form more substituted alkene in accordance with Saytzeff's rule.

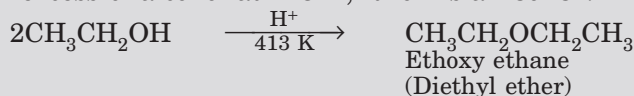
Similarly, 3,3-dimethylbutan-2-ol gives 2,3-dimethylbut-2-ene as the major product instead of expected 3,3-dimethyl but-1-ene because of 1, 2-methyl shift as :



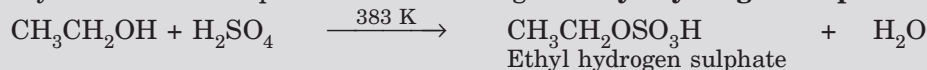
It may be noted that the reaction between alcohol and conc. H₂SO₄ depends upon the **conditions**. For example,

(i) At 443 K it gives **ethene** as the product.

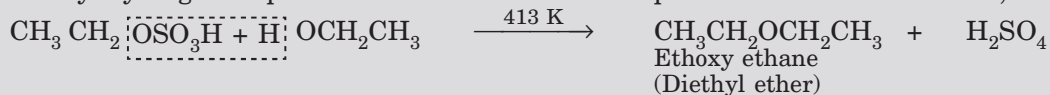
(ii) When heated with excess of alcohol at 413 K, it forms an **ether**.



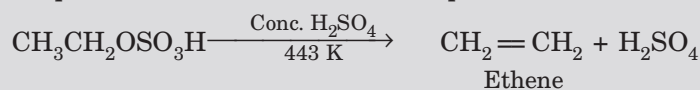
(iii) At 383 K, ethyl alcohol and sulphuric acid react to give **ethyl hydrogen sulphate**.



When ethyl hydrogen sulphate is heated to 413 K in the presence of excess of alcohol, diethyl ether is formed.

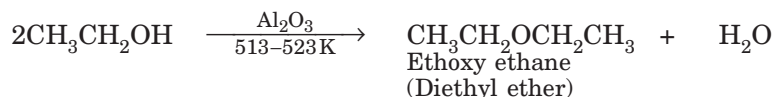


When ethyl hydrogen sulphate is heated to 443 K in the presence of excess of conc. H₂SO₄, ethene is formed.

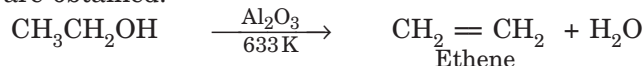


Dehydration of alcohols to ethers or alkenes can also be brought about by passing the vapour of the alcohols over **heated alumina catalyst** under different conditions :

(a) At 513–523 K, ethers are obtained.



(b) At 633 K, alkenes are obtained.



2. Oxidation. The oxidation of alcohols involves the formation of a carbon-oxygen double bond with cleavage of an O—H and C—H bonds.

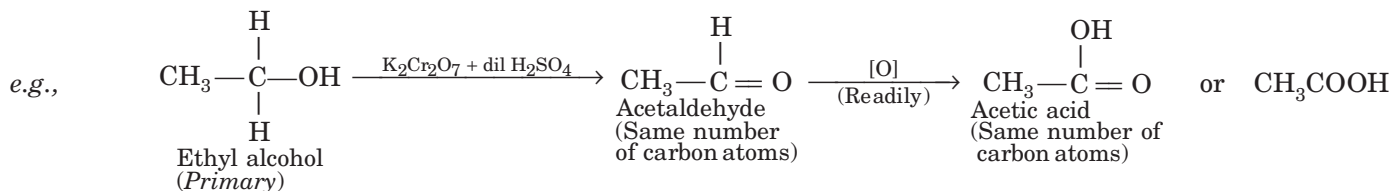
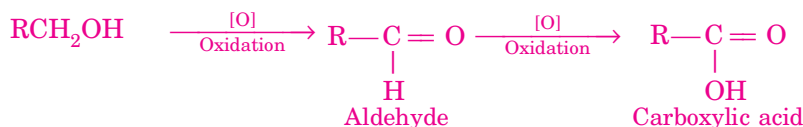


This type of cleavage and formation of bonds occur in oxidation reactions. These reactions are also called **dehydrogenation reactions** because these involve loss of hydrogen from an alcohol. The product of oxidation reaction depends upon the type of alcohol (primary, secondary or tertiary alcohol) and also on the nature of oxidising agent.

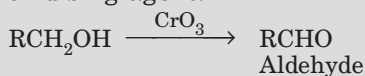
The oxidation of alcohols can be carried out by a number of reagents such as aqueous, alkaline or acidified KMnO_4 , acidified $\text{Na}_2\text{Cr}_2\text{O}_7$ or $\text{K}_2\text{Cr}_2\text{O}_7$, nitric acid, chromic acid, etc. However, different classes of alcohols differ from each other not only in their ease of oxidation but also on the nature of products formed.

(i) Primary alcohols. A primary alcohol is easily oxidised to form first an aldehyde and then a carboxylic acid. *Both the aldehyde and the acid formed contain the same number of carbon atoms as the starting alcohol.*

For example,



Strong oxidising agents such as acidified potassium dichromate convert alcohols directly to carboxylic acids. However, oxidation can be stopped at aldehyde stage by using Cr(VI) reagents in anhydrous medium (such as CH_2Cl_2) as the oxidising agent.



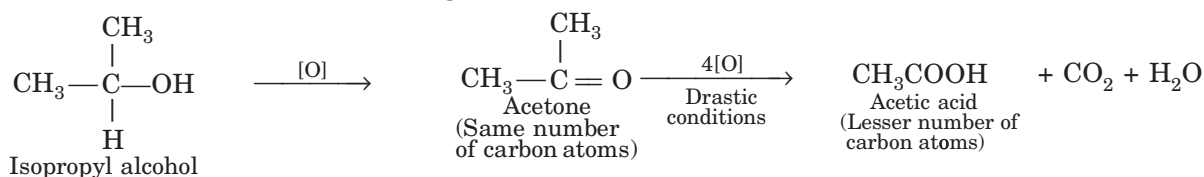
The common reagents used to stop oxidation of 1° alcohols to aldehyde stage are :

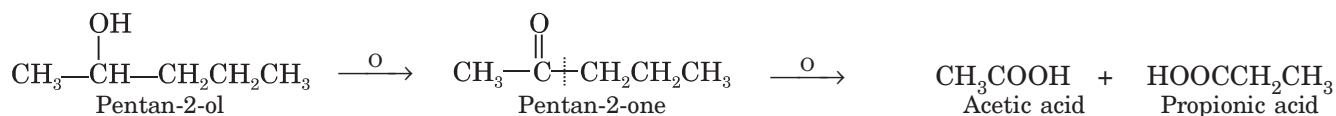
- Collins reagent : $\text{CrO}_3 \cdot 2\text{C}_5\text{H}_5\text{N}$, chromium trioxide pyridine complex
- PCC : $\text{CrO}_3 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$ or $(\text{C}_5\text{H}_5\text{NH})^+ \text{CrO}_3\text{Cl}^-$, pyridinium chlorochromate.
- PDC : $(\text{C}_5\text{H}_5\text{NH})_2^{2+} \text{Cr}_2\text{O}_7^{2-}$, pyridinium dichromate

It may be noted that these reagents are very selective because these are useful for oxidation of alcohols which contain C—C double or triple bonds, allylic or benzylic C—H bonds.

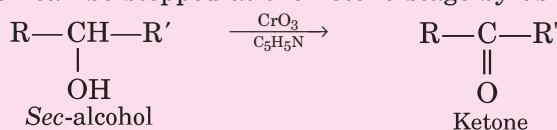


(ii) Secondary alcohols. A secondary alcohol is easily oxidised to form a ketone with chromic anhydride (CrO_3). The ketone may be further oxidised under strong conditions to form a mixture of acids. While the ketone contains the same number of carbon atoms as the starting alcohol, the acids formed contain lesser number of carbon atoms.

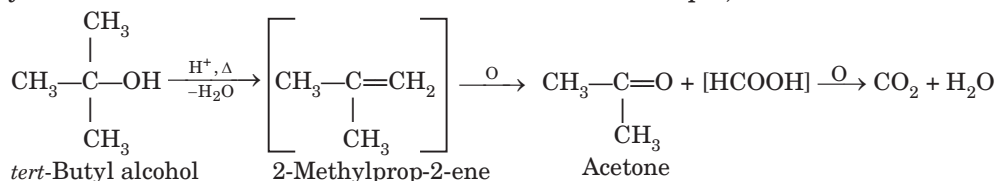




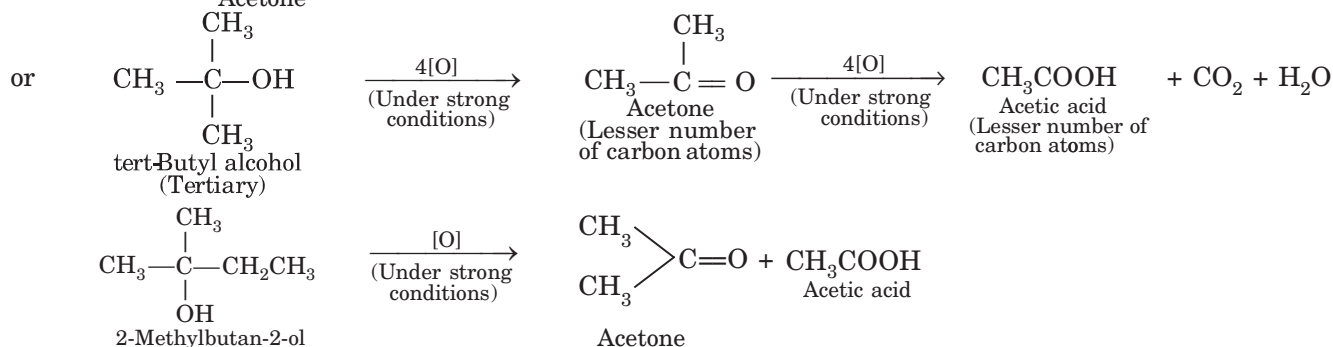
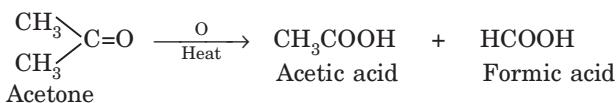
The oxidation can be stopped at the ketone stage by using chromic anhydride (CrO_3).



(iii) **Tertiary alcohols.** Tertiary alcohols are very difficult to be oxidised in neutral or alkaline KMnO_4 solution because they do not have hydrogen on carbon bearing $-\text{OH}$ group. However, when treated with acidic oxidising agents ($\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ or $\text{KMnO}_4/\text{H}_2\text{SO}_4$) under very strong conditions at elevated temperatures, cleavage of various $\text{C}-\text{C}$ bonds takes place. As a result, mixtures of ketones and carboxylic acids are formed. *Both the ketones and acids contain lesser number of carbon atoms than the starting alcohols.* The oxidation presumably occurs via alkene formation through dehydration of alcohols under acidic conditions. For example,



Acetone can further be oxidised to acetic acid and formic acid.

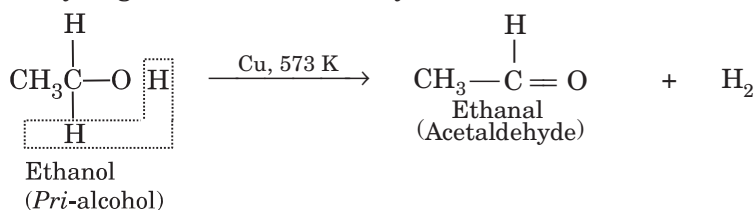


R U Curious ...

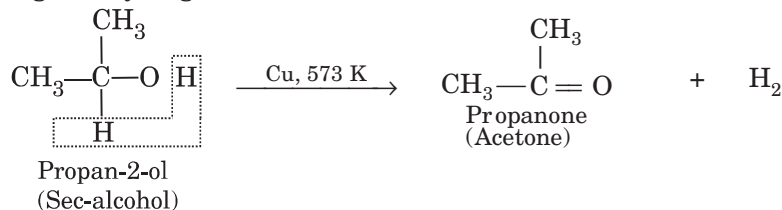
- ❑ Ethanol is generally used for drinking purposes. If a person consumes methanol by mistake, then how the person is treated for methanol poisoning!
- Biological oxidation of methanol and ethanol occurs in the body and produces the corresponding aldehyde and then the carboxylic acid. Methanol is oxidised first to methanal and then to methanoic acid while ethanol is oxidised first to ethanal and then to ethanoic acid. If an alcoholic person, by mistake, drinks denaturated alcohol (*i.e.*, ethanol mixed with methanol), the methanol is oxidised to methanoic acid, which may cause blindness and even death. A methanol poisoned patient is treated by giving intravenous infusions of diluted ethanol (about 10% solution). Ethanol gets preferentially oxidised and slows down the oxidation of methanol. The enzyme causing the oxidation of methanal (HCHO) to methanoic acid is swamped allowing time for kidneys to excrete methanol.

3. Dehydrogenation. The dehydrogenation (removal of hydrogen) of alcohols is achieved when the vapours of alcohol are passed over copper heated at 573 K. Whereas the primary and secondary alcohols get easily dehydrogenated to form aldehydes and ketones respectively, tertiary alcohols get dehydrated (loses water molecule) under the reaction conditions to alkenes.

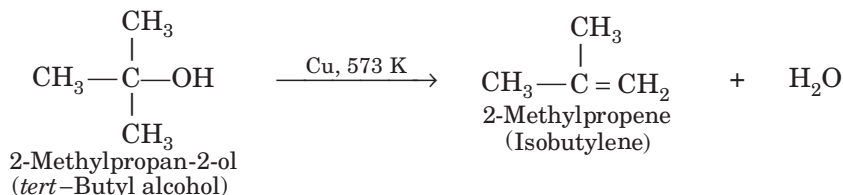
(i) *Primary alcohols* get dehydrogenated to form aldehydes.



(ii) Secondary alcohols get dehydrogenated to form ketones.



(iii) Tertiary alcohols get dehydrated on treatment with hot reduced copper to form alkenes.



CHEMICAL PROPERTIES OF PHENOLS

The phenols are reactive compounds. The chemical properties of phenols are of three types :

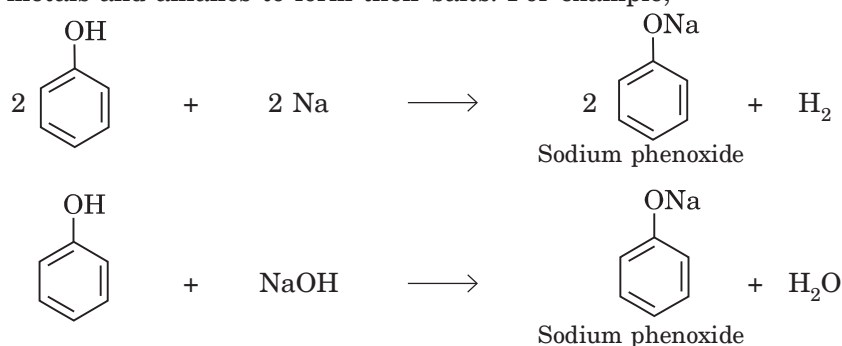
A. Reactions of phenolic group ($-\text{OH}$ group)

B. Reactions of benzene ring

C. Special reactions.

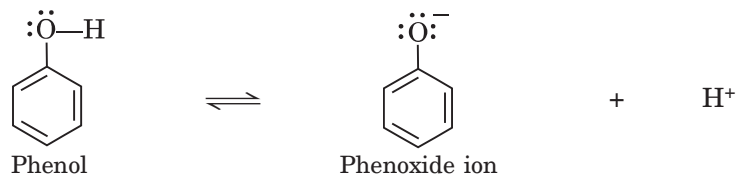
A. Reactions of Phenolic ($-\text{OH}$) Group

1. Acidic character. Phenols are weakly acidic in nature ($K_a = 10^{-8}$ to 10^{-10}). They turn blue litmus red and react with alkali metals and alkalies to form their salts. For example,

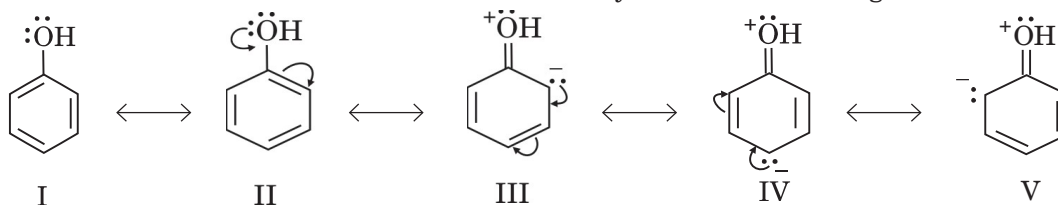


However, phenol is weaker acid than carboxylic acid. Therefore, like carboxylic acids, phenol does not react with sodium carbonate (Na_2CO_3) and sodium bicarbonate (NaHCO_3) evolving CO_2 .

The acidic character of phenol is because of the presence of polar $\text{O}-\text{H}$ group. The hydroxyl group in phenol is directly attached to the sp^2 hybridised carbon of benzene ring which acts as an electron withdrawing group. Due to the higher electronegativity of sp^2 hybridised carbon of phenol to which $-\text{OH}$ is attached, electron density on oxygen decreases. This increases the polarity of $\text{O}-\text{H}$ bond and results in an increase in ionisation of phenols. As a result H^+ ion can be easily released from aqueous solution as :

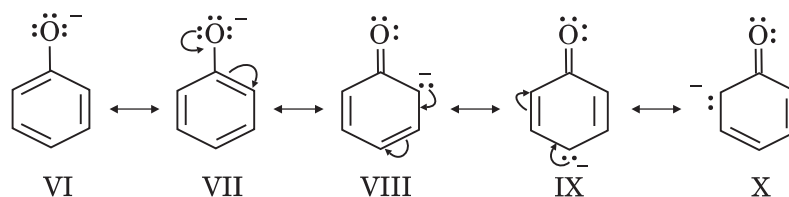


Phenols are more acidic than alcohols. The greater acidic character of phenols as compared to alcohols can be explained on the basis of resonance. Phenol is a resonance hybrid of the following structures :



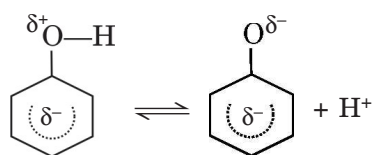
It is clear that three structures of phenol (III, IV and V) have +ve charge on oxygen of $-\text{OH}$ group. This oxygen

attracts the electron pair of O—H bond strongly towards itself, weakens the O—H bond and, therefore, facilitates the release of H^+ . Similarly, the phenoxide ion is resonance stabilized as follows :



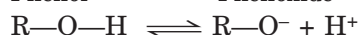
Thus, we observe that both phenol and phenoxide ion are stabilized by resonance. Now if we carefully observe the resonance structures, we observe that *phenoxide ion is more resonance stabilised than phenol*. In phenol three contributing structures (III, IV and V) have both positive and negative charges and therefore, these will be unstable. These structures will require energy to separate the charge and therefore, will be unstable. On the other hand, there is no structure in phenoxide ion which requires charge separation. Thus, the resonance hybrid of phenol is less stable than phenoxide ion and the reaction is very much in favour of the phenoxide ion. Therefore, the phenol is more acidic.

On the other hand, in case of alcohols, neither the alcohol nor the alkoxide ion is stabilized by resonance.



Phenol

Phenoxide



No resonance

Phenoxide ion is more resonance stabilized.

No resonance stabilization for alcohol or alkoxide ion.

Thus, phenols are more acidic than alcohols. However, phenols are less acidic than carboxylic acids which is supported by their dissociation constant (K_a) values.

HELP

The acidic character of an acid is expressed in terms of K_a (dissociation constant).

The stronger the acid, the larger will be its K_a value.

Alternately, K_a may also be expressed as pK_a , which is defined as : $pK_a = -\log K_a$.

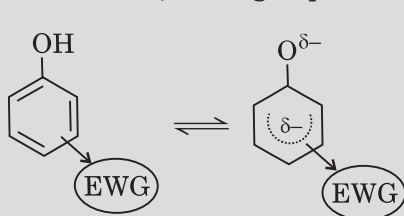
Smaller the pK_a value, stronger is the acid.

Compound	Ethanol	Phenol	Ethanoic acid
K_a	10^{-18}	10^{-10}	10^{-5}

Effect of Substituents on the Acidic Character of Phenols

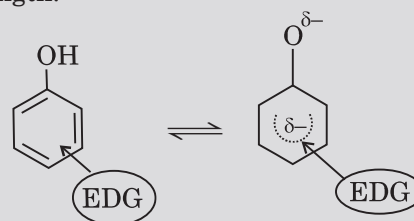
The effect of substituents on the acidic character of phenols can be easily understood in terms of stability of phenoxide ion relative to phenol. Any group that stabilizes the phenoxide ion more than the acid would make the reaction more towards forward direction and would increase the acidity. On the other hand, a group that makes the phenoxide ion less stable would decrease the acidity.

(a) **Electron withdrawing substituents (EWG)** like $-\text{NO}_2$, $-\text{CN}$, $-\text{X}$ (halogen), etc. withdraw electrons and disperse the negative charge on phenoxide ion. Therefore, these substituents stabilize the phenoxide ion relative to phenols. Thus, these groups will increase the acidic strength.



Electron withdrawing group withdraws electrons, disperses the negative charge and therefore stabilizes the phenoxide ion w.r.t. phenol.

Acidic strength increases.



Electron donating group donates electrons, intensifies the $-ve$ charge and therefore destabilizes the phenoxide ion w.r.t. phenol.

Acidic strength decreases

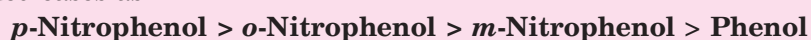
(b) **Electron donating groups (EDG)** like $-\text{R}$ (alkyl), $-\text{NH}_2$, $-\text{OR}$ (alkoxy), etc. give electrons and intensify the negative charge on phenoxide ion. Therefore, these substituents destabilize the phenoxide ion relative to phenol. Thus, these groups will decrease the acidic character.

The acidity constant (pK_a) of some phenols are given below :

Electron withdrawing groups		Electron releasing groups	
Phenol	pK_a	Phenol	pK_a
<i>p</i> -Chlorophenol	9.38	<i>p</i> -Aminophenol	10.46
<i>p</i> -Bromophenol	9.3	<i>p</i> -Methoxyphenol	10
<i>p</i> -Nitrophenol	7.15	<i>p</i> -Methyl phenol	10.
2, 4, 6-Trinitrophenol	0.6		
	Phenol	9.98	

(c) The particular effect is more significant when the substituent is present in *o*- or *p*-position than *m*-position to the —OH group. This means that *o*- and *p*-nitrophenols, will be more acidic than *m*-nitrophenol while *o*- and *p*-methylphenols (cresols) will be less acidic than *m*-cresol.

Thus, acidic strength decreases as



Similarly,



Alcohol	pK_a	Alcohol	pK_a
<i>o</i> -Nitrophenol	7.22	<i>o</i> -Cresol	10.28
<i>m</i> -Nitrophenol	8.30	<i>m</i> -Cresol	10.08
<i>p</i> -Nitrophenol	7.15	<i>p</i> -Cresol	10.14

Presence of more than one substituents also increases or decreases the acidic strength.

For example,

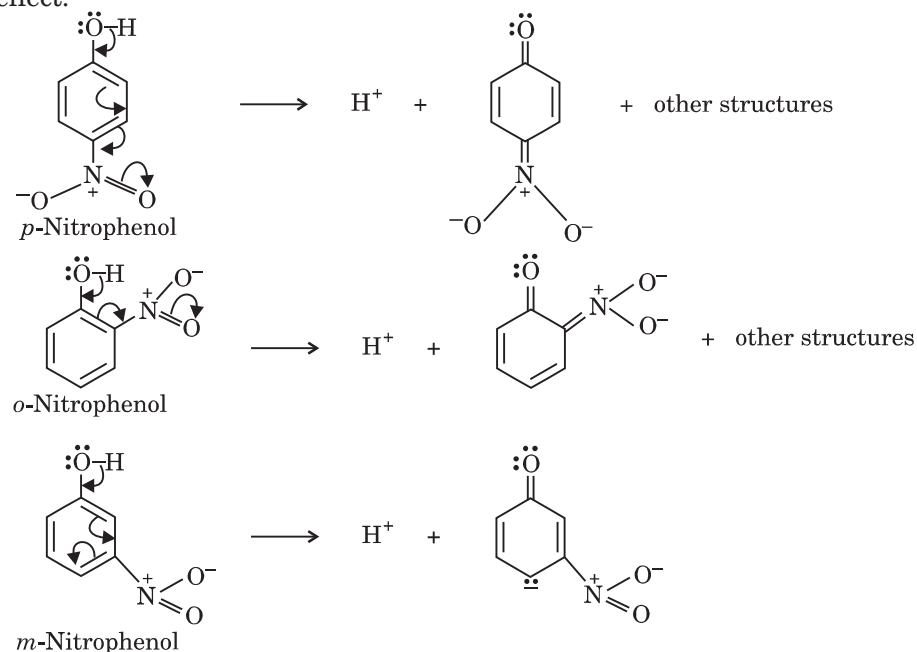


pK_a	0.71	4.0	7.15	9.98
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COMPARISON OF ACIDIC STRENGTH OF PHENOLS

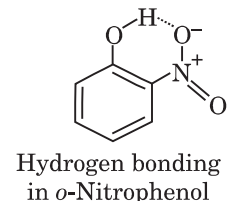
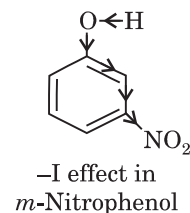
(a) Comparison of acidic strength of nitrophenols

The nitro group ($-\text{NO}_2$) has both $-\text{R}$ effect and $-\text{I}$ effect. But the $-\text{R}$ effect predominates over the $-\text{I}$ effect. Due to strong electron withdrawing nature of $-\text{NO}_2$ group, all the **nitrophenols are more acidic than phenol**. When $-\text{NO}_2$ group is present at *o*- and *p*-positions, it withdraws electrons of the O—H bond towards it by stronger $-\text{R}$ effect whereas when $-\text{NO}_2$ group is present at *m*-position, it withdraws electrons of O—H bond only by weaker $-\text{I}$ effect.



When $-\text{NO}_2$ is at *o*- and *p*-position the conjugation is extended up to oxygen atom of the nitro group and the anion is more stable than *m*-nitrophenoxide where no such conjugation is possible.

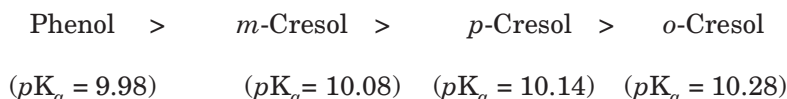
It is clear from the above structures that when $-\text{NO}_2$ group is at *o*- and *p*-positions, nitrophenoxide ion is more resonance stable because the conjugation is extended upto oxygen atom of the nitro group. But the *m*-nitrophenoxide ion is less stable because no such conjugation is possible in its structures. Thus, *o*- and *p*-nitrophenols are more acidic than *m*-nitrophenol. The larger acidic character of *m*-nitrophenol is only because of $-I$ effect as shown.



However, *o*-nitrophenol is slightly weaker acid than *p*-nitrophenol because of **intramolecular hydrogen bonding which makes loss of a proton little difficult**.

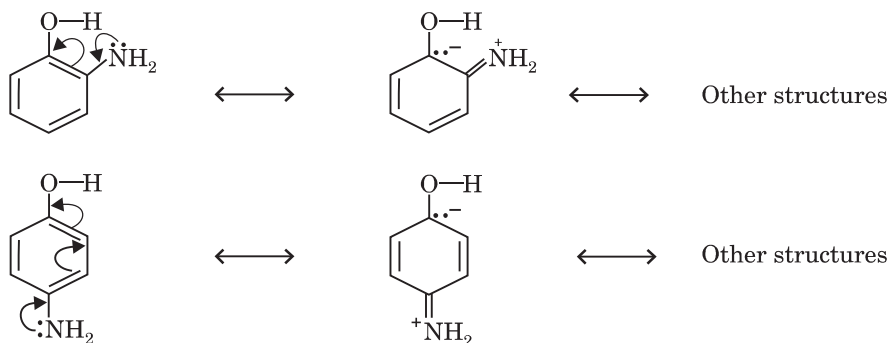
(b) Comparison of acidic strength of cresols (methylphenols)

Methyl group ($-\text{CH}_3$) has $+I$ effect and hyperconjugation effect. But the hyperconjugation effect predominates over $+I$ effect. Both these effects, increase the electron density in the $\text{O}-\text{H}$ bond so that the loss of proton becomes little difficult. Hence, **all the cresols are weaker acids than phenol**. Since hyperconjugation effect can operate only at *o*- and *p*-positions and not through *m*-position, therefore, *o*- and *p*-cresols are less acidic than *m*-cresol. However, as we know, that $+I$ effect of a substituent decreases with the increase in distance from the reaction centre, therefore, $+I$ effect will be more at *o*-position than at *p*-position. Due to stronger $+I$ effect at *o*-position than at *p*-position, *o*-cresol is a weaker acid than *p*-cresol. Thus, acidic strength decreases as:

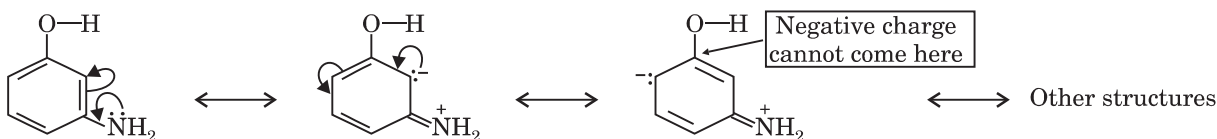


(c) Acidic strength of aminophenols and methoxyphenols

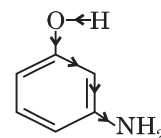
An amino group ($-\text{NH}_2$) and a methoxy group ($-\text{OCH}_3$) when attached to the benzene ring have $+R$ effect due to the presence of lone pair of electrons on N or O atom as well as $-I$ effect due to electron withdrawing nature of these groups (N and O are more electronegative than C). When $-\text{NH}_2$ group (or $-\text{OCH}_3$) group is present at *o*- or *p*-position w.r.t. OH group, it increases electron density in the $\text{O}-\text{H}$ bond by $+R$ effect of $-\text{NH}_2$ group (or $-\text{OCH}_3$) group.



However, when $-\text{NH}_2$ group (or $-\text{OCH}_3$) group is present at *m*-position, it cannot push electrons into the $\text{O}-\text{H}$ bond because negative charge cannot move to the carbon atom to which OH bond is attached.

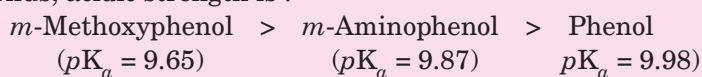


Since NH_2 group cannot exert $+R$ effect at *m*-position, therefore it exerts only $-I$ effect. Therefore, it withdraws electrons from all the nuclear positions of the benzene ring and hence withdraws electrons of $\text{O}-\text{H}$ bond. As a result, the electron density in $\text{O}-\text{H}$ bond decreases and hence *m*-aminophenol is more acidic than *o*- and *p*-aminophenols.



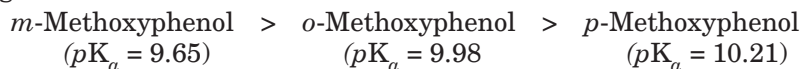
Similarly, *m*-methoxyphenol is more acidic than *o*- and *p*-methoxyphenols due to $-I$ effect of $-\text{OCH}_3$ group.

Now $-I$ effect of methoxy group ($-\text{OCH}_3$) is more than that of $-\text{NH}_2$ group, therefore, *m*-methoxyphenol is more acidic than *m*-amino phenol. Thus, acidic strength is :



On comparing *o*- and *p*-methoxyphenols, +R effect on *o*-position is less than at *p*-position because of steric hindrance. As a result, the increase in electron density in O—H bond is less in case of *o*-methoxyphenol than *p*-methoxyphenol. Consequently, *o*-methoxyphenol is slightly more acidic than corresponding *p*-isomer.

Thus, the acidic strength is

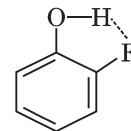
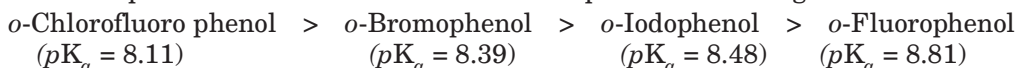


(d) Comparison of acidic strength of halophenols

Halogens have both +R effect and –I effect but –I effect predominates over the +R effect. Therefore, all **halophenols (except *p*-fluorophenol) are more acidic than phenol**. As we know, –I effect decreases with distance, therefore, acidic strength of halophenols is

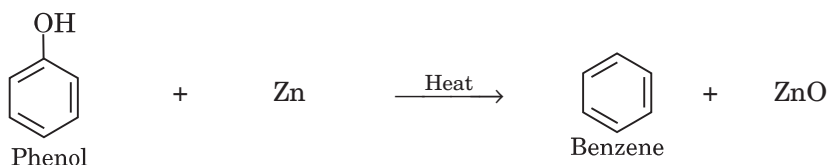


Amongst *o*-halophenols, the acidic strength of halophenols decreases as –I effect of the halogen decreases except for *o*-fluorophenol. *o*-Fluorophenol is the weakest acid due to the presence of strong intramolecular hydrogen bonding.



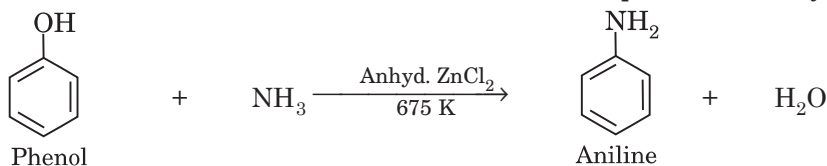
2. Action with zinc dust.

When heated with zinc dust, phenol is reduced to benzene.

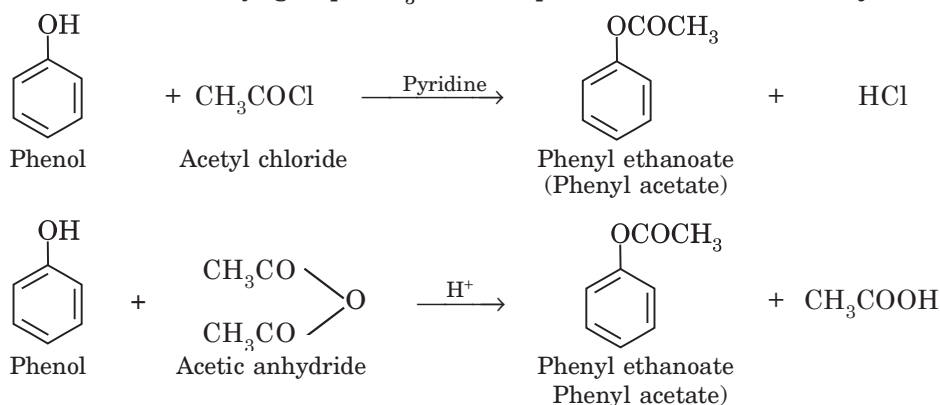


3. Action with ammonia.

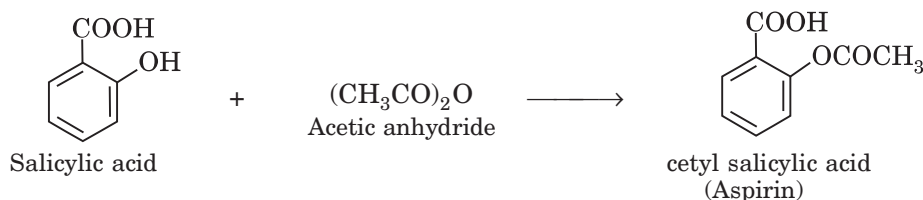
Phenol reacts with ammonia in the presence of anhydrous zinc chloride to give aniline.



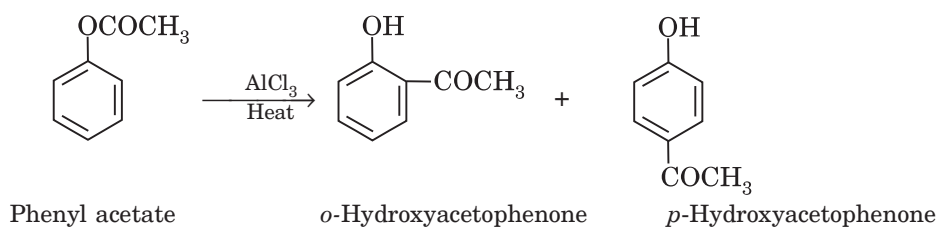
4. Action with acid chlorides and acid anhydrides (acylation). When treated with acetyl chloride (in the presence of pyridine) or acetic anhydride (in the presence of small amount of conc. H_2SO_4) esters are formed. This reaction is reversible in nature. The pyridine (base) removes HCl formed. It also shifts the equilibrium to the right hand side. The introduction of acetyl group (CH_3CO —) in phenols is known as **acetylation reaction**.



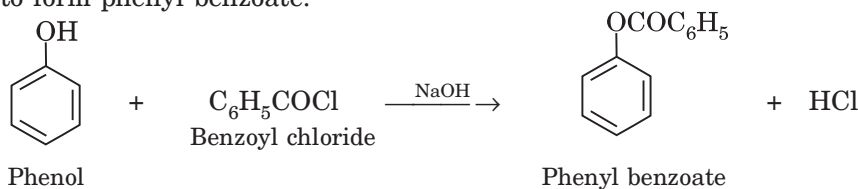
Acetylation of salicylic acid produces **aspirin** (acetyl salicylic acid), which has analgesic, anti-inflammatory and anti-pyretic properties.



When phenyl acetate is heated with anhydrous AlCl_3 , it undergoes rearrangement in which acyl group migrates from the phenolic oxygen to an ortho and para positions forming ortho and para hydroxy ketones. This reaction is called **Fries rearrangement**.

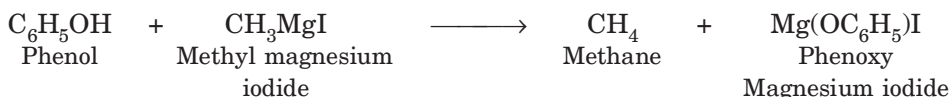


5. Action with benzoyl chloride (benzoylation). Phenols react with benzoyl chloride in the presence of aqueous NaOH to form phenyl benzoate.



This reaction is called **Schotten Baumann reaction**.

6. Reaction with Grignard reagent. Like alcohols, phenols also react with Grignard reagent to form alkanes.

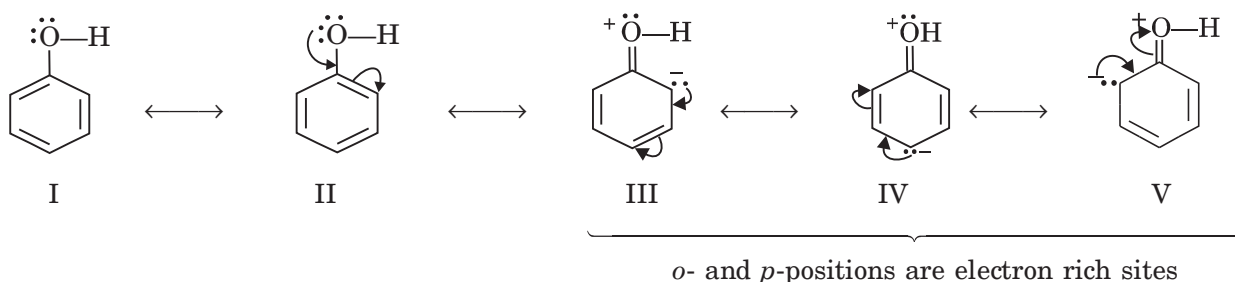


NOTE

As in case of alcohols, the alkane formed corresponds to the alkyl group of the Grignard reagent.

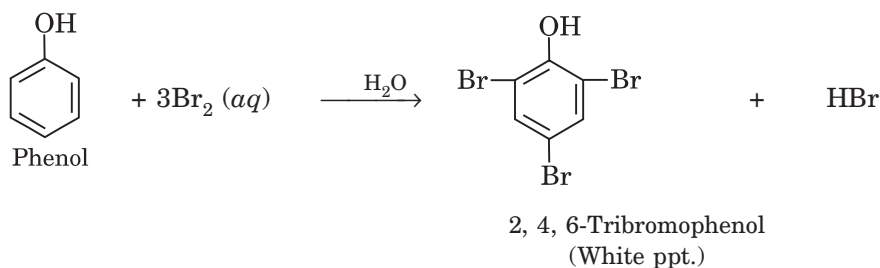
B. Reactions of Benzene Ring : Electrophilic Substitution Reactions

Apart from reactions that directly affect the —OH group, phenols undergo *electrophilic aromatic substitution reactions*. As the —OH group is an activating group, these reactions occur at a faster rate than reactions of benzene itself. The —OH group is **ortho-para directing** and therefore, incoming group comes at ortho or para position. This is due to the reason that because of electronic effects caused by —OH group, the ortho and para positions become electron rich as shown below :

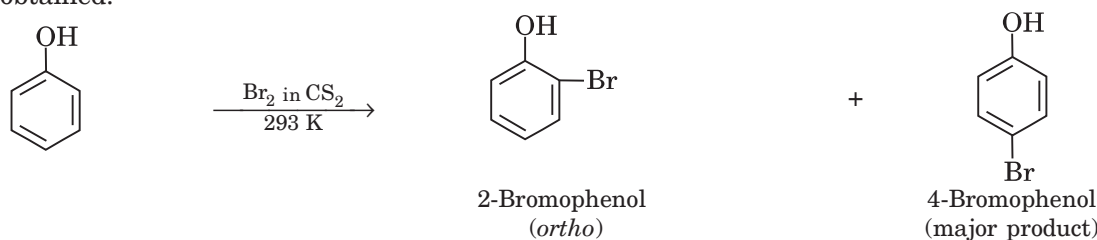


Some common examples are :

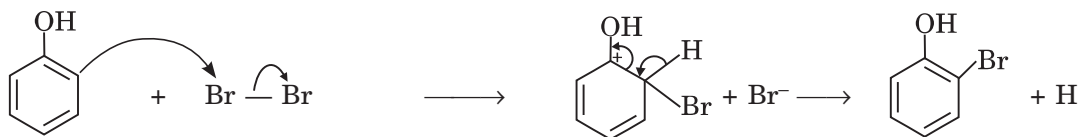
1. Bromination. Phenol reacts with bromine water (aqueous solution) to give a precipitate of 2, 4, 6-tribromophenol.



However, if the reaction is carried out in CS₂ or CCl₄, at a low temperature, a mixture of *ortho* and *para* bromophenol is obtained.

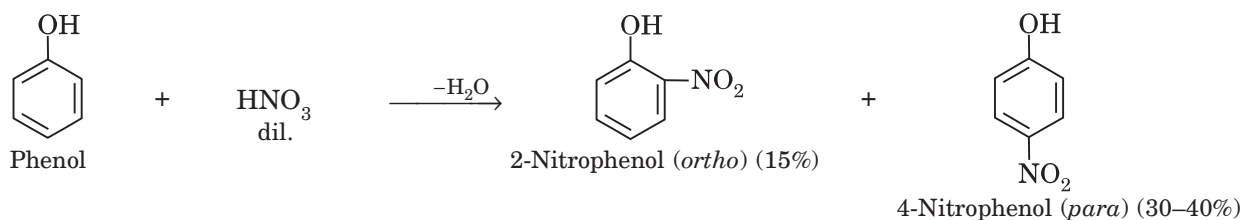


It may be noted that the usual halogenation is carried out in the presence of Lewis acid, FeBr_3 which polarises the halogen molecule. In case of phenol, the polarisation of bromine occurs even in the absence of Lewis acid. This is because of highly activating effect of $-\text{OH}$ group on the benzene ring. The reaction is believed to occur as :

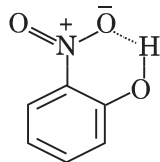


Explanation. In aqueous solution, phenol ionizes to give phenoxide ion. Due to the presence of the negative charge, the oxygen atom of the phenoxide ion donates electrons to the benzene ring to a large extent. As a result, the ring gets highly activated leading to the formation of trisubstituted product. On the other hand, in the non-polar solvents, the ionization of phenol does not occur to a large extent. As a result, the $-\text{OH}$ group donates electrons to the benzene ring only to a small extent. Consequently, the ring is activated slightly and, therefore, only monosubstitution occurs.

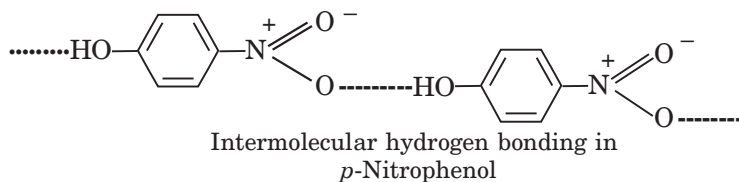
2. Nitration. Phenol reacts with dilute nitric acid at low temperature (298 K) to give a mixture of ortho and para nitrophenol.



The ortho and para isomers can be separated by steam distillation. *o*-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile because of intermolecular hydrogen bonding which causes the association of molecules.

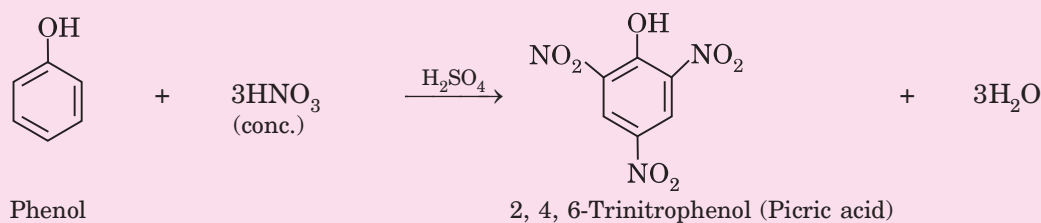


Intramolecular hydrogen bonding in *o*-Nitrophenol

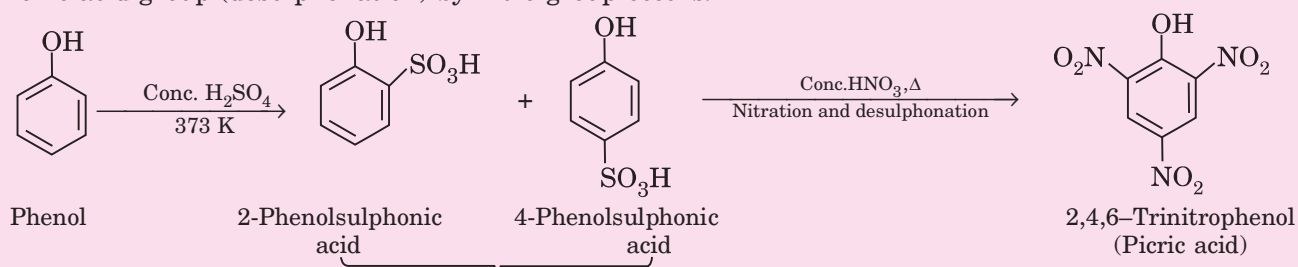


Intermolecular hydrogen bonding in *p*-Nitrophenol

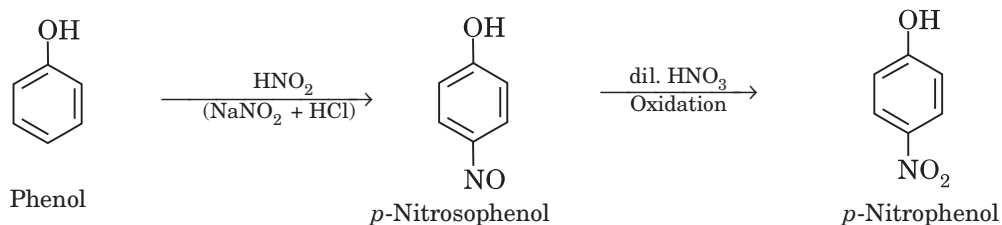
With conc. nitric acid, in the presence of sulphuric acid, phenol gives 2, 4, 6-trinitrophenol (picric acid). The yield of nitro product is low because of the oxidation of ring by conc. HNO_3 .



Now a days picric acid is prepared by treating phenols first with conc. H_2SO_4 at 373 K when a mixture of 2-phenol sulphonic acid and 4-phenolsulphonic acid is formed. This mixture is then heated with conc. HNO_3 to form 2,4,6-trinitrophenol (picric acid) in about 90% yield. During this reaction, nitration with simultaneous replacement of the sulphonic acid group (desulphonation) by nitro group occurs.

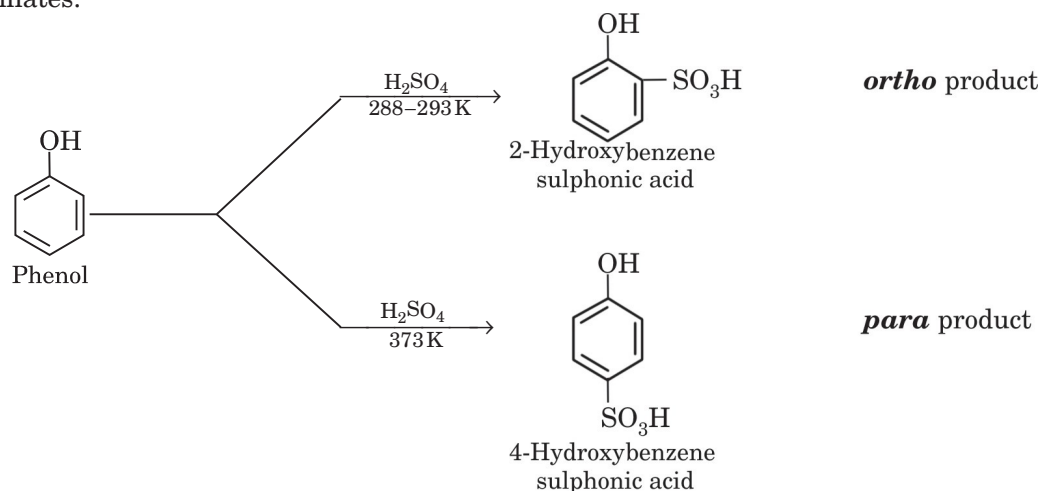


3. Nitrosation. Phenol reacts with nitrous acid ($\text{NaNO}_2 + \text{HCl}$) at low temperature (280 K) to form *p*-nitrosophenol. The reaction which involves the substitution by nitroso group ($-\text{NO}$) is called **nitrosation**. The *p*-nitrosophenol can be further oxidised with dil. HNO_3 to give *p*-nitrophenol.



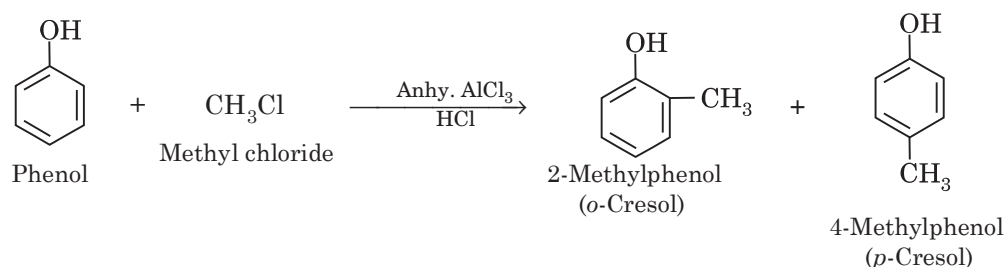
Therefore, the above method is used to get better yield of nitrophenols.

4. Sulphonation. Phenol reacts with conc. sulphuric acid to form a mixture of *o*- and *p*-phenol sulphonic acid. At low temperature (288 K), *ortho* isomer is the main product while at higher temperature (373 K), the *para* isomer predominates.



When 2-hydroxybenzene sulphonic acid is heated to 373 K, it gives thermodynamically controlled 4-hydroxybenzene sulphonic acid.

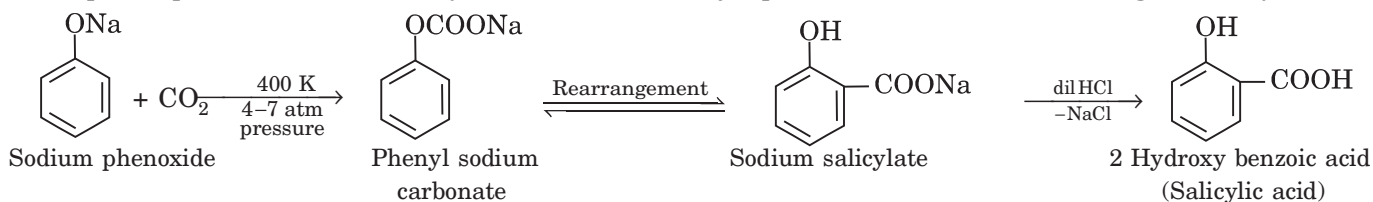
5. Friedel Crafts Alkylation. When phenol is heated with alkyl halides in the presence of anhydrous aluminium chloride, it forms cresols. The reaction is called **Friedel Crafts alkylation reaction**.



The yield of alkyl phenols is generally low because AlCl_3 coordinates with the oxygen atom.

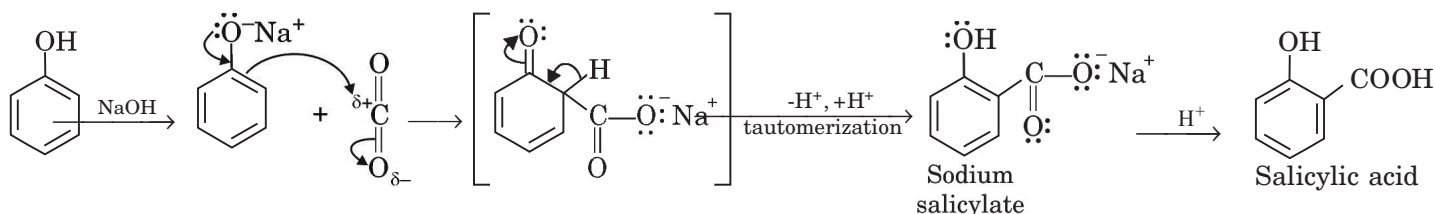
C. Special Reactions of Phenol

1. Kolbe's reaction. When sodium phenoxide is heated with carbon dioxide at about 400 K and under 4 to 7 atmospheric pressure, sodium salicylate is formed as major product. This on acidification gives salicylic acid.



A small amount of *para* isomer is also obtained and if the temperature be allowed to rise above 410 K, the *para* isomer dominates. The reaction is called **Kolbe's reaction**. In the Kolbe's reaction, carbon dioxide acts as the

electrophile. The mechanism involves the attack of CO_2 on highly activated phenoxide ion.

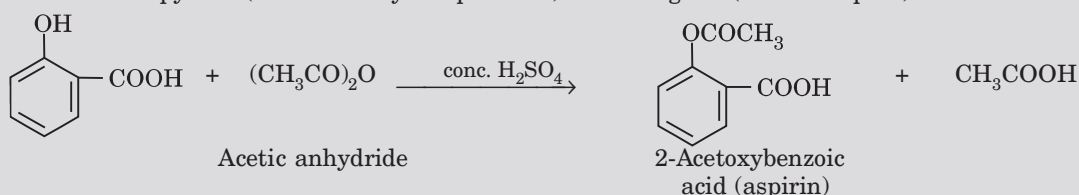


The reaction is usually carried out by allowing sodium phenoxide to absorb carbon dioxide and then heating the product to 400 K and 4–7 atm pressure. First unstable intermediate is formed which undergoes a proton shift to form sodium salicylate. The subsequent acidification of sodium salicylate gives salicylic acid.

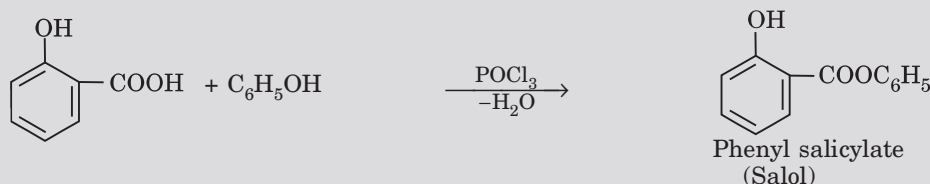
Salicylic acid is the starting material for the manufacture of a number of **important compounds**.

For example :

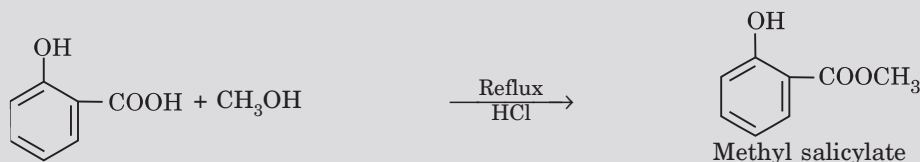
(i) **Aspirin (2-acetoxy benzoic acid)**—It is obtained by acetylating salicylic acid with acetic anhydride and conc. H_2SO_4 . Aspirin is used as antipyretic (to lower body temperature) and analgesic (to relieve pain).



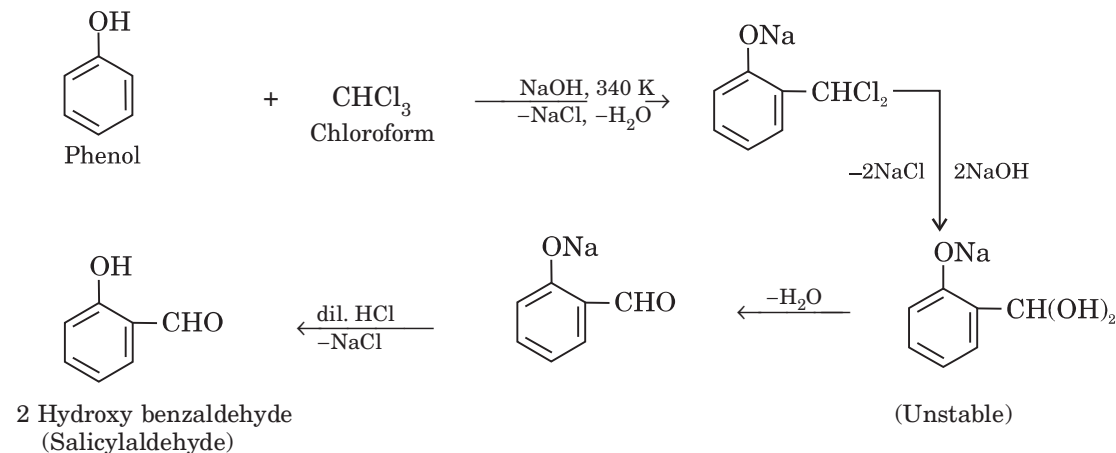
(ii) **Salol (phenyl salicylate)**. It may be prepared by heating salicylic acid with phenol in the presence of phosphoryl chloride. Salol is used as an intestinal antiseptic.



(iii) **Methyl salicylate (constituent of oil of winter green)**. It is prepared by refluxing salicylic acid with methyl alcohol. It is used in perfumery as a flavouring agent.



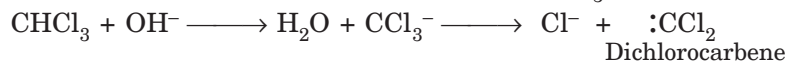
2. Reimer-Tiemann reaction. When phenol is refluxed with chloroform in the presence of aqueous sodium hydroxide at 340 K followed by hydrolysis, an aldehydic group ($-\text{CHO}$) gets introduced in the ring at a position ortho to the phenolic group. Ortho hydroxy benzaldehyde or salicylaldehyde is formed as the product of the reaction.



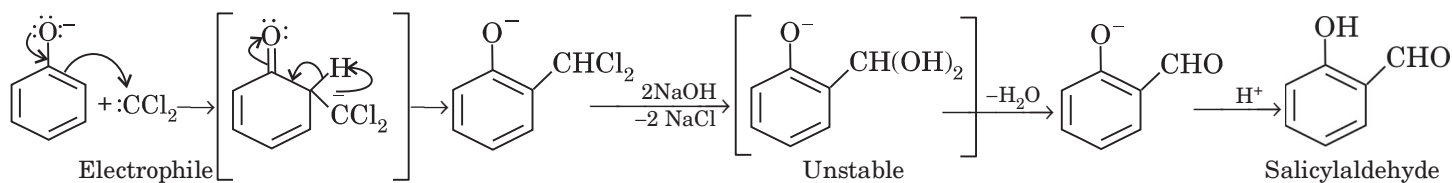
This reaction is called **Reimer-Tiemann reaction**. In addition to *o*-salicylaldehyde, small amount of *p*-salicylaldehyde is also formed but the major product is *ortho*.

Mechanism :

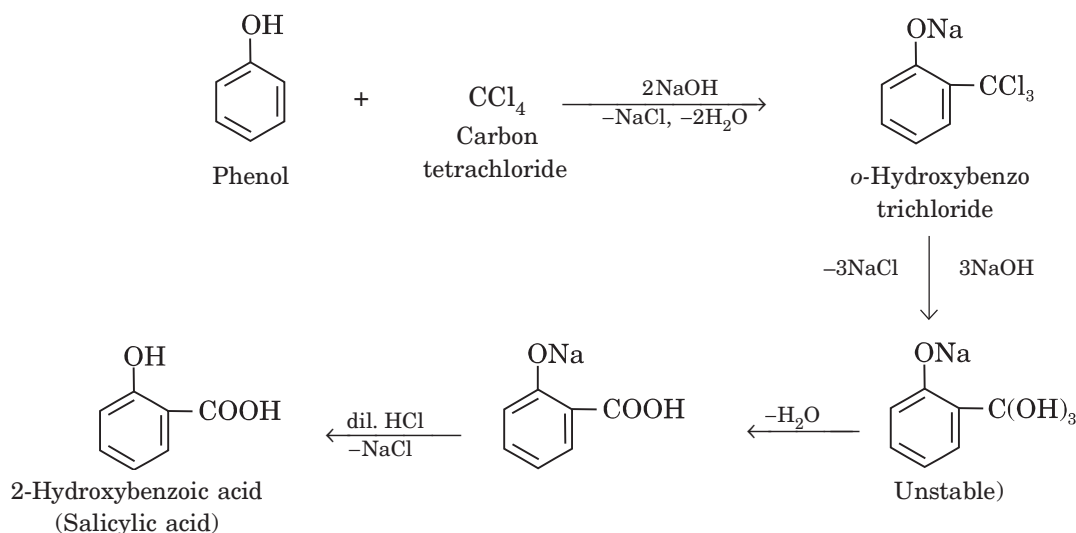
The Reimer-Tiemann reaction involves electrophilic substitution reaction. In this case, the electrophile is dichlorocarbene : CCl_2 . This is generated by the reaction of chloroform (CHCl_3) and NaOH as :



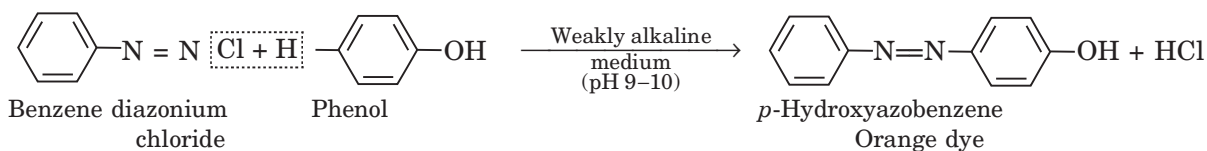
Dichlorocarbene contains carbon atom with sextet of electrons and hence is a strong electrophile. The electrophilic substitution reaction occurs as :



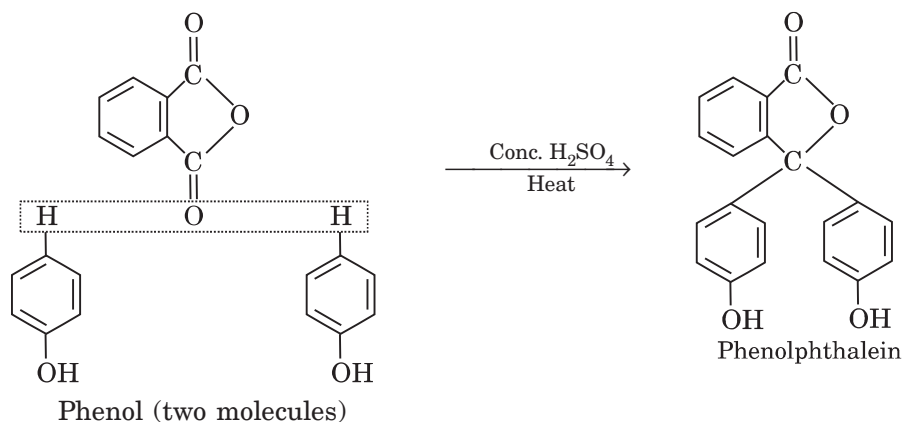
In **Reimer-Tiemann reaction**, carbon tetrachloride may also be used in place of chloroform. In this case *o*-salicylic acid is formed as the major product.



3. Coupling reaction. In the alkaline medium, an ice-cold solution of phenol combines with an ice-cold solution of benzene diazonium chloride to form coloured substances called **azo dyes**. This reaction is called **coupling reaction**.

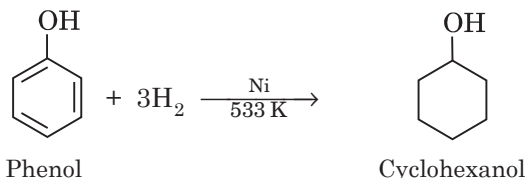


4. Reaction with phthalic anhydride. Phenol reacts with phthalic anhydride in the presence of conc. H_2SO_4 to give phenolphthalein.

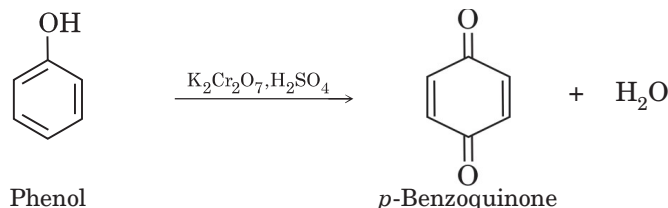


5. Condensation with formaldehyde. Phenol condenses with formaldehyde in the presence of dil. acid or alkali (as catalyst) to give a cross-linked polymer called bakelite. This reaction has been discussed in detail in Unit 15.

6. Hydrogenation or reduction. Phenol can be hydrogenated in the presence of finely divided nickel catalyst at 533 K to give cyclohexanol.

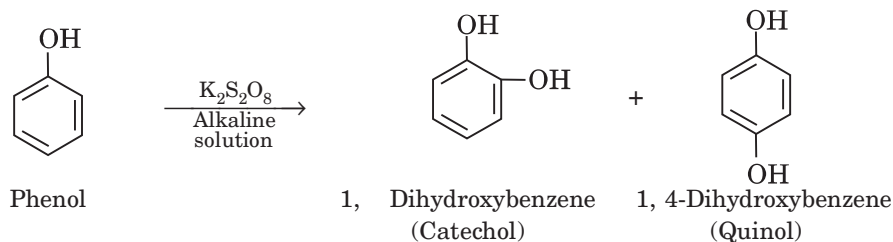


7. Oxidation. Phenol undergoes oxidation with chromic acid and produces a conjugated diketone known as *p*-benzoquinone.



When exposed to air, phenols are slowly oxidised to dark coloured mixtures containing quinones.

Phenol can also be oxidised by potassium per sulphate ($\text{K}_2\text{S}_2\text{O}_8$) in alkaline solution and gives a mixture of catechol and quinol.



This reaction is called **Elbs persulphate oxidation**.

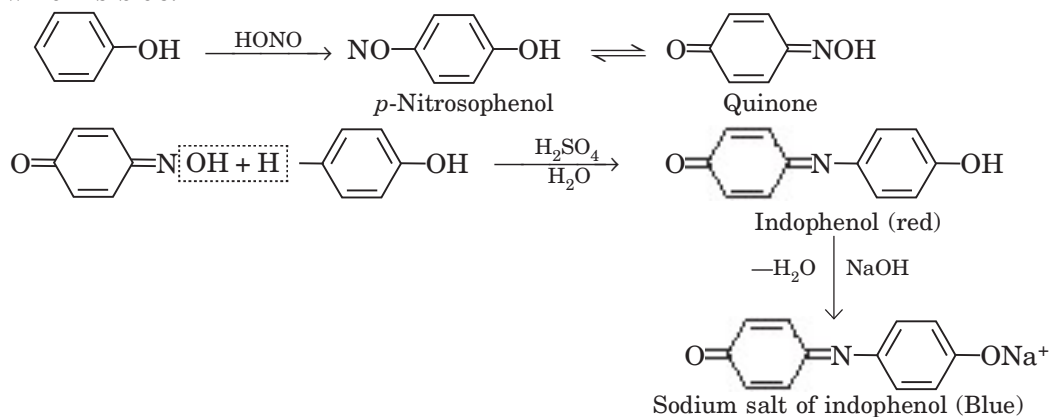
8. Reaction with ferric chloride. Phenols react with neutral ferric chloride to form coloured water soluble complex compounds. Different phenols give different colours (violet, red, green, blue, etc.) and therefore, **this reaction serves as a test for phenols**.



In fact, all compounds containing *enolic* group ($=\text{C}-\text{OH}$) give this test.

9. Libermann's test. Most of the phenols give this test. On warming with conc. H_2SO_4 and sodium nitrite, phenols give red or brown colouration. The colour changes to blue or green by the addition of aqueous NaOH.

Phenols react with nitrous acid to give *p*-nitrosophenol which rearranges to quinone. In the presence of conc. H_2SO_4 , quinone condenses with phenol to give indophenol which is red. With excess of NaOH, sodium salt of indophenol is obtained which is blue.

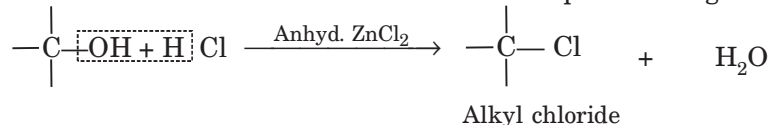


This test can be used to distinguish phenols from alcohols.

DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY ALCOHOLS

Primary, secondary and tertiary alcohols can be distinguished by the following tests/reactions.

1. Lucas test. In this test, an alcohol is treated with an equimolar mixture of concentrated hydrochloric acid and anhydrous ZnCl_2 (called *Lucas reagent*). The alcohols get converted into alkyl halides. Since the alkyl halides are insoluble in water, their formation is indicated by the *appearance of turbidity* in the reaction mixture. Since the order of reactivity of alcohols with halogen acids is *tertiary > secondary > primary*, the time required for the appearance of cloudiness will be different in different alcohols and this test helps to distinguish them from one another.



- (i) If turbidity appears **immediately**, the alcohol is **tertiary**.
 (ii) If turbidity appears **within five minutes**, the alcohol is **secondary**.
 (iii) If turbidity appears **only upon heating**, the alcohol may be **primary**.

2. Victor Meyer's test. This test involves the following steps :

- (i) The given alcohol is treated with red phosphorus and iodine resulting in the formation of corresponding alkyl iodide.
- (ii) The alkyl iodide is treated with silver nitrite to form corresponding nitroalkane.
- (iii) The nitroalkane is finally reacted with nitrous acid (*i.e.*, $\text{NaNO}_2 + \text{dil. H}_2\text{SO}_4$) and the resulting solution is made alkaline.

- Formation of a **blood red colour** indicates the primary alcohol.
- Formation of a **blue colour** shows the original alcohol to be secondary while.
- A **colourless solution** means that the alcohol is a tertiary alcohol.

The different reactions taking place are shown below :

Primary alcohol	Secondary alcohol	Tertiary alcohol
RCH_2OH $\downarrow \text{P} + \text{I}_2$ RCH_2I $\downarrow \text{AgNO}_2$ RCH_2NO_2 $\downarrow \text{HNO}_2$ $\text{R}-\text{C}-\text{NO}_2$ $\parallel$ NOH (Nitrolic acid) blood red colour when made alkaline	R_2CHOH $\downarrow \text{P} + \text{I}_2$ R_2CHI $\downarrow \text{AgNO}_2$ R_2CHNO_2 $\downarrow \text{HNO}_2$ $\text{R}_2\text{C}-\text{NO}_2$ $ $ NO Pseudo nitrol blue colour with alkali	$\text{R}_3\text{C}-\text{OH}$ $\downarrow \text{P} + \text{I}_2$ R_3CI $\downarrow \text{AgNO}_2$ R_3CNO_2 $\downarrow \text{HNO}_2$ No action Colourless solution

The primary, secondary and tertiary alcohols can also be distinguished by the following tests, which have already been discussed :

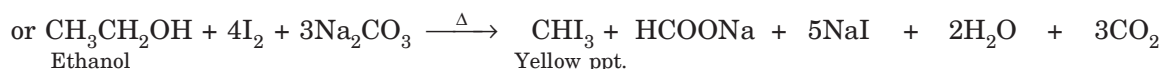
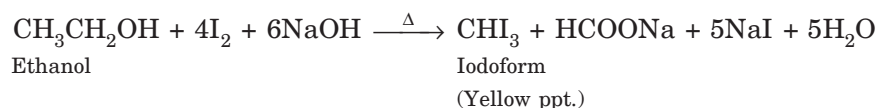
3. Oxidation reaction (Property C. 2)
4. Reduction with copper metal at 573 K (Property C. 3).

5. Iodoform Test

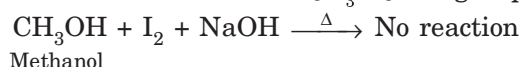
$\begin{array}{c} \text{OH} \\ | \\ \text{CH}_3\text{CH}- \end{array}$

All alcohols containing $\text{CH}_3\text{CH}-$ group linked to carbon or hydrogen atom (*i.e.*, methyl carbinols) can be distinguished from other alcohols by iodoform test. This test is performed by heating the alcohol with aqueous NaOH

or Na_2CO_3 and iodine solution. On warming the reaction mixture, yellow precipitate of iodoform indicates positive iodoform test. For example, ethanol gives iodoform test as :



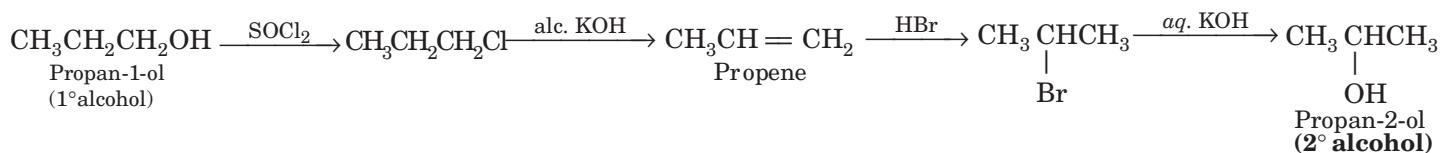
However, methanol does not have $\text{CH}_3\text{—}\overset{\text{OH}}{\underset{|}{\text{CH}}}\text{—}$ group and therefore, does not give iodoform test.



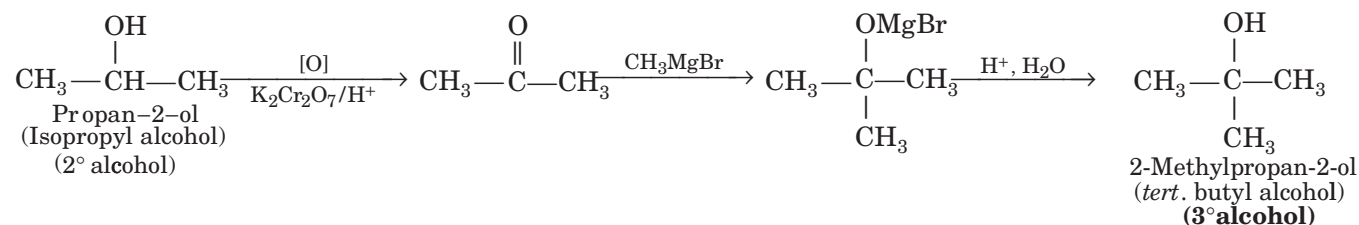
I O D O F O R M T E S T	
	Thus, the alcohols containing $\text{CH}_3\text{—}\overset{\text{OH}}{\underset{ }{\text{CH}}}\text{—}$ group give positive iodoform test. Therefore, iodoform test can be used to distinguish between :
	(i) Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and methanol (CH_3OH) Ethanol gives this test.
	(ii) Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) and propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) Ethanol gives this test.
	(iii) Propan-2-ol($\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$) and propan-1-ol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) Propan-2-ol gives this test.
	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + 4\text{I}_2 + 6\text{NaOH} \xrightarrow{\Delta} \underset{\text{Yellow ppt.}}{\text{CHI}_3} + \text{CH}_3\text{COONa} + 5\text{NaI} + 5\text{H}_2\text{O}$ Propan-2-ol
	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{I}_2 + \text{NaOH} \xrightarrow{\Delta} \text{No reaction.}$ Propan-1-ol
	(iv) Butan-2-ol($\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$) and butan-1-ol($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$) Butan-2-ol gives this test.
	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3 + 4\text{I}_2 + 6\text{NaOH} \xrightarrow{\Delta} \underset{\text{Yellow ppt.}}{\text{CHI}_3} + \text{CH}_3\text{CH}_2\text{COONa} + 5\text{NaI} + 5\text{H}_2\text{O}$ Butan-2-ol
	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{I}_2 + \text{NaOH} \longrightarrow \text{No reaction}$ Butan-1-ol

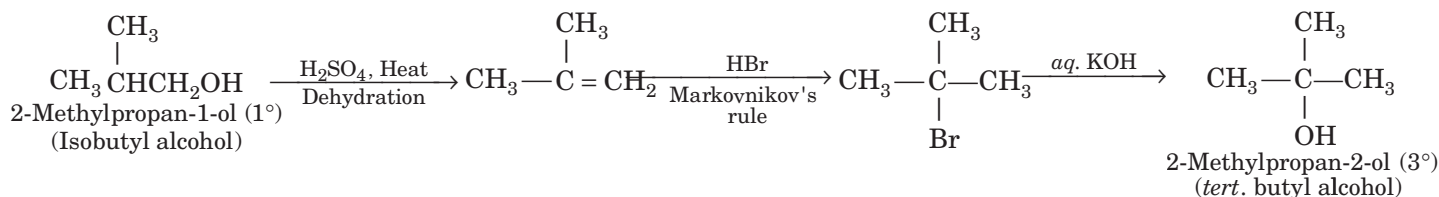
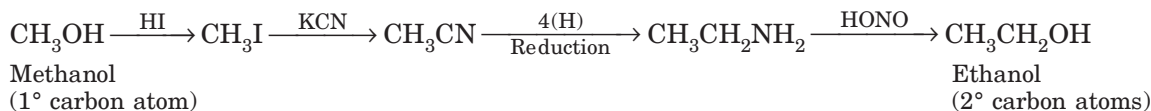
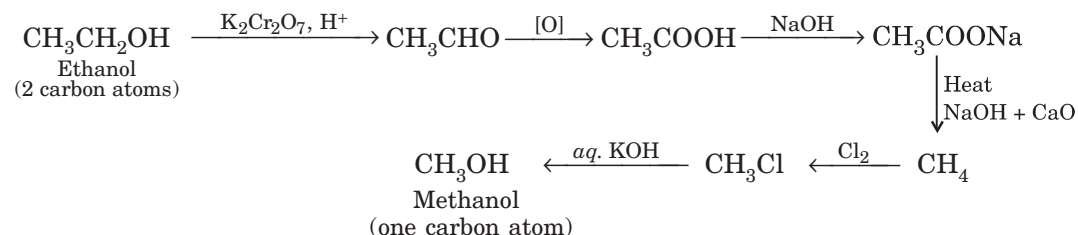
INTERCONVERSIONS OF ALCOHOLS

(a) **Primary alcohol into secondary alcohol.** For example,

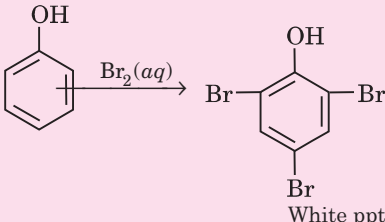
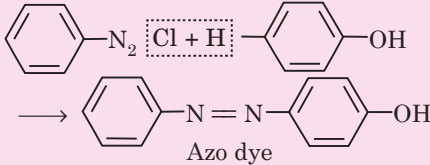


(b) **Secondary alcohol into tertiary alcohol.**



(c) Primary alcohol into tertiary alcohol.**(d) Lower alcohol into higher alcohol (ascent of series).****(e) Higher alcohol into lower alcohol (descent of series).****DISTINCTION BETWEEN ALCOHOLS AND PHENOLS**

Alcohols and phenols can be distinguished by the following tests :

Test	Phenol	Alcohol
1. litmus test	Phenols turn blue litmus red.	Alcohols do not have any effect on litmus solution.
2. With ferric chloride solution	Phenols react with neutral FeCl_3 solution to give characteristic colours (blue, green, violet).	Alcohols do not give any colour with neutral FeCl_3 solution.
3. Bromine water test	Phenols give white ppt. with bromine water due to the formation of 2, 4, 6-tribromophenol. 	Alcohols do not give white ppt. with Br_2 water.
4. Coupling reaction	Phenols give coloured dye (yellow, orange or red) with ice cold solution of benzene diazonium chloride 	Alcohols do not form any dye with benzene diazonium chloride.
5. Sodium hydroxide solution	Phenols react with sodium hydroxide solution and form sodium salt.	Alcohols do not react with sodium hydroxide solution.
6. Libermann's test	Phenols give red colouration on warming with sodium nitrite dissolved in conc. H_2SO_4 . The colour changes to blue on the addition of NaOH .	No colour is produced.

SOLVED EXAMPLES

□ Example 5.

Arrange the following sets of compounds in order of their increasing boiling points :

(a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.

(b) Pentan-1-ol, n-butane, pentanal, ethoxy ethane.

N.C.E.R.T.

Solution : Increasing order of boiling points :

(a) Methanol < ethanol < propan-1-ol < butan-2-ol < butan-1-ol < pentan-1-ol

(b) n-Butane < ethoxy ethane < pentanal < pentan-1-ol

□ Example 6.

Name the reagents used in the following reactions :

(a) dehydration of propan-2-ol to propene

(b) oxidation of primary alcohol to carboxylic acid

(c) oxidation of primary alcohol to an aldehyde

(d) butan-2-one to butan-2-ol

(e) cyclohexanone to 1-ethylcyclohexanol

Solution : (a) 85% H_2SO_4 , 443 K (b) alkaline KMnO_4 (c) PCC (d) NaBH_4 , H_2 (e) $\text{CH}_3\text{CH}_2\text{MgBr}$ (ether), H_3O^+

□ Example 7.

Convert phenol into

(i) Salicylaldehyde

(Hr. S.B. 2012)

(ii) Benzene

(Hr. S.B. 2012)

(iii) Picric acid

(Hr. S.B. 2012)

iv) Benzoic acid

(Hr. S.B. 2005)

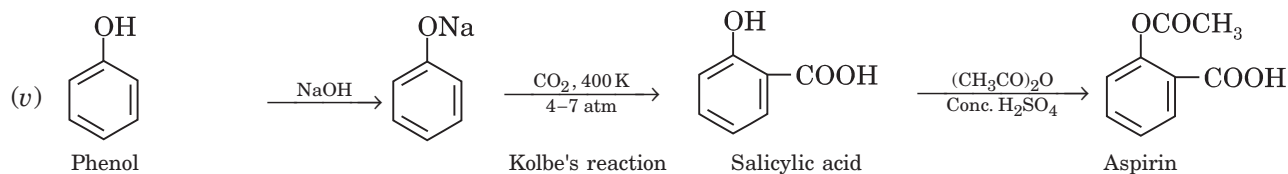
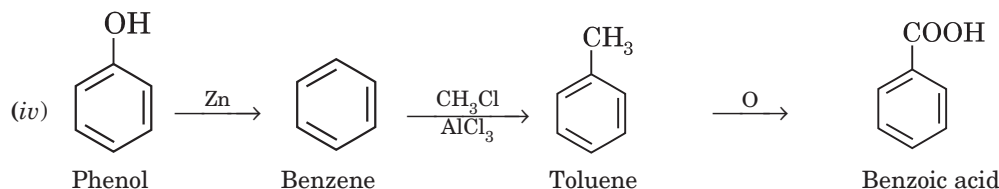
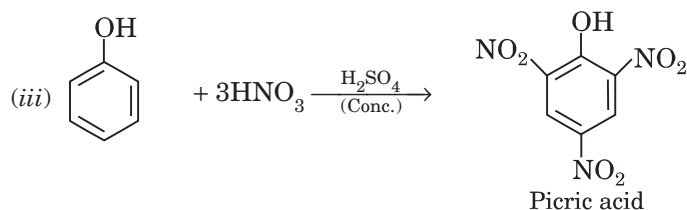
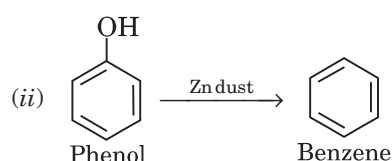
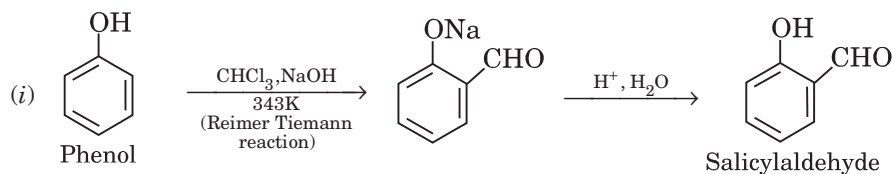
(v) Aspirin

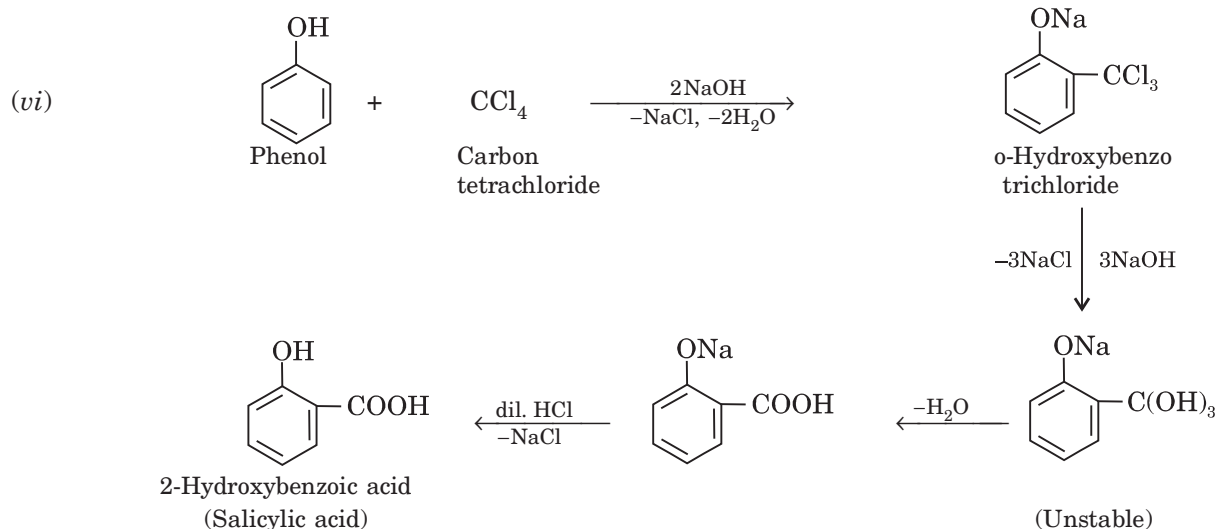
(H.P. S.B. 2010S)

(vi) Salicylic acid

(Hr. S.B. 2012, Meghalaya S.B. 2018)

Solution :





Example 8.

Write the structures of the major products expected from the following reactions :

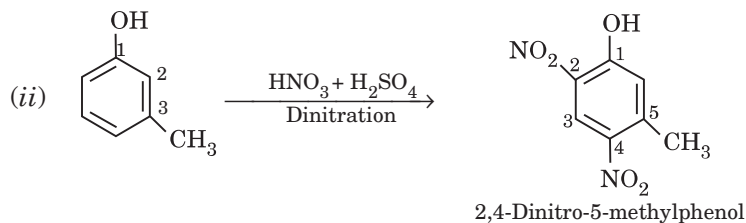
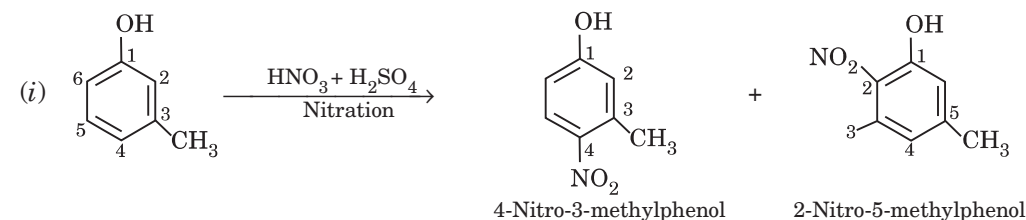
(i) Mononitration of 3-methyl phenol

(ii) Dinitration of 3-methyl phenol

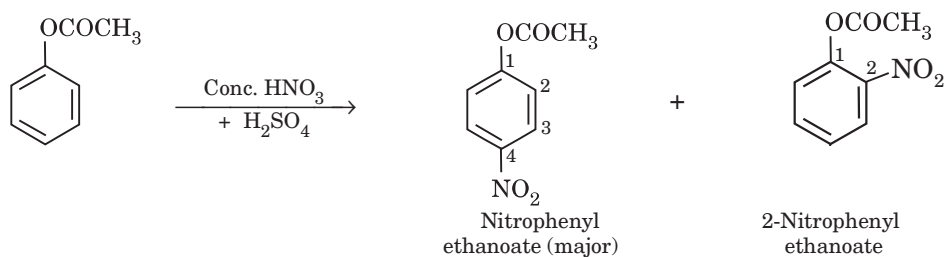
(iii) Mononitration of phenylethanoate

N.C.E.R.T.

Solution : Both OH and CH_3 groups are *o*- and *p*- directing. Therefore, position 2,4 and 6 are activated. But due to steric hindrance, substitution does not occur at position 2, i.e., in between two groups.

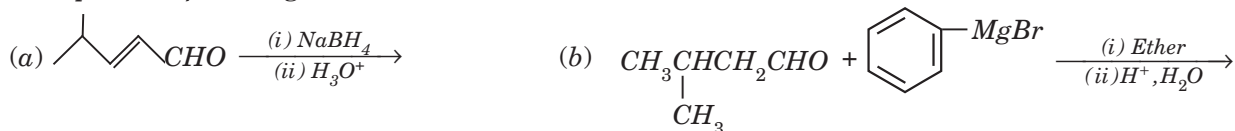


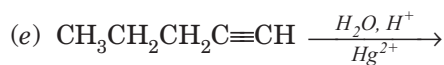
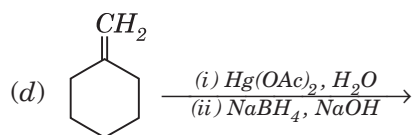
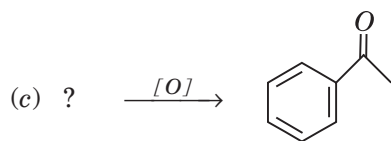
(iii) OCOCH_3 — is *o*, *p*-directing but due to steric hindrance, *p*-product predominates.



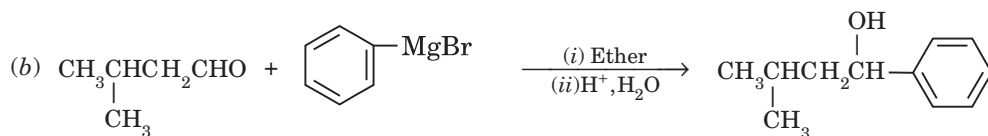
Example 9.

Complete the following reactions :



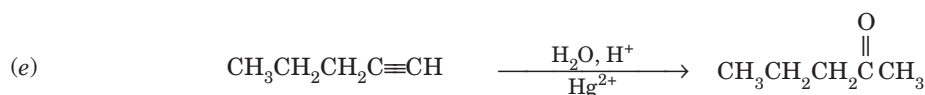
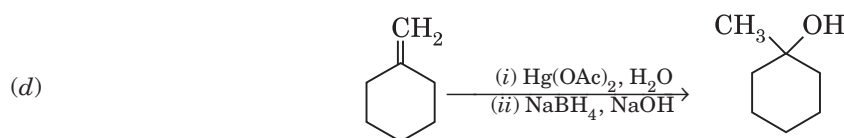
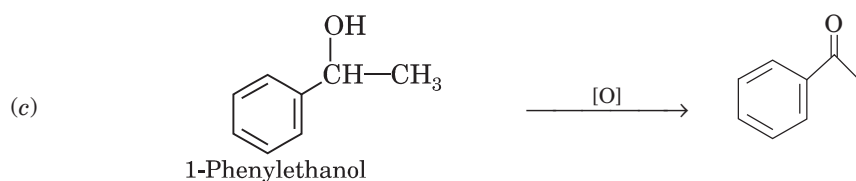


Solution :



NOTE

Oxymercuration reduction proceeds according to Markovnikov rule.

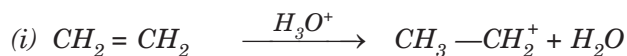


□ **Example 10.**

(a) Arrange the following compounds in the increasing order of their acid strength:

p-cresol, *p*-nitrophenol, phenol

(b) Write the mechanism (using curved arrow notation) of the following reaction:



Or

Write the structures of the products when butan-2-ol reacts with following:

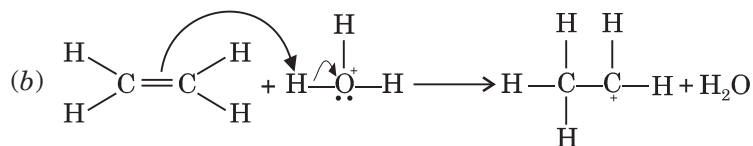
(a) CrO_3

(b) SOCl_2

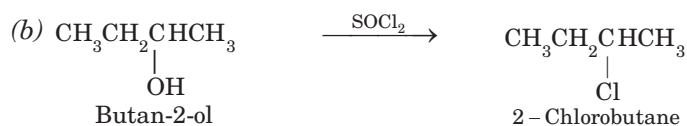
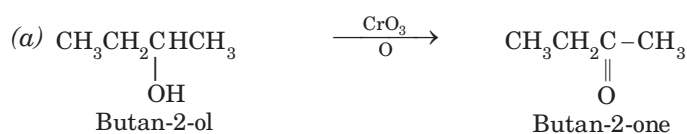
(A.I.S.B. 2017)

Solution :

(a) *p*-cresol < phenol < *p*-nitrophenol



Or



Example 11.

How are the following conversions carried out ?

(i) Benzyl chloride to benzyl alcohol

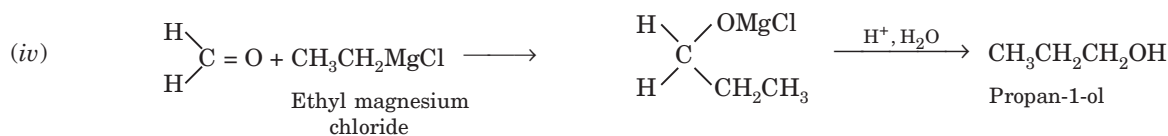
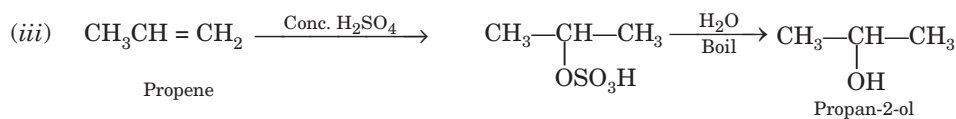
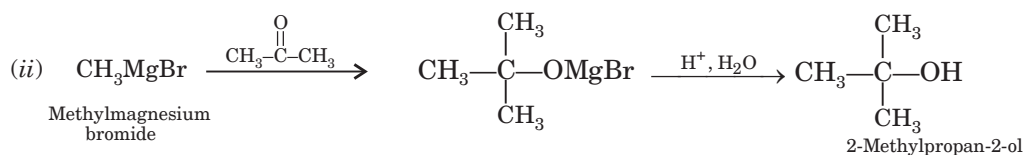
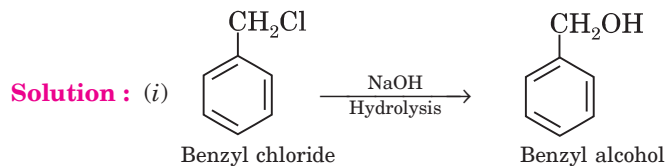
(Hr.S.B. 2018)

(ii) Methylmagnesium bromide to 2-methylpropan-2-ol.

(iii) Propene to propan-2-ol

(iv) Ethylmagnesium chloride to propan-1-ol.

D.S.B. 2010, 2013, Hr.S.B. 2018)



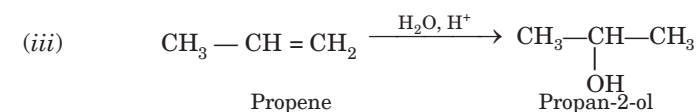
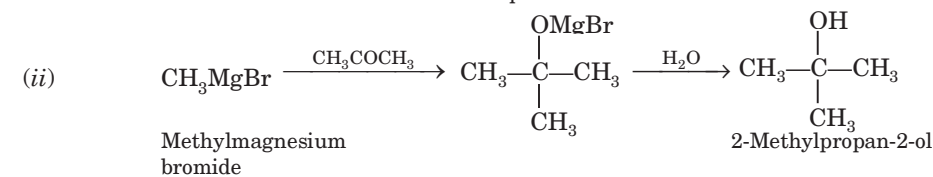
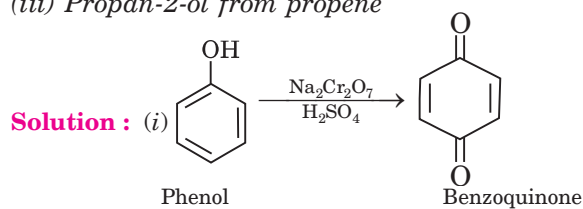
Example 12.

How would you obtain the following :

(i) Benzoquinone from phenol (ii) 2-Methylpropan-2-ol from methyl magnesium bromide

(iii) Propan-2-ol from propene

(A.I.S.B. 2011)



Example 13.

How will you convert :

(i) Propene to propan-2-ol

(ii) Phenol to 2, 4, 6-trinitrophenol

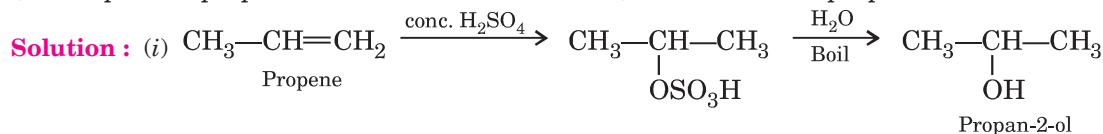
(iii) Propan-2-ol to propanone

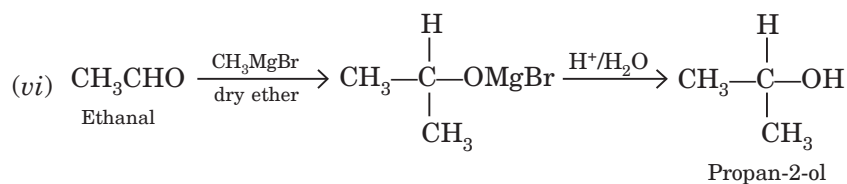
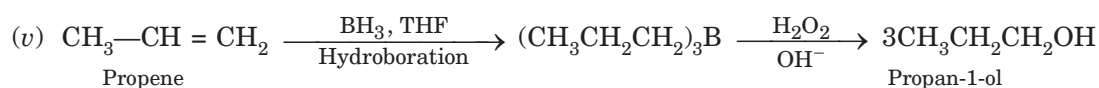
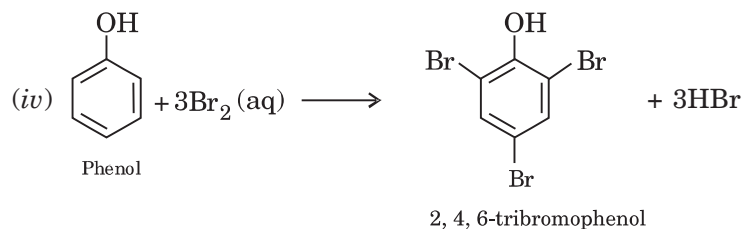
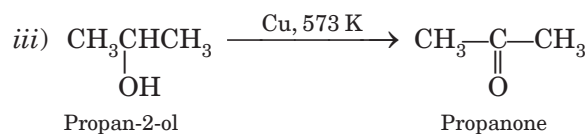
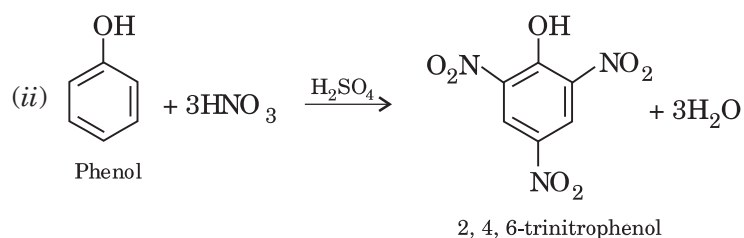
(iv) Phenol to 2, 4, 6-tribromophenol

(v) Propene to propan-1-ol

(vi) Ethanal to propan-2-ol

(D.S.B. 2013)





Example 14.

How will you convert.

(i) Propan-2-ol to 2-methylpropan-2-ol

(D.S.B. 2015)

(ii) Aniline to phenol

(D.S.B. 2015)

(iii) Ethanol to propanenitrile

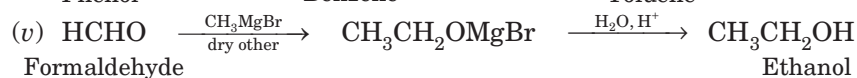
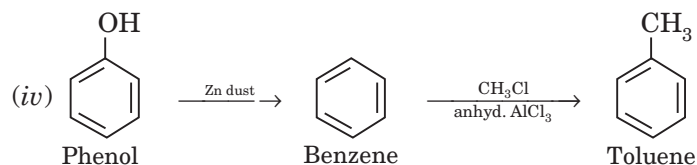
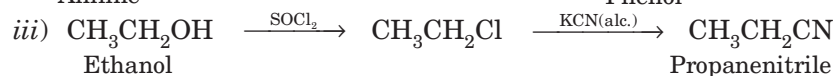
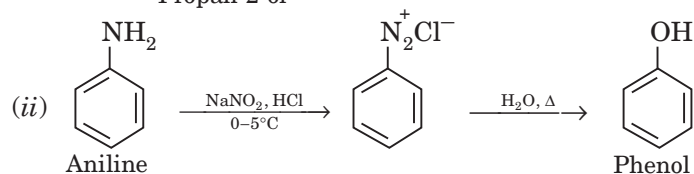
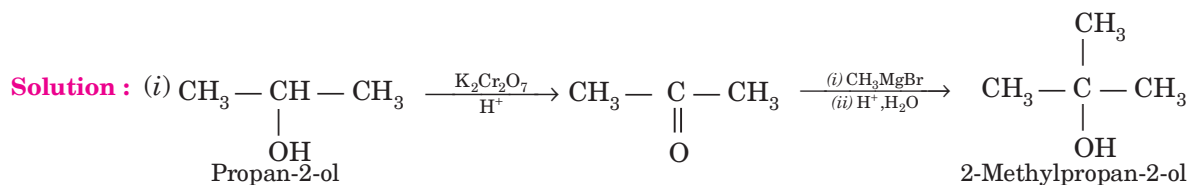
(A.I.S.B. 2015)

(iv) Phenol to toluene

(A.I.S.B. 2016)

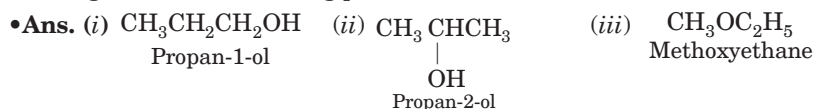
(v) Formaldehyde to ethanol

(A.I.S.B. 2016)



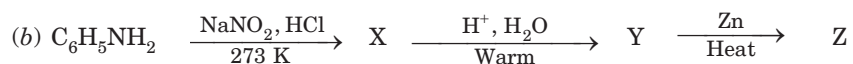
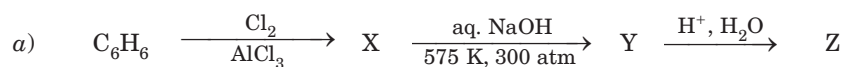
Practice Problems

7. Give the structural formulae and IUPAC names of the isomers with the molecular formula C_3H_8O . Arrange them in increasing order of their boiling point.

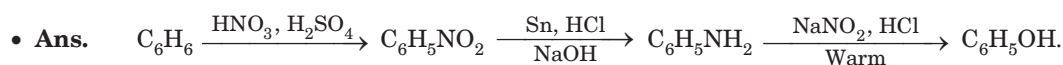


The increasing order of boiling point: (iii) < (ii) < (i)

8. Which structural isomer of $C_4H_{10}O$ cannot be dehydrogenated by copper at 575K ?
 • **Ans.** $(CH_3)_3COH$
9. Arrange the following in order of increasing reactivity towards Lucas reagent: butan-1-ol, 2-methylpropan-2-ol, butan-2-ol.
 • **Ans.** butan-1-ol, butan-2-ol, 2-methylpropan-2-ol
10. What is the major product when butan-2-ol is heated with H_2SO_4 at 443 K ?
 • **Ans.** $CH_3CH=CHCH_3$ (But-2-ene)
11. What products are obtained when ethyl alcohol is treated with H_2SO_4 at (i) 443 K (ii) 413 K at (iii) 383 K ?
 • **Ans.** (i) ethene (ii) ethoxy ethane (iii) ethyl hydrogen sulphate
12. What happens when tert. butyl alcohol is treated with reduced copper at 573K ?
 • **Ans.** 2-Methylpropene is obtained.
13. Complete the following reactions :
- (a) $CH_3COCl + C_2H_5OH \xrightarrow{\text{Pyridine}}$ (b) $(CH_3)_2CO \xrightarrow{CH_3MgBr} ? \xrightarrow{H^+}$
 (c) $(CH_3)_2CO \xrightarrow{LiAlH_4}$ (d) $CH_3CH_2OH + SOCl_2 \longrightarrow$
- **Ans.**
- (a) $CH_3COCl + C_2H_5OH \xrightarrow{\text{Pyridine}} CH_3-\overset{\overset{O}{||}}{C}-OC_2H_5$ (b) $CH_3-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow{CH_3MgBr} CH_3-\overset{\overset{CH_3}{|}}{C}-OMgBr \xrightarrow[H_2O]{H^+} CH_3-\overset{\overset{CH_3}{|}}{C}-OH$
 (c) $CH_3-\overset{\overset{O}{||}}{C}-CH_3 \xrightarrow{LiAlH_4} CH_3-CH_2-CH_2-OH$ (d) $CH_3CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + SO_2 + HCl$
14. Arrange the following in the decreasing order of acidic strength : H_2O , CH_3OH , $(CH_3)_2CHOH$.
 • **Ans.** $H_2O > CH_3OH > (CH_3)_2CHOH$.
15. What is the main product formed when phenol is subjected to Kolbe's reaction ?
 • **Ans.** Salicylic acid.
16. Arrange the following in the increasing order of acidic strength : phenol, ethanol, *o*-nitrophenol
 • **Ans.** Ethanol, phenol, *o*-nitrophenol.
17. What happens when phenol is hydrogenated ?
 • **Ans.** Cyclohexanol is formed.
18. Two isomeric aromatic compounds A and B have the molecular formula C_7H_7OH . A gives purple colour with $FeCl_3$ solution while B does not. What are A and B ?
 • **Ans.** A is cresol, B is benzyl alcohol.
19. Identify X, Y and Z in the following reactions :



20. Give a method of converting benzene to phenol via nitrobenzene.

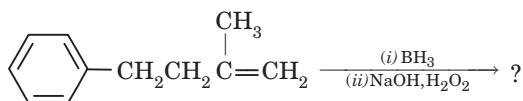


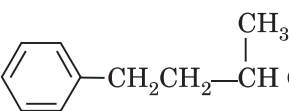
21 Predict which is stronger acid in each of the following pairs :

- (a) Phenol or cyclohexanol (b) Phenol or *p*-nitrophenol
 (c) *p*-Nitrophenol or *p*-chlorophenol (d) 2, 4, 6-Trinitrophenol or 2, 4-dinitrophenol.
 (e) *p*-Cyanophenol or phenol (f) $(\text{CH}_3)_2\text{CHOH}$ or $(\text{CF}_3)_2\text{CHOH}$
 (g) Phenol or benzyl alcohol

- **Ans.** (a) Phenol (b) *p*-Nitrophenol (c) *p*-Nitrophenol (d) 2, 4, 6-Trinitrophenol (e) *p*-Cyanophenol
 (f) $(\text{CF}_3)_2\text{CHOH}$ (g) Phenol.

22. Predict the product of the following reaction :

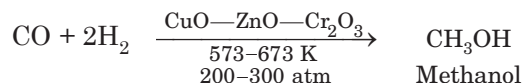


- **Ans.**  : 2-Methyl-4-phenylbutan-1-ol.
 (Hydroboration reaction proceeds according to anti-Markovnikov rule).

SOME COMMERCIALY IMPORTANT ALCOHOLS

1. Methanol

Methanol or methyl alcohol is also known as *wood spirit* or *wood alcohol* because it was originally prepared by destructive distillation of wood. Nowadays, it is manufactured by catalytic hydrogenation of carbon monoxide or water gas. A mixture of carbon monoxide and hydrogen is passed over a catalyst (consisting of oxides of copper, zinc and chromium) at 573–673 K and under 200–300 atm pressure, when methanol is formed.



Methanol is also prepared as a by-product during destructive distillation of wood.

Properties. Methanol is a colourless liquid with b.p. 337 K. It is miscible with water in all proportions. It is highly poisonous in nature and when taken internally it causes blindness or even death. It gives most of the general reactions of alcohols.

Uses of Methanol. Methanol is used

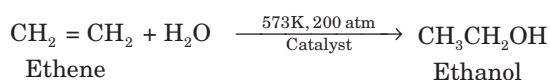
- (i) as a solvent for paints and varnishes.
- (ii) as an antifreeze for automobile radiators.
- (iii) in the manufacture of formaldehyde which is very widely used in the manufacture of plastics.
- (iv) for denaturing ethyl alcohol *i.e.*, to make it unfit for drinking purposes. Denatured alcohol is commonly known as methylated spirit.
- (v) as a motor fuel.
- (vi) in the manufacture of perfumes, drugs and varnishes.

2. Ethanol

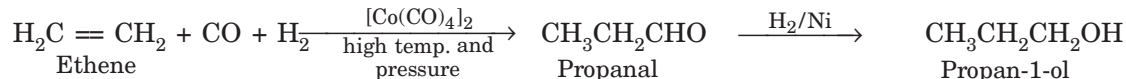
It is the most important member of the alcohol series and is simply known as **alcohol**. It is also known as **grain alcohol** because it can be prepared from starchy grains.

It can be manufactured by the following processes:

(i) **Hydration of ethene.** Ethanol is prepared by the hydration of ethene at 573 K under 200 atm pressure and in the presence of a catalyst.

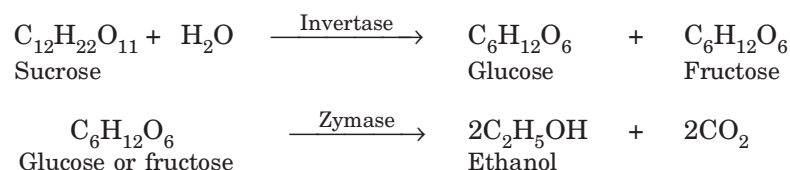


(ii) **Oxo process.** Ethene reacts with carbon monoxide and hydrogen in the presence of cobalt carbonyl $[\text{Co}(\text{CO})_4]_2$ as catalyst at high temperature and pressure to give aldehydes. *The catalytic hydrogenation of aldehydes gives primary alcohols.*



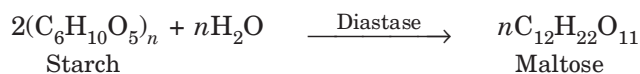
(iii) **Fermentation of carbohydrates.** Ethanol is manufactured by fermentation of *starch or sugar*. Fermentation is a process in which complex organic compounds are broken down into simpler molecules by the action of biological catalysts known as *enzymes*. **Enzymes** are complex organic compounds which act as catalysts in reaction taking place in living organisms. These are also called **bio-catalysts**.

(a) **Ethanol from sugar solution (molasses).** Molasses is a non-crystalline form of sugar obtained as the mother liquor after crystallisation of sugar from sugar solution. This contains about 50% sugar. It is diluted to about 10% solution and yeast is added and kept for about 2–3 days. Yeast supplies the enzymes invertase and zymase. The enzyme invertase hydrolyses sucrose to glucose and fructose. The enzyme zymase (found in yeast) converts glucose and fructose to ethanol.

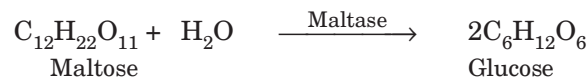


The fermented liquid which contains about 8–10% ethanol is called *wash*. It is fractionally distilled to rectified spirit containing 95.6% alcohol. Further dehydration with quick lime and distilling with sodium or calcium gives 99.8% ethanol.

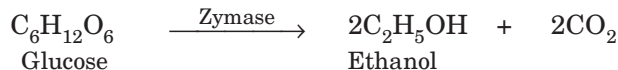
(b) **Ethanol from starch.** Ethanol is also prepared industrially from starchy substances like potato, barley, yam, etc. Starchy substances are made into a paste by heating with super-heated steam at about 335 K and malt is added. The malt contains the enzyme *diastase* which converts starch into maltose.



The product is cooled to about 305K and yeast is added. It gives enzyme maltase which converts maltose to glucose



The enzyme zymase also provided by yeast converts glucose into ethanol.



In wine making, grapes are the source of sugars and yeast. As grapes ripen, the quantity of sugar increases and the yeast grows on the skin of the grapes. When the grapes are crushed, sugar and enzyme come in contact and fermentation starts. Fermentation takes place under **anaerobic conditions** (*i.e.*, in the absence of air). During fermentation CO_2 is released.

The action of enzyme is inhibited when the concentration of alcohol exceeds 14%. If air enters the fermentation mixture, the O_2 of the air oxidises ethanol to ethanoic acid which spoils the taste of alcoholic drinks and makes it sour.

Properties. It is a colourless, volatile liquid with characteristic pleasant odour. It has boiling point of 351K. It gives all general reactions of alcohols.

Uses of Ethanol. Ethyl alcohol is used

- (i) as an industrial solvent for paints, lacquers, dyes, varnishes, cosmetics, perfumes, etc.
- (ii) in the manufacture of alcoholic beverages.
- (iii) in the preparation of ether, chloroform, iodoform, acetaldehyde, acetic acid, etc.
- (iv) in scientific instruments such as thermometers and spirit levels.
- (v) as an antifreeze in automobile radiators.
- (vi) as a preservative for biological specimens.

- (vii) as a fuel in spirit lamps and stoves.
- (viii) in hospitals as an antiseptic.
- (ix) in the manufacture of drugs, flavouring extracts, perfumes, etc.

3. Industrial Alcohols

Ethyl alcohol is one of the most important raw materials which is quite frequently used. It is sold in different grades of purity for different purposes. These are described below :

(i) **Absolute alcohol.** It is 100% pure ethanol. The fermentation of carbohydrates gives ethanol containing water. The fractional distillation of aqueous solution of ethanol gives a constant boiling azeotropic mixture which contains 95% ethanol. To get 100% ethanol, a small amount of benzene is added with azeotropic mixture and then distilled. The first fraction (at 337.8 K) consists of water, ethanol and benzene. After all water is removed, the second fraction (at 341.2 K) consists of benzene and ethanol. Finally, pure ethanol is distilled as the last fraction (351.1 K).

(ii) **Methylated spirit or denatured alcohol.** It is 95% ethyl alcohol. To avoid the misuse of alcohol meant for industries for drinking purposes, it is made unfit by mixing in it methanol, some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid), etc. The process is called denaturation of alcohol and the alcohol, thus obtained, is called methylated spirit or denatured alcohol. It is quite cheap and can be used for non-drinking purposes and particularly in industries.

(iii) **Power alcohol.** It is a mixture of 20% ethanol and 50% gasoline. Since alcohol does not mix with petrol, therefore, a third solvent such as benzene, ether or (tetrahydronaphthalene) is added. Due to the increased world consumption of petrol and its limited natural sources, petrol generally remains in a short supply. The use of power alcohol as a substitute for gasoline has promised bright future in India because we can manufacture large quantities of alcohol from molasses.

(iv) **Alcoholic beverages.** Liquors used for drinking purposes contain alcohol as the principal intoxicating agent. These are also called **alcoholic beverages**. They are prepared from different substances and contain different percentages of alcohol. There are mainly two types of beverages : *distilled* and *undistilled*. Undistilled beverages are prepared from grapes and other fruit juices and are called **wines**. The liquors obtained by distillation have higher alcoholic contents and have different trade names such as *whisky*, *rum*, *brandy*, *gin*, etc.

Toxicity of Alcohols

The toxicity of alcohols is mainly due to their biological oxidation taking place in living organisms. Methyl alcohol is highly toxic and its consumption causes blindness and death. Ethyl alcohol is non-toxic but produces physiological effects disturbing brain activity on drinking. The commercial alcohol is made unfit for drinking by mixing in it copper sulphate (which gives it colour) and pyridine which makes it foul smelling liquid. It is known as denaturation of alcohol.

4. Phenol or Carbohic acid

Phenol was first isolated from coal tar. Nowadays, it is manufactured by Dow's process (from chlorobenzene) or by cumene process.

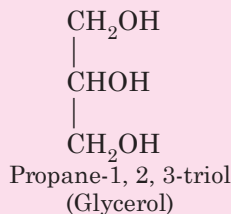
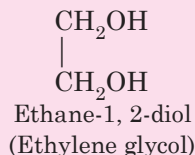
It is colourless, hygroscopic crystalline solid. Its melting point is 315K and boiling point is 455K. The liquid form of phenol containing about 5% water is known as *carbolic acid*. It turns pink on exposure to air and light.

Uses of Phenol. Phenol is used

- (i) for the manufacture of bakelite by polymerising with formaldehyde.
- (ii) in the manufacture of drugs like aspirin, salol, phenacetin, etc.
- (iii) as an antiseptic in soaps, lotions, etc.
- (iv) for preparing phenolphthalein used as an indicator in acid-base titrations.
- (v) as a preservative for ink.
- (vi) for the manufacture of cyclohexanol used as a solvent for rubber and lacquers.
- (vii) in the manufacture of azo dyes.
- (viii) in the manufacture of picric acid used in making explosives.

POLYHYDRIC ALCOHOLS

In addition to monohydrate alcohols, two polyhydric alcohols are also commercially important. These are the compounds which contain two or more hydroxyl groups ($-\text{OH}$) in the molecule. The compounds which contain two $-\text{OH}$ groups are called **diols**. Their IUPAC names are obtained by adding the suffix **diol** to the name of the parent alkane. The compounds containing three $-\text{OH}$ groups are called **triols**. Their IUPAC names are obtained by adding the suffix **triol** to the name of the parent alkane. The two common examples are :



add on

Conceptual Questions 1

Q.1. Arrange the following compounds in increasing order of their acid strength :

Propan-1-ol, 2, 4, 6-trinitrophenol, nitrophenol, 3, 5-dinitrophenol, phenol, 4-methyl phenol. **N.C.E.R.T.**

Ans. Increasing order of acid strength is :

Propan-1-ol, 4-methylphenol, phenol, 3-nitro phenol, 3, 5-dinitrophenol, 2, 4, 6-trinitrophenol.

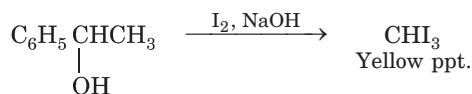
Q. 2. In the process of wine making, ripened grapes are crushed so that sugar and enzyme should come in contact with each other and fermentation should start. What will happen if anaerobic conditions are not maintained during this process?

(CBSE Sample Paper 2017-18)

Ans. Ethanol will be converted into ethanoic acid.

Q. 3. How will you distinguish between 1-phenylethanol and 2-phenylethanol ?

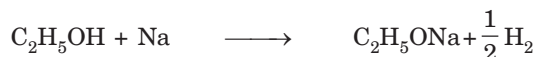
Ans. 1-Phenylethanol, $\text{C}_6\text{H}_5\text{CH}(\text{OH})\text{CH}_3$ contains the grouping $\text{—CH}(\text{OH})\text{CH}_3$ and therefore, will give iodoform test.



On the other hand, 2-Phenylethanol, $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$ does not contain $\text{—CH}(\text{OH})\text{CH}_3$ group and therefore, it will not give iodoform test.

Q.4. Sodium metal can be used for drying diethyl ether and benzene and not ethanol.

Ans. Ethanol has a replaceable hydrogen atom and therefore, reacts with sodium :



While benzene and diethyl ether do not have replaceable hydrogen atom and hence do not react with sodium. Therefore, these can be dried by sodium metal.

Q.5. Arrange the following compounds in the order of increasing boiling points :

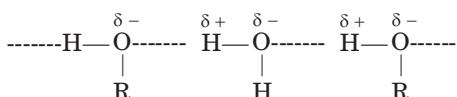
Ethanol, Propan-1-ol, Butan-1-ol, Butan-2-ol

(Kerala S.B. 2017)

Ans. Ethanol < Propan-1-ol < Butan-2-ol < Butan-1-ol

Q.6. Explain why alcohols are comparatively more soluble in water than the corresponding hydrocarbon.

Ans. The comparatively higher solubility of alcohols in water in comparison to hydrocarbons is due to the formation of hydrogen bonds between alcohol and water molecules.



Q.7. Arrange the following compounds in the decreasing order of their boiling points.

(i) Pentan-1-ol

(ii) 2-Methylbutan-2-ol

(iii) 3-Methylbutan-2-ol

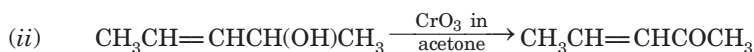
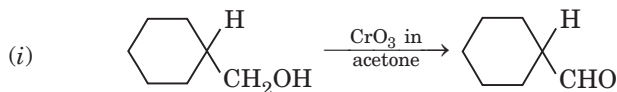
Ans. (i) > (iii) > (ii). This is because with branching the shape becomes spherical and therefore, van der Waals forces decrease. As a result, boiling point decreases.

Q.8. What is Jones reagent ? Give the product of oxidation of



(ii) $\text{CH}_3\text{CH}=\text{CHCH}(\text{OH})\text{CH}_3$ by Jones reagent.

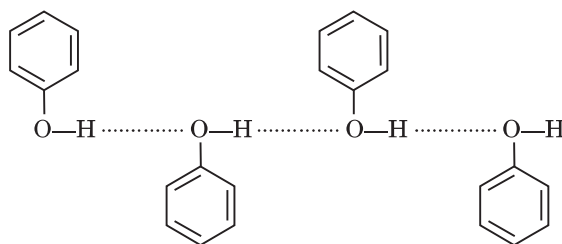
Ans. Jones reagent is CrO_3 in aqueous acetone solution. This is a mild reagent so that it oxidises alcohols without oxidising or rearranging double bonds.



Q.9. Why has phenol higher boiling point than toluene ?

(Pb.S.B. 2015)

Ans. Phenol (molecular mass 94) has higher boiling point than toluene (molecular mass 92). This is due to the fact that phenol forms intermolecular hydrogen bonding leading to association of its molecules. Consequently, additional energy is needed to break hydrogen bonds which raises its boiling point.



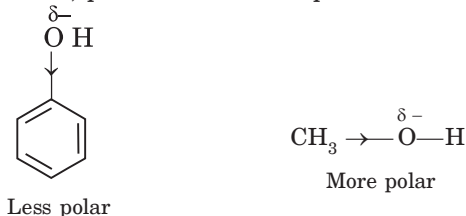
On the other hand, toluene does not form hydrogen bonds and therefore, its boiling point is less.

Q.10. Out of phenol and benzene, which is more easily nitrated and why ?

Ans. Phenol can be more easily nitrated than benzene. This is because, $-\text{OH}$ group is electron releasing group and it increases electron density on the benzene ring, particularly at the ortho and para positions. Since nitration involves attack of nitronium (NO_2^+) ion, its attack on phenol will be easier than on benzene where no electron releasing group is present.

Q.11. Why has phenol smaller dipole moment than methanol ?

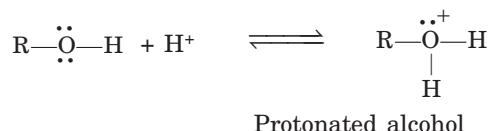
Ans. CH_3 group is electron releasing group and therefore, it increases the negative charge on the oxygen atom in CH_3OH . Therefore, $\text{C}-\text{O}$ bond in it is more polar and hence methanol has high dipole moment. Phenyl group is electron attracting group and it reduces negative charge on the oxygen in $\text{C}_6\text{H}_5\text{OH}$. As a result, $\text{C}-\text{O}$ bond is less polar in phenol and therefore, phenol has small dipole moment.



Q.12. Alcohols are easily protonated in comparison to phenols. Explain.

(A.I.S.B. 2016)

Ans. In alcohols, the electron releasing inductive effect (+ I effect) of the alkyl group attached to the carbon having the $-\text{OH}$ group increases the electron density on the oxygen atom. Therefore, alcohols are easily protonated.



On the other hand, in the case of phenol, the oxygen atom acquires a partial positive charge due to resonance. Thus, it is not protonated.

Q.13. How do you account for the fact that unlike phenol, 2,4-dinitrophenol and 2, 4, 6-trinitrophenol are soluble in aqueous sodium carbonate solution ?

Ans. Nitro group is electron withdrawing group and it stabilizes the phenoxide ion by dispersing the negative charge on the oxygen. As a result, the acidic strength of nitro phenols is more than that of phenol. This effect is more pronounced at *o*- and *p*-positions. Therefore, 2, 4-dinitrophenol and 2, 4, 6-trinitrophenols are more acidic than phenol. As a result, they are stronger acids than carbonic acid (H_2CO_3). Hence, they react with Na_2CO_3 to form their corresponding salts and dissolve in aqueous sodium carbonate solution with the evolution of CO_2 .

Q.14. Why do alcohols have higher boiling points than haloalkanes of the same molecular mass ?

Ans. The boiling points of alcohols are higher than the corresponding haloalkanes of the same molecular mass. This is mainly due to strong intermolecular hydrogen bonding between alcohol molecules. Because of hydrogen bonding in alcohols, energy has to be supplied to overcome the force of attraction and consequently boiling points are high. No such hydrogen bonding exists in haloalkanes. For example, b.pt. of CH_3OH is 337.5 K while that of CH_3Cl is only 249 K.

Q.15. While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which is more volatile. Give reason.

Ans. *Ortho* nitrophenol is more volatile. This is because it has weak intramolecular hydrogen bonding while *p*-nitrophenol is associated with strong intermolecular hydrogen bonding.

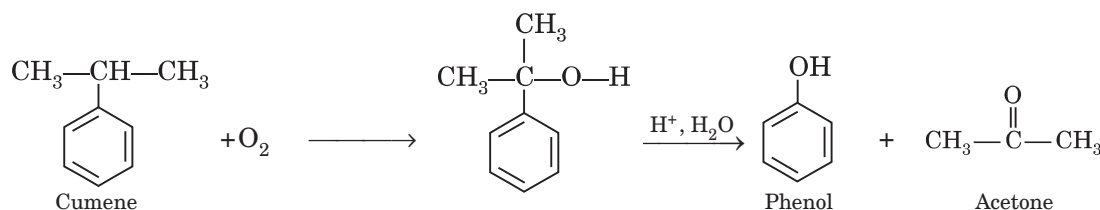
Q.16. Explain why *ortho* nitrophenol is more acidic than *ortho* methoxy phenol. (H.P.S.B. 2015, A.I.S.B. 2015)

Ans. This is because $-\text{NO}_2$ (nitro group) is electron withdrawing group and will increase the +ve charge on oxygen to make it more acidic. On the other hand, $-\text{OCH}_3$ group is electron releasing group and will decrease +ve charge on oxygen making it less acidic as $\text{O}-\text{H}$ bond will not break easily.

Q.17. Write reaction for the preparation of phenol from cumene.

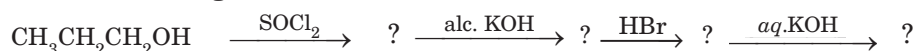
(Uttarakhand S.B. 2014)

Ans.

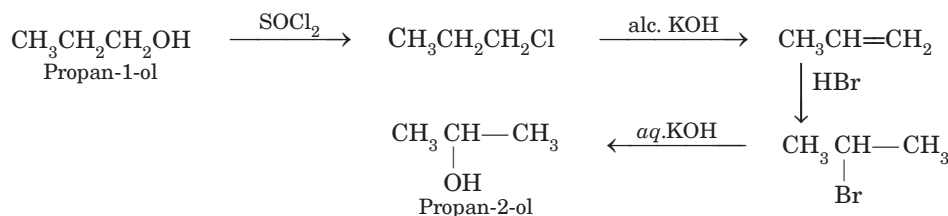


Q.18. Complete the following reactions:

(r. S.B. 2006)

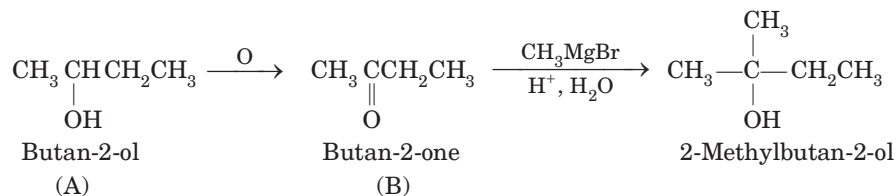


Ans.



Q.19. A compound (A) with molecular formula $\text{C}_4\text{H}_{10}\text{O}$ on oxidation forms compound (B). The compound (B) gives positive iodoform test and on reaction with CH_3MgBr followed by hydrolysis gives (C). Identify A, B and C and give the sequence of reactions.

Ans. Since B gives positive iodoform test, it must be methyl ketone, $\text{CH}_3\text{COCH}_2\text{CH}_3$ (B). It will be obtained by the oxidation of 2-butanol (A). The reactions are :



Q.20. A compound (A) reacts with thionyl chloride to give compound (B). (B) reacts with magnesium to form a Grignard reagent which is treated with acetone and the product is hydrolysed to give 2-methyl-2-butanol. What are (A) and (B) compounds ?

$$\begin{array}{ccccccc} \text{CH}_3\text{CH}_2\text{OH} & \xrightarrow{\text{SOCl}_2} & \text{CH}_3\text{CH}_2\text{Cl} & \xrightarrow{\text{Mg}} & \text{CH}_3\text{CH}_2\text{MgCl} & \xrightarrow[\text{H}^+/\text{H}_2\text{O}]{(\text{CH}_3)_2\text{C}=\text{O}} & \begin{array}{c} \text{OH} \\ | \\ \text{CH}_3\text{CH}_2-\text{C}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array} \\ \text{(A)} & & \text{(B)} & & & & \text{2-Methylbutan-2-ol} \end{array}$$

(CBSE Sample Paper 2012)

(D.S.B. 2013, A.I.S.B. 2013)

Q.23. Write the IUPAC name of the given compound:

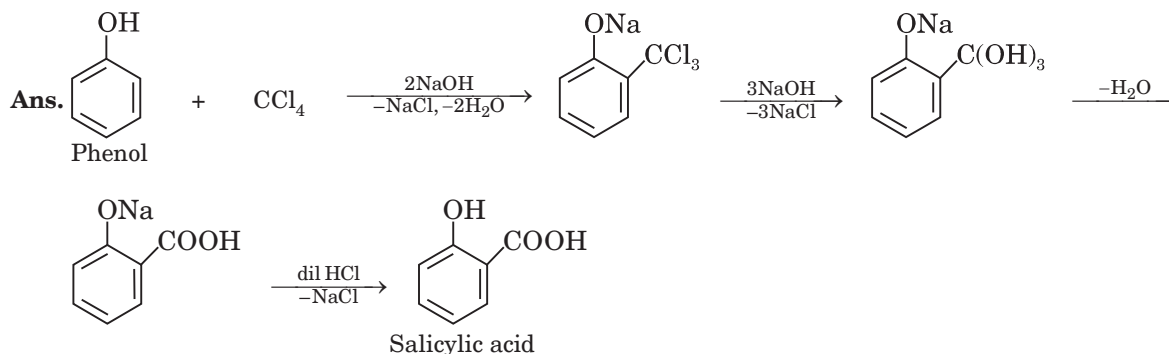


(Pb, S.B. 2017)

(Pb. S.B. 2018)

Phenolphthalein

(H. P. S. B. 2018, Meghalaya S.B. 2018)

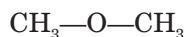


PART B

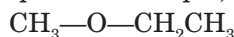
ETHERS

Ethers are the compounds having —O— as the functional group. The general formula of ethers is R—O—R where R may be alkyl or aryl group. Ethers may be classified as :

Aliphatic ethers in which R and R' are both alkyl groups. For example,

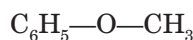


Dimethyl ether

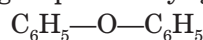


Ethyl methyl ether

Aromatic ethers in which either one or both R and R' groups are aryl groups. For example,



Methyl phenyl ether

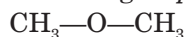


Diphenyl ether

Aromatic ethers may be further sub-divided as :

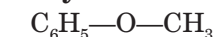
(i) *Ethers in which one of the groups is aryl while the other is alkyl* are called **alkyl aryl ethers** or **phenolic ethers**.

(ii) *Ethers in which both the groups are aryl* are called **diaryl ethers**. For example,



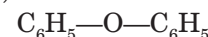
Dimethyl ether

(Aliphatic ether)



Methyl phenyl ether

(alkyl aryl ether)



Diphenyl ether

(diaryl ether)

Aromatic ethers

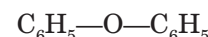
Symmetrical and unsymmetrical ethers. When the two alkyl groups in an ether are same, the ether is said to be **symmetrical** or **simple ether**. For example,



Dimethyl ether

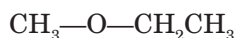


Diethyl ether

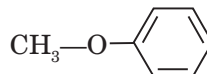


Diphenyl ether

When the two alkyl groups in an ether are different, the ether is said to be **unsymmetrical** or **mixed ether**. For example,



Ethyl methyl ether



Methyl phenyl ether

NOMENCLATURE OF ETHERS

According to **common system**, ethers are named according to *alkyl group attached to the oxygen atom*. The names of the two alkyl or aryl groups linked to oxygen are written as separate words alphabetically followed by the word 'ether'. For example,



Dimethyl ether



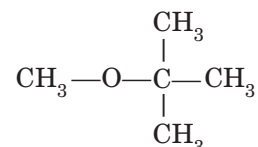
Ethyl methyl ether

CH₃

Methyl isopropyl ether



Methyl phenyl ether

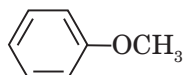


tert-Butyl methyl ether



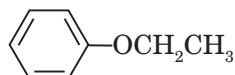
Ethyl phenyl ether

Some aromatic ethers have special common names. For example,



Anisole

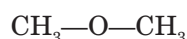
(Methyl phenyl ether)



Phenetole

(Ethyl phenyl ether)

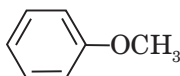
According to **IUPAC system**, ethers are named as **alkoxyalkanes**. The larger alkyl group forms the parent chain while lower alkyl group is taken with the ethereal oxygen and forms a part of *alkoxy group*. For example,



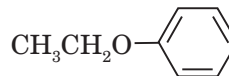
Methoxymethane



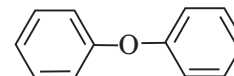
Methoxyethane



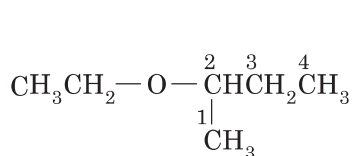
Methoxybenzene



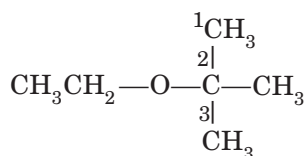
Ethoxybenzene



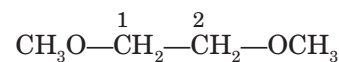
Phenoxybenzene



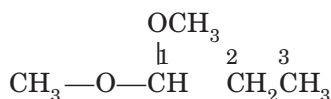
2-Ethoxybutane



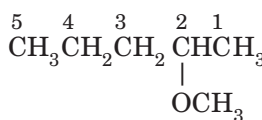
2-Ethoxy-2-methylpropane



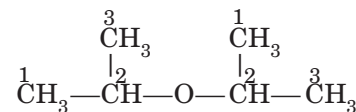
1, 2 Dimethoxyethane



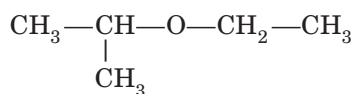
1, 1-Dimethoxypropane



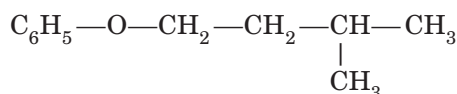
2-Methoxypentane



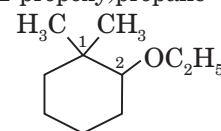
2-(2 propoxy)propane



2-Ethoxypropane

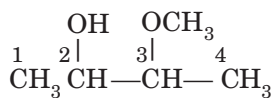


Methylbutoxybenzene

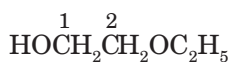


2-Ethoxy-1, 1-dimethylcyclohexane

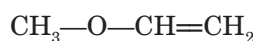
If any other functional group is also present, then that group gets priority and becomes the *principal group*. For example,



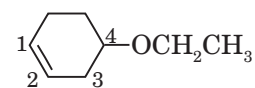
3-Methoxybutan-2-ol



2-Ethoxyethanol



Methoxyethene



4-Ethoxycyclohexene

The common and IUPAC names of some ethers are given below :

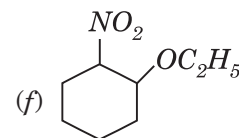
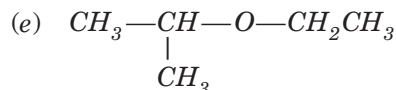
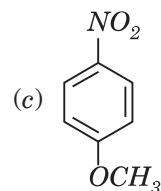
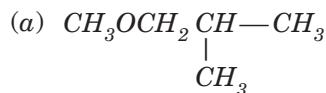
Table 1 Common and IUPAC names of some ethers.

Compound	Common name	IUPAC name
CH_3OCH_3	Dimethyl ether	Methoxymethane
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	Diethyl ether	Ethoxyethane
$\text{CH}_3\text{OC}_2\text{H}_5$	Ethyl methyl ether	Methoxyethane
$\text{CH}_3\text{OC}_3\text{H}_7$	Methyl <i>n</i> -propyl ether	1-Methoxypropane
$\text{C}_6\text{H}_5\text{OCH}_3$	Methyl phenyl ether (anisole)	Methoxy benzene
$\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$	Ethyl phenyl ether (phenetole)	Ethoxybenzene
$\text{C}_6\text{H}_5\text{O}(\text{CH}_2)_6\text{CH}_3$	Heptyl phenyl ether	1 Phenoxyheptane
$\text{CH}_3\text{O}\overset{\overset{2}{\text{CH}}}{\underset{\underset{3}{\text{CH}_3}}{ }}\overset{\overset{1}{\text{CH}_3}}{ }$	Methyl isopropyl ether	2-Methoxypropane
$\text{CH}_3-\overset{\overset{1}{\text{OCH}_2}}{ }-\overset{\overset{2}{\text{CH}_2}}{ }-\text{OCH}_3$		1, 2-Dimethoxyethane
$\text{C}_6\text{H}_5-\text{O}-\overset{\overset{1}{\text{CH}_2}}{ }-\overset{\overset{2}{\text{CH}_2}}{ }-\overset{\overset{3}{\text{CH}}}{\underset{\underset{\text{CH}_3}{ }}{ }}-\overset{\overset{4}{\text{CH}_3}}{ }$	Isopentyl phenyl ether	3-Methylbutoxybenzene
$\text{Cl}-\overset{\overset{3}{\text{CH}_2}}{ }-\overset{\overset{2}{\text{CH}}}{\underset{\underset{\text{O}}{ }}{ }}-\overset{\overset{1}{\text{CH}_2}}{ }$	Epichlorohydrin	3-Chloro-1, 2-epoxypropane

SOLVED EXAMPLES

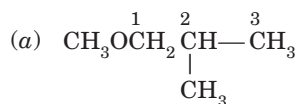
□ Example 15.

Give IUPAC names of the following :



N.C.E.R.T.

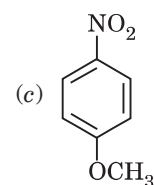
Solution: IUPAC names



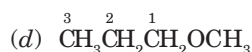
1-Methoxy-2-methylpropane



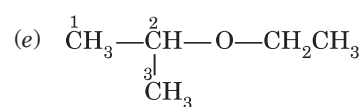
2-Chloro-1-methoxyethane



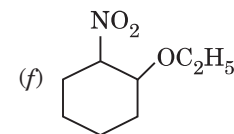
4-Nitro anisole



1-Methoxypropane



2-Ethoxypropane



1-Ethoxy-2-nitrocyclohexane

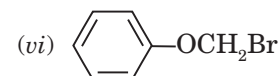
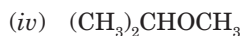
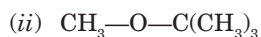
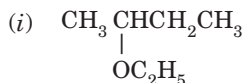
Practice Problems

23. Write the IUPAC names of the following ethers whose common names are given :

- (i) Isopropyl methyl ether (ii) Phenetole (iii) β -chloro ethyl methyl ether (iv) Cyclohexyl *n*-propyl ether

●Ans. (i) 2-Methoxypropane (ii) Ethoxy benzene (iii) 1-chloro-2-methoxyethane (iv) *n*-propoxycyclo hexane

24. Write the IUPAC names of the following :



●Ans. (i) 2-Ethoxybutane

(ii) 2-Methoxy-2-methylpropane

(iii) Ethoxy benzene

(iv) 2-Methoxypropane

(v) 1-Ethoxy-2-methoxyethane

(vi) (Bromomethoxy) benzene

25. Write the structural formula of the following :

(i) Di-isopropyl ether

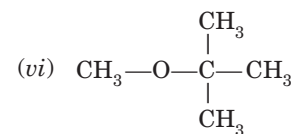
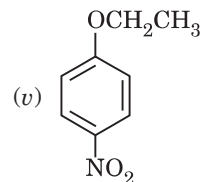
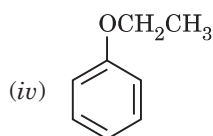
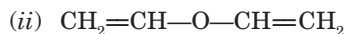
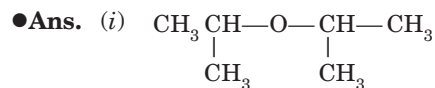
(ii) Divinyl ether

(iii) Bis (2-methoxyethyl) ether

(iv) Phenetole

(v) *p*-Nitrophenetole

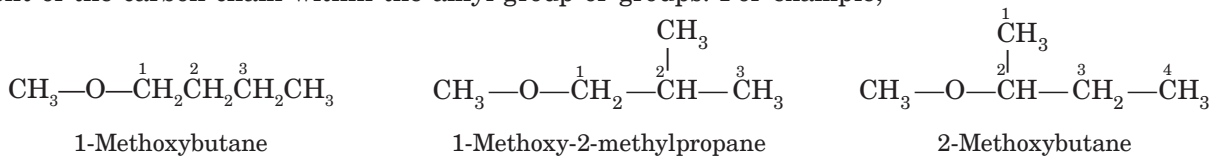
(vi) *tert*-Butyl methyl ether



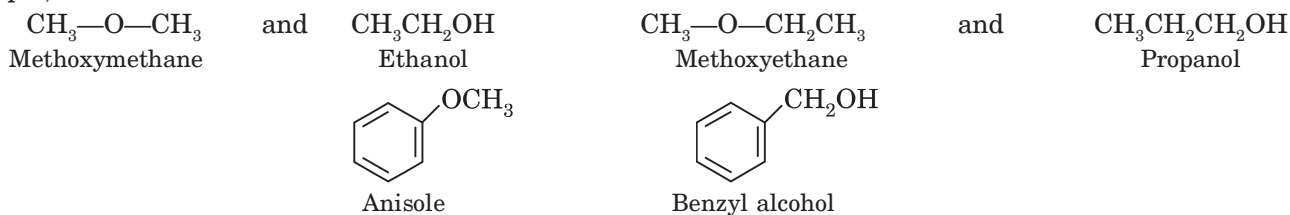
ISOMERISM IN ETHERS

Ethers show the following types of isomerism :

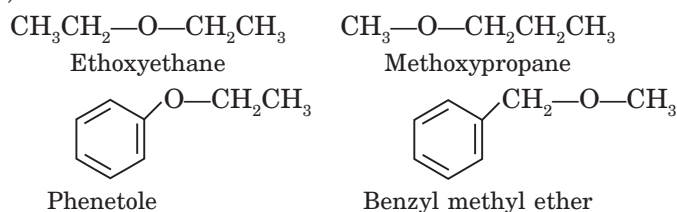
1. Chain isomerism. These have the same alkyl groups on either side of the oxygen atom but different arrangement of the carbon chain within the alkyl group or groups. For example,



2. Functional isomerism. Ethers containing two or more carbon atoms are functional isomer of alcohols. For example,



3. Metamerism. These ethers have the same molecular formula but different alkyl groups on either side of the oxygen atoms. For example,



STRUCTURE OF ETHERS

Ethers have structure similar to that of water (H_2O). In this case, oxygen undergoes sp^3 hybridisation forming four sp^3 hybrid orbitals. Two of the four sp^3 hybrid orbitals of the oxygen atom overlap with sp^3 hybrid orbitals of two alkyl groups forming sigma (σ) bonds. The remaining sp^3 hybrid orbitals of oxygen contain a lone pair of electrons each as shown in Fig. 2. The C—O—C bond angle in ethers is tetrahedral angle. For example, in dimethyl ether, the C—O—C bond angle is 111.7° and C—O bond is 141 pm, which is almost same as in alcohols. *The larger bond angle in ethers may be because of greater repulsive interactions between bulkier alkyl groups as compared to the smaller H-atoms in water.* Thus, ethers have **bent or angular** structure.

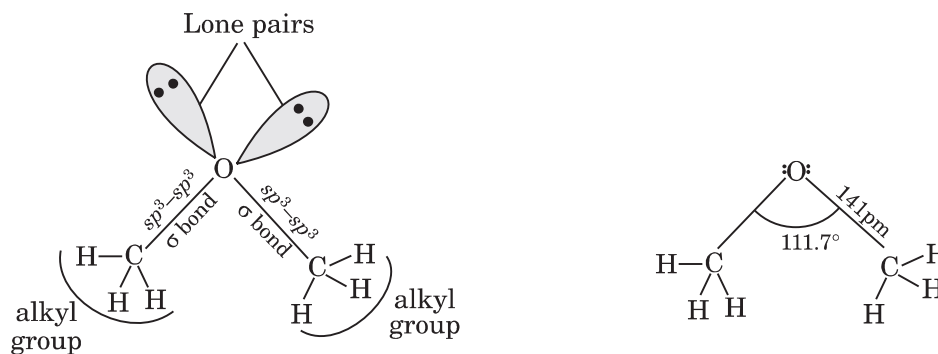


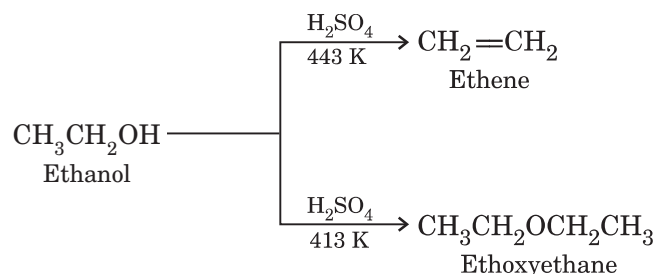
Fig. 2. Structure of dimethyl ether

METHODS OF PREPARATION OF ETHERS

Ethers can be prepared by the following general methods:

1. Dehydration of alcohols

Alcohols undergo dehydration in the presence of protonic acids such as H_2SO_4 , H_3PO_4 , etc. to give either alkenes or ethers. The formation of product, alkene or ether depends upon the reaction conditions. For example, when ethanol is heated with conc. H_2SO_4 at 443 K, ethene is formed as the major product. However, at 413 K, ethoxyethane is obtained as the major product.



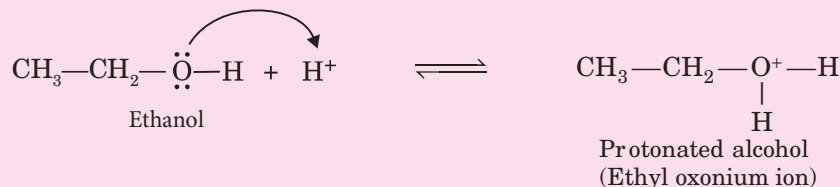
Thus, symmetrical ethers can be prepared by the dehydration of alcohols with conc. H_2SO_4 at 413 K.

The formation of ether is a nucleophilic bimolecular substitution reaction ($\text{S}_\text{N}2$) involving the attack of the alcohol molecule on a protonated alcohol as given below :

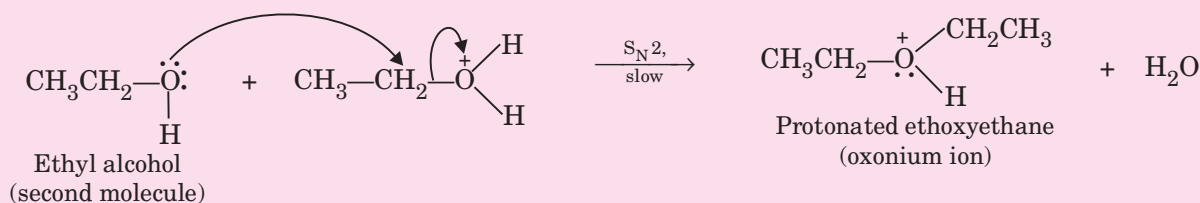
Mechanism : Formation of diethyl ether from ethanol

The **mechanism** for the formation of diethyl ether from ethanol at 413 K is given below :

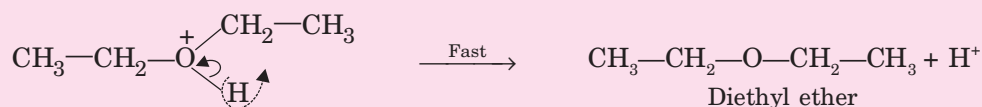
(i) Ethyl alcohol gets protonated in the presence of H^+



(ii) Due to the presence of a +ve charge on the oxygen atom, the carbon of CH_2 part of CH_3CH_2 becomes electron deficient. As a result, nucleophilic attack by another alcohol molecule (unprotonated) occurs on the protonated alcohol with the elimination of a molecule of water.



(iii) Oxonium ion loses a proton to form an ether.

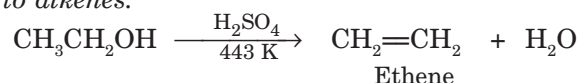


This step is fast and hence does not affect the rate of reaction.

This method is suitable for the preparation of ethers having primary alkyl groups only.

The following are **some facts** about the reaction :

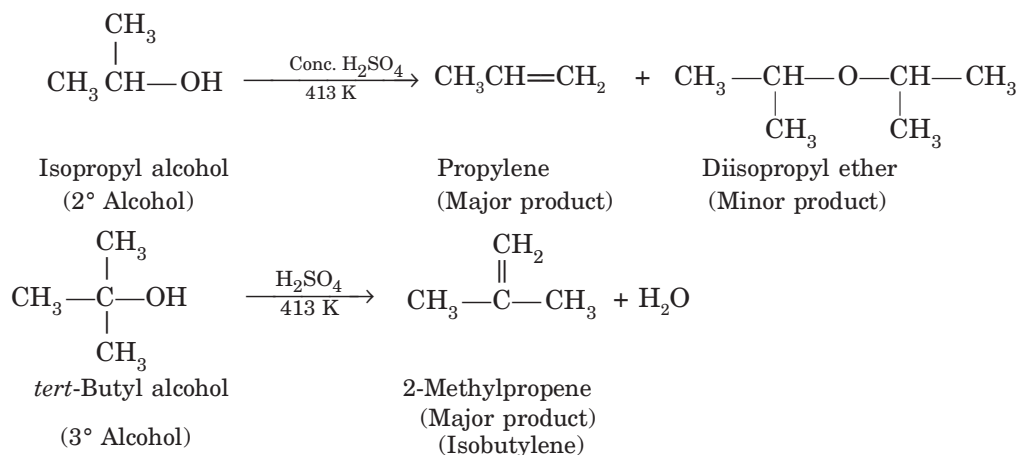
(i) **The formation of ethers may be accompanied by the formation of some amounts of alkenes.** In order to avoid this, *temperature of the reaction must be properly controlled because at higher temperature (443 K), the alcohols get dehydrated to alkenes.*



(ii) **A large excess of alcohols should be used.**

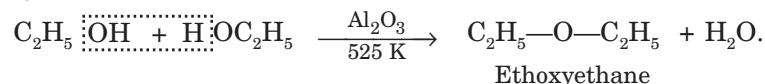
(iii) **The alkyl group should be unhindered.**

The above method is mainly used for the dehydration of **primary alcohols** because *secondary and tertiary alcohols give alkenes as major products under the reaction conditions.* The reaction with secondary and tertiary alcohols follows $\text{S}_\text{N}1$ pathway. For example,



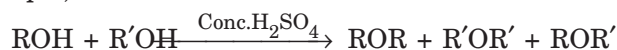
Thus, the order of dehydration of alcohols to form ethers follows the order :
primary > secondary > tertiary.

The dehydration of alcohols may also be carried out by passing the vapours of alcohols over a heated catalyst like alumina (Al_2O_3) at about 525 K.

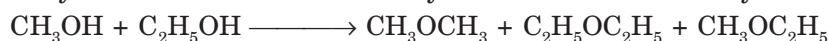


Thus, for the formation of ethers, the alkyl group should be unhindered and the temperature be kept low, otherwise, the reaction favours the formation of alkene.

Limitation. This method is generally not used for the preparation of unsymmetrical ethers because mixtures may be obtained. For example,

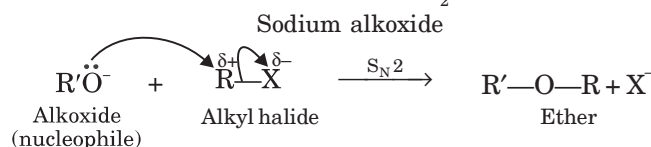
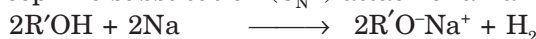


For example, ethylmethyl ether cannot be obtained by this method from methyl alcohol and ethyl alcohol.



2. From alkyl halides by Williamson's synthesis

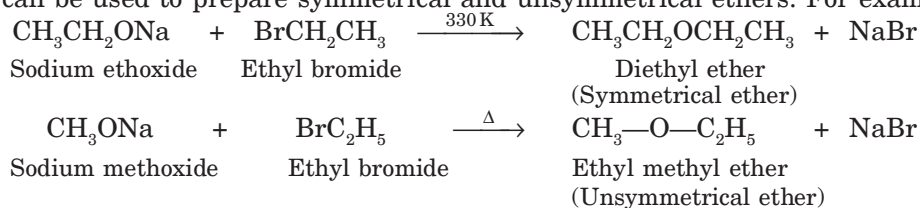
This is one of the best methods for preparing symmetrical and unsymmetrical ethers in laboratory. In this method an alkyl halide is treated with a suitable sodium alkoxide prepared by the action of sodium on a suitable alcohol. The reaction involves nucleophilic substitution ($\text{S}_{\text{N}}2$) attack of an alkoxide ion on primary alkyl halide.



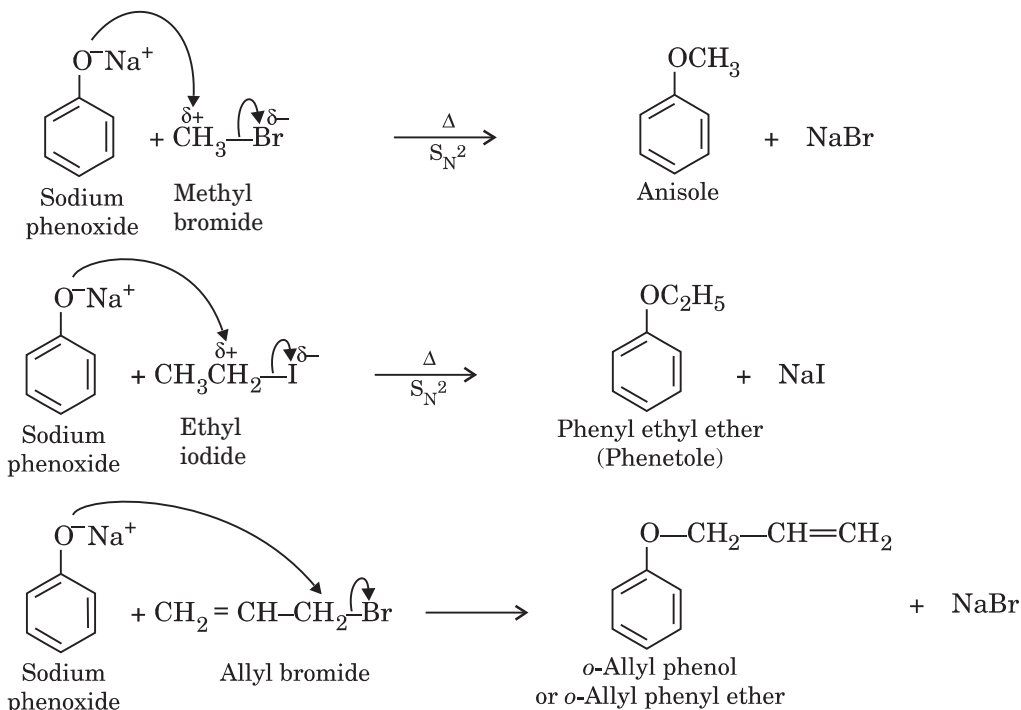
or



This reaction can be used to prepare symmetrical and unsymmetrical ethers. For example,



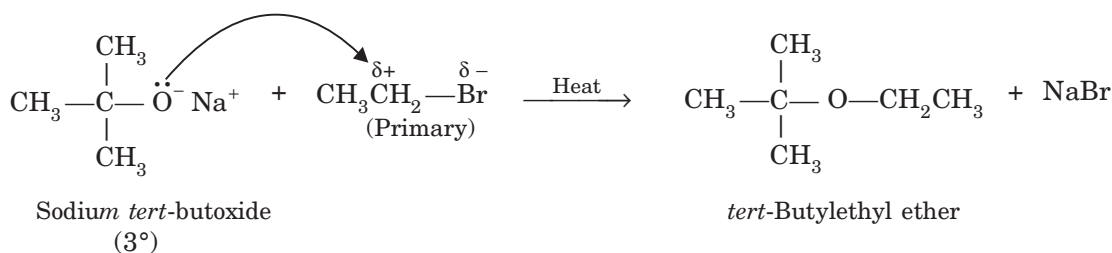
Similarly, alkyl aryl ethers (phenolic ethers) can be easily prepared by treating phenoxide with a suitable alkyl halide.



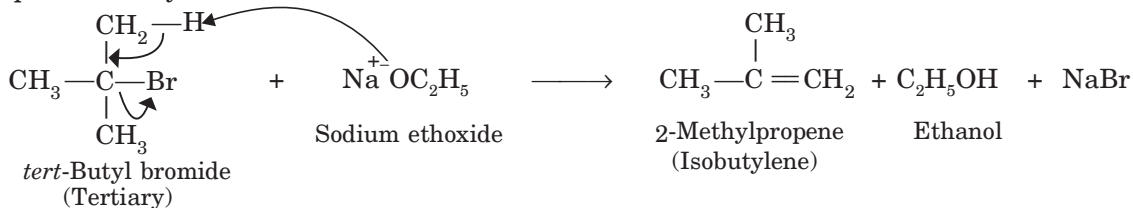
NOTE

It may be noted that phenols are more acidic than alcohols and therefore, these can be converted to sodium phenoxides by treating with NaOH. In alcohols, metallic sodium is used to convert alcohols to alkoxide ions.

Limitation. It may be noted that for preparing unsymmetrical ethers, the halide used should **preferably be primary** because Williamson synthesis occurs by S_N2 mechanism and primary alkyl halides are most reactive in S_N2 reactions. Therefore **best yields of unsymmetrical ethers can be obtained when alkyl halides are primary**. However, the alkoxides may be primary, secondary or tertiary. The secondary and tertiary alkyl halides if used may form alkenes as major product due to elimination process. For 2° and 3° alkyl halide, elimination competes over substitution. If a 3° alkyl halide is used, an alkene is the only product and no ether is formed. For example, if we want to prepare tert-butyl ethyl ether, then we should take ethyl bromide and sodium tert-butoxide.

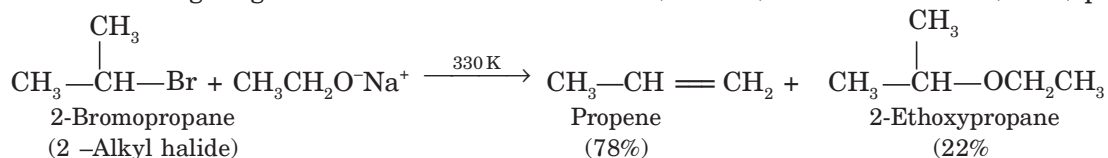


However, if we use tert-butyl bromide and sodium ethoxide as reactants, then the major products would be 2-methylpropene (isobutylene) and ethanol.

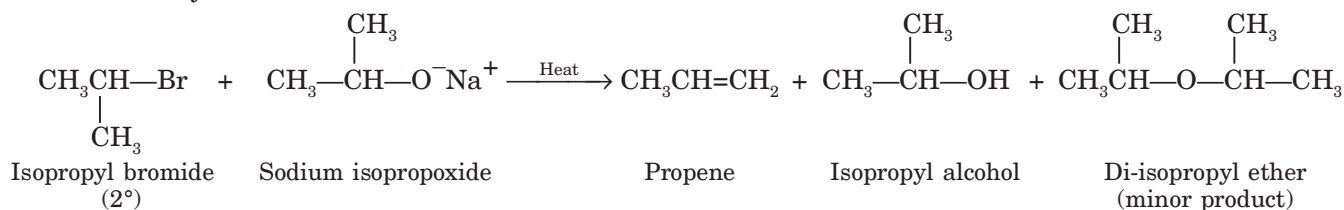


This is because alkoxides are not only nucleophiles but strong bases as well. They react with alkyl halides leading to elimination reaction.

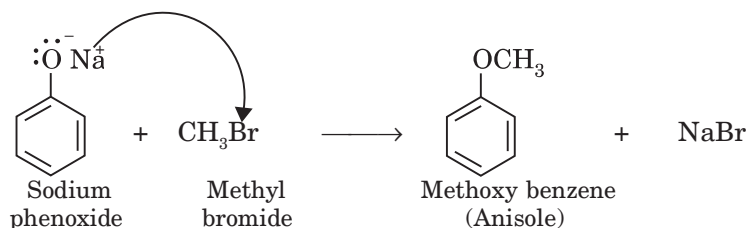
It may be noted that due to steric hindrance, secondary alkyl halides also prefer to undergo elimination rather than substitution giving a mixture of both elimination (alkenes) and substitution (ether) products. For example,



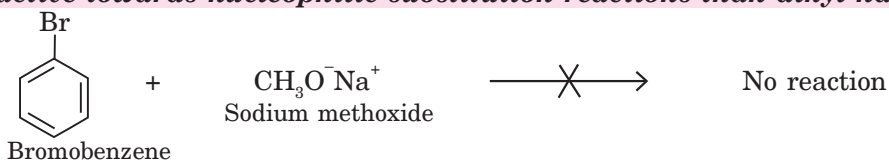
Since secondary and tertiary alkyl halides prefer to undergo elimination rather than substitution, therefore, even symmetrical ethers containing secondary and tertiary alkyl groups cannot be prepared in good yields by **Williamson's synthesis**. For example, di-isopropylether or di-*tert*-butylether cannot be prepared in good yields by Williamson's synthesis.



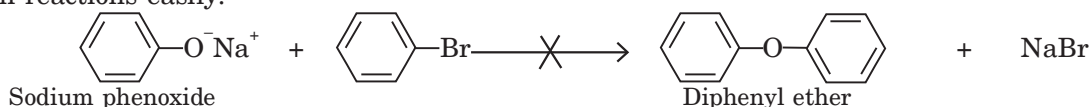
Further, alkyl aryl ethers (phenolic ethers) can be easily prepared by using sodium phenoxide and alkyl halides. For example,



However, aryl halide and sodium alkoxide cannot be used for preparing phenolic ethers because aryl halides are less reactive towards nucleophilic substitution reactions than alkyl halides.

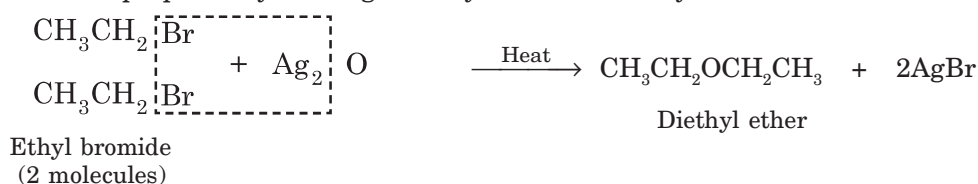


Similarly, this method cannot be used for preparing diarylethers because aryl halides do not undergo nucleophilic substitution reactions easily.



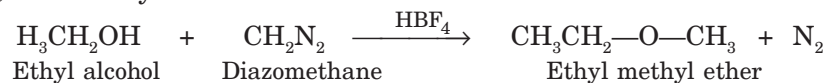
3. From alkyl halides by treating with dry silver oxide

Ethers can also be prepared by heating an alkyl halide with dry silver oxide.



4. By the action of diazomethane on alcohols

Methyl ethers can also be prepared by the action of diazomethane (CH_2N_2) on alcohols in the presence of fluoroboric acid (HBF_4) as a catalyst.

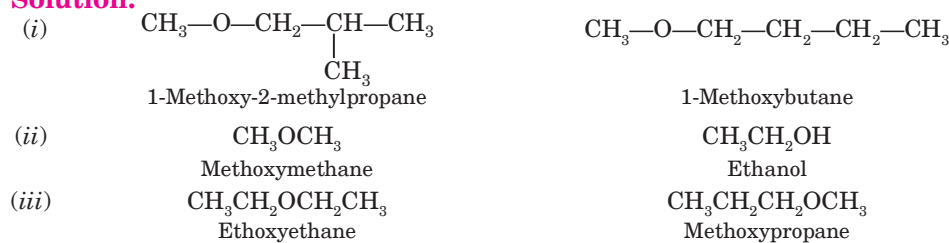


SOLVED EXAMPLES

- **Example 16.**
- Write one chain isomer of 1-methoxy-2-methyl propane.
 - Write one functional isomer of methoxymethane
 - Write one metamer of ethoxyethane

(Pb.S.B. 2009)

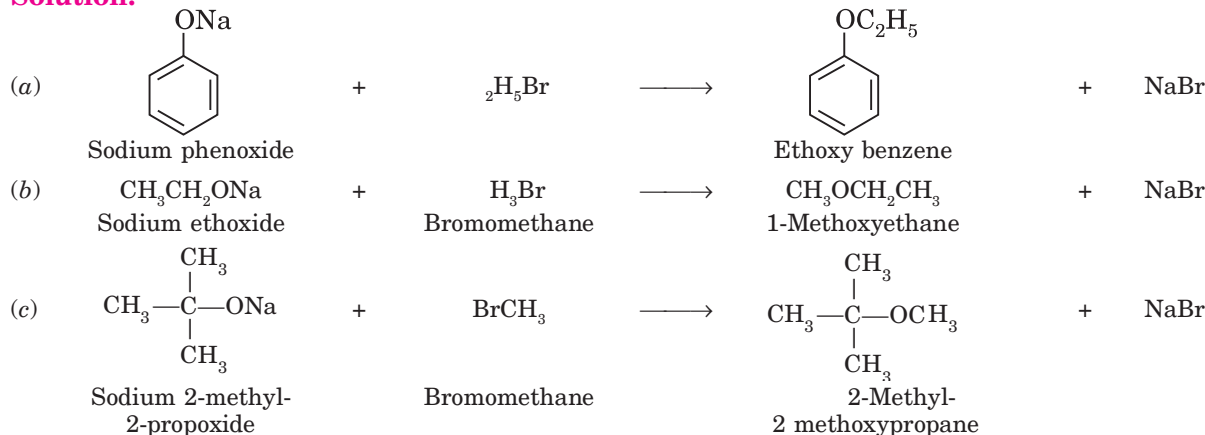
Solution:

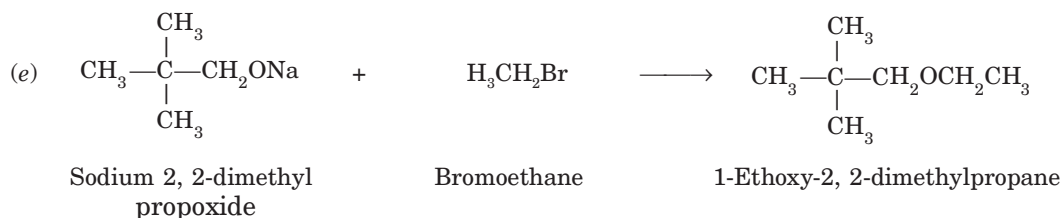
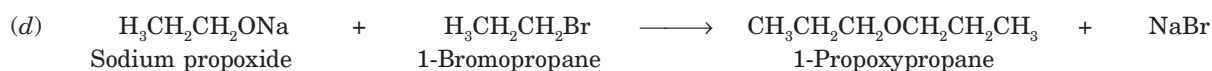


- **Example 17.** Write equations for the preparation of the following ethers by Williamson's synthesis.

- | | | |
|----------------------|-----------------------------------|-------------------------------|
| (a) Ethoxy benzene | (b) 1-Methoxyethane | (c) 2-Methyl-2-methoxypropane |
| (d) 1-Propoxypropane | (e) 1-Ethoxy-2, 2-dimethylpropane | |

Solution:





Practice Problems

26. Suggest three methods for preparing di-*n*-propyl ether.
 27. Suggest a methods to prepare ethyl-*n*-propyl ether starting from alcohol of three C-atoms or less.
 28. Name the major product in the following reactions:



● **Ans.** (a) Ethoxy benzene ($\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$) (b) Ethyl methyl ether ($\text{C}_2\text{H}_5\text{OCH}_3$)

c) Isobutylene ($\text{CH}_3-\text{C}=\text{CH}_2$) (d) Tert-butyl ethyl ether
 $\quad \quad \quad |$
 $\quad \quad \quad \text{CH}_3$

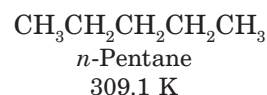
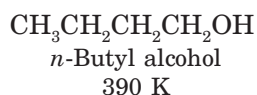
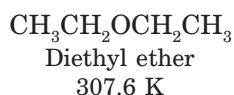
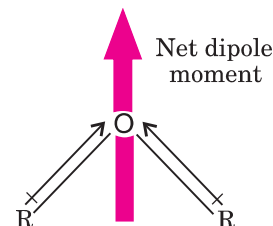
PHYSICAL PROPERTIES OF ETHERS

The important physical properties of ethers are :

1. Physical state. Lower members (dimethyl ether, methyl ethyl ether) are gases and higher members are low boiling liquids with a pleasant smell.

2. Dipole moments. Ethers have bent or angular structure like water. Due to greater electronegativity of oxygen than carbon, the C—O bonds are slightly polar and therefore, the ethers have resultant dipole moment. Since the two C—O bonds are inclined to each other at an angle of about 110° , two dipoles do not cancel each other. As a result, ethers have resultant dipole moment. For example, dipole moment of dimethylether is 1.3D and that of diethylether is 1.18D.

3. Boiling points. Ethers have low polarity and as a result do not show any association by intermolecular hydrogen bonding. Therefore, ethers have low boiling points and lower than that of isomeric alcohols and almost same as those of alkanes of comparable molecular masses.



The large difference in boiling points of alcohols and ethers is due to the presence of hydrogen bonding in alcohols.

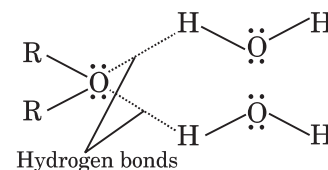
The boiling points of ethers increase with increase in number of carbon atoms. Due to weak dipole-dipole forces, the boiling points of lower members such as dimethyl ether and ethyl methyl ether are only slightly higher than those of the corresponding *n*-alkanes of comparable molecular masses. The boiling point of diethyl ether is almost the same (307.6 K) as that of *n*-pentane (309.1 K) having comparable molecular masses. However, as the hydrocarbon part increases beyond four carbon atoms, the boiling points of ethers are even slightly lower than corresponding *n*-alkanes of comparable molecular masses. This is because of the presence of oxygen atom, ether molecules are less symmetrical than *n*-alkanes of comparable molecular masses. Therefore, the van der Waals' forces of attraction between ether molecules are slightly less than those in little more symmetrical *n*-alkanes of comparable molecular masses. For example,

Ether	CH_3OCH_3	$\text{CH}_3\text{OC}_2\text{H}_5$	$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$	$\text{C}_2\text{H}_5\text{OC}_3\text{H}_7$	$\text{C}_2\text{H}_5\text{OC}_4\text{H}_9$
Molecular mass	46	60	74	88	102
Boiling point (K)	250	283	307.6	366.6	366

<i>n</i> -Alkane	Propane	<i>n</i> -Butane	<i>n</i> -Pentane	<i>n</i> -Hexane	<i>n</i> -Heptane
Molecular mass	44	58	72	86	100
Boiling point (K)	233	273	309.1	342	371

4. Solubility. The solubility of ethers is comparable to those of corresponding alcohols of the same molecular mass. For example, like ethanol, dimethyl ether is completely miscible with water.

Similarly, both ethoxyethane and butan-1-ol are soluble in water to almost the same extent i.e., 7.5 and 9.0 g. per 100 mL water respectively. On the other hand, pentane is almost immiscible with water. Solubility of ethers in water is due to the fact that like alcohols, the oxygen of ether can also form hydrogen bonds with water molecules as shown below:



However, the solubility of ethers in water decreases from lower members to higher members. *This may be due to increase in size of the alkyl group which decreases the tendency to form hydrogen bonding.* Ethers are however, fairly soluble in common organic solvents such as alcohols, chloroform, acetone, benzene, etc.

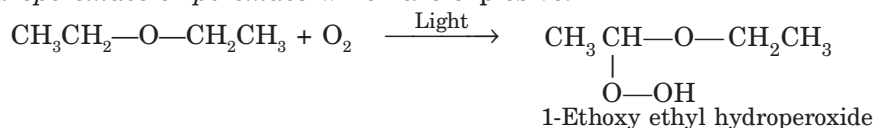
5. Density. All ethers are lighter than water.

CHEMICAL PROPERTIES OF ETHERS

Ethers are quite inert and **stable compounds**. *They are the least reactive of the functional groups.* These are not easily attacked by alkalis, dilute mineral acids, active metals, reducing agents or oxidising agents under ordinary conditions. This is because the functional group of ethers (—O—) does not contain any active site in their molecules as compared to hydroxyl (—OH) group of alcohols or phenols even though the oxygen atom in both these functional groups contains two lone pairs of electrons. However, under specific conditions, ethers undergo some chemical reactions. The important chemical properties of ethers are :

A : Reactions of Ethereal Oxygen

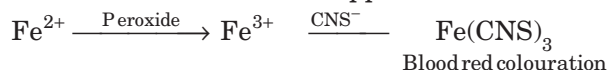
1. Action of air (formation of peroxides). On exposure to sunlight, ethers slowly react with oxygen from air to form *hydroperoxides or peroxides* which are explosive.



In this case, the oxidation occurs at the carbon atom next to the ethereal oxygen to form hydroperoxide.

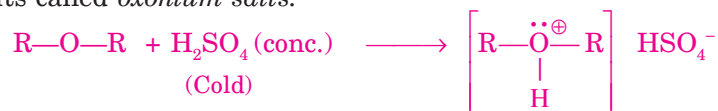
These peroxides are unstable compounds and hazardous because they decompose violently on heating. Therefore, proper care should be taken while distilling the old samples of ether. Serious accidents may occur during the distillation if the old samples contain some peroxides.

The presence of peroxides in ethers can be detected by shaking them with freshly prepared FeSO_4 solution followed by the addition of KCNS. The appearance of blood red colour indicates the presence of peroxides.

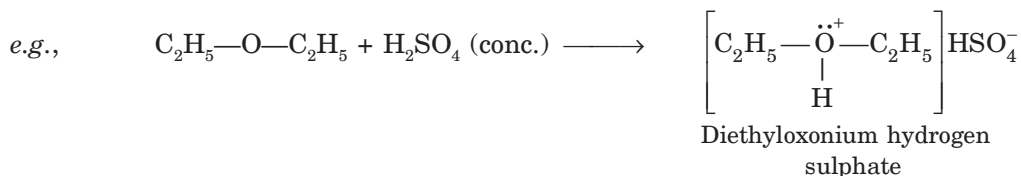


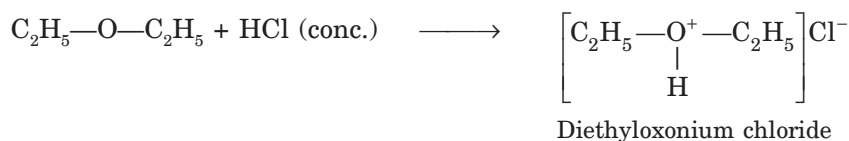
The peroxides can be removed from ethers by shaking with either an aqueous solution of KI or ferrous sulphate. The ether peroxides are reduced to ether and I^- ion is oxidised to I_2 or Fe^{2+} salts are oxidised to Fe^{3+} salts. The Fe^{3+} salts thus formed are removed from the reaction mixture by washing with water. I_2 is removed by first shaking with sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$) and then washing with water. The resulting ether is dried over anhydrous CaCl_2 and then distilled to get peroxide free pure ether.

2. Action with concentrated acids (formation of oxonium salts). The oxygen atom in ether molecule has two lone pairs of electrons. Therefore, ethers act as **Lewis bases** and dissolve in cold concentrated mineral acids (H_2SO_4 , HCl) to form salts called *oxonium salts*.



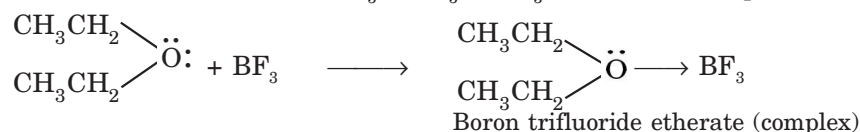
Dialkyloxonium
hydrogen sulphate



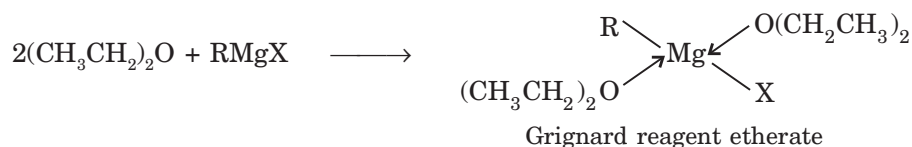


This reaction can be used to distinguish between ethers and alkanes because alkanes do not react with dilute acids.

3. Reaction with Lewis acids (formation of coordination complexes). Being Lewis bases, ethers form coordination complexes with Lewis acids such as BF_3 , AlCl_3 , FeCl_3 , etc. These complexes are called **etherates**.



Similarly, diethyl ether reacts with Grignard reagent forming Grignard reagent etherate.

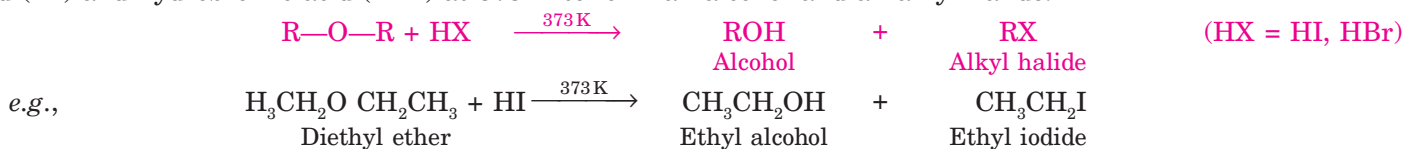


Due to the formation of the etherate, Grignard reagents dissolve in ether. That is why Grignard reagents are usually prepared in ethers. However, they cannot be prepared in benzene, because benzene has no lone pair of electrons and therefore, cannot form complexes with them.

B. Reactions Involving Cleavage of C—O Bond

Ethers are the least reactive of the functional groups. Carbon-oxygen bond in ethers can be cleaved under drastic conditions as given below :

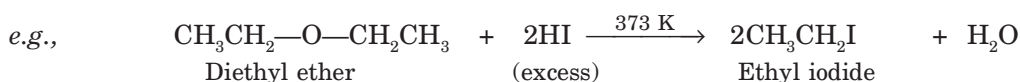
1. Cleavage by halogen acids. The carbon-oxygen bond in ethers can be cleaved by heating with hydroiodic acid (HI) and hydrobromic acid (HBr) at 373 K to form an alcohol and an alkyl halide.



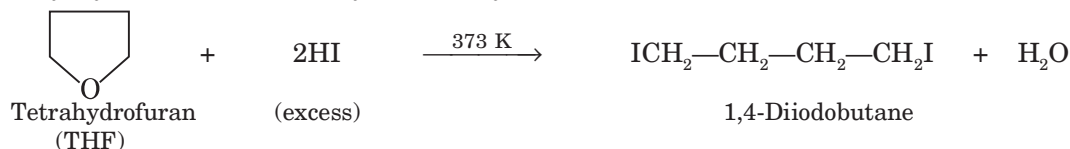
However, if excess acid is used, the alcohol first formed reacts further with the halogen acid to form alkyl halide.



The overall reaction may be written as :



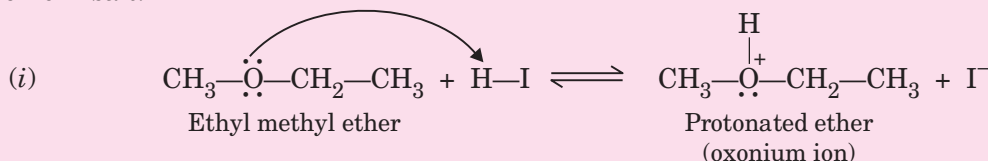
Similarly, cyclic ethers are easily cleaved by HBr or HI to form dihaloalkanes.



Mechanism : Cleavage of C—O bond in ethers by halogen acids.

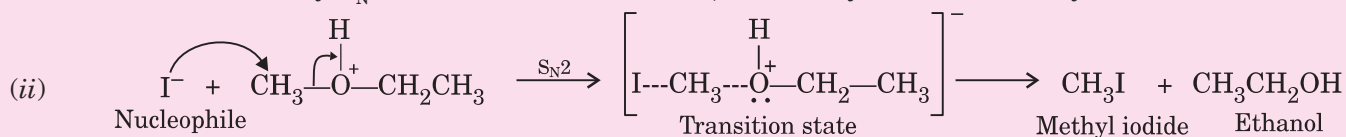
The cleavage reaction follows the following mechanism:

1. The ether molecule being Lewis base gets protonated by the hydrogen of the acid to form protonated ether or oxonium salt.

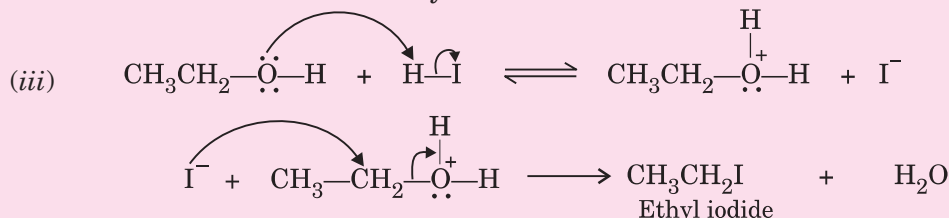


The reaction takes place with HBr and HI because these reagents are sufficiently acidic.

2. Iodide ion, I^- is a good nucleophile. The protonated ether undergoes nucleophilic attack by iodide ion (I^-) and displaces an alcohol molecule by $\text{S}_{\text{N}}2$ mechanism and therefore, forms alkyl alcohol and alkyl halide.



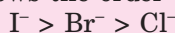
3. When HI is in excess and the reaction is carried out at high temperature, ethanol formed reacts with another molecule of HI and is converted into ethyl iodide :



The order of **reactivity of halogen acids** is :

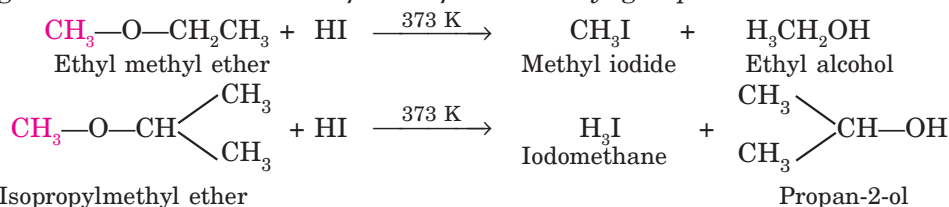


As discussed above, the cleavage of ethers by halogen acids involves nucleophilic attack by halide ion (X^-) on the protonated ether. Therefore, greater the nucleophilicity of the halide ion, more reactive is the halogen acid. As we know, nucleophilicity of the halide ions follows the order :

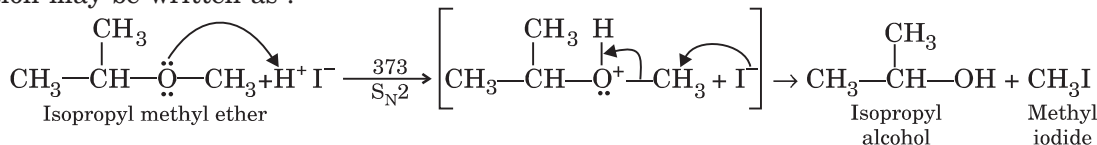


Therefore, the reactivity of the halogen acids follows the same sequence *i.e.*, $\text{HI} > \text{HBr} > \text{HCl}$

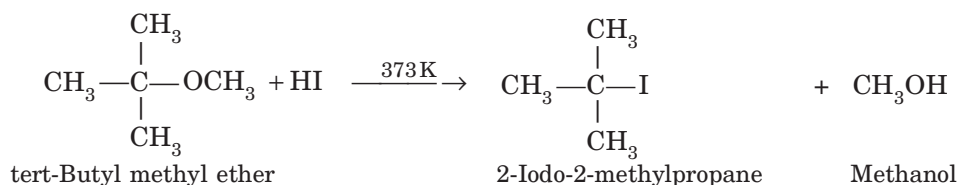
● **Cleavage of unsymmetrical alkyl ethers (site of cleavage).** In case of unsymmetrical ethers having two different alkyl groups, the alcohol and the alkyl halide formed, depend upon the nature of the alkyl groups. If primary and secondary alkyl groups are present then the reaction occurs by **$\text{S}_{\text{N}}2$ mechanism**. The halide ion attacks the smaller alkyl group because of less steric hindrance. Thus, in case of *unsymmetrical ethers with two different alkyl groups, the site of cleavage is such that the halide is formed from the alkyl group which is smaller in size*. For example,



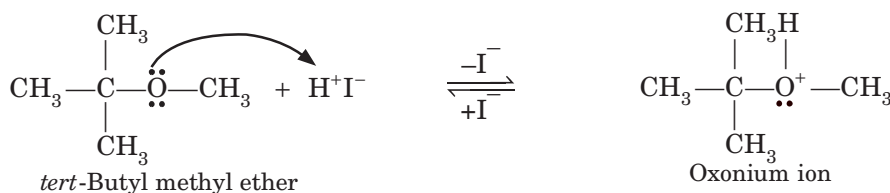
The reaction may be written as :

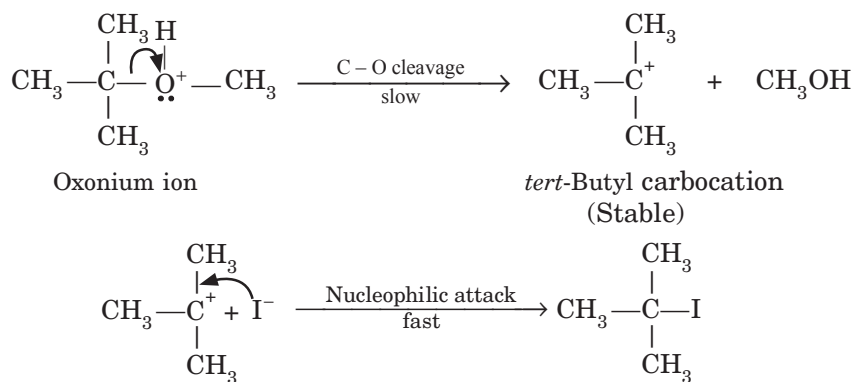


If, however, one of the alkyl groups is tertiary group, the alkyl halide is formed from the tertiary alkyl group.

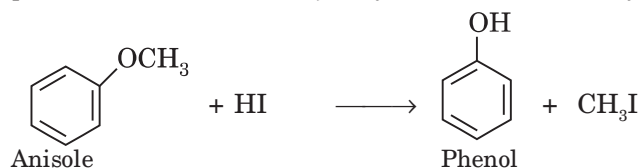


This is because the reaction now occurs by **$\text{S}_{\text{N}}1$ mechanism**. The formation of products is governed by the stability of the carbocation formed from the cleavage of C—O bond in the protonated ether (oxonium ion). Since *tert*-butyl carbocation $[(\text{CH}_3)_3\text{C}^+]$ is more stable than the methyl carbocation (CH_3^+), therefore, cleavage of C—O bond gives a more stable carbocation $[(\text{CH}_3)_3\text{C}^+]$ and methanol. Then, iodide ion, I^- attacks this *tert*-butyl carbocation to form *tert*-butyl iodide.





● **Cleavage of alkyl aryl (phenolic) ether.** With **alkyl aryl ethers** (phenolic ethers) the cleavage with hydrogen halide always gives phenol and a molecule of alkyl halide and not aryl halide and alcohol.

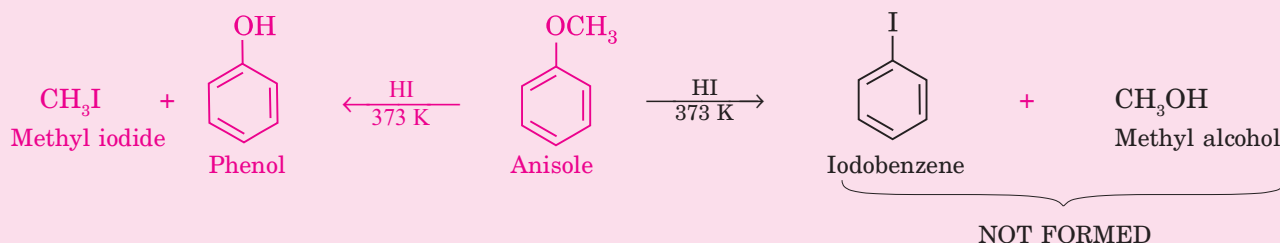
**NOTE**

Unlike alkyl alcohols, phenol does not react further with HI to give aryl halide because of strong carbon-oxygen bond in phenol.

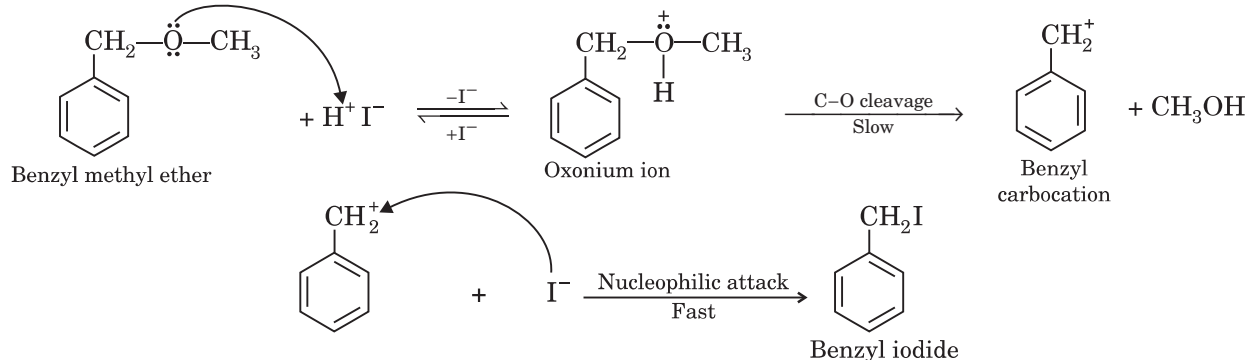
In case of anisole, methylphenyl oxonium ion, $\text{C}_6\text{H}_5 - \overset{+}{\text{O}}(\text{H}) - \text{CH}_3$ is formed by the protonation of ether. The bond

between $\text{O}-\text{CH}_3$ is weaker than the bond between $\text{O}-\text{C}_6\text{H}_5$ because the carbon of phenyl group is sp^2 hybridised and there is partial double bond character. Therefore, the attack of halide ion breaks $\text{O}-\text{CH}_3$ bond to form CH_3I . It may be noted that phenols do not react further to give halides because the sp^2 hybridised carbon of phenol does not undergo nucleophilic substitution reaction. This can also be explained on the basis of **steric hindrance**. The alkyl halide is formed by the attack of halide ion on the protonated ether. Therefore, the attack of halide ion occurs at smaller alkyl group which offers less hindrance.

Therefore, alkyl halide is formed from smaller alkyl group. Thus,

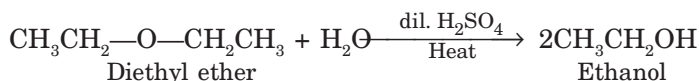
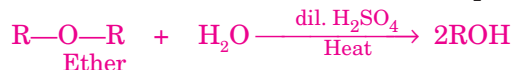


● **Cleavage of benzyl alkyl ethers.** In case of benzyl alkyl ethers containing a primary alkyl group such as benzyl methyl ether, the reaction proceeds by $\text{S}_\text{N}1$ mechanism. Since the benzyl carbocation is more stable than the methyl carbocation, the cleavage of $\text{C}-\text{O}$ bond gives benzyl carbocation and methyl alcohol. The halide ion then attacks carbocation to form benzyl iodide.

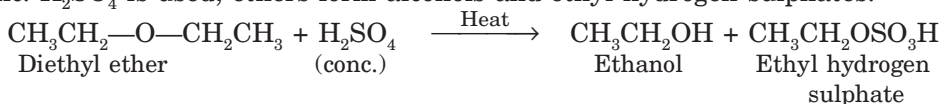


● **Cleavage of diaryl ethers.** It may be noted that diaryl ethers such as diphenyl ether are not cleaved by HI. This is because the $\text{C}-\text{O}$ bonds have some double bond character due to resonance between the lone pairs of electrons on the O atom and the C atoms of aryl groups (benzene ring) directly bonded to the O atom.

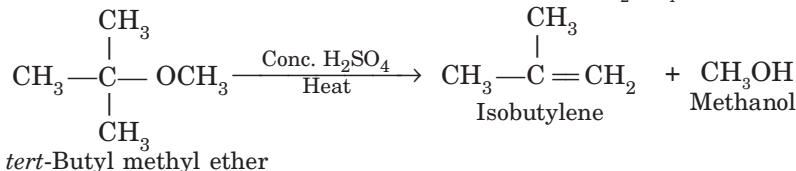
2. Cleavage by sulphuric acid. On heating with dil H_2SO_4 under pressure, ethers are hydrolysed to give alcohols.



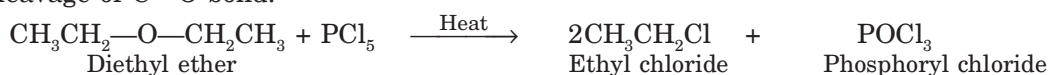
If conc. H_2SO_4 is used, ethers form alcohols and ethyl hydrogen sulphates.



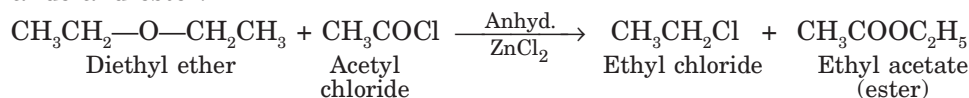
Secondary and tertiary ethers, however, form alkenes with conc. H_2SO_4



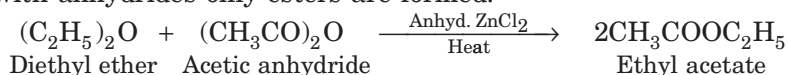
3. Cleavage with phosphorus pentachloride. Ethers react with PCl_5 on heating to form alkyl chloride as a result of cleavage of C—O bond.



4. Cleavage by acid chlorides. Ethers react with acetyl chloride in the presence of anhydrous ZnCl_2 to give alkyl halide and ester.

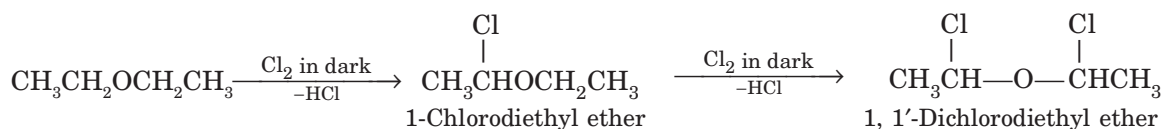


However, with anhydrides only esters are formed.

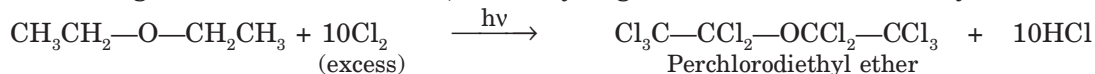


C. Reactions of Alkyl Group

1. Halogenation. Ethers react with chlorine or bromine in the dark to give substituted products. The extent of substitution depends upon the reaction conditions. For example, diethyl ether reacts with chlorine in the dark to give 1, 1-dichlorodiethyl ether in which the halogenation preferentially occurs at α -carbon atoms.



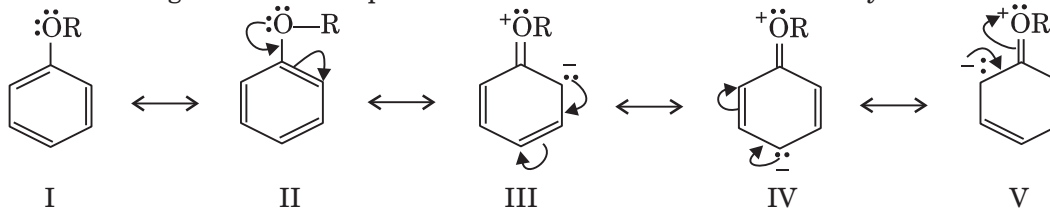
However, in the presence of light and excess of chlorine, all the hydrogen atoms are substituted by chlorine atoms.



D. Ring Substitution in Aromatic Ethers

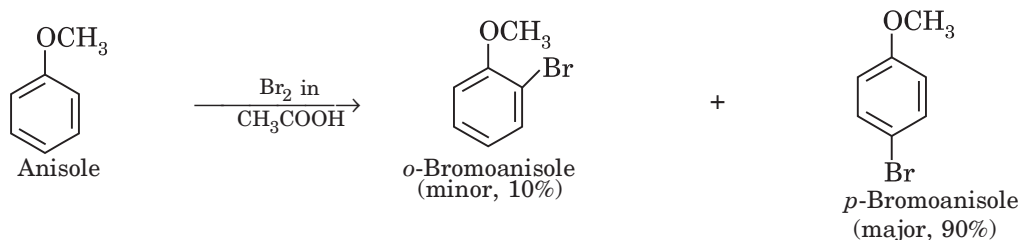
Alkoxy group is **ortho and para directing** and it directs the incoming groups to *ortho* and *para* positions.

It activates the aromatic ring towards electrophilic substitution reaction in the same way as in alcohols as given below :



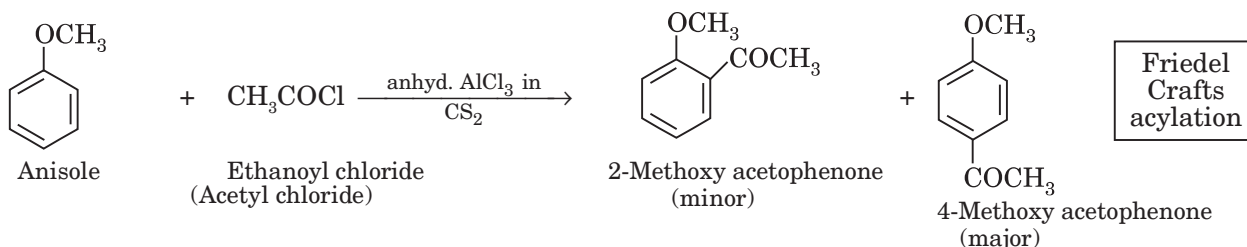
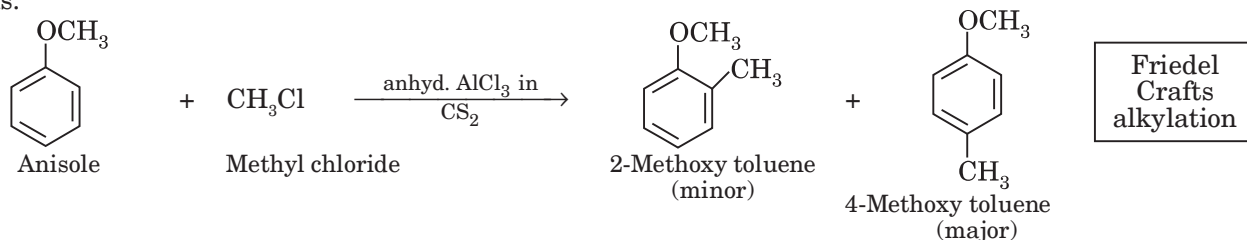
As is clear that structures III, IV and V show high electron density at *ortho* and *para* positions as compared to *meta* position. Therefore, electrophilic substitution reactions occur mainly at *o*- and *p*- positions.

1. Halogenation. Phenyl alkyl ethers undergo usual halogenation in the benzene ring. For example, bromination of anisole gives *ortho* and *para* bromo derivatives even in the absence of iron (III) bromide catalyst. It is due to the activation of benzene ring by methoxy group.

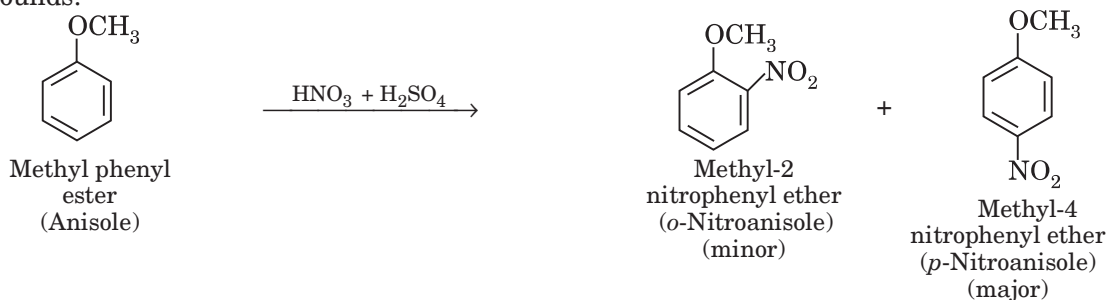


Para isomer is obtained in 90% yield.

2. Friedel Crafts reaction. Anisole undergoes **Friedel Craft alkylation** and acylation reaction in the presence of anhydrous aluminium halide (a Lewis acid) as catalyst in which alkyl and acyl groups are introduced at *ortho* and *para* positions.



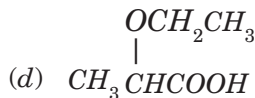
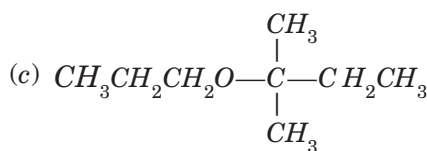
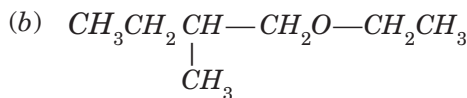
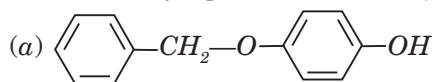
3. Nitration. When treated with a mixture of concentrated HNO_3 and H_2SO_4 , anisole gives a mixture of *o*- and *p*-nitro compounds.



It may, however, be noted that ethers are relatively **less reactive** than phenols towards electrophilic substitution reactions.

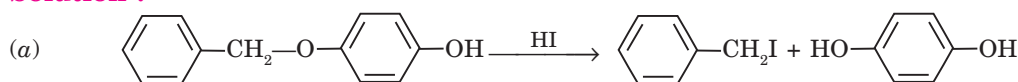
SOLVED EXAMPLES

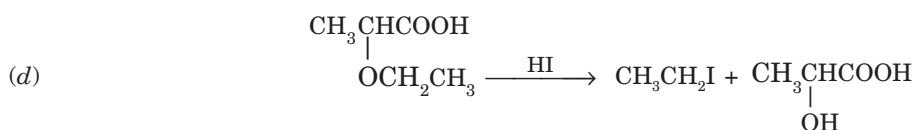
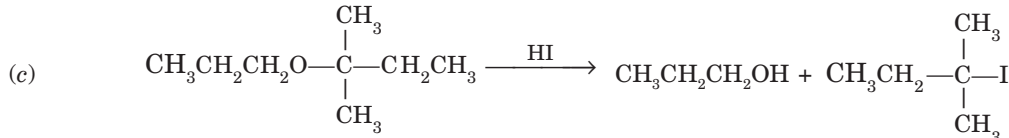
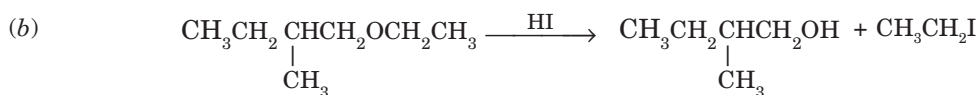
□ **Example 18.** Give the major products that are formed by heating each of the following ethers with HI .



N.C.E.R.T.

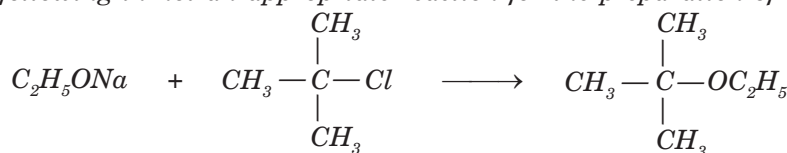
Solution :





 Example 19.

The following is not an appropriate reaction for the preparation of *t*-butyl ether :

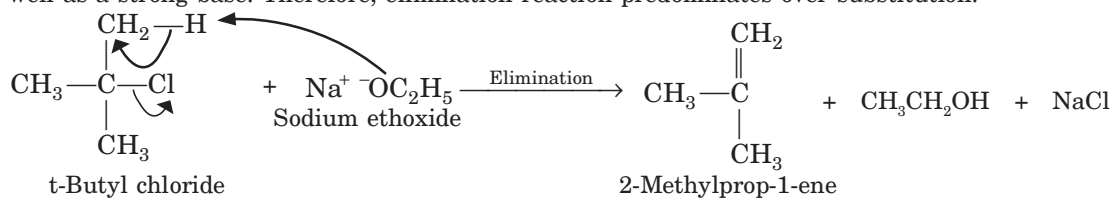


(i) What would be the major product of the reaction?

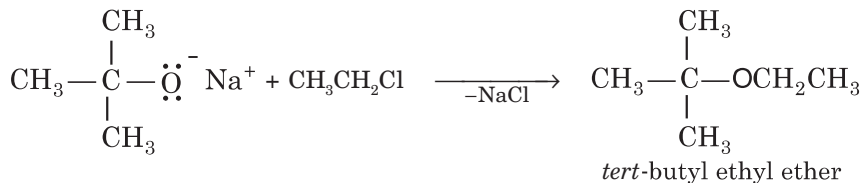
(ii) Write a suitable reaction for the preparation of tert-butyl ethyl ether.

N.C.E.R.T.

Solution : (i) The major product of the given reaction is 2-methylprop-1-ene. This is because sodium ethoxide is a strong nucleophile as well as a strong base. Therefore, elimination reaction predominates over substitution.



(ii) To prepare *tert*-butyl ethyl ether, the alkyl halide should be 1° (chloroethane) and the nucleophile should be sodium *tert*-butoxide.

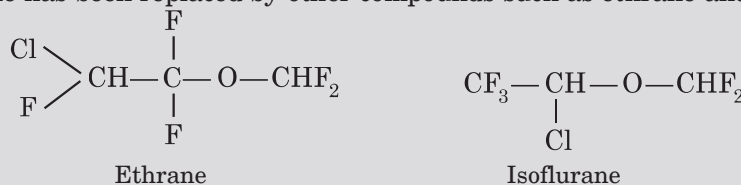


USES OF ETHERS

Ethers are widely used as a solvents both in laboratory as well as in industry because of their almost inert nature and good dissolving power. Among these diethyl ether is very common. The important uses of **diethyl ether** are :

1. Diethyl ether is an industrial solvent for oils, fats, gums, resins, etc.
2. It is used in surgery as an anaesthetic.

Ethoxy ethane has widely been used as an inhalation anaesthetic. However, because of its slow effect and unpleasant recovery period, ethoxy ethane has been replaced by other compounds such as ethrane and isoflurane as anaesthetics.



3. It is also used as a refrigerant.
4. It is also used as a reaction medium in LiAlH_4 reductions and Grignard synthesis.
5. It is used as an extracting solvent in laboratory and industry.
6. When mixed with alcohol it acts as a denaturant and the mixture is used as petrol substitute under the trade name *Natalite*.
7. It is used in perfumery and in the manufacture of smokeless powder.

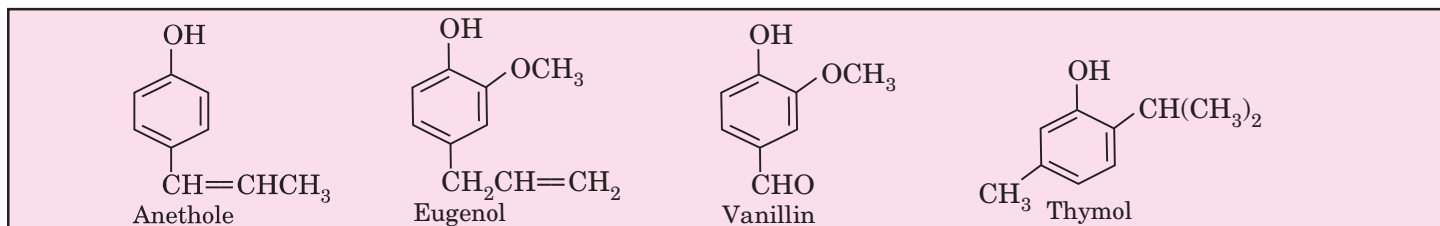
Dimethyl ether is used in the form of compressed liquid as a refrigerant, low temperature solvent and propellant for sprays. It is also used for storing food stuffs by freezing on direct contact because it does not leave any undesirable taste or smell.

Di-isopropyl ether is used as an industrial solvent and for reducing knocking of petrol.

Divinyl ether is used as an anaesthetic and is considered better than diethyl ether because of its rapid action and rapid recovery from anaesthesia.

Phenyl ether has been used as heat transfer medium because of its high boiling point (531 K).

A number of naturally occurring phenols and ethers, particularly ring substituted anisoles are used as flavouring and in perfumes because of their pleasant odour. For example, **anethole**—a constituent of anise seed, **eugenol**—present in oil of cloves, **vanillin**—present in oil of vanilla bean and **thymol**—present in thymine and mint are some common examples of phenols and ethers used in perfumes and flavourings.



add on

Conceptual Questions 2

Q. 1. Write the structure of phenyl isopentylether.

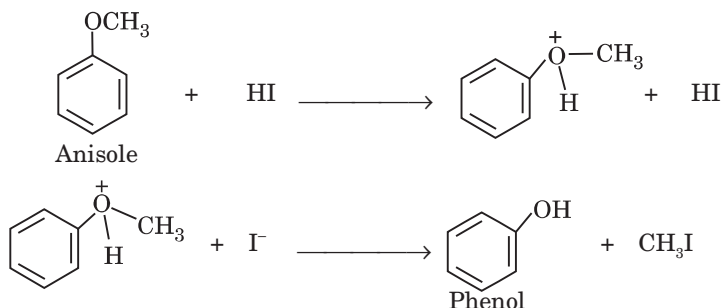
(CBSE Sample Paper 2011)

Ans. $\text{C}_6\text{H}_5\text{—O—CH}_2\text{—CH}_2\text{—CH(CH}_3\text{)—CH}_2\text{—CH}_3$

Q. 2. Anisole on reaction with HI gives phenol and CH_3I as main products and not iodobenzene and CH_3OH .

(A.I.S.B. 2016)

Ans. In this reaction protonated anisole i.e., methylphenyl oxonium ion is first formed and then the halide ion attacks this protonated anisole. Due to steric hindrance of bulky phenyl group, the attack preferably occurs to the alkyl group forming methyl iodide and phenol.

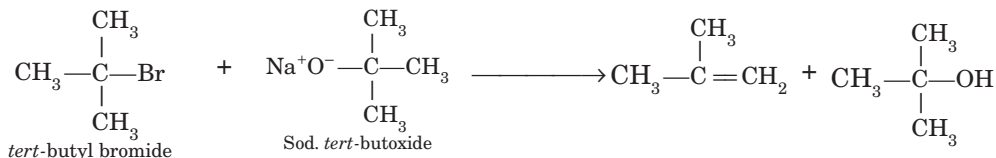


Q. 3. Why are ethers relatively inert compounds ?

Ans. Ethers are inert compounds because the functional group of ethers (—O—) does not contain any active site. Therefore, under ordinary conditions, they are stable to bases, dilute acids and other oxidising and reducing agents.

Q. 4. Why di-*tert*-butyl ether cannot be prepared by Williamson synthesis ?

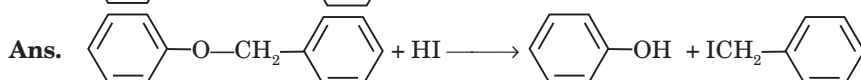
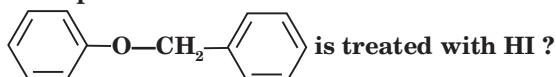
Ans. To prepare di-*tert*-butyl ether by Williamson's synthesis, we require *tert*-butyl bromide and sodium *tert*-butoxide. Since *tert*-butyl bromide is a 3° alkyl halide, it prefers to undergo elimination rather than substitution. Therefore, isobutylene is obtained as the product rather than di-*tert* butyl ether.



Q.5. Name the pair of alkyl halide and alkoxide for the preparation of ethyl *tert*. butyl ether.

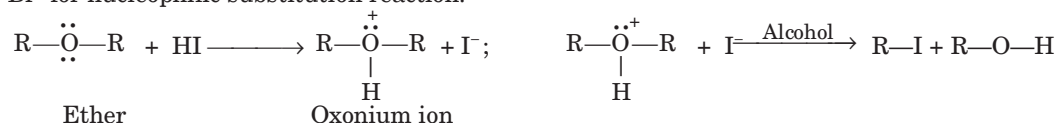
Ans. Ethyl iodide and sodium *tert* butoxide.

Q. 6. What products are obtained when



Q. 7. I is a better reagent than HBr for cleavage of ether. Explain.

Ans. HI is a stronger acid than HBr and therefore, oxonium ion is readily formed. I^- is also a better nucleophile than Br^- for nucleophilic substitution reaction.



Q. 8. The boiling points of ethers are lower than their corresponding isomeric alcohols. Explain.

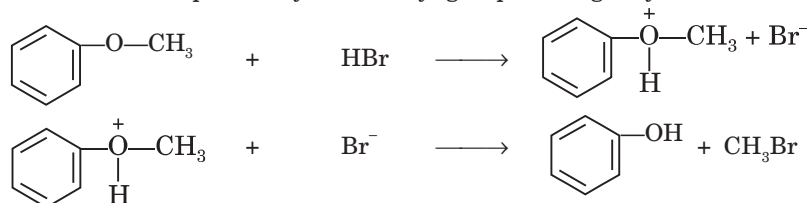
(A.I.S.B. 2012, Meghalaya S.B. 2015, Pb.S.B. 2017)

Ans. Ethers have low polarity and therefore, do not show any association by intermolecular hydrogen bonding. On the other hand, their isomeric alcohols have strong intermolecular hydrogen bonding and therefore, their boiling points are high.

Q. 9 Explain why cleavage of phenyl alkyl ethers with HBr always produces phenol and alkyl bromide and not bromobenzene and alkanols.

(A.I.S.B. 2010)

Ans. This is because during the reaction, the attack of halide ion occurs to the protonated ether. Due to steric hindrance of bulky phenyl group, the attack occurs preferably to the alkyl group forming alkyl bromide.



Q. 10. Ethers possess a dipole moment even if the alkyl radicals in the molecule are identical. Explain.

(Pb.S.B. 2012)

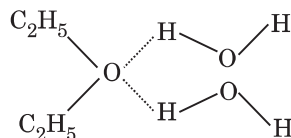
Ans. Ethers have angular structure similar to water, in which oxygen involves sp^3 hybridisation. Oxygen is surrounded by two O—R bonds and two lone pairs. Due to angular structure, ethers have dipole moment even if the two alkyl groups are identical because two C—O moments do not cancel each other. For example, dimethyl ether has dipole moment of 1.3 D.

Q.11. Why a non-symmetrical ether is not prepared by heating a mixture of ROH and R'OH in acid?

Ans. During this reaction, a mixture of three ethers, $\text{R}-\text{O}-\text{R}$, $\text{R}'-\text{O}-\text{R}'$ and $\text{R}-\text{O}-\text{R}'$ is obtained.

Q.12 How do you account for the miscibility of ethoxyethane with water ? (C.B.S.E. Sample Paper 2007)

Ans. Ethoxy ethane is miscible in water because of hydrogen bonding. Oxygen of ether can form hydrogen bonds with water molecules as :



Q. 13. Butan-1-ol has a higher boiling point than diethyl ether.

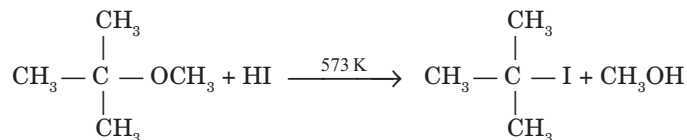
(A.I.S.B 2015)

Ans. Butan-1-ol has intermolecular hydrogen bonding between their molecules. Therefore, it exists as associated molecules and large amount of energy is required to break these bonds and hence its boiling point is high. But diethyl ether does not show any association by intermolecular hydrogen bonding. Hence, its boiling point is low.

Q.14. $(\text{C}_3)_3\text{C}-\text{O}-\text{CH}_3$ on reaction with HI gives $(\text{CH}_3)_3\text{C}-\text{I}$ and CH_3-OH as the main products and not $(\text{CH}_3)_3\text{C}-\text{OH}$ and CH_3-I .

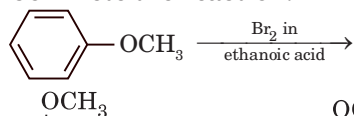
(A.I.S.B 2015)

Ans. The reaction:

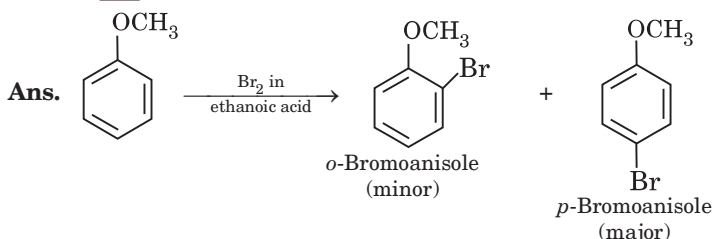


gives $(\text{CH}_3)_3\text{C}-\text{I}$ and CH_3OH as the main products and not $(\text{CH}_3)_3\text{COH}$ and CH_3I . This is because the reaction occurs by $\text{S}_{\text{N}}1$ mechanism and the formation of products is governed by the stability of carbocation formed from the cleavage of C—O bond in the protonated ether. Since *tert.* butyl carbocation, $(\text{CH}_3)_3\text{C}^+$ is more stable than methyl carbocation, CH_3^+ therefore, the cleavage of C—O gives a more stable carbocation, $[(\text{CH}_3)_3\text{C}]^+$ and methanol. Then iodide ion, I^- attacks this *tert.* butyl carbocation to form *tert.* butyl iodide.

Q.15 Complete the reaction:



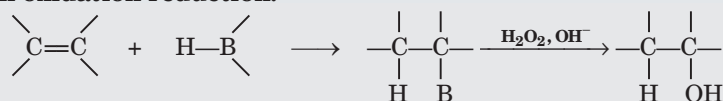
(Assam S.B. 2018)



Chapter Summary

Key Terms & Name Reactions

- **Esterification.** The reaction of alcohols and carboxylic acids in the presence of conc. H_2SO_4 to form esters.
- **Hydrogenolysis.** Catalytic hydrogenation is called hydrogenolysis.
- **Hydroboration oxidation reduction.**



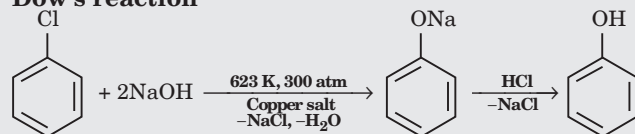
e.g., $\text{CH}_3\text{CH}=\text{CH}_2 \xrightarrow[\text{(ii) H}_2\text{O}_2, \text{OH}^-]{\text{(i) BH}_3, \text{THF}} \text{CH}_3-\text{CH}_2-\text{CH}_2\text{OH}$ (according to Anti-Markovnikov's rule)

- **Oxymercuration-demercuration reaction**

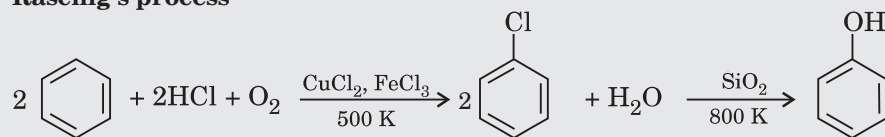


e.g., $\text{CH}_3-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}_2 \xrightarrow[\text{(ii) NaBH}_4]{\text{(i) Hg}(\text{OAc})_2, \text{THF}} \text{CH}_3\text{CH}_2-\text{C}(\text{CH}_3)(\text{OH})-\text{CH}_3$ (according to Markovnikov's rule)

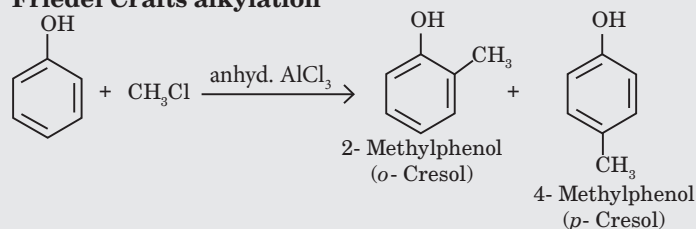
- **Dow's reaction**



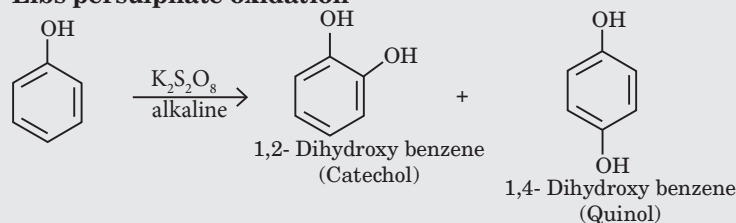
- **Raschig's process**



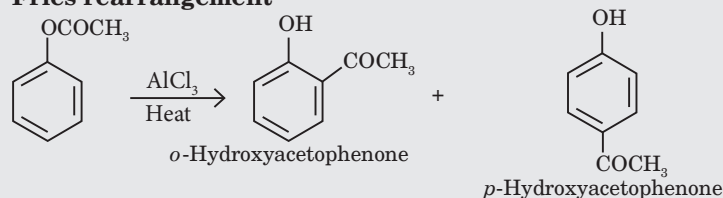
- **Friedel Crafts alkylation**



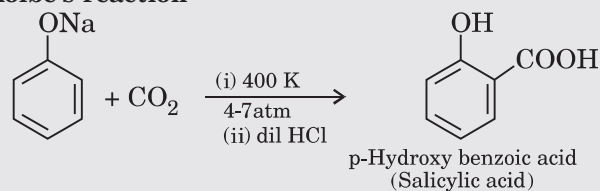
- **Elbs persulphate oxidation**



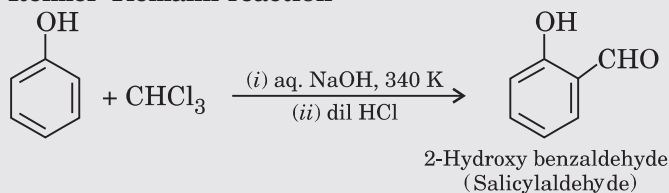
- **Fries rearrangement**



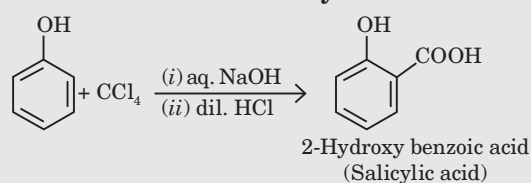
- Kolbe's reaction**



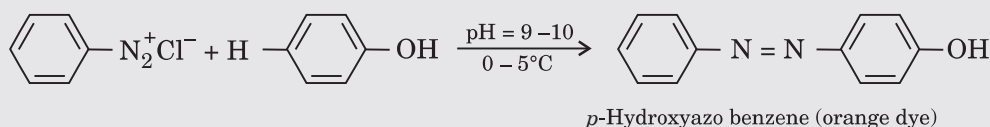
- Reimer Tiemann reaction**



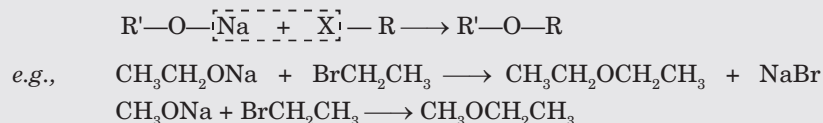
Carbon tetrachloride may also be used in place of chloroform.



- Coupling reactions**



- Williamson's synthesis**



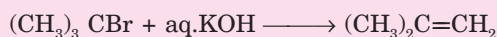
QUICK CHAPTER ROUND UP

Preparation of Alcohols

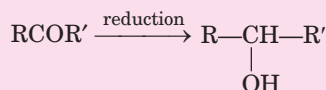
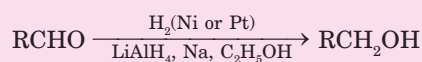
- Hydrolysis of alkanes



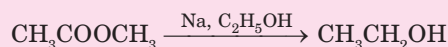
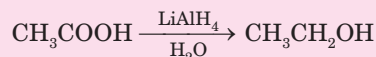
tert. alcohols give alkenes



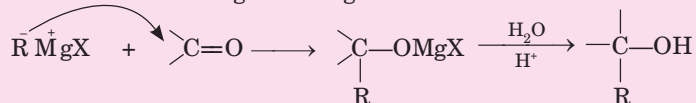
- Reduction of aldehydes/ketones



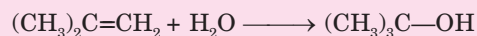
- Reduction of carboxylic acids/esters



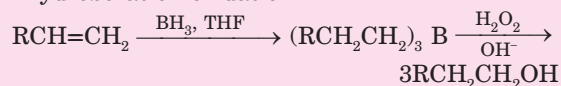
- From Grignard reagent



- From alkenes hydrolysis

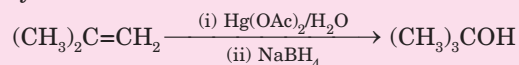


- Hydroboration-oxidation



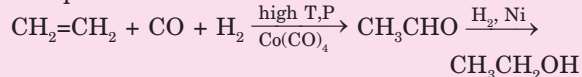
(anti-Markovnikov rule)

- Oxymercuration-demercuration



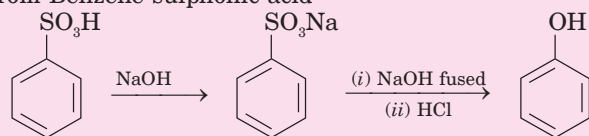
Markovnikov's addition reaction

- Oxo process

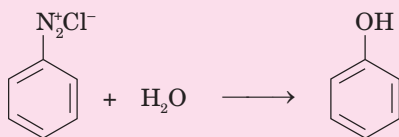


Preparation of Phenols

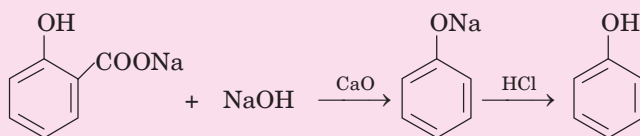
- From Benzene sulphonic acid



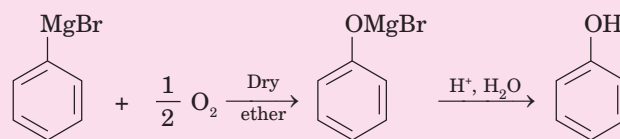
- From diazonium salt



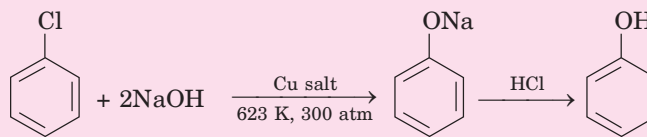
- By decarboxylation



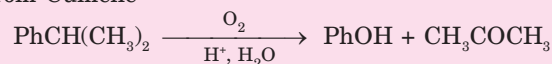
- From Grignard reagent



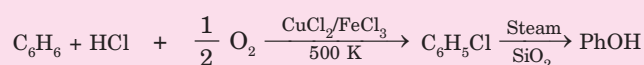
- Dow's process (Commercial)



- From Cumene



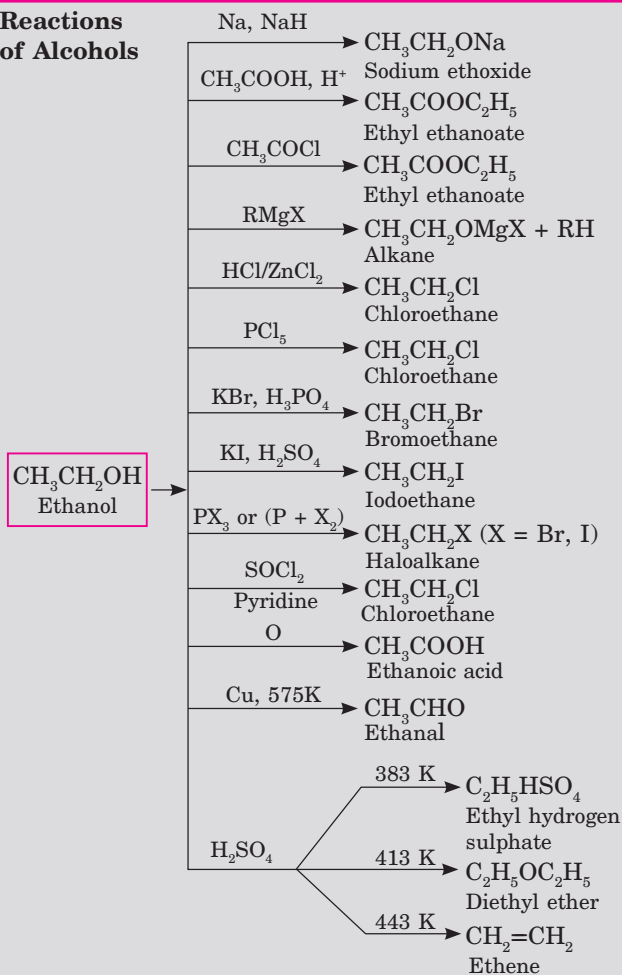
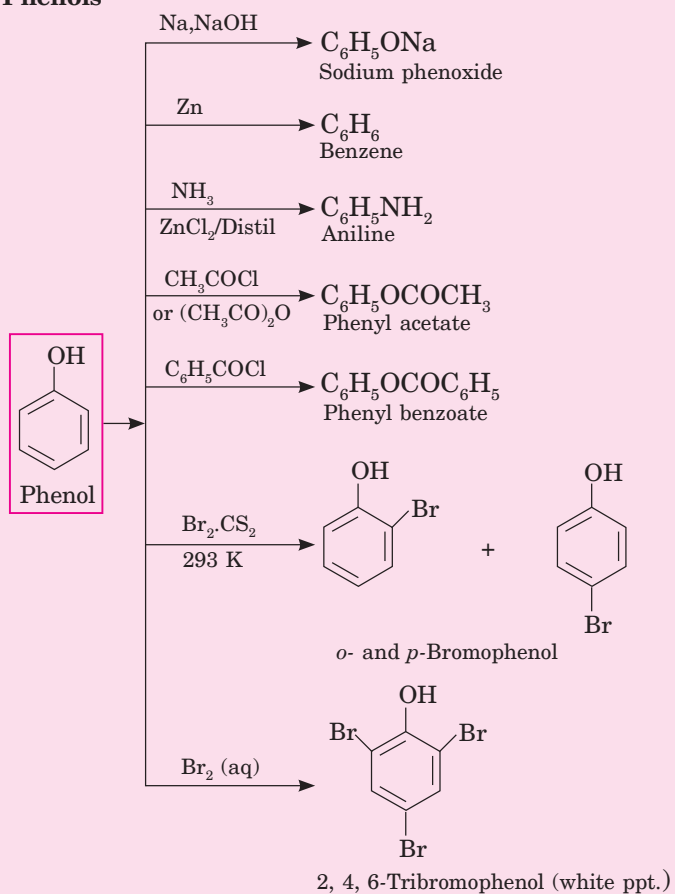
- Raschig's method

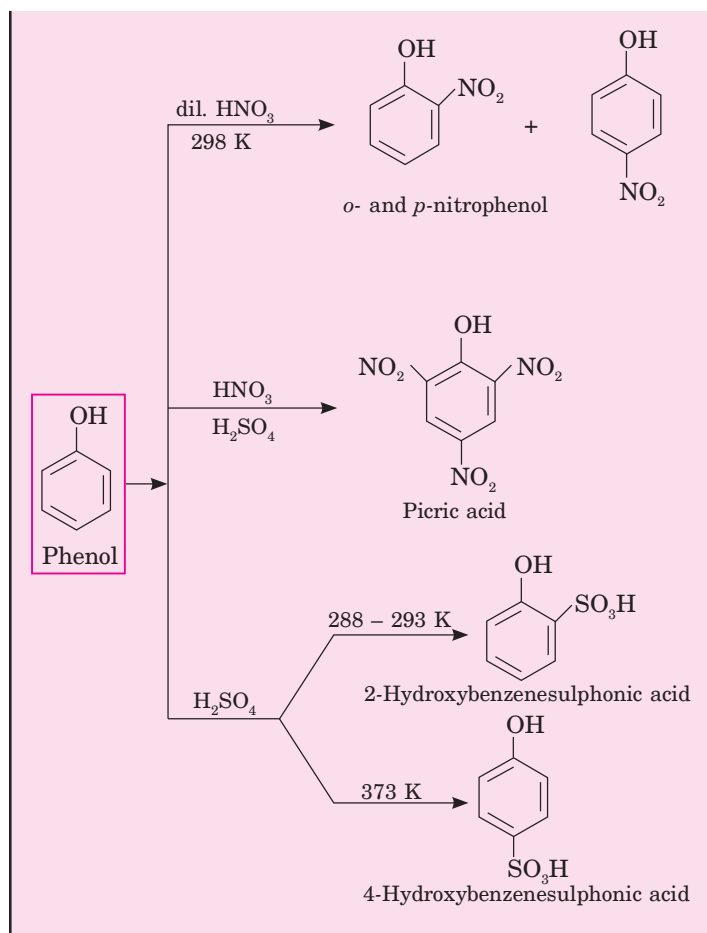


Alcohols are **weaker acids** than water

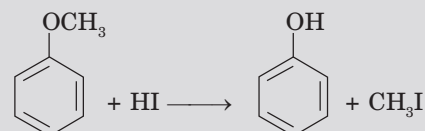
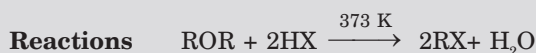
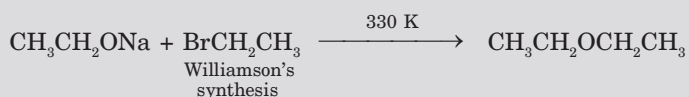
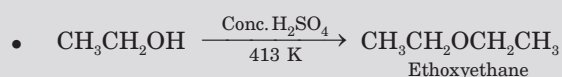
Phenol is **more acidic** than ethyl alcohol

- Electron withdrawing groups ($-\text{NO}_2$, $-\text{CN}$, X) **increase acidic strength**.
- Electron donating groups ($-\text{R}$, $-\text{NH}_2$, $-\text{OR}$) **decrease acidic strength**.

Reactions of Alcohols**Reactions of Phenols**

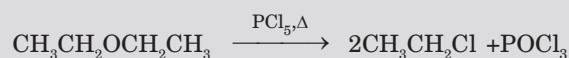
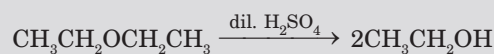


Ethers are called alkoxy alkanes.



• In alkyl aryl ethers, the products are always phenol and alkyl halide, and never an aryl halide and alcohol.

• Diaryl ethers such as diphenyl ethers are not cleaved by HI.



Alkoxy group is *o*- and *p*-directing group in electrophilic substitution reactions.



NCERT FILE

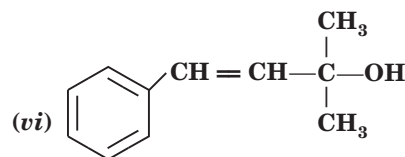
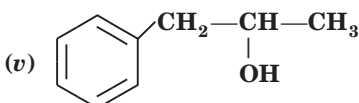
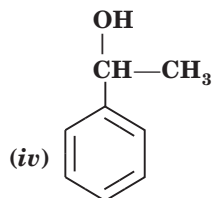
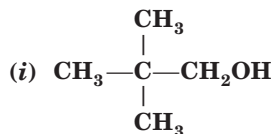
Solved



NCERT

In-text Questions

Q.1. Classify the following as primary, secondary and tertiary alcohols :

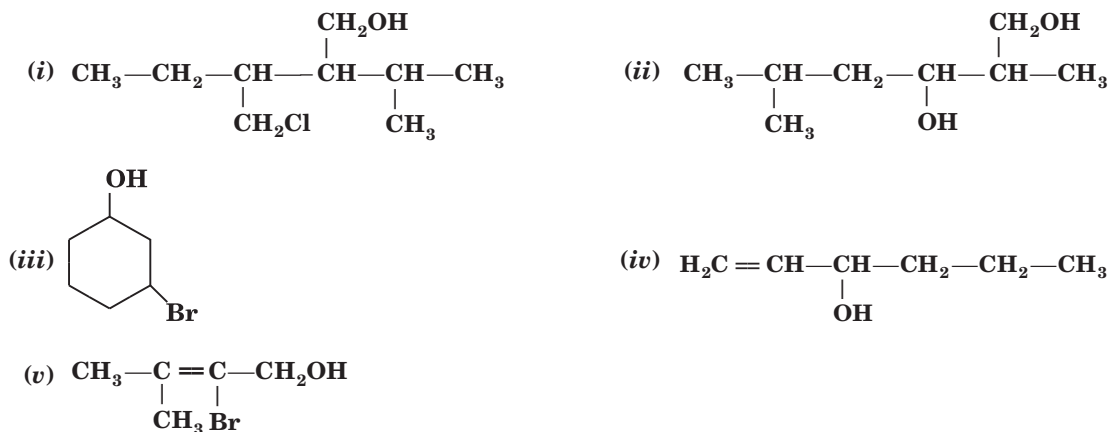


Ans. (i) Primary alcohol (ii) Primary alcohol (iii) Primary alcohol (iv) Secondary alcohol (v) Secondary alcohol (vi) Tertiary alcohol.

Q.2. Identify allylic alcohols in the above examples.

Ans. (ii) and (vi) are allylic alcohols.

Q.3. Name the following compounds according to IUPAC system :

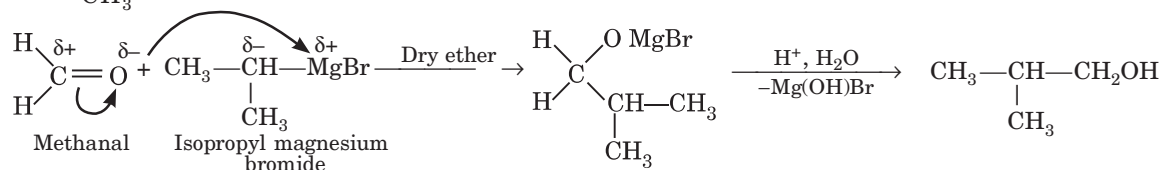


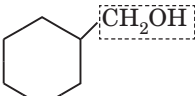
Ans. Refer Solved Example 2, page 8.

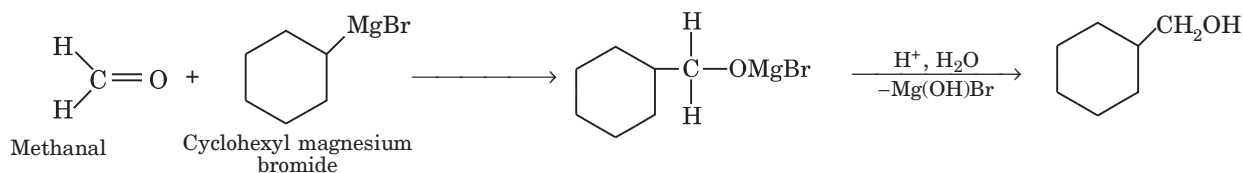
Q.4. Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal ?



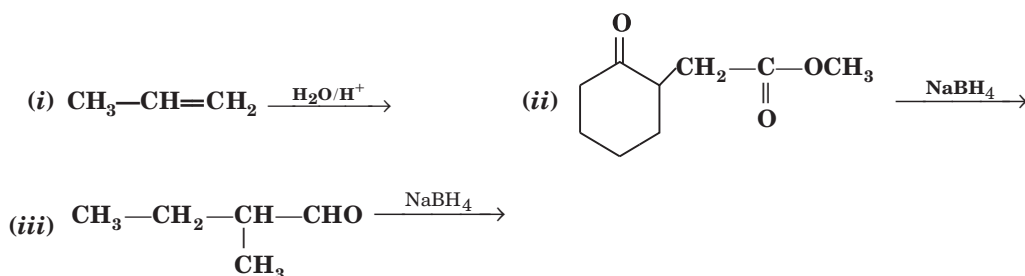
Ans. (i) $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\boxed{\text{CH}_2\text{OH}}$. The enclosed part comes from methanal and the remaining part comes from the Grignard reagent.



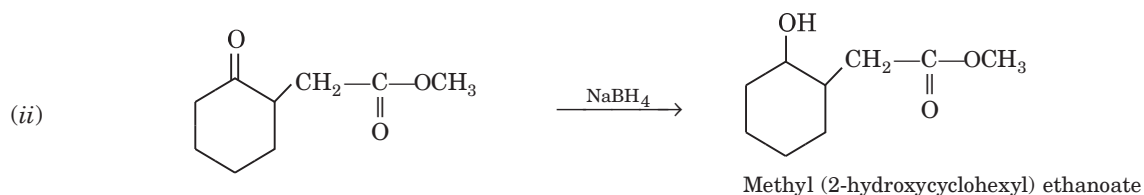
(ii) . The enclosed part comes from methanal and the remaining part from the Grignard reagent.



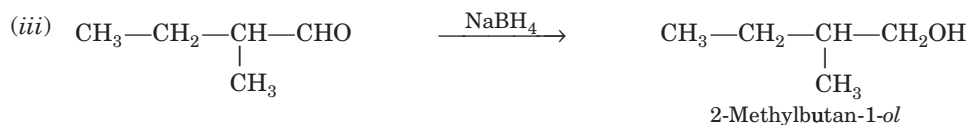
Q.5. Write structures of the products of the following reactions:



Ans. (i) $\text{CH}_3-\text{CH}=\text{CH}_2 \xrightarrow[\text{Markovnikov rule}]{\text{H}^+, \text{H}_2\text{O}} \text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$
Propan-2-ol

**HELP**

NaBH_4 is a weak reducing agent and reduces the aldehydes and ketones and not the esters.

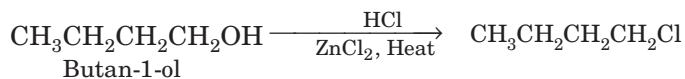


Q.6. Give structures of the products you would expect when each of the following alcohol reacts with (a) $\text{HCl}-\text{ZnCl}_2$, (b) HBr and (c) SOCl_2 .

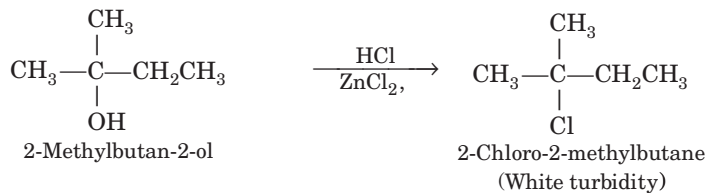
(i) Butan-1-ol

(ii) 2-Methylbutan-2-ol

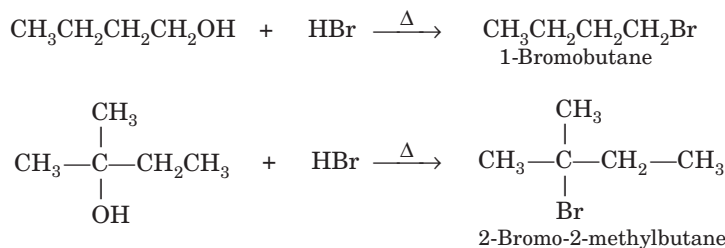
Ans. (a) $\text{HCl}-\text{ZnCl}_2$. It is Lucas reagent. Butan-1-ol does not react with $\text{HCl}-\text{ZnCl}_2$ at room temperature. However, turbidity appears only upon heating.



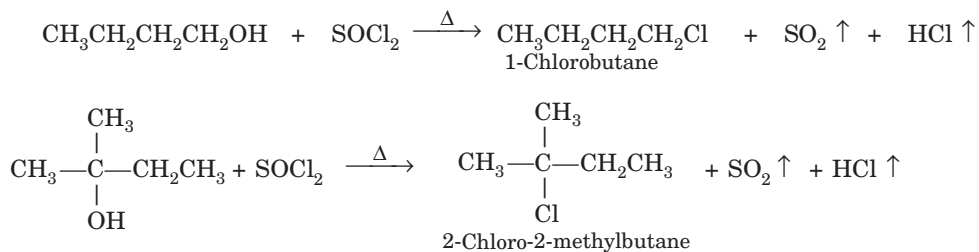
But 2-methylbutan-2-ol (3°) reacts at room temperature giving turbidity immediately.



(b) HBr . Both alcohols react with HBr to give corresponding alkyl bromides.

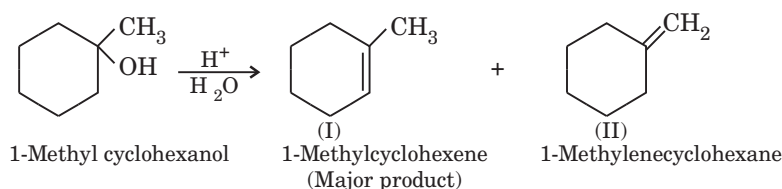


(c) SOCl_2 . Both alcohols react to give corresponding alkyl chlorides.

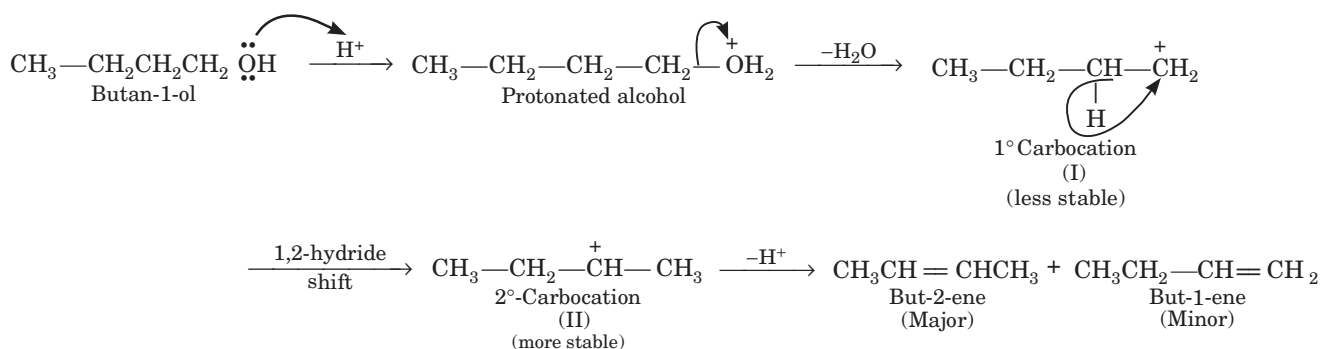


Q.7. Predict the major product of acid catalysed dehydration of (i) 1-methyl cyclohexanol and (ii) butan-1-ol

Ans. (i) Acid catalysed dehydration of 1-methylcyclohexanol gives two products I and II. But product I is highly substituted and hence, according to Saytzeff rule, is major product.

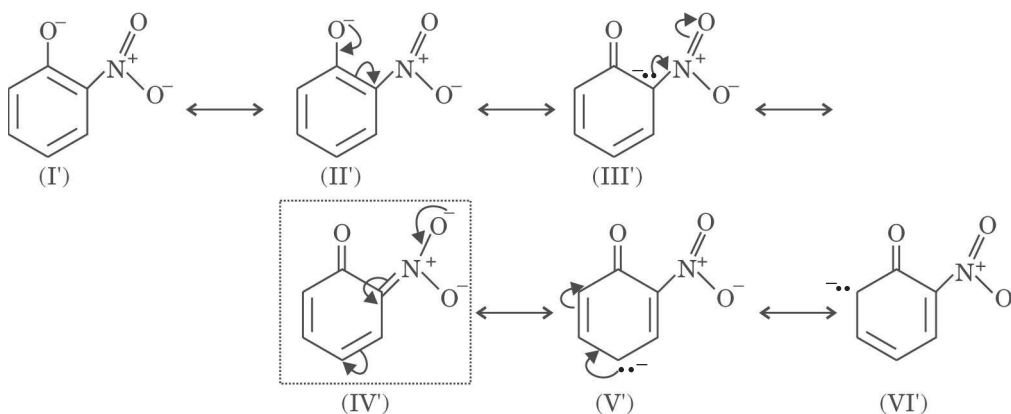
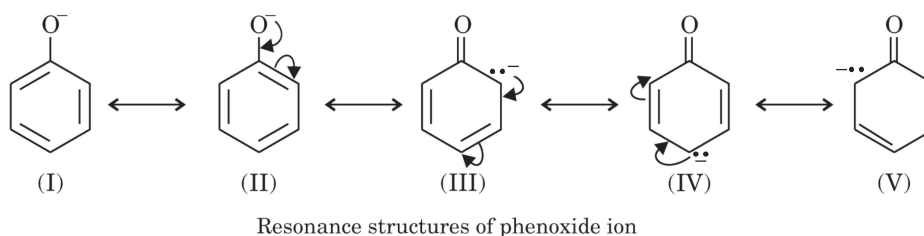


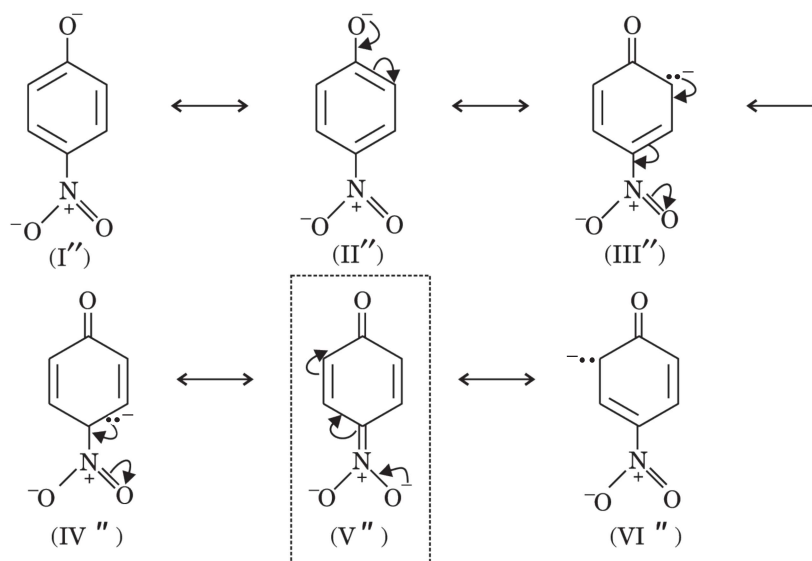
(ii) The acid-catalysed dehydration of butan-1-ol produces but-2-ene as the major product and but-1-ene as the minor product. This is because dehydration of alcohols occurs through the formation of carbocation intermediates. During the reaction, it first forms 1°-carbocation (I) which undergoes 1, 2-hydride shift to form 2°-carbocation (II). This then loses a proton to form more stable but-2-ene instead of but-1-ene. This is because but-2-ene is more stable and, according to Saytzeff rule, is preferably formed.



Q.8. Ortho and para nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.

Ans. The resonating structures of phenoxide ion and *ortho* and *para* nitrophenoxide ions are :



Resonance structures of *p*-nitrophenoxide ion

It is clear from the above structures that due to $-I$ effect of $-\text{NO}_2$ group, *o*- and *p*-nitrophenoxide ions are more stable because they have additional resonance structures (IV') and (V') than phenoxide ion. Hence, *o*- and *p*-nitrophenols are more acidic than phenol.

Q.9. Write the equations involved in the following reactions :

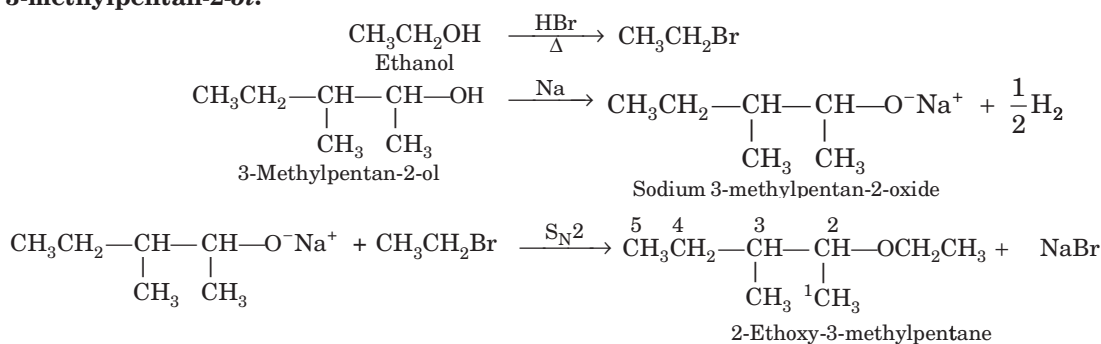
(i) Reimer Tiemann reaction

(ii) Kolbe's reaction

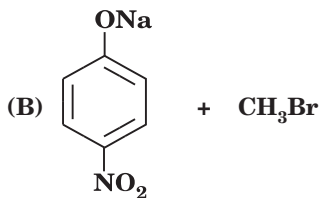
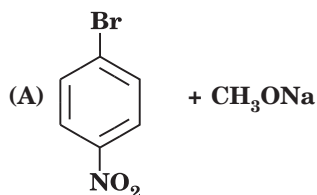
Ans. Refer special reactions of phenols (i) 2 and (ii) 1 (Text Book page 40–41).

Q.10. Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol.

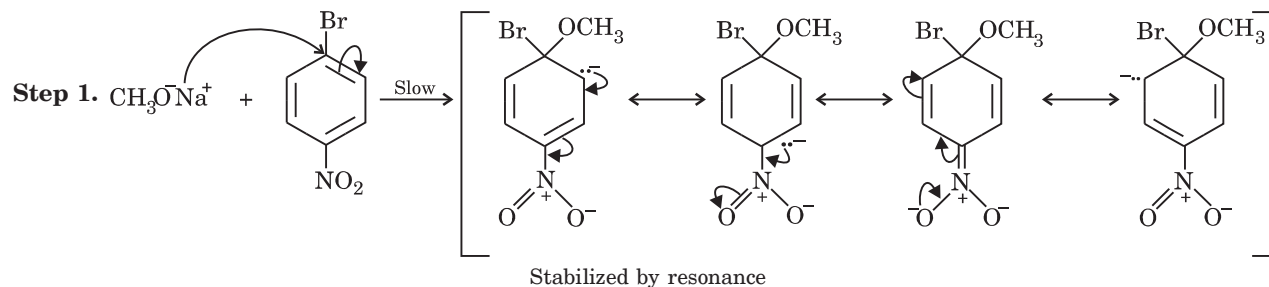
Ans.

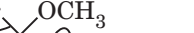


Q.11. Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why ?



Ans. Chemically both sets are equally probable. In set (A) the Br group is activated by the electron withdrawing effect of $-\text{NO}_2$ group. Therefore, nucleophilic attack of CH_3ONa followed by elimination of NaBr gives the desired ether.





 1-Methoxy-4-nitrobenzene

um 4-nitrophenoxide ion

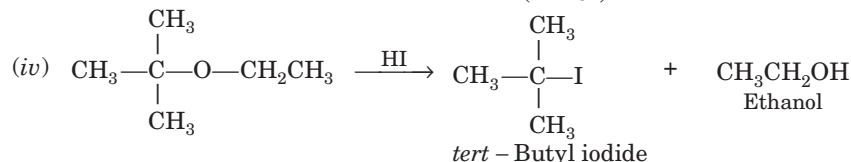
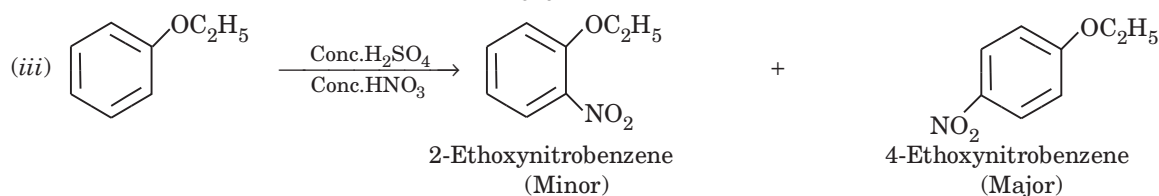
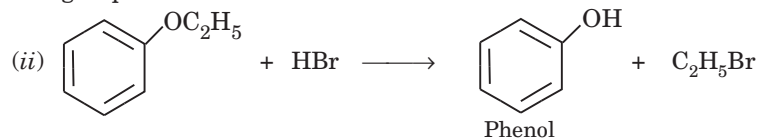
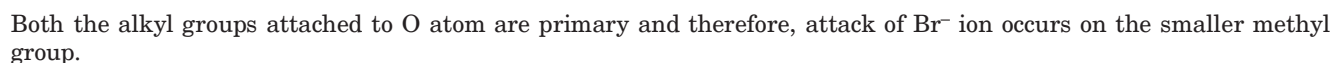
1-Methoxy-4-nitrobenzene

(i) $\text{CH}_3\text{---CH}_2\text{---CH}_2\text{---O---CH}_3 + \text{HBr} \longrightarrow$

(ii)  + $\text{HBr} \longrightarrow$

iii)  $\xrightarrow[\text{Conc. HNO}_3]{\text{Conc. H}_2\text{SO}_4}$

(iv) $(\text{CH}_3)_3\text{C---OC}_2\text{H}_5 \xrightarrow{\text{HI}}$

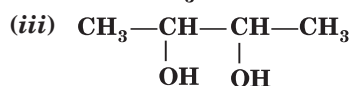
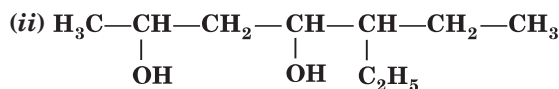


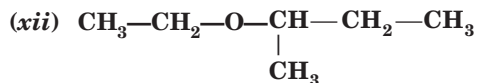
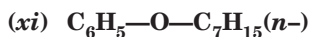
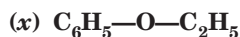
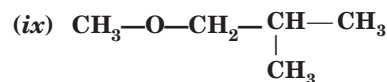
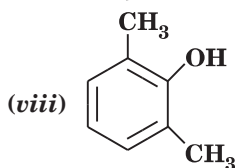
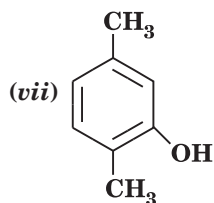
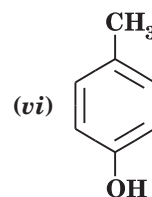
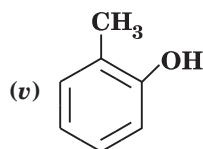
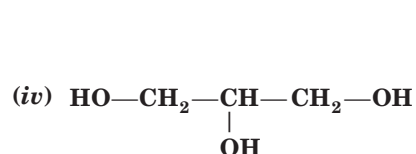
When one of the groups in unsymmetrical ether is tertiary, then the halide formed is tertiary halide.



NCERT

Textbook Exercises

$$(i) \text{ CH}_3 - \underset{\text{CH}_3}{\underset{|}{\text{CH}}} - \text{CH}_2 - \underset{\text{OH}}{\underset{|}{\text{CH}}} - \overset{\text{CH}_3}{\underset{\text{CH}_3}{\underset{|}{\text{C}}} - \text{CH}_3$$




Ans. (i) 2,2,4-Trimethylpentan-3-ol

(ii) 5-Ethylheptane-2,4-diol

(iii) Butane-2,3-diol

(iv) Propane-1,2,3-triol

(v) 2-Methylphenol

(vi) 4-Methylphenol

(vii) 2,5-Dimethylphenol

(viii) 2,6-Dimethylphenol

(ix) 1-Methoxy-2-methylpropane

(x) Ethoxybenzene

(xi) 1-Phenoxyheptane

(xii) 2-Ethoxybutane

Q.2. Write structures of the compounds whose IUPAC names are as follows :

(i) 2-Methylbutan-2-ol

(ii) 1-Phenylpropan-2-ol

(iii) 3, 5-Dimethylhexane-1, 3, 5-triol

(iv) 2, 3-Diethylphenol

(v) 1-E oxypropane

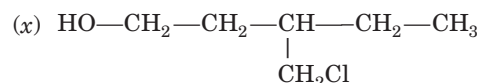
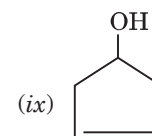
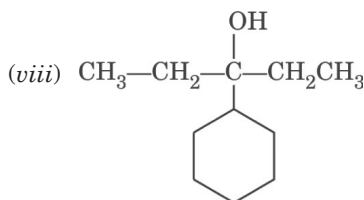
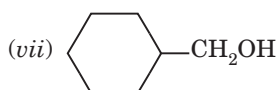
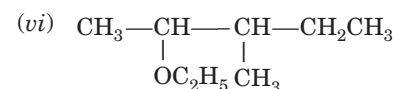
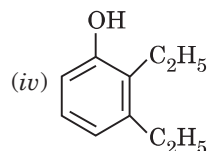
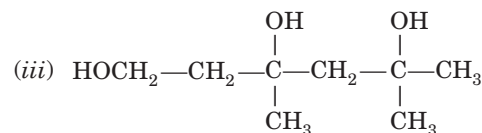
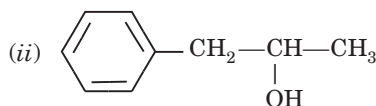
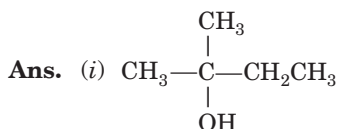
(vi) 2-E oxy-3-methylpentane

(vii) Cyclohexylmethanol

(viii) 3-Cyclohexylpentan-3-ol

(ix) Cyclopent-3-en-1-ol

(x) 3-Chloromethylpentan-1-ol



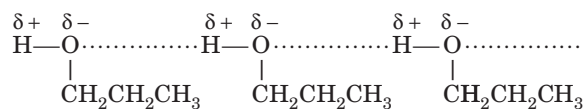
Q.3. (a) Draw the structures of all isomeric alcohols of molecular formula $\text{C}_5\text{H}_{12}\text{O}$ and give their IUPAC names.

(b) Classify the isomers of alcohols in question 3(a) as primary, secondary and tertiary alcohols.

Ans. Refer Solved Example 1. (Page 8)

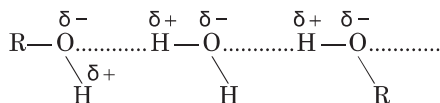
Q.4. Explain why propanol has higher boiling point than that of the hydrocarbon, butane ?

Ans. The molecules of propanol are held together by intermolecular hydrogen bonding while butane molecules have only weak van der Waals forces of attraction. Since hydrogen bonds are stronger than van der Waals forces, therefore, propanol has higher boiling point than butane.



Q.5. Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

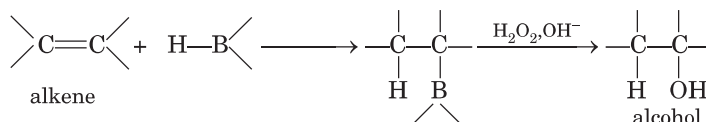
Ans. Alcohols can form hydrogen bonds with water and break the hydrogen bonds existing between water molecules. Hence, they are soluble in water.



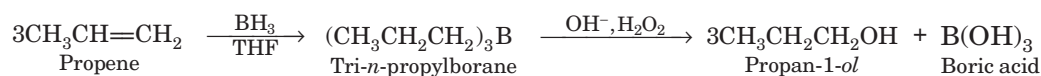
On the other hand, hydrocarbons cannot form hydrogen bonds with water molecules and hence are insoluble in water.

Q.6. What is meant by hydroboration-oxidation reaction ? Illustrate it with an example.

Ans. The addition of diborane to alkenes to form trialkylboranes followed by their oxidation with alkaline hydrogen peroxide to form alcohols is called hydroboration-oxidation reaction.

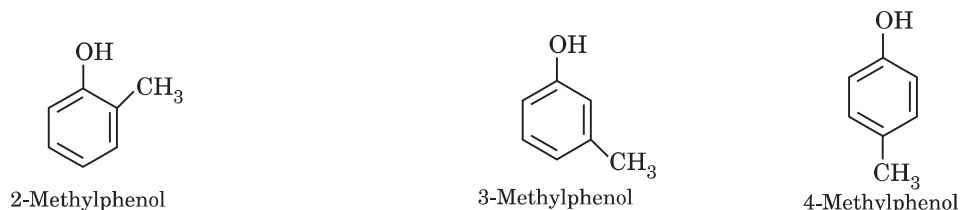


For example,



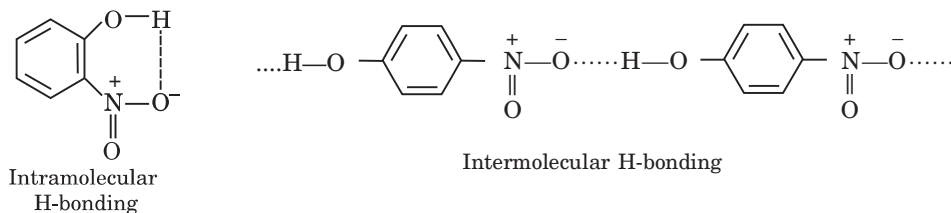
Q.7. Give the structures and IUPAC names of monohydric phenols of molecular formula, C₇H₈O.

Ans. Three isomers are possible

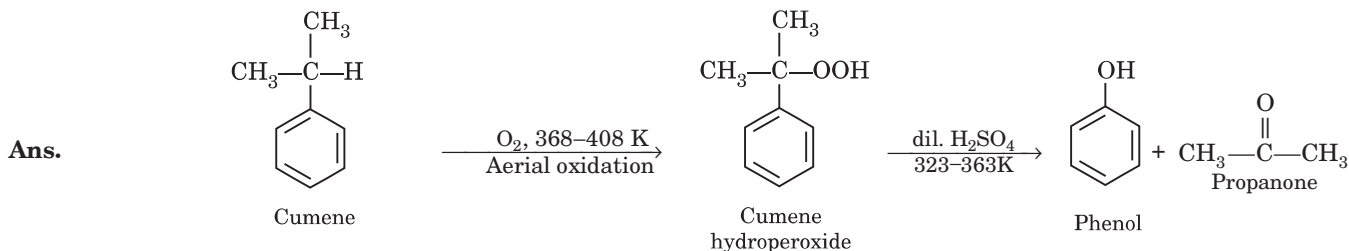


Q.8. While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

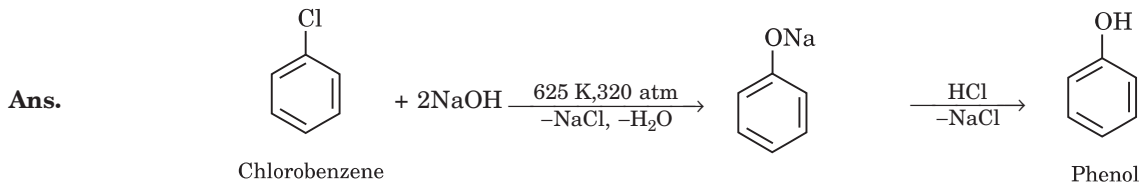
Ans. *o*-Nitrophenol is steam volatile due to chelation because of intramolecular hydrogen bonding. On the other hand, *p*-nitrophenol is not steam volatile because of intermolecular hydrogen bonding. Hence, *o*-nitrophenol can be separated from *p*-nitrophenol by steam distillation.



Q.9. Give the equations of reactions for the preparation of phenol from cumene.

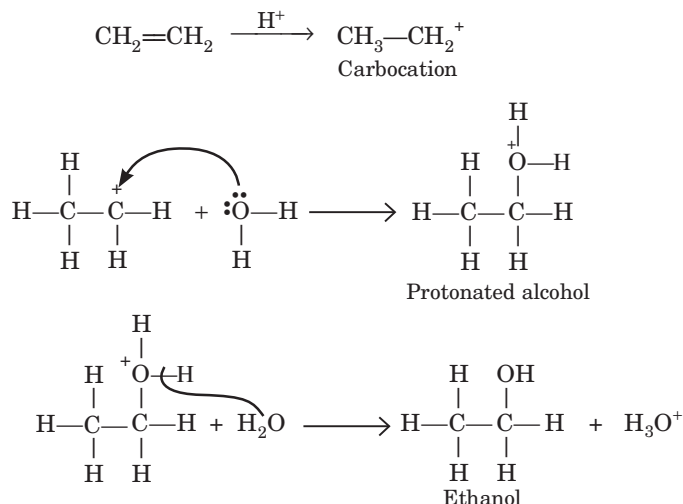
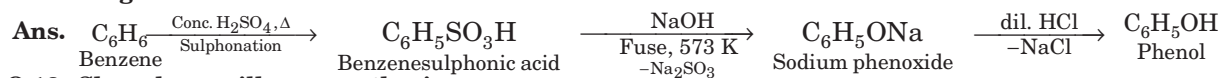


Q.10. Write chemical reaction for the preparation of phenol from chlorobenzene.

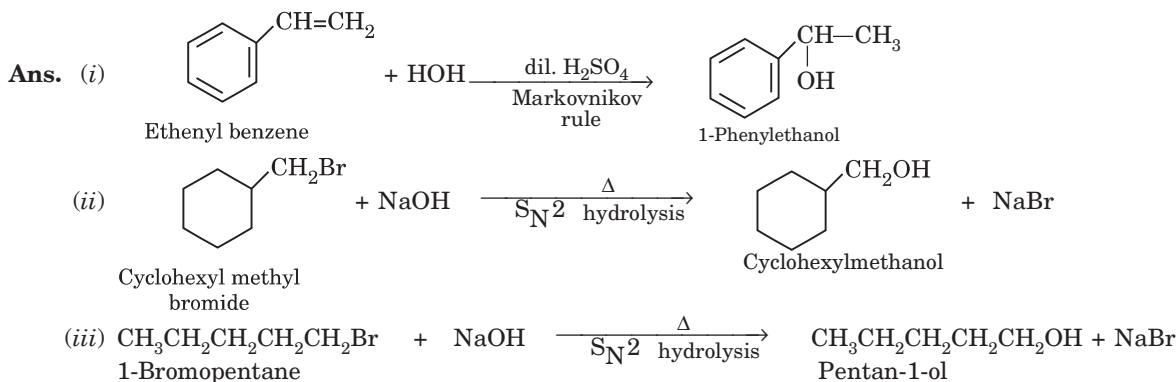


Q.11 Write the mechanism of hydration of ethene to yield ethanol.

Ans. It is an example of electrophilic addition. The water molecule with a little polarity is not in a position to give H^+ for the initial attack. Therefore, it is an acid catalysed reaction. The H^+ of the acid initially attacks the alkene to form carbocation, which then takes up an electron pair from H_2O molecule.

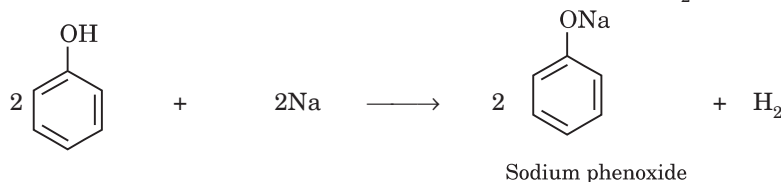
**Q.12. You are given benzene, conc. H_2SO_4 and NaOH . Write the equations for the preparation of phenol using these reagents.****Q.13. Show how will you synthesize**

- 1-phenylethanol from a suitable alkene,
- cyclohexylmethanol using an alkyl halide by an $\text{S}_\text{N}2$ reaction,
- pentan-1-ol using a suitable alkyl halide ?

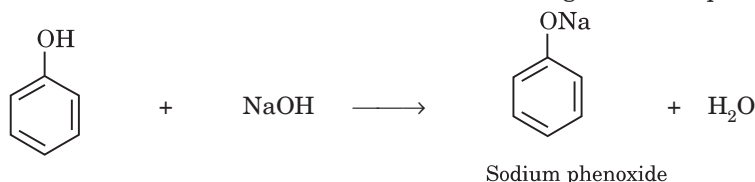
**Q.14. Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.**

Ans. The reactions showing acidic character of phenol are :

- (i) **Reaction with sodium.** Phenol reacts with sodium to give H_2 gas



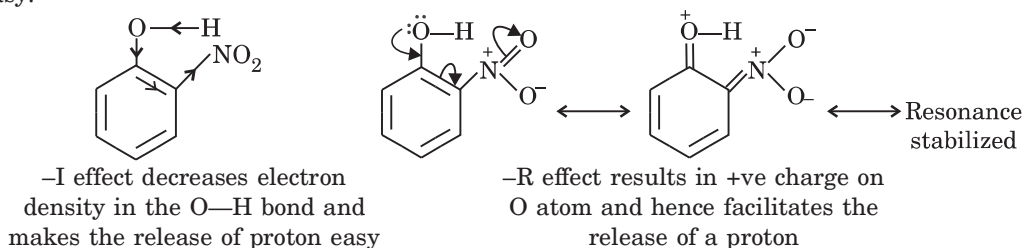
- (ii) **Reaction with NaOH .** Phenol dissolves in NaOH to give sodium phenoxide and water



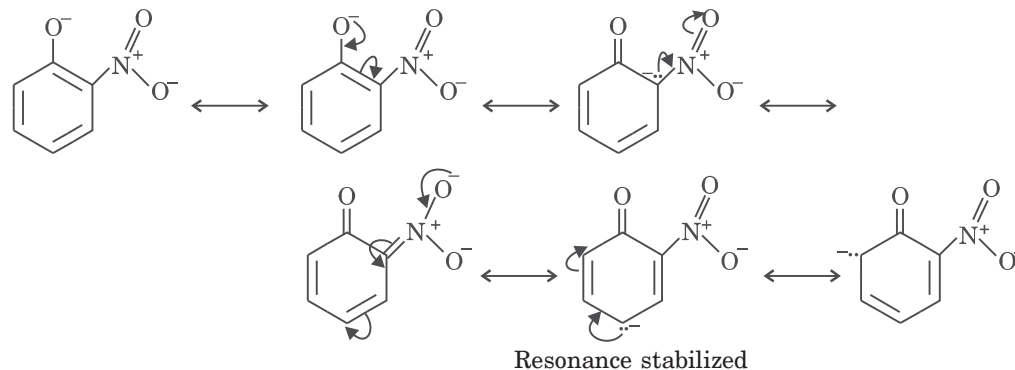
Phenol is more acidic than ethanol because of more resonance stabilized structures of phenoxide. Refer Text Book page 33–34.

Q.15. Explain why is *ortho* nitrophenol more acidic than *ortho* methoxyphenol ?

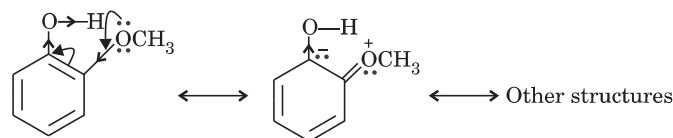
Ans. Due to strong $-R$ and $-I$ effect of $-\text{NO}_2$ group, electron density in $\text{O}-\text{H}$ bond decreases and hence the loss of a proton becomes easy.



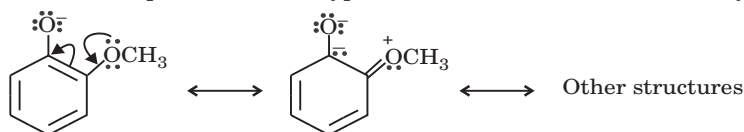
Moreover, the *o*-nitrophenoxide formed after the loss of a proton is stabilized by resonance.



o-nitrophenoxide ion is stabilized by resonance and hence *o*-nitrophenol is a stronger acid. On the other hand, due to $+R$ effect of the $-\text{OCH}_3$ group, the electron density in the $\text{O}-\text{H}$ bond increases and this makes the loss of proton difficult.



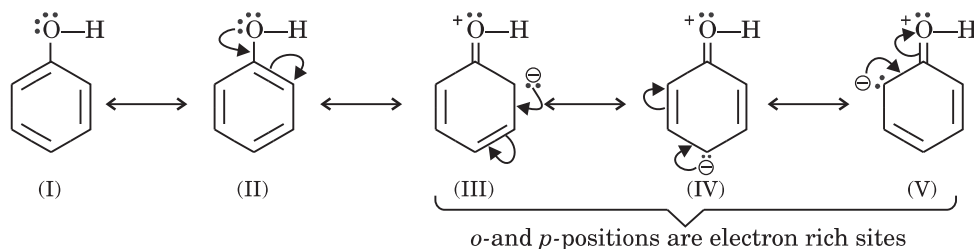
Furthermore, after the loss of proton *o*-methoxyphenoxide ion left is destabilized by resonance.



The two negative charges repel each other and therefore, destabilize the *o*-methoxyphenoxide ion. Thus, *o*-nitrophenol is more acidic than *o*-methoxyphenol.

Q.16. Explain how does the $-\text{OH}$ group attached to a carbon of benzene ring activate it towards electrophilic substitution ?

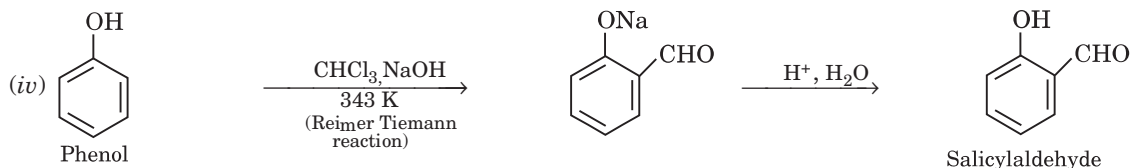
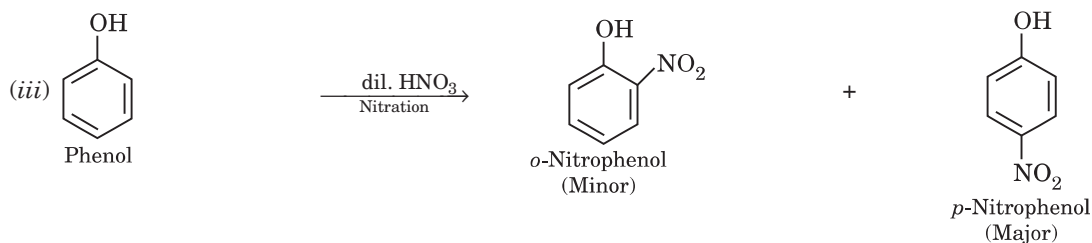
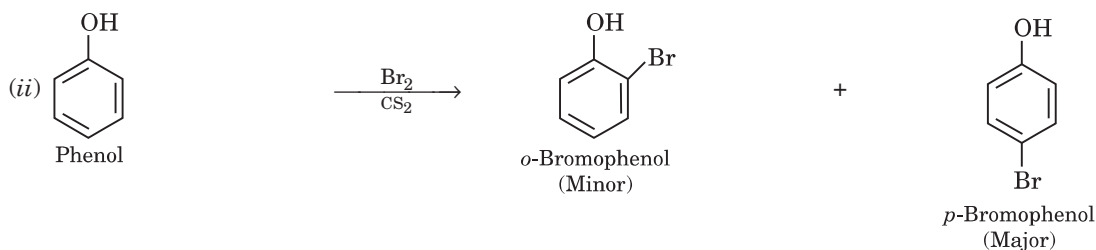
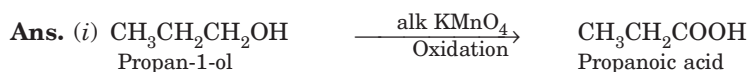
Ans. Phenol is a resonance hybrid of the following structures :



As a result of $+R$ effect of the OH group, the electron density in the benzene ring increases and thereby facilitating the attack of the electrophile. Hence, presence of OH group activates the benzene ring towards electrophilic substitution reaction. Thus, because the $-\text{OH}$ group is an activating group, these reactions occur at a faster rate than reactions of benzene itself. Further, it is clear from the resonating structures, the electron density is relatively higher at *o*-and *p*-positions and therefore, electrophilic substitution occurs preferentially at *o*-and *p*-positions. Thus, the $-\text{OH}$ group is ***ortho*-*para* directing** and therefore, incoming group comes at *ortho* or *para* position.

Q.17. Give equations of the following reactions :

- (i) Oxidation of propan-1-ol with alkaline KMnO_4 solution.
- (ii) Bromine in CS_2 with phenol.
- (iii) Dilute HNO_3 with phenol.
- (iv) Treating phenol with chloroform in presence of aqueous NaOH .



Q.18. Explain the following with an example :

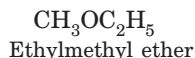
- (i) Kolbe's reaction
- (ii) Reimer-Tiemann reaction
- (iii) Williamson ether synthesis
- (iv) Unsymmetrical ether

Ans. (i) Refer special reactions of phenol, reaction 1 (Text Book Page 40)

(ii) Refer special reactions of phenols, reaction 2 (Text Book Page 41)

(iii) Refer general methods of preparation of ether, reaction 2 (Text Book Page 66)

(iv) If the alkyl or aryl groups attached to the O-atom of the ethers are different, ethers are called unsymmetrical ethers. For example,

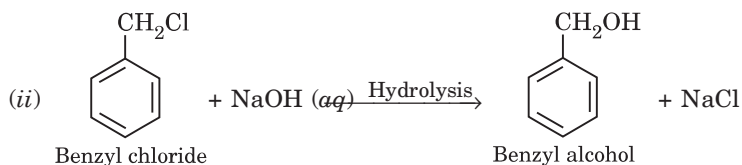
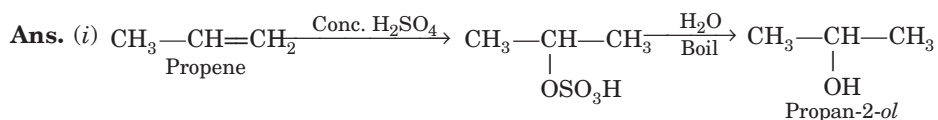


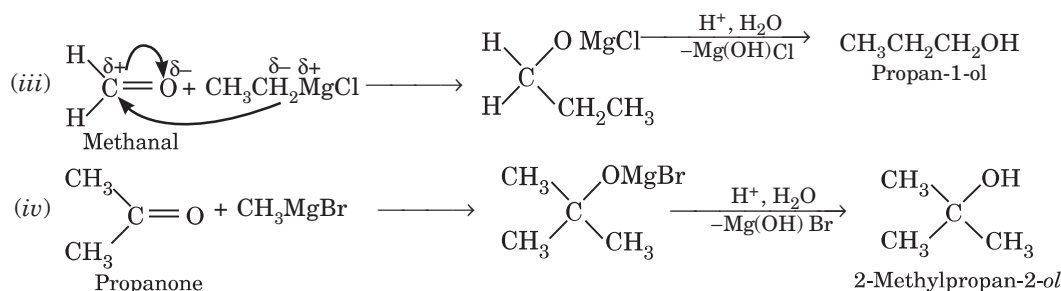
Q.19. Write mechanism of acid dehydration of ethanol to yield ethene.

Ans. Refer Text Book Page 29.

Q.20. How are the following conversions carried out ?

- (i) Propene $\longrightarrow$ Propan-2-ol
- (ii) Benzyl chloride $\longrightarrow$ Benzyl alcohol
- (iii) Ethyl magnesium chloride $\longrightarrow$ Propan-1-ol
- (iv) Methyl magnesium bromide $\longrightarrow$ 2-Methylpropan-2-ol





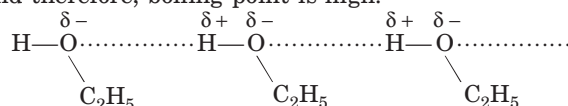
Q.21. Name the reagents used in the following reactions :

- Oxidation of a primary alcohol to carboxylic acid
- Oxidation of a primary alcohol to aldehyde
- Bromination of phenol to 2,4,6-tribromophenol
- Benzyl alcohol to benzoic acid
- Dehydration of propan-2-ol to propene
- Butan-2-one to butan-2-ol

Ans. (i) Acidified $K_2Cr_2O_7$ or $KMnO_4$
 (ii) Pyridinium chlorochromate (PCC) in CH_2Cl_2 or Pyridinium dichromate (PDC) in CH_2Cl_2 .
 (iii) Aqueous Br_2 i.e., Br_2/H_2O
 (iv) Acidified or alkaline $KMnO_4$ followed by hydrolysis with dil. H_2SO_4 .
 (v) Conc. H_2SO_4 at 443 K
 (vi) $NaBH_4$ or Ni/H_2

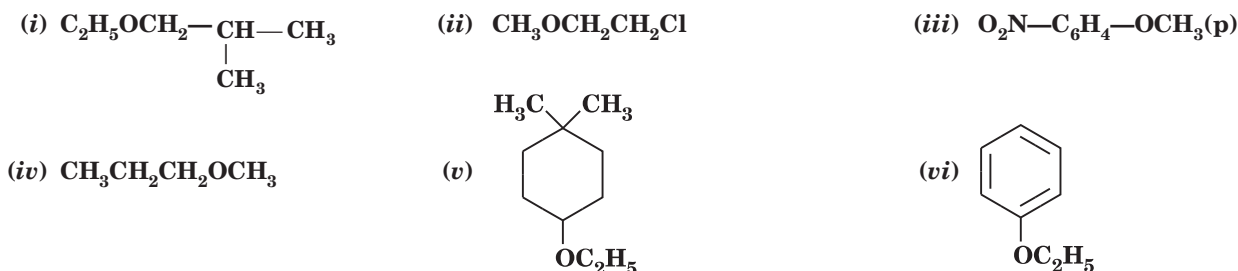
Q.22. Give reason for the higher boiling point of ethanol in comparison to methoxymethane.

Ans. The boiling point of ethanol is higher than methoxymethane because of the presence of strong intermolecular hydrogen bonding between ethanol molecules. Because of hydrogen bonding, energy has to be supplied to overcome the forces of attraction between molecules and therefore, boiling point is high.



However, no such hydrogen bonding exists in methoxymethane.

Q.23. Give IUPAC names of the following ethers :



Ans. (i) 1-Methoxy-2-methylpropane (ii) 2-Chloro-1-methoxyethane (iii) 4-Nitroanisole
 (iv) 1-Methoxypropane (v) 4-Ethoxy-1, 1-dimethylcyclohexane (vi) Ethoxybenzene

Q.24. Write the names of reagents and equations for the preparation of the following ethers by Williamson's synthesis:

- 1-Propoxypropane
- Ethoxybenzene
- 2-Methoxy-2-methylpropane
- 1-methoxyethane

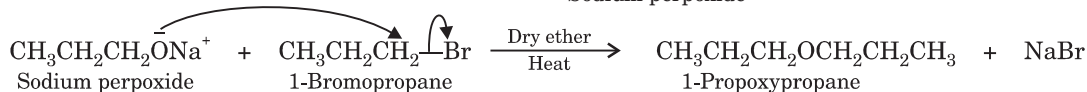
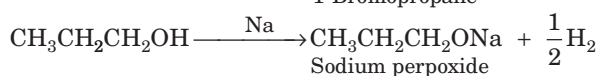
Ans. Refer Solved Example 17. (Page 67)

Q.25. Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.

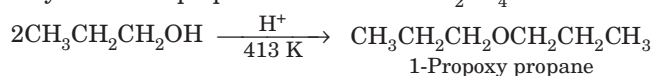
Ans. Refer Text Book Page 66)

Q.26. How is 1-propoxypropane synthesized from propan-1-ol ? Write mechanism of this reaction.

Ans. Williamson synthesis $CH_3CH_2CH_2OH \xrightarrow{P, Br_2} CH_3CH_2CH_2Br + H_3PO_3$
 1-Bromopropane

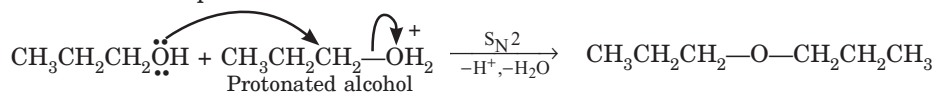


It can also be prepared by dehydration of propan-1-ol with conc. H_2SO_4 at 413 K.

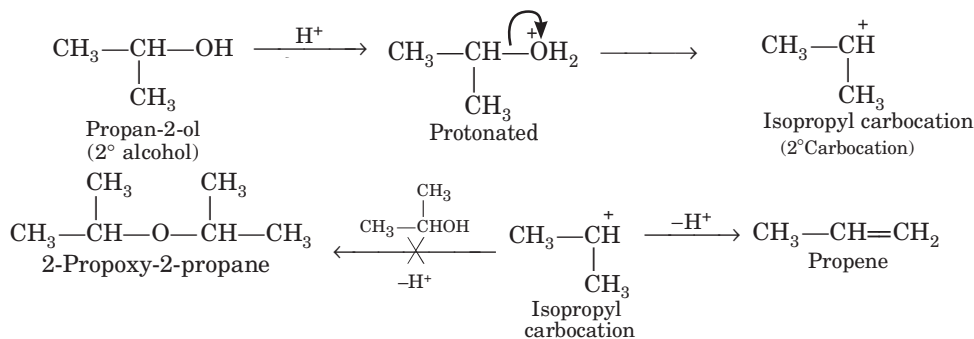


Q.27. Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

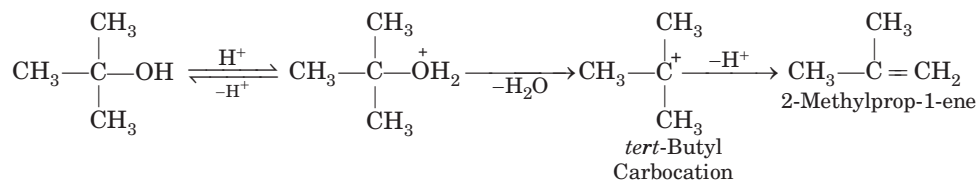
Ans. Acid-catalysed dehydration of 1° alcohols to ethers takes place by S_N2 reaction involving nucleophilic attack by the alcohol molecule on the protonated alcohol molecule as :



However, under these conditions, 2° and 3° alcohols give alkenes rather than ethers. This is because of the steric hindrance, nucleophilic attack by the alcohol on the protonated alcohol molecule does not take place. Instead of this, the protonated 2° and 3° alcohols lose a molecule of water to form stable 2° and 3° carbocations. These carbocations then prefer to lose a proton to form alkenes rather than undergoing nucleophilic attack by alcohol molecule to form ethers.

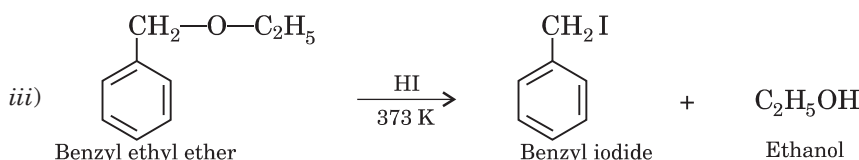
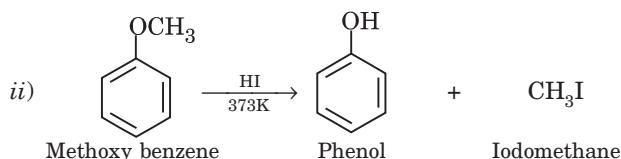
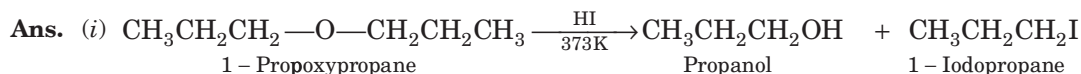


Similarly, 3° alcohols give alkenes.



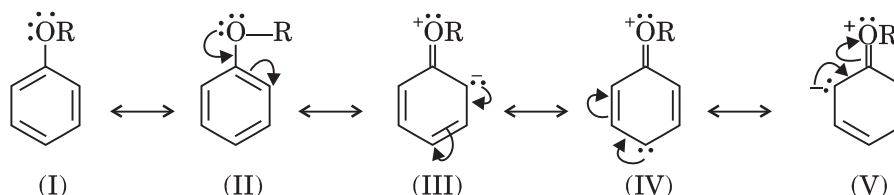
Q.28. Write the equation of the reaction of hydrogen iodide with

(i) 1-propanoxypropane, (ii) methoxybenzene and (iii) benzyl ethyl ether.



Q.29. Explain the fact that in aryl alkyl ethers (i) the alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming substituents to *ortho* and *para* position in benzene ring.

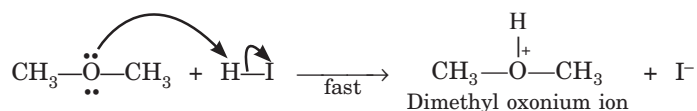
Ans. The alkoxy group increases the electron density on the benzene ring and therefore, activates the aromatic ring towards electrophilic substitution reaction as given below :



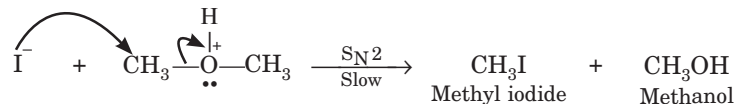
As is clear, structures III, IV and V show high electron density at *ortho* and *para* positions and therefore, direct the incoming substituents to *o*- and *p*-position in the benzene ring.

Q.30. Write mechanism of the reaction of HI with methoxymethane.

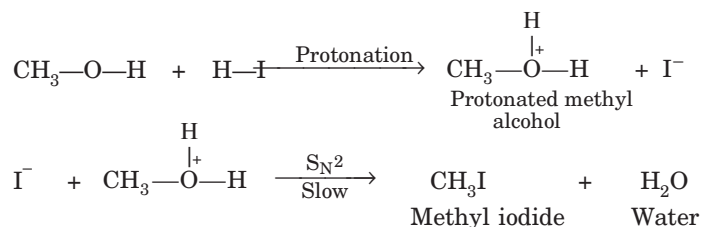
Ans. Step 1. Ether molecule gets protonated



Step 2. The protonated ether undergoes $\text{S}_{\text{N}}2$ attack by I^- ion



If HI is in excess, the methanol formed in step 2 is also converted into methyl iodide as :

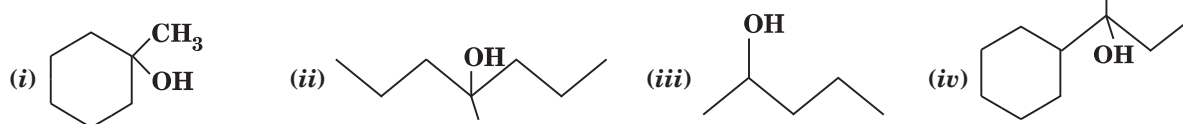


Q.31. Write equations of the following reactions.

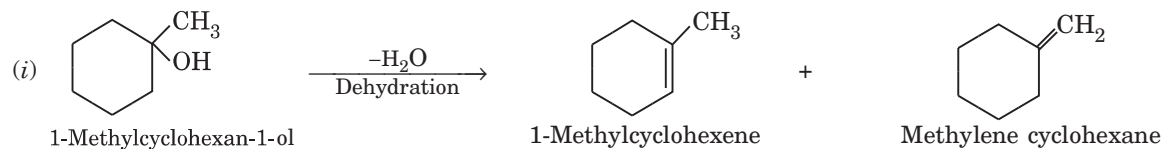
- (i) Friedel Crafts reaction – alkylation of anisole
- (ii) Nitration of anisole
- (iii) Bromination of anisole in ethanoic acid medium
- (iv) Friedel Craft's acetylation of anisole

Ans. Refer ring substitution reactions of aromatic ethers (Text Book Page 73–74).

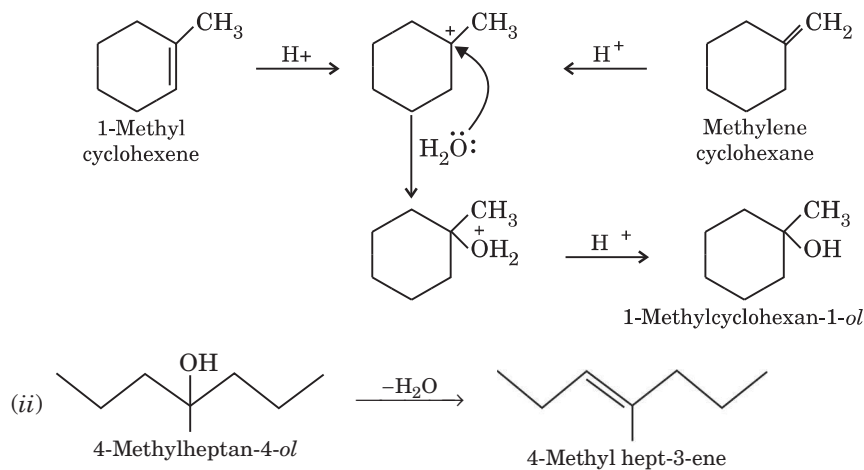
Q.32. Show how would you synthesize the following alcohols from appropriate alkenes ?



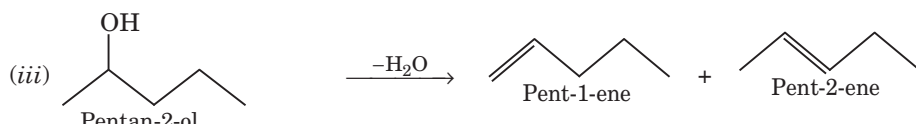
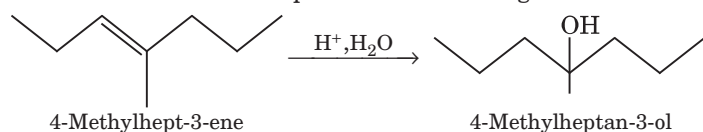
Ans. The alkenes for synthesising the alcohols can be predicted by first dehydrating the alcohol to give single alkene or a mixture of alkenes. If a mixture of alkenes is possible, then find out which alkene gives the desired alcohol. It must be remembered that acid catalysed addition of H_2O to alkenes occurs in accordance with Markovnikov's rule.



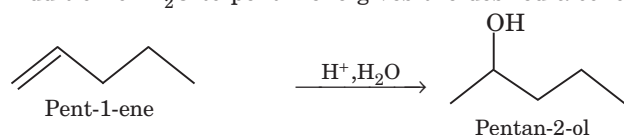
The desired alcohol can be obtained by addition of H_2O to either of these,



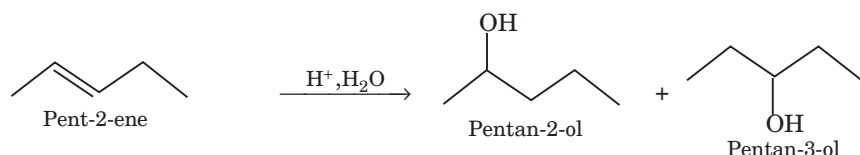
Addition of water in the presence of an acid gives the desired alcohol.



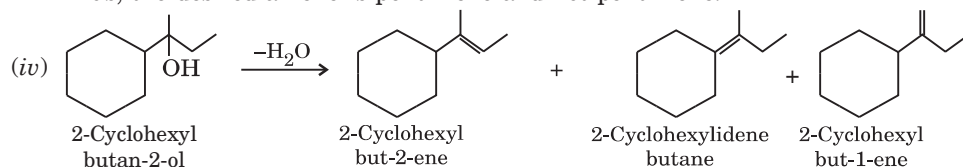
Addition of H_2O to pent-1-ene gives the desired alcohol.



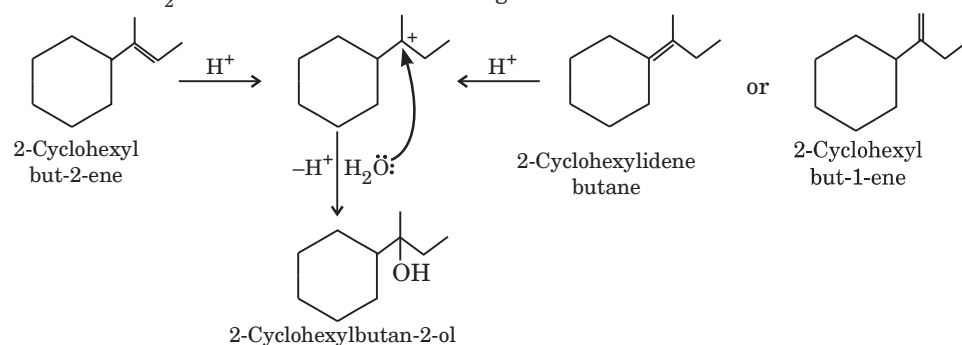
However, pent-2-ene will give two products.



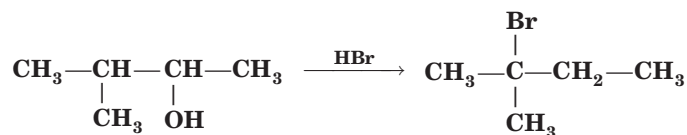
Thus, the desired alkene is pent-1-ene and not pent-2-ene.



Addition of H_2O to either of these alkenes gives the desired alcohol.

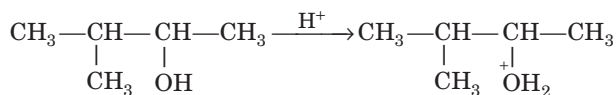


Q.33. When 3-methylbutan-2-ol is treated with HBr following reaction takes place ;

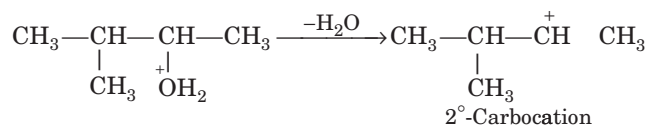


Give a mechanism for this reaction.

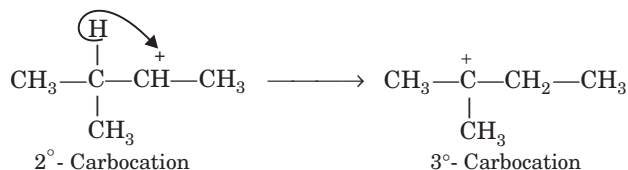
Ans. (i) Alcohol gets protonated.



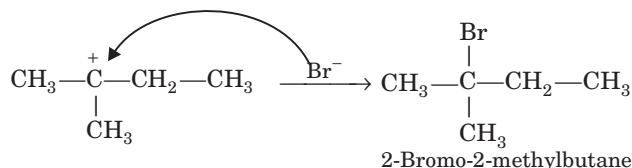
(ii) Protonated alcohol loses H_2O molecule to form 2° carbocation.



(iii) 1, hydride shift of 2-carbocation gives more stable 3° carbocation.



(iv) Nucleophilic attack by Br^- ion gives alkyl halide.



NCERT

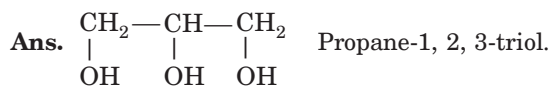
Exemplar Problems

Subjective Questions

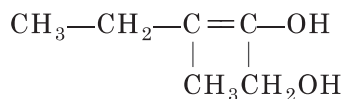
Note: Objective Questions from Exemplar Problems are given in Competition File, page 131.

III. Short Answer Type Questions

Q.1. What is the structure and IUPAC name of glycerol?



Q.2. Write the IUPAC name of the compound given below.



Ans. 3-Methylpent-2-ene-1, 2-diol.

Q.3. Name the factors responsible for the solubility of alcohols in water.

Ans. The factors responsible for the solubility of alcohols in water are:

- Hydrogen bonding.
- Size of alkyl or aryl group.

Q.4. What is denatured alcohol ?

Ans. It is 95% ethyl alcohol. To avoid misuse of alcohol for drinking it is made unfit by mixing some copper sulphate and pyridine in it. This is called denatured alcohol.

Q.5. Suggest a reagent for the following conversion.



Ans. Pyridinium chlorochromate, $\text{CrO}_3 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$.

Q.6. Out of 2-chloroethanol and ethanol which is more acidic and why ?

Ans. 2-Chloroethanol is more acidic because of $-\text{I}$ effect of chlorine atom.

Q.7. Suggest a reagent for conversion of ethanol to ethanal.

Ans. Pyridinium chlorochromate, $\text{CrO}_3 \cdot \text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$.

Q.8. Suggest a reagent for conversion of ethanol to ethanoic acid.

Ans. Any oxidising agent *e.g.*, acidified KMnO_4 , acidified $\text{K}_2\text{Cr}_2\text{O}_7$.

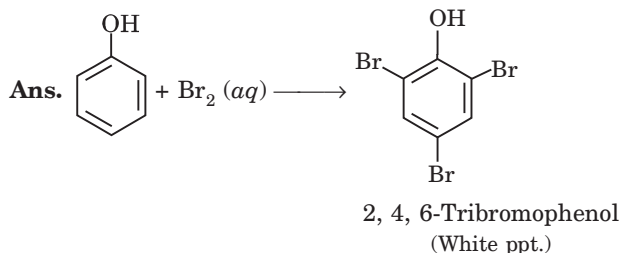
Q.9. Out of *o*-nitrophenol and *p*-nitrophenol, which is more volatile ? Explain.

Ans. *Ortho*-nitrophenol is more volatile because there is intramolecular hydrogen bonding in *o*-nitrophenol. *p*-Nitrophenol has intermolecular hydrogen bonding.

Q.10. Out of *o*-nitrophenol and *o*-cresol, which is more acidic ?

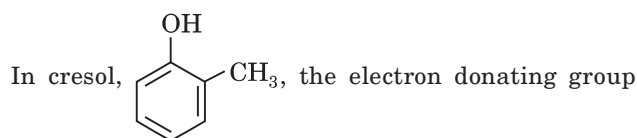
Ans. *o*-Nitrophenol because nitro group is electron withdrawing group and it increases acidic strength.

Q.11. When phenol is treated with bromine water, white precipitate is obtained. Give the structure and the name of the compound formed.



Q.12. Arrange the following compounds in increasing order of acidity and give a suitable explanation. Phenol, *o*-nitrophenol, *o*-cresol.

Ans. Increasing order of acidity:
o-Cresol < Phenol < *o*-Nitrophenol

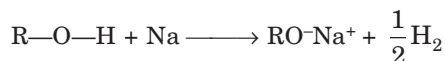


($-\text{CH}_3$) gives electrons and intensify the charge on phenoxide ion and therefore makes it unstable. Therefore, *o*-cresol is less acidic than phenol. In *o*-nitrophenol, the electron withdrawing ($-\text{NO}_2$) group withdraws electrons and disperses the $-ve$ charge and stabilizes the phenoxide ion. Therefore, *o*-nitrophenol is more acidic than phenol.

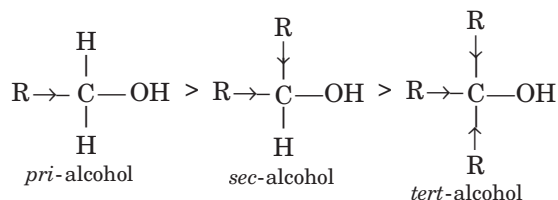
Q.13. Icohols react with active metals e.g. Na, K etc. to give corresponding alkoxides. Write down the decreasing order of reactivity of sodium metal towards primary, secondary and tertiary alcohols.

Ans. Decreasing order of reactivity of sodium metal is
 $1^\circ > 2^\circ > 3^\circ$

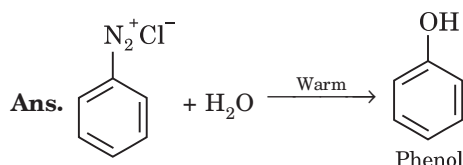
Alcohols react with sodium metal to form alkoxides and hydrogen is liberated:



The order of reactivity of alcohols is primary > secondary > tertiary. This can be explained on the basis of cleavage of $\text{O}-\text{H}$ bond. The alkyl groups are electron releasing groups (+I effect) and they increase the electron density around the oxygen. As a result, the electrons of $\text{O}-\text{H}$ bond cannot be withdrawn strongly towards oxygen and $\text{O}-\text{H}$ remains strong. Therefore, greater is the number of alkyl groups present, smaller will be reactivity of alcohol.



Q.14. What happens when benzene diazonium chloride is heated with water ?



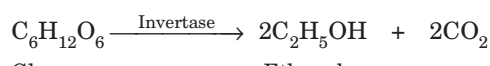
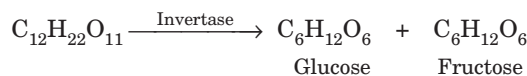
Q.15. Arrange the following compounds in decreasing order of acidity.



Ans. $\text{H}_2\text{O} > \text{ROH} > \text{HC} \equiv \text{CH}$

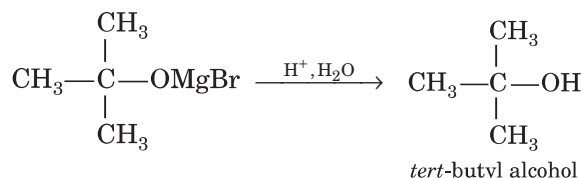
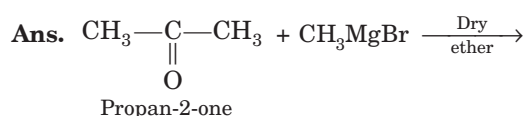
Q.16. Name the enzymes and write the reactions involved in the preparation of ethanol from sucrose by fermentation.

Ans. Invertase and zymase

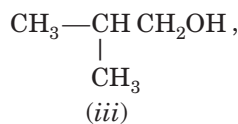
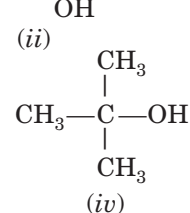
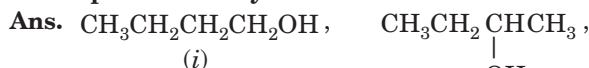


or Fructose

Q.17. How can propan-2-one be converted into *tert*-butyl alcohol ?



Q.18. Write the structures of the isomers of alcohols with molecular formula $\text{C}_4\text{H}_{10}\text{O}$. Which of these exhibits optical activity ?



(ii) is optically active.

Q.19. Explain why is OH group in phenols more strongly held as compared to OH group in alcohols.

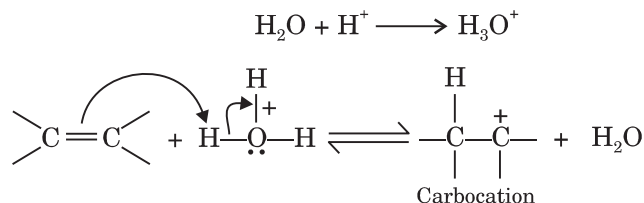
Ans. The OH group in phenol is more strongly held because of double bond character between C and O due to resonance.

Q.20. Explain why nucleophilic substitution reactions are not very common in phenols.

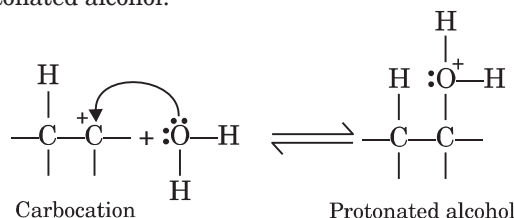
Ans. In phenols, the $-\text{OH}$ group is activating group and increases the electron density at ortho and para positions. Therefore, phenols undergo electrophilic substitution reactions and not nucleophilic substitution.

Q.21. Preparation of alcohols from alkenes involves the electrophilic attack on alkene carbon atom. Explain its mechanism.

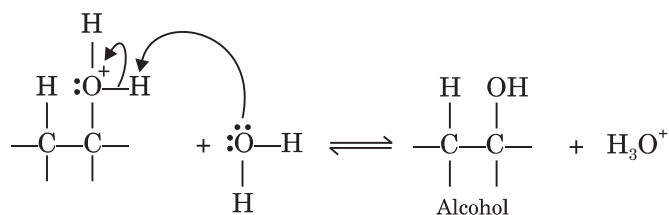
Ans. (a) Alkenes get protonated by the electrophilic attack of H_3O^+ .



(b) Nucleophile (H_2O) attacks the carbocation forming protonated alcohol.



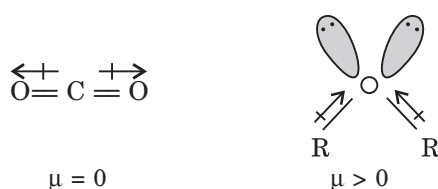
(c) Loss of H^+ from oxygen (deprotonation) to form alcohol.



Q.22. Explain why is $\text{O}=\text{C}=\text{O}$ non-polar while $\text{R}-\text{O}-\text{R}$ is polar.

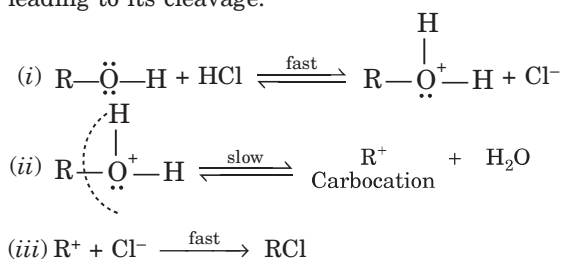
Ans. $\text{O}=\text{C}=\text{O}$ molecule is linear so that the polarities of two $\text{C}-\text{O}$ bonds get cancelled and the molecule is linear.

Ethers have structures similar to water and have angular or bent structure. Therefore, the polarity of two $\text{R}-\text{O}$ groups does not get cancelled and these have net dipole moment. Thus, $\text{R}-\text{O}-\text{R}$ is polar.



Q.23 Why is the reactivity of all the three classes of alcohols with conc. HCl and ZnCl_2 (Lucas reagent) different?

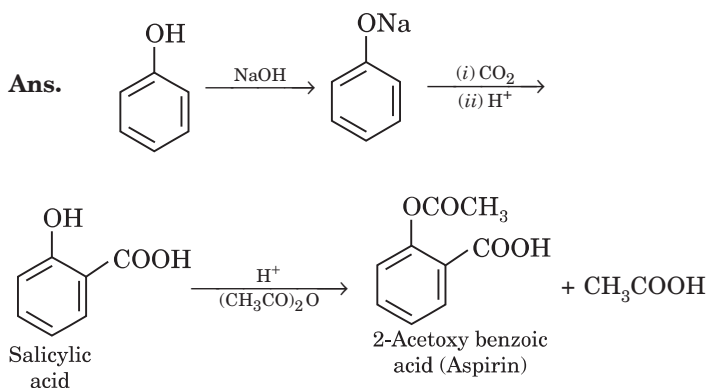
Ans. The alcohols combine with HCl to form protonated alcohol. The positive charge on oxygen weakens the $\text{C}-\text{O}$ bond leading to its cleavage.



The rate determining step in the above mechanism is (ii), which is a slow step reaction. The stability of carbocation will determine the reactivity of the reaction. Since the order of stability of carbocation is:

pri. < *sec.* < *tert.* Hence the order of formation of alkyl halide in the above reaction is *pri.* < *sec.* < *tert.*

Q.24. Write steps to carry out the conversion of phenol to aspirin.



Q.25. Nitration is an example of aromatic electrophilic substitution and its rate depends upon the group already present in the benzene ring. Out of benzene and phenol, which one is more easily nitrated and why?

Ans. Phenol is more easily nitrated than benzene. The presence of $-\text{OH}$ group in phenol increases the electron density at ortho and para positions in benzene ring by +R effect. Since nitration is an electrophilic substitution reaction, it will be more reactive at position where the electron density is more.

Q.26. In Kolbe's reaction, instead of phenol, phenoxide ion is treated with carbon dioxide. Why?

Ans. Phenoxide ion is more reactive than phenol towards electrophilic aromatic substitution. There it undergoes electrophilic substitution with carbon dioxide which is a weak electrophile.

Q.27. Dipole moment of phenol is smaller than that of methanol. Why?

Ans. In phenol, $\text{C}-\text{O}$ bond is less polar due to electron-withdrawing effect of benzene ring. In methanol, $\text{C}-\text{O}$ bond is more polar due to electron-releasing effect of $-\text{CH}_3$ group. Therefore, phenol is less polar than methanol.

Q.28. Ethers can be prepared by Williamson synthesis in which an alkyl halide is reacted with sodium alkoxide. Di-*tert*-butyl ether can't be prepared by this method. Explain.

Ans. In *tert*-butyl halides, elimination is favoured over substitution, and therefore, alkene is the only reaction product and ether is not formed.

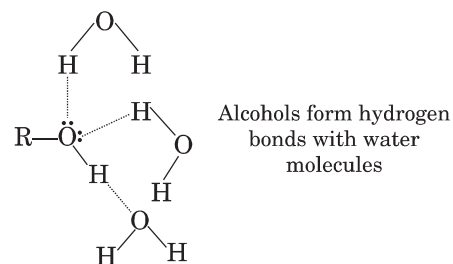
Q.29. Why is the $\text{C}-\text{O}-\text{H}$ bond angle in alcohols slightly less than the tetrahedral angle whereas the $\text{C}-\text{O}-\text{C}$ bond angle in ether is slightly greater?

Ans. The $\text{C}-\text{O}-\text{H}$ bond angle in alcohols is slightly less than the tetrahedral angle (109.5°) because of larger repulsions between the lone pairs of electrons. For example in methanol, $\text{C}-\text{O}-\text{H}$ bond angle is 108.9° .

In ethers, the $\text{C}-\text{O}-\text{C}$ bond angle is slightly greater than tetrahedral angle. For example in dimethyl ether, $\text{C}-\text{O}-\text{C}$ bond angle is 111.7° . The larger bond angle in ethers may be because of greater repulsions between bulkier alkyl groups as compared to one H in alcohols.

Q.30. Explain why low molecular mass alcohols are soluble in water.

Ans. The lower members of alcohols are highly soluble in water but the solubility decreases with increase in molecular weight. The solubility of lower alcohols in water is due to the formation of hydrogen bonds between alcohols and water molecules.



However, as the size of alcohol molecule increases, the alkyl group becomes larger and prevents the formation of hydrogen bonds with water molecules and hence the solubility goes on decreasing with increase in length of carbon chain (or molecular mass of alcohol).

Q.31. Explain why *p*-nitrophenol is more acidic than phenol.

Ans. The electron withdrawing group $-\text{NO}_2$, withdraws electrons and disperses the negative charge. Therefore, $-\text{NO}_2$ group stabilizes the phenoxide ion. Hence *p*-nitrophenol is more acidic than phenol.

Q.32. Explain why alcohols and ethers of comparable molecular mass have different boiling points?

Ans. Ethers have low polarity and as a result do not show any association by intermolecular hydrogen bonding. Therefore, ethers have low boiling points and lower than that of isomeric alcohols and almost same as those of alkanes of comparable molecular masses.

$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
Diethyl ether	<i>n</i> -Butyl alcohol	<i>n</i> -Pentane
307.6 K	390 K	309.1 K

The large difference in boiling points of alcohols and ethers is due to the presence of hydrogen bonding in alcohols.

Q.33. The carbon-oxygen bond in phenol is slightly stronger than that in methanol. Why?

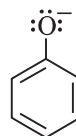
Ans. C—O bond in phenol is stronger than that in methanol due to the fact that

(i) In phenol, conjugation of lone pair of electrons on oxygen with aromatic ring results in partial double bond character in carbon-oxygen bond.

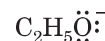
(ii) In phenol, oxygen is bonded to a sp^2 hybridised carbon atom while in methanol, it is bonded to a sp^3 hybridised carbon atom. The bond formed between oxygen and sp^2 hybridised carbon is more stable than that formed between oxygen and sp^3 hybridised carbon.

Q.34. Arrange water, ethanol and phenol in increasing order of acidity and give reason for your answer.

Ans. Increasing order of acidity is: ethanol < water < phenol. The phenoxide ion obtained after the removal of a proton is stabilised by resonance whereas the ethoxide ion obtained after the removal of a proton is destabilised by '+I' effect of $-\text{C}_2\text{H}_5$ group. Therefore phenol is stronger acid than ethanol.



Phenoxide ion
(resonance stabilised)



Ethoxide ion (no
resonance stabilisation)

On the other hand ethanol is weaker acid than water because electron releasing $-\text{C}_2\text{H}_5$ group in ethanol increases the electron density on oxygen and hence the polarity of O—H bond in ethanol decreases. This results in the decreasing acidic strength. Hence acidic strength increases in the order given above.



QUICK

MEMORY TEST

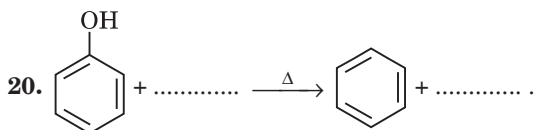
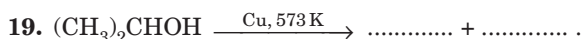
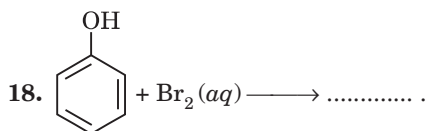
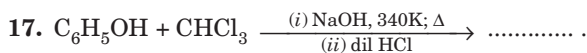
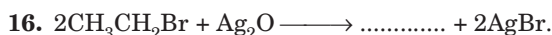
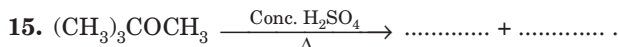
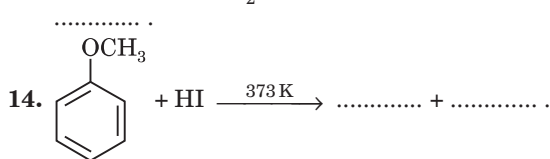
A. Say True or False

- Ethers are more polar than isomeric alcohols.
- The boiling points of ethers are lower than those of isomeric alcohols.
- Bond angle in dimethyl ether is more than in water.
- Sodium ethoxide can be prepared by the reaction of ethanol with aqueous sodium hydroxide.
- tert*-butyl alcohol is more soluble in water than *n*-butyl alcohol.
- m*-methoxyphenol is a weaker acid than phenol.
- 2, 4-dinitrophenol is less acidic than phenol.
- Reactivity of ethanol is less with sodium than that of *iso*-propyl alcohol.
- Alcohols are stronger acids than water.
- Primary alcohols undergo dehydration more easily than secondary and tertiary alcohols.
- Phenols turn blue litmus red.
- Primary alcohols on dehydrogenation give aldehydes.
- Phenetole reacts with HI at 373 K to give ethanol and iodobenzene.
- Acetone reacts with methyl magnesium bromide followed by hydrolysis to give secondary alcohols.
- Reactivity of halogen acids towards ethers follows the sequence :
 $\text{HI} > \text{HBr} > \text{HCl}$.

B. Complete the missing links

- Dehydration of ethyl alcohol with conc. H_2SO_4 at 413 K gives
- Lower alcohols are highly soluble in water due to
- 100% pure ethanol is called
- Tertiary alcohol when passed over heated copper at 573 K gives
- Amongst the three isomers of nitrophenol, the one that is least soluble in water is
- In the formation of salicylic acid by Reimer Tiemann reaction, phenol is heated with in the presence of NaOH.
- An enzyme which can convert glucose into ethanol is
- Reaction of phenol with in the presence of aqueous NaOH is called Schotten Baumann reaction.
- Ortho* and *para* nitrophenols can be separated by distillation.
- Phenol forms coloured complexes with neutral
- Absolute alcohol can be prepared from rectified spirit by distillation.
- The lowest molecular mass alcohol which is optically active is

13. The main product obtained when sodium phenoxide is treated with CO_2 at 400 K under 4–7 atm. pressure is



C Choose the correct alternative

1. *o*-Nitrophenol has *lower/higher* pK_a value than *m*-nitrophenol.
2. $\text{C}_6\text{H}_5\text{OH}$ is *weaker/stronger* acid than $\text{C}_6\text{H}_{11}\text{OH}$.
3. Water is *weaker/stronger* acid than ethanol.
4. Ketones are reduced to $1^\circ/2^\circ$ alcohols.
5. Phenol has *smaller/larger* dipole moment than methanol.
6. Benzene-1, 2, 3-triol is called *hydroquinol/pyrogallol*.
7. Oxirane reacts with Grignard reagent to form *primary/secondary* alcohol.
8. Cumene on aerial oxidation and on subsequent hydrolysis gives *phenol/phenetole*.
9. Butan-2-ol has *higher/lower* boiling point than butan-1-ol.
10. Ethanol on treatment with conc. H_2SO_4 at 443 K gives *ethene/ethoxyethane*.
11. Picric acid is obtained by heating phenol in the presence of conc. H_2SO_4 with *conc. HNO_3 /conc. HNO_2* .
12. Treatment of sodium phenoxide with CO_2 at 400 K under a pressure of 4–7 atm followed by acidification gives *salicylic acid/salicylaldehyde*.

Answers

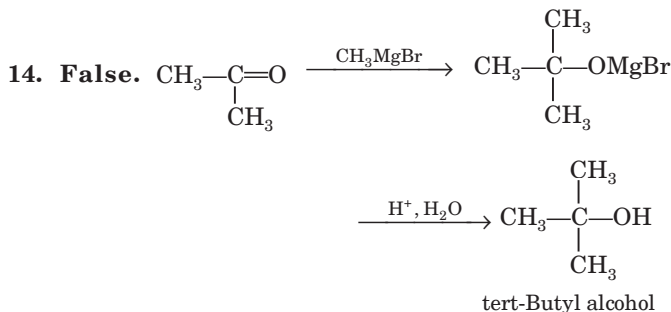
QUICK

MEMORY TEST



A. Say True or False

1. False 2. True 3. True
4. **False.** Ethanol is weaker acid than water and therefore, it does not react with aqueous NaOH to form sodium ethoxide.
5. **True.** Solubility increases with branching.
6. **False.** Due to $-I$ effect of methoxy group at *m*-position, *m*-methoxy phenol is a stronger acid than phenol.
7. False 8. False 9. False 10. False
11. True 12. True
13. **False.** It gives phenol and ethyl iodide.

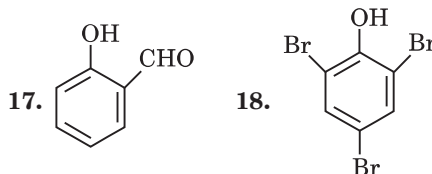
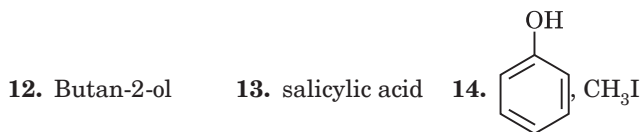


15. True.

B. Complete the missing links

1. diethyl ether 2. hydrogen bonding

3. absolute alcohol 4. alkenes 5. *o*-nitrophenol
6. CCl_4 7. zymase 8. benzoyl chloride
9. steam 10. ferric chloride 11. azeotropic



C. Choose the correct alternative

1. lower 2. stronger 3. stronger
4. 2° 5. smaller 6. hydroxy quinol
7. primary 8. phenol 9. lower
10. ethene 11. conc. HNO_3 12. salicylic acid

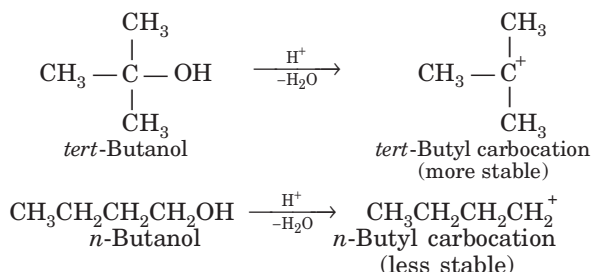
HOTS

Higher Order Thinking Skills & Advanced Level

QUESTIONS WITH ANSWERS

1. Acid-catalysed dehydration of *tert*-butanol is faster than that of *n*-butanol. Explain.

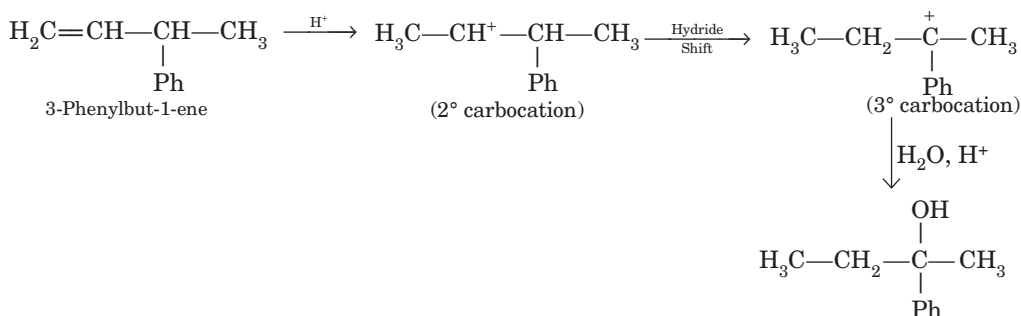
Ans. Acid-catalysed dehydration of alcohols occurs through the formation of carbocation intermediate as:



Since *t*-butyl carbocation (3°) is more stable than *n*-butyl carbocation (1°), therefore, acid-catalysed dehydration of *t*-butanol takes place faster than that of *n*-butanol.

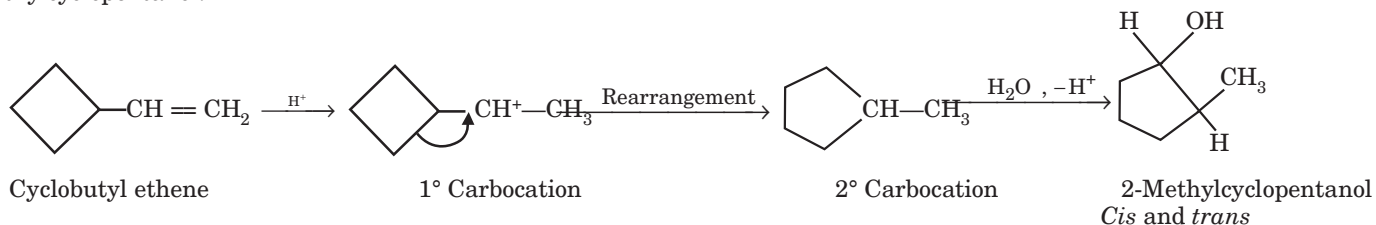
2. Hydration of 3-phenyl-1-butene with dil. H_2SO_4 is not a satisfactory method for preparing 3-phenyl-2-butanol because 2-phenyl-2-butanol is obtained instead. Explain.

Ans. Hydration form 2° carbocation which undergoes a hydride shift to stable benzylic carbocation.

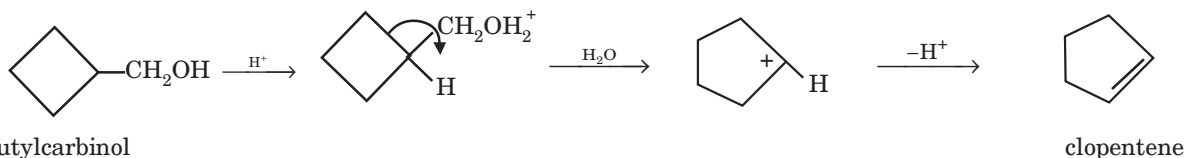


3. Give the product and show the steps in (i) the hydration of cyclobutylethene in dil. H_2SO_4 , (ii) dehydration of cyclobutylcarbinol.

Ans. (i) In this reaction, the addition of H^+ to C^1 gives a 1° carbocation, which rearranges by ring expansion. Finally, it gives 2-methylcyclopentanol.



(ii) This reaction results in the expansion of four membered to a five membered ring.



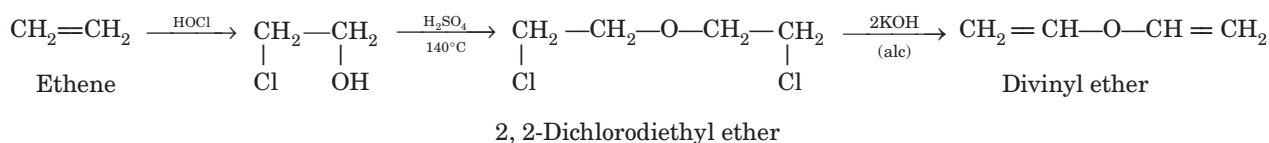
4. Arrange the following alcohols in the increasing order of reactivity with HBr :



Ans. $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OH} < p\text{-Cl C}_6\text{H}_4\text{CH}_2\text{OH} < \text{C}_6\text{H}_5\text{CH}_2\text{OH} < (\text{C}_6\text{H}_5)_2\text{CHOH} < (\text{C}_6\text{H}_5)_3\text{COH}$

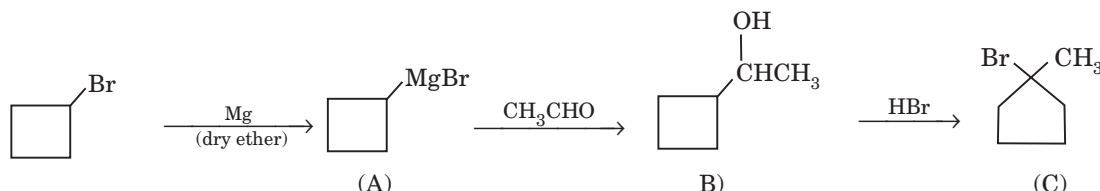
5. Show steps for the conversion of ethene to divinyl ether.

Ans.

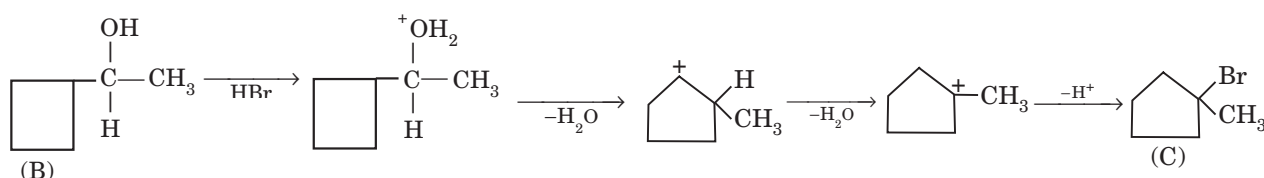


6. Cyclobutylbromide on treatment with magnesium in dry ether forms an organometallic A. The organo-metallic reacts with ethanal to give an alcohol B after mild acidification. Prolonged treatment of alcohol B with an equivalent amount of HBr gives 1-bromo-1-methyl cyclopentane(C). With the structures of A, B and explain how C is obtained from B.

Ans.

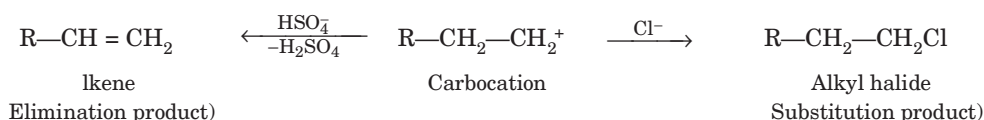


Conversion of B to C occurs as :



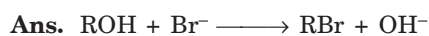
7. Explain why dehydration of alcohols to form alkenes is always carried out with conc. H_2SO_4 and not with conc. HCl or HNO_3 ?

Ans. Dehydration of alcohols to alkenes occurs through the formation of carbocation intermediate. If HCl is used then chloride (Cl^-) ion being a good nucleophile will result into substitution reaction forming alkyl chloride.



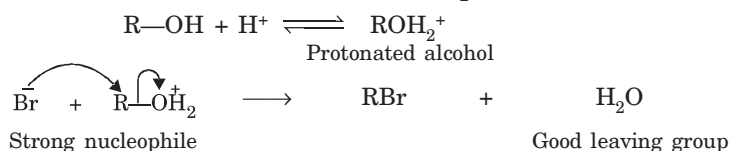
However, if H_2SO_4 is used, then the bisulphate (HSO_4^-) ion being very weak nucleophile cannot result into substitution reaction. Rather the carbocation loses a proton to form elimination product alkene. On the other hand, conc. HNO_3 also cannot be used because it is a strong oxidising agent and will preferentially result into the oxidation of alcohols to aldehydes, ketones or carboxylic acids. Thus, the dehydration of alcohols to form alkenes is always carried out with such strong acids (H_2SO_4 , H_3PO_4 , etc.) which have non-nucleophilic anions.

8. Alcohols donot react with NaBr but when H_2SO_4 is added they form alkyl bromides. Explain.

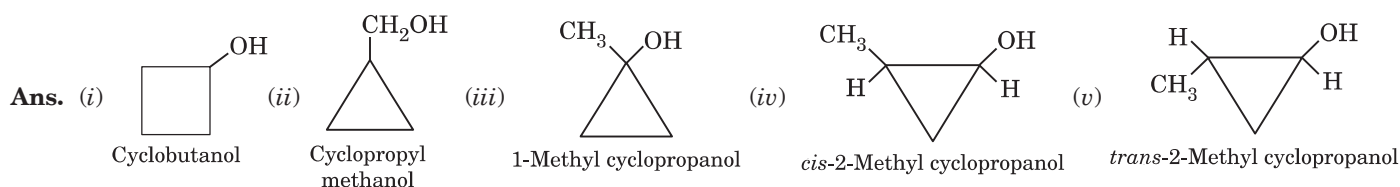


Although Br^- is a strong nucleophile, yet OH^- being a strong base is a very poor leaving group. Therefore, Br^- cannot displace OH^- from ROH to form RBr . Hence, alcohols donot react with NaBr .

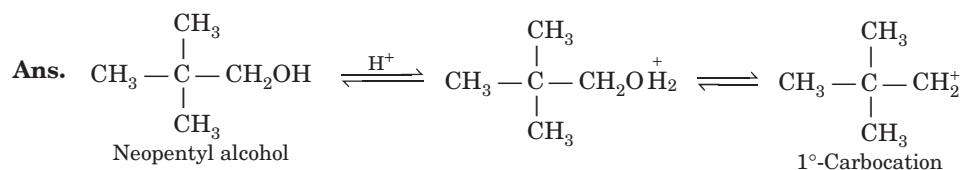
However, when H_2SO_4 is added, protonation of alcohols takes place and $-\text{OH}$ group gets converted to $-\text{OH}_2^+$. Since water is a weak base, therefore, it is a good leaving group. Hence, Br^- can displace H_2O from protonated alcohol to form RBr .



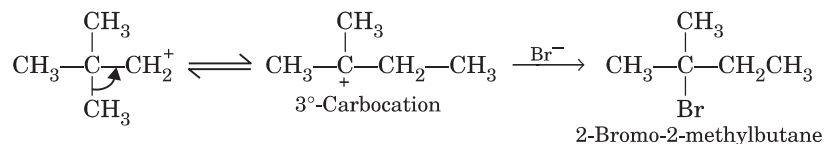
9. Cyclic $\text{C}_4\text{H}_7\text{OH}$ has five isomers. Write their structure and names.



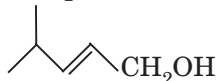
10. Neopentyl alcohol reacts with concentrated HBr to give 2-bromo-2-methylbutane. Write the mechanism for the formation of this product.



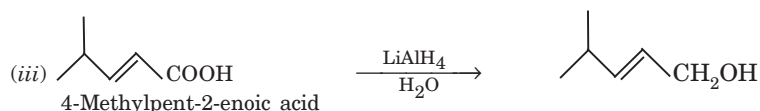
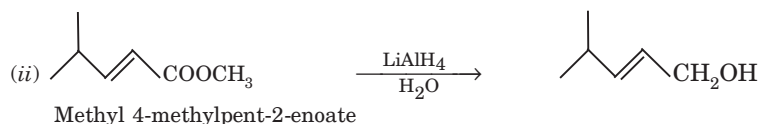
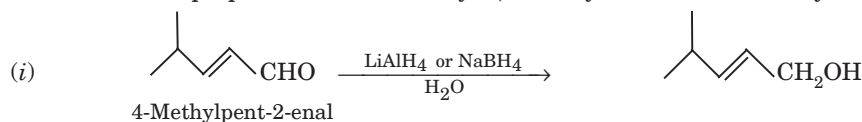
A methyl shift changes 1° carbocation to a stable 3° carbocation.



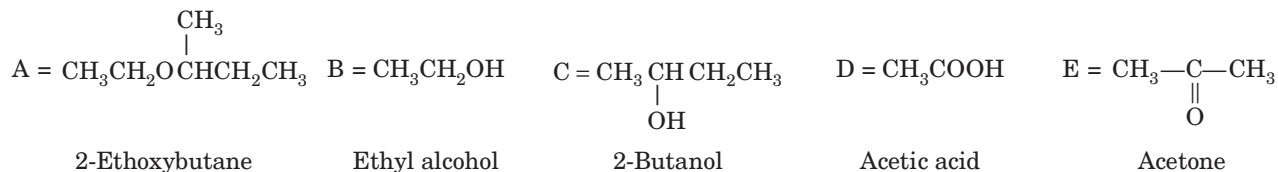
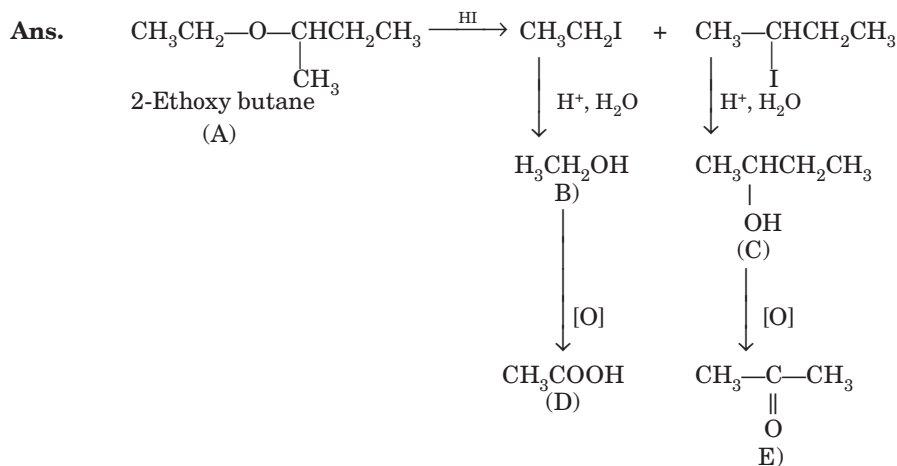
11. Write three carbonyl compounds which may be used to prepare :



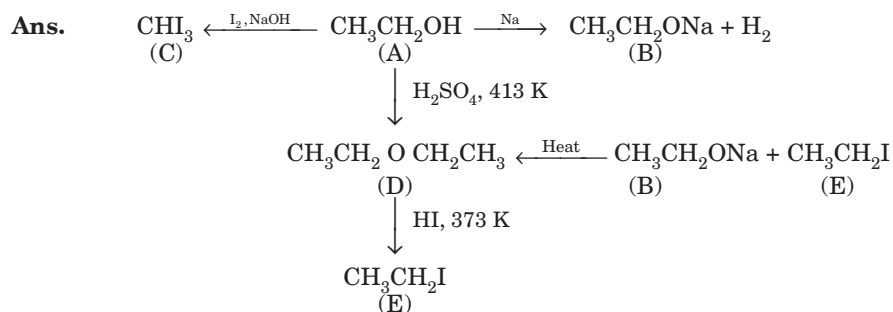
Ans : It can be prepared from an aldehyde, carboxylic acid and ester by reduction with $\text{LiAlH}_4/\text{H}_2\text{O}$.



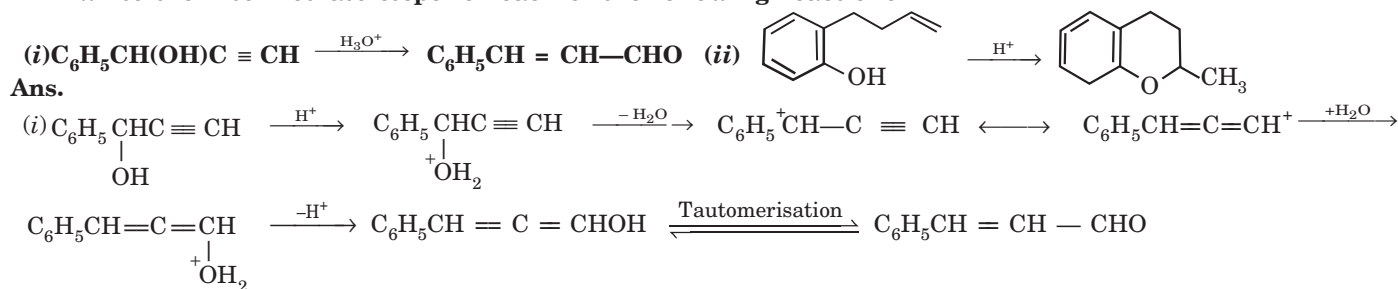
12. An ether (A) $\text{C}_6\text{H}_{14}\text{O}$ when heated with excess of hot conc. HI produced two alkyl halides which on hydrolysis form compounds (B) and (C). Oxidation of (B) gave an acid (D) whereas oxidation of (C) gave a ketone (E). Deduce the structural formulae of (A), (B), (C), (D) and (E).



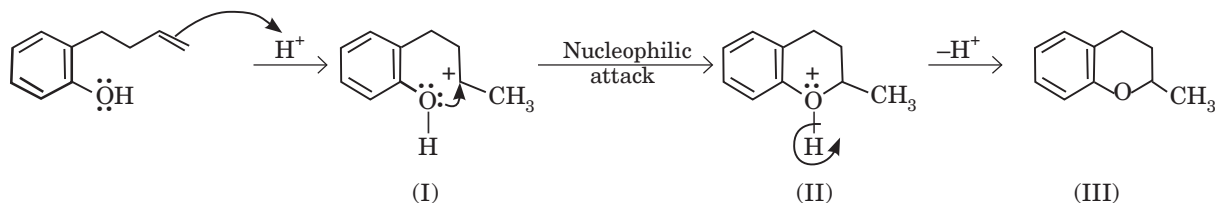
13. An organic compound A ($\text{C}_2\text{H}_6\text{O}$) reacts with sodium to form a compound B with the evolution of H_2 and gives a yellow compound C when treated with iodine and NaOH. When heated with conc. H_2SO_4 at 413 K, it gives a compound D ($\text{C}_4\text{H}_{10}\text{O}$) which on treatment with conc. HI at 373 K gives E. D is also obtained when B is heated with E. Identify A, B, C, D and E and write equations for the reactions involved.



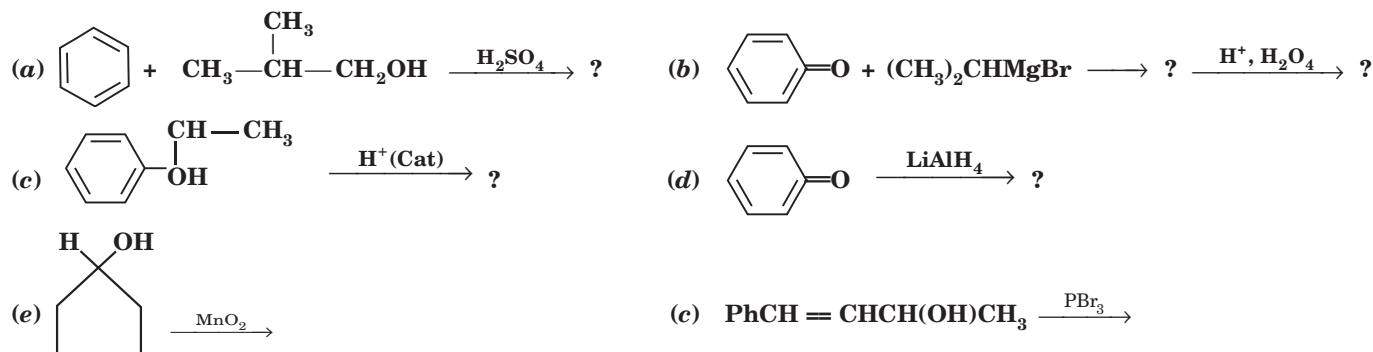
14. Write the intermediate steps for each of the following reactions :



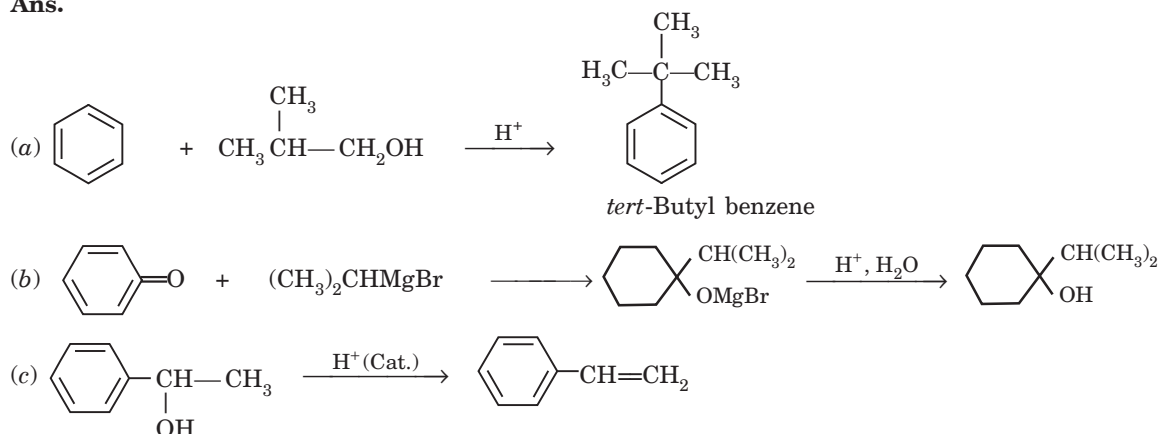
(ii) The addition of H^+ to the double bond takes place in accordance with Markovnikov's rule to form more stable carbocation (I). Nucleophilic attack by OH group on I gives the cyclized product (II) which readily loses a proton to form the final product (III).

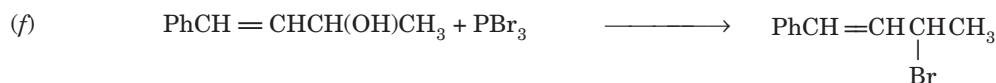


15. Complete the following reactions :



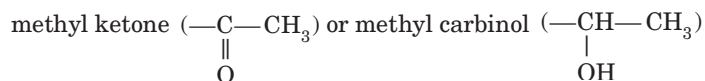
Ans.





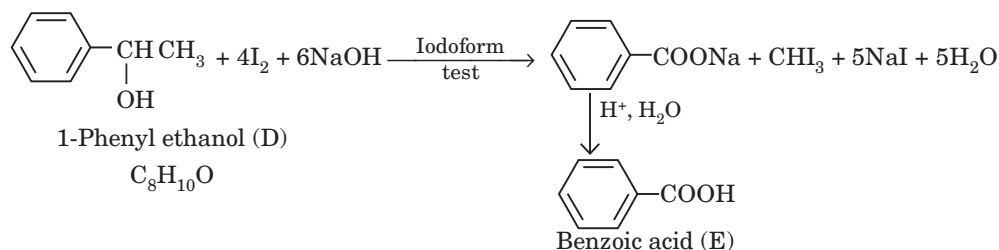
16. A compound D ($\text{C}_8\text{H}_{10}\text{O}$) upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid E ($\text{C}_7\text{H}_6\text{O}_2$). Write the structures of D and E and explain the formation of E.

Ans. Since compound D ($\text{C}_8\text{H}_{10}\text{O}$) upon treatment with alkaline solution of I_2 gives yellow ppt. therefore, D may be either



The molecular formula of D suggests it to be 1-phenyl ethanol; $\text{C}_6\text{H}_5\text{CH(OH)CH}_3$

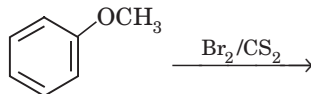
The reaction may be explained as :



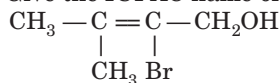
Revision Exercises

Very Short Answer Questions carrying 1 mark

- What is the major product formed when 2-butanol is treated with conc. H_2SO_4 at 443 K?
- What is the order of reactivity of 1° , 2° and 3° alcohols with sodium metal?
- Name the main product obtained when vapour of tert-butyl alcohol are passed over heated copper at 573 K.
- Phenol is heated with CHCl_3 and NaOH at 350 K. What is the product formed? Give the name of the reaction.
- What happens when phenol is warmed with CO_2 in the presence of aqueous NaOH ? (Meghalaya S.B.2015)
- What happens when phenol is oxidised? (Uttarakhand S.B.2015)
- Write the structural formula of propane -1, 2, 3- triol. (Assam S.B. 2016)
- Name the products obtained when anisole is treated with HI .
- Why is special care taken to distil old samples of ether?
- Name the products obtained when anisole is treated with a mixture of conc. HNO_3 and conc. H_2SO_4 .
- Complete the reaction :



- Give the IUPAC name of the following compound :

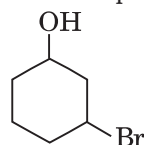


(D.S.B. 2009)

- Draw the structural formula of 2-methylpropan-2-ol molecule. (D.S.B. 2012)

- Draw the structure of hex-1-en-3-ol compound. (D.S.B. 2012, Tripura S.B. 2016)

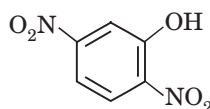
- Name the compound according to IUPAC rule :



(Assam S.B. 2013)

- Which of the following isomers is more volatile : o-nitrophenol or p-nitrophenol ? (D.S.B. 2014)

- Write the IUPAC name of



(D.S.B. 2015)

- Complete the reaction:



(Hr.S.B. 2018)

19. Give the IUPAC name of:



20. Give the IUPAC name of:



CBSE QUESTIONS

21. Write the structure of the molecule of a compound whose IUPAC name is 1-Phenylpropan-2-ol.

(A.I.S.B. 2010)

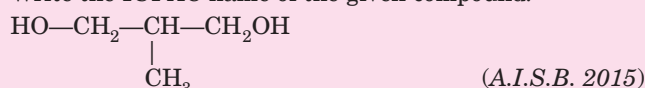
22. How would you convert ethanol to ethene?

(A.I.S.B. 2012, Hr.S.B. 2014)

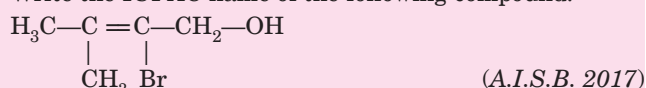
23. Why is (±)-butan-2-ol optically inactive?

(D.S.B. 2013, A.I.S.B. 2013)

24. Write the IUPAC name of the given compound:



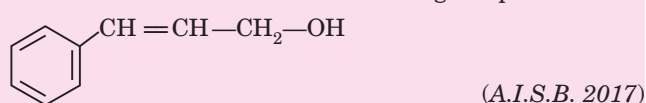
25. Write the IUPAC name of the following compound:



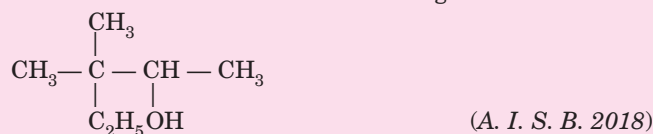
26. Write the IUPAC name of the following compound:



27. Write the IUPAC name of the following compound:



28. Write the IUPAC name of the following:



MCQs from State Boards' Examinations

29. Dehydration of tertiary alcohols with Cu at 573 gives

- (a) Aldehydes (b) Ketones
(c) Alkenes (d) None of these (Hr. S.B. 2013)

30. Molecular formula of ethers is:

- (a) $\text{C}_n\text{H}_{2n+2}\text{OH}$ (b) $\text{C}_n\text{H}_{2n}\text{O}$
(c) $\text{C}_n\text{H}_{2n+1}\text{O}$ (d) None of these
(Hr. S.B. 2014, 2017)

31. Williamson's synthesis is an example of:

- (a) Nucleophilic substitution reaction
(b) Nucleophilic addition
(c) Electrophilic substitution
(d) None of the above (Hr. S.B. 2014)

32. Reaction used for the preparation of ethers is

- (a) Reimer-Tiemann reaction
(b) Williamson's synthesis
(c) Wurtz reaction
(d) Cannizzaro reaction (H.P.S.B. 2014)

33. The test used to distinguish alcohols from one another is known as

- (a) Hinsberg's test (b) 2, 4-DNP test
(c) Iodoform test (d) Lucas Test

(H.P.S.B. 2014)

34. The IUPAC name of CH_2OH is



- (a) Propane -1, 3-diol (b) Propane -1, 2-diol
(c) Propane -1, 2, 3-triol (d) Glycerol

(Mizoram S.B. 2015)

35. Ethers on hydrolysis give

- (a) carboxylic acid (b) alcohol
(c) ester (d) ketone

(Nagaland S.B. 2015)

36. Which of the following has highest boiling point?

- (a) Methanol (b) Ethanol
(c) Propan-1-ol (d) Butan-1-ol

(Hr. S.B. 2015)

37. Which has highest value of pK_a ?

- (a) Phenol (b) Ethanol
(c) o-Nitrophenol (d) o-Cresol (Hr.S. B. 2016)

38. Which of the following is most acidic?

- (a) Benzyl alcohol (b) Cyclohexanol
(c) Phenol (d) m-Chlorophenol.

(r.S. B. 2017)

39. Phenols on reaction with conc. HNO_3 in the presence of conc. H_2SO_4 gives

- (a) o-nitrophenol (b) m-nitrophenol
(c) p-nitrophenol (d) 2,4,6-trinitrophenol.

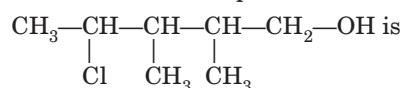
(Nagaland S.B. 2017)

40. Methanol and ethanol can be distinguished by using

- (a) Fehling's test (b) Iodoform test
(c) Tollen's test (d) Carbylamine test.

(Mizoram S.B. 2017)

41. The IUPAC name of the compound



- (a) 2-Chloro-3,4-dimethyl-n-pentyl alcohol
(b) 2-Chloro-3,4-dimethylpentan-5-ol
(c) 4-Chloro-2,3-dimethylpentan-1-ol
(d) 2,3-Dimethyl-4-chloropentan-1-ol. (Mizoram S.B. 2017)

42. $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow[413 \text{ K}]{\text{conc. H}_2\text{SO}_4} \text{A'}$, A' will be:

- (a) $\text{CH}_2=\text{CH}_2$ (b) $\text{C}_2\text{H}_5\text{OCH}_3$
(c) $(\text{C}_2\text{H}_5)_2\text{O}$ (d) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
(Hr.S.B. 2018)

43. Which is weakest acid in the following?

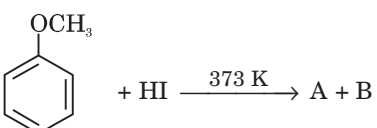
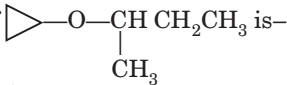
- (a) CH_3OH (b) $(\text{CH}_3)_2\text{CHOH}$
(c) $\text{CH}_3\text{CH}_2\text{OH}$ (d) $(\text{CH}_3)_3\text{COH}$

(Hr.S.B. 2018)

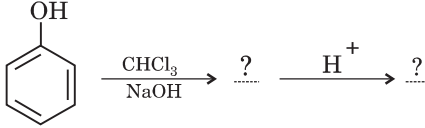
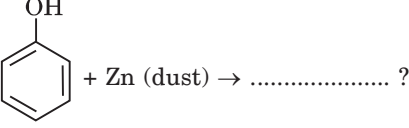
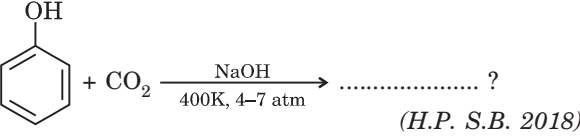
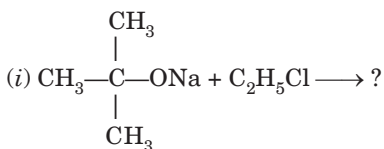
44. Williamson synthesis is used to prepare:

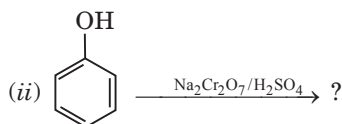
- (a) Alcohol (b) Amine
(c) Ketone (d) Ether

(Hr.S.B. 2018)

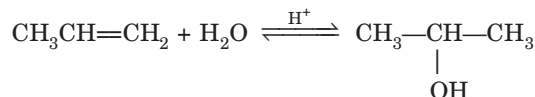
45. In the reaction  A and B are:
 (a) C_6H_5I , CH_3OH (b) C_6H_5OH , CH_3I
 (c) $C_6H_5CH_2OH$, CH_3I (d) CH_3CH_2I , C_6H_5OH
 (Hr.S.B. 2018)
46. The IUPAC name of  is—
 (a) 2-Cyclopropoxybutane
 (b) 2-Propoxybutane
 (c) 2-Propoxypropane
 (d) 2-Methyl-2-propoxypropane (Mizoram S.B. 2018)
47. Neutral ferric chloride test can be used to distinguish between
 (a) Alcohols and ethers (b) Aldehydes and ketones
 (c) Amines and aldehyde (d) Phenols and alcohols
 (Mizoram S.B. 2018)
48. On reaction with aqueous bromine at room temperature phenol forms which of the following?
 (a) *meta*-Bromophenol (b) 2, 6-Dibromophenol
 (c) 2, 4, 6-Tribromophenol (d) 3, 5-Dibromophenol
 (W.B. S.B. 2018)

Short Answer Questions carrying 2 or 3 marks

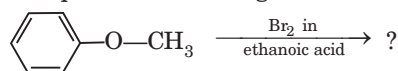
- Write the structural formulae of all the isomeric compounds that can be represented by the molecular formula $C_4H_{10}O$. Write their IUPAC names.
- How is anisole prepared? How does it react with
 (a) Br_2 in CS_2
 (b) HNO_3 in the presence of H_2SO_4
 (c) HI at 393–403 K?
- Explain the following :
 (a) Phenyl methyl ether reacts with HI to give phenyl and methyl iodide and not iodobenzene and methyl alcohol.
 (b) Dimethyl ether is completely soluble in water but diethyl ether is soluble in water to small extent.
 (c) $C-O-C$ bond angle in ether is higher than the $H-O-H$ bond angle in water though oxygen is sp^3 hybridized in both these cases. (Pb.S.B. 2011)
- How would you account for the following :
 (i) Phenol is more acidic than ethanol. (Pb. S.B. 2016, Hr. S.B. 2016)
 (ii) The boiling points of ethers are much lower than those of the alcohols of comparable molar masses. (D.S.B. 2007, Pb.S.B. 2017, Meghalaya S.B. 2017)
 (iii) Why do ethers possess dipole moment? (Pb. S.B. 2017)
- Write the equations for the reaction of phenol with the following:
 (i) Br_2 water
 (ii) $CHCl_3 + NaOH$
 (iii) $Na_2Cr_2O_7 + Conc.H_2SO_4$ (Hr. S.B. 2018)
- Explain the mechanism of the following reactions :
 (i) Acid catalysed dehydration of an alcohol forming an alkene. (D.S.B. 2009, Mizoram S.B. 2017, 2018)
- (ii) Acid catalysed hydration of an alkene forming alcohol. (D.S.B. 2009)
- Illustrate the following reactions giving a chemical equation for each :
 (i) Kolbe's reaction (D.S.B. 2010)
 (ii) Williamson's synthesis. (D.S.B. 2010, Pb. S.B. 2017)
 (iii) Friedel Crafts alkylation. (Pb. S.B. 2017)
- How can you distinguish primary, secondary and tertiary alcohols by Lucas test? (H.P.S.B. 2011, 2017)
- (a) Convert phenol into salicylic acid. (H.P.S.B. 2018)
 (b) How can you distinguish primary, secondary and tertiary alcohols by Lucas test? (H.P.S.B. 2018, Jammu S.B. 2018)
 (c) Explain Williamson synthesis. (H.P.S.B. 2018)
 (d) Dimethyl ether has less boiling point than ethyl alcohol. Explain. (H.P.S.B. 2018)
- How will you obtain :
 (i) Picric acid (2, 4, 6-trinitro phenol) from phenol.
 (ii) 2-Methyl propene from 2-methyl propanol. (D.S.B. 2011)
- (a) Complete the following reaction :

 (b) Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular mass. (H.P.S.B. 2012, 2016, Meghalaya S.B. 2016)
- (a) Name the reagents and give the equation for the preparation of 2-methyl-2-methoxypropane $[CH_3-C(OCH_3)(CH_3)_2]$ by Williamson's method.
 (b) Explain why 4-nitrophenol is more acidic than 4-methoxyphenol. (Meghalaya S.B. 2013)
- Complete the following reactions:
 (a) 
 (b)  (H.P. S.B. 2018)
- Give an example for each of the following :
 (i) Kolbe reaction
 (ii) Reimer Tiemann reaction (Jharkhand S.B. 2013)
- How will you convert
 (i) Propene to propan-2-ol
 (ii) Phenol to 2, 4, 6-trinitrophenol? (D.S.B. 2013)
- How will you convert the following :
 (i) Propan-2-ol to propanone
 (ii) Phenol to 2, 4, 6-tribromophenol (D.S.B. 2013)
- (a) How will you distinguish between propan-1-ol and 2-methylpropan-2-ol?
 (b) Complete the following reactions:




18. (a) Write a chemical test to distinguish between phenol and benzoic acid.
 (b) How will you convert phenol to benzoic acid ?
 (c) How will you convert sodium phenoxide to salicylic acid ? (Pb. S.B. 2014)
19. (i) Give a method of preparation of 3° alcohol.
 (ii) State the mechanism of the reaction:

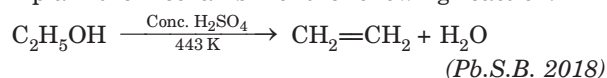


- (iii) Complete the following reaction:

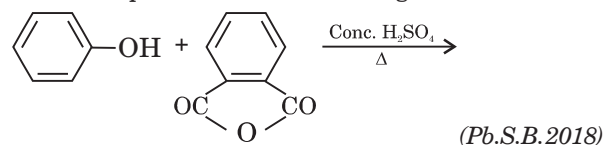


- (iv) Explain why alkoxy group (–OR) is ortho, para-directing and activates the aromatic ring towards electrophilic substitution. (Assam S.B. 2018)
20. (a) Arrange the following compounds in increasing order of acidity:
 H_2O , $\text{C}_2\text{H}_5\text{OH}$ and phenol
 (b) How can the following pair be chemically distinguished?
 Phenol and ethyl alcohol
 Or
 (a) Write the structural formulae of all the possible ethers having the molecular formula $\text{C}_4\text{H}_{10}\text{O}$ and give their IUPAC names.
 (b) Why are boiling points of ethers lower than those of alcohols? (Meghalaya S.B. 2015)
21. What are primary, secondary and tertiary alcohols? What happens when primary, secondary and tertiary alcohols are oxidized using acidified KMnO_4 ? (Uttarakhand S.B. 2015)

22. (a) Why are phenols acidic in nature?
 (b) Explain the mechanism of the following reaction:



- (c) Predict the products in the following reaction:



23. (a) How will you prepare phenol from chlorobenzene ? Write equation.
 (b) Explain, why the boiling points of ethers are much lower than those of alcohols of comparable molecular masses.
 (c) How is picric acid prepared ? (H.P.S.B. 2015)
24. (a) Why are phenols more acidic than alcohols? What happens when phenol is treated with excess of aqueous bromine solution? (Nagaland S.B. 2018)
 (b) Write the mechanism of acid catalyzed dehydration of ethanol to ethane.
 (c) Between phenol and alcohol which is more acidic? Why? (Karnataka S.B. 2018)

25. (a) Discuss dehydrogenation of primary and secondary alcohol.
 (b) What happens when vapours of primary, secondary and tertiary alcohols are passed over heated copper at 573 K. ? (Hr.S.B. 2015)

26. Explain the following behaviours:

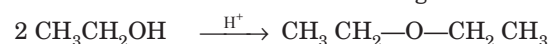
- (i) Alcohols are more soluble in water than the hydrocarbons of comparable molecular masses.
 (ii) Ortho-nitrophenol is more acidic than ortho-methoxyphenol.
 (iii) Cumene is a better starting material for the preparation of phenol. (CBSE Sample Paper 2017-18)

27. How do you convert the following :

- (i) Phenol to anisole
 (ii) Propan-2-ol to 2-methylpropan-2-ol
 (iii) Aniline to phenol

Or

- (a) Write the mechanism of the following reaction



- (b) Write the equation involved in the acetylation of salicylic acid. (D.S.B. 2015)

28. (a) Give a simple chemical test to distinguish between primary, secondary and tertiary alcohols.

(H.P.S.B. 2016)



Give structures of A and B products. (Hr.S.B. 2016)

- (c) Compare the acidic strength of primary, secondary and tertiary alcohols. (Nagaland S.B. 2015)

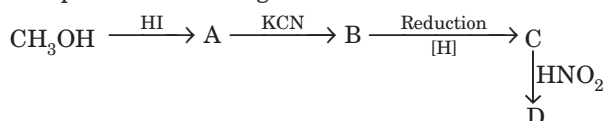
29. (a) How would you convert the following:

- (i) Phenol to benzene
 (ii) Phenol to benzoquinone
 (iii) Propene to propan-2-ol

- (b) How will you distinguish between benzyl alcohol and phenol?

or

- (a) Complete the following reaction:



- (b) How do you account the miscibility of ethoxyethane in water?
 (c) Among HI and HBr, which is a better reagent for cleavage of ether? (Hr.S.B. 2016)

30. (a) Give the chemical equation for the reaction of ethanol with conc. H_2SO_4 at 440 K.

- (b) Convert phenol to salicylic acid (2-hydroxybenzoic acid).

(Meghalaya S.B. 2018)

31. (i) Why have ethers low boiling points than isomeric alcohols?
 (ii) Give the position isomer of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (Butan-1-ol). (Pb.S.B. 2016)

32. (a) Differentiate between primary, secondary and tertiary alcohols by chemical test. (Pb.S.B. 2016)

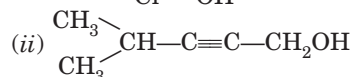
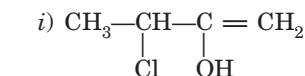
- (b) Why are primary alcohols more acidic than secondary alcohols?

- (c) Discuss the dehydrogenation of primary, secondary and tertiary alcohols. (Pb.S.B. 2016)

33. (i) Ethers possess a dipole moment even if the alkyl radicals in the molecule are identical. Explain.

- (ii) Give the position isomer of $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (Propan-1-ol). (Pb.S.B. 2016)

34. (a) Write the IUPAC names of the following compounds:



(b) Starting from phenol how phenolphthalein is obtained? (J.K. S.B. 2016)

35. (a) Give one example of each of the following reactions:

i) Reimer Tiemann reaction

(ii) Williamson's synthesis

(b) Convert: Propanone to 2-methylpropanol.

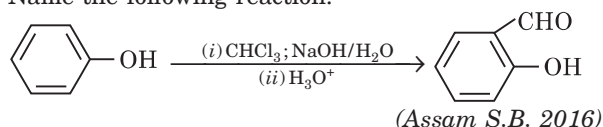
(Tripura S.B. 2016)

36. An organic compound A ($\text{C}_2\text{H}_6\text{O}$) reacts with sodium to form compound B and hydrogen gas. When heated with conc. H_2SO_4 at 413K, A produces C ($\text{C}_4\text{H}_{10}\text{O}$). C on treatment with conc. HI at 373K forms D. C is also obtained when B is heated with D. Identify A, B, C and D and write chemical equations for the formation of B from A and formation of C from B and D. (Kolkata S.B. 2016)

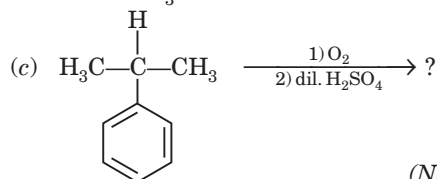
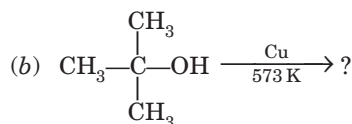
37. (a) Explain why alcohols are more soluble in water compared to ether?

(b) What happens when phenol is heated with Zn dust? Give equation.

(c) Name the following reaction:

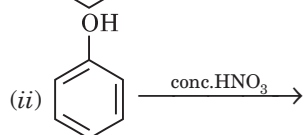
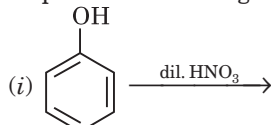


38. Complete the following reactions:



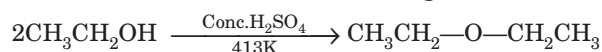
(Nagaland S.B. 2016)

39. (a) Complete the following reactions:

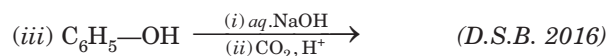
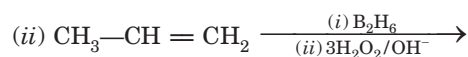
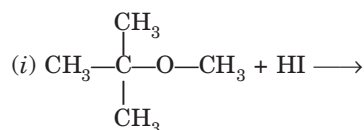


(b) Explain Williamson synthesis. (Kerala S.B. 2016)

40. (a) Write the mechanism of the following reaction:



(b) Write the main product(s) in each of the following reactions:



41. (i) Phenol has higher boiling point than toluene. Why?
(ii) Why are alcohols easily protonated but phenols are not protonated? (Pb.S.B. 2017)

42. (a) Discuss the acidic nature of phenols. (Hr.S.B. 2017)

(b) Name any two tests to distinguish alcohol from phenol.

(c) *p*-Nitrophenol is more acidic than phenol. Explain why? (Hr.S.B. 2017)

43. How do primary, secondary and tertiary alcohols differ towards oxidation reaction? (Nagaland S.B. 2017)

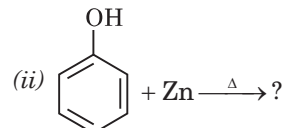
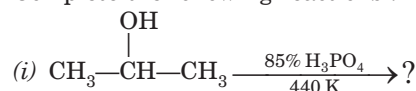
44. (a) Give reason why phenols are acidic in nature.

(b) Give one general method of preparation of 3° alcohol. Give equation.

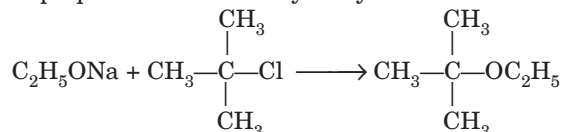
(c) Complete the following reaction and name the product.



45. (a) Complete the following reactions:



(b) The following is not an appropriate reaction for the preparation of *tert*-butyl ethyl ether:



Write a suitable reaction for the preparation of *tert*-butyl ethyl ether. (Meghalaya S.B. 2017)

46. (a) Arrange the following compounds in the order of increasing boiling points:

Ethanol, Propan-1-ol, Butan-1-ol, Butan-2-ol.

(b) In the lab, students were asked to carry out the reaction between phenol and conc. HNO_3 . But one student, 'A' carried out the reaction between phenol and dil. HNO_3 . Do you think that the student 'A' got the same result as others. Substantiate with suitable explanations.

[Also write the chemical equations wherever necessary.] (Kerala S.B. 2017)

47. Lucas test is used to identify primary, secondary and tertiary alcohols.

(a) Explain the process.

(b) Name the reagents used in the test.

(Kerala S.B. 2018)



CBSE QUESTIONS



48. Explain

(i) Ortho nitrophenol is more acidic than ortho-methoxyphenol.

(ii) $-\text{OH}$ group attached to the carbon of benzene ring activates it towards electrophilic substitution.

(A.I.S.B. 2005)

49. How would you convert the following:

(i) Phenol to benzoquinone

(ii) Propanone to 2-methyl propan-2-ol

(iii) Propene to propan-2-ol

(A.I.S.B. 2010)

50. How would you obtain the following :

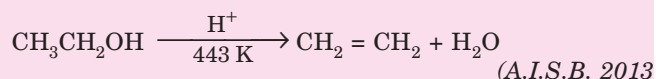
- (i) Benzoquinone from phenol
- (ii) 2-Methylpropan-2-ol from methyl magnesium bromide
- (iii) Propan-2-ol from propene. (A.I.S.B. 2011)

51. Explain the mechanism of acid catalysed hydration of an alkene to form corresponding alcohol. (A.I.S.B. 2012)

52. Explain the following :

- (i) Alcohols are more soluble in water than hydrocarbons of comparable molecular masses.
- (ii) Ortho nitrophenol is more acidic than ortho methoxyphenol. (A.I.S.B. 2012)

53. Explain the mechanism of the following reaction :



54. Write the mechanism of the following reaction :



55. Give reasons for the following:

- (i) o-nitrophenol is more acidic than o-methoxyphenol.
- (ii) Butan-1-ol has a higher boiling point than diethyl ether.
- (iii) $(\text{CH}_3)_3\text{C}-\text{O}-\text{CH}_3$ on reaction with HI gives $(\text{CH}_3)_3\text{C}-\text{I}$ and CH_3-OH as the main products and not $(\text{CH}_3)_3\text{C}-\text{OH}$ and CH_3-I . (A.I.S.B. 2015)

56. Write the chemical equations involved in the following reactions:

- (i) Kolbe's reaction
- (ii) Friedel Crafts acetylation of anisole

Or

How do you convert:

- (i) Phenol to toluene
- (ii) Formaldehyde to ethanol (A.I.S.B. 2016)

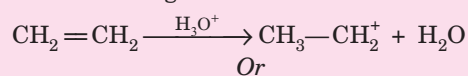
57. Give reasons for the following:

- (a) Protonation of phenols is difficult whereas ethanol easily undergoes protonation.
- (b) Boiling point of ethanol is higher than that of dimethyl ether.
- (c) Anisole on reaction with HI gives phenol and CH_3-I as main products and not iodobenzene and CH_3OH . (A.I.S.B. 2016)

58. (a) Arrange the following compounds in the increasing order of their acid strength:

p-cresol, *p*-nitrophenol, phenol

- (b) Write the mechanism (using curved arrow notation) of the following reaction :



Or

Write the structures of the products when Butan-2-ol reacts with the following :

- (a) CrO_3
- (a) SOCl_2 (A.I.S.B. 2017)

Or

- (a) Discuss the dehydrogenation of primary alcohols.

- b) Write the following reactions :

- (i) Diethyl ether with HI
- (ii) Phenol with benzene diazonium chloride
- (iii) Alcohol with SOCl_2 (Pb. S.B. 2012)

- 2. (a) Discuss the acidic dehydration of primary alcohols at 443 K.

- (b) Write Reimer-Tiemann reaction.

- c) Write two uses of ethanol.

Or

- (a) Why are ethers relatively inert compounds ?

- (b) Write the following reactions :

- i) Diethyl ether with Cl_2
- (ii) Phenol with zinc dust
- (iii) Alcohol with PCl_5 (Pb. S.B. 2012)

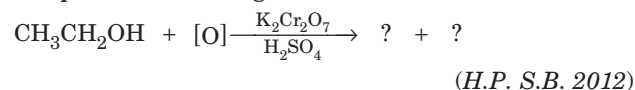
- 3. Account for the following :

- (i) Out of phenol and benzene which is more easily nitrated and why ?

- (ii) How will you convert benzene diazonium chloride to phenol ?

- (iii) Friedel Crafts alkylation reaction.

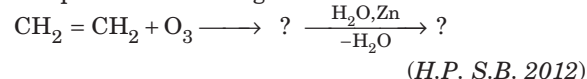
Complete the following reaction :



- 4. (a) Write short notes on :

- (i) Wurtz reaction
- (ii) Finkelstein reaction
- (iii) Saytzeff's rule

- b) Complete the following reactions :



- 5. (a) Write IUPAC names of all the possible isomers with the molecular formula $\text{C}_3\text{H}_8\text{O}$.

- (b) Phenol is usually manufactured from cumene. Write the structure of cumene.

- (c) Primary, secondary and tertiary alcohols can be distinguished by Lucas test.

- (i) What is Lucas reagent ?

- (ii) Write the observation for primary, secondary and tertiary alcohols in Lucas test. (Kerala S.B. 2013)

- 6. (a) What happens when phenol is treated with

- (i) CO_2 at 4–7 atm pressure

- (ii) Br_2/CS_2

- (iii) CHCl_3 , NaOH at 340 K

Give reactions also.

- (b) How will you distinguish between isopropyl alcohol and ethyl alcohol. (Hr. S.B. 2013)

- 7. (a) Explain the mechanism of dehydration of alcohols to give alkenes.

- b) What happens when phenol is treated with

- (i) dil. HNO_3 (ii) Conc. HNO_3

- c) How will you prepare phenol from

- (i) Haloarenes (ii) Diazonium salts

- (iii) Cumene (Hr. S.B. 2013)

- 8. (a) How will you prepare the following compounds using Grignard reagent

- (i) Primary alcohol

- (ii) Secondary alcohol ?

- (b) How will you distinguish primary and secondary alcohols using Lucas test ?

Long Answer Questions

carrying 5 marks

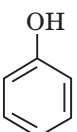
- 1. (a) Discuss the acidic dehydration of primary alcohols at 443 K.

- (b) Write Kolbe reaction of phenol.

- (c) Write two uses of methanol.

- (c) Write the correct pair of reactants for the preparation of *t*-butyl ethyl ether by Williamson synthesis.

(Kerala S.B. 2014)

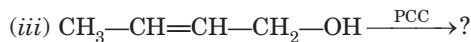
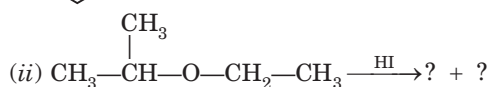
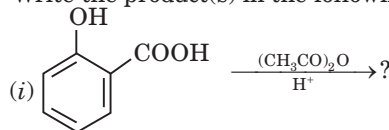
9. Give chemical reactions when  is reacted with

- (i) Zn (ii) Conc. HNO_3
(iii) Bromine water (iv) CHCl_3 + aq. NaOH
(v) Chromic acid

Or

Explain with examples the preparation of alcohols by using hydroboration oxidation of aldehydes and ketones. Also give chemical reactions involved. (Hr. S.B. 2015)

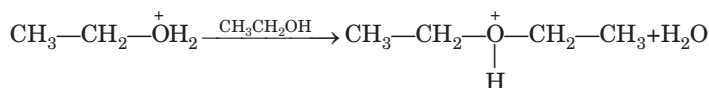
10. (a) Write the product(s) in the following reactions:



- (b) Give simple chemical tests to distinguish between the following pairs of compounds :
(i) Ethanol and Phenol
(ii) Propanol and 2-methylpropan-2-ol

Or

- (a) Write the formula of reagents used in the following reactions :
(i) Bromination of phenol to 2,4,6-tribromophenol
(ii) Hydroboration of propene and then oxidation to propanol.
(b) Arrange the following compound groups in the increasing order of their property indicated :
(i) *p*-nitrophenol, ethanol, phenol (acidic character)
(ii) Propanol, Propane, Propanal (boiling point)
(c) Write the mechanism (using curved arrow notation) of the following reaction :

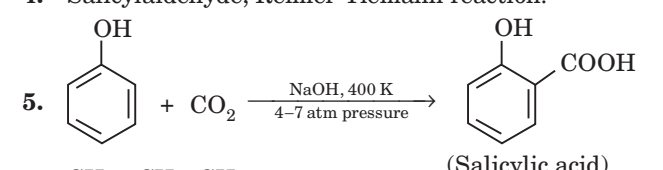


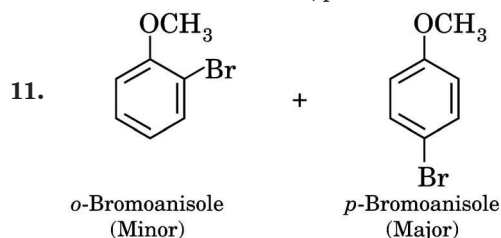
(D.S.B. 2017)

Hints & Answers

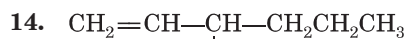
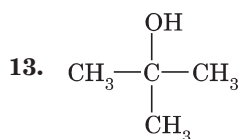
for Revision Exercises

Very Short Answer Questions

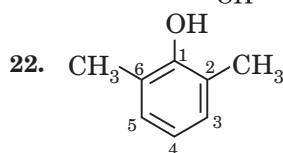
- But-2-ene, $\text{CH}_3\text{CH}=\text{CHCH}_3$
- $1^\circ > 2^\circ > 3^\circ$
- 2-Methylpropene
- Salicylaldehyde, Reimer-Tiemann reaction.
- 
- $\text{CH}_2\text{—CH—CH}_2$
 $\text{OH} \quad \text{OH} \quad \text{OH}$
- Phenol and iodomethane.
- The old samples of ethers may contain some peroxides because of their oxidation in the presence of light. The peroxides of ethers may decompose violently on heating resulting serious accidents.
- o*-nitroanisole (minor), *p*-nitroanisole (major).



12. 2-Bromo-3-methylbut-2-en-1-ol



- 3-Bromocyclohexanol
- p*-Nitrophenol
- 2, 5-Dinitrophenol
- $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + 2\text{HI} \xrightarrow{373\text{ K}} 2\text{C}_2\text{H}_5\text{I} + \text{H}_2\text{O}$
- 2-Ethoxyphenol
- 1, 1-Dimethoxyethane
- $\text{C}_6\text{H}_5\text{CH}_2\text{—CH—CH}_3$
 OH



- (±)-Butan-2-ol represents racemic mixture of (+)-butan-2-ol and (−)-butan-2-ol which rotates the plane polarised light in different directions but to equal extent. Therefore, (±) -butan-2-ol is optically inactive.
- 2-Methyl-propan-1,3-diol.
- 2-Bromo-3-methylbut-2-en-1-ol.
- 2-Methoxy-2-methylpropane.
- 3-Phenylprop-2-en-1-ol.
- 3, 3 Dimethylpentan-2-ol
- (c) 30. (b) 31. (a) 32. (b) 33. (d)
- (c) 35. (b) 36. (d) 37. (b) 38. (d)
- (d) 40. (b) 41. (c) 42. (c) 43. (a)
- (d) 45. (b) 46. (a) 47. (d) 48. (c)

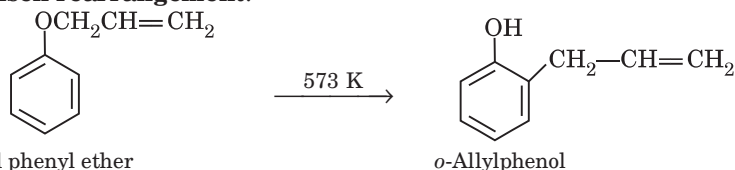
Competition File

Additional Useful Information and Objective Questions

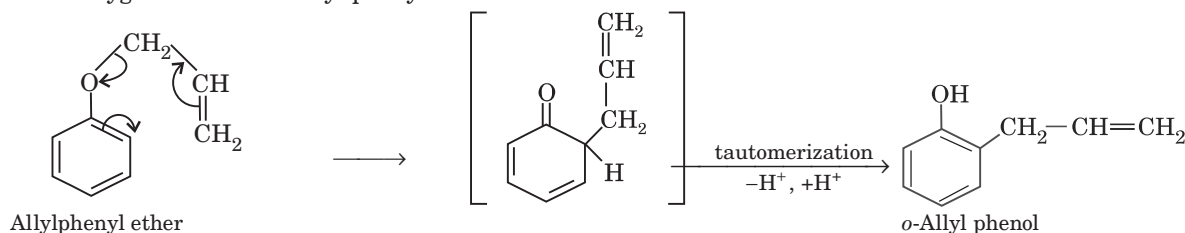
ADDITIONAL USEFUL INFORMATION

► SOME MORE NAME REACTIONS

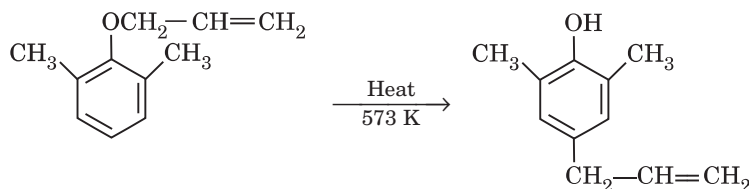
Claisen rearrangement. When allyl phenyl ethers are heated to 573 K, they undergo intramolecular rearrangement in which the allyl group migrates from the phenolic oxygen atom to *ortho* position of the benzene ring forming *o*-allyl phenol. This reaction is called **Claisen rearrangement**.



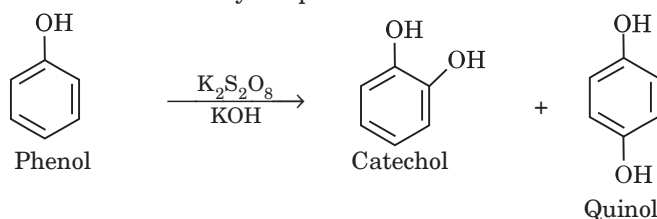
In this reaction, the bond between C-3 of the allyl group and the *ortho* position of the benzene ring forms at the same time so that the carbon—oxygen bond of the allyl phenyl ether breaks.



If both the *ortho* positions are occupied, then the allyl group migrates to the *para* position.

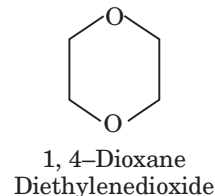
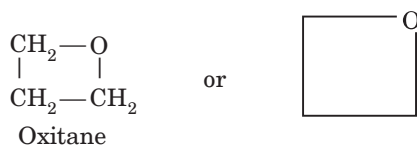
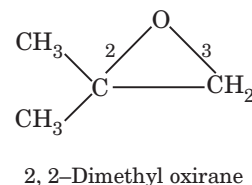
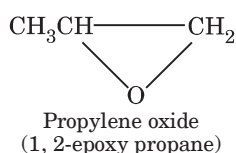
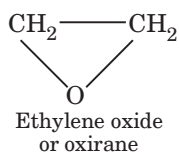


Elbs persulphate oxidation. Monohydric phenols on oxidation with alkaline potassium persulphate give dihydric phenols.



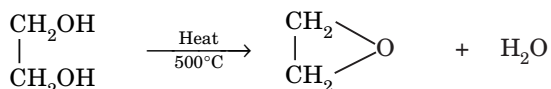
► CYCLIC ETHERS

In addition to normal ethers, some cyclic ethers are also important. Cyclic ethers are named as oxides or epoxy compounds. The three and four membered cyclic ethers are named as **oxiranes** and **oxitanes** respectively. In cyclic ethers, numbering is done in such a way that oxygen is assigned number 1. Some common examples are :

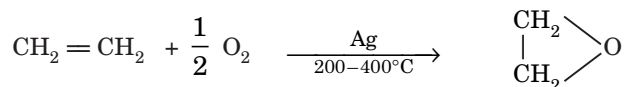


Competition File

Epoxides are prepared by heating ethylene glycol at 500°C.



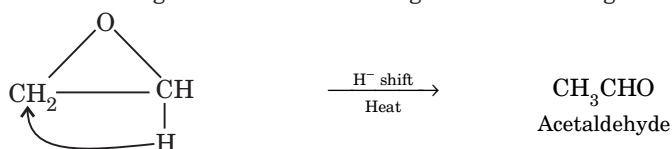
It is manufactured by heating ethylene and oxygen under pressure in the presence of silver catalyst at 200–400°C



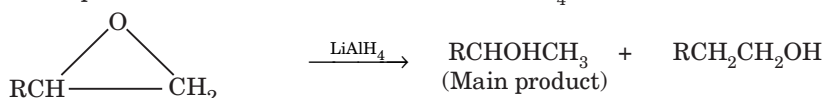
It may also be prepared by distilling ethylene chlorohydrin with concentrated aqueous solution of NaOH.



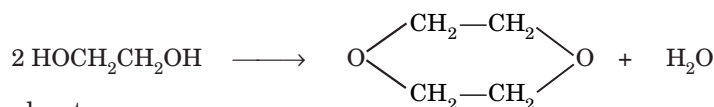
Ethylene oxide undergoes molecular rearrangement on heating to form acetaldehyde



The substituted epoxides are reduced to alcohols with LiAlH_4 .



Dioxane is manufactured by distilling ethylene glycol with fuming H_2SO_4 .



It is a very useful solvent.

OBJECTIVE TYPE QUESTIONS

Multiple Choice Questions

M. C. Q.

A

Topicwise MULTIPLE CHOICE QUESTIONS
with only one correct answer

Alcohols

A1. When ketones are treated with Grignard reagent followed by hydrolysis with dilute acid, the product is:

- (a) Primary alcohol (b) Secondary alcohol
(c) Tertiary alcohol (d) Alkene

A2. Propene on hydroboration oxidation produces

- (a) Propan-1-ol (b) Propan-2-ol
(c) Propane-1, 3-diol (d) Propane-1, 2-diol

A3. The product of acid-catalysed hydration of 2-phenylpropene gives

- (a) 2-phenylpropan-2-ol (b) 1-phenylpropan-2-ol
(c) 2-phenylpropan-1-ol (d) 3-phenylpropan-1-ol

A4. Which one of the following compounds would not be easily oxidised by $\text{K}_2\text{Cr}_2\text{O}_7$ and sulphuric acid?

- (a) $\text{CH}_3\text{CH}_2\text{OH}$ (b) $(\text{CH}_3)_2\text{CHOH}$
(c) $(\text{CH}_3)_3\text{COH}$ (d) CH_3CHO

A5. Which of the following alcohols is most reactive with HCl in the presence of ZnCl_2 ?

- (a) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} - \text{OH} \\ | \\ \text{CH}_3 \end{array}$ (b) $\begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2\text{OH} \\ | \\ \text{CH}_3 \end{array}$

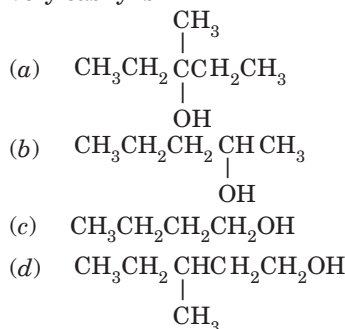
Answers

- A1.** (c) **A2.** (a) **A3.** (a) **A4.** (c) **A5.** (a)

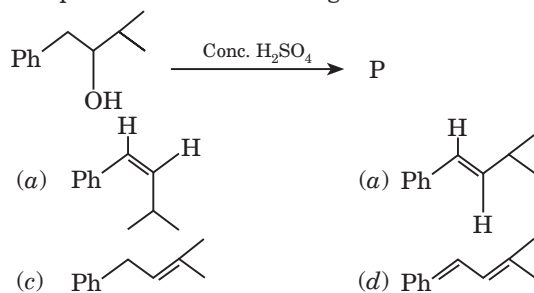
Competition File

- (c) $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{OH}$ (d) CH_3OH .
- A6.** Isopropyl alcohol is oxidised with $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 to give :
 (a) CH_3CHO (b) CH_3COCH_3
 (c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ (d) $\text{CH}_3\text{CH}=\text{CH}_2$.
- A7.** An alcohol of molecular formula $\text{C}_5\text{H}_{11}\text{OH}$ on dehydration gives an alkene, which on oxidation yields a mixture of ketone and an acid. The alcohol is
 (a) $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$
 (b) $\text{CH}_3\underset{\text{OH}}{\text{CH}}\text{CH}_2\text{CH}_2\text{CH}_3$
 (c) $(\text{H}_3)_2\text{CHCH}(\text{OH})\text{CH}_3$
 (d) $(\text{H}_3)_3\text{CCH}_2\text{OH}$
- A8.** Ethanol on warming with conc. H_2SO_4 at 413 K gives
 (a) ethene
 (b) diethyl ether
 (c) dimethyl ether
 (d) ethyl hydrogen sulphate.
- A9.** Which one/ones of the following reactions will give propan-2-ol ? Choose the right answer from (a), (b), (c) and (d).
- I. $\text{CH}_2=\text{CH}-\text{CH}_3 + \text{H}_2\text{O} \xrightarrow{\text{H}^+}$
- II. $\text{CH}_3\text{CHO} \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) CH}_3\text{MgI}}$
- III. $\text{CH}_2\text{O} \xrightarrow[\text{(ii) H}_2\text{O}]{\text{(i) C}_2\text{H}_5\text{MgI}}$
- IV. $\text{CH}_2=\text{CH}-\text{CH}_3 \xrightarrow{\text{Neutral KMnO}_4}$
- (a) I and II (b) II and III
 (c) III and I (d) II and IV
- A10.** How many optically active stereoisomers are possible for butane-2, 3-diol ?
 (a) 1 (b) 2
 (c) 3 (d) 4
- A11.** 1 propanol and 2-propanol can be best distinguished by
 (a) oxidation with alkaline KMnO_4 followed by reaction with Fehling solution
 (b) oxidation with acidic dichromate followed by reaction with Fehling solution
 (c) oxidation by heating with copper followed by reaction with Fehling solution
 (d) oxidation with conc. H_2SO_4 followed by reaction with Fehling solution

- A12.** During dehydration of alcohols to alkenes by heating with conc. H_2SO_4 , the initial step is
 (a) formation of an ester
 (b) protonation of alcohol molecule
 (c) formation of carbocation
 (d) elimination of water
- A13.** Which of the following will not form a yellow precipitate on heating with an alkaline solution of iodine ?
 (a) $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ (b) CH_3OH
 (c) $\text{CH}_3\text{CH}_2\text{OH}$ (d) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$
- A14.** Among the following compounds which can be dehydrated very easily is

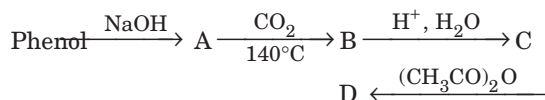


- A15.** The product P in the following reaction is



Phenols

- A16.** Phenol is more acidic than ethyl alcohol because
 (a) phenoxide ion is more resonance stabilised than phenol
 (b) there is more hydrogen bonding in phenol than ethyl alcohol
 (c) ethoxide ion is less resonance stabilised than ethyl alcohol
 (d) phenol has higher boiling point than ethyl alcohol.
- A17.** Reimer-Tiemann reaction is useful for the preparation of :
 (a) benzaldehyde (b) salicylaldehyde
 (c) toluene (d) acetophenone.
- A18.** Phenol on distillation with zinc dust gives :
 (a) benzene (b) benzaldehyde
 (c) benzoic acid (d) benzophenone.
- A19.** The end product in the following sequence is :



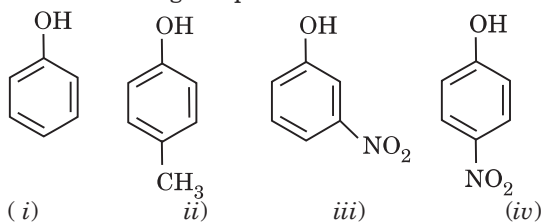
Answers

- A6.** (b) **A7.** (c) **A8.** (b) **A9.** (a) **A10.** (b) **A11.** (c) **A12.** (b) **A13.** (b) **A14.** (a) **A15.** (b)
A16. (a) **A17.** (b) **A18.** (a) **A19.** (d)

Competition File

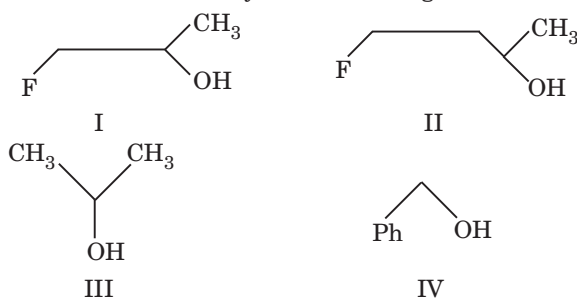
- (a) Salicylic acid (b) Salicylaldehyde
(c) Phenyl acetate (d) Aspirin.
- A20.** Which of the following reagent cannot be used to distinguish between phenol and benzyl alcohol ?
(a) NaOH (b) NaHCO_3
(c) Br_2/CCl_4 (d) FeCl_3
- A21.** Phenol reacts with bromine water in CS_2 at low temperature to give
(a) *o*-Bromophenol (b) *o*- and *p*-Bromophenol
(c) *p*-Bromophenol (d) 2,4,6-Tribromophenol

A22. In the following compounds :



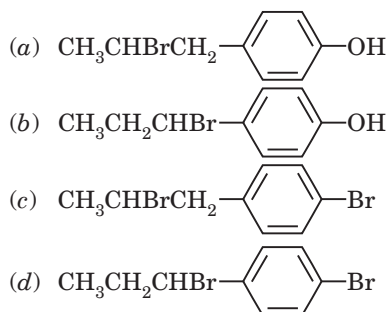
The order of acidity is

- (a) (iii) > (iv) > (i) > (ii)
(b) (i) > (iv) > (iii) > (ii)
(c) (ii) > (i) > (iii) > (iv)
(d) (iv) > (iii) > (i) > (ii)
- A23.** The order of reactivity of the following alcohols



towards conc. HCl is

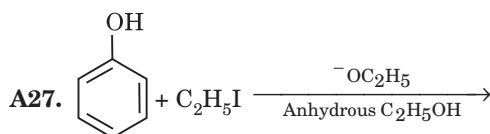
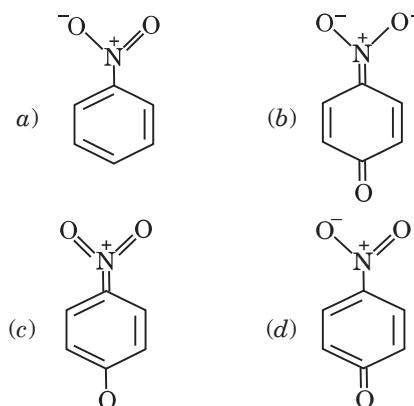
- (a) I > II > III > IV (b) I > III > II > IV
(c) IV > III > II > I (d) IV > III > I > II
- A24.** The reaction of $\text{CH}_3\text{CH}=\text{CH}-\text{C}_6\text{H}_4-\text{OH}$ with HBr gives



A25. Which of the following will give phenol with CaO and NaOH ?

- (a) Salicylic acid
(b) Picric acid
(c) Benzoic acid
(d) Amino acid

A26. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is :



- (a) $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$ (b) $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$
(c) $\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$ (d) $\text{C}_6\text{H}_5\text{I}$

A28. When phenol is treated with CHCl_3 and NaOH, the product formed is

- (a) Benzaldehyde (b) Salicylaldehyde
(c) Salicylic acid (d) Benzoic acid

A29. When phenol is treated with conc. HNO_3 in the presence of conc. H_2SO_4 , the product is

- (a) Picric acid (b) *p*-nitrophenol
(c) *o*-nitrophenol (d) *m*-nitrophenol

A30. Which of the following is the strongest acid?

- (a) *o*-methoxyphenol (b) *p*-methoxyphenol
(c) *m*-methoxyphenol (d) phenol

Ethers

A31. Ethers are isomeric with

- (a) aldehydes
(b) vinyl alcohols
(c) alcohols
(d) ketones.

Answers

- A20.** (b) **A21.** (b) **A22.** (d) **A23.** (c) **A24.** (b) **A25.** (a) **A26.** (c) **A27.** (b) **A28.** (b)
A29. (a) **A30.** (c) **A31.** (c)

Competition File

- A32.** Diethyl ether on treatment with excess Cl_2 gives
- perchlorodiethyl ether
 - ethyl chloride
 - ethanoyl chloride
 - diethyl ether peroxide.
- A33.** Anisole reacts with HI at 373 K to give
- $\text{C}_6\text{H}_5\text{I} + \text{CH}_3\text{OH}$
 - $\text{CH}_3\text{I} + \text{C}_6\text{H}_5\text{OH}$
 - $\text{C}_6\text{H}_5\text{CH}_2\text{OH} + \text{CH}_3\text{I}$
 - $\text{CH}_3\text{CH}_2\text{I} + \text{C}_6\text{H}_5\text{OH}$.
- A34.** Ethers can be distinguished from alcohols by the following reaction :
- reaction with Na
 - reaction with PCl_5
 - reaction with 2, 4-dinitrophenyl hydrazine
 - none of these.
- A35.** In the reaction :
- $$\text{CH}_3\underset{\text{Br}}{\text{CH}}\text{CH}_3 \xrightarrow[\text{KOH}]{\text{alc}} \text{A} \xrightarrow[\text{Peroxide}]{\text{HBr}} \text{B} \xrightarrow{\text{CH}_3\text{ONa}} \text{C},$$
- C is
- Diethyl ether
 - 1-Methoxypropane
 - Isopropyl alcohol
 - Propylene glycol.
- A36.** The compound which is not isomeric with diethyl ether is
- n*-propyl methyl ether
 - 2-methyl propan-2-ol
 - Butanone
 - Butan-1-ol
- A37.** How many isomeric acyclic alcohols and ethers are possible for $\text{C}_4\text{H}_8\text{O}$?
- 3
 - 4
 - 5
 - 7
- A38.** Diethyl ether on heating with conc. HI gives two moles of
- ethanol
 - iodoform
 - ethyl iodide
 - methyl iodide
- A39.** An ether is more volatile than alcohol having the same molecular formula. This is due to
- intermolecular hydrogen bonding in alcohols
 - dipolar character of ethers
 - alcohols having resonance structures
 - intermolecular hydrogen bonding in ethers.
- A40.** The major organic product in the reaction
- $$\text{CH}_3\text{—O—CH}(\text{CH}_3)_2 + \text{HI} \longrightarrow \text{Product is}$$
- $\text{ICH}_2\text{OCH}(\text{CH}_3)_2$
 - $\text{CH}_3\text{OC}(\text{CH}_3)_2$
I
 - $\text{CH}_3\text{I} + (\text{CH}_3)_2\text{CHOH}$
 - $\text{CH}_3\text{OH} + (\text{CH}_3)_2\text{CHI}$
- Answers**

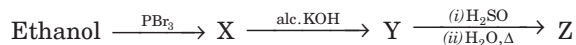
Answers

A32.(a) **A33.** (b) **A34.** (a) **A35.** (b) **A36.** (b) **A37.** (d) **A38.** (c) **A39.** (a) **A40.** (c)

B MULTIPLE CHOICE QUESTIONS
from competitive examinations

AIPMT & Other State Boards' Medical Entrance

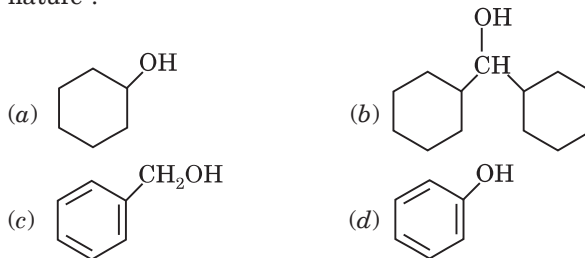
- B1.** Consider the following reaction :



The product Z is

- (a) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ (b) $\text{CH}_3\text{CH}_2\text{O}-\text{SO}_3\text{H}$
 (c) $\text{CH}_3\text{CH}_2\text{OH}$ (d) $\text{CH}_2=\text{CH}_2$
 (C.B.S.E. PMT 2009)

- B2.** Phenol $\xrightarrow{\text{Zn, dust}}$ X $\xrightarrow[\text{Anhyd. AlCl}_3]{\text{CH}_3\text{Cl}}$ Y $\xrightarrow[\text{KMnO}_4]{\text{Alkaline}}$ Z
The product Z is
(a) Benzaldehyde (b) Benzoic acid
(c) Benzene (d) Toluene
(C.B.S.E. PMT 2009)
- B3.** Which one of the following compounds has the most acidic nature ?



(C.B.S.E. P.M.T. 2010)

Answers

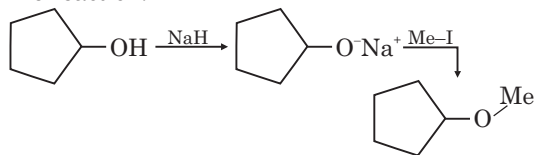
B1. (c) **B2.** (b) **B3.** (d)

Competition File

B13. Which of the following reagent would distinguish *cis*-cyclopenta-1, 2-diol from *trans*-isomer?

- (a) MnO_2 (b) luminium isopropoxide
(c) Acetone (d) Ozone (NEET 2016)

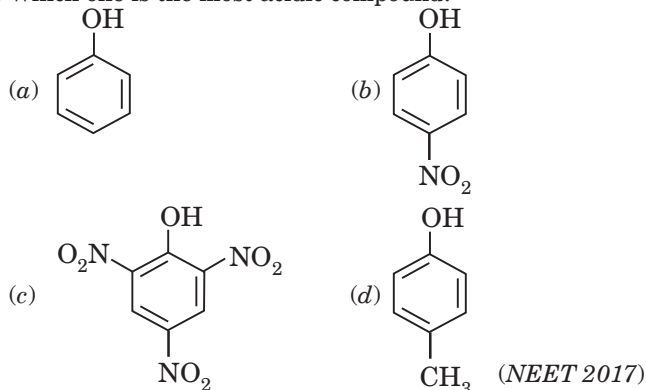
B14. The reaction.



can be classified as

- (a) dehydration reaction
(b) Williamson alcohol synthesis reaction
(c) Williamson ether synthesis reaction
(d) alcohol formation reaction (NEET 2016)

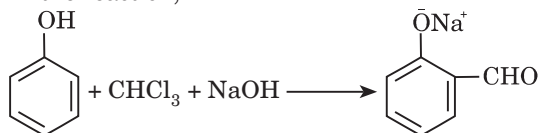
B15. Which one is the most acidic compound?



B16. The heating of phenyl methyl ether with HI produces

- (a) iodobenzene (b) phenol
(c) benzene (d) ethyl chloride (NEET 2017)

B17. In the reaction,



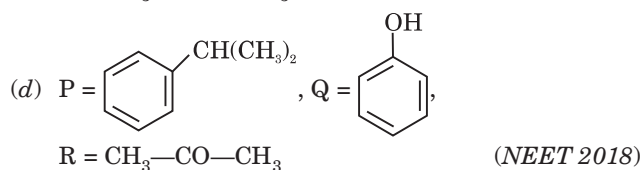
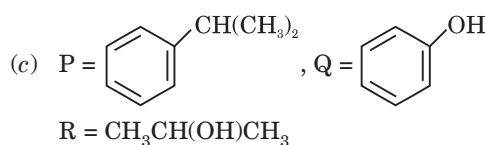
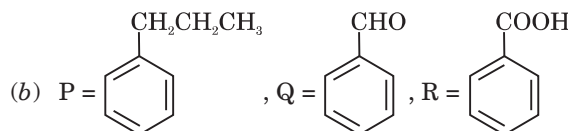
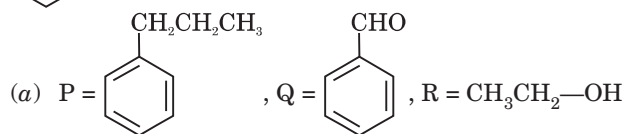
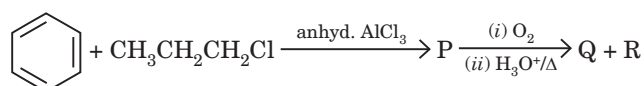
the electrophile involved is

- (a) dichloromethyl cation (CHCl_2^+)
(b) formyl cation (CHO^+)
(c) dichloromethyl anion (CHCl_2^-)
(d) dichlorocarbene ($:\text{CCl}_2$) (NEET 2018)

B18. The compound A on treatment with Na gives B, and with PCl_5 gives C. B and C react together to give diethyl ether. A, B and C are in the order

- (a) $\text{C}_2\text{H}_5\text{OH}$, C_2H_6 , $\text{C}_2\text{H}_5\text{Cl}$
(b) $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_2\text{H}_5\text{Cl}$, $\text{C}_2\text{H}_5\text{ONa}$
(c) $\text{C}_2\text{H}_5\text{Cl}$, C_2H_6 , $\text{C}_2\text{H}_5\text{OH}$
(d) $\text{C}_2\text{H}_5\text{OH}$, $\text{C}_2\text{H}_5\text{ONa}$, $\text{C}_2\text{H}_5\text{Cl}$ (NEET 2018)

B19. Identify the major products P, Q and R in the following sequence of reactions:



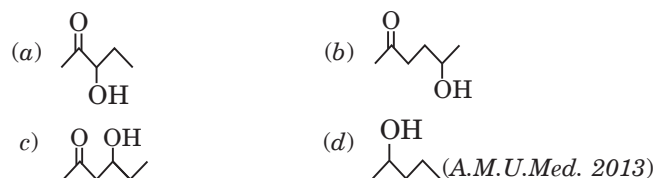
B20. The major product formed when 3,3-dimethylbutan-2-ol is heated with concentrated sulphuric acid is

- (a) 2, 3- dimethyl-2-butene
(b) 2,3-dimethyl-1-butene
(c) 3,3 dimethyl-1-butene
(d) *cis*- and *trans*-isomers of 2,3-dimethyl-1-butene
(e) *cis*- and *trans*-isomers of 3,3-dimethyl-2-butene (Kerala P.M.T. 2007)

B21. Which of the following alcohols gives the best yield of dialkyl ether on being heated with a trace of sulphuric acid?

- (a) Pentan-2-ol (b) Cyclopentanol
(c) 2-Methyl butan-2-ol (d) Propan-2-ol
(e) Pentan-1-ol (Kerala P.M.T. 2011)

B22. Which of the following will be most readily dehydrated in acidic conditions?



B23. Which one of the following phenols has the highest pK_a value?

- (a) *o*-Nitrophenol (b) Phenol
(c) *m*-Nitrophenol (d) Picric acid
(e) *p*-Cresol (Kerala PMT 2014)

Answers

B13. (c) **B14.** (c) **B15.** (c) **B16.** (b) **B17.** (d) **B18.** (d) **B19.** (d) **B20.** (a) **B21.** (e) **B22.** (c) **B23.** (e)

Competition File

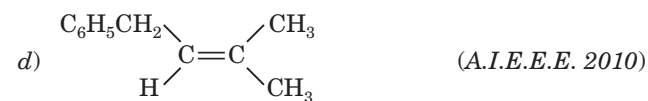
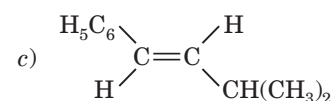
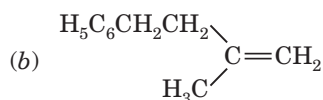
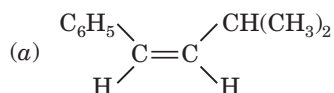
JEE (Main) & Other State Boards' Engineering Entrance

B24. The major product obtained on interaction of phenol with NaOH and CO₂ is

- (a) Benzoic acid (b) Salicylaldehyde
(c) Salicylic acid (d) Phthalic acid

(A.I.E.E.E. 2009)

B25. The main product of the following reaction



B26. The correct order of acidic strength of the following compounds :

- I. Phenol II. *p*-Cresol
III. *m*-Nitrophenol IV. *p*-Nitrophenol

is

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

(A.I.E.E.E. 2011)

B27. Which of the following reagents may be used to distinguish between phenol and benzoic acid ?

- (a) Molisch reagent (b) Neutral FeCl₃
(c) Aqueous NaOH (d) Tollen's reagent

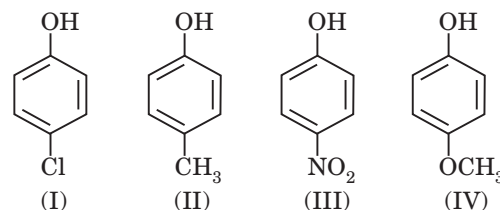
(A.I.E.E.E. 2011)

B28. *Ortho*-nitrophenol is less soluble in water than *p*- and *m*-nitrophenols because

- (a) *o*-nitrophenol shows intramolecular H-bonding
(b) *o*-nitrophenol shows intermolecular H-bonding
(c) melting point of *o*-nitrophenol is lower than those of *m*- and *p*-isomers
(d) *o*-nitrophenol is more volatile in steam than those of *m*- and *p*-isomers

(A.I.E.E.E. 2012)

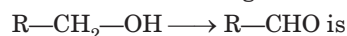
B29. Arrange the following compounds in order of decreasing acidity.



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

(JEE Main 2013)

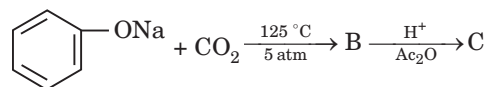
B30. The most suitable reagent for the conversion of



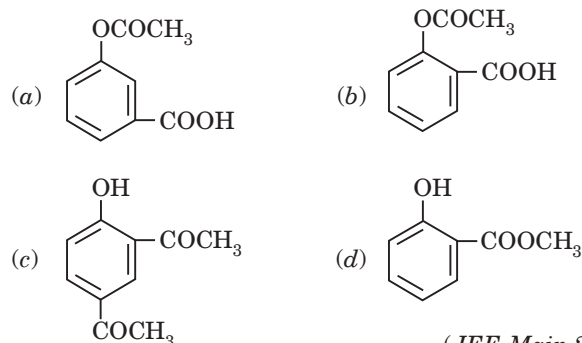
- (a) PCC (Pyridinium chlorochromate)
(b) KMnO₄
(c) K₂Cr₂O₇
(d) CrO₃

(JEE Main 2014)

B31. Sodium phenoxide when heated with CO₂ under pressure at 125°C yields a product which on acetylation produces C.

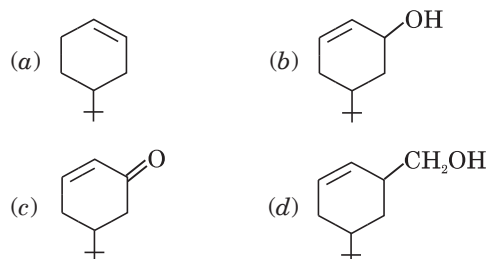
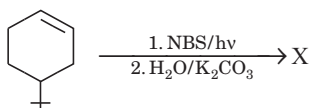


The major product C would be



(JEE-Main 2014)

B32. The product of the reaction given below is:



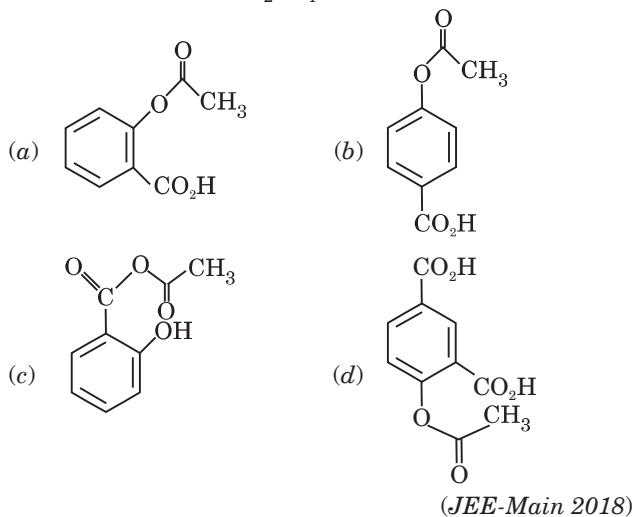
(JEE-Main 2016)

Answers

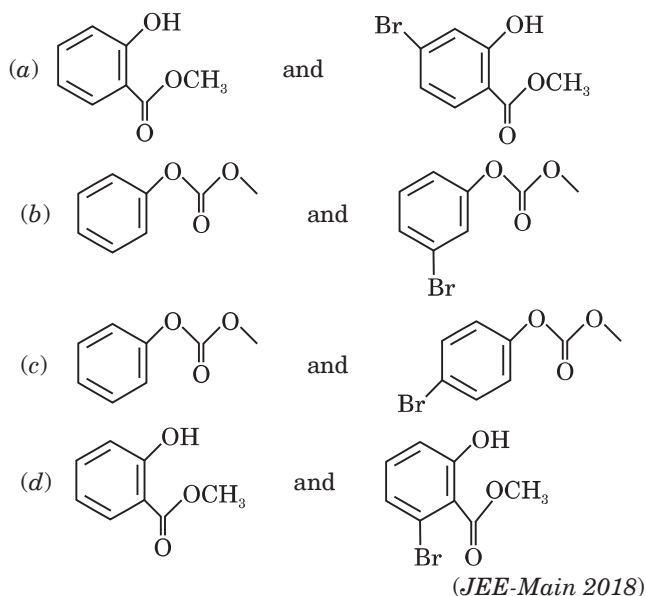
B24. (c) B25. (c) B26. (a) B27. (b) B28. (a) B29. (d) B30. (a) B31. (b) B32. (b)

Competition File

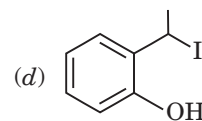
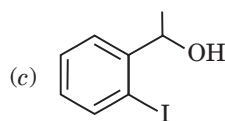
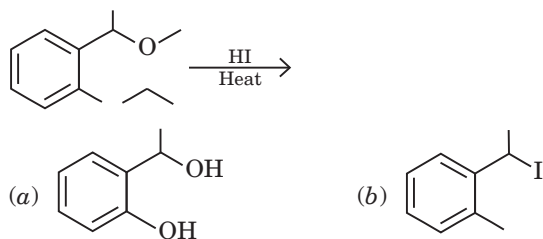
B33. Phenol on treatment with CO_2 in the presence of NaOH followed by acidification produces compound X as the major product. X on treatment with $(\text{CH}_3\text{CO})_2\text{O}$ in the presence of catalytic amount of H_2SO_4 produces:



B34. Phenol reacts with methyl chloroformate in the presence of NaOH to form product A. A reacts with Br_2 to form product B. A and B are respectively:

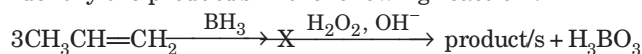


B35. The major product formed in the following reaction is:



(JEE Main 2018)

B36. Identify the product/s in the following reaction :

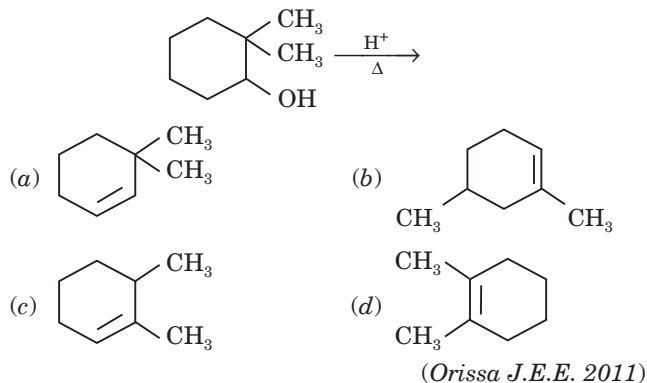


- (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (b) $\text{CH}_3\text{CHOHCH}_3$
 (c) $\text{CH}_3\text{CH}_2\text{CHO}$ (d) $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{OH}$
 (e) $\text{CH}_3\text{CHO} + \text{CH}_3\text{OH}$ (Kerala C.E.T. 2007)

B37. The hydroxyl compound that gives a precipitate immediately when treated with concentrated hydrochloric acid and anhydrous zinc chloride is

- (a) 3-methyl-2-butanol (b) 3-methyl-1-butanol
 (c) 1-butanol (d) 2-methyl-2-butanol
 (e) 2, 3-dimethyl-1-butanol (Kerala P.E.T. 2011)

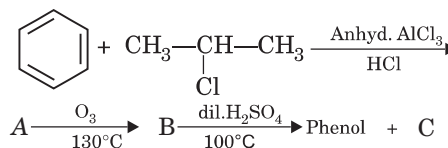
B38. Find the product of the given reaction



B39. An oxygen containing organic compound was found to contain 52% carbon and 13% of hydrogen. Its vapour density is 23. The compound reacts with sodium metal to liberate hydrogen. A functional isomer of this compound is

- (a) Ethanol (b) Ethanal
 (c) Methoxy methane (d) Methoxy ethane
 (Karnataka C.E.T. 2012)

B40. Identify 'C' in the following



- (a) Water (b) Ethanol
 (c) Propanone (d) Cumene hydroperoxide
 (Karnataka C.E.T. 2012, 2018)

B41. Salicylaldehyde can be prepared from phenol by

- (a) Schotten-Baumann reaction
 (b) Kolbe's reaction
 (c) Reimer-Tiemann reaction
 (d) Perkin reaction
 (e) Cannizzaro reaction (Kerala P.E.T. 2013)

Answers

B33. (a) **B34.** (c) **B35.** (d) **B36.** (a) **B37.** (d) **B38.** (d) **B39.** (c) **B40.** (c) **B41.** (c)

Competition File

B42. The total number of acyclic structural isomers possible for compound with molecular formula $C_4H_{10}O$ is

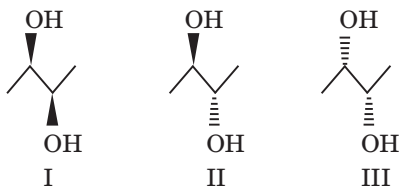
- (a) 9 (b) 7
(c) 5 (d) 6
(e) 8

(Kerala P.E.T. 2013, 2016)

B43. Compound 'A' of molecular formula $C_4H_{10}O$ on treatment with Lucas reagent at room temperature gives compound 'B'. When compound 'B' is heated with alcoholic KOH, it gives isobutene. Compound 'A' and 'B' are respectively

- (a) 2-methyl-2-propanol and 2-methyl-2-chloropropane
(b) 2-methyl-1-propanol and 1-chloro-2-methylpropane
(c) 2-methyl-1-propanol and 2-methyl-2-chloropropane
(d) butan-2-ol and 2-chlorobutane
(e) butan-1-ol and 1-chlorobutane (Kerala P.E.T. 2013)

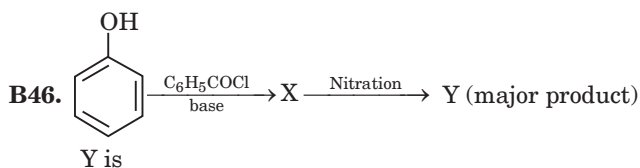
B44. The correct statement regarding the following compounds is



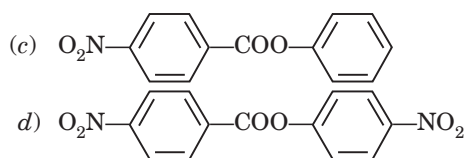
- (a) all three compounds are chiral
(b) only I and II are chiral
(c) I and III are diastereomers
(d) only I and III are chiral. (WB JEE 2014)

B45 Williamson's synthesis of preparing dimethyl ether is a/an

- (a) electrophilic substitution
(b) S_N1 reaction
(c) electrophilic addition
(d) S_N2 reaction
(e) free radical substitution. (Kerala PMT 2014)



- (a)
(b)



(Karnataka CET 2014)

B47. 0.44 g of a monohydric alcohol when added to methylmagnesium iodide in ether liberates at S.T.P., 112 cm^3 of methane. With PCC the same alcohol forms a carbonyl compound that answers silver mirror test. The monohydric alcohol is

- (a) $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{CH}_3$
(b) $(\text{CH}_3)_3\text{C}-\text{CH}_2\text{OH}$
(c) $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_2-\text{CH}_2-\text{CH}_3$

- (d) $(\text{CH}_3)_2\text{CH}-\text{CH}_2\text{OH}$ (Karnataka CET 2014)

B48. Arrange the following compounds in the increasing order of their acidic strength :

- (i) *m*-Nitrophenol (ii) *m*-Cresol
(iii) Phenol (iv) *m*-Chlorophenol
(a) $ii < iv < iii < i$ (b) $ii < iii < i < iv$
(c) $iii < ii < i < iv$ (d) $ii < iii < iv < i$

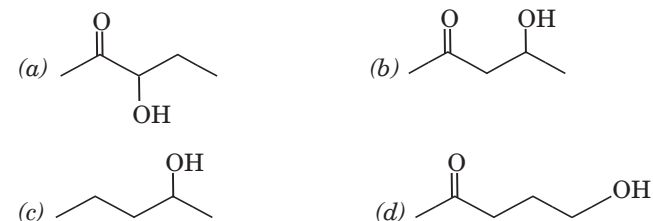
(Karnataka CET 2015)

B49. Which of the following compound would not react with Lucas reagent at room temperature?

- (a) $\text{H}_2\text{C}=\text{CHCH}_2\text{OH}$ (b) $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$
(c) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (d) $(\text{CH}_3)_3\text{COH}$

(W.B JEE 2016)

B50. Which of the following will be dehydrated most readily in alkaline medium?



(W.B JEE 2016)

B51. Isopropyl methyl ether when treated with cold hydrogen iodide gives:

- (a) Isopropyl iodide and methyl iodide
(b) Isopropyl alcohol and methyl iodide
(c) isopropyl alcohol and methyl alcohol
(d) isopropyl iodide and methyl alcohol

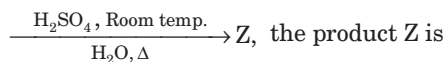
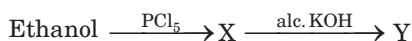
(M.H. CET 2016)

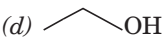
Answers

B42. (b) **B43.** (a) **B44.** (d) **B45.** (d) **B46.** (a) **B47.** (b) **B48.** (d) **B49.** (c) **B50.** (b) **B51.** (b)

Competition File

B52. In the reaction :



- (a) C_2H_4 (b) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$
 (c) $\text{CH}_3\text{CH}_2\text{OSO}_3\text{H}$ (d) 
 (Karnataka CET 2016)

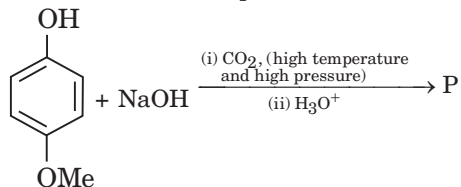
B53. The reaction which involves dichlorocarbene as an electrophile is

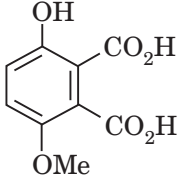
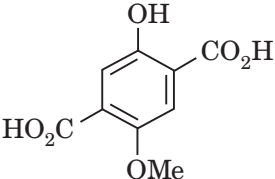
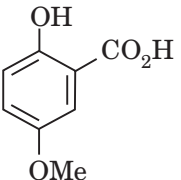
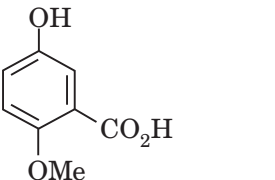
- (a) Reimer-Tiemann reaction (b) Kolbe's reaction
 (c) Friedel-Crafts' acylation (d) Fitting's reaction
 (Karnataka CET 2016)

B54. Ethanol is converted into ethoxyethane

- (a) by heating excess of ethanol with conc. H_2SO_4 at 140°C
 (b) by heating ethanol with excess of conc. H_2SO_4 at 443 K
 (c) by treating with conc. H_2SO_4 at room temperature
 (d) by treating with conc. H_2SO_4 at 273 K .
 (Karnataka CET 2016)

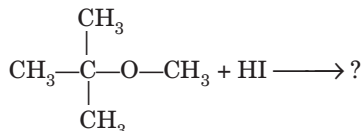
B55. The structure of the product P of the following reaction is



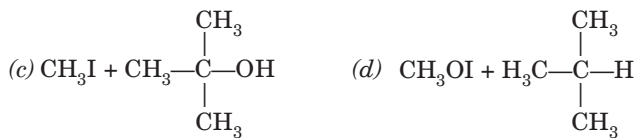
- (a) 
 (b) 
 (c) 
 (d) 

(W.B. JEE 2017)

B56. The products formed during the following reaction are



- (a) $\text{CH}_3\text{OH} + \text{CH}_3\text{C}(\text{CH}_3)_2\text{I}$ (b) $\text{CH}_4 + \text{H}_3\text{C}-\text{C}(\text{CH}_3)_2\text{OI}$



(Karnataka CET 2017)

B57. Which of the following cannot be used to oxidise primary alcohols to aldehydes?

- (a) CrO_3 in anhydrous medium
 (b) Pyridinium chlorochromate
 (c) KMnO_4 in acidic medium
 (d) Heating in presence of Cu at 573 K

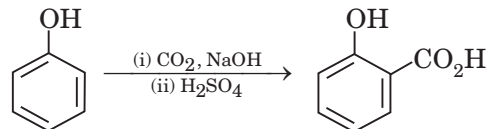
(Karnataka CET 2017)

B58. Which of the following orders is true regarding the acidic nature of phenols?

- (a) Phenol > o-cresol > o-nitrophenol
 (b) o-cresol < phenol < o-nitrophenol
 (c) Phenol < o-cresol > o-nitrophenol
 (d) Phenol < o-cresol < o-nitrophenol

(Karnataka CET 2017)

B59. Name of the following reaction is



- (a) Reimer-Tiemann (b) Kolbe-Schmitt
 (c) Cannizzaro (d) Gattermann
 (e) Gattermann-Koch. (Kerala PET 2017)

B60. What product is formed when phenol is treated with CHCl_3 and NaOH?

- (a) 3-Hydroxybenzaldehyde
 (b) 2-Hydroxybenzoic acid
 (c) 3-Hydroxybenzoic acid
 (d) 2-Hydroxybenzaldehyde

(J.K. CET 2018)

B61. Methoxybenzene on treatment with HI produces

- (a) iodobenzene and methanol
 (b) phenol and methyl iodide
 (c) iodobenzene and methyl iodide
 (d) phenol and methanol.

(WB JEE 2018)

B62. The intramolecular hydrogen bond is present in

- (a) phenol (b) o-nitrophenol
 (c) p-nitrophenol (d) p-cresol

(Karnataka CET 2018)

B63. Phenol can be distinguished from ethanol by the reagent

- (a) bromine water (b) sodium metal
 (c) iron metal (d) chlorine water

(Karnataka CET 2018)

Answers

- B52.** (d) **B53.** (c) **B54.** (a) **B55.** (c) **B56.** (a) **B57.** (c) **B58.** (b) **B59.** (b) **B60.** (d) **B61.** (b)
B62. (b) **B63.** (a)

Competition File

B64. When the vapours of tertiary butyl alcohol are passed through heated copper at 573 K, the product formed is

- (a) but-2-ene (b) butan-2-one
(c) 2-methylpropene (d) butanal

(Karnataka CET 2018)

B65. What is the increasing order of acidic strength among the following?

- (i) p-methoxy phenol, (ii) p-methyl phenol, (iii) p-nitrophenol
(a) $ii < iii < i$ (b) $iii < ii < i$
(c) $i < ii < iii$ (d) $i < iii < ii$

(Karnataka CET 2018)

B66. Oxidation of 1° alcohols to aldehydes is very successful for the alcohols like

- (a) pent-2-yn-1-ol (b) hexan-1-ol
(c) n-propylalcohol (d) pentan-1-ol
(e) octan-1-ol

(Kerala PET 2018)

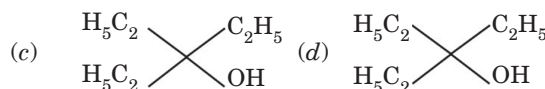
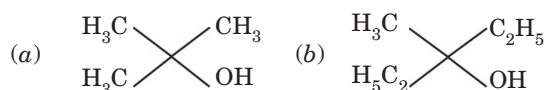
B67. The halogen compound which will not react with phenol to give ethers is

- (a) ethyl chloride (b) methyl chloride
(c) benzyl chloride (d) vinyl chloride
(e) allyl chloride

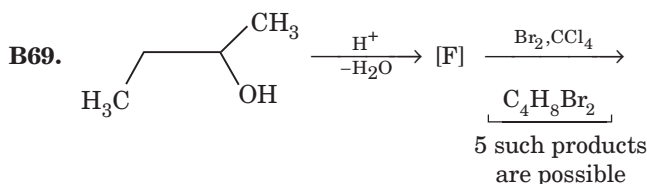
(Kerala PET 2018)

JEE (Advance) for IIT Entrance

B68. Ethyl ester $\xrightarrow[\text{excess}]{\text{CH}_3\text{MgBr}}$ P. The product P is



(I.I.T. 2003)

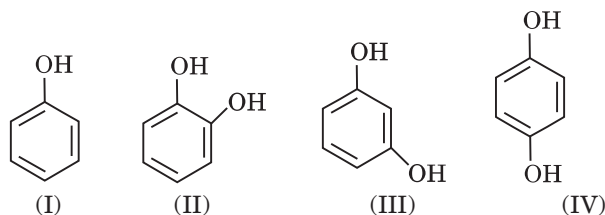


How many structures of F are possible ?

- (a) 2 (b) 5
(c) 6 (d) 3.

(I.I.T. 2003)

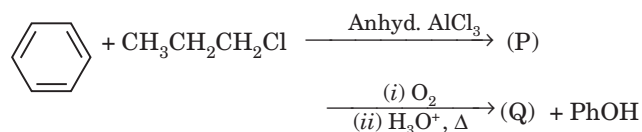
B70. Arrange the following compounds according to decreasing boiling points :

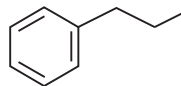
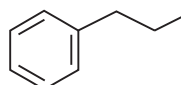
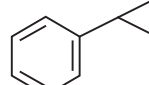
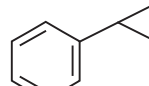


- (a) (IV) > (III) > (II) > (I) (b) (III) > (IV) > (II) > (I)
(c) (I) > (II) > (III) > (IV) (d) (III) > (II) > (I) > (IV)

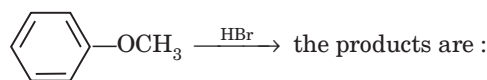
(I.I.T. 2006)

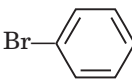
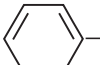
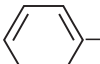
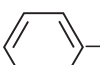
B71. Identify the major products (P) and (Q) in the following reaction :



- (a)  and CH_3COCH_3
(b)  and $\text{CH}_3\text{CH}_2\text{CHO}$
(c)  and CH_3COCH_3
(d)  and $\text{CH}_3\text{CH}_2\text{CHO}$ (I.I.T. 2006)

B72. In the reaction :



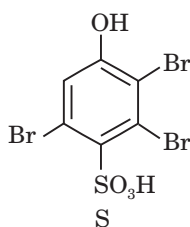
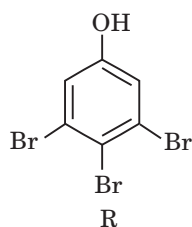
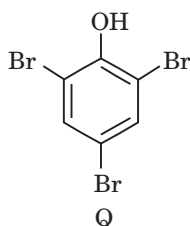
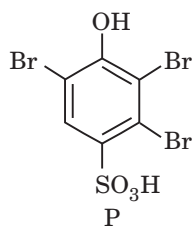
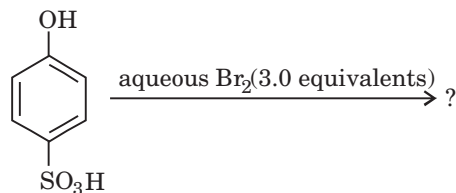
- (a)  and H_2
(b)  and CH_3Br
(c)  and CH_3OH
(d)  and CH_3Br (I.I.T. 2010)

Answers

B64. (c) **B65.** (c) **B66.** (e) **B67.** (d) **B68.** (a) **B69.** (d) **B70.** (a) **B71.** (c) **B72.** (d)

Competition File

B73. The major product(s) of the following reaction is (are)



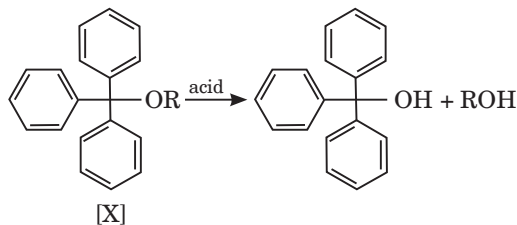
(a) P

(b) Q

(c) R

(d) SQ (JEE Advance 2013)

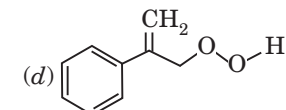
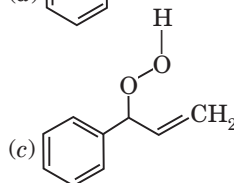
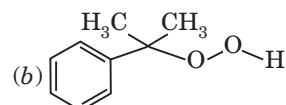
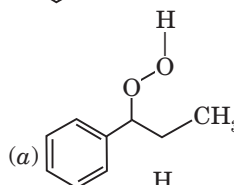
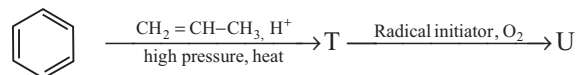
B74. The acidic hydrolysis of ether (X) shown below is fastest when



- (a) one phenyl group is replaced by a methyl group
 (b) one phenyl group is replaced by a para-methoxyphenyl group
 (c) two phenyl groups are replaced by two para-methoxyphenyl group
 (d) no structural change is made to X.

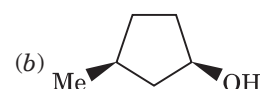
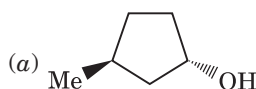
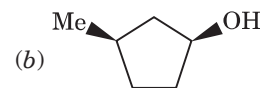
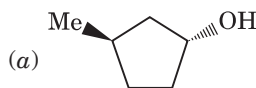
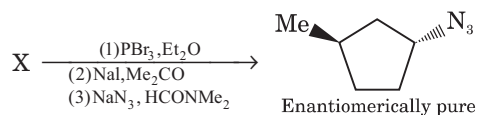
(JEE Advance 2014)

B75. The major product U in the following reaction is



(JEE Advance 2015)

B76. In the following reaction sequence, the correct structure(s) of X is (are)



(JEE Advance 2018)

Answers

B73. (b) **B74.** (c) **B75.** (b) **B76.** (b)

C

MULTIPLE CHOICE QUESTIONS with more than one correct answer

- C1.** Which of the following alcohols on dehydration with conc. H_2SO_4 give but-2-ene ?
 (a) 2-Methyl propan-2-ol
 (b) Butan-1-ol
 (c) 2-Methyl propan-1-ol
 (d) Butan-2-ol

C2. Which of the following alcohols give iodoform test ?

- (a) Butan-1-ol (b) Propan-1-ol
 (c) Propan-2-ol (d) Ethanol

C3. Which of the following are weaker acids than phenol ?

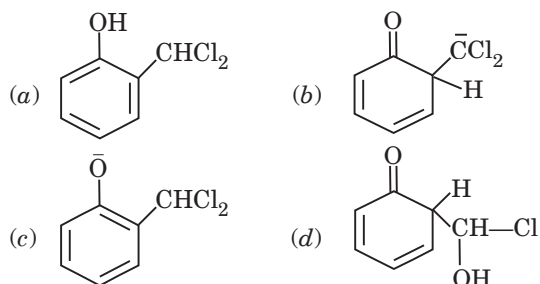
- (a) 4-Methoxy phenol (b) 3,5-dinitrophenol
 (c) 4-Methyl phenol (d) 4-Nitro phenol

Answers

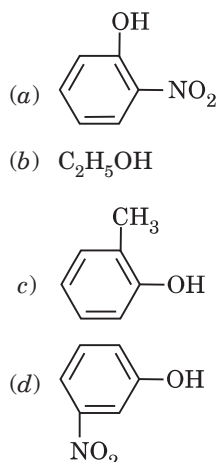
C1. (b, d) **C2.** (c, d) **C3.** (a, c)

Competition File

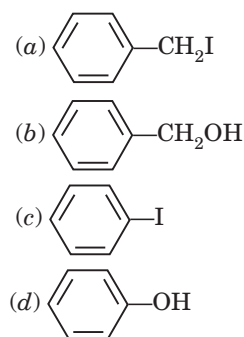
C4. When phenol is treated with CHCl_3 and NaOH followed by acidification, salicylaldehyde is formed. Which of the following species are involved in the above mentioned reaction as intermediate?



C5. Which of the following are less acidic than $\text{C}_6\text{H}_5\text{OH}$?

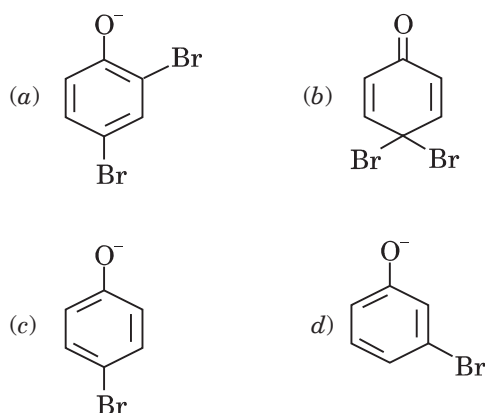
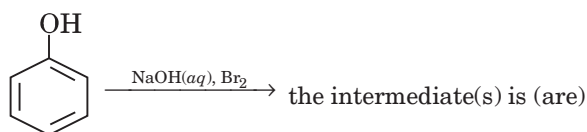


C6. The ether when treated with HI produces



(Kerala PMT 2014)

C7. In the reaction



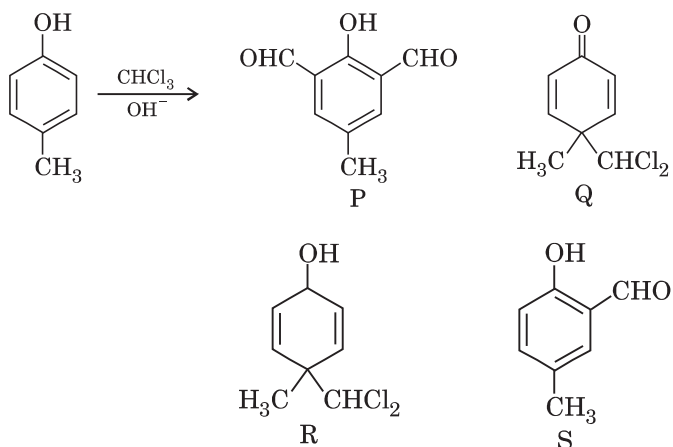
(I.I.T. 2010)

C8. Correct statement(s) in cases of *n*-butanol and *t*-butanol is (are)

- (a) both are having equal solubility in water
 (b) *t*-butanol is more soluble in water than *n*-butanol
 (c) boiling point of *t*-butanol is lower than *n*-butanol
 (d) boiling point of *n*-butanol is lower than *t*-butanol

(W.B. JEE Engg. 2013)

C9. In the following reaction, the product(s) formed is (are)



- (a) P (major) (b) Q (minor)
 (c) R (minor) (d) S (major)

(JEE Advance 2013)

C10. The correct combination of names for isomeric alcohols with molecular formula $\text{C}_4\text{H}_{10}\text{O}$ is/are

- (a) *tert*-butanol and 2-methylpropan-2-ol
 (b) *tert*-butanol and 1, 1-dimethylethan-1-ol
 (c) *n*-butanol and butan-1-ol
 (d) *iso*-butyl alcohol and 2-methylpropan-1-ol.

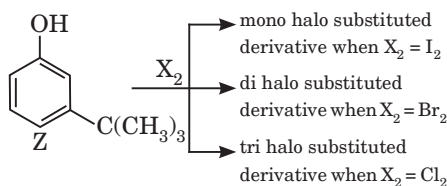
(JEE Advance 2014)

Answers

C4. (b, c) **C5.** (b, c) **C6.** (a, d) **C7.** (a, c) **C8.** (b, c) **C9.** (b, d) **C10.** (a, c, d)

Competition File

C11. The reactivity of compound Z with different halogens under appropriate conditions is given below :

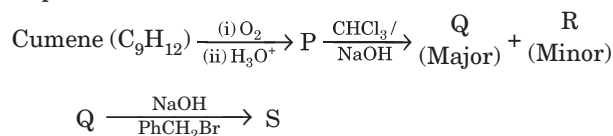


The observed pattern of electrophilic substitution can be explained by

- (a) the steric effect of the halogen
- (b) the steric effect of the *tert*-butyl group
- (c) the electronic effect of the phenolic group
- (d) the electronic effect of the *tert*-butyl group

JEE Advance 2014

C12. The correct statement(s) about the following reaction sequence is(are)



- (a) R is steam volatile
- (b) Q gives dark violet colouration with 1 % aqueous FeCl_3 solution
- (c) S gives yellow precipitate with 2, 4-dinitro-phenylhydrazine
- (d) S gives dark violet colouration with 1% aqueous FeCl_3 solution.

(JEE Advance 2016)

Answers

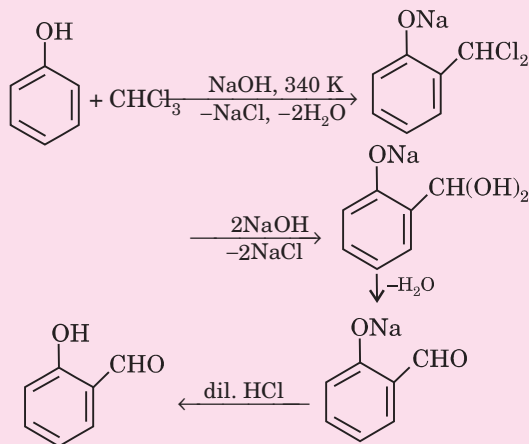
C11. (a, b, c) **C12.** (b, c)

D

MULTIPLE CHOICE QUESTIONS based on the given passage/comprehension

Passage-I

Phenols react with chloroform in the presence of aqueous KOH at 340 K followed by hydrolysis of the resulting product give salicylaldehyde as :



Answer the following questions :

- D1.** The above reaction is
 - (a) Reimer-Tiemann reaction
 - (b) Kolbe's reaction
 - (c) Cannizzaro's reaction
 - (d) Fries rearrangement.
- D2.** The electrophile in this electrophilic substitution reaction is
 - (a) $^-\text{CCl}_3$
 - (b) $:\text{CCl}_2$
 - (c) CHCl_2^+
 - (d) Cl^-
- D3.** When CCl_4 is used in place of CHCl_3 in the above reaction, the product formed is
 - (a) 2-Acetoxybenzoic acid
 - (b) 2-Hydroxybenzoic acid
 - (c) 2-Carboxyphenol
 - (d) none of these.
- D4.** When the product in D3 is heated with acetic anhydride and conc. H_2SO_4 , the final product formed is used as :
 - (a) antiseptic
 - (b) tranquilizer
 - (c) analgesic
 - (d) antibiotic
- D5.** When product in D3 is heated with phenol, the new product formed is called
 - (a) oil of winter green
 - (b) salol
 - (c) carbolic acid
 - (d) aspirin

Answers

Passage I. **D1.** (a) **D2.** (b) **D3.** (b) **D4.** (c) **D5.** (b)

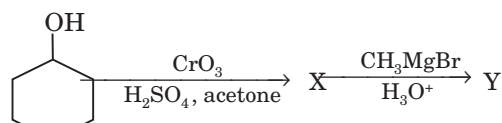
Competition File

Passage-II

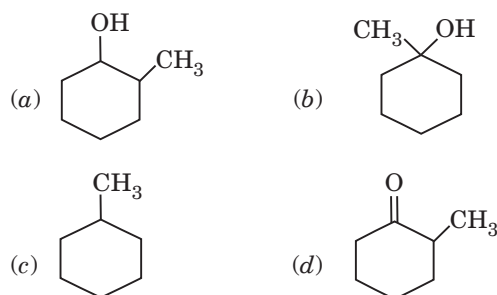
Primary and secondary alcohols are dehydrogenated by copper at 573 K to aldehydes and ketones respectively. In contrast tertiary alcohols are dehydrated to alkenes by heating with copper at 573 K. Similarly, primary alcohols are easily oxidised to form first an aldehyde and then a carboxylic acid while secondary alcohols are oxidised to ketones which are further oxidised to form a mixture of acids. Tertiary alcohols are oxidised with difficulty and with strong oxidising agents in acidic medium. They form first ketones and then acids. In the case of alcohols containing carbon-carbon double bond, some oxidising agents oxidise both double bond and —OH group while other reagents do not affect C=C bond.

Answer the following questions :

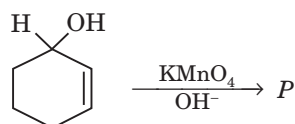
D6. In the reaction :



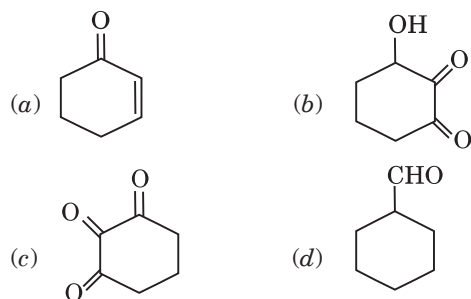
the product Y is



D7. In the reaction



The product P is



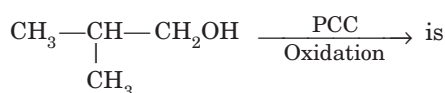
D8. Butan-2-ol on heating with Cu at 573 K gives

- (a) butanal (b) 2-butanone
(c) propanone (d) but-2-ene

D9. The reagent which oxidises 1° alcohol to aldehyde without affecting C=C double bond is

- (a) CrO_3 in aqueous acetone solution
(b) aqueous $\text{K}_2\text{Cr}_2\text{O}_7$
(c) alkaline KMnO_4
(d) none of these.

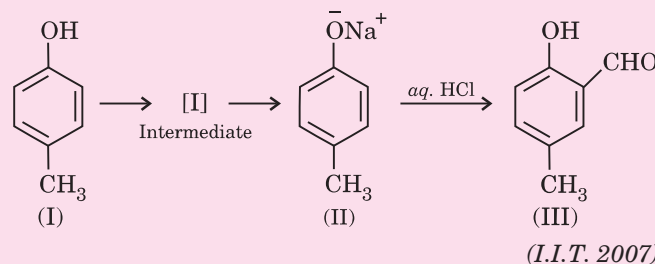
D10. The product of the reaction :



- (a) 2-Methylpropanal
(b) 2-Methylpropanoic acid
(c) Butanoic acid
(d) Butan-2-one

Passage-III

Riemer Tiemann reaction introduces an aldehyde group, on to the aromatic ring of phenol, ortho to the hydroxyl group. This reaction involves electrophilic aromatic substitution. This is a general method of the synthesis of substituted salicylaldehydes as depicted below :



Answer the following questions :

D11. Which one of the following reagents is used in the above reaction ?

- (a) aq. $\text{NaOH} + \text{CH}_3\text{Cl}$
(b) aq. $\text{NaOH} + \text{CH}_2\text{Cl}_2$
(c) aq. $\text{NaOH} + \text{CHCl}_3$
(d) aq. $\text{NaOH} + \text{CCl}_4$

D12. The electrophile in this reaction is

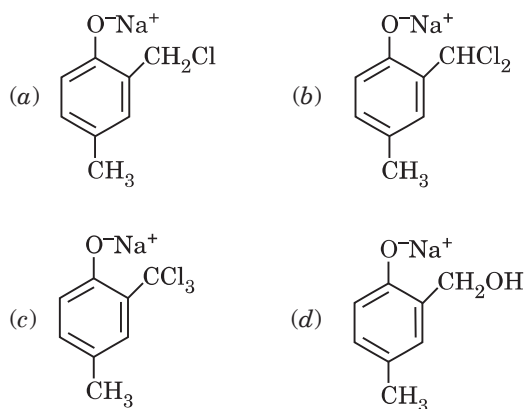
- (a) $:\text{CHCl}$ (b) $^+\text{CHCl}_2$
(c) $:\text{CCl}_2$ (d) $^+\text{CCl}_3$

Answers

Passage II. D6. (b) D7. (c) D8. (b) D9. (a) D10. (a) Passage III D11. (c) D12. (c)

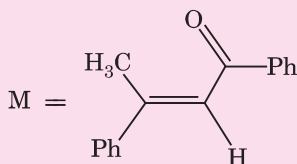
Competition File

D13. The structure of the intermediate I is



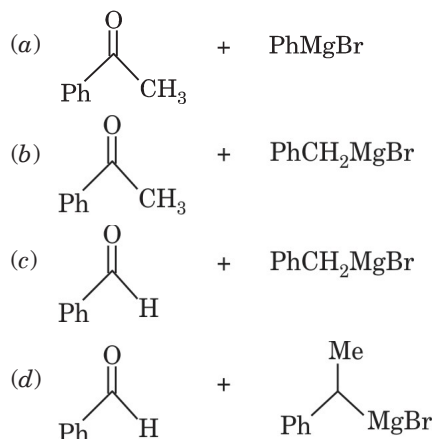
Passage-IV

A tertiary alcohol **H** upon acid catalysed dehydration gives a product **I**. Ozonolysis of **I** leads to compounds **J** and **K**. Compound **J** upon reaction with KOH gives benzyl alcohol and a compound **L**, whereas **K** on reaction with KOH gives only **M**.

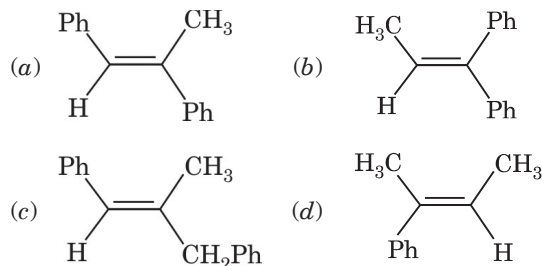


Answer the following questions :

D14. Compound **H** is formed by the reaction of



D15. The structure of compound **I** is



D16. The structures of compounds **J**, **K** and **L** respectively, are

- (a) PhCOCH_3 , $\text{PhCH}_2\text{COCH}_3$ and $\text{PhCH}_2\text{COO}^-\text{K}^+$
 (b) PhCHO , PhCH_2CHO and PhCOO^-K^+
 (c) PhCOCH_3 , PhCH_2CHO and $\text{CH}_3\text{COO}^-\text{K}^+$
 (d) PhCHO , PhCOCH_3 and PhCOO^-K^+ (I.I.T. 2008)

Answers

Passage III. D13. (b) Passage IV. D14. (b) D15. (a) D16. (d)

Assertion Reason Type Questions

The question given below consist of an Assertion and the Reason. Use the following key to choose the appropriate answer.

- (a) If both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
 (b) If both assertion and reason are CORRECT, but reason is NOT THE CORRECT explanation of the assertion.
 (c) If assertion is CORRECT but reason is INCORRECT.
 (d) If assertion is INCORRECT but reason is CORRECT.
 (e) If both assertion and reason are INCORRECT.

Answers

1 (c) 2. (b) 3. (b) 4. (a)

1. **Assertion:** The boiling points of alcohols are higher than those of hydrocarbons of comparable molecular mass.

Reason : Alcohols show intramolecular hydrogen bonding.

2. **Assertion:** Phenol undergoes Kolbe's reaction but ethanol does not.

Reason : Phenol is more acidic than ethanol.

3. **Assertion:** The C—O—C bond angle in ethers is higher than H—O—H bond angle in water.

Reason : Oxygen in both ethers and water is sp^3 hybridized.

4. **Assertion:** The boiling point of diethyl ether is much less than that of ethanol.

Reason : In ethanol, the molecules are associated by the formation of intermolecular hydrogen bonding whereas in diethyl ether, it is not possible.

Competition File

5. Assertion: Alcohols have higher boiling points than ethers of comparable molecular masses.

Reason : Alcohols and ethers are isomeric compounds.

6. Assertion: *o*- and *p*-nitrophenols can be separated by steam distillation.

Reason : *o*- isomer is steam volatile due to chelation while *p*-isomer is not steam volatile due to association of molecules by intermolecular H-bonding.

Answers

5. (b) 6. (a)

Matrix Match Type Questions

Each question contains statements given in two columns, which have to be matched. Statements in Column I are labelled as A, B, C and D whereas statements in Column II are labelled as *p*, *q*, *r* and *s*. Match the entries of Column I with appropriate entries of Column II. Each entry in Column I may have one or more than one correct option from Column II. The answers to these questions have to be appropriately bubbled as illustrated in the following example.

	p	q	r	s
A	☐ p	☒ q	☐ r	☐ s
B	☒ p	☐ q	☐ r	☒ s
C	☐ p	☐ q	☐ r	☒ s
D	☐ p	☒ q	☐ r	☐ s

If the correct matches are A-*q*, A-*r*, B-*p*, B-*s*, C-*r*, C-*s* and D-*q*, then the correctly bubbled matrix will look like the following:

1. Match the compounds in Column I with the properties in Column II.

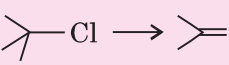
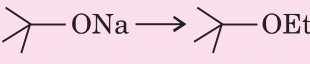
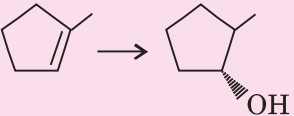
Column I	Column II
(A) butan-2-ol	(<i>p</i>) less acidic than phenol
(B) 3-nitrophenol	(<i>q</i>) gives alkene with Cu at 573K
(C) <i>p</i> -cresol	(<i>r</i>) more acidic than ethanol
(D) 2-methylpropan-2-ol	(<i>s</i>) gives toluene on reduction with zinc dust.

Answers

(1) : (A) – (*p*) (B) – (*r*) (C) – (*p*), (*s*) (D) – (*p*), (*q*)

Matching List Type Questions

1. Match the chemical conversions in List I with the appropriate reagents in List II and select the correct answer using the code given below the lists:

List I	List II
P. 	1. (i) Hg(OAc) ₂ (ii) NaBH ₄
Q. 	2. NaOEt
R. 	3. EtBr
S. 	4. (i) BH ₃ (ii) H ₂ O ₂ /NaOH

	P	Q	R	S
(a)	2	3	1	4
(b)	3	2	1	4
(c)	2	3	4	1
(d)	3	2	4	1

Competition File

2. List-I contains reactions and List-II contains major products.

List I	List II
P.  +  $\longrightarrow$	1. 
Q.  + HBr $\longrightarrow$	2. 
R.  + NaOMe $\longrightarrow$	3. 
S.  + MeBr $\longrightarrow$	4. 
	4. 

Match each reaction in List-I with one or more products in List-II and choose the correct option. The correct option is

- (a) P $\rightarrow$ 1, 5; Q $\rightarrow$ 2; R $\rightarrow$ 3; S $\rightarrow$ 4
 (b) P $\rightarrow$ 1, 4; Q $\rightarrow$ 2; R $\rightarrow$ 4; S $\rightarrow$ 3
 (c) P $\rightarrow$ 1, 4; Q $\rightarrow$ 1, 2; R $\rightarrow$ 3, 4; S $\rightarrow$ 4
 (d) P $\rightarrow$ 4, 5; Q $\rightarrow$ 4; R $\rightarrow$ 4; S $\rightarrow$ 3, 4

(JEE Advanced 2018)

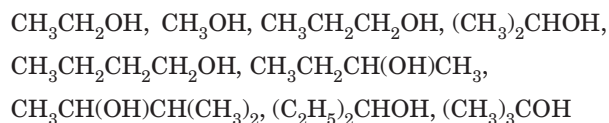
Answers

(1) : (a) (2) : (b)

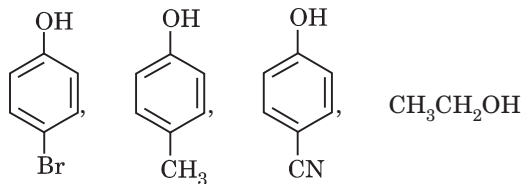
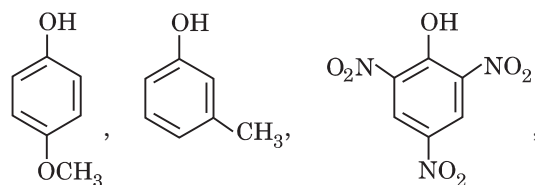
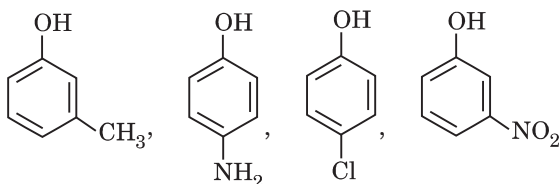
Integer Type or Numerical Value Type Questions

Integer Type: The answer to each of the following question is a **single-digit**-integer ranging from 0 to 9.

1. The number of alcohols giving iodoform test among the following is



2. How many of the following compounds have lower pK_a value than phenol ?



3. How many of the structurally isomeric pentyl alcohols will give immediate turbidity in Lucas test ?
 4. The total number of structural isomers having the molecular formula $\text{C}_5\text{H}_{12}\text{O}$ is

Answers

1. 4 2. 6 3. 1 4. 8

Competition File

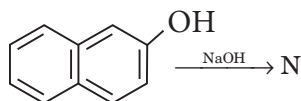
5. How many of the following compounds give 1° alcohol with Grignard reagent (CH_3MgBr) is :

Acetaldehyde, Formaldehyde, Ethylethanoate, Acetone, Oxirane, Acetyl chloride, Acetamide, Carbon dioxide, Methyl methanoate.

6. How many of the following of ethers cannot be prepared by Williamson's synthesis

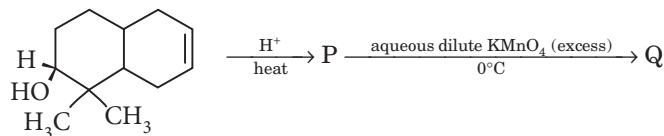
$\text{CH}_3\text{OC}_2\text{H}_5$, $(\text{C}_6\text{H}_5)_2\text{O}$, $\text{C}_6\text{H}_5\text{OCH}_3$, $\text{C}_6\text{H}_5\text{OC}_2\text{H}_5$,
 $(\text{CH}_3)_3\text{COC}(\text{CH}_3)_3$, $(\text{C}_2\text{H}_5)_2\text{O}$, $\text{C}_6\text{H}_5\text{CH}_2\text{OC}_6\text{H}_5$,
 $(\text{CH}_3)_3\text{COCH}_3$, $(\text{CH}_3)_3\text{COCH}_2\text{CH}_3$,

7. The number of resonance structures of N is



(JEE Advance 2015)

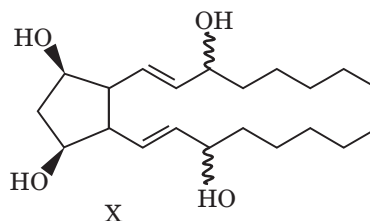
8. The number of hydroxyl group(s) in Q is



(JEE Advance 2015)

Numerical Value Type: Give the correct numerical value (in decimal notation truncated/rounded off to the second decimal place).

9. For the given compound X, the total number of optically active stereoisomers is _____.



◀ This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is fixed.

~~~~ This type of bond indicates that the configuration at the specific carbon and the geometry of the double bond is NOT fixed.

(JEE Advance 2018)

## Answers

5. 2      6. 2      7. 9      8. 4      9. 7.00



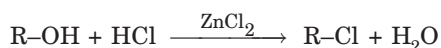
**NCERT**

## Exemplar Problems

### Objective Questions

#### Multiple Choice Questions (Type-I)

- Monochlorination of toluene in sunlight followed by hydrolysis with aq. NaOH yields
  - o*-Cresol
  - m*-Cresol
  - 2, 4-Dihydroxytoluene
  - Benzyl alcohol
- How many alcohols with molecular formula  $\text{C}_4\text{H}_{10}\text{O}$  are chiral in nature?
  - 1
  - 2
  - 3
  - 4
- What is the correct order of reactivity of alcohols in the following reaction?



- $1^\circ > 2^\circ > 3^\circ$
- $1^\circ < 2^\circ > 3^\circ$
- $3^\circ > 2^\circ > 1^\circ$
- $3^\circ > 1^\circ > 2^\circ$

4.  $\text{CH}_3\text{CH}_2\text{OH}$  can be converted into  $\text{CH}_3\text{CHO}$  by \_\_\_\_\_.

- catalytic hydrogenation
- treatment with  $\text{LiAlH}_4$
- treatment with pyridinium chlorochromate
- treatment with  $\text{KMnO}_4$

5. The process of converting alkyl halides into alcohols involves \_\_\_\_\_.

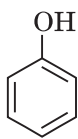
- addition reaction
- substitution reaction
- dehydrohalogenation reaction
- rearrangement reaction

## Answers

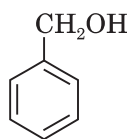
1. (d)      2. (a)      3. (c)      4. (c)      5. (b)

## Competition File

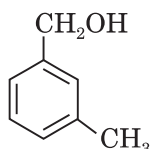
6 Which of the following compounds is aromatic alcohol?



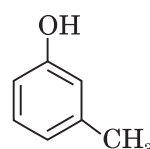
(A)



(B)



(C)



(D)

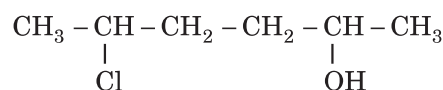
(a) A, B, C, D

(b) A, D

(c) B, C

(d) A

7. Give IUPAC name of the compound given below.



(a) 2-Chloro-5-hydroxyhexane

(b) 2-Hydroxy-5-chlorohexane

(c) 5-Chlorohexan-2-ol

(d) 2-Chlorohexan-5-ol

8. IUPAC name of *m*-cresol is \_\_\_\_\_.

(a) 3-methylphenol

(b) 3-chlorophenol

(c) 3-methoxyphenol

(d) benzene-1,3-diol

9. IUPAC name of the compound  $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{OCH}_3$  is

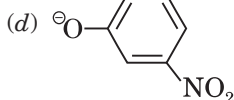
(a) 1-methoxy-1-methylethane

(b) 2-methoxy-2-methylethane

(c) 2-methoxypropane

(d) isopropylmethyl ether

10. Which of the following species can act as the strongest base?

(a)  $^-\text{OH}$ (b)  $^-\text{OR}$ (c)  $^-\text{OC}_6\text{H}_5$ 

11. Which of the following compounds will react with sodium hydroxide solution in water?

(a)  $\text{C}_6\text{H}_5\text{OH}$ (b)  $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ (c)  $(\text{CH}_3)_3\text{COH}$ (d)  $\text{C}_2\text{H}_5\text{OH}$ 

12. Phenol is less acidic than \_\_\_\_\_.

(a) ethanol

(b) *o*-nitrophenol(c) *o*-methylphenol(d) *o*-methoxyphenol

13. Which of the following is most acidic?

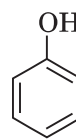
(a) Benzyl alcohol

(b) Cyclohexanol

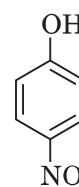
(c) Phenol

(d) *m*-Chlorophenol

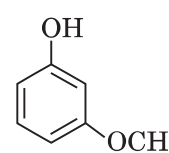
14. Mark the correct order of decreasing acid strength of the following compounds.



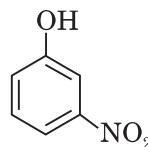
(A)



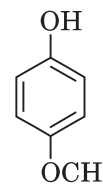
(B)



(C)



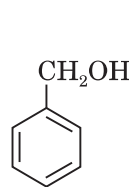
(D)



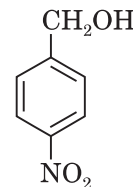
(E)

(a)  $\text{E} > \text{D} > \text{B} > \text{A} > \text{C}$ (b)  $\text{B} > \text{D} > \text{A} > \text{C} > \text{E}$ (c)  $\text{D} > \text{W} > \text{C} > \text{B} > \text{A}$ (d)  $\text{E} > \text{D} > \text{C} > \text{B} > \text{A}$ 

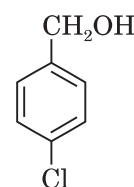
15. Mark the correct increasing order of reactivity of the following compounds with  $\text{HBr}/\text{HCl}$ .



(i)



(ii)



(iii)

(a)  $(i) < (ii) < (iii)$ (b)  $(ii) < (i) < (iii)$ (c)  $(ii) < (iii) < (i)$ (d)  $(iii) < (ii) < (i)$ 

16. Arrange the following compounds in increasing order of boiling point.

Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol

(a) Propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol

(b) Propan-1-ol, butan-1-ol, butan-2-ol, pentan-1-ol

(c) Pentan-1-ol, butan-2-ol, butan-1-ol, propan-1-ol

(d) Pentan-1-ol, butan-1-ol, butan-2-ol, propan-1-ol

## Answers

6. (c)    7. (c)    8. (a)    9. (c)    10. (b)    11. (a)    12. (b)    13. (d)    14. (b)    15. (c)    16. (a)

# Competition File

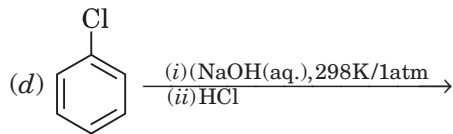
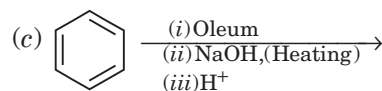
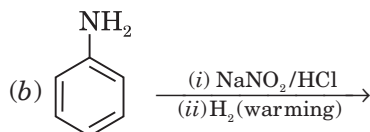
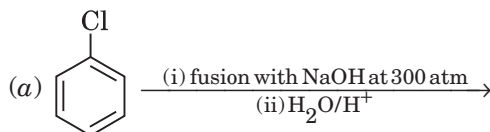
## Multiple Choice Questions (Type-II)

**Note :** In the following questions two or more options may be correct.

17. Which of the following are used to convert  $\text{RCHO}$  into  $\text{RCH}_2\text{OH}$  ?

- (a)  $\text{H}_2/\text{Pd}$
- (b)  $\text{LiAlH}_4$
- (c)  $\text{NaBH}_4$
- (d) Reaction with  $\text{RMgX}$  followed by hydrolysis

18. Which of the following reactions will yield phenol ?



19. Which of the following reagents can be used to oxidise primary alcohols to aldehydes ?

- (a)  $\text{CrO}_3$  in anhydrous medium.
- (b)  $\text{KMnO}_4$  in acidic medium.
- (c) Pyridinium chlorochromate.
- (d) Heat in the presence of  $\text{Cu}$  at  $573\text{K}$ .

20. Phenol can be distinguished from ethanol by the reactions with \_\_\_\_\_.

- (a)  $\text{Br}_2/\text{water}$
- (b)  $\text{Na}$
- (c) Neutral  $\text{FeCl}_3$
- (d) All the above

21. Which of the following are benzylic alcohols?

- (a)  $\text{C}_6\text{H}_5\text{—CH}_2\text{—CH}_2\text{OH}$
- (b)  $\text{C}_6\text{H}_5\text{—CH}_2\text{OH}$
- (c)  $\text{C}_6\text{H}_5\text{—}\underset{\text{CH}_3}{\text{CH}}\text{—OH}$
- (d)  $\text{C}_6\text{H}_5\text{—CH}_2\text{—}\underset{\text{CH}_3}{\text{CH}}\text{—OH}$

## Answers

17. (a), (b), (c)

18. (a), (b), (c)

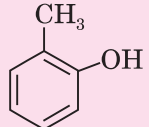
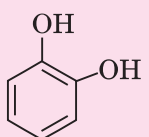
19. (a), (c), (d)

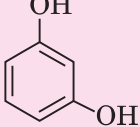
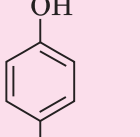
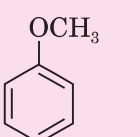
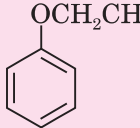
20. (a), (c)

21. (b), (c)

## Matching Type Questions

22. Match the items of Column I and Column II in the following questions.

| Column I                                                                                | Column II        |
|-----------------------------------------------------------------------------------------|------------------|
| (a)  | (i) Hydroquinone |
| (b)  | (ii) Phenetole   |

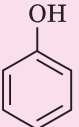
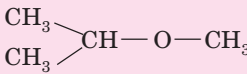
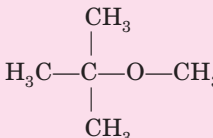
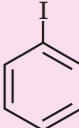
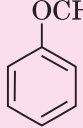
|                                                                                          |                 |
|------------------------------------------------------------------------------------------|-----------------|
| (c)  | (iii) Catechol  |
| (d)  | (iv) o-Cresol   |
| (e)  | (v) Quinone     |
| (f)  | (vi) Resorcinol |
|                                                                                          | (vii) Anisole   |

## Answers

22. (a) (iv); (b) (iii); (c) (vi); (d) (i); (e) (vii); (f) (ii)

## Competition File

23. Match the starting materials given in Column I with the products formed by these (Column II) in the reaction with HI.

| Column I                                                                              | Column II                                                                                                          |
|---------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|
| (a) $\text{CH}_3\text{—O—CH}_3$                                                       | (i)  + $\text{CH}_3\text{I}$      |
| (b)  | (ii) $\text{CH}_3\text{—}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{—I} + \text{CH}_3\text{OH}$  |
| (c)  | (iii)  + $\text{CH}_3\text{OH}$   |
| (d)  | (iv) $\text{CH}_3\text{—OH} + \text{CH}_3\text{—I}$                                                                |
|                                                                                       | (v)  + $\text{CH}_3\text{I}$     |
|                                                                                       | (vi)  + $\text{CH}_3\text{OH}$  |
|                                                                                       | (vii) $\text{CH}_3\text{—}\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}\text{—OH} + \text{CH}_3\text{I}$ |

24. Match the items of column I with items of column II.

| Column I                                          | Column II                   |
|---------------------------------------------------|-----------------------------|
| (a) Antifreeze used in car engine                 | (i) Neutral ferric chloride |
| (b) Solvent used in perfumes                      | (ii) Glycerol               |
| (c) Starting material for picric acid             | (iii) Methanol              |
| (d) Wood spirit                                   | (iv) Phenol                 |
| (e) Reagent used for detection of phenolic group  | (v) Ethylene glycol         |
| (f) By product of soap industry used in cosmetics | (vi) Ethanol                |

25. Match the items of column I with items of column II.

| Column I                               | Column II                                           |
|----------------------------------------|-----------------------------------------------------|
| (a) Methanol                           | (i) Conversion of phenol to o-hydroxysalicylic acid |
| (b) Kolbe's reaction                   | (ii) Ethyl alcohol                                  |
| (c) Williamson's synthesis             | (iii) Conversion of phenol to salicylaldehyde       |
| (d) Conversion of 2° alcohol to ketone | (iv) Wood spirit                                    |
| (e) Reimer-Tiemann reaction            | (v) Heated copper at 573K                           |
| (f) Fermentation                       | (vi) Reaction of alkyl halide with sodium alkoxide  |

## Answers

23. (a) (iv); (b) (v); (c) (ii); (d) (i)    24. (a) (v); (b) (vi); (c) (iv); (d) (iii); (e) (i); (f) (ii)    25. (a) (iv); (b) (i); (c) (vi); (d) (v); (e) (iii); (f) (ii)

## Assertion and Reason Type Questions

**Note :** In the following questions 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 and reason is correct explanation of assertion.  
 (b) Assertion and reason both are wrong statements.  
 (c) Assertion is correct statement but reason is wrong statement.  
 (d) Assertion is wrong statement but reason is correct statement.  
 (e) Both assertion and reason are correct statements but reason is not correct explanation of assertion.
26. **Assertion :** Addition reaction of water to but-1-ene in acidic medium yields butan-1-ol  
**Reason :** Addition of water in acidic medium proceeds through the formation of primary carbocation.

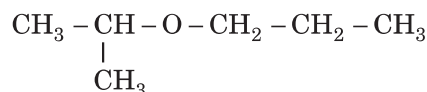
## Answers

26. (b)    27. (a)    28. (d)    29. (d)    30. (b)

27. **Assertion :** p-nitrophenol is more acidic than phenol.

**Reason :** Nitro group helps in the stabilisation of the phenoxide ion by dispersal of negative charge due to resonance.

28. **Assertion :** IUPAC name of the compound



is 2-Ethoxy-2-methylethane.

**Reason :** In IUPAC nomenclature, ether is regarded as hydrocarbon derivative in which a hydrogen atom is replaced by —OR or —OAr group [where R = alkyl group and Ar = aryl group]

29. **Assertion :** Bond angle in ethers is slightly less than the tetrahedral angle.

**Reason :** There is a repulsion between the two bulky (—R) groups.

30. **Assertion :** Boiling points of alcohols and ethers are high.

**Reason :** They can form intermolecular hydrogen-bonding.

# Competition File

**31. Assertion :** Like bromination of benzene, bromination of phenol is also carried out in the presence of Lewis acid.

**Reason :** Lewis acid polarises the bromine molecule.

**32. Assertion :** *o*-Nitrophenol is less soluble in water than the *m*- and *p*-isomers.

**Reason :** *m*- and *p*-Nitrophenols exist as associated molecules.

**33. Assertion :** Ethanol is a weaker acid than phenol.

**Reason :** Sodium ethoxide may be prepared by the reaction of ethanol with aqueous NaOH.

**34. Assertion :** Phenol forms 2, 4, 6 – tribromophenol on treatment with  $\text{Br}_2$  in carbon disulphide at 273K.

**Reason :** Bromine polarises in carbon disulphide.

**35. Assertion :** Phenols give *o*- and *p*-nitrophenol on nitration with conc.  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  mixture.

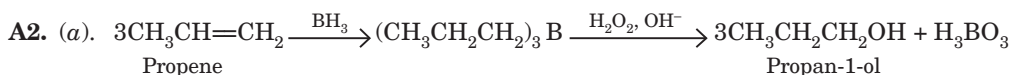
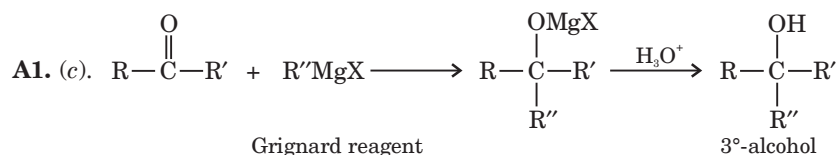
**Reason :** —OH group in phenol is *o*-, *p*-directing.

# Answers

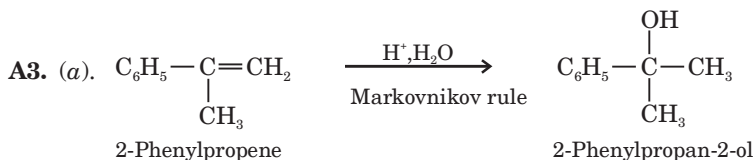
**31.** (d)      **32.** (e)      **33.** (c)      **34.** (b)      **35.** (d)

## Hints & Explanations for *Difficult Objective Type Questions*

### A. mcq with only one correct answer

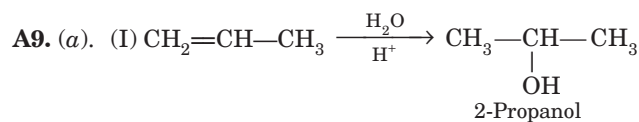
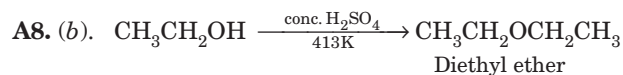
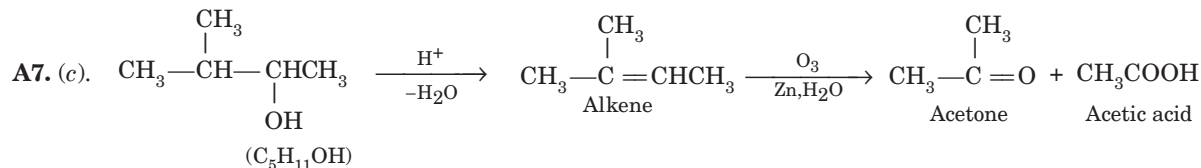
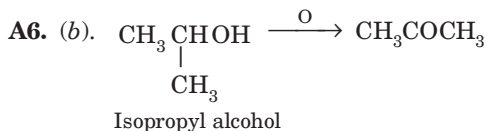


The reaction hydroboration oxidation involves addition of water molecule in accordance with Markovnikov's rule.

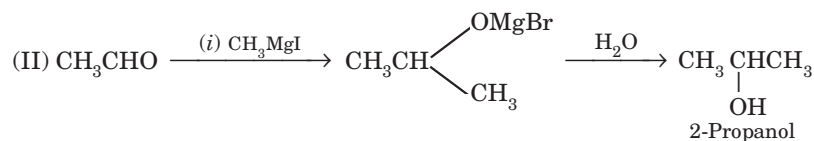


**A4.** (c). A tertiary alcohol is very difficult to be oxidised because it does not have hydrogen on the carbon bearing  $\text{—OH}$  group.

**A5.** (a). Tertiary alcohols have greater reactivity ( $3^\circ > 2^\circ > 1^\circ$ )



## Competition File

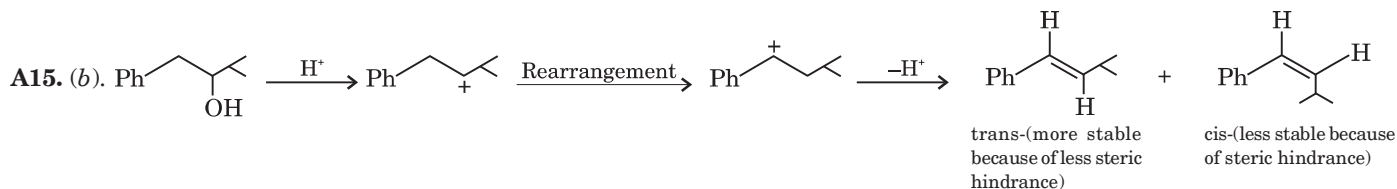


**A11. (c).** 1-Propanol and 2-Propanol in the presence of copper (heat) undergo dehydration to give  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{COCH}_3$  respectively. These can be easily distinguished by Fehling solution.

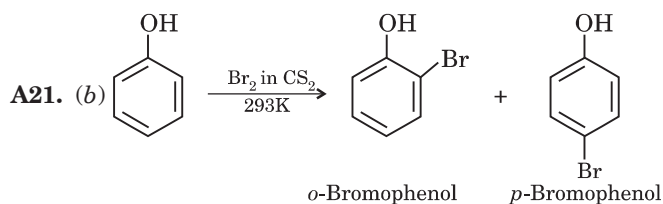
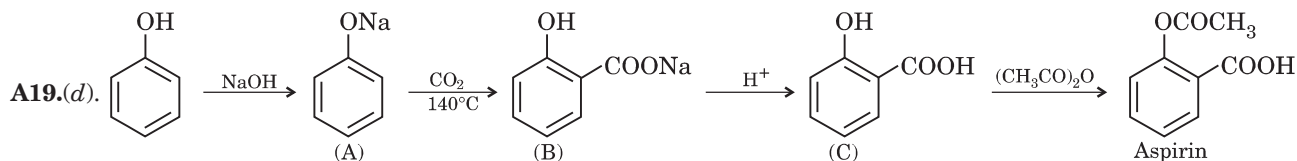
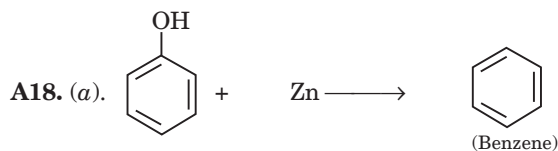
**A12. (b).** First step is protonation of alcohol.  $\text{RCH}_2\text{OH}_2 + \text{H}^+ \longrightarrow \text{RCH}_2\text{OH}_2^+$   
Protonated alcohol

**A13. (b).** The compound which does not contain  $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-$  group will not give iodoform test.

**A14. (a).** The compound  $\text{CH}_3\text{CH}_2\underset{\text{OH}}{\text{C}}(\text{CH}_3)\text{CH}_2\text{CH}_3$  produces most stable  $3^\circ$  carbocation and, therefore, the compound will undergo dehydration most easily.



**A16. (a).** The greater acidic character of phenol is due to more resonance stability of phenoxide ion than phenol.



**A22. (d).** Phenol is more acidic than cresol but less acidic than nitrophenol. *p*-nitrophenol is more acidic than *m*-nitrophenol. Thus, the correct order is *p*-nitrophenol > *m*-nitrophenol > phenol > cresol.

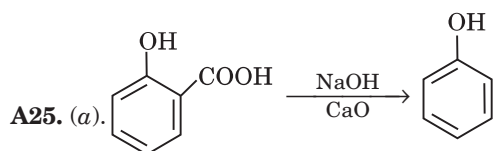
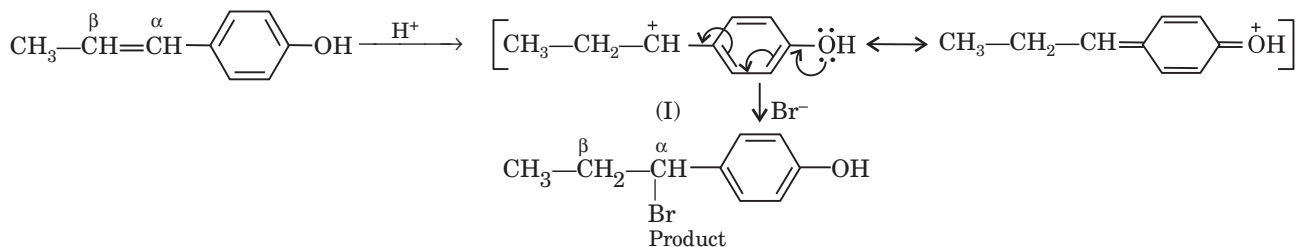
**A23. (c).** The order of reactivity depends upon the stability of carbocations formed. The relative stability of the carbocations follows the order :

$\text{Ph}\overset{+}{\text{C}}\text{H}_2 > \text{CH}_3\overset{+}{\text{C}}\text{H}\text{CH}_3 > \text{FCH}_2\text{CH}_2\overset{+}{\text{C}}\text{H}\text{CH}_3 > \text{FCH}_2\overset{+}{\text{C}}\text{H}\text{CH}_3$ . Therefore, the order of reactivity of corresponding alcohols follows the order : (IV > III > II > I)

**A24. (b).** The addition of a proton at  $\beta$ -carbon gives a carbocation (I) which is resonance stabilized because of electron donating effect of  $-\text{OH}$  group. The addition of  $\text{Br}^-$  ion to the carbocation gives the main product.



## Competition File

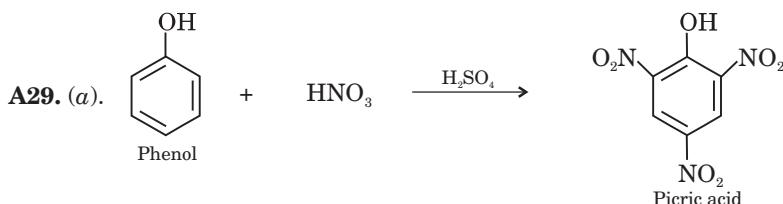
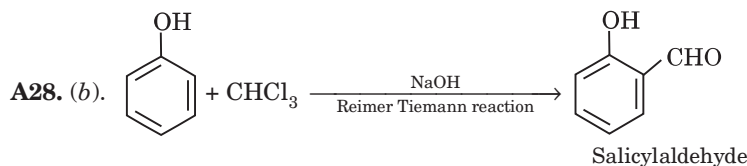


Salicylic acid

Phenol

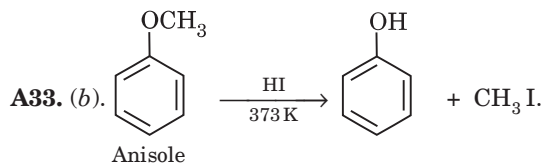
**A26. (c).** Nitrogen cannot have 10 electrons (more than octet) in its valence shell.

**A27. (b).**  $\text{C}_2\text{H}_5\text{O}^-$  is better nucleophile to attack  $\text{C}_2\text{H}_5\text{I}$  than  $\text{C}_6\text{H}_5\text{O}^-$ . In  $\text{C}_6\text{H}_5\text{O}^-$ , the negative charge is delocalised over the benzene ring.

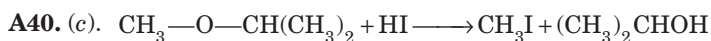
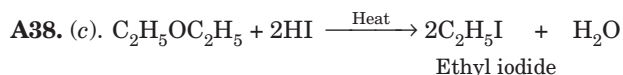
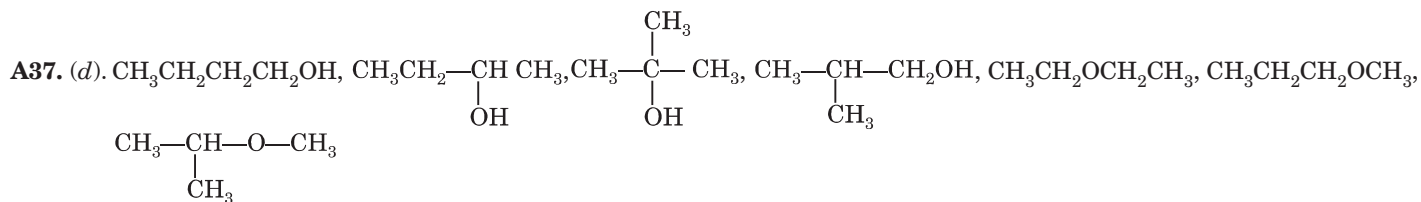
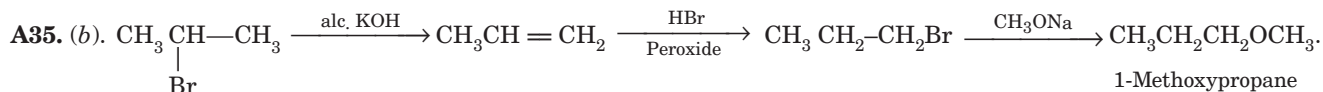


**A30. (c).** At *m*-position,  $-\text{OCH}_3$  group does not exert its +R effect. Instead, it exerts its -I effect and therefore, *m*-methoxyphenol is the strongest acid among phenols, *o*-, *m*- or *p*-methoxyphenol.

**A31. (c).** Ethers and alcohols are functional isomers. :  $\text{CH}_3\text{CH}_2\text{OH}$  or  $\text{CH}_3\text{OCH}_3$

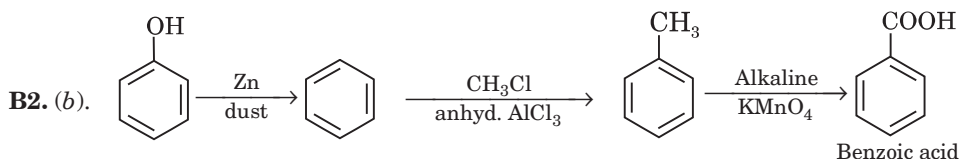
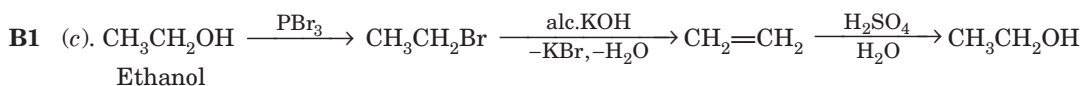


**A34. (a).** Alcohols react with sodium while ethers do not react.



## Competition File

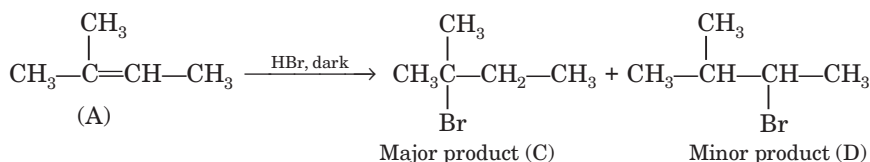
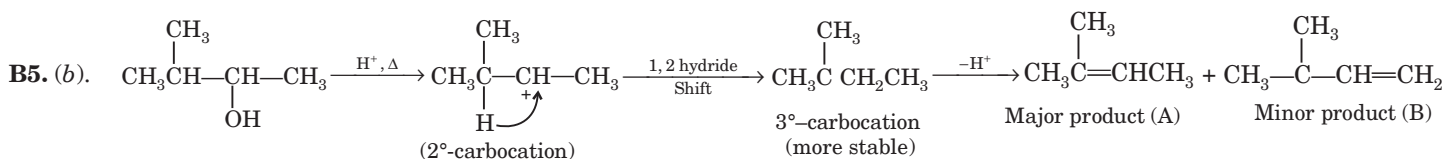
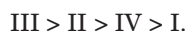
### B. mcq from Competitive Examination



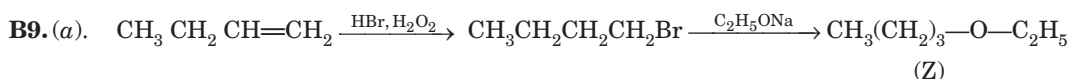
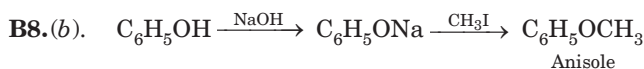
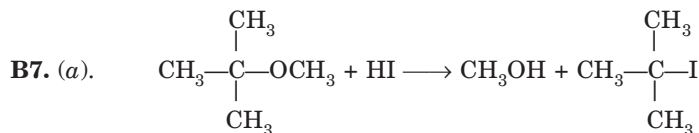
**B3. (d).** Phenol is the most acidic among these.

**B4. (c).** Phenols and carboxylic acids are more acidic than aliphatic alcohols, therefore, cyclohexanol (I) is least acidic. Out of two phenols, III is more acidic than IV because of the presence of three electron withdrawing  $-\text{NO}_2$  groups on the benzene ring which make O—H bond as highly polarized. Acetic acid (II) is more acidic than phenols and cyclohexanol but less acidic than trinitrophenol.

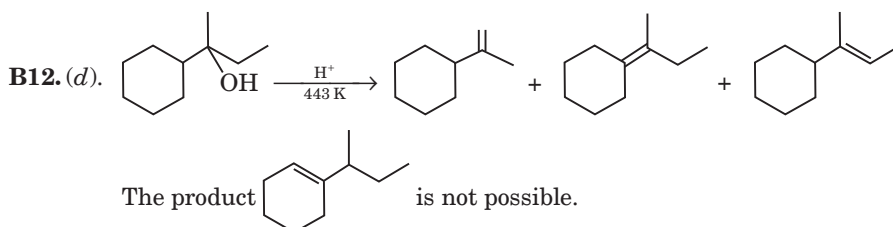
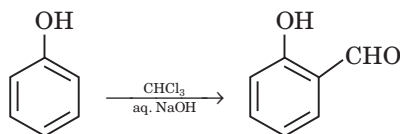
Therefore, correct order is :



**B6. (b).** Electron donating effect decreases in the order :  $-\text{OH} > -\text{OCH}_3 > -\text{NHCOCH}_3 > -\text{CH}_3 > -\text{CH}_2\text{OH}$ . Therefore,  $-\text{OH}$  group is most strongly electron donating group and hence (b) i.e., *o*-cresol is most reactive towards electrophilic reagent.

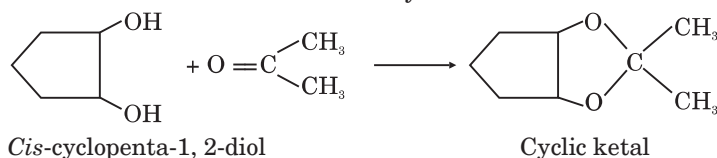


**B11. (b).** The reaction of phenol with chloroform in the presence of dil. NaOH is called Reimer Tiemann reaction.

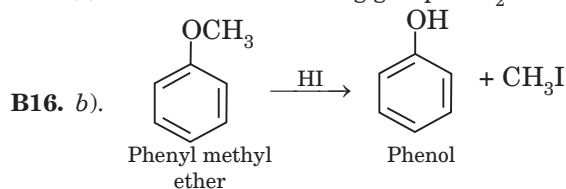


## Competition File

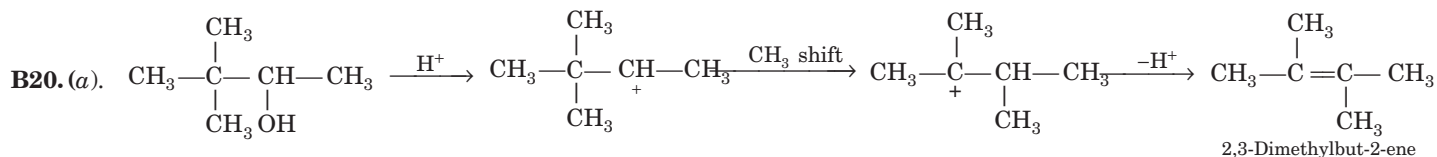
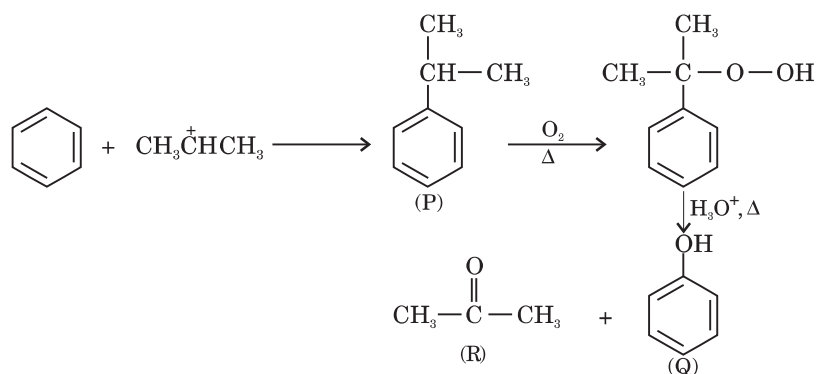
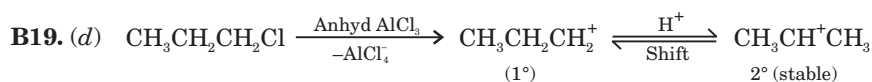
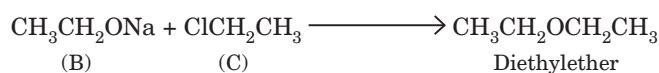
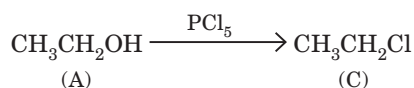
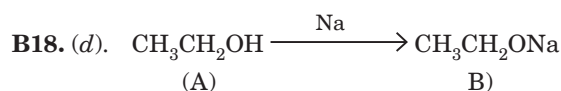
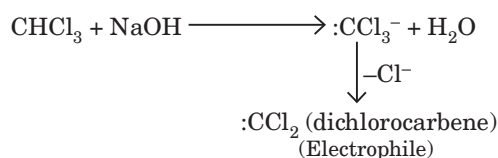
- B13. (c).** Acetone can be used to distinguish between *cis*- and *trans*- diols. *Cis*- cyclopenta -1, 2-diol forms cyclic ketal with acetone, whereas *trans*-isomer cannot form cyclic ketal.



- B15. (c).** Electron withdrawing group  $-\text{NO}_2$  increases the acidity of phenol.



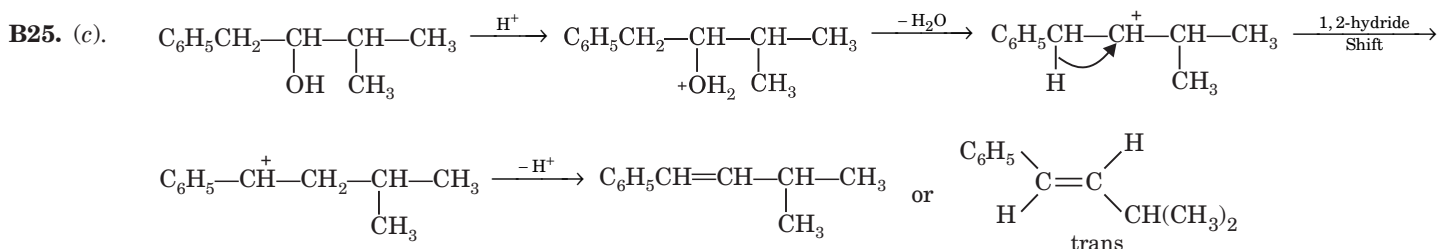
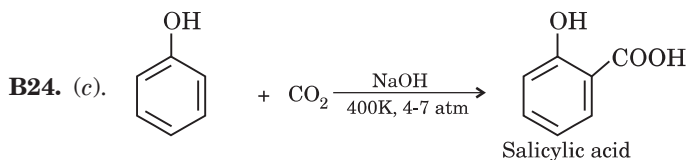
- B17. (d).** It is a Reimer Tiemann reaction and the electrophile is dichlorocarbene ( $:\text{CCl}_2$ )



- B21. (e).** Primary alcohol (pentan-1-ol) readily forms ethers when heated with conc. H<sub>2</sub>SO<sub>4</sub> and gives best yield.

- B23. (e).**  $\text{CH}_3$ --OH; *p*-cresol contains electron donating group ( $-\text{CH}_3$ ) which decreases acidity. Hence,  $pK_a$  value is highest for *p*-cresol.

## Competition File



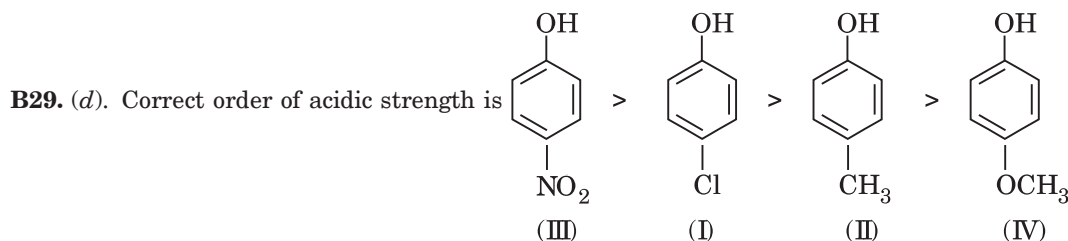
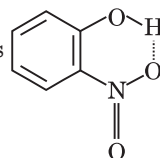
### NOTE

Dehydration occurs in such a way that the double bond comes in conjugation with the  $C_6H_5$  group.

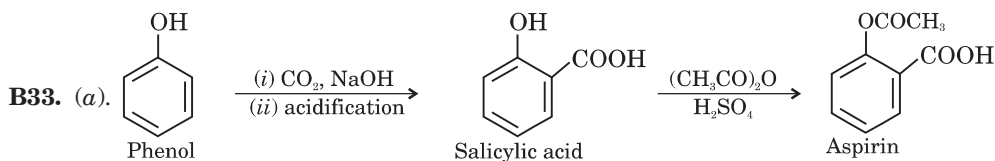
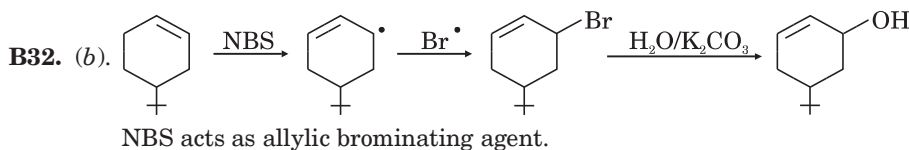
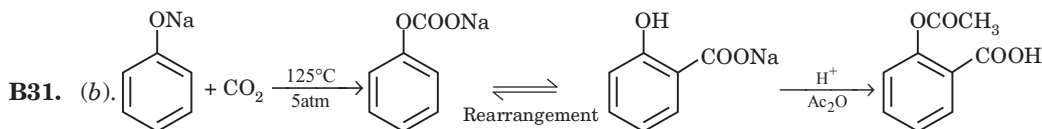
**B26. (a).**  $p$ -nitrophenol >  $m$ -nitrophenol > phenol > cresol

**B27. (b).** Phenol gives violet colour with neutral  $FeCl_3$  and benzoic acid gives buff coloured ppt.

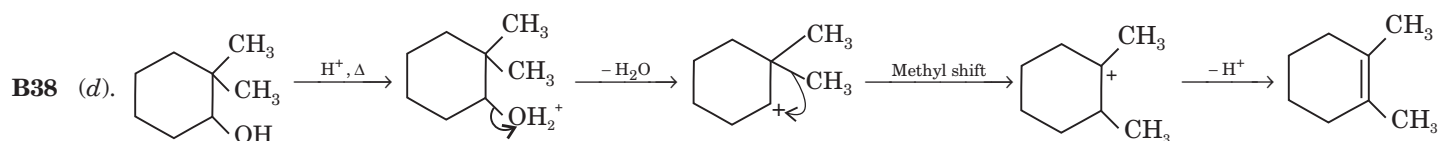
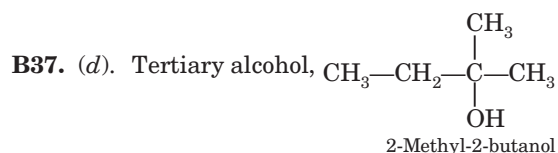
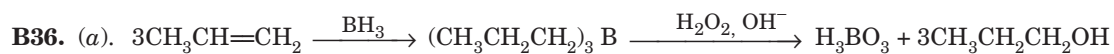
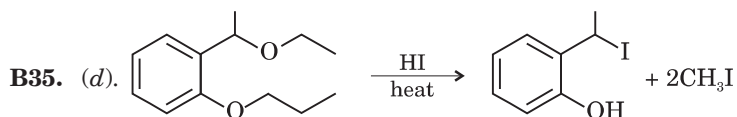
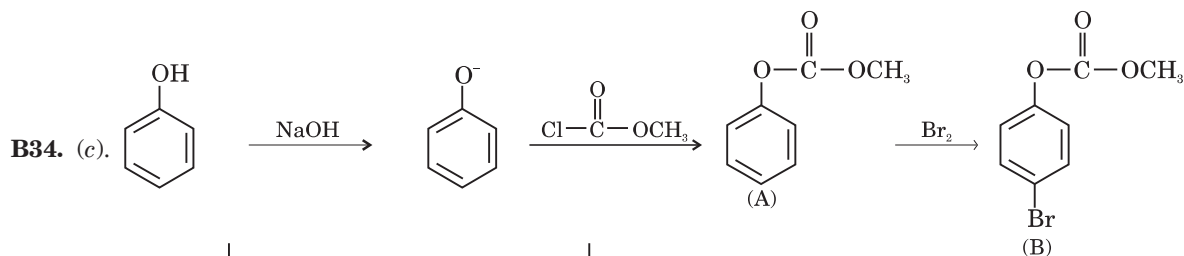
**B28. (a).** Because  $o$ -nitrophenol shows intra-molecular hydrogen bonding as



**B30. (a).** PCC is highly effective for oxidising  $1^\circ$  alcohols to aldehydes.



## Competition File



**B39. (c).** Molecular formula can be calculated as:

| Element | Percentage | Atomic mass | Moles of atoms         | Mole ratio              |
|---------|------------|-------------|------------------------|-------------------------|
| C       | 52         | 12          | $\frac{52}{12} = 4.33$ | $\frac{4.33}{2.19} = 2$ |
| H       | 13         | 1           | $\frac{13}{1} = 13$    | $\frac{13}{2.19} = 6$   |
| O       | 35         | 16          | $\frac{35}{16} = 2.19$ | $\frac{2.19}{2.19} = 1$ |

Empirical formula =  $\text{C}_2\text{H}_6\text{O}$

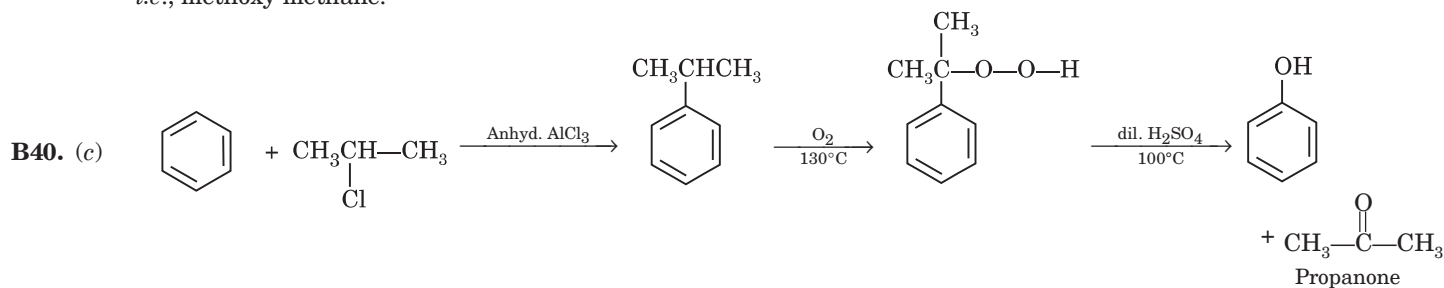
Molecular mass =  $2 \times 23 = 46$

Empirical formula mass =  $2 \times 12 + 6 \times 1 + 1 \times 16 = 46$

$$n = \frac{46}{46} = 1$$

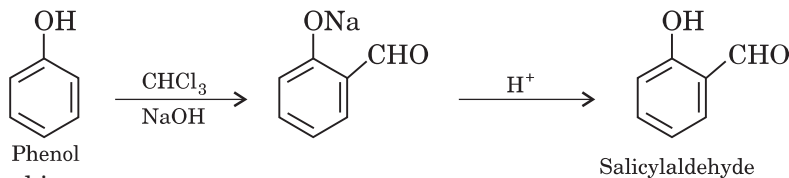
$\therefore$  Molecular formula =  $\text{C}_2\text{H}_6\text{O}$

Since it liberates hydrogen by reacting with sodium, it is an alcohol *i.e.*,  $\text{CH}_3\text{CH}_2\text{OH}$ . Its functional isomer is  $\text{CH}_3\text{OCH}_3$  *i.e.*, methoxy methane.

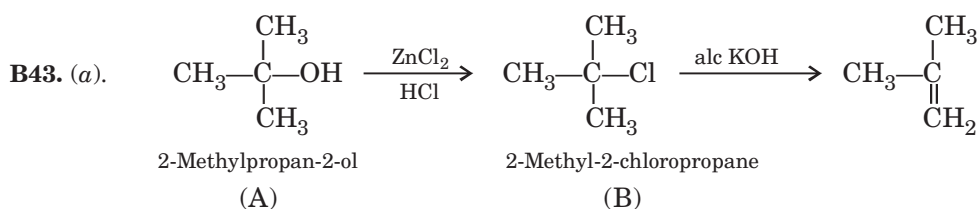
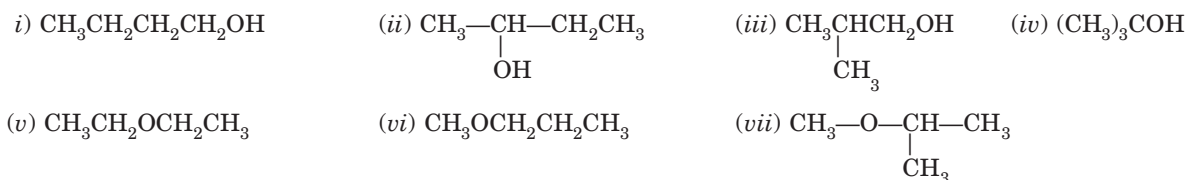


## Competition File

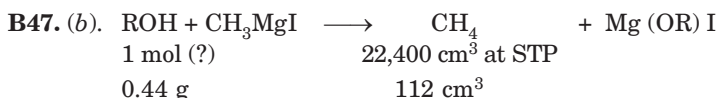
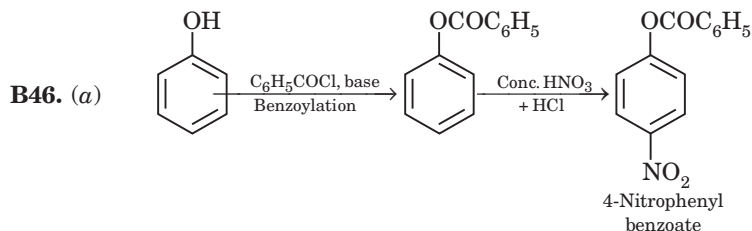
- B41. (c)** Salicylaldehyde can be prepared from phenol by Reimer Tiemann reaction



- B42. (b)** Acyclic structural isomers are :



- B45. (d).** Williamson's synthesis is a nucleophilic substitution reaction and proceeds via  $\text{S}_{\text{N}}2$  mechanism.

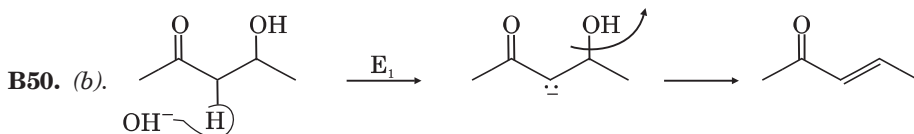


112 cm<sup>3</sup> of CH<sub>4</sub> is obtained from alcohol = 0.44 g.

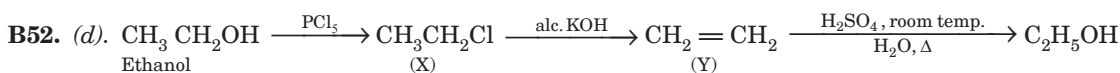
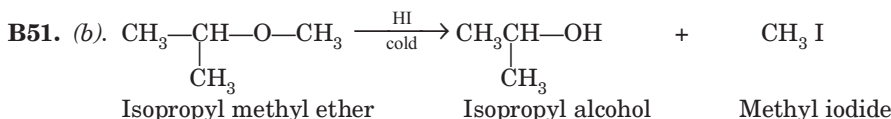
$$22,400 \text{ cm}^3 \text{ of CH}_4 \text{ will be obtained from alcohol} = \frac{0.44 \times 22400}{112} = 88 \text{ g}$$

Alcohol must be a primary alcohol because it reacts with PCC to give carbonyl compound which answers silver mirror test. Therefore, (b) or (d) is correct. But (b) is correct because it has molar mass 88 g.

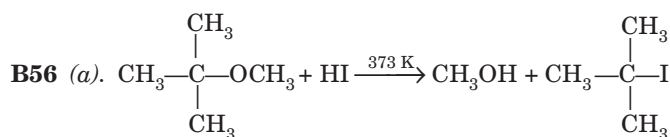
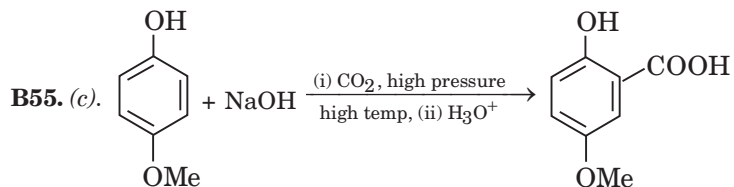
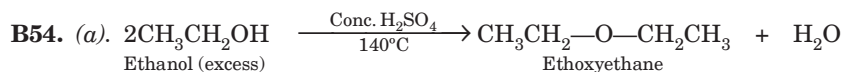
- B49. (c).** The order of reactivity of alcohols towards Lucas reagent is  $3^\circ > 2^\circ > 1^\circ$ . Therefore,  $1^\circ$ -alcohols donot react with Lucas reagent at room temperature. The benzyl and allyl alcohols react as rapidly as  $3^\circ$  alcohols with Lucas reagent because their carbocations are resonance stabilised and are stable. Thus,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  ( $1^\circ$  alcohol) is least reactive.



$\text{OH}^-$  is not a good leaving group but its expulsion becomes easy due to conjugated structure.

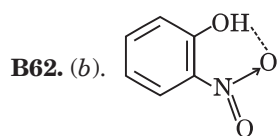
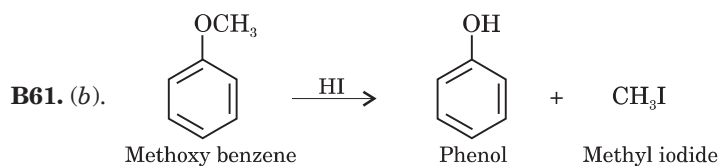
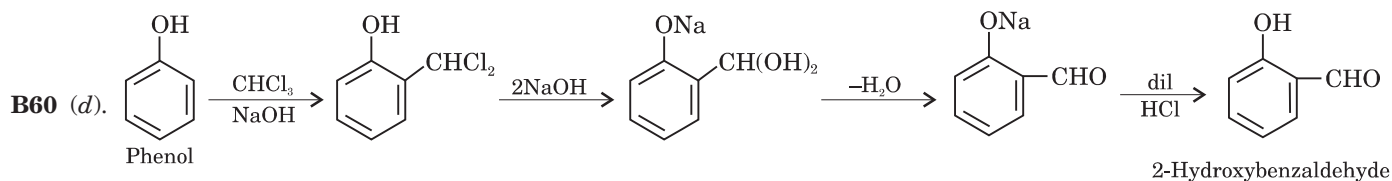


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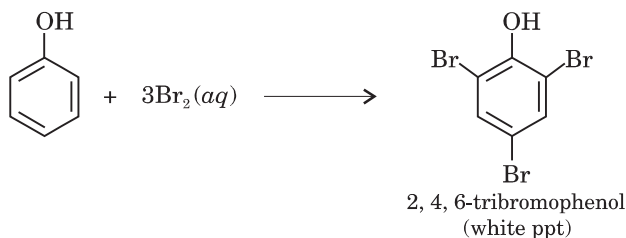


**B57. (c).** Acidified  $\text{KMnO}_4$  oxidises alcohols to carboxylic acids directly. Aqueous or alkaline  $\text{KMnO}_4$  can be used to oxidise alcohols to aldehydes.

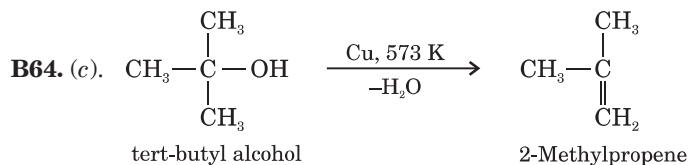
**B58. (b).** Electron releasing group ( $-\text{CH}_3$ ) decreases acidity of phenol and electron withdrawing group ( $-\text{NO}_2$ ) increases acidity of phenol. Thus, *o*-cresol < phenol < *o*-nitrophenol.



**B63. (a).** Phenol gives white precipitate with excess of bromine water due to the formation of 2, 4, 6-tribromophenol.



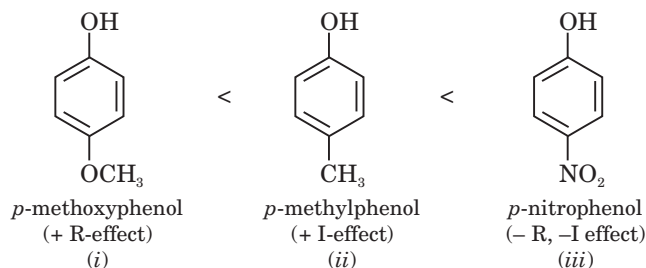
Alcohol does not react with bromine water.



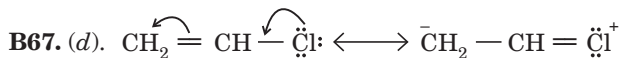


## Competition File

**B65. (c).** Electron withdrawing group increases acidic strength while electron donating group decreases the acidic strength of phenol.

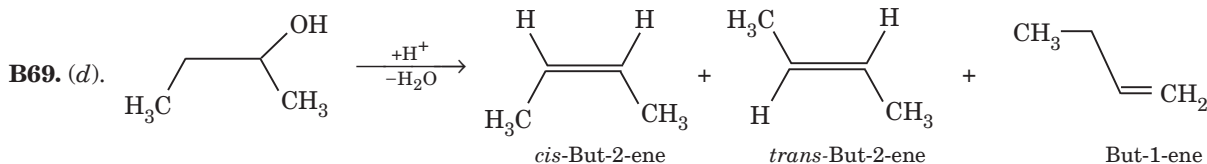
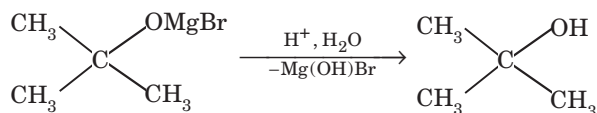
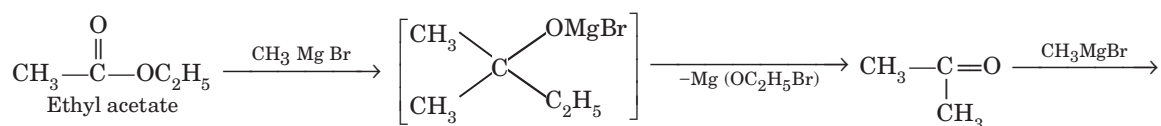


**B66. (e).** Long chain alcohols are successfully oxidised to aldehydes.

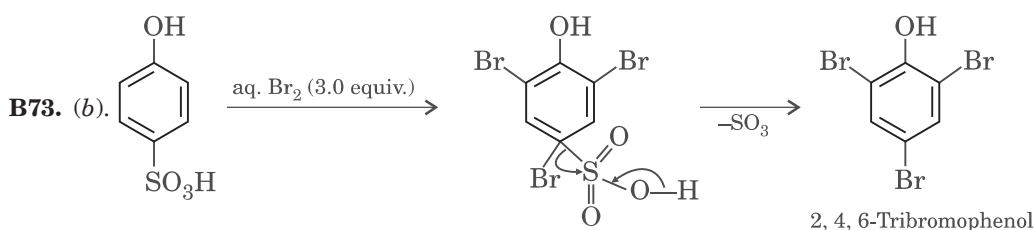
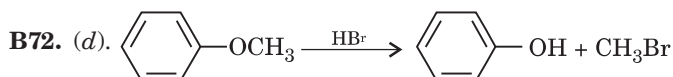
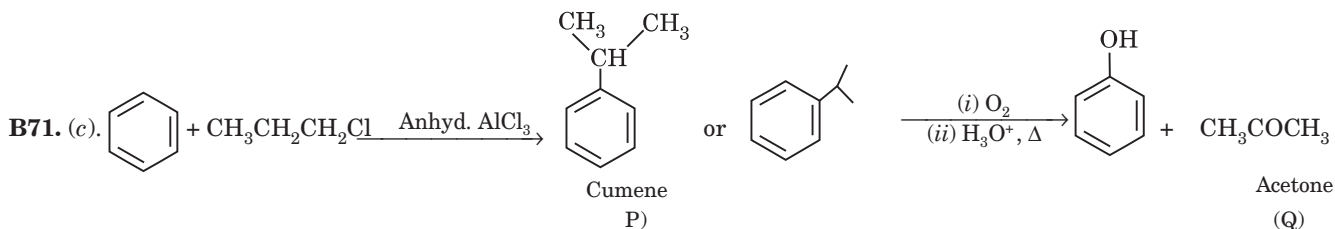


Since C-Cl bond acquires partial double bond character, it will not undergo substitution.

**B68. (a).** Esters add two moles of Grignard reagent to form 3° alcohols. Since the Grignard reagent is  $\text{CH}_3\text{MgBr}$ , the product must contain at least two methyl groups. Therefore, the only choice having two  $\text{CH}_3$  group is (a).



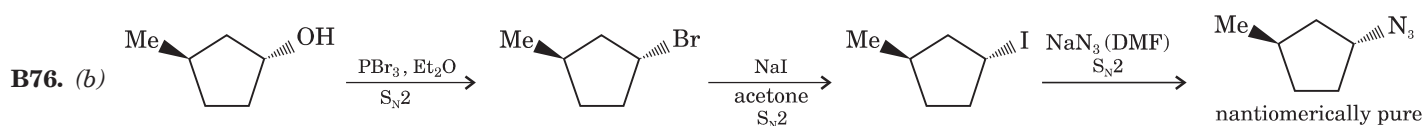
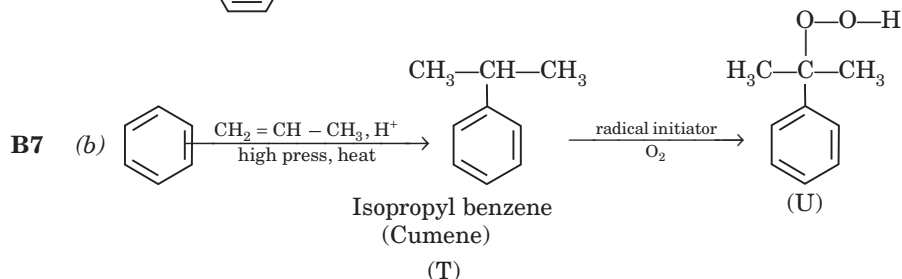
**B70. (a).** Increase in number of hydroxyl groups increases the boiling points. Among isomeric dihydroxy benzenes, as the distance between the —OH group increases, the repulsion between them decreases and hence boiling point increases. (I) Phenol = 181.7°C, (II) catechol = 245.5°C, (III) resorcinol = 281°C and (IV) quinol = 285°C.



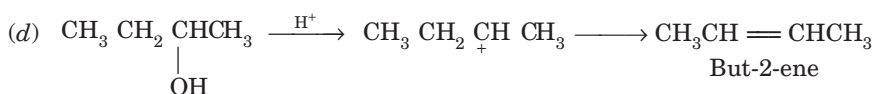
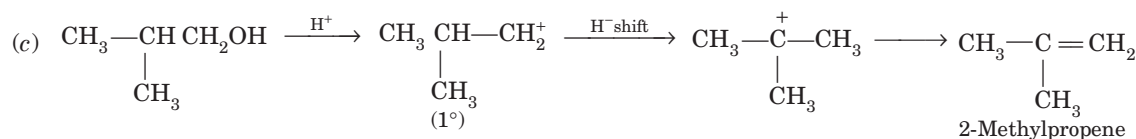
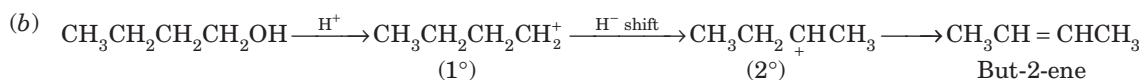
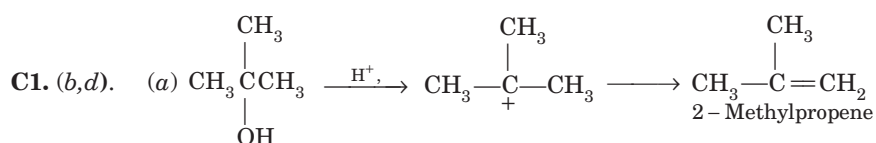
## Competition File

**B74.** (c). Rate of  $S_N1$  reaction is proportional to the stability of carbocation. When two phenyl groups are replaced by two

$\text{MeO}-\text{C}_6\text{H}_4-$  groups, the carbocation formed will be more stable. Therefore, the reaction is the fastest.



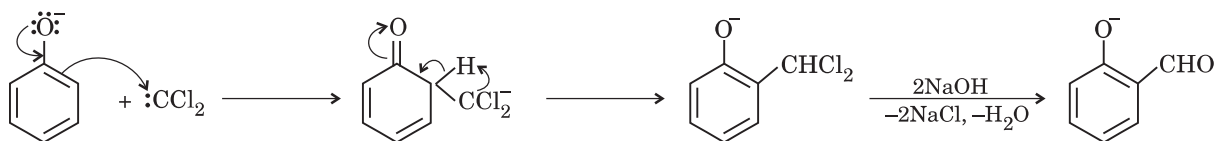
### C. mcq with more than one correct answer



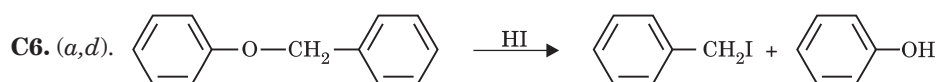
**C2.** (c,d). Alcohols containing  $\text{CH}_3\text{CHOH}$  group, i.e.,  $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$  give iodoform test. Butan-1-ol ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ) and propan-1-ol ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ) do not give this test.

**C3.** (a,c). 3,5-dinitrophenol and 4-nitrophenols are stronger acids than phenol because nitro group increases the acidity of phenols.

**C4.** (b,c). The reaction mechanism is :

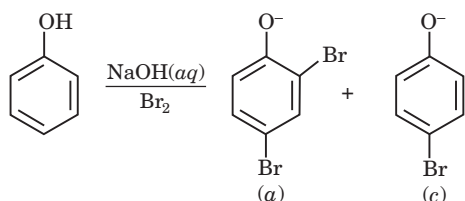


**C5.** (b,c).  $\text{C}_2\text{H}_5\text{OH}$  and *o*-cresol are less acidic than phenol whereas nitrophenols are more acidic.

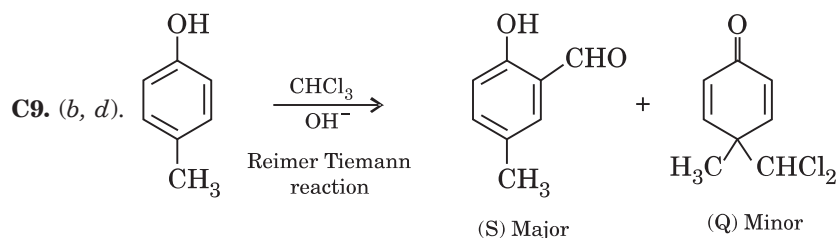


## Competition File

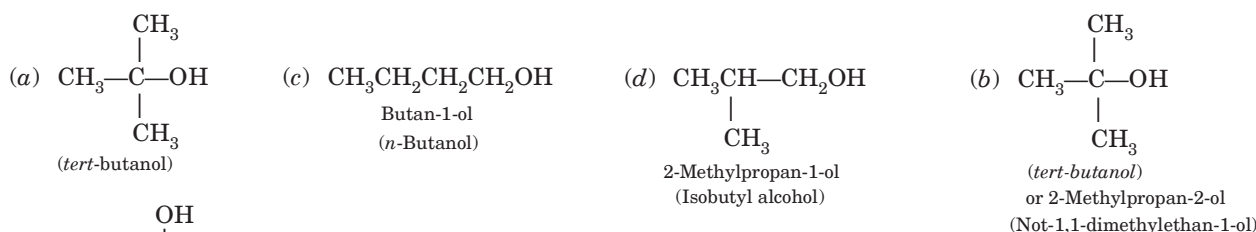
**C7.** (a, c). Phenol being acidic, reacts with NaOH to form phenoxide ion. Since —OH group is *o*-, *p*-directing, therefore, Br enters at *o*- and *p*-positions.



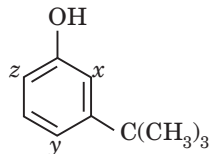
**C8.** (b, c). Boiling point decreases as branching increases. Solubility increases with branching.



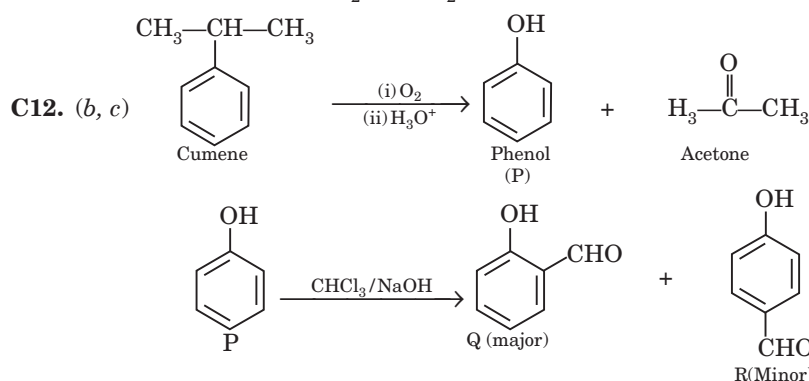
**C10.** (a, c, d).  $\text{C}_4\text{H}_{10}\text{O}$  is a monohydric alcohol *i.e.*,  $\text{C}_4\text{H}_9\text{OH}$ . Its isomeric alcohols are



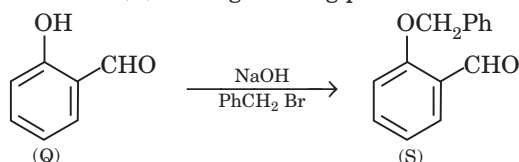
**C11.** (a, b, c)



*x*, *y* and *z* are suitable positions for attack as per electronic effect of —OH group. Due to steric effect of *tert*-butyl group, the bulky electrophiles are less likely to attack at positions *y* and *z*. Hence, position *x* is suitable for  $\text{I}_2$ , positions *x* and *z* are suitable for  $\text{Br}_2$ . But  $\text{Cl}_2$  being smaller can attack all the three positions *i.e.*, *x*, *y* and *z*.



(Q) forms intramolecular hydrogen bonding and (R) forms intermolecular hydrogen bonding. Therefore, (Q) has low boiling point and is steam volatile while (R) has high boiling point and is not steam volatile.



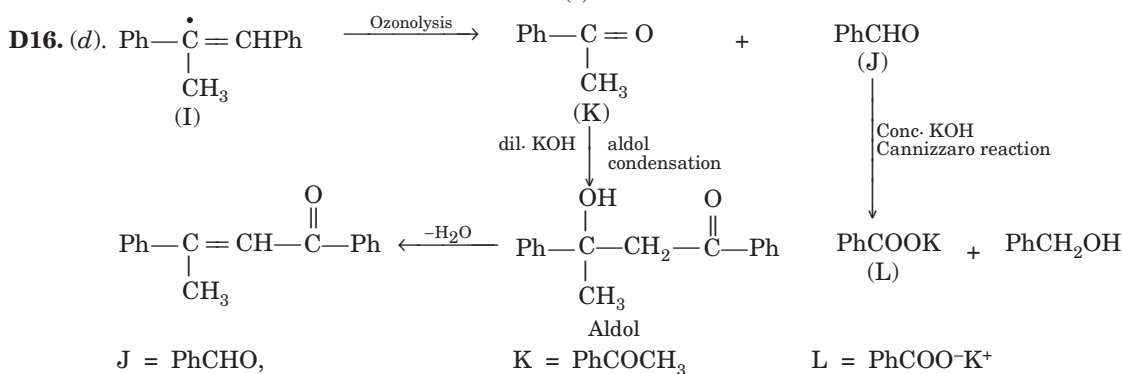
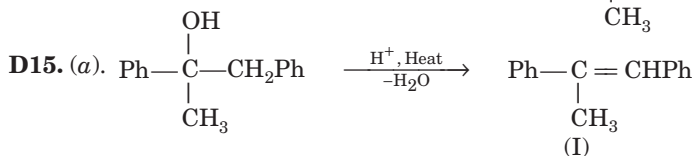
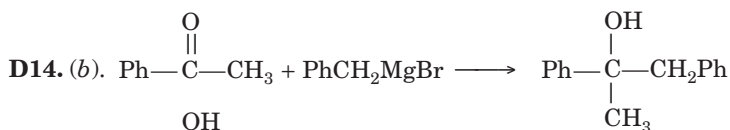
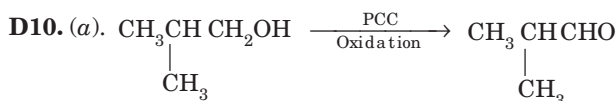
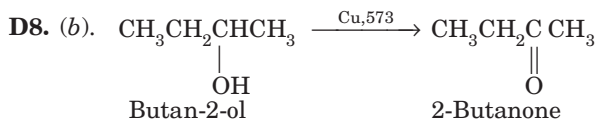
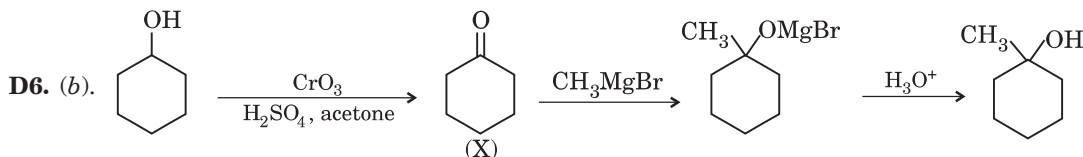
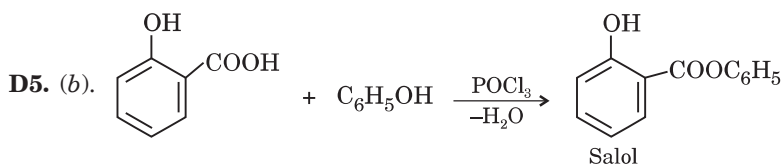
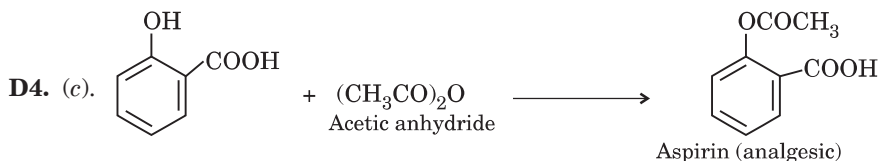
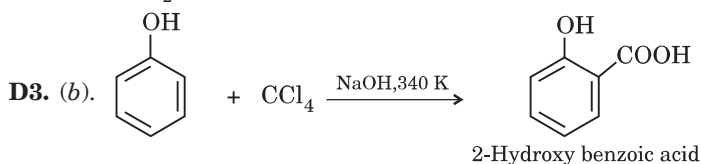
(Q) gives dark violet colouration with 1% aqueous  $\text{FeCl}_3$  solution because it has phenolic (—OH) group. (S) gives yellow ppt. with 2,4- dinitrophenyl hydrazine because it has carbonyl (—CHO) group but does not give violet colouration with 1% aqueous  $\text{FeCl}_3$  because it does not have —OH group.

## Competition File

### D. mcq based on comprehension

D1. (a). The reaction is Reimer Tiemann reaction.

D2. (b).  $\cdot\text{CCl}_2$  contains sextet of electrons and hence is a strong electrophile.

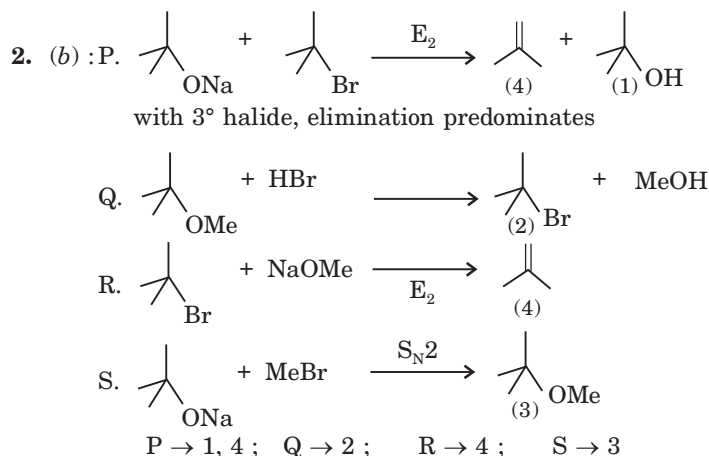
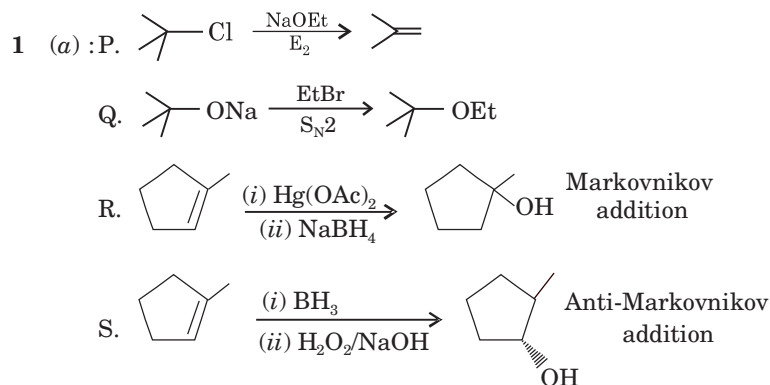


#### HELP

With PCC, oxidation can be stopped to aldehyde stage.

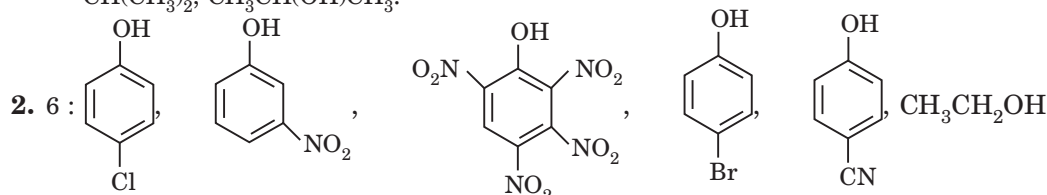
# Competition File

## Matching Type Questions



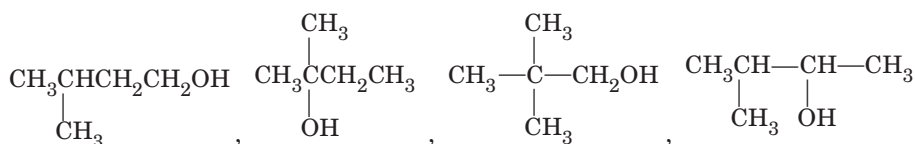
## Integer Type and Numerical Value Type Questions

1. 4 : Alcohols containing  $\text{CH}_3\text{CHOH}$ -group give iodoform test. These are  $\text{CH}_3\text{CH}_2\text{OH}$ ,  $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ ,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{CH}_3)_2$ ,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$ .



3. 1 : Only tertiary alcohol give turbidity in Lucas test i.e.,  $\text{CH}_3-\overset{\text{CH}_3}{\underset{\text{OH}}{\text{C}}}-\text{CH}_2\text{CH}_3$ . All others will be 1° or 2°.

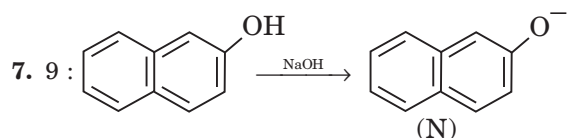
4. 8 :  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_3$ ,  $\text{CH}_3\text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_2\text{CH}_3$ ,  $\text{CH}_3\text{CH}_2\underset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{OH}$ ,



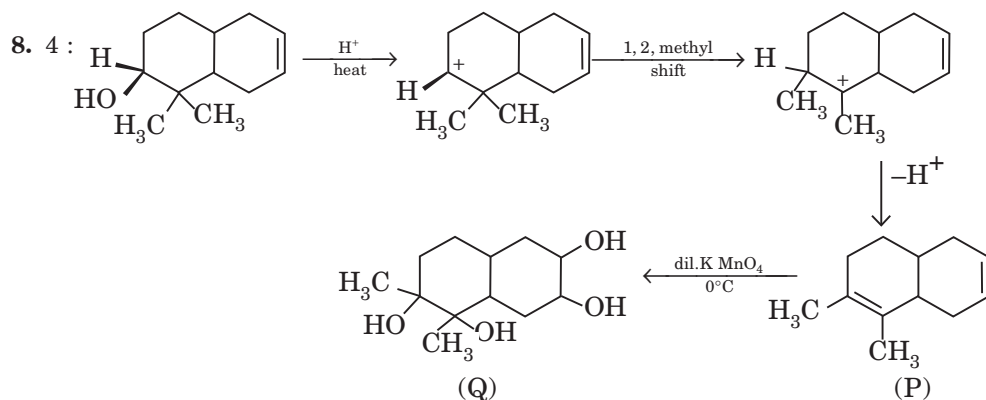
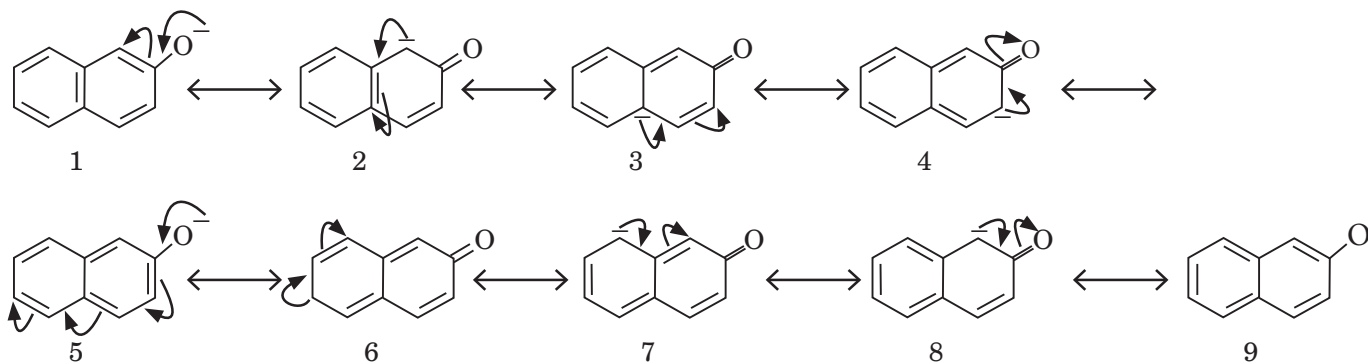
5. 2 : Formaldehyde and oxirane give primary alcohols.

6. 2 : Williamson's synthesis requires that the alkyl halide should be primary and alkoxide may be primary, secondary or tertiary. Hence, two ethers which cannot be prepared by Williamson's synthesis are  $(\text{C}_6\text{H}_5)_2\text{O}$ ,  $(\text{CH}_3)_3\text{COC}(\text{CH}_3)_3$ .

## Competition File

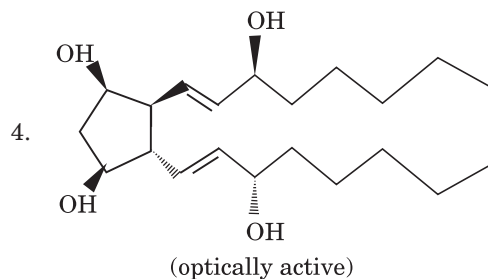
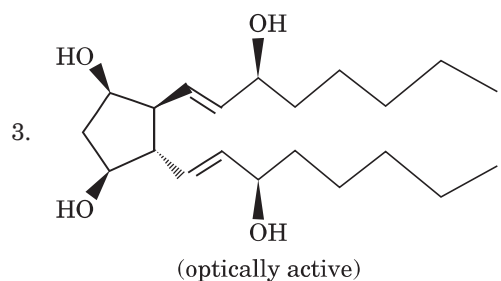
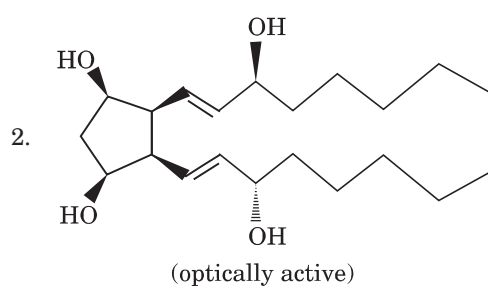
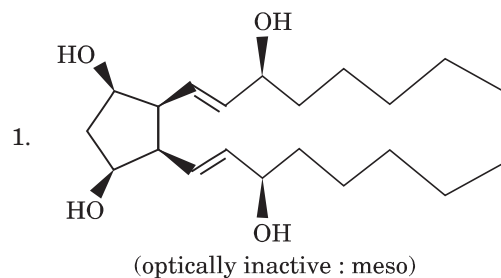


The resonating structures of N are:



There are four hydroxyl groups in (Q).

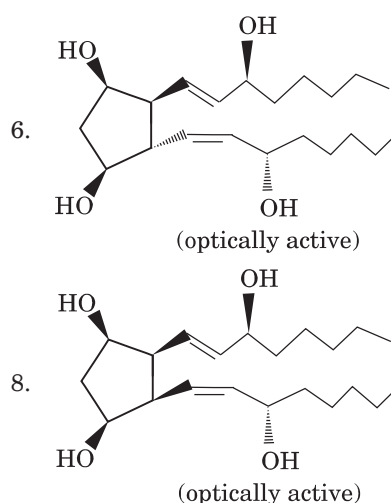
9. 7.00 : These are eight isomers and one of these *i.e.*, first (1) is optically inactive. Therefore, the number of optically active isomers is 7.



7

(optically active)

(optically active)


$$\begin{array}{ccc} & \text{CH}_3 & \\ & | & \\ \text{CH}_3 - \text{C} - \text{CH}_3, & & \text{CH}_3\text{CH}_2\text{C}^* - \text{CH}_3 \\ & | & | \\ & \text{OH} & \text{OH} \end{array}$$

(Chiral)

- Chemical structures showing the relative reactivity of various substituted phenols in electrophilic aromatic substitution, ordered from highest to lowest reactivity:
- Oc1ccc([N+](=O)[O-])cc1
- >
- Oc1cccc([N+](=O)[O-])c1
- >
- Oc1ccccc1
- >
- COc1cccc(O)c1
- >
- COc1ccc(O)cc1

- $$\text{NO}_2\text{-C}_6\text{H}_4\text{-CH}_2^+ < \text{Cl-C}_6\text{H}_4\text{-CH}_2^+ < \text{C}_6\text{H}_5\text{-CH}_2^+$$

16. (a) : Boiling point increases with increase in molecular mass of the alcohols. Among isomeric alcohols 1° alcohols have higher boiling points than 2° alcohols. Thus, correct order is:

**NCERT Exemplar Problems : MCQs Type-II**

17. : (a), (b), (c) : Except  $\text{RMgX}$ , all other reagents reduce  $\text{RCH}_2\text{OH}$  to  $\text{RCHO}$ .
18. : (a), (b), (c) : Chlorobenzene does not undergo hydrolysis on treatment with  $\text{NaOH}$  at 298 K. All other three options are correct.



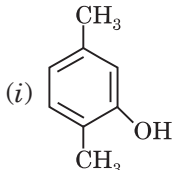


# Unit Practice Test

## for Board Examination

Time allowed : 2 Hrs.

Maximum Marks : 35

- Write chemical equation for the preparation of phenol from chlorobenzene. (1)
- Predict the products of the reaction :  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3 + \text{HBr} \longrightarrow$  (1)
- Why di-tert-butyl ether cannot be prepared by Williamson's synthesis? Explain. (1)
- Which of the two: phenol or o-nitrophenol are more acidic and why? (1)
- What is the order of reactivity of 1°, 2° and 3° alcohols with sodium metal? (1)
- Write the reactions and conditions involved in the conversion of  
 (i) Propene to propan-1-ol (ii) Phenol to salicylic acid. (2)
- Write the IUPAC names of the following :  
 (i)  (ii)  $\text{CH}_3\text{CH}_2\text{OCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$  (2)
- Write mechanism of acid dehydration of ethanol to give ethene. (2)
- Which of the two :  $\text{C}_6\text{H}_5\text{OH}$  or  $\text{C}_2\text{H}_5\text{OH}$  is more acidic and why? (2)
- Write the equations involved in the following reactions :  
 (i) Kolbe's reaction  
 (ii) Reimer-Tiemann reaction  
 (iii) Williamson ether synthesis (3)
- Write chemical equations for the following reactions :  
 (i) Friedel Craft's acylation of anisole  
 (ii) Bromination of phenol  
 (iii) Sulphonation of phenol. (3)
- Give chemical tests to distinguish between  
 (a) Methanol and ethanol  
 (b) 1-Propanol and 2-Propanol  
 (c) n-Propyl chloride and iso-propyl chloride (3)
- How will you convert the following :  
 (i) Propene to propan-2-ol  
 (ii) Phenol to benzoic acid  
 (iii) Propan-1-ol to propan-2-ol (3)
- Explain  
 (i) Ethers possess dipole moment even if the alkyl radicals in the molecule are identical.  
 (ii) Boiling points of ethers are lower than their corresponding alcohols.  
 (iii) Ethers are relatively inert. (3)
- (a) Explain how an -OH group attached to a carbon in the benzene ring activates benzene towards substitution ?  
 (b) Discuss the oxidation of 1°, 2° and 3° alcohols.  
 (c) Explain hydroboration reaction with an example. (2,2,1)

► To check your performance, see HINTS AND SOLUTIONS TO SOME QUESTIONS at the end of Part II of the book.