DAY THIRTY ONE

Alcohols , Phenols and Ethers

Learning & Revision for the Day

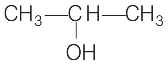
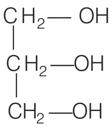
- Alcohols
- Phenols
- Ethers

- Alcohols and phenols are formed when a hydrogen atom from a hydrocarbon, aliphatic or aromatic is replaced by — OH group. The substitution of a hydrogen atom from a hydrocarbon by an alkoxy or aryloxy group ($R—O$ / $Ar—O$) gives ethers.

Alcohols

- The hydroxy derivatives of aliphatic hydrocarbons are called alcohols. They are obtained by replacing one or more hydrogen atoms of a hydrocarbon by the — OH group. These are classified as mono, -di, -tri or polyhydric compounds depending on wheather they contain one, two, three or more —OH groups respectively in their structures.
- **Nomenclature** According to IUPAC system of nomenclature, the suffixes-ol,-diol, or-triol are used for monohydric, dihydric on trihydric alcohols respectively.

  IUPAC names of some alcohols are given below:

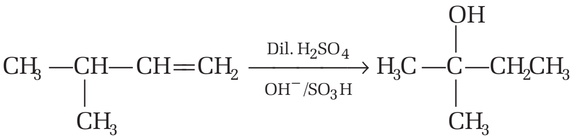
Type of alcohol	Structural formula	IUPAC name
Monohydric alcohols	$CH_3—CH_2—OH$  $CH_3—\underset{\mid \atop OH}{CH}—CH_3$	Ethanol Propan - 2 - ol
Dihydric alcohols	$HO—CH_2—CH_2—OH$	Ethan - 1, 2 - diol
Trihydric alcohols	 $\begin{array}{l}CH_2—OH\\ \mid\\ CH_2—OH\\ \mid\\ CH_2—OH\end{array}$	Propan -1, 2, 3 - trial

Methods of Preparation

The important methods used to prepare alcohols are as follows:

1. From Alkenes

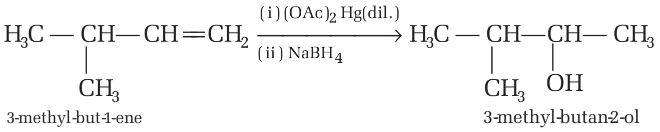
- Alkenes react with water in the presence of dilute H_2SO_4 to form alcohols. This reaction is called **acid catalysed hydration**.



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH=CH_2 \xrightarrow[OH^-/SO_3H]{\text{Dil. } H_2SO_4} H_3C-\overset{\displaystyle OH}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2CH_3$$

In this reaction, intermediate carbocation is formed and rearrange, therefore — OH gets attached at maximum degree of carbon.

- Alkenes react with mercuric acetate to form oxymercuration products, which upon reduction with $NaBH_4$ in basic medium give alcohols. This reaction is called as **oxymercuration-demercuration reaction**.

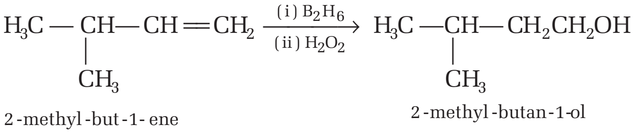


$$H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH=CH_2 \xrightarrow[\text{(ii) } NaBH_4]{\text{(i) } (OAc)_2\,Hg(\text{dil.})} H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

3-methyl-but-1-ene 3-methyl-butan-2-ol

Intermediate carbocation is not formed and alcohol is formed according to **Markownikoff's rule.**

- Diborane reacts with alkenes to form trialkyl boranes, which on oxidation with alkaline H_2O_2 give alcohols. This reaction is called **hydroboration-oxidation reaction**



$$H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH=CH_2 \xrightarrow[\text{(ii) } H_2O_2]{\text{(i) } B_2H_6} H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2CH_2OH$$

2-methyl-but-1-ene 2-methyl-butan-1-ol

Intermediate carbocation is not formed and alcohol is formed according to **anti-Markownikoff's rule**.

2. By Reduction of Carbonyl Compounds

Aldehydes on reduction give primary alcohols and ketones give secondary alcohols in the presence of weak reducing agent ($NaBH_4$).

$$RCHO \xrightarrow{NaBH_4} \underset{1^\circ\text{-alcohol}}{RCH_2OH} \qquad RCOR' \xrightarrow{NaBH_4} R-\underset{\displaystyle OH}{\underset{|}{CH}}-R'$$

2°-alcohol

3. By Reduction of Acids and Esters

Carboxylic acids and esters on reduction, in the presence of strong reducing agent ($LiAlH_4$), give primary alcohols.

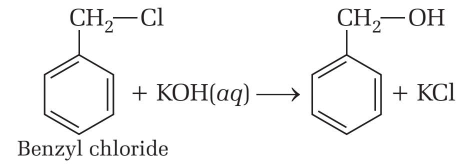
$$\underset{\text{Ethanol acid}}{CH_3COOH} \xrightarrow{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2-OH}$$

$$\underset{\text{Methyl butyate}}{CH_3COOCH_2-CH_2-CH_3} \xrightarrow[+4H]{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH} + \underset{\text{Propane}}{CH_3CH_2CH_2OH}$$

NOTE $LiAlH_4$ and $NaBH_4$ are highly specific reducing agents. $LiAlH_4$ reduces a number of organic compounds to the corresponding alcohols without attacking the double bond, if present.

4. By Hydrolysis of Alkyl Halides

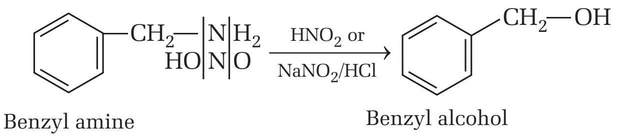
Haloalkanes on hydrolysis, with aqueous soldium or potassium hydroxide gives alcohols.



$$CH_3-CH_2\,Br + NaOH(aq) \longrightarrow CH_3-CH_2-OH + NaBr$$

5. From Primary Aliphatic Amines

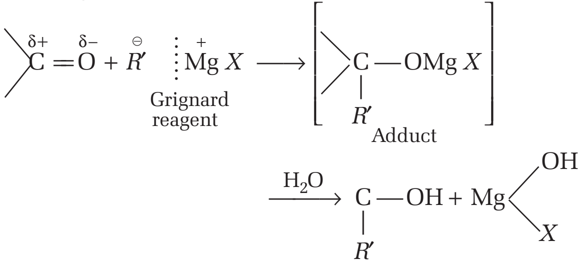
Aliphatic primary amines on treatment with nitrous acid give primary alcohols.



6. From Grignard Reagent

Grignard reagent ($R'\,Mg\,X$) on reaction with aldehydes or ketones followed by hydrolysis gives alcohols.

The nature of alcohol formed depends upon the aldehyde or ketone taken, e.g. if the reacting aldehyde is formaldehyde, primary alcohol $-CH_2OH$ is obtained while other aldehydes give secondary alcohols ($-CHOH$) with Grignard reagent. Ketones give tertiary alcohols with Grignard reagent.



Physical Properties

The detailed description of physical properties of alcohols, i.e. their boiling points, solubility are given below:

1. Boiling Points

Alcohols have higher boiling point than haloalkanes of comparable molecular mass because alcohols have intermolecular hydrogen bonding. As the number of carbon atoms increases, boiling point increases. The boiling point decreases with increase of branching in carbon chain.

2. Solubility

Alcohols are soluble in water due to ability to form hydrogen bonds with water. As the number of carbon atoms increases, solubility decreases.

Chemical Properties

The chemical properties of alcohol depend on the order of reactivity of alcohols as given below:

Order of reactivity of alcohols:

1° alcohol > 2° alcohol > 3° alcohol.

The chemical reactions of alcohols can be divided into following two categories:

1. Reactions Involving Cleavage of O — H Bond

- Alcohols are acidic in nature and hence **reacts with metals** to form metals alkoxides.

$$\underset{\text{Alcohol}}{2R—OH} + 2Na \longrightarrow \underset{\text{Sodium alkoxides}}{2R—O—Na} + H_2$$

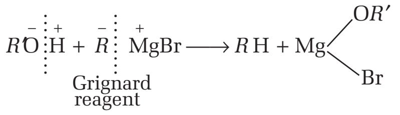
Electron releasing group decreases the polarity of —OH bond. This decreases the acidic strength Acidity of alcohols in decreasing order :

Primary alcohols > secondary alcohols > tertiary alcohols

- Alcohols when react with carboxylic acids, acid chlorides acid anhydrides, form esters. This reaction is called **esterification**.

$$R\overset{\ominus}{O}\overset{+}{H} + \underset{\text{Carboxylic acid}}{R'\overset{+}{C}O\,\overset{-}{O}H} \xrightleftharpoons{H^+} \underset{\text{Ester}}{R'COOR} + H_2O$$

- Alcohols when react with Grignard reagent to give alkanes.



$$R\overset{-}{O}\overset{+}{H} + \underset{\text{Grignard reagent}}{\overset{-}{R}\,\overset{+}{MgBr}} \longrightarrow RH + Mg\begin{array}{l}OR'\\Br\end{array}$$

2. Reactions Involving Cleavage of Carbon Oxygen (C — O) Bond

Some important reactions of alcohols involving C—O bond cleavage are discussed below:

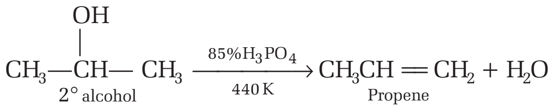
Alcohols react **with halogen acids** to form haloalkanes and water.

$$ROH + HX \longrightarrow R—X + H_2O$$

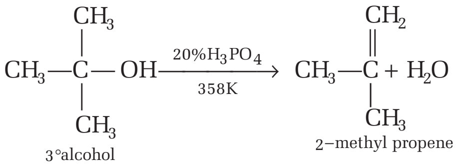
Reactivity of alcohols in decreasing order 3° > 2° > 1°.

Dehydration of alcohols in the presence of protic acids like conc. H_2SO_4 or H_3PO_4 or in the presence of catalysts such as anhy. $ZnCl_2$ or Al_2O_3 leads to the formation of alkenes or ethers.

$$\underset{1^{\circ}\text{ alcohol}}{C_2H_5OH} \xrightarrow[443K]{H_2SO_4} \underset{\text{Ethene}}{CH_2 = CH_2} + H_2O$$



$$\underset{2^{\circ}\text{ alcohol}}{CH_3—\overset{\overset{\large OH}{|}}{CH}—CH_3} \xrightarrow[440\,K]{85\% H_3PO_4} \underset{\text{Propene}}{CH_3CH = CH_2} + H_2O$$



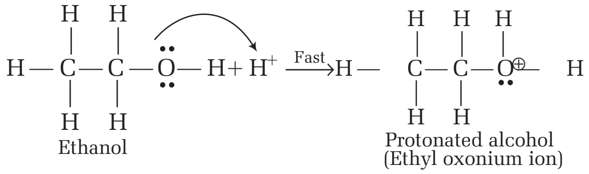
$$\underset{3^{\circ}\text{alcohol}}{CH_3—\overset{\overset{\large CH_3}{|}}{\underset{\underset{\large CH_3}{|}}{C}}—OH} \xrightarrow[358K]{20\% H_3PO_4} \underset{2\text{–methyl propene}}{CH_3—\overset{\overset{\large CH_2}{||}}{\underset{\underset{\large CH_3}{|}}{C}}} + H_2O$$

Ease of dehydration of alcohols 3° > 2° > 1°

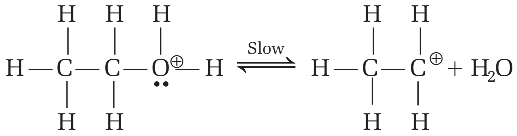
Mechanism of Dehydration

Mechansm of dehydraton of alcohols to form alkenes occurs in three steps :

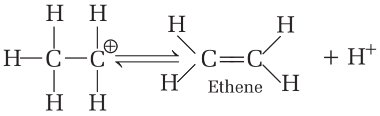
- **Formation of protonated alcohol**



- **Formation of carbocation**



- **Formation of ethene by elimination of a proton**



3. Oxidation

Oxidation of alcohols involves the formation of C = O double bond with cleavage of O—H.

(a) $\underset{1^{o}\text{alcohol}}{RCH_2OH} \xrightarrow[\text{Acidified } KMnO_4]{[O]} \underset{\text{Aldehyde}}{R—CHO} \xrightarrow{[O]} \underset{\text{Carboxylic acid}}{RCOOH}$

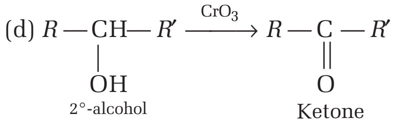
(b) $RCH_2OH \xrightarrow[CH_2Cl_2]{CrO_3} RCHO$

(c) $CH_3—CH = CH—CH_2OH \xrightarrow{PCC}$

$$CH_3—CH = CH—CHO$$

(PCC = pyridinium chloro chromate is a better reagent to convert 1° alcohol to aldehyde.)

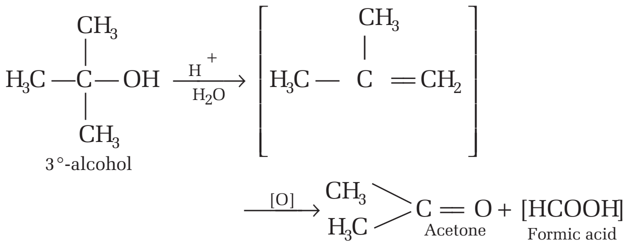
(d)



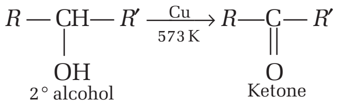
$$\underset{2^{\circ}\text{-alcohol}}{R—\underset{\underset{\large OH}{|}}{CH}—R'} \xrightarrow{CrO_3} \underset{\text{Ketone}}{R—\underset{\underset{\large O}{||}}{C}—R'}$$

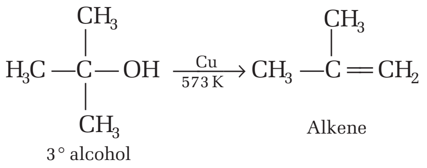
NOTE
- Ethylene glycol on reaction with HIO_4 (periodic acid) gives formaldehyde.
- Oxidation of methyl benzene with CrO_3 to benzaldehyde is carried out in the presence of acetic anhydride to prevent its further oxidation to benzoic acid.

- Tertiary alcohols do not undergo oxidation reaction. In the presence of strong oxidising agent ($KMnO_4$) and at high temperature, cleavage of C—C bond takes place and a mixture of carboxylic acids containing lesser number of carbon atoms is formed.



4. Action of Heated Copper

- $RCH_2OH \xrightarrow[573\,K]{Cu} R—CHO$
  1° alcohol Aldehyde
- 
  $R—\underset{OH}{CH}—R' \xrightarrow[573\,K]{Cu} R—\underset{O}{\overset{\|}{C}}—R'$

- 

Uses

- Methanol and ethanol are two commercially important alcohols. Methanol is used as a solvent in paints, varnishes and mainly for making formaldehyde.
- It is highly poisonous in nature. Ingestion of even small quantities of methanol can cause blindness and large quantities cause even death.
- Ethanol is used as a solvent in paint industry and in preparation of a number of carbon compounds.
- Commercial alcohol is made unfit for drinking by mixing $CuSO_4$ and pyridine (denaturation of alcohol).
- Ethanol is mainly used in alcoholic beverages.

Identification of Primary, Secondary and Tertiary Alcohols

With Lucas Reagent (conc. HCl and $ZnCl_2$),

- tertiary alcohols give turbidity immediately.
- secondary alcohols give turbidity with in five minutes.
- primary alcohols do not produce turbidity at room temperature.

Victor-Meyer's Test It has following indications:

- blood red colour indicates 1° alcohols.
- blue colour indicates 2° alcohols.
- colourless solution indicates 3° alcohols.

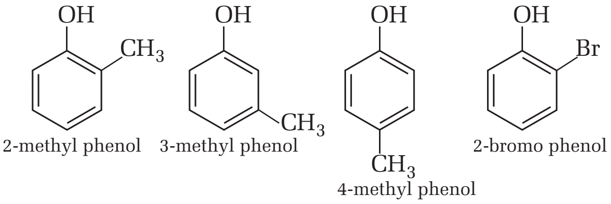
Iodoform Test All alcohols containing CH_3CHOH- group can be distinguished from other alcohols by this test. In this test, the given alcohol is treated with I_2/NaOH, if yellow ppt. of iodoform is produced, alcohols contain the grouping —$CHOHCH_3$, otherwise not. Hence, this can be used to distinguish.

- methanol from ethanol.
- *n* - propyl alcohol from isopropyl alcohol.
- 2- butanol from 1- butanol , 2- methyl - 1 propanol and 2- methyl - 2 - propanol.

Phenols (C_6H_5OH)

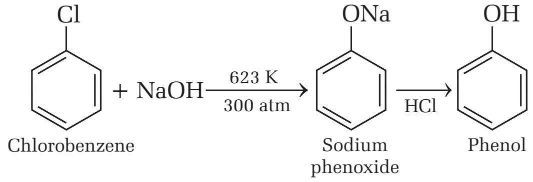
Aromatic compounds in which hydroxyl group (— OH) is directly attached with benzene nucleus are called phenols.

Nomenclature All substituted phenols are named as phenol in the IUPAC system. Also, the position of the substituents w.r.t. —OH group is indicated by arabic numerals with the some phenols. With their IUPAC names are given below :

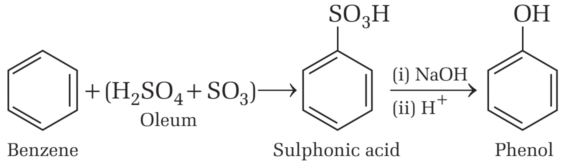


Methods of Preparation

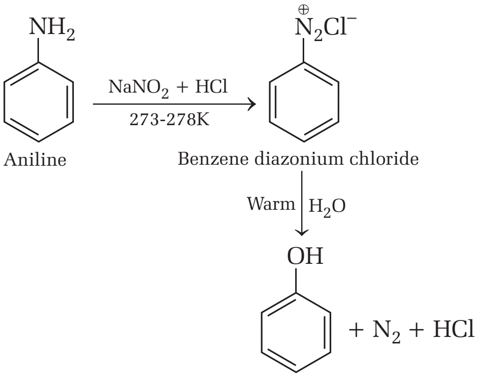
- Chlorobenzene is fused with NaOH at 623 K and 320 K atmosphere pressure and forms sodium phenoxide which on acidification.



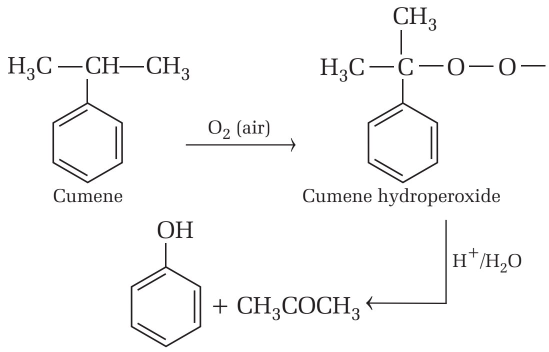
- Benzene is sulphonated with oleum to form benzene sulphuric acid, which on acidification gives phenol.



- Diazonium salt is formed by treating an aromatic primary amine with nitrous acid at 0-5℃, which on hydrolysis gives phenol.

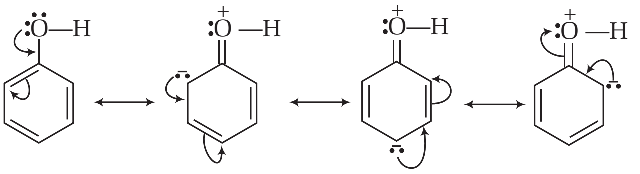


- Cumene is oxidised in the presence of air to cumene hydroperoxide, which is converted to phenol and acetone by treating with dil.acid.



Physical Properties

- Phenol has higher boiling point and soluble in water due to its ability to form hydrogen bond with water.
- **Acidic Nature of Phenol** Phenols are **acidic in nature**, The more acidic character of phenols (than corresponding aliphatic alcohols) is due to conjugation between lone pair of oxygen and benzene nucleus, i.e.



- The positive charge on oxygen signifies the weakening of O—H bond. Presence of electron releasing group like $—CH_3$, $—C_2H_5$ over benzene nucleus destabilises the phenoxide ion, thus, decreases the acidity of phenol whereas, presence of electron withdrawing groups like $—NO_2$, —CN, etc., stabilises the phenoxide ion and thus, increases the acidity of phenol.

Chemical Properties

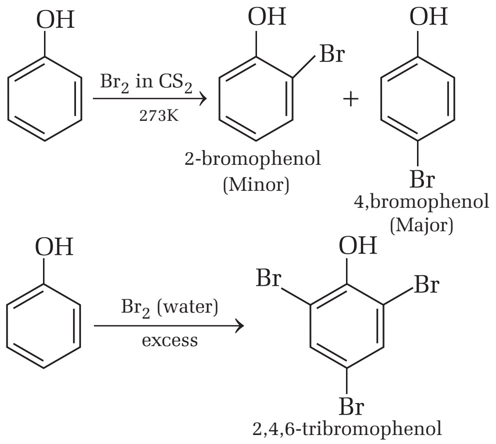
Phenols exhibit the following chemical properties.

1. Electrophilic Substitution Reactions

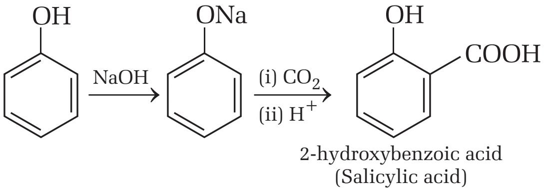
- In phenol, the —OH group shows $+R$ and $-I$ effect and hence, highly activates the benzene ring towards electrophilic substitution reaction. It is *ortho* and *para* directing group.
- With dilute HNO_3 at low temperature phenol yield mixture of *o*- and *p*-nitrophenol. This reaction is called **nitration.** With conc HNO_3, phenol is converted to 2, 4-trinitro phenol.

NOTE 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 due to intermolecular hydrogen bonding.

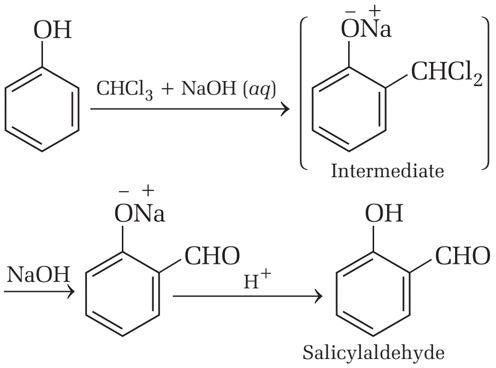
- On treating phenol with bromine different reaction products are formed under different experimental conditions. This reaction is called **halogenation**.



- Phenoxide ion generated by treating phenol with NaOH undergoes reaction with CO_2 and forms salicylic acid. This reaction is called as **Kolbe's reaction**.



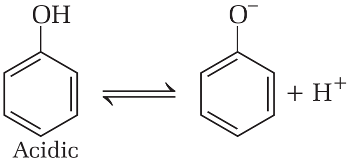
- On treating phenol with chloroform in the presence of NaOH, salicyldehyde forms. This reaction is called Riemer-Tiemann reaction.

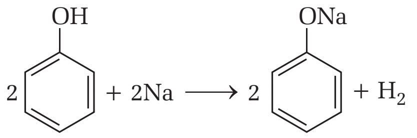


Electrophile-CCl_2 (dichlorocarbene) .

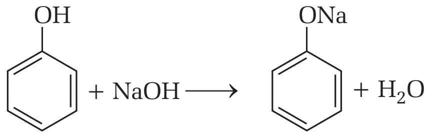
2. Reactions Involving Breaking of O — H Bond

Phenols are acidic in nature and hence react with metals or aqueous alkalies to form phenoxide ion.



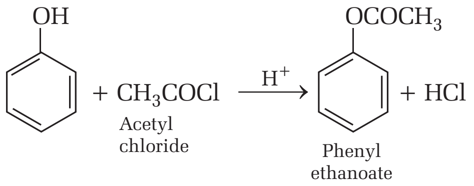


Sodium phenoxide

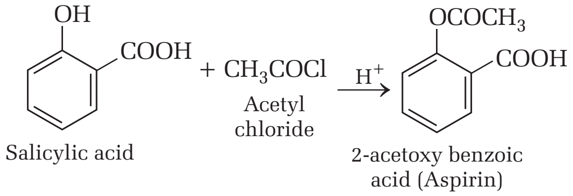


Sodium phenoxide

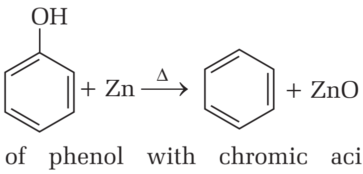
- Phenol reacts with acid chlorides and anhydrides to give phenyl ethanoate. This reaction is called **acylation**



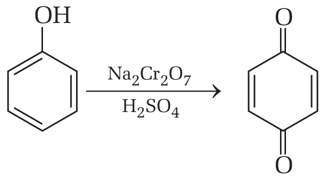
Salicylic acid reacts with acid chloride to give aspirin.



- Phenol on distillation **with zinc dust** give the corresponding aromatic hydrocarbon.



- Oxidation of phenol with chromic acid produces benzoquinone.



Benzoquinone

Uses

- Phenol is used in the manufacture of bakelite, soaps, lotions, etc.
- It is used in the manufacture of drugs like aspirin, salol, phenacetin, etc.

Ethers

These are the organic compounds having —O— functional group. Thus, these may look like

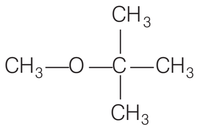
$$R'—O—R''$$

- In other words, ethers are the derivatives of water as these are obtained when both the H-atoms of H_2O are replaced by *R* groups.
- The *R* groups may be same or different. When both the *R* groups (alkyl groups) are same, the ethers are called **simple** or **symmetrical ether** and when both the groups are different, the ethers are called **mixed** or **unsymmetrical ethers**, e.g.

$CH_3—O—CH_3$ (Simple or symmetrical ethers) $CH_3OC_2H_5$ (Mixed ether)

- **Nomenclature** In the IUPAC system, ethers are named as alkoxy alkanes.
- The ethereal oxygen is taken with the smaller alkyl group and forms a part of the alkoxy group, while the larger alkyl group is considered to be a part of alkane.

IUPAC names of some ethers are given below:

Structural Formula	IUPAC Name
$CH_3—O—CH_3$	Methoxy methane
$CH_3—O—CH_2CH_3$	Methoxy ethane
 $CH_3—O—\overset{\overset{CH_3}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}}—CH_3$	2- methoxy - 2- methyl propane
$C_6H_5—O—CH_3$	Methoxy benzene

Methods of Preparation

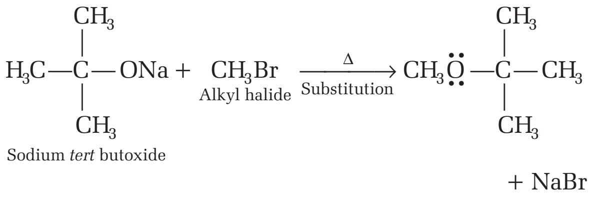
General methods used to synthesis ethers are as follows :

- Alcohols undergo dehydration in the presence of protic acids to form ethers.

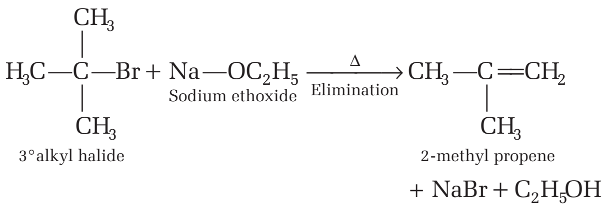
$$\underset{\text{Excess}}{2CH_3CH_2—OH} \xrightarrow[413\,K]{H_2SO_4(\text{conc.})} CH_3—CH_2—\ddot{\underset{\cdot\cdot}{O}}—CH_2—CH_3 + H_2O$$

- Only primary alkyl halides when react with sodium alkoxide give ether while tertiary alkyl halide give alkene due to steric hindrance. This reaction is called **Williamson's synthesis.**

$$CH_3CH_2Br + \underset{\text{Sodium ethoxide}}{CH_3CH_2ONa} \xrightarrow[\text{(Substitution)}]{\Delta} CH_3CH_2OCH_2CH_3 + NaBr$$



$$\underset{\text{Sodium } tert \text{ butoxide}}{H_3C-\overset{CH_3}{\underset{CH_3}{C}}-ONa} + \underset{\text{Alkyl halide}}{CH_3Br} \xrightarrow[\text{Substitution}]{\Delta} CH_3\ddot{\underset{\cdot\cdot}{O}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 + NaBr$$



$$\underset{3°\text{alkyl halide}}{H_3C-\overset{CH_3}{\underset{CH_3}{C}}-Br} + \underset{\text{Sodium ethoxide}}{Na-OC_2H_5} \xrightarrow[\text{Elimination}]{\Delta} \underset{\text{2-methyl propene}}{CH_3-\underset{CH_3}{C}=CH_2} + NaBr + C_2H_5OH$$

Physical Properties

Ethers are polar but insoluble in H_2O and have low boiling point than alcohols (having comparable molecular mass) because ethers do not form hydrogen bond with water.

Chemical Properties

The reactions of ethers are mainly due to lone pair of ethereal oxygen, cleavage of C—O bond and —*R* group.

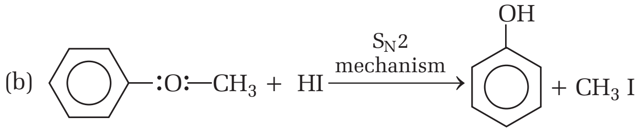
1. Reactions Involving Cleavage of C—O Bond

The reaction of dialkyl ether gives alcohol and alkyl halides, while alkyl-aryl ethers gives phenol and alkyl halide.

(a) $CH_3-CH_2-\ddot{\underset{\cdot\cdot}{O}}-CH_3 + HI \xrightarrow{S_N2 \text{ mechanism}}$

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} + \underset{\text{Methyl iodide}}{CH_3I}$$

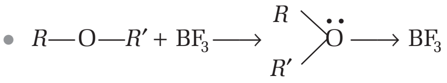
(b)

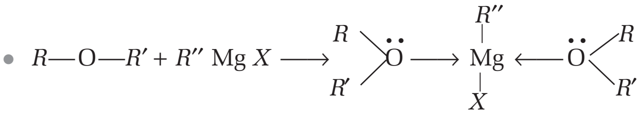


Phenol

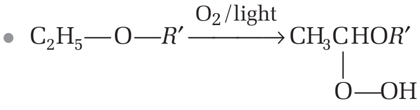
2. Addition Reactions

Ethers shows following addition reactions :





- $R-O-R' \xrightarrow[425\text{ K}]{CO/BF_3} RCOOR'$ Ester

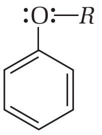


$$C_2H_5-O-R' \xrightarrow{O_2/\text{light}} CH_3\underset{O-OH}{C}HOR'$$

Peroxide

3. Electrophilic Substitution Reactions

—O*R* is *ortho, para* directing group and activates the aromatic ring towards electrophilic substitution reaction.



- Anisole undergoes bromination with bromine in ethanoic acid and forms *o*- and *p*-nitroanisole. This reaction is called halogenation.
- Anisole undergoes **Friedel-crafts alkylation and acylation** reaction with alkyl halide and acid halide in the presence of anhyd. $AlCl_3$ to give *p*-methoxy toluene and *p*-methoxy acetophenone respectively as major product.
- Anisole reacts with a mixture of conc. H_2SO_4 and nitric acid to give a mixture of *o*- and *p*-nitroanisole. This reaction is called **nitration**.

Uses

Ethers are used as a solvent for oils, fats and Grignard reagent, etc. It is used as general anaesthetic. It provides inert and moisture free medium for various reactions.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 Industrially, ethyl alcohol is prepared from ethylene by

(a) permanganate oxidation
(b) fermentation
(c) catalytic reduction
(d) absorbing in H_2SO_4 followed by hydrolysis

2 For the sequence of reactions,

$$A \xrightarrow{C_2H_5MgI} B \xrightarrow{H_2O/H^+} \textit{tert}\text{-pentyl alcohol}$$

The compound A in the sequence is

(a) 2-butanone
(b) acetaldehyde
(c) acetone
(d) propanal

3 Which of the following is not a characteristic of alcohol?

(a) They are lighter than water
(b) Their boiling points rise fairly uniformly with rising molecular weight
(c) Lower members are insoluble in water and organic solvents but the solubility regularly increases with molecular mass
(d) Lower members have a pleasant smell and burning taste, higher members are colourless and tasteless

4 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

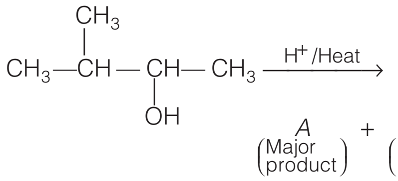
5 When primary alcohol is oxidised with Cl_2, it gives

(a) CH_3CHO
(b) CH_3COCH_3
(c) CH_3COCl
(d) $COCl_2$

6 Ethyl alcohol on oxidation with $K_2Cr_2O_7$ gives

(a) acetic acid
(b) acetaldehyde
(c) formaldehyde
(d) formic acid

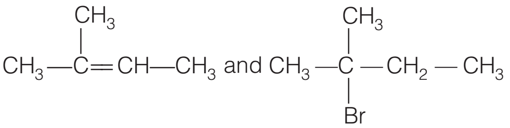
7 In the following reactions, → **CBSE-AIPMT 2011**

I. 

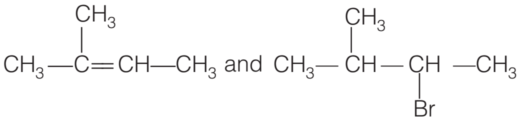
$$CH_3-\overset{CH_3}{\overset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow{H^+/\text{Heat}} \underset{\text{(Major product)}}{A} + \underset{\text{(Minor product)}}{B}$$

II. $A \xrightarrow[\text{in absence of peroxide}]{\text{HBr, dark}} \underset{\text{(Major product)}}{C} + \underset{\text{(Minor product)}}{D}$

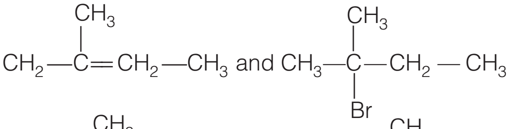
the major products A and C are respectively

(a) 

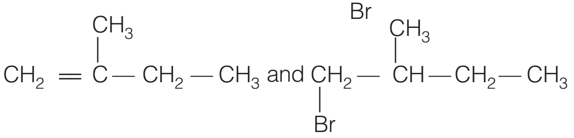
$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3$ and $CH_3-\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-CH_3$

(b) 

$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3$ and $CH_3-\overset{CH_3}{\overset{|}{CH}}-\underset{Br}{\underset{|}{CH}}-CH_3$

(c) 

$CH_2-\overset{CH_3}{\overset{|}{C}}=CH_2-CH_3$ and $CH_3-\underset{Br}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-CH_3$

(d) 

$CH_2=\overset{CH_3}{\overset{|}{C}}-CH_2-CH_3$ and $\underset{Br}{\underset{|}{CH_2}}-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_3$

8 A compound is soluble in conc. H_2SO_4. It does not decolourise Br_2 in CCl_4 but oxidised by chromic anhydride in sulphuric acid, within two seconds, turning orange solution to blue green, then opaque. The original solution contains

(a) secondary alcohol
(b) an ether
(c) an alkene
(d) a primary alcohol

9 Consider the following reaction,

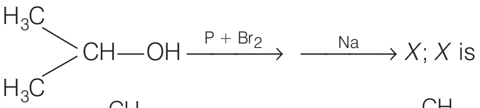
$$\text{Ethanol} \xrightarrow{PBr_3} X \xrightarrow{\text{Alc. KOH}} Y \xrightarrow[\text{(ii) } H_2O\text{, heat}]{\text{(i) } H_2SO_4\text{, room temperature}} Z$$

The product Z is → **CBSE-AIPMT 2009**

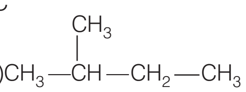
(a) $CH_2=CH_2$
(b) $CH_3CH_2OCH_2CH_3$
(c) $CH_3CH_2OSO_3H$
(d) CH_3CH_2OH

10 The alcohol that produces turbidity immediately with $ZnCl_2$/conc. HCl at room temperature is

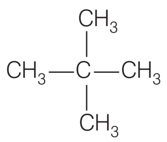
(a) 1-hydroxy butane
(b) 2-hydroxy butane
(c) 2-hydroxy-2-methyl propane
(d) 1-hydroxy-2-methyl propane

11 

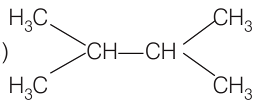
$$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>CH-OH \xrightarrow{P+Br_2} \xrightarrow{Na} X\text{; } X \text{ is}$$

(a) 

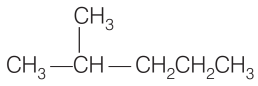
$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_3$

(b) 

$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_3$

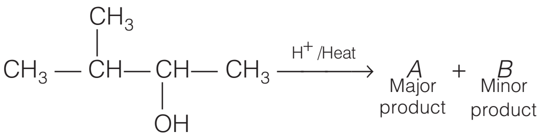
(c) 

$\begin{matrix}H_3C\\H_3C\end{matrix}\!\!>CH-CH<\!\!\begin{matrix}CH_3\\CH_3\end{matrix}$

(d) 

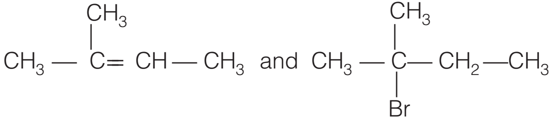
$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2CH_2CH_3$

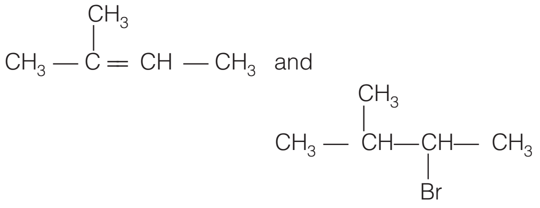
12 In the following reactions, **→ CBSE-AIPMT 2011**

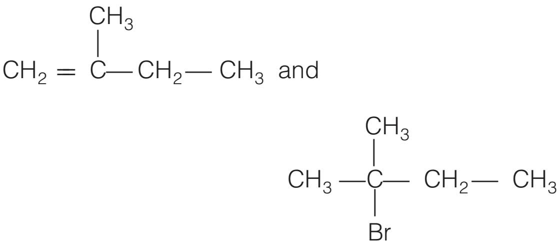
I. 
$CH_3-\overset{CH_3}{CH}-\underset{OH}{CH}-CH_3 \xrightarrow{H^+/\text{Heat}} \underset{\text{Major product}}{A} + \underset{\text{Minor product}}{B}$

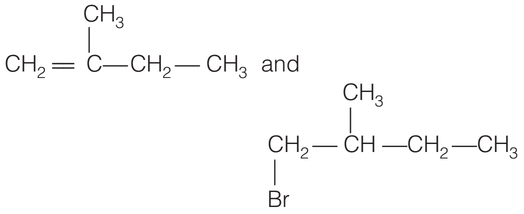
II. $A \xrightarrow[\text{in the absence of peroxide}]{\text{HBr, dark}} \underset{\text{Major product}}{C} + \underset{\text{Minor product}}{D}$

the major products *A* and *C* respectively are

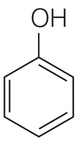
(a) 
$CH_3-\overset{CH_3}{C}=CH-CH_3$ and $CH_3-\overset{CH_3}{\underset{Br}{C}}-CH_2-CH_3$

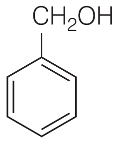
(b) 
$CH_3-\overset{CH_3}{C}=CH-CH_3$ and $CH_3-\overset{CH_3}{CH}-\underset{Br}{CH}-CH_3$

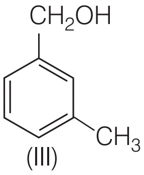
(c) 
$CH_2=\overset{CH_3}{C}-CH_2-CH_3$ and $CH_3-\overset{CH_3}{\underset{Br}{C}}-CH_2-CH_3$

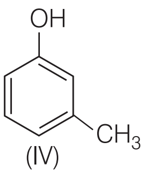
(d) 
$CH_2=\overset{CH_3}{C}-CH_2-CH_3$ and $\underset{Br}{CH_2}-\overset{CH_3}{CH}-CH_2-CH_3$

13 Which of the following compounds is aromatic alcohol?


(I)

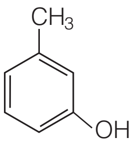

(II)

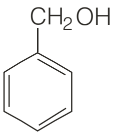

(III)

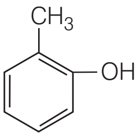

(IV)

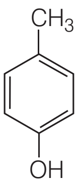
(a) I, II, III and IV (b) I and IV
(c) II and III (d) Only I

14 The structure of the compound that gives a tribromo derivative on treatment with bromine water is

(a) 

(b) 

(c) 

(d) 

15 Phenol $\xrightarrow[\text{(ii) } CO_2/140°C]{\text{(i) NaOH}} A \xrightarrow{H^+/H_2O} B \xrightarrow{Ac_2O} C$

In this reaction, the end product *C* is

(a) salicylaldehyde (b) salicylic acid
(c) phenyl acetate (d) aspirin

16 Reaction of phenol with chloroform in the presence of dilute sodium hydroxide finally introduces, which one of the following functional group? **→ CBSE-AIPMT 2015**

(a) $-CH_2Cl$ (b) $-COOH$
(c) $-CHCl_2$ (d) $-CHO$

17 Consider the following reaction,

Phenol $\xrightarrow{\text{Zn-dust}} X \xrightarrow[\text{Anhy. } AlCl_3]{CH_3Cl} Y \xrightarrow{\text{Alk. } KMnO_4} Z$

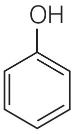
The product *Z* is **→ CBSE-AIPMT 2009**

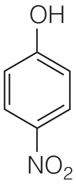
(a) toluene (b) benzaldehyde
(c) benzoic acid (d) benzene

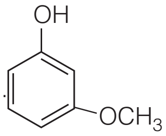
18 Which of the following will not be soluble in sodium hydrogen carbonate? **→ CBSE-AIPMT 2014**

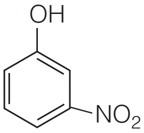
(a) 2,4,6-trinitrophenol (b) Benzoic acid
(c) *o*-nitrophenol (d) Benzene sulphonic acid

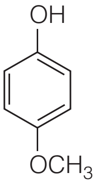
19 Mark the correct order of decreasing acidic strength of the following compounds.

I. 

II. 

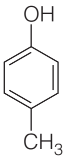
III. 

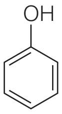
IV. 

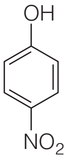
V. 

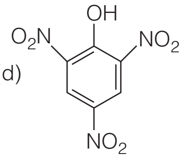
(a) V > IV > II > I > III (b) II > IV > I > III > V
(c) IV > V > III > II > I (d) V > IV > III > II > I

20 Which one is the most acidic compound? **→ NEET 2017**

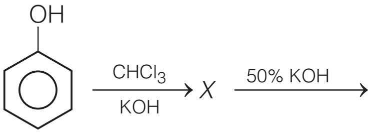
(a) 

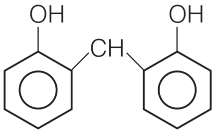
(b) 

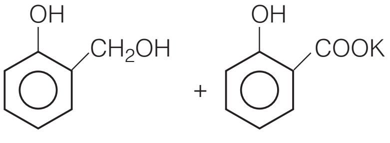
(c) 

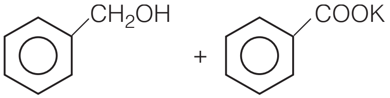
(d) 

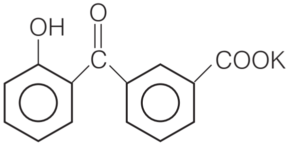
21 The final product of the following reaction is/are



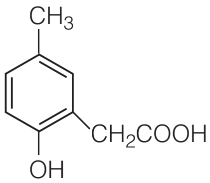
(a) 

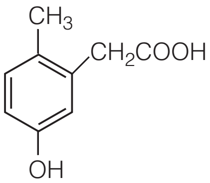
(b) 

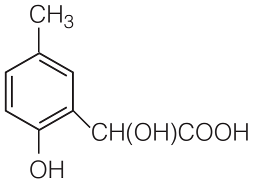
(c) 

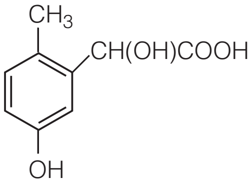
(d) 

22 *p*-cresol reacts with chloroform in alkaline medium to give a compound *A*, which adds hydrogen cyanide to form another compound *B*. This latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is

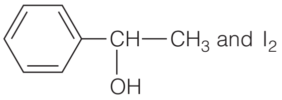
(a) 

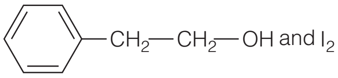
(b) 

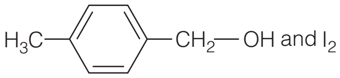
(c) 

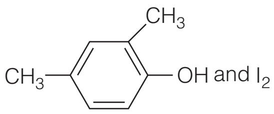
(d) 

23 Compound *A*, $C_8H_{10}O$, is found to react with NaOI (produced by reacting *Y* with NaOH) and yields a yellow precipitate with characteristic smell. *A* and *Y* are respectively. **➞ NEET 2018**

(a) 

(b) 

(c) 

(d) 

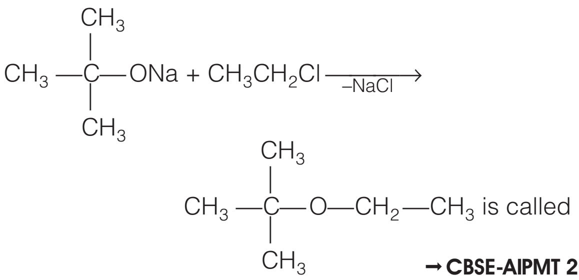
24 The heating of phenyl-methyl ethers with HI produces **➞ NEET 2017**

(a) ethyl chlorides (b) iodobenzene
(c) phenol (d) benzene

25 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 **➞ NEET 2018**

(a) C_2H_5Cl, C_2H_6, C_2H_5OH
(b) C_2H_5OH, C_2H_5Cl, C_2H_5ONa
(c) C_2H_5OH, C_2H_6, C_2H_5Cl
(d) C_2H_5OH, C_2H_5ONa, C_2H_5Cl

26 The reaction,



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-ONa + CH_3CH_2Cl \xrightarrow[-NaCl]{} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_2-CH_3$$

is called **➞ CBSE-AIPMT 2015**

(a) Williamson synthesis
(b) Williamson continuous etherification process
(c) Etard reaction
(d) Gattermann-Koch reaction

27 Identity *Z* in the sequence of reactions, **➞ CBSE-AIPMT 2014**

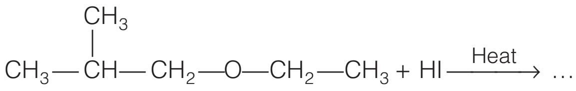
$$CH_3CH_2CH=CH_2 \xrightarrow{HBr/H_2O_2} Y \xrightarrow{C_2H_5ONa} Z$$

(a) $CH_3-(CH_2)_3-O-CH_2CH_3$
(b) $(CH_3)_2CH_2-O-CH_2CH_3$
(c) $CH_3(CH_2)_4-O-CH_3$
(d) $CH_3CH_2-CH(CH_3)-O-CH_2CH_3$

28 Among the following sets of reactants which one produces anisole? **➞ CBSE-AIPMT 2014**

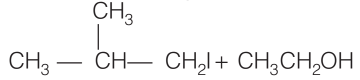
(a) CH_3CHO, $RMgX$
(b) C_6H_5OH, NaOH, CH_3I
(c) C_6H OH, neutral $FeCl_3$
(d) $C_6H_5-CH_3$, CH_3COCl, $AlCl_3$

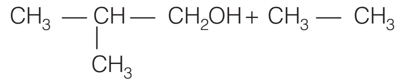
29 The reaction,

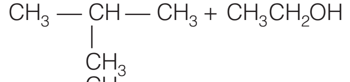


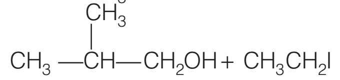
$$CH_3-\overset{CH_3}{CH}-CH_2-O-CH_2-CH_3 + HI \xrightarrow{Heat} \ldots$$

Which of the following compounds will be formed?

(a) 
$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2I+CH_3CH_2OH$

(b) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2OH+CH_3-CH_3$

(c) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3+CH_3CH_2OH$

(d) 
$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2OH+CH_3CH_2I$

30 Which one of the following reaction does not yield an alkyl halide?

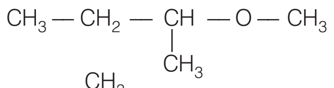
(a) Diethyl ether + Cl_2 (in the dark)
(b) Diethyl ether + PCl_5
(c) Diethyl ether + HI
(d) Divinyl ether $\xrightarrow{\text{Reduction}} X \xrightarrow{SOCl_2}$

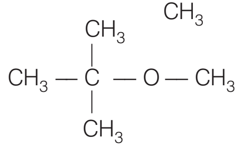
31 *Tert*-butyl methyl ether on heating with HI gives a mixture of

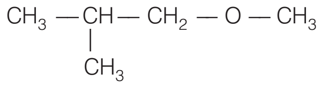
(a) *tert*-butyl alcohol and methyl iodide
(b) *tert*-butyl iodide and methanol
(c) isobutylene and methyl iodide
(d) isobutylene and methanol

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

→ **NEET 2013**

(a) 
$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O-CH_3$

(b) 
$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-O-CH_3$

(c) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-O-CH_3$

(d) $CH_3-CH_2-CH_2-CH_2-O-CH_3$

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 What will be the products of reaction of methoxy benzene with HI?

(a) Methyl alcohol (methanol) + iodobenzene
(b) Methyl iodide (iodomethane) + benzene
(c) Methyle iodide + phenol
(d) Methyl iodide + iodobenzene

2 Which of the following relation is correct regarding case of dehydration in alcohols?

(a) Primary > secondary
(b) Secondary > tertiary
(c) Tertiary > primary
(d) None of the above

3 When a mixture of ethanol and methanol is heated in the presence of conc. H_2SO_4, the resulting organic product or products is / are

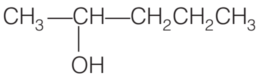
(a) $CH_3OC_2H_5$
(b) CH_3OCH_3 and $C_2H_5OC_2H_5$
(c) $CH_3OC_2H_5$ and CH_3OCH_3
(d) $CH_3OC_2H_5$, CH_3OCH_3 and $C_2H_5OC_2H_5$

4 Which of the following compounds on boiling with $KMnO_4$ (alk.) and subsequent acidification will not give benzoic acid?

(a) Benzyl alcohol
(b) Acetophenone
(c) Anisole
(d) Toluene

5 An alcohol of molecular formula $C_5H_{11}OH$ on dehydration gives an alkene, which on oxidation yields a mixture of ketone and an acid. The alcohol is

(a) $CH_3CH_2CH(OH)CH_2CH_3$

(b) 
$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2CH_2CH_3$

(c) $(CH_3)_2CHCH(OH)CH_3$
(d) $(CH_3)_3CCH_2OH$

6 Which one / ones of the following reactions give 2-propanol? Choose the right answer from (a), (b), (c) and (d).

(i) $CH_2 == CH—CH_3 + H_2O \xrightarrow{H+}$
(ii) $CH_3CHO \xrightarrow[H_2O]{CH_3MgI}$
(iii) $CH_2O \xrightarrow[H_2O]{C_2H_5MgI}$
(iv) $CH_2 = CH—CH_3 \xrightarrow{\text{Neutral } KMnO_4}$

(a) (i) and (ii)
(b) (ii) and (iii)
(c) (iii) and (i)
(d) (ii) and (iv)

7 Which of the following statements is correct ?

(a) During dehydration of alcohols to alkenes by heating with conc, H_2SO_4 the initial step is the formation of carbocation
(b) Phenol is acidic and react with $NaHCO_3$ solution
(c) Alcohols are soluble in water due to intermolecular hydrogen bonding between alcohols and water molecules
(d) The —OH group in phenol is *meta* directing

8 Phenol is heated with phthalic anhydride in the presence of conc. H_2SO_4. The product gives pink colour with alkali. The product is

(a) phenolphthalein
(b) bakelite
(c) salicylic acid
(d) salicyldehyde

9 The major product formed when 3, 3- dimethyl butan-2-ol is heated with conc. sulphuric acid is

(a) 3, 3 - dimethyl - 1 - butene
(b) 2, 3 - dimethyl - 2 - butene
(c) 2, 3 - dimethyl - 1- butene
(d) *cis* and *trans* isomers of 2, 3 - dimethyl - 1-butene

10 Which of the following order of acid strength is correct?

(a) $RCOOH > ROH > HOH > HC\equiv CH$
(b) $RCOOH > HOH > ROH > HC\equiv CH$
(c) $RCOOH > HOH > HC\equiv CH > ROH$
(d) $RCOOH > HC\equiv CH > HOH > ROH$

11 An organic compound (X) with molecular formula C_7H_8O is insoluble in aqueous $NaHCO_3$ but dissolves in NaOH. When treated with bromine water (X) rapidly gives (Y) $C_7H_5OBr_3$. The compounds (X) and (Y) respectively are

(a) *m* - cresol and 2, 4, 6 - tribromo - 3 - methyl phenol
(b) benzyl alcohol and 2, 4, 6 - tribromo - 3 - methyl benzene
(c) *o* - cresol and 3, 4, 5 tribromo - 2 - methyl phenol
(d) methoxy benzene and 2, 4, 6 - tribromo - 3 - methory benzene

12 A compound having formula $C_4H_{10}O$ reacts with Na and undergoes oxidation to give a carbonyl compound which does not reduce Tollen's reagent, the original compounds is

(a) diethyl ether (b) *n* - butyl alcohol
(c) *sec* - butyl alcohol (d) isobutyl alcohol

13 An organic compound A when treated with ethyl magnesium iodide in dry ether forms an addition product, which on hydrolysis form compound B. The compound B on oxidation form 3- pentanone. The compounds A and B are

(a) propanal, 3- pentanol (b) pentanol, 3- pentanol
(c) ethanal, pentanal (d) acetone, 3- pentanol

14 When compound X is oxidised by acidified potassium dichromate, compound Y is formed. Compound Y on reduction with $LiAlH_4$ gives X. X and Y respectively are

(a) C_2H_5OH, CH_3COOH (b) CH_3COCH_3, CH_3COOH
(c) C_2H_5OH, CH_3COCH_3 (d) CH_3CHO, CH_3COCH_3

15 Increasing order of acidic strength among *p*- methoxy phenol (I), *p*- methyl phenol (II), *p*- nitrophenol (III) is

(a) III, I, II (b) II, I, III (c) III, II, I (d) I, II, III

16 A compound X undergoes reduction with $LiAlH_4$ to yield Y. When vapours of Y are passed over freshly reduced copper at 300°C, X is formed. What is Y?

(a) CH_3COCH_3 (b) CH_3CHO
(c) CH_3CH_2OH (d) CH_3OCH_3

ANSWERS

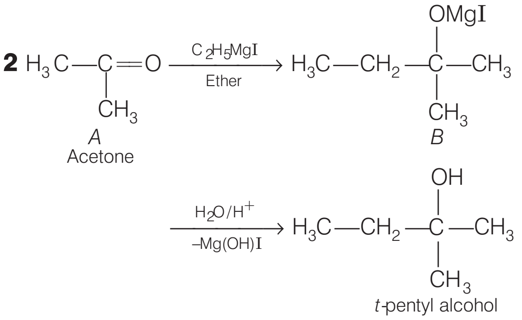
SESSION 1	**1** (d)	**2** (c)	**3** (c)	**4** (a)	**5** (a)	**6** (a)	**7** (a)	**8** (d)	**9** (d)	**10** (c)
	11 (c)	**12** (a)	**13** (c)	**14** (a)	**15** (d)	**16** (d)	**17** (c)	**18** (c)	**19** (b)	**20** (d)
	21 (b)	**22** (c)	**23** (a)	**24** (c)	**25** (d)	**26** (a)	**27** (a)	**28** (b)	**29** (d)	**30** (a)
	31 (b)	**32** (b)								
SESSION 2	**1** (c)	**2** (c)	**3** (d)	**4** (c)	**5** (c)	**6** (a)	**7** (c)	**8** (a)	**9** (b)	**10** (b)
	11 (a)	**12** (c)	**13** (a)	**14** (a)	**15** (d)	**16** (c)				

Hints and Explanations

SESSION 1

1 $CH_2{=}CH_2 + H_2SO_4 \longrightarrow C_2H_5HSO_4 \xrightarrow[-H_2SO_4]{H_2O/H^+} C_2H_5OH$

2



$$\underset{\substack{A\\ \text{Acetone}}}{H_3C-\underset{\substack{|\\CH_3}}{C}{=}O} \xrightarrow[\text{Ether}]{C_2H_5MgI} \underset{B}{H_3C-CH_2-\overset{\substack{OMgI\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_3}$$

$$\xrightarrow[-Mg(OH)I]{H_2O/H^+} \underset{t\text{-pentyl alcohol}}{H_3C-CH_2-\overset{\substack{OH\\|}}{\underset{\substack{|\\CH_3}}{C}}-CH_3}$$

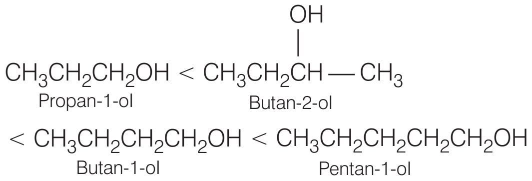
3 Lower members are soluble in water as they form H-bonding with water molecules.

Solubility of alcohols in water decreases with increase in molecular masses.

4 Boiling point of alcohols increases with molecular weight. Alcohols with same molecular weight are expected to have almost same boiling point however two more factor other than molecular weight are important, they are namely H-bonding and surface area.

Both these factors are least in 3° alcohols and maximum in 1° alcohols.

Therefore, the correct order of boiling points of alcohols will be



$$\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} < \underset{\text{Butan-2-ol}}{CH_3CH_2\overset{\substack{OH\\|}}{C}H-CH_3}$$

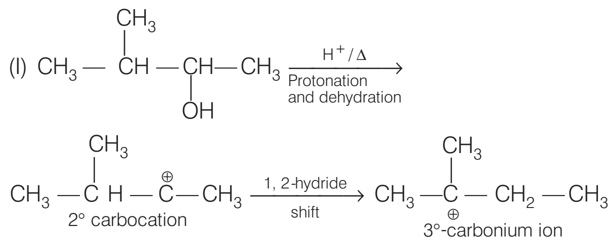
$$< \underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} < \underset{\text{Pentan-1-ol}}{CH_3CH_2CH_2CH_2CH_2OH}$$

5 A primary alcohol on oxidation with Cl_2 gives an aldehyde (CH_3CHO).

$$RCH_2OH \xrightarrow[\text{oxidation}]{Cl_2} RCHO + 2HCl$$

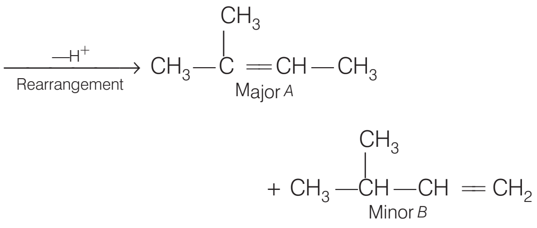
6 $\underset{\text{Ethyl alcohol}}{C_2H_5OH} + 2[O] \xrightarrow{K_2Cr_2O_7/H^+} \underset{\text{Acetic acid}}{CH_3COOH} + H_2O$

7 (I)



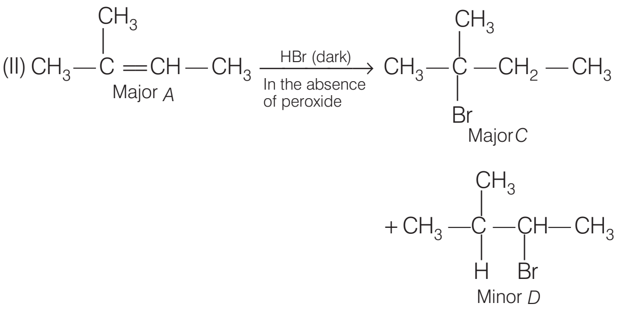
$$CH_3-\overset{\substack{CH_3\\|}}{CH}-\underset{\substack{|\\OH}}{CH}-CH_3 \xrightarrow[\text{Protonation and dehydration}]{H^+/\Delta}$$

$$\underset{2^\circ\text{ carbocation}}{CH_3-\overset{\substack{CH_3\\|}}{C}H-\overset{\oplus}{C}-CH_3} \xrightarrow[\text{shift}]{1,2\text{-hydride}} \underset{3^\circ\text{-carbonium ion}}{CH_3-\overset{\substack{CH_3\\|}}{\underset{\oplus}{C}}-CH_2-CH_3}$$



$$\xrightarrow[\text{Rearrangement}]{-H^+} \underset{\text{Major } A}{CH_3-\overset{\substack{CH_3\\|}}{C}{=}CH-CH_3} + \underset{\text{Minor } B}{CH_3-\overset{\substack{CH_3\\|}}{CH}-CH{=}CH_2}$$

A part is major because more substituted alkenes are more stable.



$$\text{(II) } \underset{\text{Major } A}{CH_3-\overset{\substack{CH_3\\|}}{C}{=}CH-CH_3} \xrightarrow[\text{In the absence of peroxide}]{\text{HBr (dark)}} \underset{\text{Major } C}{CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\Br}}{C}}-CH_2-CH_3}$$

$$+ \underset{\text{Minor } D}{CH_3-\overset{\substack{CH_3\\|}}{\underset{\substack{|\\H}}{C}}-\underset{\substack{|\\Br}}{CH}-CH_3}$$

8 Since, oxidation is easier and occurs very quickly. Hence, it must be a 1°-alcohol. The dichromate solution changes from orange to blue green.

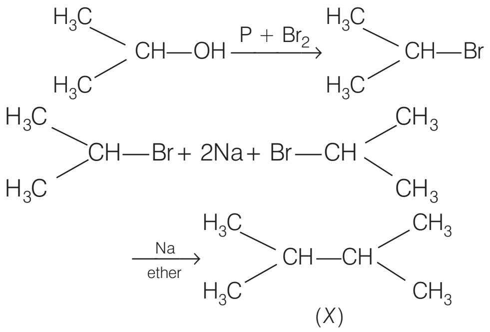
9 (d) $\underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow{PBr_3} C_2H_5Br \xrightarrow[\substack{-K\,Br, -H_2O\\ \beta\text{-elimination}}]{\text{Alc. KOH}} CH_2{=}CH_2$

$$\xrightarrow{H_2SO_4} CH_3-CH_2OSO_3H \xrightarrow[-H_2SO_4]{H_2O/\Delta} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

10 Mixture of anhydrous $ZnCl_2$ and conc. HCl is known as **Lucas reagent**. Lucas test is used for the distinction between primary, secondary and tertiary alcohols. The tertiary alcohol reacts immediately with Lucas reagent producing turbidity.

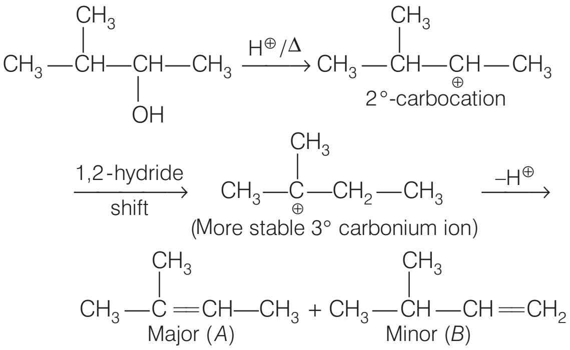
The secondary alcohol gives turbidity within 5 -10 min and primary alcohol does not give turbidity at room temperature. In the given alternates, 2-hydroxy-2-methyl propane is a 3° alcohol, so it is more reactive.

11



(X)

12 (I)



$$CH_3-\overset{CH_3}{\overset{|}{CH}}-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{H^{\oplus}/\Delta} CH_3-\overset{CH_3}{\overset{|}{CH}}-\underset{\oplus}{CH}-CH_3$$

2°-carbocation

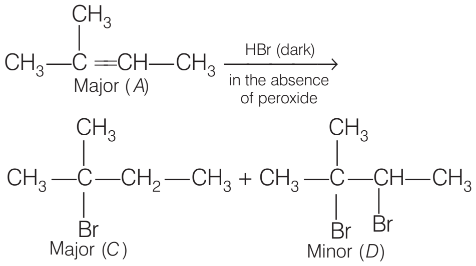
$$\xrightarrow[\text{shift}]{\text{1,2-hydride}} CH_3-\underset{\oplus}{\overset{CH_3}{\overset{|}{C}}}-CH_2-CH_3 \xrightarrow{-H^{\oplus}}$$

(More stable 3° carbonium ion)

$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3 + CH_3-\overset{CH_3}{\overset{|}{CH}}-CH=CH_2$$

Major (*A*) Minor (*B*)

(II)



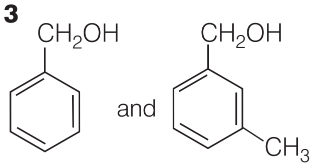
$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3 \xrightarrow[\text{in the absence of peroxide}]{\text{HBr (dark)}}$$

Major (*A*)

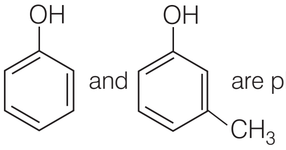
$$CH_3-\underset{\underset{Br}{|}}{\overset{CH_3}{\overset{|}{C}}}-CH_2-CH_3 + CH_3-\underset{\underset{Br}{|}}{\overset{CH_3}{\overset{|}{C}}}-\underset{\underset{Br}{|}}{CH}-CH_3$$

Major (*C*) Minor (*D*)

13

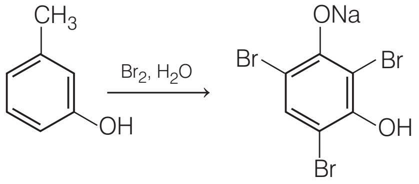


are aromatic alcohols due to the presence of benzene ring and —OH group is attached with aliphatic carbon.

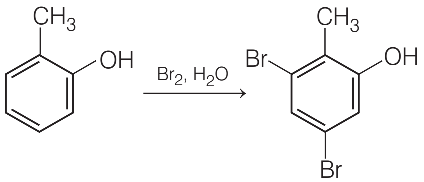


are phenols.

14 *m*-cresol due to phenoxide ion in H_2O solvent, gives tribromo derivative at all *ortho* and *para*-positions.



Tribromoderivative



Dibromoderivative

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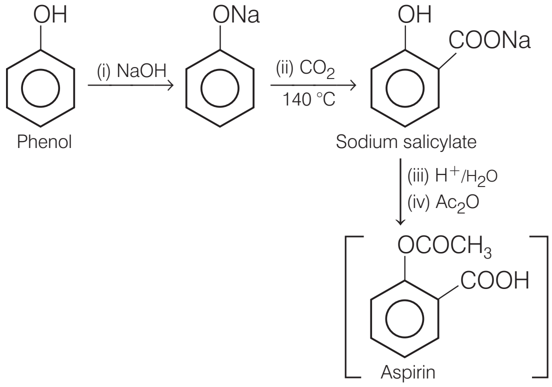

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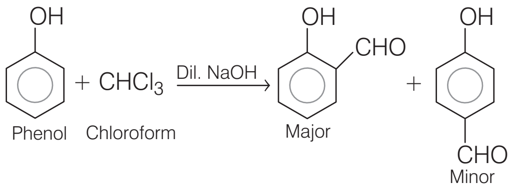
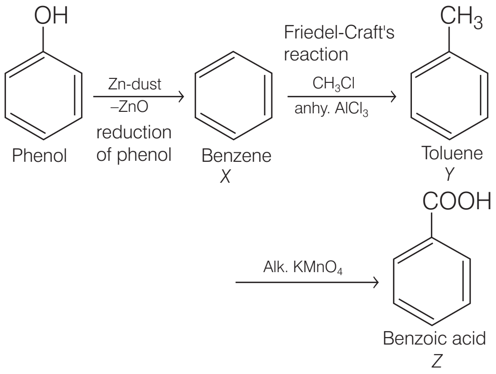


This is Reimer-Tiemann reaction. So, finally —CHO group is introduced.

17



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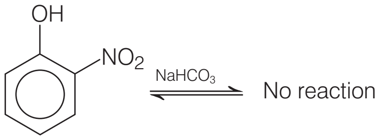


o-nitrophenol is insoluble in sodium hydrogen carbonate. While 2,4,6-trinitrophenol, benzoic acid and benzene sulphonic acid are soluble in $NaHCO_3$.

Infact, Acid + $NaHCO_3 \longrightarrow$ Salt + H_2CO_3

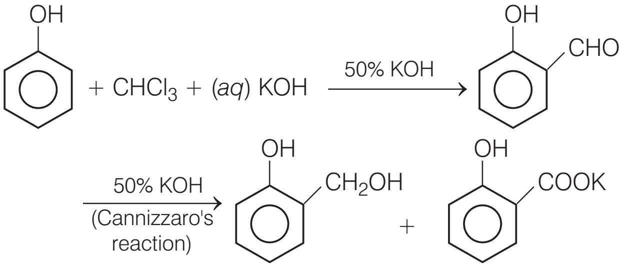
This reaction is possible in forward direction if acid is more acidic than H_2CO_3. *o*-nitrophenol is less acidic than H_2CO_3. Hence, it is not soluble in sodium hydrogen carbonate.

19 Phenols are acidic in nature due to resonance stabilisation of phenoxide ion. Presence of electron withdrawing groups (such as $—NO_2$, $—X$, $—NR_3^+$, —CHO, —COX , —COOR, —CN) in the ring stabilise phenoxide ion and increase the acidic nature of phenols. On the other hand, presence of electron releasing groups (such as —CH_3, —OR) in the ring destabilises the phenoxide ion and decreases the acidic nature of phenols.

20 This problem is based on the acidic character of phenol. Electron -withdrawing group at *o* and *p*-position w.r.t. —OH group of phenol, increase the acidic strength.

Picric acid (2, 4, 6-trinitrophenol) is extremely more acidic than given compounds because its pK_a value is close to zero also due to the presence of three strong electron withdrawing group (—NO_2group) at *ortho* and *para*-positions, picric is more acidic compound.

21 Phenol on reaction with chloroform and KOH gives salicylaldehyde, which with 50% KOH solution undergoes Cannizzaro's reaction.



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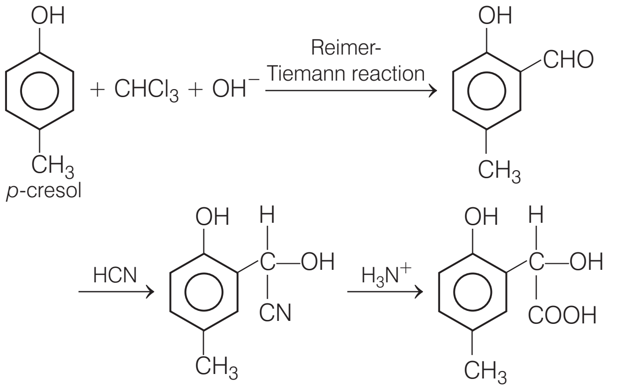


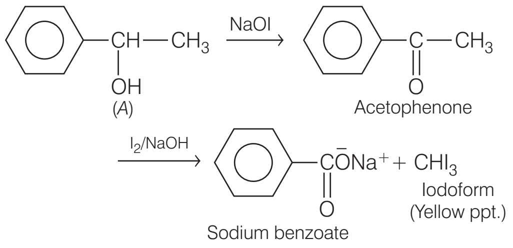
(—OH is more activating than —CH_3 in *o*, *p*-directing, thus, —CHO goes to *o*-position w.r.t —OH).

23 Iodoform reaction with sodium hypoiodite is used for the detection of CH_3CO group. Also, compounds containing $CH_3CH(OH)$ group shows positive iodoform test as it produces CH_3CO group on oxidation.

Since, among the compounds, $CH_3CH(OH)$ group is given only in the substrate of option (a) hence, it is correct.

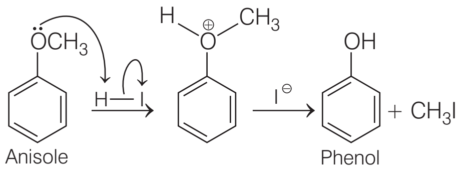
The reaction of compound *A* with NaOI is given as follows :

$$2NaOH + I_2 \longrightarrow NaOI + NaI + H_2O$$



24 This problem is based on the resonance stabilisation.

In anisole, methyl phenyl oxonium ion is formed by protonation of ether. The bond between O — CH_3 is weaker than the bond between O — C_6H_5, because the carbon of phenyl group is sp^2-hybridised and there is a partial double bond character. Thus, the reaction yields phenol and alkyl halide.



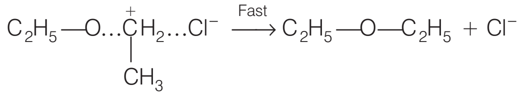
25 According to given question and options (*A*) must be C_2H_5OH, as it reacts with Na to give C_2H_5ONa. The reaction sequence is as follows :

$$\text{(i) } \underset{\substack{\text{Ethanol}\\(A)}}{C_2H_5OH} \xrightarrow{Na} \underset{\substack{\text{Sodium ethoxide}\\(B)}}{C_2H_5\bar{O}\overset{+}{Na}} \xrightarrow{PCl_5} \underset{\substack{\text{Ethyl chloride}\\(C)}}{C_2H_5Cl}$$

$$\text{(ii) } C_2H_5\bar{O}\overset{+}{Na} + C_2H_5Cl \xrightarrow{S_N2} \underset{\text{Diethyl ether}}{C_2H_5—O—C_2H_5} + NaCl$$

The above reaction is known as Williamson's ether synthesis. It involves nucleophilic attack of alkoxide ion on alkyl halide according to S_N2 mechanism.

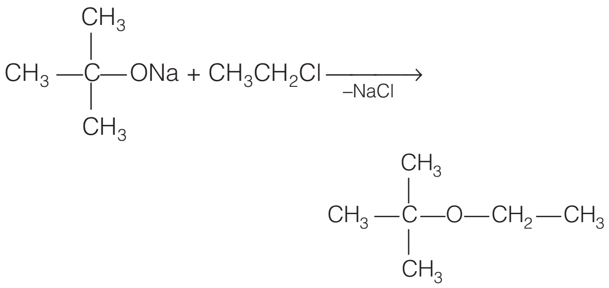
$$\underset{\substack{\text{Nucleophile}\\\text{(Alkoxide ion)}}}{C_2H_5O^-} + \underset{\substack{\text{Substrate}\\\text{(Alkyl halide)}}}{CH_3—CH_2Cl} \xrightarrow{\text{Slow}}$$



$$C_2H_5—O\ldots\underset{\underset{CH_3}{|}}{\overset{+}{C}}H_2\ldots Cl^- \xrightarrow{\text{Fast}} C_2H_5—O—C_2H_5 + Cl^-$$

26 The reaction of alkyl halides with sodium alkoxide or sodium phenoxide to form ethers is called **Williamson synthesis**. Here, in this reaction alkyl halide should be primary and alkoxide, should be bulkier as shown below,

$$\underset{\text{Alkyl halide}}{R—X} + \underset{\text{Sodium alkoxide}}{R'—ONa} \longrightarrow \underset{\text{Ether}}{R—O—R'} + NaX$$

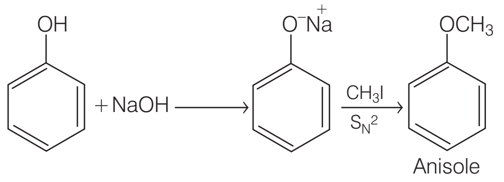


$$CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—ONa + CH_3CH_2Cl \xrightarrow[-NaCl]{} CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—O—CH_2—CH_3$$

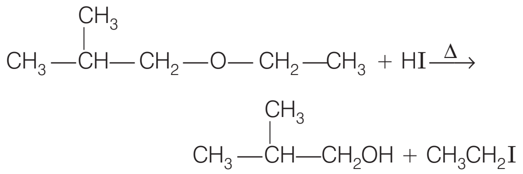
27 $$CH_3CH_2CH{=}CH_2 \xrightarrow[\textit{Anti}\text{ - Markownikoff's rule}]{HBr / H_2O_2}$$

$$\underset{\text{Bromobutane}}{CH_3CH_2CH_2CH_2Br} \xrightarrow[S_N2\text{ reaction}]{C_2H_5ONa} \underset{\substack{\text{Ethoxy-butane}\\\text{(Williamson's synthesis)}}}{CH_3CH_2CH_2CH_2OC_2H_5}$$

28 Williamson's synthesis

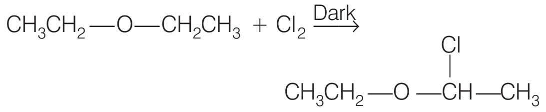


29 When conc. HI or HBr react with mixed ether, the halogen atom attaches to the smaller alkyl group due to steric effect.



$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-O-CH_2-CH_3 + HI \xrightarrow{\Delta}$$

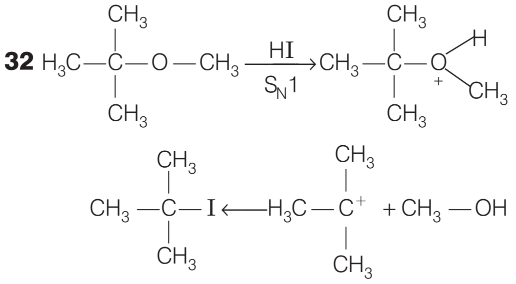
$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2OH + CH_3CH_2I$$



30 $$CH_3CH_2-O-CH_2CH_3 + Cl_2 \xrightarrow{\text{Dark}} CH_3CH_2-O-\overset{\overset{Cl}{|}}{CH}-CH_3$$

31 $(CH_3)_3C-O-CH_3 + HI \longrightarrow (CH_3)_3C-I + CH_3OH$

t-butyl methyl ether *t*-butyl iodide Methanol

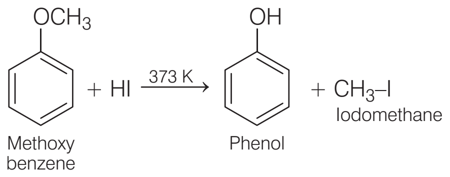


32 $$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O-CH_3 \xrightarrow[S_N1]{HI} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{+}{O}\begin{smallmatrix}H\\CH_3\end{smallmatrix}$$

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-I \longleftarrow H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C^+}} + CH_3-OH$$

SESSION 2

1 On reaction of HI with methoxy benzene, we get phenol and methyl iodide product.



2 The dehydration of alcohols depends on the degree of carbocation formed during the dehydration. More be the degree easier is the dehydration.Hence, (c) option is correct.

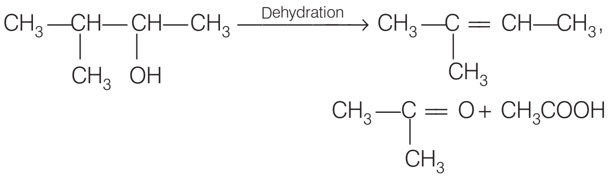
3 On heating the mixture of methanol and ethanol we can get mixture of

CH_3OCH_3 / C_2H_5 OCH_3 / $C_2H_5OC_2H_5$

$$CH_3OH + HOC_2H_5 \xrightarrow[H_2SO_4]{\text{Conc.}} CH_3OCH_3 + CH_3OC_2H_5 + C_2H_5OC_2H_5$$

4 Anisole will not give benzoic acid on boiling with $KMnO_4$ due to presence of OCH_3 (bonded directly with the benzene ring).

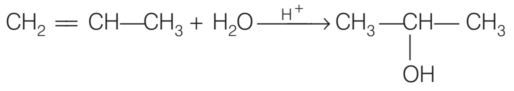
5 $C_5H_{11}OH$ has zero degree of unsaturation. Which on dehydration give alkene further alkene on oxidation gives dehydration mixture of carboxylic acid and ketone.



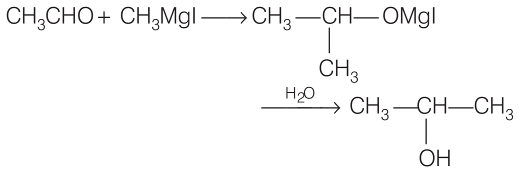
$$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow{\text{Dehydration}} CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3,$$

$$CH_3-\underset{\underset{CH_3}{|}}{C}=O + CH_3COOH$$

6 Alkenes (propene) and aldehydes (acetaldehyde) will give alcohols on the reaction with H_2O/H^+ and CH_3MgI respectively, the reaction can be written as follows



(i) $$CH_2=CH-CH_3 + H_2O \xrightarrow{H^+} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$



(ii) $$CH_3CHO + CH_3MgI \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{CH}-OMgI \xrightarrow{H_2O} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

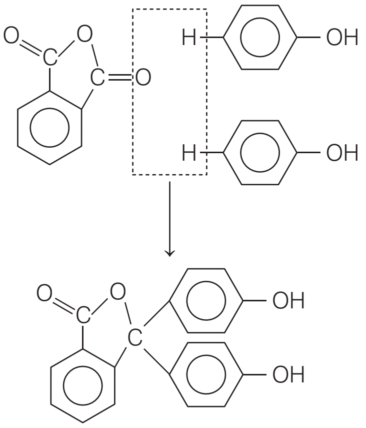
7. (a) The initial step is the protonation of alcohols using H^+-ions.

(b) Phenol does not react with $NaHCO_3$ because $NaHCO_3$ is a weak base

(c) Alcohols are soluble in water due to intermolecular molecules

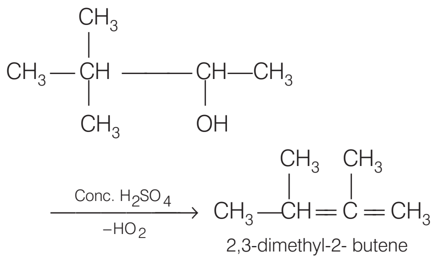
(d) ∵ –OH group is electron releasing group thus is *ortho*, *para* directive.

8 When phenol is heated with phathalic anhydride in the presence of conc. H_2SO_4 phenolphthalein is formed, which show pink colour with alkali.



Phenolphthalein

9 2,3-dimethyl but-2-ene is the major product because conc. H_2SO_4 takes out the water molecule. After the formation of carbocation, tertiary carbocation will form due to higher stability and leads to product 2,3-dimethyl but-2-ene.



10 (i) Among the given structure, those conjugate, gives resonance are more acidic than the structure does not show any resonance.

(ii) R—OH and HOH both will not show resonance but due to presence of alkyl group (R)ROH is more acidic than H_2O (HOH).

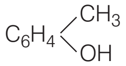
(iii) Alkynes are slightly acidic due to sp hybridisation of both the triple bonded carbon atoms the triple bonded carbon atom (∵ more be the s-character more is the acidic nature of the alkyne).

Hence, (b) is the correct option.

11 The given compound 'X' having formula C_7H_8O, thus has degree of unsaturation is 4 hence, it contain a ring and therefore the product is phenol.

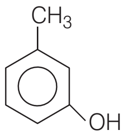
(i) Phenol will not dissolve in $NaHCO_3$ due to its weak nature.

(ii) Since, X when treated with Br_2 forms. $C_7H_5OBr_3$ (ppt.) and considering the molecular formula of X, it is most likely to be cresol.

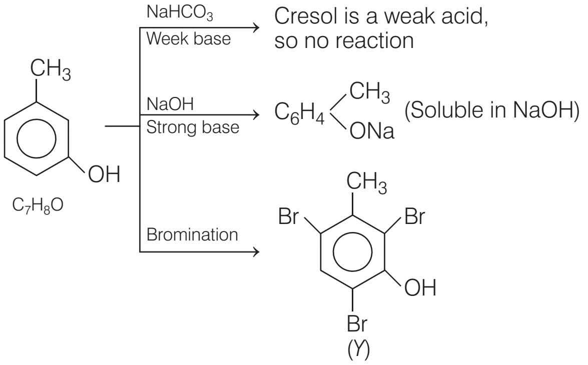


$$C_6H_4\begin{cases}CH_3\\OH\end{cases}$$

(iii) Since X on bromination forms tribromo derivative so, it is m-cresol, i.e.



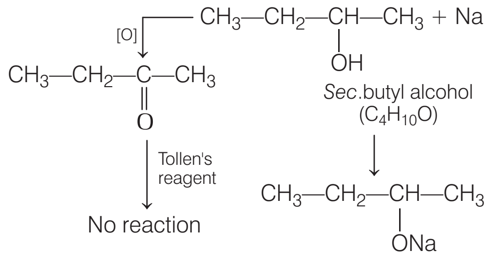
The reactions are



12 The degree of unsaturation for the formula $C_4H_{10}O$ is zero, means the given compound has no pair (π) bond or ring in its structure. As, it gives sodium salt with Na and a carbonyl compound.

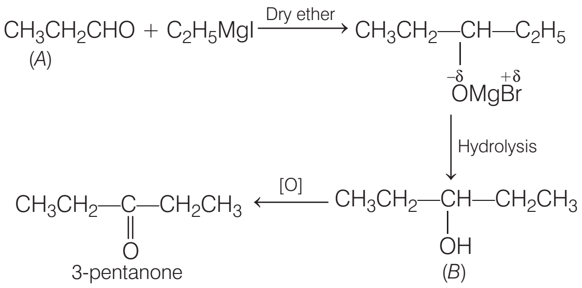
Which does not give positive test with Tollen's reagent.

Therefore, the product formed on oxidation is a ketone, the whole reaction (s) are as follows :



13

$$\begin{tikzcd}A + C_2H_5MgI \arrow[r, "\text{Dry ether}"] & \text{Addition product} \arrow[d, "\text{Hydrolysis}"] \\ \text{3-pentanone} & B \arrow[l, "{[O]}"']\end{tikzcd}$$

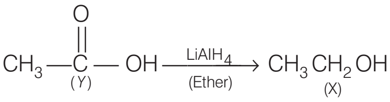


14 When ethyl alcohol is oxidised by acidified potassium dichromate. $CH_3COOH(Y)$ is obtained as

$$\underset{(X)}{3C_2H_5OH} + 2K_2Cr_2O_7 + 8H_2SO_4 \longrightarrow$$

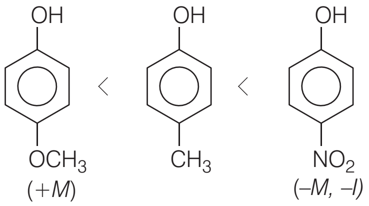
$$\underset{(Y)}{3CH_3COOH} + 2Cr_2(SO_4)_3 + 2K_2SO_4 + 11H_2O$$

Carboxylic acid undergoes reduction with $LiAlH_4$ to give primary alcohol as



$$\underset{(Y)}{CH_3-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow[\text{(Ether)}]{LiAlH_4} \underset{(X)}{CH_3CH_2OH}$$

15



(+I, Hyperconjugation)

Electron releasing group decreases while electron with drawing group increases acidic strength by destabilising and stabilising the phenoxide ion formed respectively.

16 ∵ Compound (X) on reduction with $LiAlH_4$ give (Y), which on passing over the copper at 300°C gives (X), therefore (X) is an aldehyde which on reduction with $LiAlH_4$ gives primary alcohol $(CH_3CH_2OH)\cdot CH_3CH_2OH$ gives aldehyde with copper on heating at 300° C.